Understanding Advanced Chemistry Through Problem Solving

(Revised Edition)

The Learner's Approach

Volume 2

Kim Seng Chan • Jeanne Tan

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PREFACE

When a major examination approaches, students would start going around in search for guidebooks that can help them to consolidate the important concepts that are necessary to meet the requirements of the assessments in the shortest amount of time. But unfortunately, most guidebooks are of the expository and non-refutational type, presenting facts rather than explaining them. In addition, the links between concepts are often not made explicit and presupposes that learners would be able to make the necessary integration with the multitude of concepts that they have come across in their few years of chemical education, forgetting that some learners may lack the prior knowledge and metacognitive skills to do it meaningfully. Hence, learners would at most be able to reproduce the information that is structured and organized by the guidebook writer, but not able to construct a meaningful conceptual mental model for oneself. Hence, the learners would not be able to apply what they should know fluidly across different contextual questions that appear in the major examination.

This current book is a continuation of our previous two books — *Understanding Advanced Physical Inorganic Chemistry* and *Understanding Advanced Organic and Analytical Chemistry*, retaining the main refutational characteristics of the two books by strategically planting think-aloud questions to promote conceptual understanding, knowledge construction, reinforcement of important concepts, and discourse opportunities. It is hoped that these essential questions would make learners aware of the possible conflict between their prior knowledge, which may be counterintuitive or misleading, with those presented in the text, and hence in the process, make the necessary conceptual changes. In essence, we are trying to effect metaconceptual awareness — awareness of the theoretical nature of one's thinking — while learners are trying to master the essential chemistry concepts and learn about their applications in problem solving. We hope that by pointing out the differences between possible misconceptions and the actual chemistry content, we can promote metaconceptual awareness and thus assist the learner to construct a meaningful conceptual model of understanding to meet the necessary assessment criteria. We want our learners to not only know what they know, but at the same time, have a sense of how they know what they know and how their new learning is interrelated within the discipline. This would enable the learners to better appreciate and fluidly apply what they have learned in whatever novel questions that they come across in the major examinations.

Lastly, the substance in this book would be both informative and challenging to the practices of teachers. This book would certainly illuminate the teaching of all chemistry teachers who strongly believe in teaching chemistry in a meaningful and integrative approach, from the learners' perspective. The integrated questions that are being used as problem-solving tools would certainly prove useful to students in helping them to revise fundamental concepts that they have learned from previous chapters, and also perceive the importance and relevancy in the application to their current learning. Collectively, this book offers a vision of understanding and applying chemistry meaningfully and fundamentally from the learners' approach and to fellow chemistry teachers, we hope that it would help you develop a greater insight into what makes you tick, explain, enthuse, and develop in the course of your teaching.

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We also wish to take this opportunity to express our gratitude to Yeo Yam Khoon of Raffles Institution (Year 5-6) who has been and will always be an inspiration for his unwavering commitment to the teaching of chemistry.

Special thanks to Tham Zisheng of Raffles Institution (Year 1-4), Ms Soh Xiao Fen of St. Andrew Junior College, Mdm Toh Chui Hoon of Victoria Junior College, Dr Chok Yew Keong of Eunoia Junior College and William Wong Yu Kai of Victoria Junior College for some of their invaluable suggestions and mind provoking discussions, in the past and present.

Special thanks go to all our students who have made our teaching of chemistry fruitful and interesting. We have learnt a lot from them just as they have learnt some good chemistry from us.

Finally, we thank our families for their wholehearted support and understanding throughout the period of writing this book. We would like to share with all the passionate learners of chemistry two important quotes from the *Analects of Confucius*:

學而時習之，不亦悅乎？**(Isn’t it a pleasure to learn and practice what is learned time and again?)**

學而不思則罔，思而不學則殆 **(Learning without thinking leads to confusion, thinking without learning results in wasted effort)**

CONTENTS

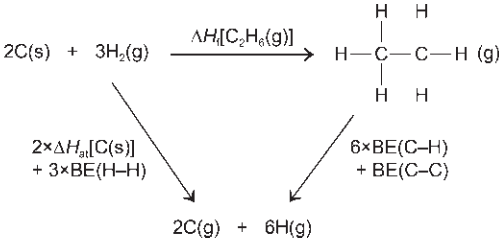
CHAPTER 1

STRUCTURE AND BONDING

1. (a) (i) The enthalpies of the formation of ethane, ethene, ethyne, and benzene are –84.7, +52.3, +227, and +82.9 kJ mol^{-1}, respectively. With the given bond energies of H−H and C−H as +436 and +412 kJ mol^{-1}, respectively, calculate the values for the carbon−carbon bond energies in the four hydrocarbons.

Explanation:

For ethane:



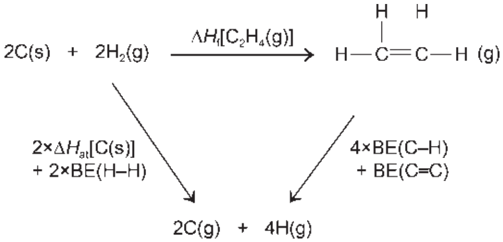
By Hess' Law, $\Delta H_f[C_2H_6(g)] = 2\Delta H_{at}[C(s)] + 3BE(H–H) - [6BE(C–H) + BE(C–C)]$

$= 2(715) + 3(436) - [6(412) + BE(C\text{-}C)]$

$= -84.7.$

$\Rightarrow$ BE(C–C) for ethane = +350.7 kJ mol^{-1}.

For ethene:



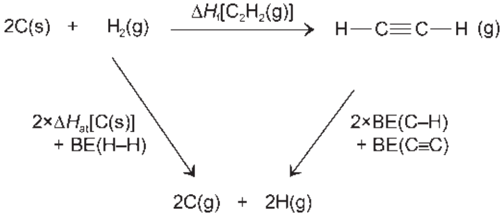
By Hess' Law, $\Delta H_f[C_2H_4(g)] = 2\Delta H_{at}[C(s)] + 2BE(H\text{–}H) - [4BE(C\text{–}H) + BE(C{=}C)]$

$= 2(715) + 2(436) - \{4(412) + BE(C{=}C)\}$

$= +52.3.$

$\Rightarrow$ BE(C=C) for ethene = +601.7 kJ mol^{-1}.

For ethyne:



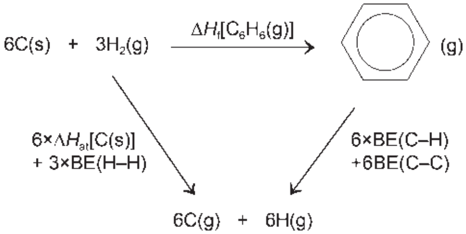
By Hess' Law, $\Delta H_f[C_2H_2(g)] = 2\Delta H_{at}[C(s)] + BE(H\text{–}H) - [2BE(C\text{–}H) + BE(C{\equiv}C)]$

$= 2(715) + (436) - [2(412) + BE(C{\equiv}C)]$

$= +227.$

$\Rightarrow$ BE(C≡C) for ethyne = +815.0 kJ mol^{-1}.

For benzene:



$$\begin{aligned}\text{By Hess' Law, } \Delta H_f[C_6H_6(g)] &= 6\Delta H_{at}[C(s)] + 3BE(H-H) - [6BE(C-H) \\ &\quad + 6BE(\text{carbon-carbon})] \\ &= 6(715) + 3(436) - [6(412) + 6BE(\text{carbon-}\\ &\quad \text{carbon})] = +82.9.\end{aligned}$$

$$\Rightarrow BE(\text{carbon–carbon}) \text{ for benzene} = +507.2 \text{ kJ mol}^{-1}.$$

Q Why did you use the term 'carbon–carbon' when you calculated the bond energy for the carbon–carbon bond in benzene?

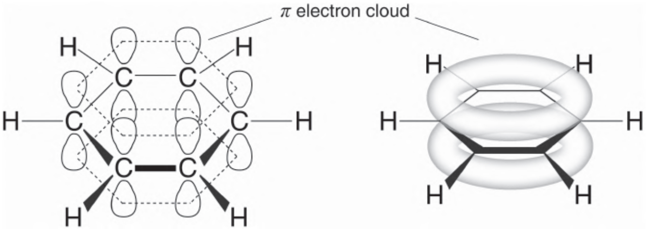
A: This is because the carbon–carbon bond in benzene is neither a C–C single nor a C=C double bond. Hence, it is inappropriate to use the term 'C–C.'

(ii) Account for the differences in the carbon−carbon bond length in the compounds ethane, ethene, ethyne, and benzene.

Explanation:

The carbon-carbon bond energies increase in the order: ethane < benzene < ethene < ethyne. Hence, the bond length would also decrease in this similar trend, with the C–C bond in ethane the longest. As the number of bonds between the two carbon atoms increases, the bond becomes stronger and shorter because there is stronger attractive force acting on the increasing number of shared electrons exerted by the two nuclei.

For benzene, the bond energy value indicates that the carbon–carbon bond is intermediate between a C–C single and a C=C double bond. This is because the pi electrons between any two carbon atoms in benzene can actually delocalize throughout all the six carbon atoms. As a result, there is only on the average one pi electron between two carbon atoms. This accounts for the weaker carbon–carbon bond in benzene as compared to ethene, but the bond is stronger than that in ethane.

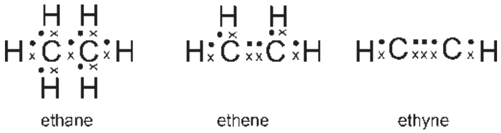


Do you know?

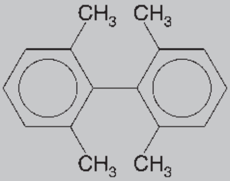
- As the number of shared electrons increases, the attractive force by the nuclei on the shared electrons increases but at the same time, the inter-electronic repulsion between the shared electrons also increases. This increase in inter-electronic repulsion would act against the attractive force. This is why it is very difficult to form four bonds between two atoms as the inter-electronic repulsion would be too strong to be contained.
- BE(C=C) – BE(C–C) = 601.7 – 350.7 = +251.0 kJ mol^{-1}, which is equivalent to the bond energy to overcome a pi bond between two carbon atoms. Did you notice that the strength of the pi bond is weaker than that of the sigma bond? This is because the formation of a sigma bond results in the accumulation of electron density within the inter-nuclei region, which buffers the inter-nuclei repulsion much better than the accumulation of electron density out of the inter-nuclei region for the pi bond. The sigma bond is able to accumulate electron density within the inter-nuclei region due to the head-on overlap of the atomic orbitals. While for pi bond, it is the side-on overlap!

(iii) Draw the dot-and-cross diagrams of ethane, ethene, and ethyne.

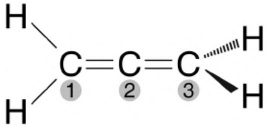
Explanation:



(b) Explain why $CH_2=C=CH_2$ is not a flat molecule and the carbon skeleton of the following molecule is not planar

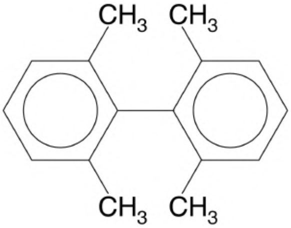


Explanation:

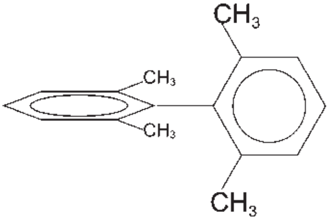


The $CH_2{=}C{=}CH_2$ is not a flat molecule because the two C–H bonds on C_1 are lying on a plane which is perpendicular to the plane that contains the two C–H bonds on C_3.

Let us label the following molecule **A:**



The 16 carbon atoms of molecule **A** cannot be lying on the same plane because there would be too much steric effect between the four $–CH_3$ groups. So instead, the two benzene rings are in fact perpendicular to each other, causing the two $–CH_3$ groups on each benzene ring to be perpendicular to each other as shown below:



Q Why are the two C–H bonds on C_1 lying on a plane that is perpendicular to the plane that contains the two C–H bonds on C_3 for $CH_2{=}C{=}CH_2$?

A: C_1 is an sp^2 hybridized atom, which means it uses an *s* orbital and two *p* orbitals to form three sp^2 hybrid orbitals. Let's say that it uses both the p_x and p_y orbitals for hybridization. It would then be left with the p_z orbital to form a pi bond with C_2. Hence, the three sp^2 hybrid orbitals on C_1 must be sitting on the *x*–*y* plane.

Now C_2 is an *sp* hybridized atom, which means it uses an *s* orbital and *p* orbitals. Let's say that it uses the p_x orbital. But do not forget that it has already used up the p_z orbital to form a pi bond with C_1. Hence, C_2 can only use its p_y orbital to form a pi bond with C_3.

As for C_3, it is also an sp^2 hybridized atom, which means it uses an *s* orbital and two *p* orbitals. Since it has already used up its p_y orbital to form a pi bond with C_2, it can only use the p_x and p_z orbitals for hybridization. Hence, the three sp^2 hybrid orbitals on C_3 must be sitting on the *x*–*z* plane, which is perpendicular to the *x*–*y* plane.

Therefore, since all the carbon and hydrogen atoms are sitting on different planes, the molecule is not planar.

Q What is steric effect?

A: Well, an atom or group of atoms occupies space. So, when another approaching species encounter the atom, the inter-electronic repulsion between these two species is termed steric effect. Hence, steric effect is none other than a type of inter-electronic repulsion.

Do you know?

— In short, to determine the hybridization state of an atom, we can make use of the following guidelines:

- *Four* single bonds *OR* *four* sigma bonds *OR* *tetrahedral* electron pair geometry (EPG) *OR* bond angle is about 109.5° ⇒ the atom is sp^3 hybridized;
- *Two* single bonds and *one* double bond *OR* *three* sigma bonds and *one* pi bond *OR* *trigonal planar* EPG *OR* bond angle is about 120° ⇒ the atom is sp^2 hybridized; and
- *One* single bond and *one* triple bond *OR* *two* double bonds *OR* *two* sigma bonds and *two* pi bonds *OR* *linear* EPG *OR* bond angle is about 180° ⇒ the atom is *sp* hybridized.

Q Can we use the shape of the molecule to predict its hybridization state? For example, CH_4 is tetrahedral, hence it is sp^3 hybridized?

A: It is not very accurate. Take for example, NH_3 is trigonal pyramidal in shape and it has a tetrahedral EPG. So, the best hybridization model to describe NH_3 is in fact sp^3 hybridization. For another instance, $AlCl_3$, it has only three single bonds and its EPG is trigonal planar, so the best model to describe it would be sp^2 hybridization.

(c) Explain in molecular terms the differences between the boiling points of;

(i) methane and *n*-butane;

Explanation:

Both methane (CH_4) and *n*-butane ($CH_3CH_2CH_2CH_3$) are non-polar molecules; hence, they both have instantaneous dipole–induced dipole interaction. Now, since *n*-butane has more electrons than methane, its id–id interaction is stronger. Therefore, *n*-butane would have a higher boiling point than methane.

(ii) *n*-butane and methylpropane;

Explanation:

Both *n*-butane ($CH_3CH_2CH_2CH_3$) and methylpropane ($CH_3CH(CH_3)_2$) are non-polar molecules having the same number of electrons; hence, they both have instantaneous dipole–induced dipole interaction. Now, since *n*-butane is more linear than methylpropane, the surface area of contact between the molecules is greater. Therefore, the id–id interaction is more extensive in *n*-butane, accounting for its higher boiling point than methylpropane.

(iii) *n*-hexane and cyclohexane;

Explanation:

Both *n*-hexane ($CH_3(CH_2)_4CH_3$) and cyclohexane ($(CH_2)_6$) are non-polar molecules having almost the same number of electrons; hence, they both have instantaneous dipole–induced dipole interaction. Now, since *n*-hexane is more linear than cyclohexane, the surface area of contact between the *n*-hexane molecules is greater. Therefore, the id–id interaction is more extensive in *n*-hexane, accounting for its higher boiling point than cyclohexane.

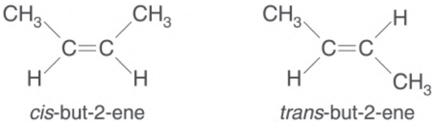
(iv) propene and ethane;

Explanation:

Both propene ($CH_3CH{=}CH_2$) and ethane (CH_3CH_3) are non-polar molecules; hence, they both have instantaneous dipole–induced dipole interaction. Now, since propene has more electrons than ethane, its id–id interaction is stronger. Therefore, propene would have higher boiling point than ethane.

(v) *cis*-but-2-ene and *trans*-but-2-ene;

Explanation:



Both *cis*-but-2-ene and *trans*-but-2-ene are relatively non-polar molecules having almost the same number of electrons; hence, they both have instantaneous dipole–induced dipole interaction. But *cis*-but-2-ene is relatively more polar than *trans*-but-2-ene, thus the permanent dipole–permanent dipole interaction in *cis*-but-2-ene causes it to have a higher boiling point than the *trans*-but-2-ene.

Q So is an alkene molecule polar or non-polar?

A: Let's just consider an unsubstituted alkene molecule consisting only of C and H atoms. Since the C atom is more electronegative than the H atom, the C–H bond is polar but can be considered as relatively non-polar when compared with bonds such as C–Cl or C–O. Thus, an unsubstituted alkene is actually relatively non-polar. But for *cis*-alkene, the distribution of electron density is higher on one side of the C=C double bond than the other as compared to the *trans*-alkene. Hence, there is a net dipole moment for the *cis*-alkene than the *trans*-alkene, causing the *cis*-alkene to have permanent dipole–permanent dipole interaction.

(vi) *n*-butane and propanone;

Explanation:

Propanone (CH_3COCH_3) is a polar molecule with permanent dipole–permanent dipole interaction, whereas *n*-butane ($CH_3CH_2CH_2CH_3$) is non-polar, with instantaneous dipole–induced dipole interaction. Now, since the pd–pd interaction is stronger than the id–id interaction, propanone has a higher boiling point than *n*-butane.

(vii) propanone and propanal;

Explanation:

Both propanone (CH_3COCH_3) and propanal (CH_3CH_2CHO) are polar molecules with permanent dipole–permanent dipole interaction. But propanone, having a greater net dipole moment than propanal, has stronger pd–pd interaction, accounting for its higher boiling point than proponal.

Q Since propanal has the structure CH_3CH_2CHO, can there be hydrogen bonding?

A: An aldehyde has the functional group –CHO. But it doesn't mean that there is an –OH group in the molecule. In –CHO, there is a C=O double bond and a C–H single bond. There is no –OH group, so how can aldehyde form hydrogen bonds between themselves?

(viii) propanone and propan-1-ol;

Explanation:

Propanone (CH_3COCH_3) is a polar molecule with permanent dipole–permanent dipole interaction. But propan-1-ol ($CH_3CH_2CH_2OH$) has a –OH group that is capable of forming hydrogen bonds. Hence, propan-1-ol has a higher boiling point than propanone.

Do uou know?

— The average number of hydrogen bonds formed per alcohol molecule is less than that of a water molecule due to the replacement of a H atom of the H_2O molecule by an alkyl group (R group). As a result, alcohol molecules with a similar molecular weight as water molecule, have lower boiling point and are more volatile.

(ix) ethylamine and dimethylamine;

Explanation:

Both ethylamine ($CH_3CH_2NH_2$) and dimethylamine ($(CH_3)_2NH$) contain a –NH group that is capable of forming hydrogen bonds. But because the lone pair of electrons in dimethylamine is more hidden than in ethylamine, the hydrogen bonds formed in dimethylamine are not as extensive as those in ethylamine due to the steric hindrance posed by the two methyl groups. Hence, dimethylamine has a lower boiling point.

Q But isn't the ethyl group of ethylamine more bulky than a methyl group?

A: Yes, an ethyl group is indeed more bulky than a methyl group, but it only takes up a corner of the space. Whereas, in dimethylamine, the two methyl groups take up more space. Hence, there is greater steric effect posed by the two methyl groups.

Q But dimethylamine has two alkyl groups whereas ethylamine has only one. Since an alkyl group is electron-donating via inductive effect, shouldn't the lone pair of electrons on dimethylamine be more available for hydrogen bond formation?

A: Indeed, more alkyl groups can help to make the lone pair of electrons more available. But unfortunately, the availability of the lone pair factor here cannot be used to account for why dimethylamine has a lower boiling point than ethylamine.

Q Then when can we use the "availability of lone pair" factor?

A: Well, if you are given two amines of similar molecular weight, where one is a primary while the other is a secondary amine, and you are told that the secondary amine has a higher boiling point than the primary amine, then you can use the "availability of lone pair" factor to account for it. This is using the appropriate theory or concept to account for the observation!

Q What would you expect the boiling point of trimethylamine to be compared to dimethylamine?

A: Since trimethylamine cannot form hydrogen bonds, we would expect its boiling point to be lower than dimethylamine.

(x) ethylamine and ethanol;

Explanation:

Both ethylamine ($CH_3CH_2NH_2$) and ethanol (CH_3CH_2OH) can form hydrogen bonds. But since the hydrogen bonds in ethanol is stronger than those in ethylamine as the O–H bond is more polar than the N–H bond, ethanol has a higher boiling point than ethylamine.

Do you know?

— The strength of a hydrogen bond depends on:

(i) The type of hydrogen bond that is being formed. A hydrogen bond that is formed between H–F:----H–F is stronger than H–O:----H–O, which in turn is stronger than H–N:----H–N. The reason is because of an increase in the polarity of the bond: H–N < H–O < H–F.

(ii) The number of hydrogen bonds that the molecule can form. For example, the H_2O (100^oC) molecule has a higher boiling point than HF ($\sim20^oC$) is because a H_2O molecule can form an average of two hydrogen bonds per molecule, whereas HF can only form one hydrogen bond. Another example is CH_3OH, which has a boiling point of $\sim65^oC$ as compared to that of H_2O. This is because CH_3OH can on the average only form one hydrogen bond per molecule.

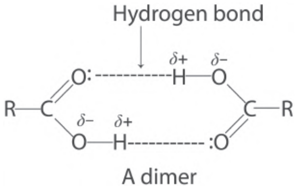
(xi) ethanol and ethanoic acid; and

Explanation:

Both ethanol (CH_3CH_2OH) and ethanoic acid (CH_3COOH) can form hydrogen bonds. But the hydrogen bonds in ethanoic acid are stronger than those in ethanol because the O–H bond in ethanoic acid is made more polar by the electron-withdrawing C=O group. Hence, there is a greater attractive force between the more electron-deficient H atom of the O–H group of ethanoic acid. Therefore, ethanoic acid has a higher boiling point than ethanol.

Do you know?

— The hydrogen bonds in carboxylic acid are so strong that they can undergo dimerization as follows:



The formation of dimers actually further increases the boiling point of the substance as now, the instantaneous dipole–induced dipole interaction between the dimer molecules is stronger than between the monomer.

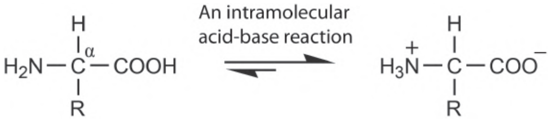
(xii) ethanoic acid and amino ethanoic acid.

Explanation:

Ethanoic acid (CH_3COOH) has hydrogen bonds whereas aminoethanoic (H_2NCH_2COOH) acid is present as a zwitterion. Hence, the ionic bonding in aminoethanoic acid causes it to have a higher boiling point than ethanoic acid.

Do you know?

— An amino acid undergoes the intramolecular acid–base reaction to produce a zwitterion. It is a species which possesses an equal number of positive and negative charges. Hence, they are ionic compound at room temperature with a high melting point.



(d) Predict whether each of the compounds below will be miscible or immiscible with water. Give reasons for your predictions.

(i) *n*-butane;

Explanation:

n-butane ($CH_3CH_2CH_2CH_3$) will be immiscible with water. This is because *n*-butane is non-polar; hence it interacts with the water molecules through instantaneous dipole–induced dipole interaction. The interaction does not release a sufficient amount of energy to overcome the strong hydrogen bonds in water.

Do you know?

— The explanation behind the maxim 'like dissolves like' is simply because if two substances are alike, then the intermolecular forces between them would be similar to those present in their pure form. Thus, because of this similar interaction, sufficient energy would be released to help overcome the intermolecular forces in their pure form, in order for them to mix.

(ii) chloroethane;

Explanation:

Chloroethane (CH_3CH_2Cl) will be immiscible with water. This is because although chloroethane is polar, it interacts with water molecules through permanent dipole–permanent dipole interaction. The interaction does not release a sufficient amount of energy to overcome the strong hydrogen bonds in water.

(iii) propanone;

Explanation:

Propanone (CH_3COCH_3)will be miscible with water. This is because the lone pair of electrons on the O atom of propanone can form hydrogen bonds with the H atom of the H_2O molecules. The interaction would release a sufficient amount of energy to overcome the strong hydrogen bonds in water.

Do you know?

— As the number of carbon atoms increases for the ketone, the solubility in water decreases. This is because it is more difficult for water molecules to form hydrogen bonds with the lone pair of electrons on the O atom of the ketone due to steric effect. As such, the interaction of the higher-molecular-weight ketone with water is mainly of the instantaneous dipole–induced dipole interaction. This would not release a sufficient amount of energy to overcome the strong hydrogen bonds in water.

— Alternatively, we can say that the higher-molecular-weight ketone is essentially non-polar or more hydrophobic. This applies to organic molecules like alcohol, amine, carboxylic acid, etc.

(iv) propan-1-ol; and

Explanation:

Propan-1-ol ($CH_3CH_2CH_2OH$) will be miscible with water. This is because the lone pair of electrons on the O atom of propan-1-ol can form hydrogen bonds with the H atom of the H_2O molecules. The interaction would release a sufficient amount of energy to overcome the strong hydrogen bonds in water.

(v) propylamine.

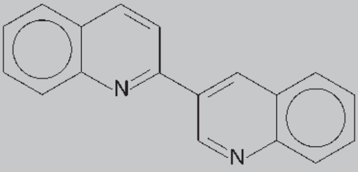
Explanation:

Propylamine ($CH_3CH_2CH_2NH_2$) will be miscible with water. This is because the lone pair of electrons and the H atoms on the N atom of propylamine can form hydrogen bonds with the H_2O molecules. The interaction would release a sufficient amount of energy to overcome the strong hydrogen bonds in water.

Q So, are we expecting the solubility of a secondary (R_2NH) and a tertiary amine (R_3N) of similar molecular weight as that of a primary amine, to be less soluble in water than that of the primary amine?

A: Comparatively, the secondary amine has a smaller number of H atoms to form hydrogen bonds, in addition to the fact that its lone pair is more sterically hindered to be available for hydrogen bond formation. On the other hand, the tertiary amine has only a lone pair of electrons on the N atom, and its lone pair is also sterically hindered. Hence, we would expect the solubility of a tertiary amine to be lower than that of a secondary amine, which in turn is lower than that of a primary amine, all of which share a similar molecular weight.

(e) 2,2’-biquinolyl is an important complexation agent used in the extraction of copper.



2,2’-Biquinolyl

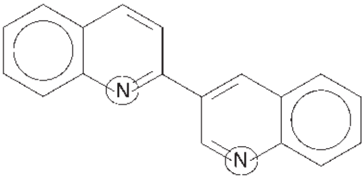
(i) Identify the type of hybridization of each of the two N atoms.

Explanation:

Since each of the N atom of 2,2′-biquinolyl has a trigonal planar EPG, it is sp^2 hybridized.

(ii) Circle the atoms that make the compound able to act as a complexation agent.

Explanation:

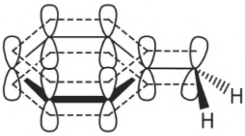


2,2′-Biquinolyl

(iii) The N atom of 2,2′-biquinolyl is more basic than the N atom of phenylamine but less basic than the N atom of an aliphatic amine. Explain.

Explanation:

The lone pair of electrons on the N atom of phenylamine ($C_6H_5NH_2$) is less available to be donated because it is delocalized into the benzene ring as shown below:



On the contrary, for 2,2′-biquinolyl, the lone pair of electrons of the N atom sits in an sp^2 hybridized orbital, which is perpendicular to the pi electron cloud of the ring. But when compared to the lone pair of electrons of an aliphatic amine, the lone pair of electrons of 2,2′-biquinolyl is less basic. This is because the lone pair of electrons in an aliphatic amine sits in an sp^3-hybridized orbital which has only 25% *s* character compared to an sp^2 hybridized orbital, which has about 33% *s* character. Since an *s* orbital is closer to the nucleus as compared to a *p* orbital, the higher the percentage of *s* character, the stronger the attractive force acting on the electrons. Thus, the lone pair of electrons on 2,2′-biquinolyl is less basic than that on an aliphatic amine.

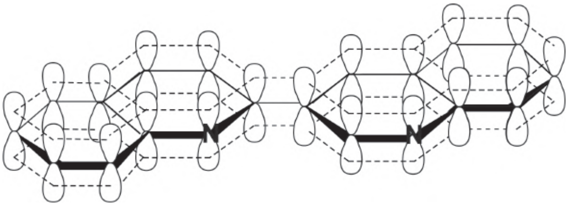
Do you know?

- According to Brønsted–Lowry's definition of acid–base: an acid is a proton donor while a base is a proton acceptor. The stronger the acid, the greater the availability of the proton for donation while the stronger the base, the more likely it is to accept a proton.
- But what does a species use to accept a proton? According to Lewis' definition: an acid is an electron pair acceptor, whereas a base is an electron pair donor. So, a base uses a pair of electrons to accept a proton.
- What happens after an acid donates a proton? It becomes its conjugate base, which is more electron-rich than its conjugate acid. So, the stronger the acid, the more stable is its conjugate base. This means if there is a factor that would help to disperse the electron density on the conjugate base, it would stabilize the base AND hence make the acid a stronger one.
- What happens after a base accepts a proton? It becomes its conjugate acid, which is less electron-rich than its conjugate base. So, the stronger the base, the more stable is its conjugate acid. This means if there is a factor that would help to enhance the electron density on the conjugate base, it would destabilize the base AND hence make the base a stronger one. Or if there is a factor that would help to disperse the electron-deficiency of the conjugate acid (a conjugate acid is more electron-deficient or less electron-rich than its conjugate base) by donating electron density to the conjugate acid, then the conjugate acid would be stabilized and becomes less acidic.
- Thus, a factor that stabilizes a base (make it less basic by withdrawing electron density away) must be the same factor that destabilizes an acid (make it more acidic by withdrawing electron density away).

(iv) Explain why the carbon skeleton of 2,2′-biquinolyl is planar.

Explanation:

All the carbon atoms and the two nitrogen atoms of 2,2′-biquinolyl are sp^2 hybridized, each with a *p* orbital parallel to each other. Hence, all these *p* orbitals can overlap collaterally (or side-on) to form a continuous pi network. Therefore, the 2,2′-biquinolyl is planar.



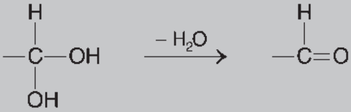
Q Is there any advantage with the delocalization of electrons over such a big surface area?

A: When the electrons are “allowed” to delocalize, it brings about added stability because the dispersion of charges, be it positive or negative, would lower the energy state of the system, hence increasing its stability.

Q Why would the dispersion of charges lower the energy state?

A: Now, electrons are negatively charged particles. If you “force” electrons to come near each other, what must you do? You need to invest energy, right? Where does the energy go to? Since energy cannot be destroyed nor created (Law of Thermodynamics), the energy would “stay” in the system. So, the energy of the system would increase, right? Hence, if forcing electrons together would increase the energy of the system, then allowing the electrons to spread out would decrease the energy. So, the same would apply if we talk about positive charge.

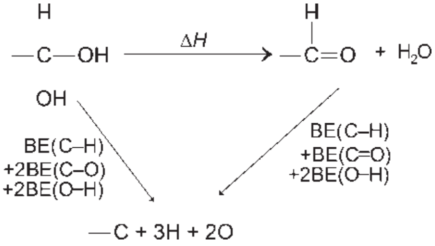
(f) Use the following bond energies to account for why the following germinal diol undergoes spontaneous intramolecular dehydration to form the aldehyde functional group.



$$-\underset{\text{OH}}{\overset{\text{H}}{\text{C}}}-\text{OH} \xrightarrow{-\,H_2O} -\overset{\text{H}}{\text{C}}=\text{O}$$

[Bond energies (in kJ mol^{-1}): C−O (358); C−H (413); C=O (736); H−O (464)]

Explanation:



By Hess's Law, $\Delta H = 2\text{BE(C–O)} - \text{BE(C=O)}$
$= 2(358) - 736 = -20$ kJ mol^{-1}.

By undergoing spontaneous intramolecular dehydration, the products formed are more stable than the reactant itself. In addition, the entropy of the product state is also higher than that of the reactant as there are more particles on the product side. Hence, the system becomes more disordered. Therefore, the intramolecular dehydration is thermodynamically spontaneous.

Q Why would the germinal diol be so unstable as compared to the aldehyde?

A: There are two highly electronegative O atoms bonded to the carbon atom. This carbon atom is highly electron-deficient and you can now imagine a lone pair of electrons from one of the O atoms "flowing into" the carbon atom. This would cause the –OH group to leave.

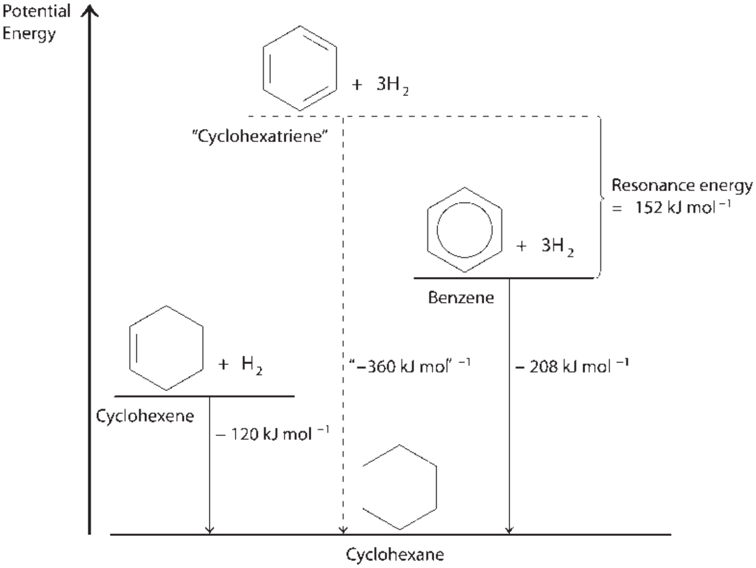
Q If the germinal diol is so unstable, how is it able to form in the first place?

A: If there are two Cl or Br groups bonded to the same carbon atom, we can replace these two halogen atoms by reacting it with NaOH(aq), and we would get the germinal diol.

(g) The enthalpy changes of hydrogenation of benzene and cyclohexatriene, both to cyclohexane, are −208 and −360 kJ mol^{-1}, respectively. Discuss the difference between these two values.

Explanation:

The enthalpy change of hydrogenation of benzene to cyclohexane is less exothermic than when cyclohexatriene is converted to cyclohexane. This is an indication that benzene has a lower energy level than cyclohexatriene. This is because the benzene molecule is resonance stabilized as the six pi electrons are delocalized throughout the ring structure.



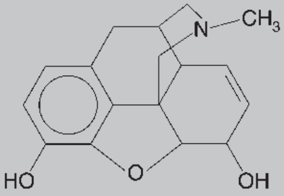
Q What is resonance?

A: Resonance refers to the delocalization of pi electrons as a result of the side-on overlapping of a few *p* orbitals that are parallel to each other. Note that the way the electrons are delocalized here is different from that in metals because of the need for *p* orbitals to be involved. In metal, this is not necessary.

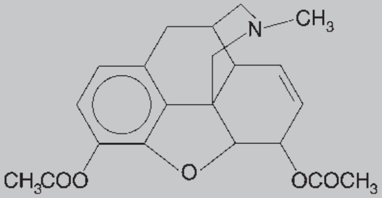
Q Is there a limit to the number of atoms that can be involved in the delocalization?

A: Minimally, there must be three atoms but there is no limit. Look at the porphyrin ring of chlorophyll, it is highly conjugated!

2. Morphine is a chemical able to act on the central nervous system to relieve pain whereas heroin, a synthetic derivative of morphine is an illegal drug. Both the structures of the compounds are shown below:



Morphine



Heroin

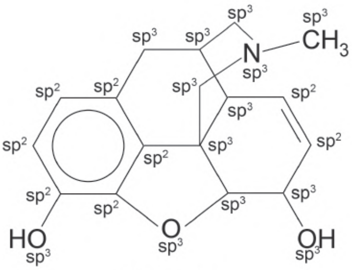
(a) Write the condensed structures (i.e., $C_wH_xN_yO_z$) for both morphine and heroin. Thus, find the relative molecular mass of these two compounds.

Explanation:

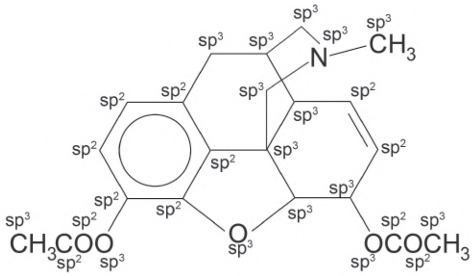
For morphine: $C_{17}H_{19}NO_3$. The Mr is 285.
For heroin: $C_{21}H_{23}NO_5$. The Mr is 369.

(b) Identify each type of hybridization used by the carbon atoms in each of the molecule and give the number of carbon atoms exhibiting each type of hybridization.

Explanation:



Morphine



Heroin

For morphine: number of $sp^2 = 8$; number of $sp^3 = 9$.
For heroin: number of $sp^2 = 10$; number of $sp^3 = 11$.

Do you know?

— We have also included the hybridization state of the O and N atoms in the answer above. The purpose is to show that we can simply assign a hybridization state for an atom by simply looking at the EPG of the atom.

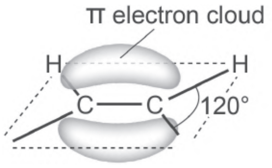
(c) Describe the bonding represented by the circle in the benzene ring of each of the molecule.

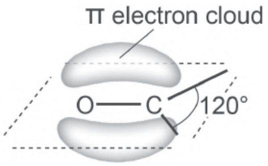
Explanation:

The circle in the benzene ring represents the delocalization of the six pi electrons throughout the ring structure via the overlapping of the six *p* orbitals.

(d) Identify a pair of atoms involved in a pi bond in each of the molecule. Sketch the pi bond and describe briefly how it is formed.

Explanation:





The atoms that are involved in forming the pi bond above are sp^2 hybridized, each with an unused *p* orbital parallel to each other. The two *p* orbitals overlap side-on to form the pi bond. The pi electron cloud is both below and above the plane. The bond angle is 120^o.

(e) Excluding the benzene ring from consideration, determine the number of pi bonds in each of the molecule.

Explanation:

For morphine: number of pi bonds = 1.
For heroin: number of pi bonds = 3.

Q Why did you exclude the benzene ring when considering the number of pi bonds?

A: To form a pi bond, there needs to be two electrons. But the "pi bond" in the benzene ring has only one pi electron between the carbon–carbon bond.

(f) In each part of the molecule linking the benzene ring to the rest of the molecule,

(i) name the groups, C−C(O)−O and C−O−C; and

Explanation:

The C−C(O)−O and C−O−C groups are ester and ether, respectively.

(ii) predict the value of the C−C−O bond angle and explain your answer.

Explanation:

The bond angle of the C−C−O is 120^{o}. This is because there are three regions of electron densities. According to the VSEPR theory, the EPG is trigonal planar with an angle of 120^{o} between two electron densities.

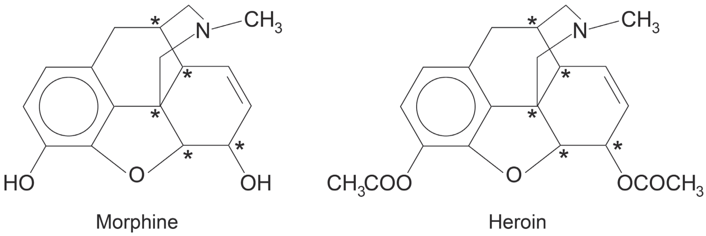
(g) Identify two different elements in each of the molecules that have lone pairs of electrons and determine the number of such lone pairs in the molecule.

Explanation:

For morphine: both nitrogen and oxygen have lone pairs of electrons. There are a total of seven lone pairs.
For heroin: both nitrogen and oxygen have lone pairs of electrons. There are a total of 11 lone pairs.

(h) Mark the chiral carbons in each molecule with asterists and hence predict the number of stereoisomers.

Explanation:



Each of the molecule has five chiral carbons, so there is a total of $2^5 = 32$ optical isomers.

Do you know?

— A C=C double bond in a cyclic ring CANNOT exhibit *cis-trans*/ geometrical isomerism.

(i) Predict whether morphine or heroin would be more soluble in water. Explain your prediction.

Explanation:

Morphine is more soluble in water than heroin because the –OH groups in morphine allow the molecule to form inter-molecular hydrogen bonds with water molecules.

CHAPTER 2

ISOMERISM IN ORGANIC COMPOUNDS

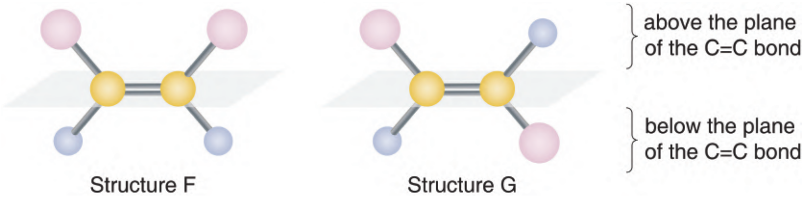
Do you know?

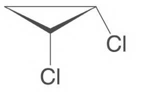
- Compounds that have the same molecular formula but different structures are known as *isomers*. This phenomenon is known as isomerism. The two main types of isomerism are constitutional/structural isomerism and stereoisomerism. These are further divided into subclasses:
  - *Constitutional/Structural isomerism*: Same molecular formula but different constitutional/structural formula. It includes chain isomerism, positional isomerism, and functional group isomerism.
  - *Stereoisomerism*: Same molecular formula and same constitutional/structural formula but differs in spatial orientation of the groups of atoms.

  Geometrical isomerism/*cis-trans* isomerism

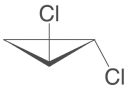
  (1) Restricted rotation about a double bond or a ring.

  (2) Two different groups of atoms bonded to each of the carbon atoms in the C=C double bond or to two carbon atoms in the ring structure.





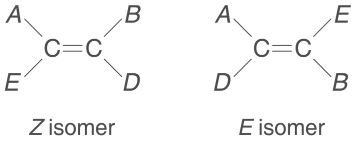
cis-1,2-dichlorocyclopropane



trans-1,2-dichlorocyclopropane

Q Must the two different groups be the same two different groups on both carbon atoms of the C=C double bond?

A: Not necessarily. Let us assume that the two groups on one carbon atom are X and Y. On the other carbon atom, it can be W and Z. Then, the way we decide *cis* or *trans* would not be so straightforward. We would need to use the *E*, *Z* notation. For the *E*, *Z* notation, substituents at each of the doubly bonded carbon atom are assigned either a "higher" or "lower" priority. If a structure has both higher-priority groups on the same side of the C=C bond, it is labeled the *Z* isomer (from the German word *zusammen* that means 'together'). When the higher-priority groups are on opposite sides of the C=C bond, it is termed the *E* isomer (from the German word *entgegen* that means 'opposite').



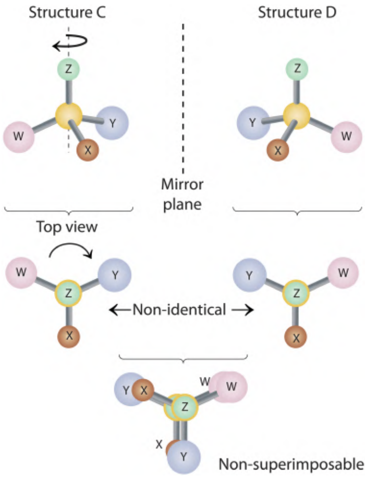
where *A* and *B* are higher priority groups; and *D* and *E* are lower priority groups

Take note that due to the dissimilarities of the four groups, the net dipole moment of the *trans* isomer may not be zero.

Do you know?

Enantiomerism

(1) Needs a chiral atom, i.e., four different groups of atoms bonded to the atom.



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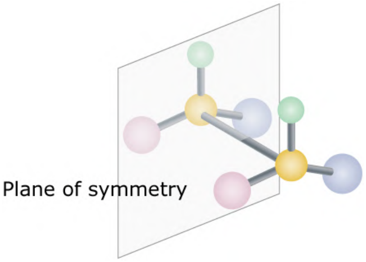
(*Continued*)

(2) A pair of enantiomers is a pair of molecules which are non-superimposable mirror images of each other. Enantiomers have the same physical properties except toward plane-polarized light. Enantiomers rotate plane-polarized light to the same extent but in the opposite direction. Enantiomers have the same chemical properties except toward other optical isomers. An equimolar mixture of a pair of enantiomers is optically inactive and is known as a racemic mixture or racemate.

(3) A meso compound is a molecule with chiral atoms but is optically inactive due to the presence of a plane of symmetry within the molecule.



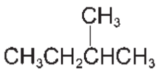
1. Discuss the various types of isomerism present in the following molecules and draw the structural formulae of all possible structural isomers and/or stereoisomers:

   (a) C_5H_{12};

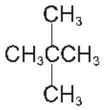
Explanation:

$CH_3CH_2CH_2CH_2CH_3$

n-pentane


$CH_3CH_2\overset{\overset{\displaystyle CH_3}{|}}{C}HCH_3$

2-methylbutane


$CH_3\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}CH_3$

2,2-dimethylpropane

The above molecules are chain isomers, i.e., they have different chain lengths and since none of the above molecules has a chiral carbon there are no optical isomers.

Q What is the trend of the boiling points of the three molecules?

A: The boiling points decrease from: *n*-pentane > 2-methylbutane > 2,2-dimethylpropane. This is because as the molecules become more spherical, the surface area of contact decreases. This decreases the extensiveness of the instantaneous dipole–induced dipole interaction.

(b) C_2H_6O;

Explanation:

CH_3CH_2OH CH_3OCH_3

ethanol dimethylether

The above molecules are functional group isomers, i.e., they have different functional groups; one is an alcohol while the other is an ether.

Q Which molecule has a higher boiling point?

A: Ethanol has a higher boiling point as it has hydrogen bonding, while dimethylether is a polar molecule with permanent dipole–permanent dipole interaction.

Do you know?

— Both alcohol and ether are analogs of H_2O. If you replace one of the H atoms of H_2O by an alkyl group, R, you get alcohol, ROH. If both H atoms are replaced, you get an ether, ROR.

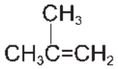
(c) alkenes of formula C_4H_8

Explanation:

Chain isomerism:

$CH_3CH_2CH{=}CH_2$

but-1-ene



$CH_3C(CH_3){=}CH_2$

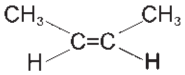
methylpropene

Positional isomerism:

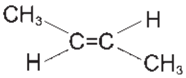
$CH_3CH_2CH{=}CH_2$ $CH_3CH{=}CHCH_3$

but-1-ene but-2-ene

Cis-trans/Geometrical isomerism:



cis-but-2-ene



trans-but-2-ene

Do you know?

— But-2-ene does not exist at all! It is either *cis*-but-2-ene or *trans*-but-2-ene.

Q Which alkene has a higher boiling point, *cis*-but-2-ene or *trans*-but-2-ene?

A: Since *cis*-but-2-ene is relatively more polar than *trans*-but-2-ene, the permanent dipole permanent dipole-interaction in *cis*-but-2-ene would cause it to have a higher boiling point than *trans*-but-2-ene.

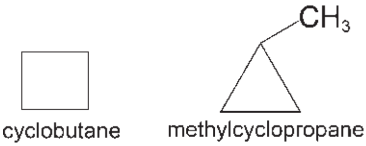
Q Would *cis*-alkene have a higher melting point than the corresponding *trans*-alkene?

A: Not necessarily! If you are told that the melting point of *cis*-alkene is higher than that of *trans*-alkene, then it may be attributed to the strength of intermolecular forces, as discussed previously. But if you are told that *trans*-alkene has a higher melting point than the corresponding *cis*-alkene, then you need to bring in the "packing factor" to account for it. *Trans*-alkene is relatively more linear than *cis*-alkene because the latter "curled up." Thus, *trans*-alkene packs better than the *cis*-alkene. As a result, the intermolecular forces between *trans*-alkene molecules are more extensive than those in *cis*-alkene when in the soild state. Hence, importantly, look at the data and see which concept is more appropriate to account for it!

(d) cycloalkane of formula C_4H_8;

Explanation:

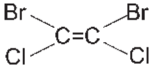
Chain isomerism:



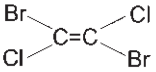
(e) 1,2-dibromo-1,2-dichloroethene;

Explanation:

Cis-trans/Geometrical isomerism:



cis-1,2-dibromo-1,2-dichloroethene

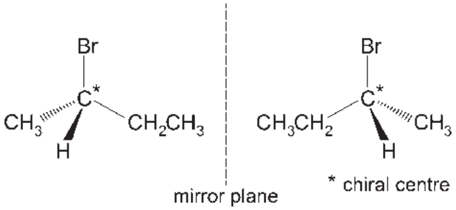


trans-1,2-dibromo-1,2-dichloroethene

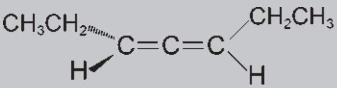
(f) 2-bromobutane;

Explanation:

Enantiomerism:

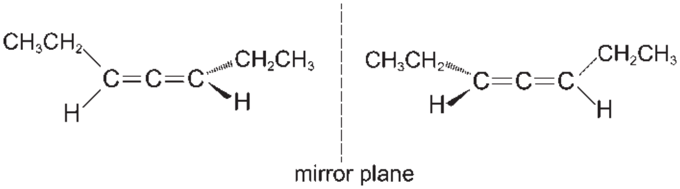


(g) 1,3-diethylallene;



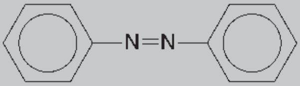
Explanation:

Enantiomerism:



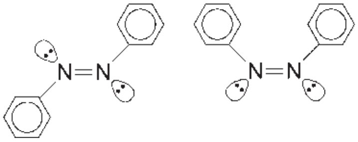
Do you know?

— The above is a good example that enantiomerism does not necessarily need a chiral carbon. So, the key concept about enantiomers is that as long as the isomers are non-superimposable mirror images of each other, it would rotate plane-polarized light in opposite directions.

(h) 
;

Explanation:

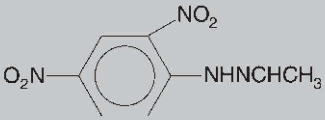
Cis-*trans*/Geometrical isomerism:



Do you know?

— *Cis*-*trans*/Geometrical isomerism is not restricted to the C=C double bond, and a lone pair of electrons can also be considered as a "group."

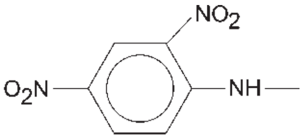
(i)

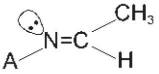


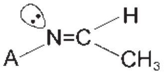
Explanation:

Cis-*trans*/Geometrical isomerism:

Let A be





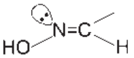


(j) HON=CHCH(OH)CH_3.

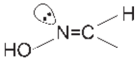
Explanation:

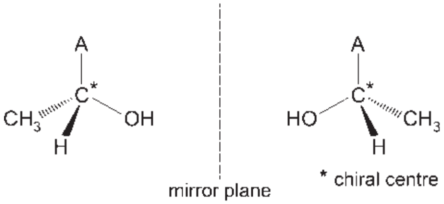
Cis-*trans*/Geometrical isomerism as well as enantiomerism:

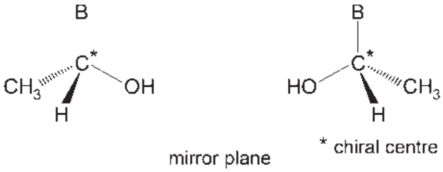
Let A be



Let B be







Since there are a total of two stereo-centers, the total number of stereoisomers is $2^2 = 4$. For a *cis*-isomer, there is a pair of enantiomers, likewise for the *trans*-isomer.

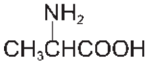
Q What is the relationship between an enantiomer of the *cis*-isomer and another enantiomer of the *trans*-isomer?

A: They are called *diastereomers*. Diastereomers are actually stereoisomers with the same constitutional/structural formula but different spatial orientations of the various groups of substituents in such a way that the molecules are non-superimposable with one another.

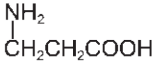
2. Using the isomeric amino acids $C_3H_7NO_2$ as examples, explain the meaning of the terms *constitutional/structural isomerism* and *enantiomerism*.

Explanation:

Constitutional/Structural isomerism refers to the phenomenon where compounds have the same molecular formula but different structures or constitutional/structural formulae. If we take the isomeric amino acids $C_3H_7NO_2$ as examples, their constitutional/structural isomers differ in the position of the $-NH_2$ group:

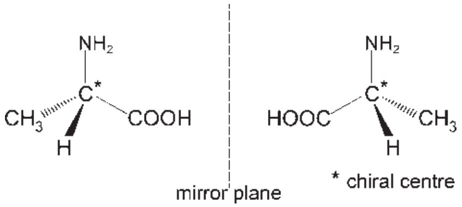


$CH_3\overset{\overset{NH_2}{|}}{C}HCOOH$



$\overset{\overset{NH_2}{|}}{C}H_2CH_2COOH$

Enantiomersim refers to the phenomenon where compounds have the same molecular formula and constitutional/structural formula, but differ in the spatial orientation of the groups of atoms. These compounds rotate plane-polarized light differently. If we take the isomeric amino acids $C_3H_7NO_2$ as examples, there is a chiral center, meaning there is an atom with four different groups of atoms bonded to it. As a result of this chiral center, the two mirror images are non-superimposable. Each mirror image rotate plane-polarized light by the same amount but in opposite directions.



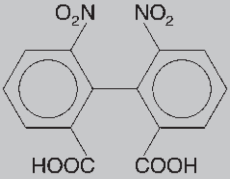
Q But how does a molecule rotate plane-polarized light?

A: Plane-polarized light consists of only one plane of changing electric field. When this plane-polarized light encounters a molecule, the electric field of the light interacts with the electron cloud. If the distribution of electron density is symmetrical, which means that there is no potential difference within the symmetrical electron cloud, the plane-polarized light is not rotated. But if the distribution of electron density is asymmetrical at every point in space, for example in a chiral molecule, then the plane-polarized light has different spatial interaction as it passes through the molecule. This results in a rotation of the plane-polarized light.

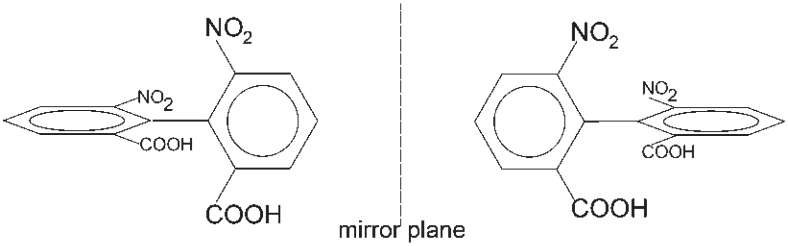
Q Then why does a pair of enantiomers rotate light in opposite directions but to the same degree?

A: A molecule of an enantiomeric pair has a asymmetrical distribution of electron density at every point in space. The other member of the same enantiomeric pair also has this same asymmetrical distribution of electron density, but it is actually a mirror image of the former. Thus, it accounts for the same degree of rotation but in opposite directions.

3. Explain how the following structure can occur as enantiomers.

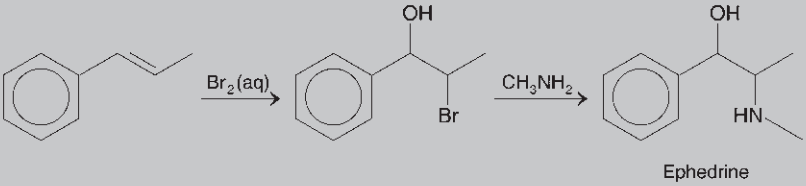


Explanation:



To minimize steric effect between the two $-NO_2$ groups and two –COOH groups, the two benzene rings are perpendicular to each other. As a result, the pair of mirror images becomes non-superimposable. Hence, they are a pair of enantiomers.

4. The synthesis of ephedrine, a decongestant medicine, is shown below:

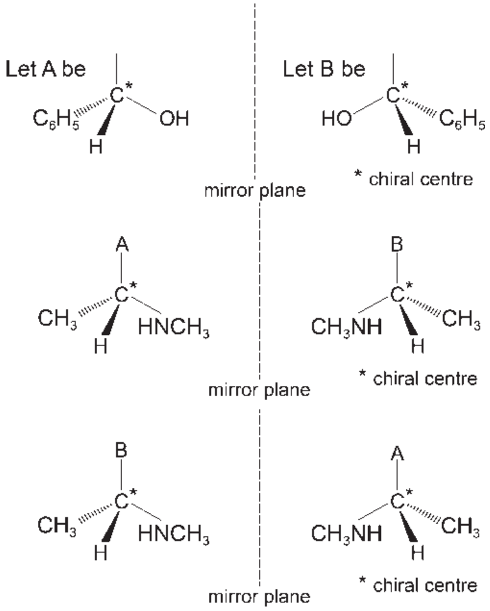


When the above synthetic route is used, four products with the same constitutional/structural formula are produced. Out of these four products, two have different melting points and solubilities in water.

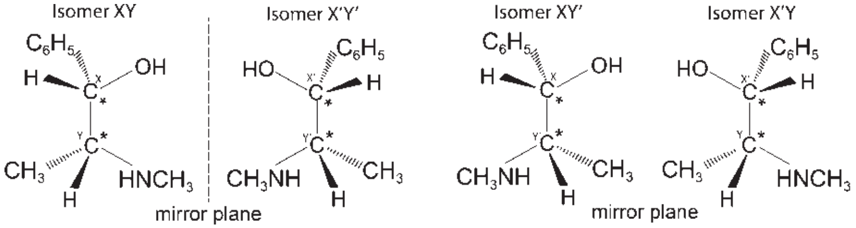
(a) Explain how four such isomers with the same constitutional/structural formula can arise and draw the three-dimensional structures to show the differences. Name the type of isomerism present.

Explanation:

There are a total of two chiral centers in ephedrine, hence a total of four possible enantiomers stereoisomers can arise. The type of isomerism is known as enantiomerism and the four isomers are shown below:



OR



(b) With the aid of labeled diagrams, explain the reasons for the differences in melting point and solubility of the four isomers.

Explanation:

A pair of enantiomers has the same melting point and solubility, but there is a difference in the rotation of plane-polarized light. From the diagram above, isomers XY and X'Y' are a pair of enantiomers, hence they have similar melting point and solubility; likewise for isomers XY' and X'Y. But isomers XY and XY' are not a pair of enantiomers; they are known as diastereomers, hence they would have different melting points and solubilities. This is similar for isomers X'Y' and X'Y.

(c) With reference to the constitutional/structural formula of ephedrine, explain why it can act as a decongestant.

Explanation:

A decongestant removes the water in the mucus that clogs the nasal passage. There is an –OH and a HN– group in ephedrine that are capable of forming hydrogen bonds with the water in the mucus that clogs the nasal passage.

5. Explain clearly each of the following terms:
   (a) empirical formula;

Explanation:

The empirical formula informs us about the simplest ratio of the *type* of atoms present in a molecule.

(b) molecular formula;

Explanation:

The molecular formula of a compound informs us of the *number* and *type* of atoms present in a molecule.

Do you know?

— The molecular formula is *n* times the empirical formula.

(c) constitutional/structural isomerism;

Explanation:

Constitutional/Structural isomerism is used to classify compounds that have the same molecular formula but different structures or constitutional/structural formulae.

(d) chain isomerism;

Explanation:

Chain isomerism is used to classify constitutional/structural isomers that have the same functional group but differ in the way that the carbon atoms are connected in the main skeletal carbon chain of their molecules. In other words, these molecules differ in the degree of branching and the length of the main carbon skeleton and hence the term *chain isomers*.

(e) positional isomerism;

Explanation:

Positional isomerism is used to classify structural isomers that have the same functional groups located at different positions along the same carbon chain. That is, the carbon skeleton of these isomers must be of the same length.

(f) functional group isomerism;

Explanation:

Functional group isomerism is used to classify structural isomers that have different functional groups.

(g) stereoisomerism;

Explanation:

Stereoisomerism is used to classify compounds that have the same molecular formula and structural formula but different spatial orientation of the atoms within their molecules.

(h) geometrical isomerism; and

Explanation:

Geometrical isomerism or *cis-trans* isomerism is a type of stereoisomerism where compounds have the same molecular formula and structural formula, but differ in the spatial orientation of groups of atoms because of restricted rotation about the C=C bond. The geometrical isomers differ in the relative spatial orientation of the substituents with respect to the C=C bond.

Do you know?

— Geometric isomerism can also arise because of restricted rotation in a cyclic structure. The criteria to exhibit geometric isomerism are exactly the same as for the C=C double bond.

(i) optical isomerism.

Explanation:

Optical isomerism is a type of stereoisomerism where compounds have the same molecular formula and structural formula, but differ in the spatial orientation of groups of atoms. These compounds rotate plane-polarized light differently.

CHAPTER 3

ORGANIC REACTIONS AND MECHANISMS

Do you know?

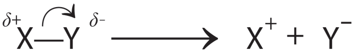
— *Types of bond cleavage*

- Homolytic bond cleavage

  The bonding electrons are equally shared by the two atoms, resulting in the formation of a free radicals.

- Heterolytic bond cleavage

  The bonding electrons are not equally shared by the two atoms, resulting in the formation of a cation (Lewis acid) and an anion (Lewis base).



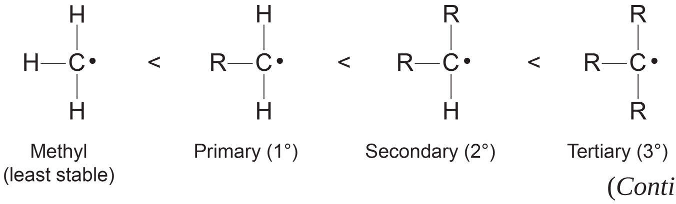
  A Lewis acid is an electron-pair acceptor while a Lewis base is an electron-pair donor.

— *Types of reaction intermediates*

- Free radical

  An electron-deficient species with unpaired electrons. The stability of a radical depends on the number of alkyl groups present.

  An alkyl group is able to diminish the electron deficiency on the carbon atom possessing the unpaired electron (sp^2 hybridized) through inductive effect.



(*Continued*)

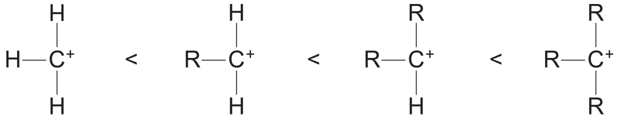
(*Continued*)

- Electrophile (Lewis acid)

  A species with an electron-deficient center, seeking out an electron-rich center.

  A carbocation (*sp*^{2} hybridized) is an electrophile, which is trigonal planar in shape. The stability of a carbocation depends on the number of alkyl groups present.

  An alkyl group is able to diminish the electron deficiency on the carbocation through inductive effect.



Methyl carbocation (least stable) 1° carbocation 2° carbocation 3° carbocation

- Nucleophile (Lewis base)

  A species with an electron-rich center, seeking out an electron-deficient center.

  A carbanion (*sp*^{3} hybridized) is a nucleophile.

— *Types of organic reactions*

- Rearrangement reaction

  Involves the shifting of atoms or bonds in a molecule to form a structural isomer of the original molecule.
- Redox reaction

  A simultaneous oxidation of a species with the reduction of another species.
- Addition reaction

  The degree of unsaturation decreases or the degree of saturation increases after the reaction.
- Elimination reaction

  The degree of unsaturation increases or the degree of saturation decreases after the reaction.
- Substitution reaction

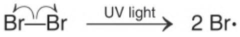
  The degree of unsaturation or saturation remains the same after the reaction.

1. Discuss the various types of reaction mechanisms between the following pairs of molecules:
   (a) butane and bromine in the presence of UV light;

Explanation:

Butane reacts with bromine in the presence of UV light via the Free Radical Substitution mechanism:

Step 1: Chain initiation with the generation of free radicals



Step 2: Chain propagation
(a) $Br\bullet + CH_3CH_2CH_2CH_3 \rightarrow CH_3CH_2CH_2CH_2\bullet + HBr$
(b) $CH_3CH_2CH_2CH_2\bullet + Br_2 \rightarrow CH_3CH_2CH_2CH_2Br + Br\bullet$
and the cycle repeats itself.

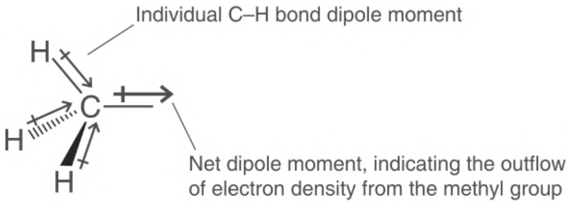
Step 3: Chain termination
$Br\bullet + CH_3CH_2CH_2CH_2\bullet \rightarrow CH_3CH_2CH_2CH_2Br$
$Br\bullet + Br\bullet \rightarrow Br_2$
$CH_3CH_2CH_2CH_2\bullet + CH_3CH_2CH_2CH_2\bullet \rightarrow CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$

Q Can the Br• radical attack any of the hydrogen atom in butane?

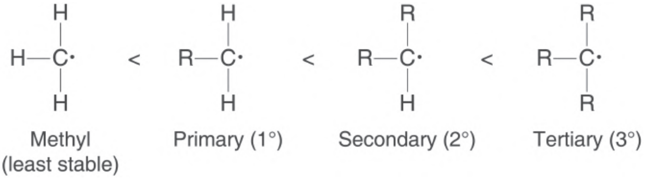
A: Yes, of course. If you look at butane, $CH_3CH_2CH_2CH_3$, there are a total of two types of H atoms: (i) six primary hydrogen atoms and (ii) four secondary hydrogen atoms. Although the Br• radical can attack any hydrogen atom, statistically we would get $CH_3CH_2CH_2CH_2Br : CH_3CH_2CHBrCH_3$ in the ratio of 6:4.

Q Would there be any differences in the stability of the different types of radicals form?

A: Yes, of course, it is known as the electronic effect. A radical is an electron-deficient species with an unpaired electron. On the other hand, an alkyl group, R, is an electron-donating group via inductive effect, as shown:



Hence, we would expect the stability of radical to increase from:



This is because, due to the electron-donating effect of the R group, the electron deficiency of the radical increases from: $R_3C\bullet < R_2CH\bullet < RCH_2\bullet < CH_3\bullet$. Thus, if we factor in this electronic effect together with the statistical factor, the ratio of $CH_3CH_2CH_2CH_2Br : CH_3CH_2CHBrCH_3$ is certainly going to be less than 6:4.

Do you know?

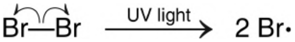
— There is no specific site on an alkane molecule that is especially electron-rich or electron-deficient, hence the species that is likely to attack an alkane would be a free radical.

(b) ethylbenzene and bromine in the presence of UV light;

Explanation:

Ethylbenzene and bromine in the presence of UV light via the Free Radical Substitution mechanism:

Step 1: Chain initiation with the generation of free radicals



Step 2: Chain propagation
(a) Br• + $C_6H_5CH_2CH_3 \rightarrow C_6H_5CH{\bullet}CH_3$+ HBr
(b) $C_6H_5CH{\bullet}CH_3 + Br_2 \rightarrow C_6H_5CHBrCH_3$ + Br•
and the cycle repeats itself.

Step 3: Chain termination
Br• + $C_6H_5CH{\bullet}CH_3 \rightarrow C_6H_5CHBrCH_3$
Br• + Br• → Br_2
$C_6H_5CH{\bullet}CH_3 + C_6H_5CH{\bullet}CH_3 \rightarrow C_6H_5(CH_3)CHCH(CH_3)C_6H_5$

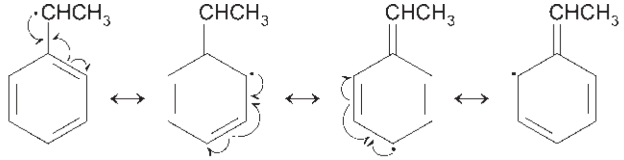
Q Why is the $C_6H_5CH{\bullet}CH_3$ radical being generated? Why can't the radical be $C_6H_5CH_2CH_2{\bullet}$?

A: Based on the statistical factor (the number of H atoms bonded to carbon atoms), the ratio would be 2:3 for (1-bromoethyl)benzene and (2-bromoethyl)benzene, respectively. On the other hand, with regard to the electronic factor, (1-bromoethyl)benzene will be the major product since it is formed from the more stable Radical 1 as compared to Radical 2 below.

Radical 1

Radical 2

Radical 1 is more stable than Radical 2. The electron deficiency on the former's carbon atom possessing the lone electron is diminished by a greater extent since it is bonded to a methyl group that is inductively electron-donating and the benzyl (–C_6H_5) group, which allows the lone electron to delocalize into the benzene ring as shown below:



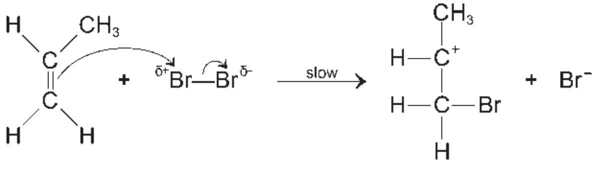
Through the delocalization, the electron deficiency is being "shared" over a greater number of atoms, hence it brings about greater stability.

(c) propene and bromine;

Explanation:

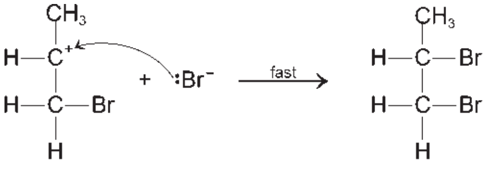
Propene reacts with bromine through the Electrophilic Addition mechanism:

Step 1: Electrophile (Lewis acid) attacks the electron-rich C=C bond (Lewis base) to form a carbocation intermediate.



carbocation

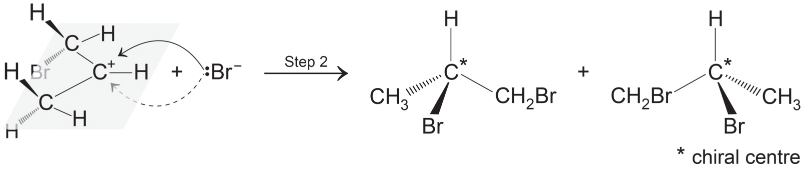
Step 2: Carbocation (Lewis acid) is readily attacked by Br^- (Lewis base) to form the final product.



halogenoalkane

Do you know:

- As the pi electron cloud of the C=C double bond is relatively electron-rich, alkene would be susceptible to attack by an electron-deficient species, i.e., an electrophile. As the pi bond is relatively weak to break compared to the formation of two C–Br sigma bonds, an alkene undergoes addition reaction.
- The carbocation is a trigonal planar sp^2 hybridized atom; as such, the products formed is a racemic mixture, which is optically inactive:

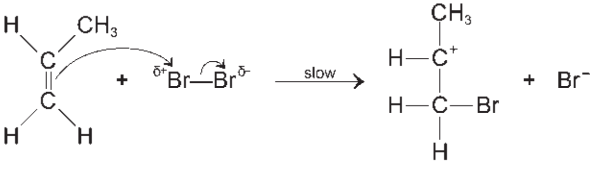


(d) propene and aqueous bromine;

Explanation:

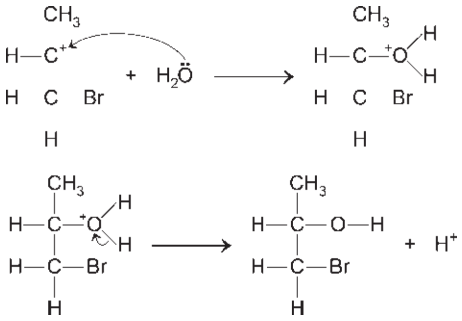
Propene reacts with aqueous bromine through the Electrophilic Addition mechanism:

Step 1: Electrophile (Lewis acid) attacks the electron-rich C=C bond (Lewis base) to form a carbocation intermediate.



carbocation

Step 2: Carbocation (Lewis acid) is readily attacked by H_2O (Lewis base), followed by losing a H^+ ion to form the final product, a bromohydrin.

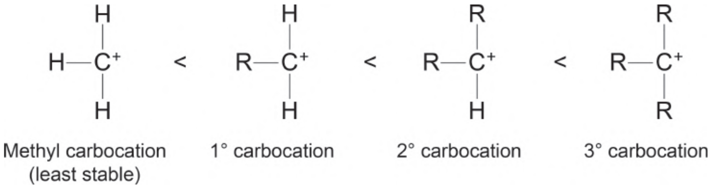


Q Why isn't the 1,2-dibromopropane the major product formed?

A: Once the carbocation is generated, as water molecules are present in abundance, it is statistically more reasonable for the carbocation to be attacked by the water molecule. Hence, the reaction generates bromohydrin as the major product.

Do you know?

- The formation of the bromohydrin is an evident that points toward the existence of the carbocation intermediate. Why is it so? Because without the carbocation as the intermediate, you won't get any 1-bromopropan-2-ol!
- Other than the formation of the above 1-bromopropan-2-ol, $CH_3CH(OH)CH_2Br$, we also have the 1,2-dibromopropane ($CH_3CHBrCH_2Br$) and 2-bromopropan-1-ol ($CH_3CHBrCH_2OH$) being formed. The $CH_3CH(OH)CH_2Br$ is formed in a larger amount than the $CH_3CHBrCH_2OH$ because the more stable secondary carbocation, $CH_3CH^+CH_2Br$, is formed in greater abundance.
- An alkyl group is known to be electron-releasing (via inductive effect) and thus, the electron deficiency on the carbon atom bearing the positive charge would be diminished by a greater extent when it is attached to more of these alkyl groups. Hence, the stability of a carbocation and its rate of formation increase in the following order:

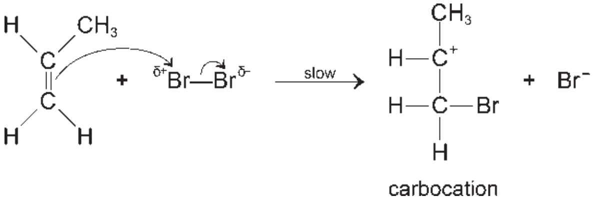


(e) propene and aqueous bromine in the presence of sodium cyanide (NaCN);

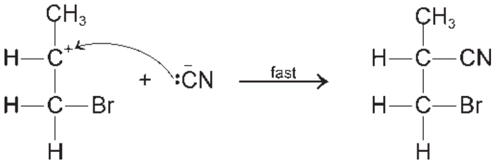
Explanation:

Propene reacts with aqueous bromine in the presence of NaCN through the Electrophilic Addition mechanism:

Step 1: Electrophile (Lewis acid) attacks the electron-rich C=C bond (Lewis base) to form a carbocation intermediate.



Step 2: Carbocation (Lewis acid) is readily attacked by CN^- (Lewis base).

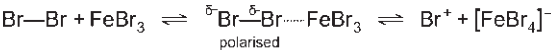


(f) benzene and bromine in the presence of $AlBr_3$ or $FeBr_3$;

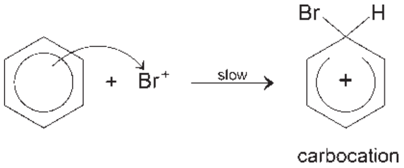
Explanation:

Benzene reacts with bromine in the presence of $FeBr_3$ via the Electrophilic Substitution mechanism:

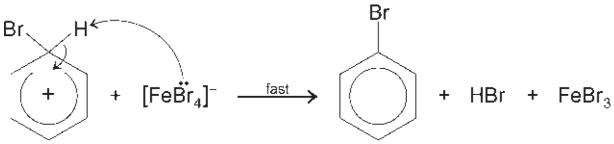
Step 1: Generation of the electrophile by the Lewis acid catalyst, $FeBr_3$.



Step 2: Electrophile (Lewis acid) attacks electron-rich benzene (Lewis base) to form a carbocation intermediate.



Step 3: The carbocation (Lewis acid) is deprotonated to regain the resonance-stabilized benzene ring, and the Lewis acid catalyst is regenerated.



Do you know:

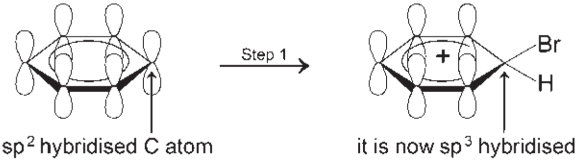
— As the pi electron cloud of the benzene ring is relatively electron-rich, benzene would be susceptible to attack by an electron-deficient species, i.e., an electrophile. But if the benzene is to undergo addition reaction like an alkene, it would lose its resonance stability. Hence, benzene undergoes the electrophilic substitution reaction instead.

— Unlike alkene, benzene needs a stronger electrophile as the attack involves destroying the resonance stability when forming the carbocation. Hence, the attack is the rate-determining step with high activation energy, and a catalyst is needed to help generate the strong electrophile.

— The regeneration of the resonance-stabilized benzene ring is a fast step.

Q What is the hybridization state of the carbocation?

A: The carbon atom under electrophilic attack changes from an sp^2 hybridized state to an sp^3 as follows:



(g) chlorobenzene with concentrated nitric and sulfuric acids;

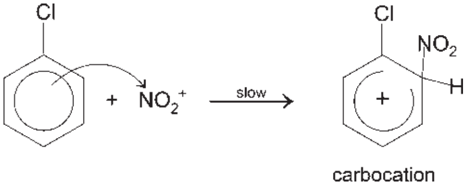
Explanation:

Chlorobenzene reacts with concentrated nitric and sulfuric acids via the Electrophilic Substitution mechanism:

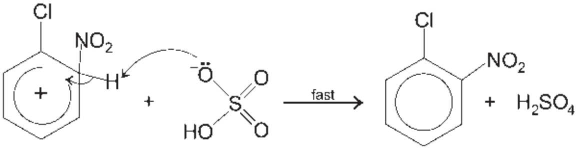
Step 1: The electrophile NO_2^+ is generated through the acid−base reaction below:

$$\underset{\text{(base)}}{HNO_3} + \underset{\text{(acid)}}{2H_2SO_4} \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-$$

Step 2: NO_2^+ electrophile (Lewis acid) attacks benzene (Lewis base) to form a carbocation intermediate.

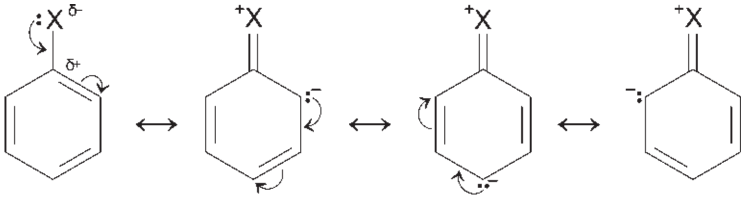


Step 3: Deprotonation of the carbocation (Lewis acid) to regain the resonance-stabilized benzene ring.



Q Why did the NO_2^+ electrophile attack the second position relative to the Cl group?

A: Actually, the electrophile could attack any of the remaining five positions but it attacks the 2nd, 4th, and 6th positions more readily. This is because the Cl group is a 2,4-director due to the delocalization of the lone pair of electrons from the Cl group into the benzene ring via *p–p* orbitals overlap:



As a result, the positions 2, 4, and 6 are much more electron-rich than position 3. Hence, the major products would be 2-nitrochlorobenzene and 4-nitrochlorobenzene.

(h) methylbenzene and chlorine in the presence of $AlCl_3$ or $FeCl_3$;

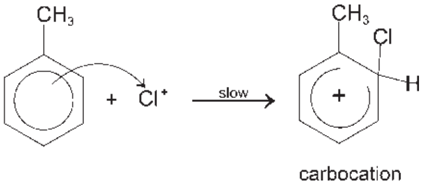
Explanation:

Methylbenzene reacts with chlorine in the presence of $AlCl_3$ via the Electrophilic Substitution mechanism:

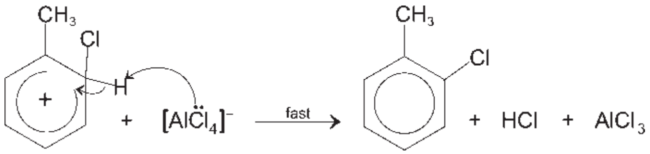
Step 1: Generation of the electrophile by the Lewis acid catalyst, $AlCl_3$.

$$Cl{-}Cl + AlCl_3 \rightleftharpoons \underset{\text{polarised}}{{}^{\delta+}Cl{-}\overset{\delta-}{Cl}\cdots AlCl_3} \rightleftharpoons Cl^+ + [AlCl_4]^-$$

Step 2: Electrophile (Lewis acid) attacks electron-rich benzene (Lewis base) to form a carbocation intermediate.

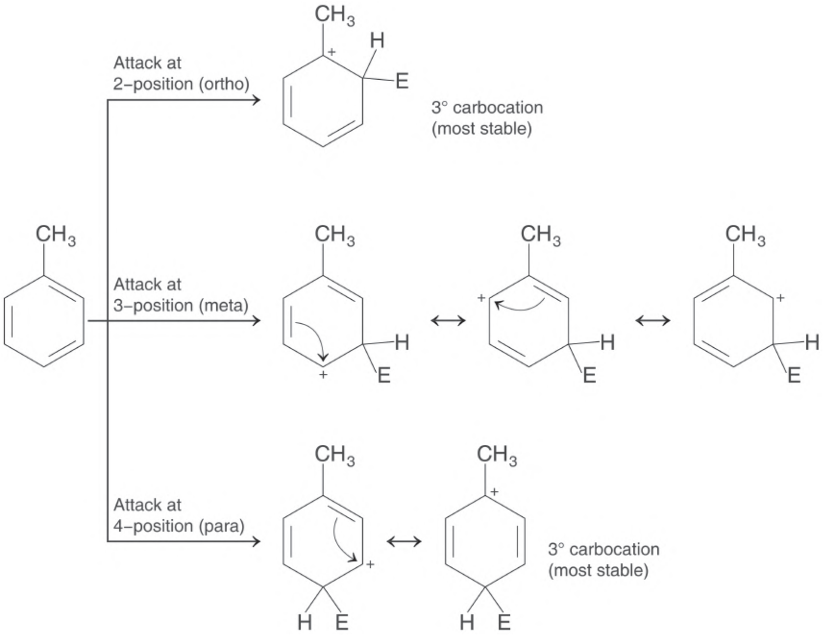


Step 3: The carbocation (Lewis acid) is deprotonated to regain the resonance-stabilized benzene ring, and the Lewis acid catalyst is regenerated.



Do you know?

— An alkyl group is a 2,4-director because of the following:



(i) 1-bromobutane and aqueous barium hydroxide with heating;

Explanation:

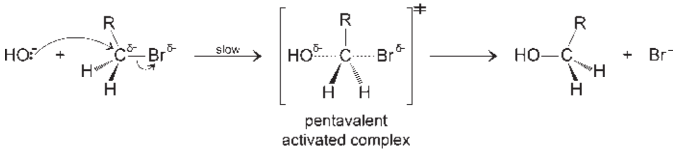
1-bromobutane reacts with aqueous barium hydroxide with heating via the Nucleophilic Substitution bimolecular (S_N2) mechanism:

Let R be $CH_3CH_2CH_2$–.

The one-step nucleophilic substitution mechanism is as follows:

- The nucleophile HO^- attacks the $^{\delta+}C$ from the side opposite to that of the C−Br bond in what is known as the “backside” attack.

- In a concerted move, the following can be thought to occur:
  - C−Br bond undergoes heterolytic cleavage and a Br^- ion is formed, which is known as the leaving group; and
  - C−OH bond is formed.



Q Why does the nucleophile approach from the "backside" route?

A: Due to the large size of the Br atom, the "backside" approach results in less steric hindrance (which is inter-electronic repulsion in nature) and hence resulting in a greater ease of accessibility to the $^{\delta+}C$ atom by the nucleophile. Furthermore, the repulsion between the electron clouds of the negatively charged HO^- and $^{\delta-}Br$ can be minimized. In addition, in order for the nucleophile to form a bond with the electron-deficient carbon atom, the donating pair of electrons has to "enter" the small lobe of the sp^3 hybrid orbital from the side that is opposite to that of the Br group.

Do you know?

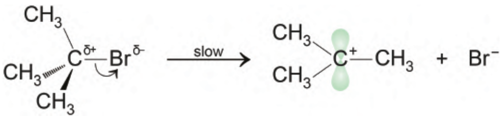
— If we start off with a molecule where the carbon atom bearing the halogen group is chiral, after going through the S_N2 mechanism, the optical activity of the product would be reversed! That is, we have an inverted product as compared to the reactant.

(j) 2-bromo-2-methylpropane and aqueous barium hydroxide with heating;

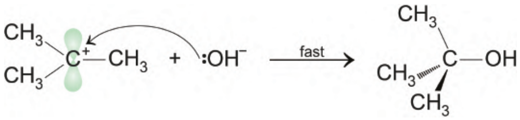
Explanation:

2-bromo-2-methylpropane reacts with aqueous barium hydroxide with heating via the Nucleophilic Substitution monomolecular (S_N1) mechanism:

Step 1: Formation of carbocation.

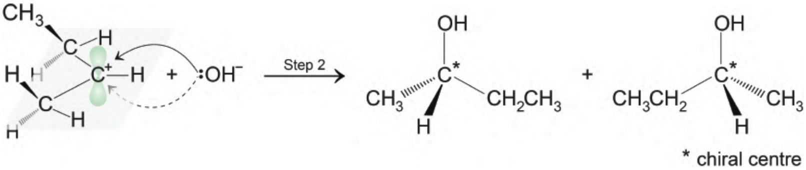


Step 2: Nucleophile (Lewis base) attacks the carbocation (Lewis acid) to form the final product.



Do you know?

— If we start off with a molecule where the carbon atom bearing the halogen group is chiral, after going through the S_N1 mechanism, we would get a racemic mixture.



This is because the carbocation formed is trigonal planar, thus the nucleophile has an equal chance of attacking from above or below the plane.

Q Step 1 of the S_N1 mechanism gives us the impression that the C−Br bond of the halogenoalkane simply cleaves on its own. Am I right about this?

A: No! The C–Br bond does not cleave "automatically." It is actually mediated by the approach of a nucleophile quite similarly to that in an S_N2. But the proximity of the nucleophile in an S_N1 reaction is farther than in an S_N2. As a result, the effect of the nucleophile is not great enough to make its "impact" visible in the rate equation. In addition, you could also imagine that as the nucleophile approaches the halogenoalkane from the "backside" route, it would repel against the electron clouds of the bulky alkyl groups. This inter-electronic repulsion would "push" the electron clouds of the bulky alkyl groups toward the Br atom. Thus, this "helps" the C–Br bond to cleave "on its own."

Q How would we know whether a particular halogenoalkane would undergo S_N1 or S_N2?

A: Usually, the more highly substituted the halogenoalkane, the more likely it would undergo the S_N1 mechanism due to (i) steric effect and (ii) electronic effect. There would be more bulky groups hindering the approach of the nucleophile for a more highly substituted halogenoalkane (steric effect). As for the electronic effect, the more highly substituted the halogenoalkane, the greater the stability of the carbocation that is being generated:

CH_3^+	<	RCH_2^+	<	R_2CH^+	<	R_3C^+
		1° carbocation		2° carbocation		3° carbocation
		(primary)		(secondary)		(tertiary)

(k) 1-bromobutane and alcoholic potassium hydroxide with heating;

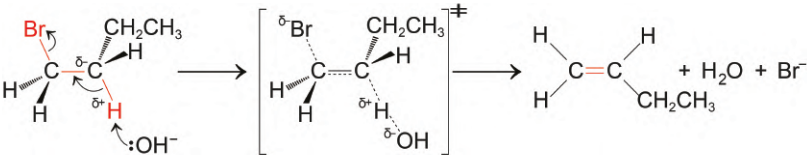
Explanation:

When 1-bromobutane reacts with alcoholic potassium hydroxide with heating, the Elimination reaction occurs.

The highly electronegative Br atom withdraws electron density inductively from the neighboring atoms. Being electron-deficient and thus acidic here, the α–H atom, on the C atom adjacent to the C−Br bond, can be easily extracted by a strong base.

In a concerted move, the following can be thought to occur:

- A strong base forms a dative covalent bond to the acidic H atom;
- Both the C−H and C−Br bonds undergo heterolytic cleavage, producing H^+ and Br^- ions as the leaving groups; and
- A pi bond is formed between these two C atoms.



Do you know?

— A nucleophile can function as a base and participate in the elimination reaction. But whether the elimination reaction would occur or not depends very much on the relative reactivity of the two reactants. Similarly, a base can also act as a nucleophile, but the nucleophilic reaction may not occur if the reactivity of the reactants are low.

— Thus, substitution and elimination are two competing reactions involving a nucleophile where both reactions will occur but to a different extent. Generally, to have elimination as the predominant reaction, a strong base is used. But if the nucleophile is a weak base or non-basic, then the main reaction will be nucleophilic substitution instead.

Q Why is the OH^- ion acting as a base in an alcoholic medium causing elimination to occur, whereas in an aqueous medium, it acts as a nucleophile?

A: The OH^- ion can be both a nucleophile and a base. In an aqueous medium, the OH^- ion is a very bulky species because it is surrounded by many layers of water molecules. The first layer of water molecules is attracted to the OH^- ion via ion–dipole interaction, and subsequent layers are attracted to each other via hydrogen bonding. But for the OH^- ion in ethanol, it is a much smaller solvated species. The first layer of ethanol molecules is attracted to the OH^- ion via ion–dipole interaction; as a result, the hydrophobic alkyl group would be pointing outward. Subsequent layers of the ethanol molecules are attracted via the weak id–id interaction.

Now, in a bulky hydrated OH^- ion, the negative charge is farther away from the peripheral than in the weakly solvated OH^- ion in ethanol. This would mean that the charge density of the hydrated OH^- ion would be much smaller than the solvated OH^- ion in ethanol. As a result, the ability of the bulky hydrated OH^- ion to "extract" the acidic hydrogen is lower than that of the solvated OH^- ion in an ethanol medium. This, renders the bulky hydrated OH^- ion a weaker base.

Q Now, based on your explanation, wouldn't the bulky hydrated OH^- ion face greater steric hindrance when trying to perform a nucleophilic attack than the weakly solvated OH^- ion?

A: You are right here. The bulky OH^- ion would face greater steric hindrance when performing a nucleophilic attack. If you have looked closely at the mechanism for elimination and compare it against nucleophilic substitution (as above), you would notice that the approach of the nucleophile or base is at the opposite direction to the halogen group for both mechanisms, but the "attacking species" are approaching the alkyl halide in the same direction relative to the position of the alkyl group. So before the "attacking species" reaches the electron-deficient carbon center, be it the highly hydrated OH^- ion or the weakly solvated OH^- ion in ethanol, the "first" atom encountered would be the acidic hydrogen. Thus, the weakly solvated OH^- ion would make elimination more likely to happen than nucleophilic substitution. Whereas for the highly hydrated OH^- ion, because the "first" contact with the acidic hydrogen would not result in elimination due to its lower charge density, further approaching the alkyl halide molecule would result in nucleophilic substitution instead. Thus, take note that in a nucleophilic substitution reaction, there is bound to be a minor amount of elimination products formed. Likewise, for the elimination reaction of alkyl halide, there is bound to have a minor nucleophilic substitution reaction.

(l) propanone and HCN with sodium hydroxide;

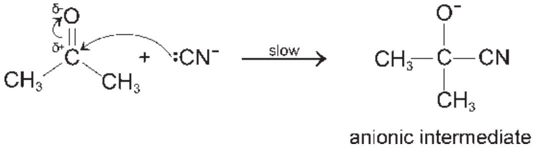
Explanation:

Propanone reacts with HCN and sodium hydroxide via the Nucleophilic Addition mechanism.

As HCN is a weak acid, $HCN \rightleftharpoons H^+ + CN^-$, the amount of CN^- is low. So, to increase the $[CN^-]$, NaOH(aq) as a catalyst is added:

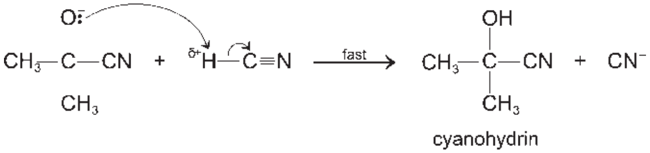
$$HCN + OH^- \rightarrow H_2O + CN^-$$

Step 1: Nucleophile (Lewis base) attacks the electron-deficient carbonyl carbon (Lewis acid) to form an anionic intermediate.

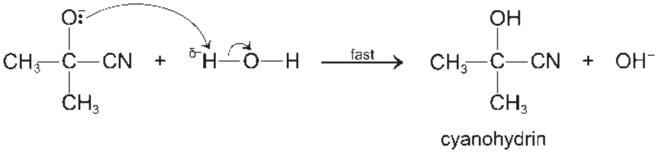


Step 2: The anionic intermediate (Lewis base) is protonated to form the final cyanohydrin product.

A proton can be extracted from the undissociated HCN (Lewis acid) molecule,



or it can be extracted from the H_2O (Lewis acid) solvent molecule.



Do you know?

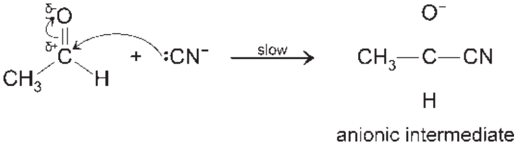
- As the NaOH is regenerated at the end of the reaction, the NaOH serves as a catalyst in the nucleophilic addition reaction.
- Nucleophilic addition of a carbonyl compound is a step-up reaction as the number of carbon atoms increases by one in the product as compared to the reactant.

(m) ethanal and KCN with sulfuric acid; and

Explanation:

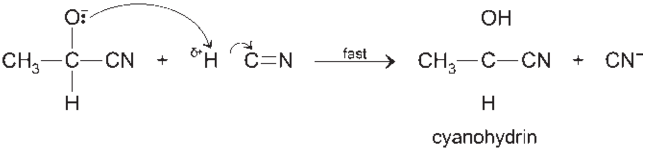
Ethanal reacts with KCN and sulfuric acid via the Nucleophilic Addition mechanism. The purpose of the sulfuric acid is to convert some of the CN^- to the HCN for Step 2.

Step 1: Nucleophile (Lewis base) attacks the electron-deficient carbonyl carbon (Lewis acid) to form an anionic intermediate.



Step 2: The anionic intermediate (Lewis base) is protonated to form the final cyanohydrin product.

A proton can be extracted from the undissociated HCN (Lewis acid) molecule.

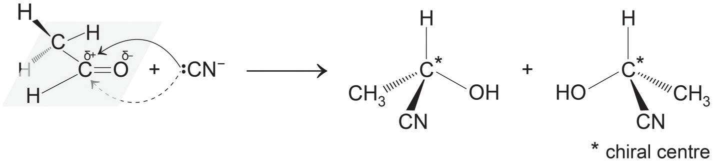


Q If the solvent can act as a proton donor and NaCN is the source of CN^-, can't we forego the use of HCN?

A: Now, the extraction of a H^+ ion from a water molecule is much more difficult than from a H–CN molecule. This is because the H–O (BE = +460 kJ mol^{-1}) bond is much stronger than the H–C bond (BE = +410 kJ mol^{-1}). Such an explanation also provides us with the understanding of why HCN, though is a weak acid, is still a stronger acid as compared to H_2O. So, in reality, extracting a H^+ ion from a water molecule to form the cyanohydrin is a minor reaction as compared to the extraction from a HCN molecule.

Do you know?

— Ethanal is an example of a prochiral molecule — an achiral molecule that can be transformed into a chiral molecule in one step. Just like a carbocation, the geometry around the *sp*^{2} hybridized carbonyl carbon atom is trigonal planar. The nucleophile can attack the carbonyl carbon from either side of the plane to form a racemic mixture (or racemate) containing equal proportions of the two optically active enantiomers.



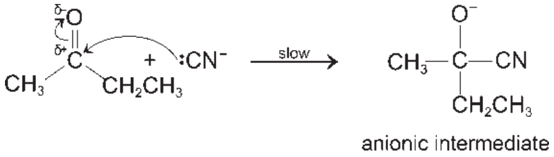
— Other than HCN/a small amount of NaOH(aq) and NaCN/H_2SO_4(aq), we can also use a combination of NaCN/HCN. The effect would still be nucleophilic addition.

(n) butanone and HCN with NaCN.

Explanation:

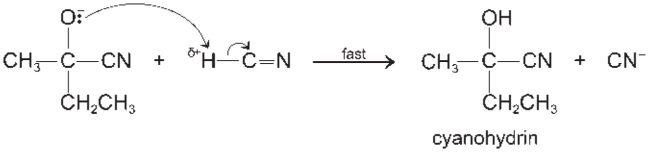
Butanone reacts with HCN and NaCN via the Nucleophilic Addition mechanism.

Step 1: Nucleophile (Lewis base) attacks the electron-deficient carbonyl carbon (Lewis acid) to form an anionic intermediate.



Step 2: The anionic intermediate (Lewis base) is protonated to form the final cyanohydrin product.

A proton can be extracted from the undissociated HCN molecule (Lewis acid).



2. (a) Describe the meaning of the term *homolytic fission*, using an organic reaction as an example.

Explanation:

In homolytic fission, when the bond breaks, the shared pair of electrons is distributed equally among the two atoms. This is common in the Free Radical Substitution reaction:

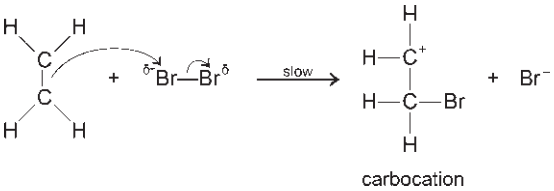
$$Br\bullet + CH_4 \rightarrow CH_3\bullet + HBr$$

(b) Describe the meaning of the term *heterolytic fission*, using an organic reaction as an example.

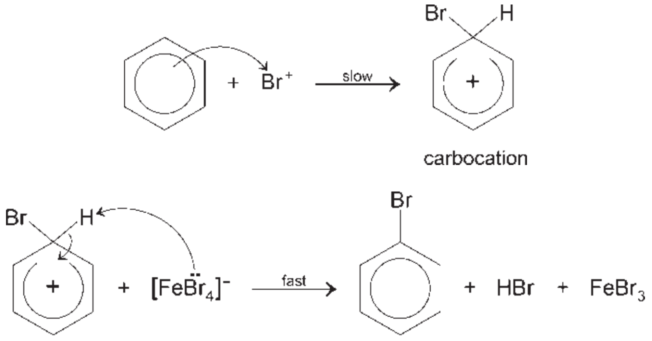
Explanation:

In heterolytic fission, when the bond breaks, the shared pair of electrons moved toward the more electronegative atom, resulting in the formation of charged species. There are many organic reactions that involve heterolytic bond cleavage:

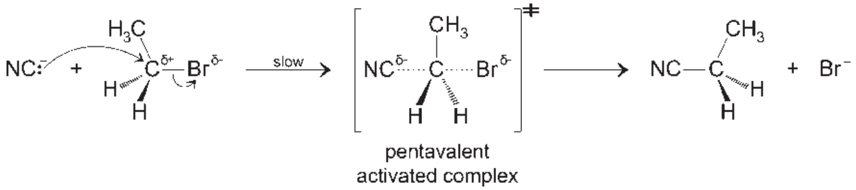
Electrophilic addition of alkene:

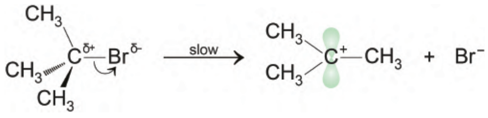


Electrophilic substitution of arene:

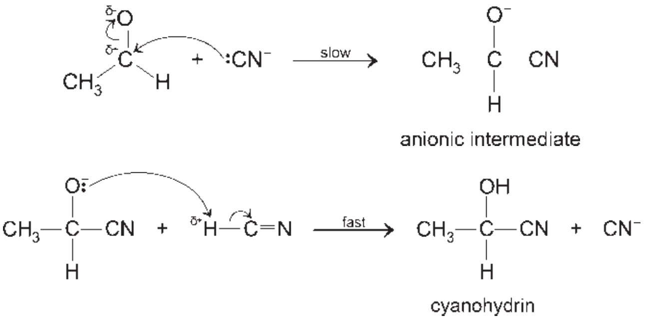


Nucleophilic substitution of halogenoalkane:

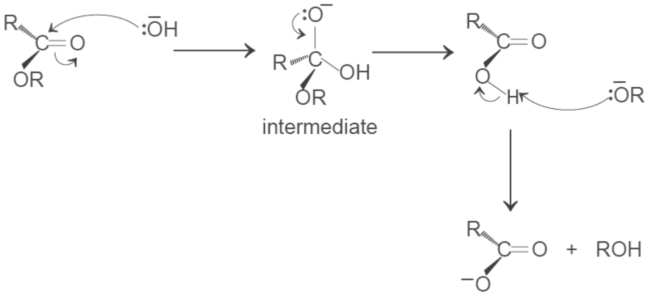




Nucleophilic addition of carbonyl:



Nucleophilic acyl substitution of carboxylic acid and its derivatives:



Do you know?

— In homolytic fission, the bond breaking is indicated by half arrows while in heterolytic bond cleavage, it is represented by a full arrow which signifies the movement of a pair of electrons.

Q The Br–Br bond is non-polar. Does this mean that it cannot undergo heterolytic cleavage?

A: No. The Br–Br bond can undergo heterolytic cleavage to give Br^+ and Br^- too. It all depends on the amount of energy that is present at the time of cleavage. If the right amount of energy is present for heterolytic cleavage to occur, then heterolytic cleavage will occur and not homolytic cleavage. Similarly, the polar H–Br bond can also undergo homolytic cleavage with the right amount of energy present.

(c) Why do halogenoalkanes react with nucleophiles at the carbon center but with electrophiles at the halogen atom?

Explanation:

In halogenoalkane, the $C^{\delta+}–X^{\delta-}$ is polar because the halogen atom, X, is more electronegative than the carbon atom. As a result, the nucleophile, which is an electron-rich species, would be attracted to the electron-deficient carbon atom. Whereas an electrophile, which is electron-deficient species, would be attracted to the electron-rich halogen atom.

(d) What do you understand by the *polarity* of a bond and what determines whether a bond is polar or not?

Explanation:

The polarity of a bond is an indication of how polar the bond is. It is usually measured by the dipole moment. How polar a bond is would depend very much on the electronegative differences between the two atoms that form the covalent bond.

CHAPTER 4

ALKANES

Do you know?

— Alkanes are non-polar molecules and only weak instantaneous dipole–induced dipole (id–id) interactions exist between their molecules. The melting and boiling points of alkanes only depend on the strength of the id–id interaction which is affected by:
  - *Number of electrons in the molecule*: The greater the number of electrons (i.e., the bigger the electron cloud), the more polarizable is the electron cloud, and the stronger is the id–id interactions; and
  - *surface area for contact of molecules*: The greater the surface area of contact possible between the molecules, the greater is the extent of id–id interactions.

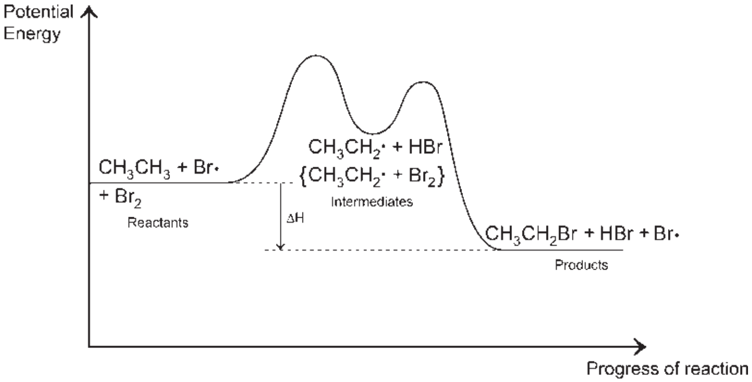
— Alkanes, being non-polar compounds, are soluble in non-polar organic solvents such as carbon tetrachloride (CCl_4), but insoluble in polar solvents such as water. This is due to the similar intermolecular attractive forces, i.e., van der Waals forces that exist between the non-polar molecules that lead to favorable mixing. In fact, hydrocarbons in the liquid state such as hexane and benzene are commonly used as non-polar solvents.

— If we look at the structure of any alkane, there are no electrostatically attractive features that draw in a potential attacking species. C−H bonds are essentially non-polar as both the carbon and hydrogen atoms have a rather smaller electronegativity difference. There are also no pi electrons as these are saturated molecules, with each carbon atom using all its valence electrons to form sigma bonds with four others. Subtly, it is this unattractive feature of the C−C and C−H bonds that form the backbone of all organic compounds and are responsible for their existence.

(*Continued*)

(*Continued*)

With their chemical inertness, reactions that do occur involve some form of energy input. Hence, the most common reaction mechanism that alkane would undergo is the Free Radical Substitution mechanism with an energy profile as shown below:



1. (a) When ethane reacts with bromine in light to produce the desired product, bromoethane, small traces of butane and other multiple brominated products are found after the reaction has completed.
   (i) Describe the mechanism for the formation of bromoethane.

Explanation:

The mechanism is the Free Radical Substitution:

Step 1: Chain initiation with the generation of free radicals

$$Br{-}Br \xrightarrow{\text{UV light}} 2\,Br\cdot$$

Step 2: Chain propagation
(a) Br• + CH_3CH_3 → CH_3CH_2• + HBr
(b) CH_3CH_2• + Br_2 → CH_3CH_2Br + Br•
and the cycle repeats itself.

Step 3: Chain termination
$Br\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2Br$
$Br\bullet + Br\bullet \rightarrow Br_2$
$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_3$

(ii) Describe the mechanism for the formation of 1,1-dibromoethane.

Explanation:

The mechanism is the Free Radical Substitution:

Step 1: Chain initiation with the generation of free radicals

Step 2: Chain propagation
(a) $Br\bullet + CH_3CH_3 \rightarrow CH_3CH_2\bullet + HBr$
(b) $CH_3CH_2\bullet + Br_2 \rightarrow CH_3CH_2Br + Br\bullet$
(c) $Br\bullet + CH_3CH_2Br \rightarrow CH_3CHBr\bullet + HBr$
(d) $CH_3CHBr\bullet + Br_2 \rightarrow CH_3CHBr_2 + Br\bullet$
and the cycle repeats itself.

Step 3: Chain termination
$Br\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2Br$
$Br\bullet + Br\bullet \rightarrow Br_2$
$Br\bullet + CH_3CHBr\bullet \rightarrow CH_3CHBr_2$
$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_3$
$CH_3CHBr\bullet + CH_3CHBr\bullet \rightarrow CH_3CHBrCHBrCH_3$
$CH_3CHBr\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CHBrCH_3$

Q Why are there more steps in the termination stage for the formation of 1,1-dibromoethane than for bromoethane?

A: This is because there are more types of radicals that are being generated during the formation of 1,1-dibromoethane. Hence, there are more possibilities for different types of radicals to meet. Some of the trace amounts of byproducts are in fact being formed during the termination stage.

(iii) Describe the mechanism for the formation of 1,2-dibromoethane.

Explanation:

The mechanism is Free Radical Substitution:

Step 1: Chain initiation with the generation of free radicals

Step 2: Chain propagation
(a) $Br\bullet + CH_3CH_3 \rightarrow CH_3CH_2\bullet + HBr$
(b) $CH_3CH_2\bullet + Br_2 \rightarrow CH_3CH_2Br + Br\bullet$
(c) $Br\bullet + CH_3CH_2Br \rightarrow CH_2\bullet CH_2Br + HBr$
(d) $CH_2\bullet CH_2Br + Br_2 \rightarrow CH_2BrCH_2Br + Br\bullet$
and the cycle repeats itself.

Step 3: Chain termination
$Br\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2Br$
$Br\bullet + Br\bullet \rightarrow Br_2$
$Br\bullet + CH_2\bullet CH_2Br \rightarrow CH_2BrCH_2Br$
$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_3$
$CH_2\bullet CH_2Br + CH_2\bullet CH_2Br \rightarrow CH_2BrCH_2CH_2CH_2Br$
$CH_2\bullet CH_2Br + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_2Br$

(iv) Describe the mechanism for the formation of 1,1,2-tribromoethane.

Explanation:

The mechanism is Free Radical Substitution, forming 1,2-dibromoethane first:

Step 1: Chain initiation with the generation of free radicals

Step 2: Chain propagation

(a) $Br\bullet + CH_3CH_3 \rightarrow CH_3CH_2\bullet + HBr$

(b) $CH_3CH_2\bullet + Br_2 \rightarrow CH_3CH_2Br + Br\bullet$

(c) $Br\bullet + CH_3CH_2Br \rightarrow CH_2\bullet CH_2Br + HBr$

(d) $CH_2\bullet CH_2Br + Br_2 \rightarrow CH_2BrCH_2Br + Br\bullet$

(e) $Br\bullet + CH_2BrCH_2Br \rightarrow CH_2BrCHBr\bullet + HBr$

(f) $CH_2BrCHBr\bullet + Br_2 \rightarrow CH_2BrCHBr_2 + Br\bullet$

and the cycle repeats itself.

Step 3: Chain termination

$Br\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2Br$

$Br\bullet + Br\bullet \rightarrow Br_2$

$Br\bullet + CH_2\bullet CH_2Br \rightarrow CH_2BrCH_2Br$

$Br\bullet + CH_2BrCHBr\bullet \rightarrow CH_2BrCHBr_2$

$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_3$

$CH_2\bullet CH_2Br + CH_2\bullet CH_2Br \rightarrow CH_2BrCH_2CH_2CH_2Br$

$CH_2\bullet CH_2Br + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_2Br$

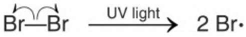
$CH_3CH_2\bullet + CH_2BrCHBr\bullet \rightarrow CH_3CH_2CHBrCH_2Br$

$CH_2BrCHBr\bullet + CH_2BrCHBr\bullet \rightarrow CH_2BrCHBrCHBrCH_2Br$

OR

The mechanism is the Free Radical Substitution, forming 1,1-dibromoethane first:

Step 1: Chain initiation with the generation of free radicals



Step 2: Chain propagation

(a) $Br\bullet + CH_3CH_3 \rightarrow CH_3CH_2\bullet + HBr$

(b) $CH_3CH_2\bullet + Br_2 \rightarrow CH_3CH_2Br + Br\bullet$

(c) $Br\bullet + CH_3CH_2Br \rightarrow CH_3CHBr\bullet + HBr$

(d) $CH_3CHBr\bullet + Br_2 \rightarrow CH_3CHBr_2 + Br\bullet$

(e) $Br\bullet + CH_3CHBr_2 \rightarrow CH_2\bullet CHBr_2 + HBr$

(f) $CH_2\bullet CHBr_2 + Br_2 \rightarrow CH_2BrCHBr_2 + Br\bullet$

and the cycle repeats itself.

Step 3: Chain termination

$Br\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2Br$

$Br\bullet + Br\bullet \rightarrow Br_2$
$Br\bullet + CH_3CHBr\bullet \rightarrow CH_3CHBr_2$
$Br\bullet + CH_2\bullet CHBr_2 \rightarrow CH_2BrCHBr_2$
$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_3$
$CH_3CHBr\bullet + CH_3CHBr\bullet \rightarrow CH_3CHBrCHBrCH_3$
$CH_3CHBr\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CHBrCH_3$
$CH_3CH_2\bullet + CH_2\bullet CHBr_2 \rightarrow CH_3CH_2CH_2CHBr_2$
$CH_2\bullet CHBr_2 + CH_2\bullet CHBr_2 \rightarrow CHBr_2CH_2CH_2CHBr_2$

(v) Describe the mechanism for the formation of butane.

Explanation:

Butane is a byproduct that is formed through the termination stage of the Free Radical Substitution mechanism:

Step 1: Chain initiation with the generation of free radicals

Step 2: Chain propagation
(a) $Br\bullet + CH_3CH_3 \rightarrow CH_3CH_2\bullet + HBr$
(b) $CH_3CH_2\bullet + Br_2 \rightarrow CH_3CH_2Br + Br\bullet$
and the cycle repeats itself.

Step 3: Chain termination
$CH_3CH_2\bullet + CH_3CH_2\bullet \rightarrow CH_3CH_2CH_2CH_3$

Did you know?

— We did not include other termination reactions as our sole purpose is to show how butane is formed when ethane reacts with bromine via the Free Radical Substitution mechanism.

(vi) How can you maximize the formation of bromoethane?

Explanation:

To obtain more of the monosubstituted product, the only way is to have more ethane than bromine. This increases the statistical chance of a bromine radical encountering an ethane molecule.

Q So, there is no way to avoid the formation of other side products?

A: You can't avoid the formation of other side products, as a radical is "blind" and remember, a reaction happens when particles collide. So, you can't prevent a radical from colliding with other parts of the molecule that are not intended to get our desired product.

(vii) How can you maximize the formation of hexabromoethane?

Explanation:

To obtain more of the highly substituted product, the only way is to have more bromine than ethane. This would allow brominated ethane to undergo further bromination.

(viii) Suggest a simple way to separate the desired product from the mixture of products.

Explanation:

The mixture of products can be separated through fractional distillation since each compound would have its own unique boiling point due to the different strengths of intermolecular forces.

(b) When 50 cm^3 of gaseous hydrocarbon, **P**, was completely combusted with 400 cm^3 of oxygen gas, the residual gases occupied 300 cm^3 at r.t.p. After passing through barium hydroxide solution, the final volume was 100 cm^3.

(i) Why was there a decrease in volume when residual gases were shaken with aqueous barium hydroxide? Give a balanced equation for the reaction.

Explanation:

The decrease in volume is brought about by the reaction of CO_2 gas with the hydroxide ions as shown below:

$$CO_2(g) + 2OH^-(aq) \rightarrow CO_3^{2-}(aq) + H_2O(l).$$

Do you know?

— CO_2 is an acidic gas that dissolves in water to give weak carbonic acid:

$$CO_2(g) + H_2O(l) \rightleftharpoons H_2CO_3(aq).$$

(ii) Determine the molecular formula of **P**.

Explanation:

Volume of O_2 used = 300 cm^3.

Volume of CO_2 used = (300 − 100) = 200 cm^3.

Let the hydrocarbon be C_xH_y:

$$C_xH_y(g) + \left(x + \frac{y}{4}\right) O_2(g) \rightarrow xCO_2(g) + \frac{y}{2}\ H_2O(l).$$

According to $pV = nRT$, under constant p and T, $V \propto n$.

Ratio of $C_xH_y : CO_2 = 50 : 200 = 1{:}4 \Rightarrow x = 4$.
Ratio of $C_xH_y : O_2 = 50 : 300 = 1{:}6 = 1 : (x + \frac{y}{4}) \Rightarrow (x + \frac{y}{4}) = 6 \Rightarrow y = 8$.
The molecular formula of **P** is C_4H_8.

Do you know?

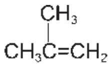
— The molecular formula of an alkane is C_nH_{2n+2} while that of cycloalkane is C_nH_{2n}, which is similar to that of alkene, C_nH_{2n}. Hence, two hydrogen atoms can "trade" for a double bond or a ring structure!

(i) Give the constitutional/structural formulae of six possible compounds with this molecular formula.

Explanation:

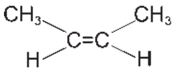
$CH_3CH_2CH{=}CH_2$

but-1-ene

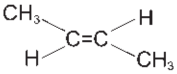


$$\begin{array}{c} \quad CH_3 \\ \quad | \\ CH_3C{=}CH_2 \end{array}$$

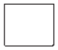
methylpropene



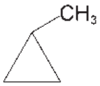
cis-but-2-ene



trans-but-2-ene



cyclobutane



methylcyclopropane

(iv) Which of the six constitutional/structural formulae show compounds which are

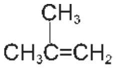
(A) constitutional/structural isomers;

Explanation:

The constitutional/structural isomers are:

$CH_3CH_2CH=CH_2$

but-1-ene



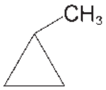
$CH_3C(CH_3)=CH_2$

methylpropene

$CH_3CH=CHCH_3$

but-2-ene

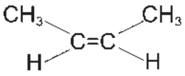
cyclobutane



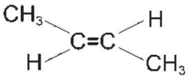
methylcyclopropane

(B) stereoisomers;

Explanation:



cis-but-2-ene



trans-but-2-ene

(C) enantiomers?

Explanation:

There is no chiral atom, hence there are no enantiomers.

(c) Methane and chlorine react only very slowly in the dark, but in bright sunlight, the reaction takes place readily to give a mixture of organic products. Explain.

Explanation:

In bright sunlight, Br_2 undergoes homolytic cleavage to give a highly reactive bromine radical which initiates the Free Radical Substitution mechanism.

(d) When pentane is treated with a solution of bromine in CCl_4 in the presence of sunlight, the reddish-brown coloration disappears and steamy white fumes evolve. Identify the white fumes.

Explanation:

The white fumes are HBr gas.

Do you know?

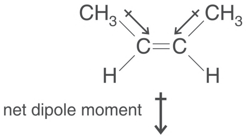
— The disappearance of the reddish-brown coloration of bromine and the appearance of the fumy HBr can serve as characteristics test for the presence of an alkane. But take note that this is only applicable if the reaction conditions consist of light or strong heating!

CHAPTER 5

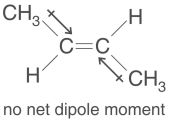
ALKENES

Do you know?

- Like alkanes, alkenes are essentially non-polar molecules. The strength of the instantaneous dipole–induced dipole interactions increases as the number of carbon atoms increases, and decreases with an increase in branching.
- Unlike alkanes, an alkene is able to exhibit *cis*-*trans*/geometrical isomerism. As a result, the *cis* alkene is relatively more polar than the *trans* alkene. This causes the *cis* alkene to have a higher boiling point than the *trans* alkene due to the presence of relatively stronger permanent dipole–permanent dipole interactions.



cis-but-2-ene
(b.p. 4 °C)



trans-but-2-ene
(b.p. 1 °C)

But if the melting point of *cis* alkene is lower than that of the *trans* alkene, then the reason is because the *trans* alkene packs more effectively than the *cis* alkene due to the *trans* alkene being a more symmetrical molecule. As a result, the intermolecular forces between the *trans* alkene molecules in the solid state are more extensive than those for the *cis* alkene.

In addition, the *trans* alkene can also have a higher boiling point than the *cis* alkene because of the presence of intra-molecular hydrogen

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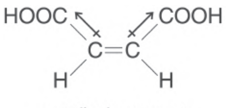
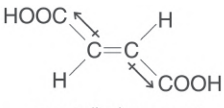
bonding brought about by the proximity of the two –COOH groups as shown below:


net dipole moment

cis-butenedioic acid
(b.p. 160 °C)

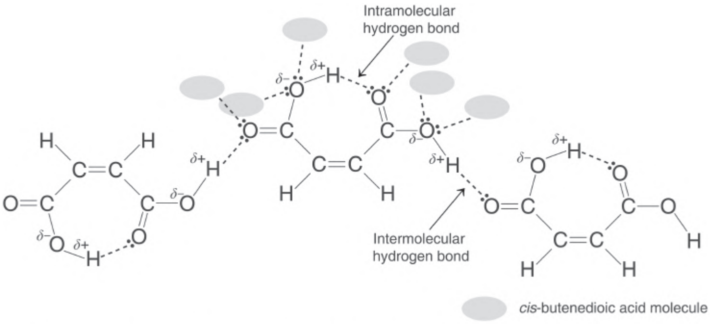

no net dipole moment

trans-butenedioic acid
(b.p. 290 °C)

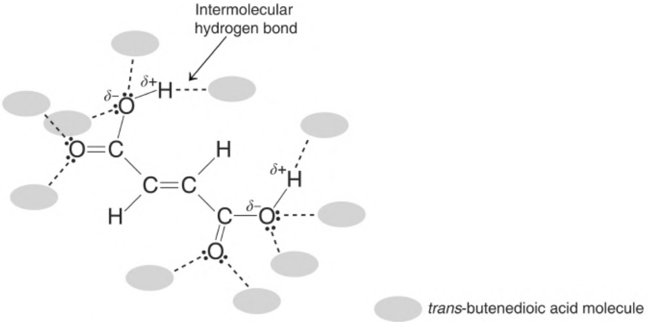
The presence of intra-molecular hydrogen bonding in the *cis* alkene limits sites available for inter-molecular hydrogen bonding to form. This thus lowers the boiling point of the compound.

Q Would *cis*-butenedioic acid have a lower solubility than *trans*-butenedioic acid?

A: Yes, we would expect *cis*-butenedioic acid to have a lower solubility than *trans*-butenedioic acid because the presence of intramolecular hydrogen bonding limits sites available for intermolecular hydrogen bond formation:



Less extensive intermolecular hydrogen bonding in *cis*-butenedioic acid



More extensive intermolecular hydrogen bonding in *trans*-butenedioic acid

Q Which is more acidic, *cis*-butenedioic acid or *trans*-butenedioic acid?

A: When *cis*-butenedioic acid dissociates, the $–COO^-$ group is near an undissociated –COOH group; the stability of the conjugate base is increased because the hydrogen bonds that are formed between the $–COO^-$ and –COOH groups help to disperse the electron density on the negatively charged $–COO^-$ group. All these are absent in the *trans*-butenedioic acid.

Q How does the formation of hydrogen bonds help to disperse the electron density?

A: When the electron-deficient H atom is attracted to the lone pair of electrons during the formation of the hydrogen bonds, the electron density of the lone pair of electrons is being "pulled away" from the donor atom. Hence, the electron density of this lone pair of electrons on the donor atom decreases.

Q How can we account for the lower acidity of the second –COOH group as compared to the first –COOH group for *cis*-butenedioic acid?

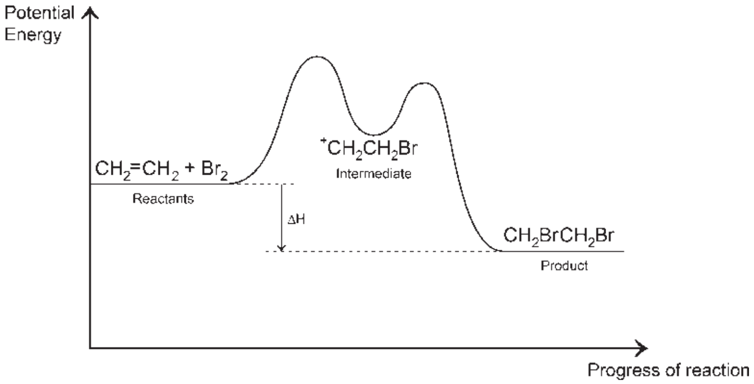
A: Normally, we would just say that the second dissociation is weaker than the first one because (i) it is more difficult to remove a H^+ ion from an already negatively charged species, and (ii) the H^+ ion that is produced from the first dissociation would suppress the second dissociation due to the common ion effect. For *cis*-butenedioic acid, we can bring in the third reason, which is, when the second dissociation occurs, the stability of the conjugate base brought about by the formation of hydrogen bonds between the $-COO^-$ and $-COOH$ groups is lost. Moreover, there is inter-electronic repulsion between the two $-COO^-$ groups which are in close proximity. Hence, the conjugate base that is formed after the second dissociation is even less stable.

Q So, based on your argument above, can we say that the second dissociation of *trans*-butenedioic acid would be greater than that of the *cis*-butenedioic acid?

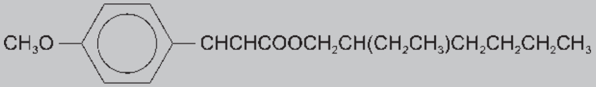
A: Yes, it should be. This is because there would be less inter-electronic repulsion between the two $-COO^-$ groups which are far apart.

Do you know?

— If we look back at the structure of an alkene, the electron-rich C=C double bond allows electron-deficient species to attack it. As the pi bond is relatively weak, it is viable for alkenes to undergo Electrophilic Addition reaction to trade the weak pi bond for two stronger sigma bonds. The energy profile of the Electrophilic Addition mechanism is shown below:



1. The following compound, **X**, 2-ethylhexyl-4-methoxycinnamate, is capable of UV absorption, hence it is commonly used in sunscreens lotion. The constitutional/structural formula of **X** is:



   (a) (i) Name three functional groups present in **X**.

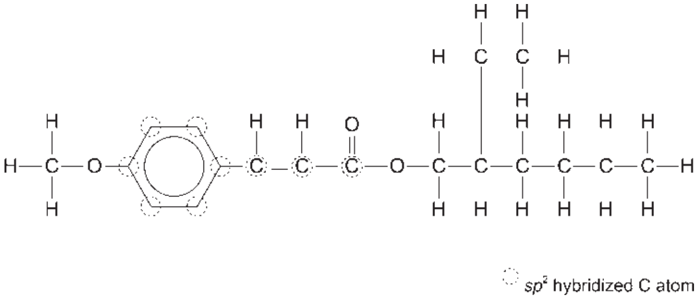
Explanation:

The three functional groups present in **X** are: alkene, ether, and ester.

(ii) Identify the *sp*^{2} hybridized carbon atoms in **X**.

Explanation:

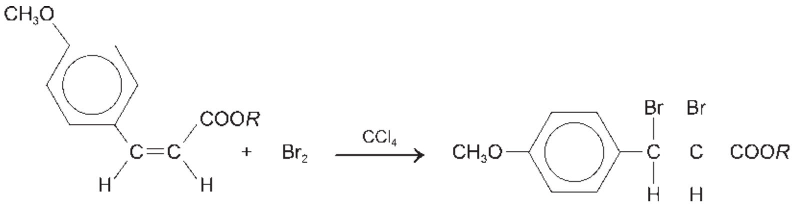
There are nine *sp*^{2} hybridized carbon atoms in **X**.



(iii) Compound **X** is an unsaturated compound. Describe a chemical test to demonstrate the presence of unsaturation in this molecule. Give the reagents, conditions, balanced equation, as well as observations.

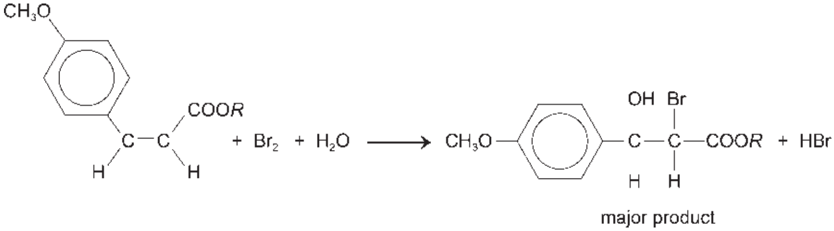
Explanation:

Test: Add Br_2 in CCl_4 to compound **X** at room temperature.
Observations: Decolorization of reddish-brown Br_2 will be observed.
Equation:



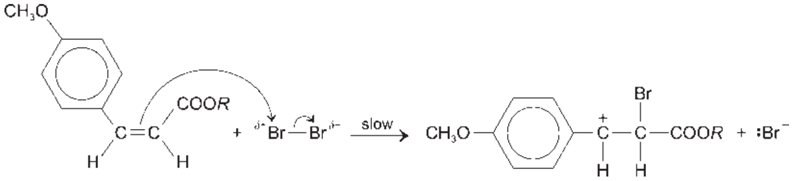
R denotes $-CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$ group

An alternative test is to use $Br_2(aq)$ at room temperature. Decolorization of yellowish-brown $Br_2(aq)$ will be observed.

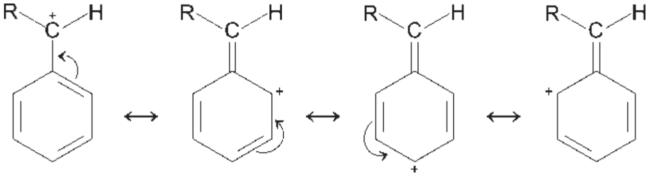


Do you know?

— Both reactions involving bromine are Electrophilic Addition reactions. In fact, the first step of both mechanisms generates the same carbocations, of which the more stable one is shown below:



The above carbocation is especially stable because the positive charge can delocalize into the benzene ring as shown below:



Different products are obtained because different nucleophiles come into the picture in the second stage. When compound **X** reacts with Br_2 in CCl_4, there is only the Br^- nucleophile. Whereas in the case of $Br_2(aq)$, not only do we have the Br^-, we also have H_2O molecules as nucleophiles. Both these species can donate an electron pair to form a bond with the electron-deficient carbocation and subsequently gives

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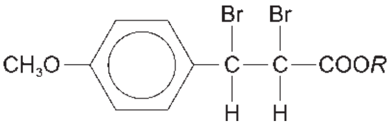
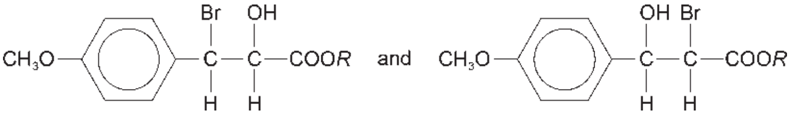
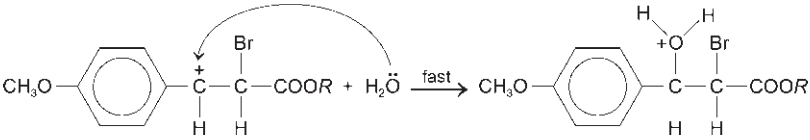
rise to different products. When Br^- attacks the carbocation, a dibromo compound is formed as the minor product:



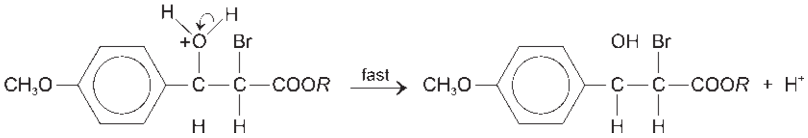
As H_2O molecules are present in much greater quantity (since water is the solvent), the chances of the carbocation reacting with H_2O are much higher, and this leads to a greater proportion of halohydrin products being formed:



In forming the halohydrin, the following subsequent steps occur in the Electrophilic Addition mechanism:



After donating a lone pair of electrons to form a dative covalent bond with the C atom, the O atom now acquires a positive charge. Since it is very electronegative, the O atom subsequently loses a proton to form the halohydrin product.

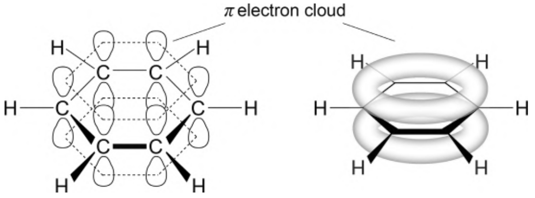


Q The positive centre of the species is residing in the nucleus, how can the "nucleus delocalize" when you said that the positive charge delocalized into the benzene ring?

A: Yes, in reality, it is not the "movement" of the positive charge, rather it is the movement of electron density out from the benzene ring to help disperse the electron-deficiency of the carbocation. But with this said, we cannot say that the benzene ring is electron-donating by resonance!

Q Arenes, like alkenes, are unsaturated hydrocarbons. Why can't we test for the presence of benzene using Br_2 in CCl_4?

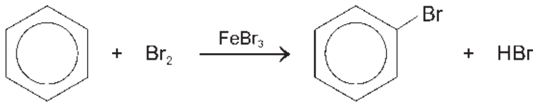
A: Benzene does not exhibit chemically similar behavior as alkenes. With the availability of pi electrons (which are less strongly bonded than sigma electrons), both benzene and alkene are susceptible to attack by electrophiles, with alkenes being more so. This is because the electron density at the alkene C=C bond is relatively higher with two pi electrons distributed between two C atoms. For benzene, the six pi electrons are delocalized over the entire network of six carbon atoms, resulting in an "average" of one pi electron between two C atoms.



More aptly, it is said that the carbon–carbon bond of a benzene molecule is intermediate between a single bond and a double bond, i.e., an average of about one and a half bond. Hence, the carbon–carbon bond of a benzene molecule is less electron-rich than the C=C bond of an alkene. Therefore, the benzene does not polarize the Br_2 molecule as greatly as an alkene. In order for benzene to react with the poor electrophile, Br_2, a Lewis acid such as anhydrous $FeBr_3$ has to be added so as to generate the stronger electrophile Br^+:

$$Br{-}Br + FeBr_3 \rightleftharpoons \underset{\text{polarised}}{\overset{\delta+}{Br}{-}\overset{\delta-}{Br}\cdots FeBr_3} \rightleftharpoons Br^+ + [FeBr_4]^-$$

Nonetheless, even with the Br^+ being generated, benzene does not undergo the Electrophilic Addition reaction as readily as alkenes. The extensive network of delocalized pi electrons confers added stability to the benzene molecule and this resonance stability would be destroyed if benzene undergoes an addition reaction. Thus, benzene undergoes mostly Electrophilic Substitution reactions such as the following:



The reaction with Br_2 in CCl_4 can thus be used to distinguish between an alkene and benzene. It also highlights the fact that benzene is less reactive than an alkene, i.e., a benzene molecule is less electron-rich than an alkene molecule.

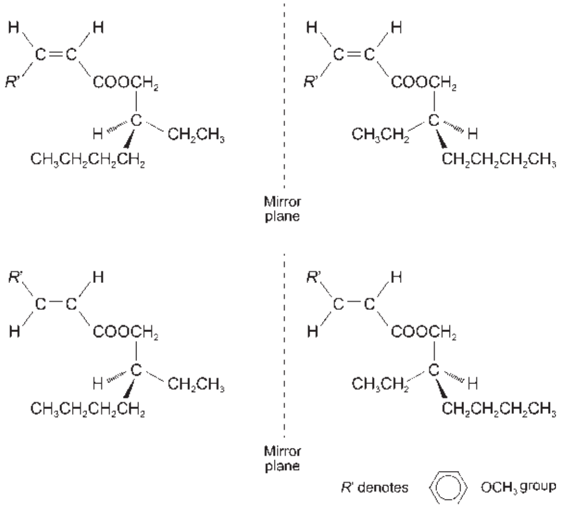
Q How does a Lewis acid polarize the Br_2 molecule?

A: A Lewis acid is an electron-pair acceptor, and in this way, it reduces the electron density on the donor atom, i.e., a Br atom in the Br_2 molecule. As a result, the Br–Br bond is weakened to an extent that it cleaves heterolytically. $FeBr_3$ is able to function as a Lewis acid because the Fe center is electron-deficient and has a low-lying vacant orbital to accommodate the lone pair of electrons from the donor atom. In addition, the high charge density of the metal center enables it to exert a stronger attraction on the electron cloud of the donor atom.

(iv) Compound **X** exhibits stereoisomerism. Name the types of stereoisomerism that is/are present in compound **X** and draw all the possible stereoisomers.

Explanation:

Compound **X** exhibits both *cis-trans*/geometrical and enantiomerism. Hence, there are four possible stereoisomers:

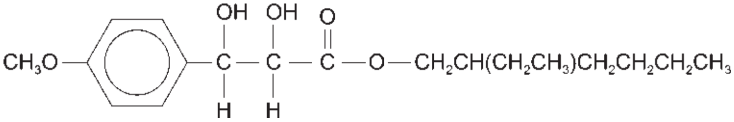


(b) Give the structures of the organic products formed when compound **X** undergoes the following reactions:

(i) addition of cold alkaline potassium manganate(VII);

Explanation:

Compound **X** undergoes mild oxidation where the carbon–carbon pi bond is cleaved and a diol is formed:



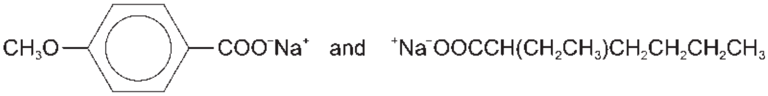
Q Would the ester functional group undergo alkaline hydrolysis here?

A: No! This is because no heating is applied.

(ii) heating under reflux with alkaline potassium manganate(VII);

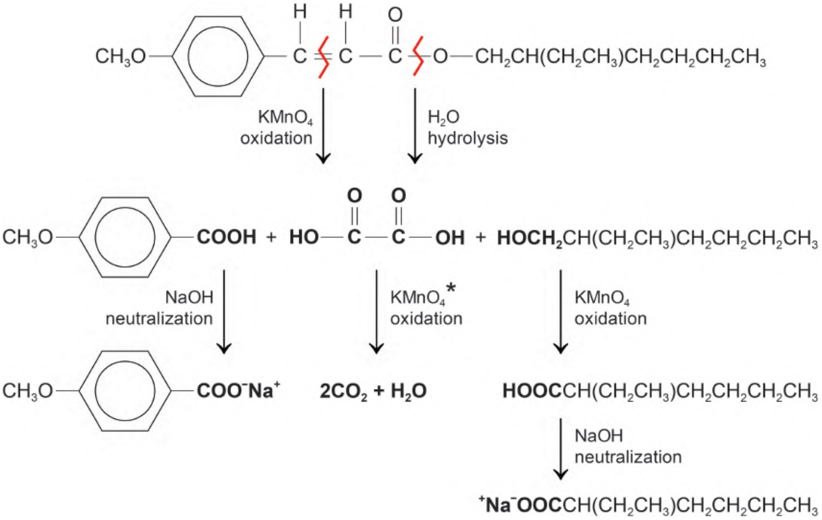
Explanation:

Three reactions would occur: alkaline hydrolysis of the ester functional group, oxidation, and an acid–base reaction. As a result, two organic products are formed:



Do you know?

— One way of solving this question is to do a step-wise tackling of each type of reaction. Begin with the hydrolysis of the ester functional group. Next, tackle all possible oxidation reactions such as the oxidative cleavage of the C=C bond and the primary alcohol formed from the hydrolysis of the ester. Take note that ethanedioic acid is further oxidized by $KMnO_4$ to give CO_2(g). Lastly, since the medium is alkaline, focus on the presence of any acidic groups as these can undergo neutralization. The following diagram shows how the final products are derived:



*On a molecular level, some ethanedioic acid would be oxidized and others neutralized to form ethanedioate salt. The latter is also oxidized by $KMnO_4$ to CO_2. Thus, although reactions in reality do not occur in such a step-wise manner, the above approach allows us to break up the problem into more manageable chunks.

Q How is it possible that ethanedioic acid is oxidized to CO_2 and not the other carboxylic acids?

A: The C–C bond in ethanedioic is relatively weak because of the electron-withdrawing effect of four highly electronegative O atoms attached to these C atoms. Hence, it is easily cleaved and readily oxidized to form CO_2 and H_2O.

Q Is it possible to oxidize the primary alcohol to a carboxylic acid without further oxidizing ethanedioic acid?

A: Yes, we can replace $KMnO_4$ with the weaker oxidizing agent $K_2Cr_2O_7$ which cannot oxidize ethanedioic acid. The weaker oxidizing strength of $K_2Cr_2O_7$ can be explained by its less positive standard reduction potential value as shown:

$$\begin{array}{ll} & \underline{E^{\theta}/V} \\ MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O & +1.52 \\ Cr_2O_7^{2-} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{3+} + 7H_2O & +1.33 \end{array}$$

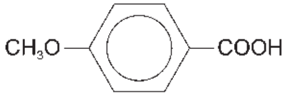
Q Why doesn't the diol obtained in part (*i*) further oxidized since both reactions in parts (*i*) and (*ii*) use alkaline $KMnO_4$?

A: The difference is attributed to the different temperatures used in each reaction. Hot alkaline $KMnO_4$ is a stronger oxidizing agent than cold alkaline $KMnO_4$. It would cause the cleavage of the C=C bond, in contrast to just pi bond cleavage when cold alkaline $KMnO_4$ is used.

(iii) heating under reflux with alkaline potassium manganate(VII), followed by acidification;

Explanation:

After obtaining the products from part (*ii*), subsequent acidification causes the protonation of the basic carboxylate ions to form the respective conjugate acids:

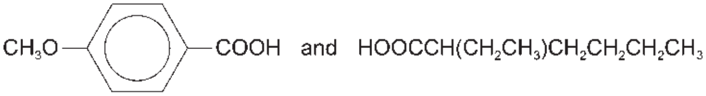


and $HOOCCH(CH_2CH_3)CH_2CH_2CH_2CH_3$

(iv) heating under reflux with acidified potassium manganate(VII);

Explanation:

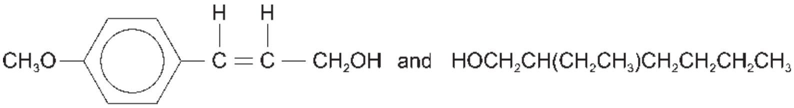
Under such conditions, three possible reactions would occur: acidic hydrolysis, oxidation and an acid–base reaction. Since there are no basic groups present, only acidic hydrolysis of the ester group and oxidation occurs to produce the following two organic products:



(v) addition of LiAlH$_4$ in dry ether, followed by warming with water;

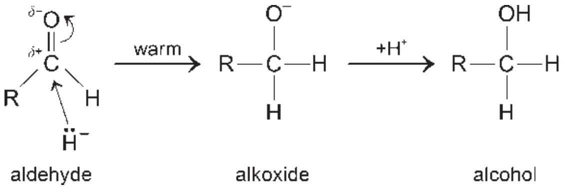
Explanation:

The reduction of the ester group results in two primary alcohol products:



Q Why can't LiAlH$_4$ be used for the reduction of alkenes?

A: LiAlH$_4$, along with NaBH$_4$, does not affect both C=C and C≡C bonds as it only attacks polar bonds such as C=O. The mechanism is rather complex but it can be thought to proceed via the following mechanism for the reduction of aldehyde:



In the first step, the reducing agent acts as a hydride ion donor (H^-) which attacks the electron-deficient carbonyl C atom in a Nucleophilic Addition reaction. Water or aqueous acid is then added in the subsequent step to protonate the alkoxide intermediate to yield the alcohol.

Q Why can't reduction using $LiAlH_4$ be carried out in the presence of water?

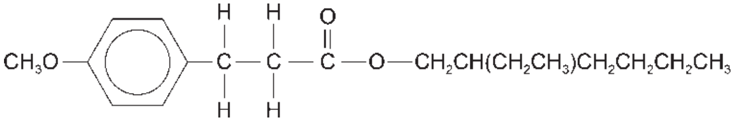
A: $LiAlH_4$ reacts vigorously with water and is thus unable to act as a H^- donor:

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2.$$

(vi) heating with hydrogen in the presence of a nickel catalyst;

Explanation:

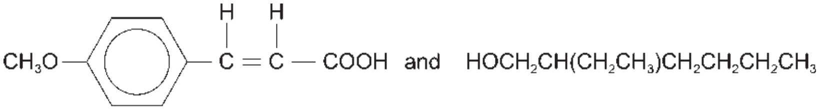
The reduction of the C = C bond occurs:



(vii) heating under reflux with aqueous hydrochloric acid; and

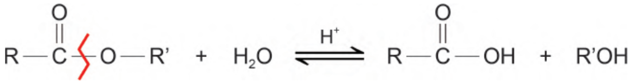
Explanation:

The ester functional group undergoes acidic hydrolysis:



Do you know?

- Hydrolysis of esters, just as that of amides and nitriles, involves the splitting of the molecules into two parts by a water molecule. One part of the molecule gains a proton and the other gains a hydroxide ion. Acids or bases are added as catalysts to speed up the hydrolysis process.
- In acidic hydrolysis, the presence of an acid will cause the protonation of basic compounds. In this case, there aren't any, so the products are basically the carboxylic acid and alcohol.



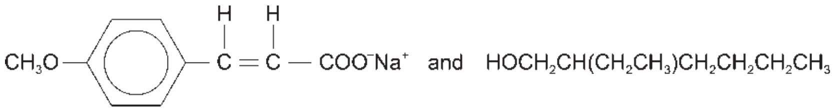
$$R-\overset{O}{\overset{\|}{C}}-O-R' + H_2O \xrightleftharpoons{H^+} R-\overset{O}{\overset{\|}{C}}-OH + R'OH$$

- Acidic hydrolysis of ester is a reversible process, the backward reaction of which is esterification. Mechanism-wise, acid hydrolysis is the opposite of that for esterification — in the former, the nucleophile is H_2O and the leaving group is the alcohol; these roles are reversed in the latter.

(viii) heating under reflux with aqueous sodium hydroxide.

Explanation:

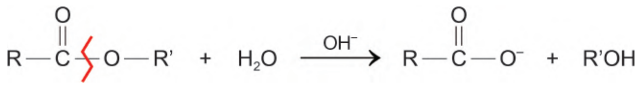
The ester functional group undergoes alkaline hydrolysis:



Do you know?

- In alkaline hydrolysis, the presence of a base will cause the deprotonation of the acidic RCOOH after it is formed, generating the carboxylate salt.

(*Continued*)



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-R' + H_2O \xrightarrow{OH^-} R-\overset{\overset{\displaystyle O}{\|}}{C}-O^- + R'OH$$

Unlike acidic hydrolysis, alkaline hydrolysis is essentially irreversible since the carboxylate ion obtained is resonance-stabilized and exhibits little tendency to react with the alcohol to form back the ester. The OH^- nucleophile, which is a stronger nucleophile than H_2O as it is more electron-rich, also helps to promote the hydrolysis of esters.

Q Why isn't the alcohol deprotonated by OH^- since it is also a weak acid?

A: Alcohol is a weaker acid than water which means the alkoxide ion, RO^-, is a stronger base than OH^-. Thus, OH^- cannot deprotonate ROH to generate H_2O and RO^- as the RO^- formed would be less stable than OH^-.

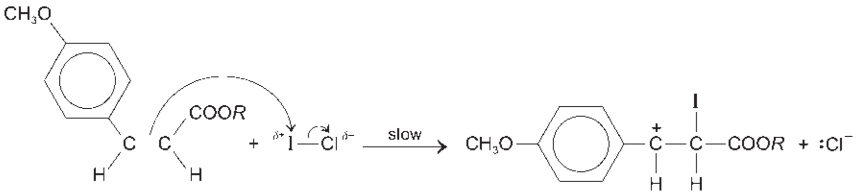
(c) Compound **X** reacts with iodine chloride (ICl) to give two different products. Give the mechanism for the formation of the major product and reasons for its formation.

Explanation:

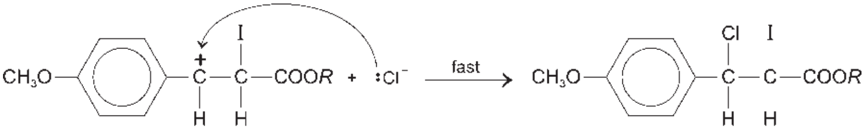
Compound **X** reacts with ICl in an electrophilic addition reaction that consists of two steps.

Step 1: Attack of an electrophile on the electron-rich C=C bond.

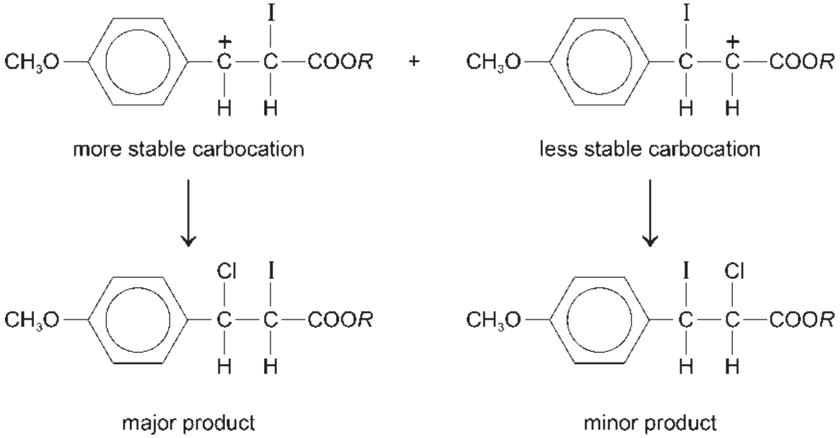
R denotes $-CH_2CH(CH_2CH_3)CH_2CH_2CH_2CH_3$ group



Step 2: Attack of a nucleophile on the carbocation to form the major product.



In fact, from Step 1 of the mechanism, two possible carbocations are obtained:



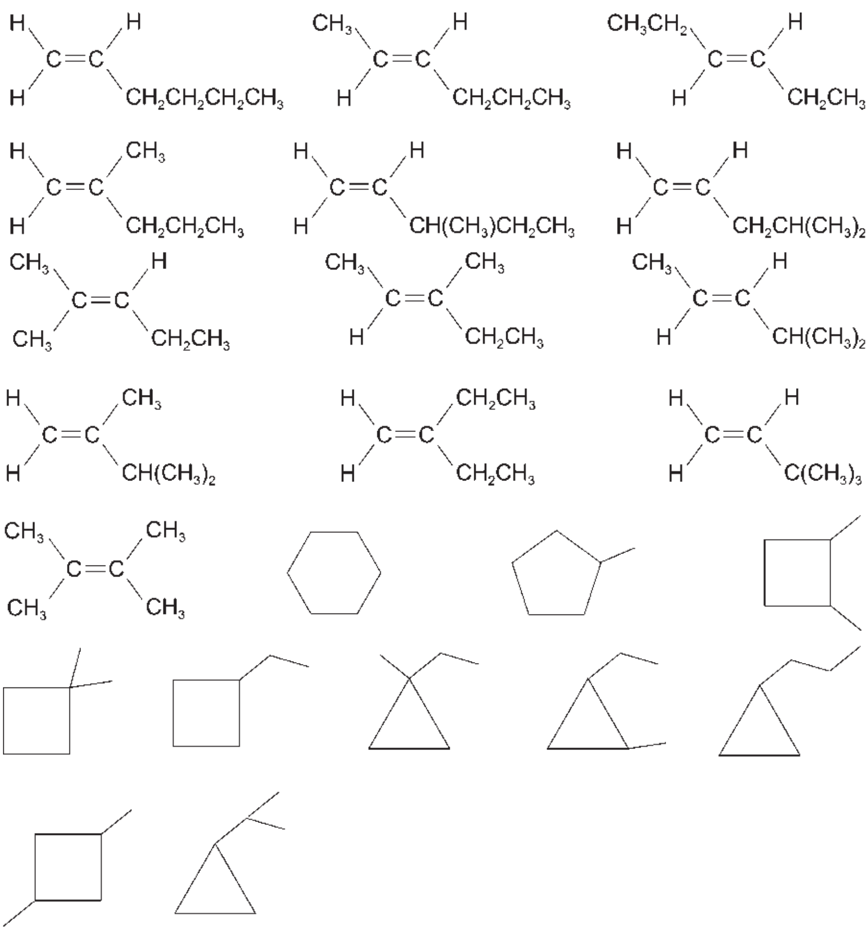
The more stable carbocation is formed faster and it subsequently reacts to produce the major product. In this case, the more stable carbocation has the positive charge on the C atom attached to the benzene ring. It is more stable because there is greater charge dispersal.

The empty *p* orbital of the sp^2 hybridized carbocation can overlap side-on with the π-electron cloud of the benzene ring. As a result, the electrons from the benzene ring can delocalize onto the carbocation, decreasing its electron-deficiency.

On the other hand, the carbocation with the positive charge on the C atom which is bonded to the ester group (–COO*R*) is less stable as the presence of electronegative O atoms withdraw electron density away from it, making the C atom more electron-deficient and hence intensifying the positive charge on it.

2. Alkenes can be selectively oxidized to give a range of products such as diols, aldehydes, ketones, carboxylic acids, and carbon dioxide. In such an experiment, an alkene, C_6H_{12}, gave an aldehyde **P** and a ketone **Q**, both with the molecular formula C_3H_6O.
   (a) Draw all the possible constitutional/structural formulae corresponding to the molecular formula C_6H_{12}.

Explanation:

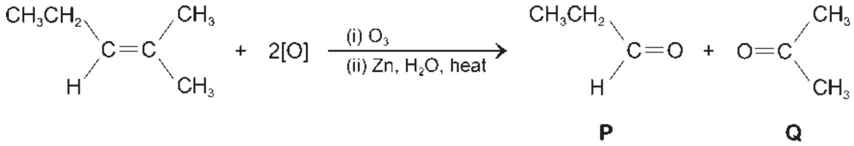


Do you know?

— Alkenes and cylcoalkanes are functional group isomers; they have the same molecular formula but different functional groups. Other common pairs of compounds that exhibit such constitutional/structural isomerism include (i) alcohols and ethers; (ii) aldehydes and ketones; and (iii) carboxylic acids and esters.

(b) Suggest a simple chemical test to differentiate **P** from **Q**.

Explanation:



Test: Add $KMnO_4$(aq) and H_2SO_4(aq) to each compound and heat.
Observations: Decolorization of purple $KMnO_4$ is observed for **P** but not for **Q**.

Alternative 1: Add $K_2Cr_2O_7$(aq) and H_2SO_4(aq) to each compound and heat.
Orange $K_2Cr_2O_7$ turns green for **P** but not for **Q**.
Alternative 2: Add Fehling's solution to each compound and heat.
A reddish-brown precipitate is observed for **P** but not for **Q**.
Alternative 3: Add Tollens' reagent to each compound and heat.
Silver mirror is observed for **P** but not for **Q**.
Alternative 4: A positive test result can be obtained for the ketone by adding I_2(aq), NaOH(aq) and warm.
Yellow crystals of CHI_3 are observed for **Q** but not for **P**.

Do you know?

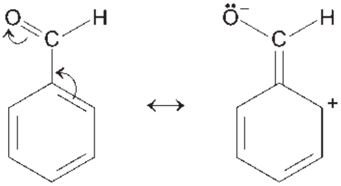
— Tollens' reagent is a stronger oxidizing agent than Fehling's solution. Tollens' reagent can be used to oxidize both aliphatic and aromatic aldehydes, whereas Fehling's solution can only oxidize aliphatic aldehydes.

Q Why is aromatic aldehyde more resistant to oxidation?

A: A stronger oxidizing agent (or reducing agent) causes a greater magnitude of change in the oxidation number of the species it oxidizes (or reduces). In the presence of either Tollens' reagent or Fehling's solution, an aliphatic aldehyde is oxidized to the carboxylate ion as the reaction medium is alkaline. There is an increase in the oxidation number of the carbonyl C atom in the aldehyde from +1 to +3 in the carboxylate.

If benzaldehyde is oxidized, the oxidation number of the carbonyl C atom has to increase from 0 to +3; this greater change in magnitude can only be brought about by the use of the stronger oxidizing agent, Tollens' reagent.

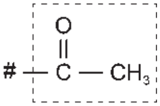
The oxidation number of the carbonyl C atom in benzaldehye can be perceived to be zero because of the delocalization of electrons as shown:



Do you know?

— The reaction involving alkaline iodine to form the yellow crystals of CHI_3 is an oxidation reaction. However, this reaction only applies to ethanol and all methyl ketones that contain the following structural unit:

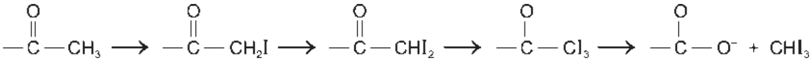
The carbonyl carbon must be bonded to either a C or H atom


$$\#-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(*Continued*)

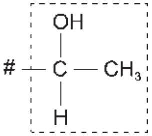
(*Continued*)

Based on the multi-step mechanism, the oxidation can be seen to occur through the formation of the following series of intermediates,



$$-\overset{O}{\overset{\|}{C}}-CH_3 \longrightarrow -\overset{O}{\overset{\|}{C}}-CH_2I \longrightarrow -\overset{O}{\overset{\|}{C}}-CHI_2 \longrightarrow -\overset{O}{\overset{|}{C}}-CI_3 \longrightarrow -\overset{O}{\overset{|}{C}}-O^- + CHI_3$$

Alcohols with the following bonding pattern also give a positive result for the tri-iodomethane test:

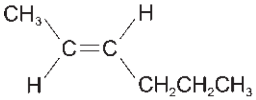


The carbon atom here must be bonded to either a C or H atom

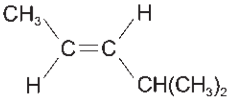
(c) (i) Draw two constitutional/structural isomers of an alkene, C_6H_{12}, which exhibits *cis-trans*/geometrical isomerism.

Explanation:

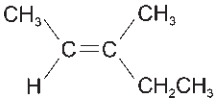
From the list of alkenes in part (*a*), only the following alkenes exhibit *cis-trans*/geometrical isomerism because each of the C atom of the C=C bond is bonded to two different substituents:



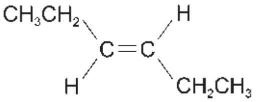
U



V



W



X

(ii) How can you use ozonolysis to differentiate between these two constitutional/structural isomers of C_6H_{12}?

Explanation:

Under ozonolysis, compounds **U** and **V** would give the following products:

$$CH_3CHO \text{ and } CH_3CH_2CH_2CHO.$$

Compounds **W** and **X** would give:

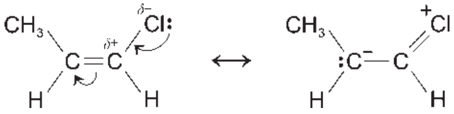
$$CH_3CHO \text{ and } CH_3CH_2COCH_3.$$

After adding Tollens' reagent to oxidize the aldehydes to the carboxylate, when we add I_2/NaOH/heat, only the $CH_3CH_2COCH_3$ would give us a yellow ppt of CHI_3.

3. Account for why $CH_3CH_2CH_2Cl$ reacts rapidly with aqueous potassium hydroxide, whereas $CH_3CH{=}CHCl$ only reacts slowly.

Explanation:

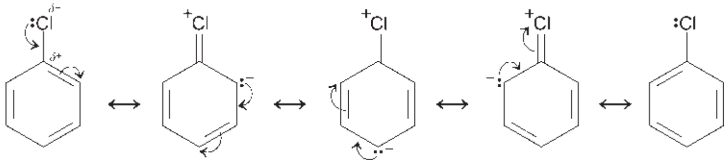
For the $CH_3CH{=}CHCl$ molecule, the lone pair of electrons on the chlorine atom can delocalize into the adjacent C=C bond. This results in the C–Cl bond bearing partial double bond character, and it is thus stronger than the C–Cl bond in the halogenoalkane.



In addition, due to the delocalization of electrons, the polarity of the C–Cl bond is decreased, and the OH^- nucleophile is less strongly attracted to the C atom of the C–Cl bond than we would expect in the case of a halogenoalkane.

Do you know?

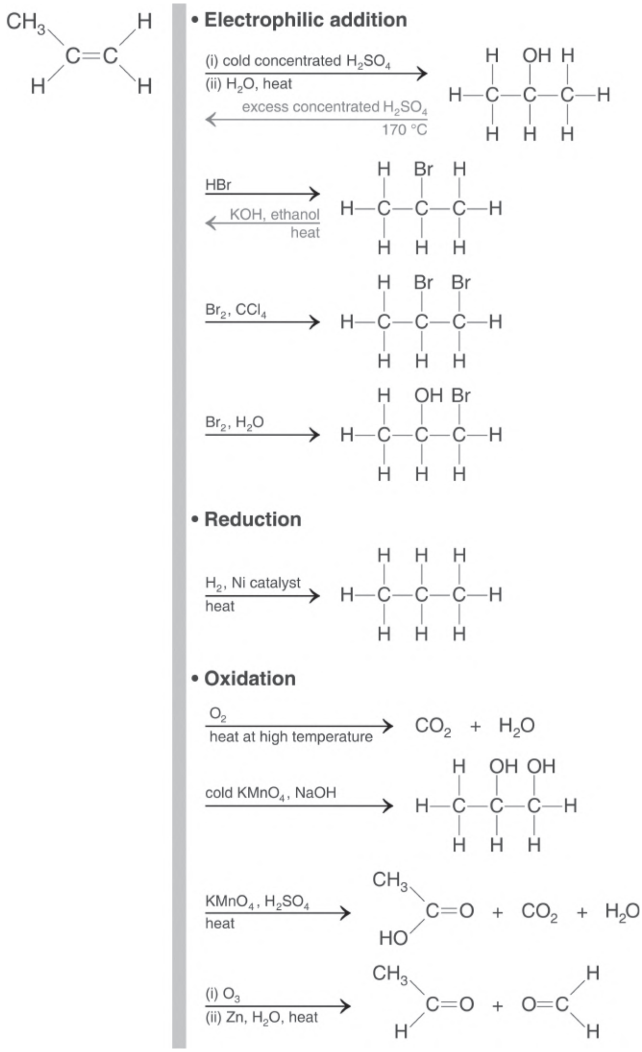
— Halogenoarenes do not undergo Nucleophilic Substitution as readily as halogenoalkanes. Their lack of reactivity can be explained by the same reasons why vinylic halides (containing a halogen bonded to a doubly bonded carbon atom) do not undergo Nucleophilic Substitution readily. The following resonance structures depict the delocalization of the lone pair of electrons on the Cl atom into the benzene ring:



A third reason for halogenoarenes' lack of reactivity toward nucleophilic attacks is the inter-electronic repulsion between the electron-rich benzene and the nucleophile which hinders the approach of the latter.

Do you know?

— A mind-map showing important chemical reactions pertaining to propene:



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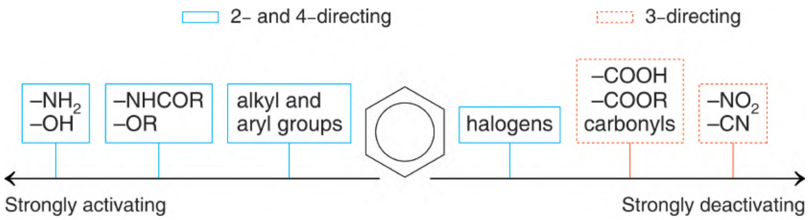
- Reactions that serve as distinguishing tests:
  - when an alkene reacts with Br_2/CCl_4 or Br_2(aq), the brown Br_2 would decolorize;
  - when an alkene reacts with hot acidified $KMnO_4$, the purple $KMnO_4$ would decolorize; and
  - when an alkene reacts with cold alkaline $KMnO_4$, the purple $KMnO_4$ would decolorize and a brown MnO_2 ppt would be observed.

CHAPTER 6

ARENES

Do you know?

- Benzene is a liquid at room temperature due to strong instantaneous dipole–induced dipole interaction. This is a result of its massive electron cloud attributed by the great number of electrons present in the molecule.
- Substituted benzene, such as chlorobenzene and nitrobenzene, are polar molecules. Therefore, there are permanent dipole–permanent dipole interactions in addition to the extensive id–id interactions.
- Different substituents bonded to the benzene ring have different effects on the benzene ring.
  - There are substituents that are both 2,4-directing and ring–activating at the same time: –OH, $–NH_2$, –alkyl, etc. Ring activators would require less drastic reaction conditions.
  - Substituents such as halogens are 2,4-directing but ring-deactivating. Ring-deactivated benzene requires more stringent reaction conditions, such as a higher temperature or pressure or the use of a catalyst, than unsubstituted benzene.
  - While groups such as –COOH, $–NO_2$, etc. are both 3-directing and ring-deactivating.



R = alkyl / aryl group

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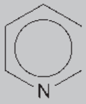
— When we say that a substituent is 2,4-directing, the major products formed would be the 1,2- and 1,4-substituted products. The 1,3-substituted product is a minor product. Similarly, for a 3-directing substituent, the 1,3-substituted product would be the major product.

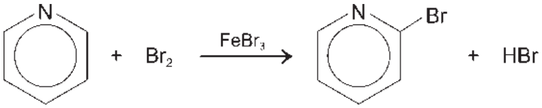
1. Benzene, C_6H_6, is an aromatic hydrocarbon with six delocalized pi electrons. On treatment with a mixture of concentrated nitric acid and sulfuric acid, benzene undergoes the Electrophilic Substitution reaction to give nitrobenzene. Pyridine, C_5H_5N, exhibits chemical properties very similar to that of benzene.



Pyridine

(a) (i) Suggest one substitution reaction of pyridine, and give the structure of a possible product.

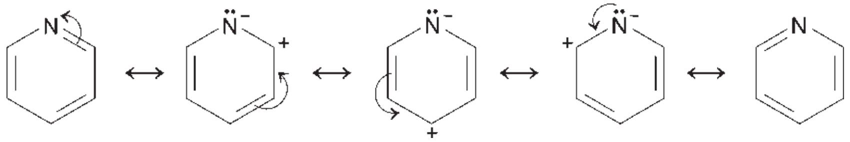
Explanation:



(ii) Pyridine does not undergo the reaction that is mentioned in (a)(i) as readily as benzene. Suggest a possible reason for this observation.

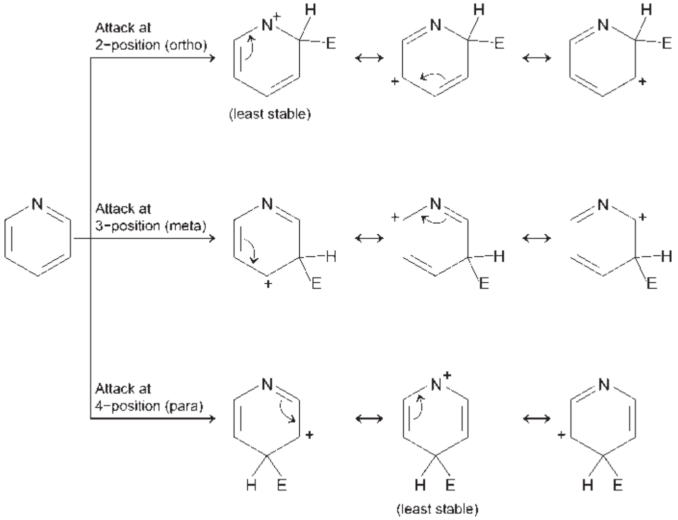
Explanation:

Due to the nitrogen atom being more electronegative than the carbon atom, it withdraws electron density toward itself via inductive efffect. In addition, the delocalization of the pi electrons onto the nitrogen atom also causes a decrease in the electron density of the ring, making it less susceptible to electrophilic attack.



Do you know?

- All the carbon atoms in pyridine are more electron-deficient than those in an unsubstituted benzene ring, but with carbon atoms 2, 4, and 6 being more electron-deficient than carbon atoms 3 and 5 since they possess the positive charge.
- Apart from influencing the reactivity of the aromatic ring toward electrophilic attack and the rate of such reaction, the nitrogen atom also exerts an influence on the position of the electrophilic attack. Referring to the diagram below, there are three different sites that an electrophile, E^+, can attack:



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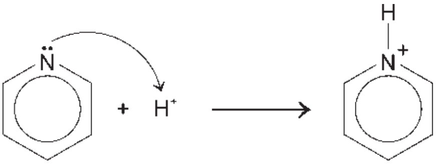
If the electrophile attacks at either the ortho or para position, the positive charge will reside on the more electronegative nitrogen atom. This presents the least stable structure. If the attack occurs at the meta position, no such destabilizing effect is observed. Hence, pyridine is 3-directing or meta-directing.

(iii) Benzene does not react with sulfuric acid but pyridine does. Explain this observation and give a balanced equation for its reaction.

Explanation:

The nitrogen atom in pyridine has a lone pair of electrons available for dative covalent bond formation with a proton. Hence, pyridine is a base, albeit a weak one, that undergoes an acid–base reaction with sulfuric acid.



Q Wouldn't the lone pair of electrons on the N atom delocalize into the ring?

A: The N atom is sp^2 hybridized. Its lone pair of electrons resides in a sp^2 hybridized orbital which cannot overlap with the *p* orbital of the adjacent C atoms since these orbitals actually lie perpendicularly to each other. Hence, the lone pair of electrons cannot delocalize into the ring and is thus available to bond with a proton.

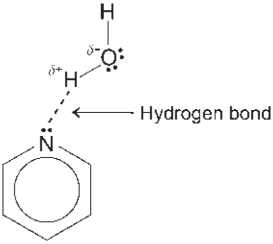
(b) Pyridine has a higher boiling point than benzene. Explain.

Explanation:

Pyridine is a polar molecule whereas benzene is non-polar. More energy is needed to overcome the stronger permanent dipole–permanent dipole interactions between molecules of pyridine than the instantaneous dipole–induced dipole interactions between molecules of benzene. Hence, pyridine has a higher boiling point than benzene.

Do you know?

— Pyridine is miscible with both water and organic solvents. The lone pair of electrons on the N atom allows pyridine to function as a hydrogen bond acceptor. This ability to form hydrogen bonds with water molecules accounts for the solubility of pyridine in water.



Pyridine is soluble in organic solvents because the hydrophobic part of its molecules can form van der Waals forces with the non-polar molecules that lead to favorable mixing.

(c) Benzene also undergoes the same reaction when treated with ethanoyl chloride (CH_3COCl), in the presence of aluminum chloride under anhydrous conditions, to give phenylethanone ($C_6H_5COCH_3$).

(i) Give the formula of the electrophile that is involved in the reaction.

Explanation:

The electrophile is CH_3CO^+.

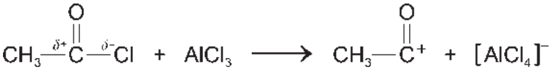
Q How is the electrophile generated?

A: The Al atom of $AlCl_3$ has a vacant orbital, hence it is an electron-deficient species. It would be able to accept a lone pair of electrons from the Cl atom of ethanoyl chloride. This would polarize the C–Cl bond and cause the generation of the electrophile.

(ii) Suggest a reason for the requirement of the anhydrous conditions.

Explanation:

$AlCl_3$ functions as a Lewis acid, i.e., an electron-pair acceptor to generate the electrophile as follows:



$$CH_3\overset{\delta+}{-}\overset{O}{\overset{\|}{C}}\overset{\delta-}{-}Cl + AlCl_3 \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}{}^+ + [AlCl_4]^-$$

Due to the high charge density of the aluminum atom, $AlCl_3$ will undergo hydrolysis in an aqueous solution, producing the complex ion, $[Al(H_2O)_6]^{3+}$, that decreases the electron deficiency of the aluminum atom, rendering it incapable of functioning as a Lewis acid.

Q Why is there a decrease in electron deficiency of the metal center?

A: In forming the complex ion, the Al^{3+} ion accepts a lone pair of electrons from each of the six H_2O molecules to form dative covalent bonds. Hence, it is no longer electron-deficient.

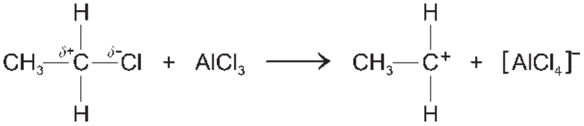
Q Why wasn’t the term “Al^{3+} ion” used above?

A: The $AlCl_3$ is a covalent compound where there are three Al–Cl bonds. Hence, it is inappropriate to use the term “Al^{3+} ion.”

(iii) If ethanoyl chloride is replaced by chloroethane under the same conditions, ethylbenzene is formed. Give a mechanistic account of the formation of ethylbenzene.

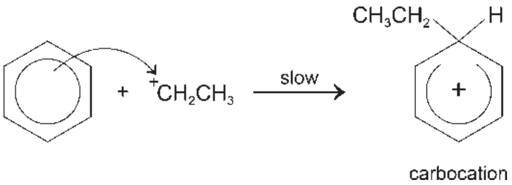
Explanation:

Step 1: Generation of electrophile.

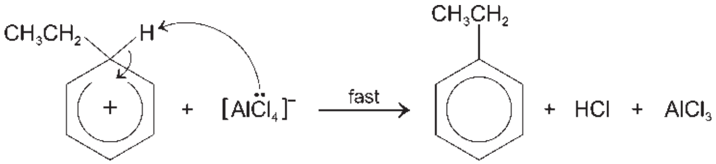


$$CH_3-\overset{\delta+}{C}H_2-\overset{\delta-}{Cl} + AlCl_3 \longrightarrow CH_3-CH_2^{+} + [AlCl_4]^{-}$$

The two-step Electrophilic Substitution mechanism is as follows:
Step 2: Electrophile (Lewis acid) attacks the electron-rich benzene (Lewis base).



Step 3: Deprotonation of carbocation (Lewis acid) to regenerate the resonance stability.



Q Is it easier to generate the $CH_3CH_2^+$ electrophile or CH_3CO^+ electrophile?

A: Due to the presence of the electron-withdrawing C=O group in CH_3COCl, the C–Cl bond is more polarized; hence, it is more likely to break.

Q Which is a stronger electrophile, $CH_3CH_2^+$ or CH_3CO^+?

A: The carbon atom of the C=O group of CH_3CO^+ is more electron-deficient than the carbocation of $CH_3CH_2^+$ due to the presence of a highly electronegative O atom bonded to the already electron-deficient carbon atom. This increases the strength of the CH_3CO^+ as an electrophile.

(d) Account for the differences in the rate of reactions nitrobenzene, phenol, and methylbenzene have with concentrated nitric acid.

Explanation:

In order of decreasing reaction rate: phenol > methylbenzene > nitrobenzene.

Nitrobenzene contains the deactivating nitro group that withdraws electrons from the benzene ring via both resonance and inductive effects. As a result, the benzene ring is least susceptible to electrophilic attack.

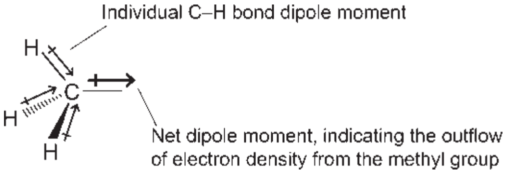
Phenol and methylbenzene contain activating groups that enhance the electron density in the benzene ring. The methyl group enhances the electron density of the ring via inductive effect only, while the OH–group of phenol increases the electron density through resonance effect only. But as the hydroxyl substituent is a stronger activating group than the methyl substituent, phenol is the most susceptible to electrophilic attack.

Do you know?

— The reactivity of these substituents influences the conditions necessary for electrophilic substitution. The most reactive phenol requires mild conditions for its electrophilic reaction, while harsher reacting conditions are needed for methylbenzene, and most so for nitrobenzene. For instance, the bromination of phenol only requires the use of Br_2(aq) at room temperature. Phenol is so reactive that even under this condition, polysubstitution occurs. On the other hand, the bromination of methyl benzene requires Br_2 in the presence of anhydrous $FeBr_3$, and only monosubstitution takes place. As for nitrobenzene, a higher reaction temperature is needed as compared to that for methylbenzene.

Q What is inductive effect and resonance effect? Which effect is more prominent for which functional group?

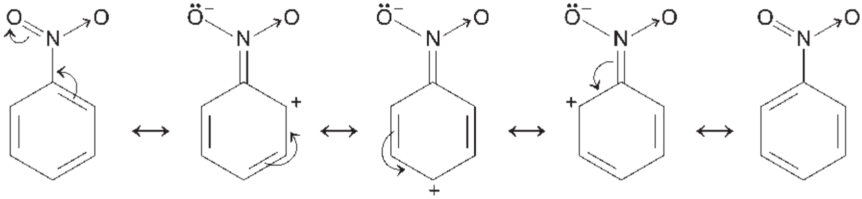
A: Inductive effect means the flow of electron density that occurs through sigma bonds, whereas resonance effect describes the electron flow that occurs through the pi bond.



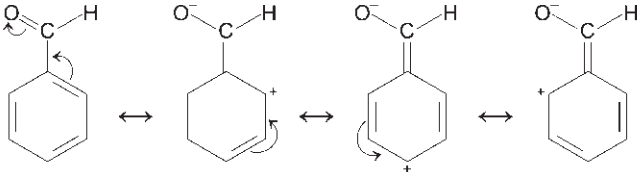
The methyl group inductively donates electrons through the sigma bond. This is possible because there is a net dipole moment pointing away from the alkyl group, toward the benzene ring.

The methyl group cannot donate electrons through the pi bond because its sp^3 hybridized carbon atom does not have a *p* orbital to overlap with the *p* orbital of the sp^2 hybridized carbon atom of the benzene ring.

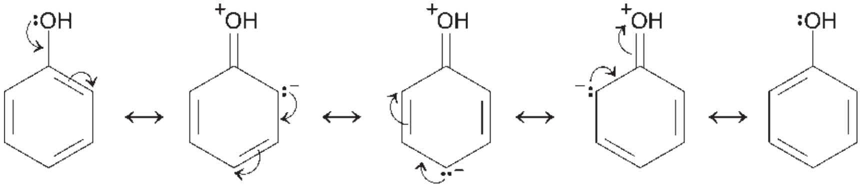
The nitro group is electron-withdrawing via both inductive (as both N and O atoms are more electronegative than the C atom) and resonance effects. The resonance effect arises as nitrogen atom is sp^2 hybridized and its *p* orbital overlaps with the *p* orbital of the carbon atom of the benzene ring to which it is bonded. As a result, there is delocalization of electrons over both the benzene ring and nitro group. But as oxygen is the most electronegative atom present, it withdraws electron density from the benzene ring, causing carbon atoms 2, 4, and 6 to acquire the positive charge:



In addition to the nitro group, an aldehyde, ketone, ester, or amide functional groups that is bonded to the benzene ring also exhibits the same effect as that of the nitro group as shown below:



The hydroxyl group is electron-withdrawing via inductive effect because of the greater electronegativity of the oxygen atom that is bonded adjacent to the carbon atom of the benzene ring. However, the hydroxyl group is also electron-donating via resonance effect:



In this case, the electron-donating via resonance effect outweighs the electron-withdrawing via inductive effect. Overall, the electron density of the benzene ring is enhanced and the hydroxyl group is considered an activating group.

(e) A catalyst is required for the reaction of benzene with bromine but not for the reaction of ethene with bromine. Explain.

Explanation:

On the average, benzene is less electron-rich than an alkene. There are two pi electrons between the carbon atoms in ethene. On average, there is only one pi electron between two carbon atoms in benzene. Thus, the pi electron cloud of benzene is not strong enough to polarize the bromine molecule. To circumvent the lower reactivity of benzene than an alkene, a Lewis acid catalyst is used to generate a more reactive attacking species, which in this case is the Br^+ ion which is a stronger electrophile than a partially polarized Br_2 molecule.

In addition, after the electrophile has attacked the benzene ring, the benzene ring would lose its resonance stability. This thus increases the activation energy for the reaction. Hence, to overcome this, a stronger electrophile is needed.

2. To prepare methyl 3-nitrobenzoate, methyl benzoate is dissolved in concentrated sulfuric acid and the mixture is cooled in an ice bath. The nitrating agent is then added to the cooled methyl benzoate, maintaining the temperature of the mixture at about 8°C.
   (a) (i) Give the reagents that are required to make the nitrating agent.

Explanation:

Concentrated nitric acid and concentrated sulfuric acid are required to make the nitrating agent, NO_2^+.

(ii) Suggest reasons why dilute sulfuric acid is not used as the medium to dissolve methyl benzoate.

Explanation:

Concentrated H_2SO_4 plays two roles in the reaction. One of its roles is that of an acid. Being a stronger acid than HNO_3, H_2SO_4, donates a proton to HNO_3, and subsequent dehydration results in the formation of the NO_2^+ electrophile:

$$HNO_3 + H_2SO_4 \rightleftharpoons NO_2^+ + H_2O + HSO_4^-.$$

Concentrated H_2SO_4 also serves as a dehydrating agent. By removing water, it helps to drive the forward reaction in producing more NO_2^+, which leads to an increase in rate of electrophilic reaction. Thus, in dilute sulfuric acid, the H_2SO_4 has already dissociated in water to give H^+ and HSO_4^-, which cannot further function as a proton donor anymore.

Q Why is H_2SO_4 a stronger acid than HNO_3?

A: There are four highly electronegative oxygen atoms in a H_2SO_4 molecule, while there are only three of them in HNO_3. Hence, the H atoms of H_2SO_4 are more electron-deficient than those in HNO_3, making H_2SO_4 a stronger acid as the H atoms are more likely to be extracted by a Brønsted–Lowry base. So, this is a very good example to demonstrate that an acid can assume the role of a base in the presence of a stronger acid. Hence, acidity or basicity is very relative!

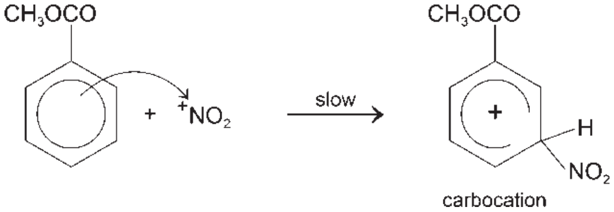
Q How does concentrated H_2SO_4 function as a dehydrating agent? Does the acid molecule absorb water molecules or does it react chemically with water?

A: Basically, concentrated sulfuric acid contains undissociated H_2SO_4 molecules. These molecules contain a lone pair of electrons on the oxygen atoms of the molecule and also H atoms bonded to the oxygen atoms. The lone pair of electrons of H_2SO_4 can attract the H atoms of a water molecule, while the H atoms can attract the lone pair of electrons on the H_2O molecule. This would thus help to "pull" H_2O molecule from a substance, causing the dehydrating effect. And after the "extraction," the water molecules would be strongly attracted to the H_2SO_4 molecule through strong hydrogen bonds. So, the water molecules are somehow being "absorbed" by the H_2SO_4 molecules.

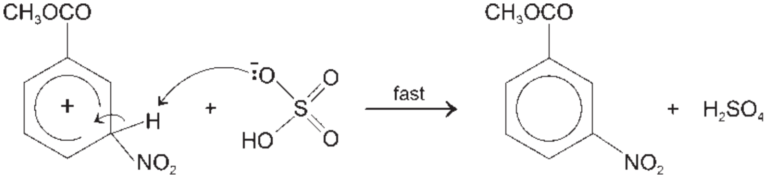
(iii) Give the mechanism showing the nitration of methyl benzoate.

Explanation:

The two-step Electrophilic Substitution mechanism is as follows:
Step 1: An electrophile (Lewis acid) attacks the electron-rich benzene (Lewis base).



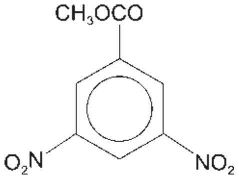
Step 2: Deprotonation of the carbocation (Lewis acid) to regenerate the resonance stability.



(iv) The amount of methyl 3-nitrobenzoate formed would decrease once the temperature is above 8°C. Suggest a reason for the observation.

Explanation:

If temperature is above 8°C, further nitration will occur, resulting in poly-nitrated products, e.g.,



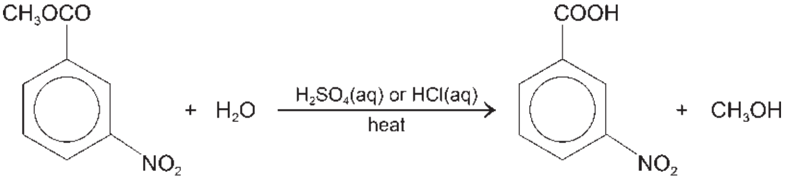
Q Why would further nitration occur at a higher temperature?

A: A nitro group is an electron-withdrawing group. Hence, the nitrated methyl benzoate would be less susceptible to electrophilic attack than the methyl benzoate as the benzene ring now becomes even more electron-deficient. At a higher temperature, the electrophile becomes more energetic to attack the more electron-deficient benzene ring. Or rather, the reactants now possess a greater amount of kinetic energy to overcome the activation energy that is needed.

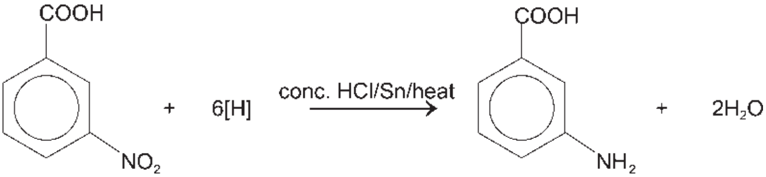
(b) Write balanced equations for the conversion of methyl 3-nitrobenzoate to each of the following compounds:
 (i) 3-aminobenzoic acid;

Explanation:

The first step is the acidic hydrolysis of the ester into benzoic acid and methanol:



The second step is the reduction of the nitrobenzene group by heating with Sn and concentrated HCl, followed by adding NaOH(aq):



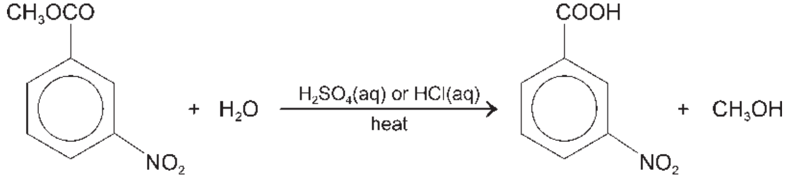
Q Can we use $LiAlH_4$/dry ether to reduce a nitrobenzene to phenylamine?

A: Yes, actually you can use it but we do not want to emphasize it here because it can also reduce other functional groups such as esters, carboxylic acids, etc. But Sn/conc. HCl can only reduce nitrobenzene and NOT the rest.

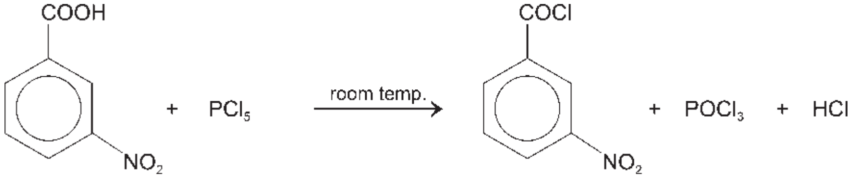
(ii) 3-nitrobenzoyl chloride;

Explanation:

The first step is the acidic hydrolysis of the ester into benzoic acid and methanol:



The second step is the Nucleophilic Acyl Substitution of carboxylic acid:



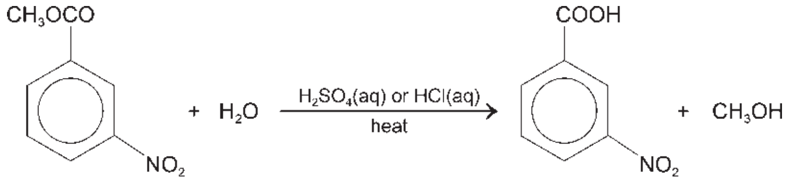
Q Is it better to use $SOCl_2$ instead of PCl_5 or PCl_3?

A: Certainly! As $SOCl_2$ would give HCl and SO_2 as the gaseous products, we would have fewer problems in purification.

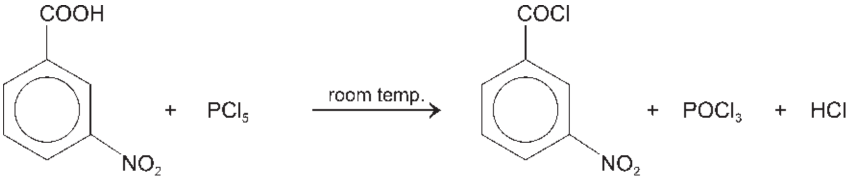
(iii) *N*-methyl-3-nitrobenzamide; and

Explanation:

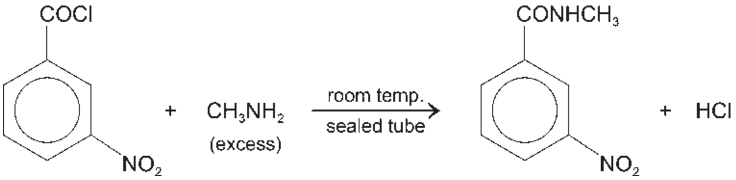
The first step is the acidic hydrolysis of the ester into benzoic acid and methanol:



The second step is the Nucleophilic Acyl Substitution of carboxylic acid:



The third step is the Nucleophilic Acyl Substitution of the acid chloride:



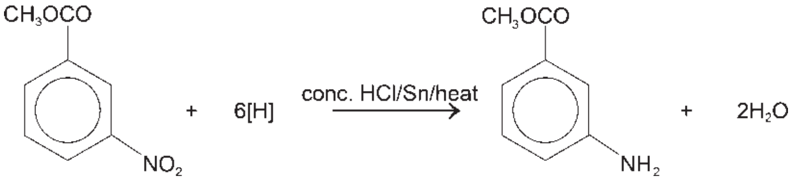
Q Why can't we simply react the amine with the carboxylic acid to get the amide?

A: Carboxylic acid is a weak acid while amine is a weak base. They would undergo an acid–base reaction instead when mixed to give you the salt.

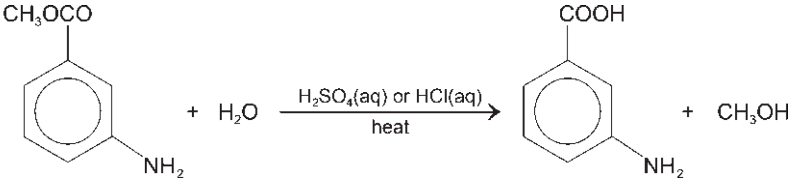
(iv) (3-aminophenyl) methanol.

Explanation:

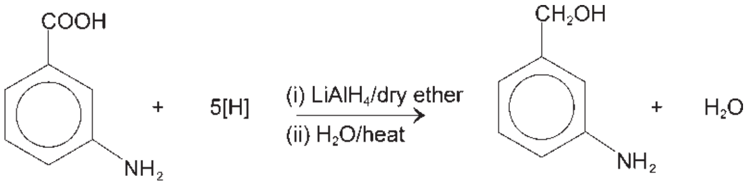
The first step is the reduction of the nitro group to the amino group:



The second step is the acidic hydrolysis of the ester to the aminobenzoic acid and methanol:



The third step is the reduction of the benzoic acid functional group to the alcohol:



Q Can we just simply reduce the ester and nitro functional groups using $LiAlH_4$ in dry ether, rather than going through the three stages?

A: Yes, you can, since the nitro group can be reduced by $LiAlH_4$ in dry ether. But for learning purposes, we would like to emphasize the reduction of the nitro group by Sn/conc. HCl/heat to phenylamine.

Q When Sn/conc. HCl/heat is used to reduce the nitro group to phenylamine, wouldn't the ester group undergo acidic hydrolysis since conc. HCl is used?

A: Yes, indeed, the ester group would not be spared from being hydrolyzed. But since we are using conc. HCl, we are assuming that the amount of water may not be sufficient to effect the appropriate amount of hydrolysis.

(c) With appropriate reagents and conditions, describe a simple chemical test to differentiate the following pair of compounds:

(i) methyl 3-nitrobenzoate and methyl benzoate;

Explanation:

Step 1: Add Sn/conc. HCl and heat {Reduction}

The nitro group of the methyl 3-nitrobenzoate would be reduced to form the phenylamine functional group.

Step 2: Add Br_2(aq) to both of the reduced product in Step 1. {Electrophilic Substitution}

Only the reduced product of methyl 3-nitrobenzoate, which contains a phenylamine functional group, would give a white ppt and decolorized brown bromine.

Alternatively,

Step 2: Add $NaNO_2$(s)/HCl(aq)/0–5°C, followed by water/heat. {Diazotization followed by hydrolysis}:

Only the reduced product of methyl 3-nitrobenzoate, which contains a phenylamine functional group, would give effervescence of N_2 gas.

(ii) methyl 3-nitrobenzoate and 3-aminobenzoic acid;

Explanation:

To differentiate between methyl 3-nitrobenzoate and 3-aminobenzoic acid, just use any of the following tests:

(1) Use PCl_5 and test for HCl(g):

methyl 3-nitrobenzoate: No white fumes of HCl(g).
3-aminobenzoic acid: White fumes of HCl(g) observed.
3-aminobenzoic acid contains a –COOH group.
$–COOH + PCl_5 \rightarrow –COCl + POCl_3 + HCl(g)$. {Nucleophilic Acyl Substitution}

(2) Use $SOCl_2$ and test for HCl(g):

methyl 3-nitrobenzoate: No white fumes of HCl(g).
3-aminobenzoic acid: White fumes of HCl(g) observed.
3-aminobenzoic acid contains a –COOH group.
$–COOH + SOCl_2 \rightarrow –COCl + SO_2 + HCl(g)$. {Nucleophilic Acyl Substitution}

(3) Use $Na_2CO_3(s)$ and test for $CO_2(g)$:

methyl 3-nitrobenzoate: No gas evolved gave white ppt with $Ca(OH)_2(aq)$.
3-aminobenzoic acid: Gas evolved gave white ppt with $Ca(OH)_2(aq)$.
3-aminobenzoic acid contains a –COOH group.
$2–COOH + CO_3^{2-} \rightarrow 2–COO^- + CO_2 + H_2O$. {Acid–base reaction}

(4) Use (i) $NaNO_2$/HCl(aq)/0–5°C, (ii) water/heat. {Diazotization followed by hydrolysis}

methyl 3-nitrobenzoate: No evolution of $N_2(g)$.
3-aminobenzoic acid: Evolution of $N_2(g)$.
3-aminobenzoic acid contains a $–NH_2$ group.

(5) Use aqueous Br_2:

methyl 3-nitrobenzoate: No decolorization of brown Br_2.
3-aminobenzoic acid: Brown Br_2 decolorized. White ppt formed.
3-aminobenzoic acid contains a phenylamine functional group {Electrophilic Substitution}

(iii) 3-aminobenzoic acid and 3-nitrobenzoyl chloride;

Explanation:

To differentiate between 3-aminobenzoic acid and 3-nitrobenzoyl chloride, just use any of the following tests:

(1) Add water to each of the unknown, the one that evolves white fumes of HCl(g) is 3-nitrobenzoyl chloride. This is because 3-nitrobenzoyl chloride undergoes hydrolysis to give HCl gas.

Alternatively, if $AgNO_3$(aq) is used, there would be a white ppt of AgCl observed in addition to the white HCl fumes.

(2) Use PCl_5 and test for HCl(g):

3-nitrobenzoyl chloride: No white fumes of HCl(g).
3-aminobenzoic acid: White fumes of HCl(g) observed.
3-aminobenzoic acid contains a –COOH group.
$–COOH + PCl_5 \rightarrow –COCl + POCl_3 + HCl(g)$. {Nucleophilic Acyl Substitution}

(3) Use $SOCl_2$ and test for HCl(g):

3-nitrobenzoyl chloride: No white fumes of HCl(g).
3-aminobenzoic acid: White fumes of HCl(g) observed.
3-aminobenzoic acid contains a –COOH group.
$–COOH + SOCl_2 \rightarrow –COCl + SO_2 + HCl(g)$. {Nucleophilic Acyl Substitution}

(4) Use Na_2CO_3(s) and test for CO_2(g):

3-nitrobenzoyl chloride: No gas evolved gave white ppt with $Ca(OH)_2$(aq).
3-aminobenzoic acid: Gas evolved gave white ppt with $Ca(OH)_2$(aq).
3-aminobenzoic acid contains a –COOH group.
$2–COOH + CO_3^{2-} \rightarrow 2–COO^- + CO_2 + H_2O$. {Acid–base reaction}

(5) Use (i) $NaNO_2$/HCl(aq)/0–5°C, (ii) water/heat. {Diazotization followed by hydrolysis}

3-nitrobenzoyl chloride: No evolution of N_2(g).
3-aminobenzoic acid: Evolution of N_2(g).
3-aminobenzoic acid contains a $–NH_2$ group.

(6) Use aqueous Br_2:

3-nitrobenzoyl chloride: No decolorization of brown Br_2.
3-aminobenzoic acid: Brown Br_2 decolorized. White ppt formed.
3-aminobenzoic acid contains a phenylamine functional group.
{Electrophilic Substitution}

(iv) (3-aminophenyl) methanol and 3-nitrobenzoyl chloride; and

Explanation:

To differentiate between (3-aminophenyl) methanol and 3-nitrobenzoyl chloride, just use any of the following tests:

(1) Add water to each of the unknown, the one that evolves white fumes of HCl(g) is 3-nitrobenzoyl chloride. This is because 3-nitrobenzoyl chloride undergoes hydrolysis to give HCl gas.

Alternatively, if $AgNO_3$(aq) is used, there would be a white ppt of AgCl observed in addition to the white HCl fumes.

(2) Use PCl_5 and test for HCl(g):

3-nitrobenzoyl chloride: No white fumes of HCl(g).
(3-aminophenyl) methanol: White fumes of HCl(g) observed.
3-aminobenzoic acid contains a $–CH_2OH$ group.

$–CH_2OH + PCl_5 \rightarrow –CH_2Cl + POCl_3 + HCl(g)$. {Nucleophilic Substitution}

(3) Use $SOCl_2$ and test for HCl(g):

3-nitrobenzoyl chloride: No white fumes of HCl(g).
(3-aminophenyl) methanol: White fumes of HCl(g) observed.

(3-aminophenyl) methanol contains a $–CH_2OH$ group.

$–CH_2OH + SOCl_2 \rightarrow –CH_2Cl + SO_2 + HCl(g)$. {Nucleophilic Substitution}

(4) Use (i) $NaNO_2/HCl(aq)$/0-5°C, (ii) water/heat. {Diazotization followed by hydrolysis}

3-nitrobenzoyl chloride: No evolution of $N_2(g)$.
(3-aminophenyl) methanol: Evolution of $N_2(g)$.
(3-aminophenyl) methanol contains a $–NH_2$ group.

(5) Use $KMnO_4/H_2SO_4$/heat:

3-nitrobenzoyl chloride: No decolorization of purple $KMnO_4$.
(3-aminophenyl) methanol: Purple $KMnO_4$ decolorized.
(3-aminophenyl) methanol contains a $–CH_2OH$ group bonded to benzene that is oxidizable.

$2–CH_2OH + 4[O] \rightarrow 2–COOH + 2H_2O$. {Oxidation}

(6) Use $KMnO_4$/NaOH/heat:

3-nitrobenzoyl chloride: No decolorization of purple $KMnO_4$.
(3-aminophenyl) methanol: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.
(3-aminophenyl) methanol contains a $–CH_2OH$ group bonded to benzene that is oxidizable.

$–CH_2OH + OH^- + 2[O] \rightarrow –COO^- + 2H_2O$. {Oxidation}

(7) Use $K_2Cr_2O_7/H_2SO_4$/heat:

3-nitrobenzoyl chloride: No orange solution turned green.
(3-aminophenyl) methanol: Orange solution turned green.
(3-aminophenyl) methanol contains a $–CH_2OH$ group bonded to benzene that is oxidizable.

$2–CH_2OH + 4[O] \rightarrow 2–COOH + 2H_2O$. {Oxidation}

(8) Use Na metal:

3-nitrobenzoyl chloride: No gas evolved that extinguished a lighted splint with a ‘pop’ sound.

(3-aminophenyl) methanol: Gas evolved that extinguished a lighted splint with a 'pop' sound. Gas is H_2.
(3-aminophenyl) methanol contains a –OH group that is acidic.

$2\text{–}CH_2OH + 2Na \rightarrow 2\text{–}CH_2ONa + H_2$. {Acid–metal reaction}

(9) Use aqueous Br_2:

3-nitrobenzoyl chloride: No decolorization of brown Br_2.
(3-aminophenyl) methanol: Brown Br_2 decolorized. White ppt formed.
(3-aminophenyl) methanol contains a phenylamine functional group.
{Electrophilic Substitution}

Do you know?

— When $KMnO_4$ and $K_2Cr_2O_7$ acts as oxidizing agents in an acidic medium, they would be reduced as follows:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O; \text{ and}$$
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O.$$

— Under alkaline or neutral conditions, the $KMnO_4$ would be reduced to MnO_2 as follows:

$$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O.$$

(v) *N*-methyl-3-nitrobenzamide and 3-nitrobenzoyl chloride.

Explanation:

To differentiate between *N*-methyl-3-nitrobenzamide and 3-nitrobenzoyl chloride, just use any of the following tests:

(1) Add water to each of the unknown, the one that evolves white fumes of HCl(g) is 3-nitrobenzoyl chloride. This is because 3-nitrobenzoyl chloride undergoes hydrolysis to give HCl gas.

Alternatively, if $AgNO_3(aq)$ is used, there would be a white ppt of AgCl observed in addition to the white HCl fumes.

(2) Add NaOH(aq) and heat:

3-nitrobenzoyl chloride: No gas evolved that turned moist red litmus paper blue.

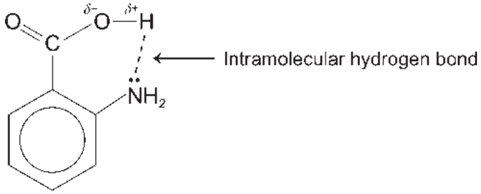
N-methyl-3-nitrobenzamide: Gas evolved that turned moist red litmus paper blue. Gas is methylamine.

N-methyl-3-nitrobenzamide contains an amide functional group, which undergoes alkaline hydrolysis to release the basic amine gas. {Alkaline hydrolysis}

(d) The melting point of 2-aminobenzoic acid is lower than that of 4-aminobenzoic acid. State the type of isomerism that both compounds exhibit and give reasons for the difference in the observed melting points.

Explanation:

Both compounds exhibit positional isomerism where the same functional groups are located at different positions on the benzene ring.



In 2-aminobenzoic acid, the close proximity of the carboxylic acid and amino functional groups allows the formation of intramolecular hydrogen bonds within themselves. Hence, there is less extensive intermolecular hydrogen bonding between molecules of 2-aminobenzoic acids which requires less energy to be overcome than in the case of 4-aminobenzoic-acid. Thus, 2-aminobenzoic acid has a lower melting point.

Q Can the aminobenzoic acid exist as a zwitterion? And if it does, how can we use the zwitterion concept to explain the discrepancy between the melting points?

A: Yes, in the solid state, the aminobenzoic acid can be perceived to exist in the form of a zwitterion, with the formation of the –COO^- and –NH_3^+ groups. For 2-aminobenzoic acid, these two oppositely charged groups are in close proximity, attracting each other and forming intramolecular ionic bonding. So, for example, the –COO^- group would repel other –COO^- groups from nearing the –NH_3^+ group that it is attracted to. Likewise for the –NH_3^+ group, it would repel other –NH_3^+ group from attracting "its" –COO^- group. These diminish the formation of intermolecular ionic bonding. As for the 4-aminobenzoic acid, because the two charged groups are far apart, there is minimal intramolecular ionic bonding. Hence, this allows other species the ease of formation of intermolecular ionic bonding.

(e) The solubility of 2-nitrobenzoic acid is lower than that of 4-nitrobenzoic acid. Give reasons for the observation.

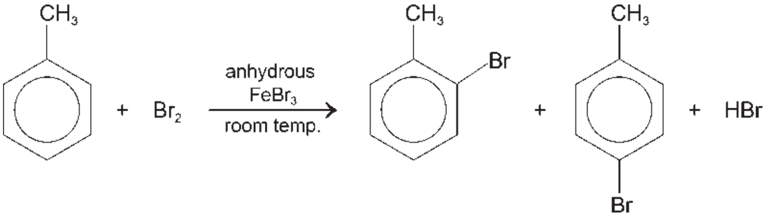
Explanation:

In 2-nitrobenzoic acid, the close proximity of the carboxylic acid and nitro functional groups allows the formation of intramolecular hydrogen bonds within themselves. Hence, there is less extensive intermolecular hydrogen bonding between molecules of 2-nitrobenzoic acid and water compared to that between molecules of 4-nitrobenzoic acid and water. Thus, 2-nitrobenzoic acid has a lower solubility in water.

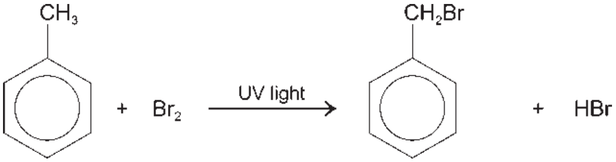
3. By reference to the reaction of methylbenzene with bromine, show how the experimental conditions are important in determining the nature of the products of an organic reaction.

Explanation:

Electrophilic Substitution occurs when methylbenzene is reacted with bromine in the presence of a Lewis acid such as $FeBr_3$.



However, if reaction takes place in the presence of UV light or heat, Free Radical Substitution would also occur at the alkyl side-chain.



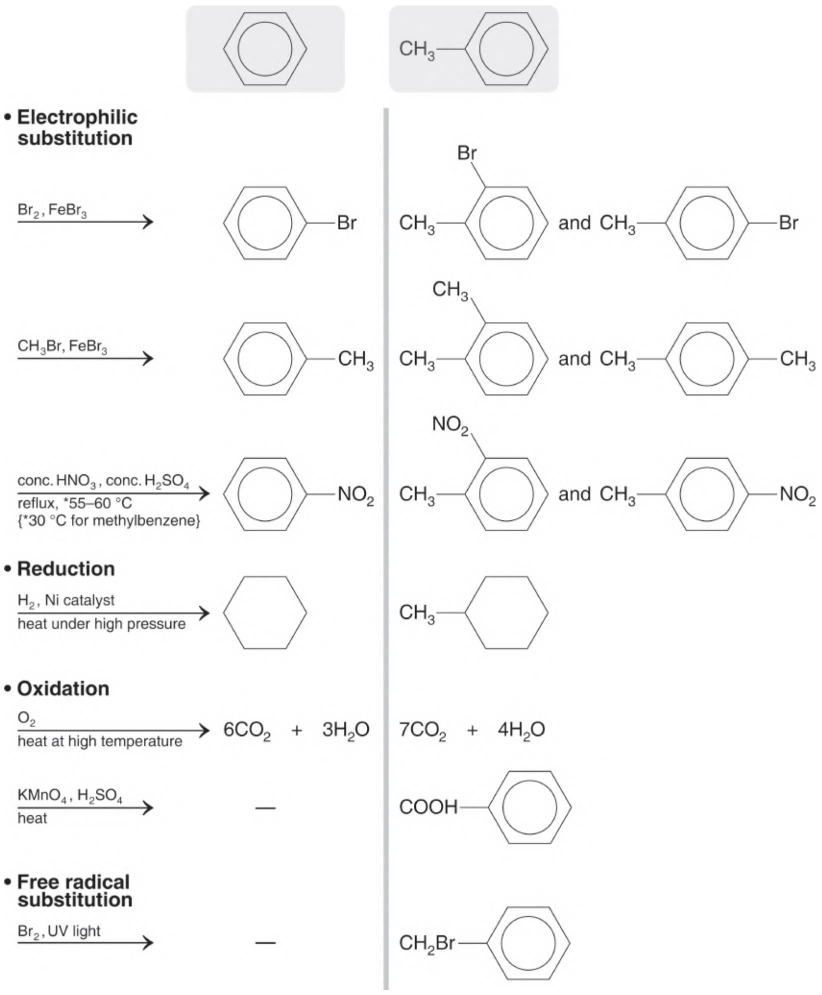
Thus, if the aim is to only brominate the benzene ring, the electrophilic reaction has to take place in the dark to prevent the free radical reaction from occurring.

Q Can the radical attack the benzene ring?

A: Yes, of course. That is why benzene and alkene can undergo Free Radical Addition. It is logically simple; the radical does not have "eyes," so it won't know which to attack and which not to.

Do you know?

— A mind-map showing the important chemical reactions pertaining to benzene and methylbenzene:



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- Reactions that serve as distinguishing tests:
  - When methylbenzene reacts with hot acidified $KMnO_4$, the purple $KMnO_4$ would decolorize. In addition, a white ppt of benzoic acid would form. If a longer alkyl chain is attached to the benzene ring, CO_2 would evolve.
  - When methylbenzene reacts with hot alkaline $KMnO_4$, the purple $KMnO_4$ would decolorize and brown MnO_2 ppt would be observed.

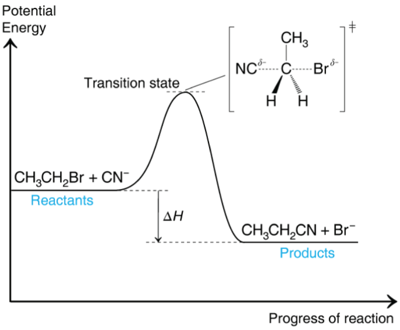
CHAPTER 7

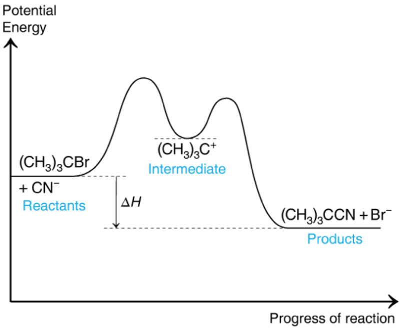
HALOGEN DERIVATIVES

Do you know?

— Halogenolalkanes are polar molecules. Therefore, there are permanent dipole–permanent dipole interaction in addition to the instantaneous dipole–induced dipole interaction that is present. Since the polarity of the bond increases in the order: C–I < C–Br < C–Cl < C–F, the pd–pd interaction should also increase in the same order. But the boiling point of RX increases from RCl < RBr < RI. The observed trend is due to the increase in the number of electrons from RCl to RBr to RI, which leads to an increase in the strength of the id–id interaction.

— Halogenoalkanes are polar molecules with the C atom of the C−X bond bearing the partial positive charge. Nucleophiles are attracted to this electron-deficient site and depending on the nature of the halogenoalkane, the substitution mechanism can be either S_N1 or S_N2. The energy profiles are shown below:





— The strength of the C–X bond decreases from C–Cl > C–Br > C–I, due to the decrease in the effective overlap of orbitals in the covalent bond.

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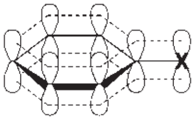
This leads to a decrease in the bond energy. As a result, when reacting with the same nucleophile, the rate of reaction increases from: R−Cl < R−Br < R−I. In fact, fluoroalkanes are generally unreactive toward Nucleophilic Substitution. The explanation for this is similar to that being used to account for the differences in H−X bond strength, i.e., in terms of the effectiveness of orbital overlap in covalent bond formation.

Q Shouldn't the C−F bond be the most polar among all? And thus shouldn't the carbon atom of the C−F bond be more susceptible to nucleophilic attack?

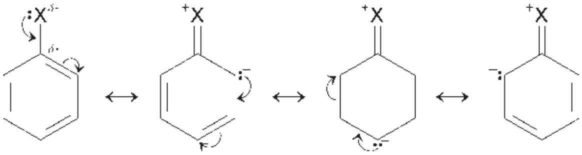
A: Yes, you are right about the C−F bond being the most polar among all. But unfortunately, the trend for the ability to be attacked by a nucleophile: C−F > C−Cl > C−Br > C−I, cannot be used to account for the observed experimental data here, which is, the rate of reaction decreases in the order of: C−I > C−Br > C−CI > C−F.

Do you know?

— It is difficult for halogenoarenes to undergo the Nucleophilic Substitution reaction like its corresponding halogenoalkane. The C−X bond in halogenoarenes (C_6H_5X) has a partial double bond characteristic due to the delocalization of the lone pair of electrons from the halogen atom into the benzene ring via resonance.



The delocalization of electrons also decreases the polarity of the C−X bond. Due to the extended network of delocalized electrons over the halogen and the six sp^2 hybridized carbon atoms, a nucleophile is not as strongly drawn to the C atom of the C−X bond as you would expect in the case of a halogenoalkane. This is because the electron deficiency on the carbon atom has been diminished as shown in the following resonance structures:



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Lastly, a nucleophile is an electron-rich species, thus the inter-electronic repulsion between the electron-rich benzene ring and nucleophile hinders the approach of the nucleophile.

— Though polar, both halogenoalkanes and halogenoarenes have poor solubility in water, especially for molecules with higher molecular weights. The type of interaction that the halogenoalkane molecule could possibly form with water (i.e., pd−pd interaction for lower molecular weight molecule and id–id interaction for higher molecular weight molecule) is much weaker than the hydrogen bonding that exists between the water molecules. These hydrogen bonds need to be overcome first before the halogenolkane molecule can interact with the water molecules. Such a process needs energy. Unfortunately, the intermolecular forces between the halogenoalkane and water molecules do not release a sufficient amount of energy to overcome the strong hydrogen bonds. This would be especially true with the presence of the hydrophobic benzene ring for halogenoarenes, as the id–id interaction of the halogenoarenes and water molecules is relatively weak. Similarly for the halogenoalkanes, when the alkyl group gets bigger, the molecules become more hydrophobic in nature.

1. (a) Outline, by giving reagents and conditions for each step, the sequence of reactions by which you would convert a three-carbon-atom organic molecule such as 1-bromopropane into the next higher member of the same homologous series. Give a mechanistic account for the first step in the conversion process.

Explanation:

To convert: $CH_3CH_2CH_2Br \rightarrow CH_3CH_2CH_2CH_2Br$

Step 1: $CH_3CH_2CH_2Br \rightarrow CH_3CH_2CH_2CN$ {Nucleophilic Substitution}
Reagents/Conditions: NaCN(aq)/ethanol/heat.

Step 2: $CH_3CH_2CH_2CN \rightarrow CH_3CH_2CH_2COOH$ {Acidic hydrolysis}
Reagents/Conditions: H_2SO_4(aq)/heat.

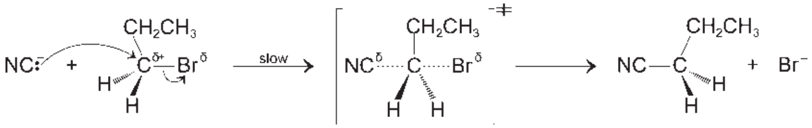
Step 3: $CH_3CH_2CH_2COOH \rightarrow CH_3CH_2CH_2CH_2OH$ {Reduction}
Reagents/Conditions: (i) $LiAlH_4$/dry ether, (ii) H_2O/heat.

Step 4: $CH_3CH_2CH_2CH_2OH \rightarrow CH_3CH_2CH_2CH_2Br$ {Nucleophilic Substitution}

Reagents/Conditions: $PBr_3(l)$.

Since 1-bromopropane is a primary halogenoalkane, we assume it undergoes the one-step Nucleophilic Substitution bimolecular mechanism, S_N2, as follows:

- The nucleophile NC^- attacks the $^{\delta+}C$ from the side opposite to that of the C–Br bond in what is known as the "backside" attack.
- In a concerted move, the following is thought to occur:
  - ○ The C–Br bond undergoes heterolytic cleavage and a Br^- ion is formed, which is known as the leaving group; and
  - ○ C–CN bond is formed.



pentavalent activated complex

(b) With appropriate reagents and conditions, describe a simple chemical test to differentiate the following pair of compounds:

(i) hexane and hex-1-ene;

Explanation:

(1) Use Br_2/CCl_4/dark:

Hexane: No decolorization of brown Br_2.

Hex-1-ene: Brown Br_2 decolorized.

$CH_3(CH_2)_3CH{=}CH_2 + Br_2 \rightarrow CH_3(CH_2)_3CHBrCH_2Br$. {Electrophilic Addition}

(2) Use $Br_2(aq)$/dark:

Hexane: No decolorization of brown Br_2.

Hex-1-ene: Brown Br_2 decolorized.

$CH_3(CH_2)_3CH{=}CH_2 + Br_2 + H_2O \rightarrow CH_3(CH_2)_3CH(OH)CH_2Br + HBr$. {Electrophilic Addition}

(3) Use $KMnO_4/H_2SO_4$/heat:
Hexane: No decolorization of purple $KMnO_4$.
Hex-1-ene: Purple $KMnO_4$ decolorized.
$CH_3(CH_2)_3CH{=}CH_2 + 5[O] \rightarrow CH_3(CH_2)_3COOH + CO_2 + H_2O$.
{Oxidation}

(4) Use $KMnO_4$/NaOH/cold:
Hexane: No decolorization of purple $KMnO_4$.
Hex-1-ene: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.
$CH_3(CH_2)_3CH{=}CH_2 + [O] + H_2O \rightarrow CH_3(CH_2)_3CH(OH)CH_2OH$.
{Oxidation}

(ii) 3-chloromethylbenzene and (chloromethyl)benzene; and

Explanation:

Test: Add NaOH(aq) to each of these compounds and heat. Next, cool the mixture followed by adding HNO_3(aq). Lastly, add $AgNO_3$(aq).

Observation: Only a white ppt of AgCl would be observed for (chloromethyl)benzene.

Q Why isn't any AgCl formed for 3-chloromethylbenzene?

A: This is because the Cl-group of 3-chloromethylbenzene is bonded to the benzene. The lone pair of electrons on the Cl atom delocalizes into the benzene ring and this results in a partial double bond characteristic between the carbon–chlorine bond, which is difficult to break.

Q So can the halogenoarenes undergo Nucleophilic Substitution at all?

A: Under extreme conditions of heating or at high pressures, yes!

Q What is the purpose of cooling the mixture and adding HNO_3(aq) before the addition of $AgNO_3$(aq)?

A: Cooling is needed to prevent $AgNO_3$ from decomposing since it is thermally unstable. The acidification using HNO_3 is to remove the excess NaOH. If not, when $AgNO_3$ is added, Ag(OH) may be precipitated out. Using HNO_3 instead of HCl or H_2SO_4 for acidification prevents introducing anions into the system that may be precipitated out by the Ag^+ ion.

(iii) (chloromethyl)benzene and (bromomethyl)benzene.

Explanation:

Test: Add NaOH(aq) to each of these compounds and heat. Next, cool the mixture before adding HNO_3(aq). Lastly, add $AgNO_3$(aq).

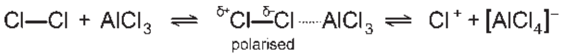
Observation: (Chloromethyl)benzene: White ppt of AgCl observed.
(Bromomethyl)benzene: Cream ppt of AgBr observed.

(c) (i) 3-chloromethylbenzene can be synthesized from methylbenzene. Give an account of the mechanism for the conversion, stating the reagents and conditions.

Explanation:

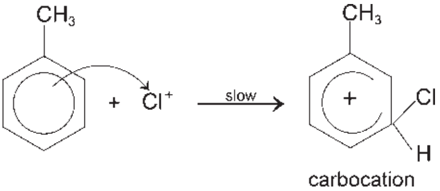
3-chloromethylbenzene can be synthesized from methylbenzene using Cl_2 in the presence of $AlCl_3$ or $FeCl_3$. The reaction mechanism is Electrophilic Substitution:

Step 1: Generation of the electrophile by the Lewis acid catalyst, $AlCl_3$.

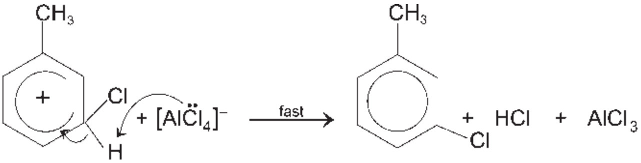


$$Cl{-}Cl + AlCl_3 \rightleftharpoons \underbrace{\overset{\delta+}{Cl}{-}\overset{\delta-}{Cl}\cdots AlCl_3}_{\text{polarised}} \rightleftharpoons Cl^+ + [AlCl_4]^-$$

Step 2: The electrophile attacks the electron-rich benzene to form a carbocation intermediate.



Step 3: The carbocation is deprotonated to regain the resonance-stabilized benzene ring and the Lewis acid catalyst is regenerated.



Q Since a methyl group is a 2,4-director, shouldn't the yield of 3-chloromethylbenzene be low if we proceed by the above pathway?

A: Yes, indeed the yield of 3-chloromethylbenzene would be low as it is a minor product compared to the other two major products, 2-chloromethylbenzene and 4-chloromethylbenzene. But what can we do? As the question requires us to propose a direct synthetic pathway, we need to answer according to what the question asks for.

Q Why is the $AlCl_3$ or $FeCl_3$ able to act as a Lewis acid catalyst?

A: A Lewis acid is an electron-pair acceptor. Both the Al and Fe atoms are electron-deficient species. They have a vacant low-lying orbital to accept a lone pair of electrons. In addition, they are able to do this because of their high charge density that allows them to polarize the lone pair of electrons from the Lewis base, which is an electron-pair donor.

Q Why did we need a catalyst then?

A: Without the catalyst, if benzene is mixed with halogen in the absence of light, there would not be any reaction. But if the halogen is mixed with an alkene, there would be reaction. So, the comparison shows that benzene, though a relatively electron-rich species than an alkene, is less susceptible to electrophilic attack. Of course, the reason is ascribed to its resonance stability. Thus, in order to "force" a reaction on benzene, we need to create a stronger electrophile, hence the need of a catalyst.

Q Would the HCl gas evolve as white fumes?

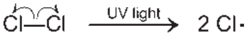
A: Yes, hence this may serve as some form of characteristic test for benzene-containing compounds.

(ii) (Chloromethyl)benzene can also be synthesized from methylbenzene under a different set of conditions. Give an account of the mechanism for the conversion, stating the reagents and conditions.

Explanation:

(Chloromethyl)benzene can be synthesized from methylbenzene using Cl_2 in the presence of light or strong heating. The reaction mechanism is Free Radical Substitution:

Step 1: Chain initiation with the generation of free radicals



Step 2: Chain propagation
(a) $Cl\bullet + C_6H_5CH_3 \rightarrow C_6H_5CH_2\bullet + HCl$
(b) $C_6H_5CH_2\bullet + Cl_2 \rightarrow C_6H_5CH_2Cl + Cl\bullet$
and the cycle repeats itself.

Step 3: Chain termination
$Cl\bullet + C_6H_5CH_2\bullet \rightarrow C_6H_5CH_2Cl$
$Cl\bullet + Cl\bullet \rightarrow Cl_2$
$C_6H_5CH_2\bullet + C_6H_5CH_2\bullet \rightarrow C_6H_5CH_2CH_2C_6H_5$

(iii) (Chloromethyl)benzene yields a white precipitate when warmed with aqueous silver nitrate solution, whereas 3-chloromethylbenzene does not. Explain the observations.

Explanation:

The lone pair of electrons of the –Cl group in 3-chloromethylbenzene delocalizes into the benzene ring and results in a partial double bond characteristic between the carbon–chlorine bond, which is difficult to break. In addition, because of this delocalization, the carbon atom that is bonded to the Cl group becomes less electron-deficient. There is also the interelectronic repulsion between the electron-rich benzene ring and nucleophile, which thus hinders the approach of the nucleophile. Hence, the –Cl group of 3-chloromethylbenzene cannot undergo Nucleophilic Substitution as readily as the (chloromethyl)benzene, releasing a chloride ion.

2. (d) Gaseous compound **P** has a density of 4.6 kg m^{-3} at s.t.p. **P** contains only the elements carbon, hydrogen, oxygen, and chlorine. On combustion, 0.158 g of **P** gave 0.225 g of carbon dioxide and 0.089 g of water. On treatment with aqueous silver nitrate solution, 0.158 g of silver chloride evolved.

   (i) Determine the empirical and molecular formula of P.

Explanation:

Volume of 0.158 g of **P** = $(1.58 \times 10^{-4})/4.6 = 3.435{\times}10^{-5}$ $m^{3.}$
Amount of **P** in 0.158 g = $3.435 \times 10^{-5}/0.0224 = 1.53{\times}10^{-3}$ mol.
Amount of CO_2 in 0.225 g = $0.225/44 = 5.11 \times 10^{-3}$ mol.
Amount of H_2O in 0.089 g = $0.089/18 = 4.94 \times 10^{-3}$ mol.
Amount of AgCl in 0.158 g = $0.158/143.5 = 1.10 \times 10^{-3}$ mol.
The molar ratio C : H : Cl = $5.11 \times 10^{-3} : 2 \times 4.94 \times 10^{-3} : 1.10 \times 10^{-3}$
$= 4.65 : 8.99 : 1$
$= 5 : 9 : 1.$
The empirical formula of **P** is C_5H_9Cl.
Molar mass of **P** = $0.158/1.53 \times 10^{-3} = 103.3$ g mol^{-1}.
Molecular formula = $n \times$ Empirical formula
$\Rightarrow n \times (5 \times 12 + 8 \times 1 + 35.5 \times 1) = 103.3$
$\Rightarrow n = 1.$
Molecular formula = C_5H_9Cl.

Do you know?

— A halogen atom, like a hydrogen atom, forms a single bond with the carbon atom. Thus, we can treat a halogen atom just like a hydrogen atom. The molecular formula of C_5H_9Cl can be treated as equivalent to C_5H_{10}, which means that for a molecule containing five carbon atoms, the maximum number of hydrogen atoms should be 10. Therefore, the compound with the molecular formula C_5H_9Cl has either a double bond or a ring structure.

(ii) Give two possible constitutional/structural formulae for **P**.

Explanation:

The two possible constitutional/structural formulae for **P** are $CH_2{=}CHCH_2CH_2CH_2Cl$ and $CH_2{=}CHCH_2CH(Cl)CH_3$.

Q Can we propose $ClCH{=}CHCH_2CH_2CH_3$ or $CH_2{=}C(Cl)CH_2CH_2CH_3$?

A: No! This is because for both molecules, the –Cl group is bonded to an sp^2 hybridized carbon atom involved in a pi bond formation. So, like what happens in chlorobenzene, C_6H_5Cl, the lone pair of electrons on the –Cl group of can $ClCH{=}CHCH_2CH_2CH_3$ and $CH_2{=}C(Cl)CH_2CH_2CH_3$ can delocalize into the C=C double bond. As a result, there is also partial double bond characteristic between the carbon–chlorine bond in these two compounds. Thus, the –Cl group is less susceptible to Nucleophilic Substitution and this won't fit the given information in the question.

(e) Explain why when chloroethane is treated with aqueous potassium hydroxide, it undergoes substitution of Cl by OH, whereas CH_3CH_2CN does not undergo replacement of CN by OH.

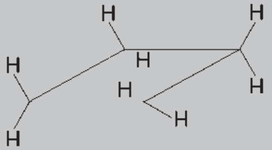
Explanation:

In chloroethane, the carbon atom is directly bonded to the —Cl group. Due to the higher electronegativity of the Cl atom than that of the carbon atom, the carbon atom of the C—Cl bond is electron-deficient. Hence, it can attract a nucleophile, which is an electron-rich species. But for CH_3CH_2CN, the carbon atom that is bonded to the –CN group is not directly bonded to the N atom (C—C≡N). As such, it is not electron-deficient enough to attract a nucleophile.

Do you know?

- If you compare the bond energy of a C–C bond (+350 kJ mol^{-1}) to that of a C–Cl (+340 kJ mol^{-1}), it is easier to break the C–Cl bond. This, thus makes the substitution of the CN by the OH in CH_3CH_2CN less favorable.
- In addition, even if you can substitute the –CN group, it would be given out as a ^{-}CN with a negative charge residing on a lowly electronegative carbon atom. This would be a strong nucleophile instead.

2. The three-dimensional structure of cyclobutane is shown below:



(a) Explain why the C−C bond energy for butane is greater than that for cyclobutane.

Explanation:

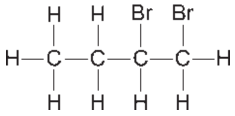
In cyclobutane, the carbon atom is not really of the tetrahedral configuration as the C–C–C bond angle is about 90°. Hence, the inter-electronic repulsion between the C—C bonds would weaken the C—C bonds. This is called ring strain. Thus, a smaller amount of energy is required to break the C─C bond in cyclobutane than in butane.

Do you know?

— As the number of carbon atoms in a ring gets greater, the amount of ring strain decreases. That is why cyclopropane is highly unstable among the cycloalkanes.

(b) Give the three-dimensional structure of the compound, 1,2-dibromobutane, like for cyclobutane above.

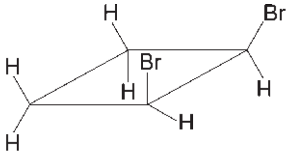
Explanation:



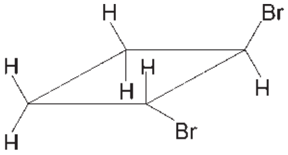
$$\begin{array}{ccccccccc} & & H & & H & & Br & & Br & \\ & & | & & | & & | & & | & \\ H & — & C & — & C & — & C & — & C & — & H \\ & & | & & | & & | & & | & \\ & & H & & H & & H & & H & \end{array}$$

(c) (i) Use the diagram in (*a*) to explain how 1,2-dibromocyclobutane exhibits *cis-trans*/geometrical isomerism.

Explanation:



cis-1,2-dibromocyclobutane



trans-1,2-dibromocyclobutane

As the ring has restricted rotation and plus there are two different groups of atoms bonded to each of the two carbon atoms, 1,2-dibromocyclobutane is able to exhibit *cis-trans*/geometrical isomerism.

(ii) State with reasons, which of the *cis* or *trans* isomer would have the higher boiling point.

Explanation:

The *cis* isomer would have a higher boiling point than the *trans* isomer as the *cis* isomer is more polar than the *trans* isomer. Hence, the permanent dipole–permanent dipole interaction in the *cis* isomer is stronger.

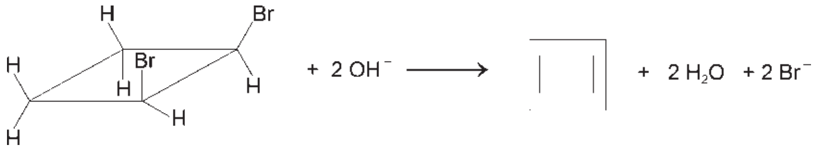
Q Would the ring strain of 1,2-dibromocyclobutane be greater than that of cyclobutane?

A: Of course. The –Br group is bigger than a H atom, hence the inter-electronic repulsion between the two –Br groups would weaken the C–C bond further in 1,2-dibromocyclobutane. In addition, we would also expect the ring strain of *cis*-1,2-dibromocyclobutane to be greater than that of *trans*-1,2-dibromocyclobutane as the two –Br groups are on the same side of the plane; hence, there is greater inter-electronic repulsion as compared to if they are on opposite sides as in *trans*-1,2-dibromocyclobutane.

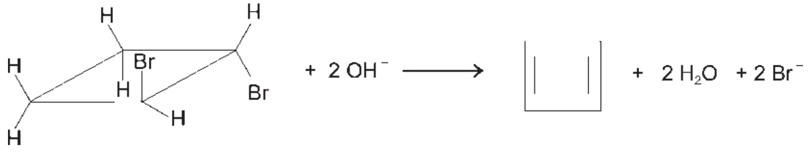
(iii) Both *cis-trans*/geometrical isomers react with alcoholic KOH to give one product of the same molecular formula C_4H_4. Write balanced equations to show their formation.

Explanation:

For *cis*-1,2-dibromocyclobutane:



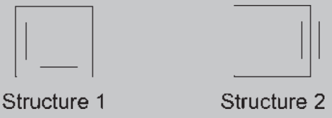
For *trans*-1,2-dibromocyclobutane:



Do you know?

— NaOH(aq) with heating would encourage Nucleophilic Substitution, whereas NaOH in ethanol with heating would encourage mostly Elimination reaction. This is because the same OH^- in water is a strong nucleophile but in ethanol, it is a strong base (refer to Chapter 3).

Q Can we obtain the following compounds from the elimination of 1,2-dibromocyclobutane?

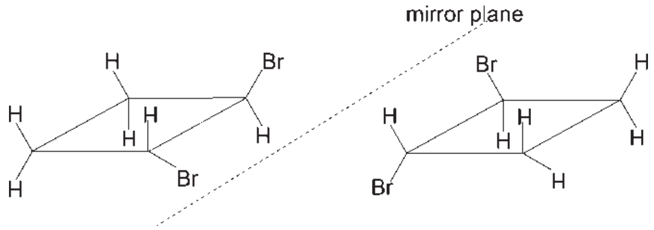


A: Quite impossible. For Structure 1, the carbon atom that forms two C=C double bonds is likely to be *sp* hybridized, which should have a theoretical bond angle of 180^o. But the angle would be about 90^o in the ring. There would be too much ring strain. As for Structure 2, the two carbon atoms forming the C≡C should also be *sp* hybridized with a bond angle of 180^o. Again, there is too much ring strain. Hence, due to ring strain, the above two compounds would be highly unstable.

(d) One of the *cis-trans*/geometrical isomers in (*b*) also exhibits enantiomerism. Draw the pair of enantiomers and explain why the enantiomers have different optical activities.

Explanation:

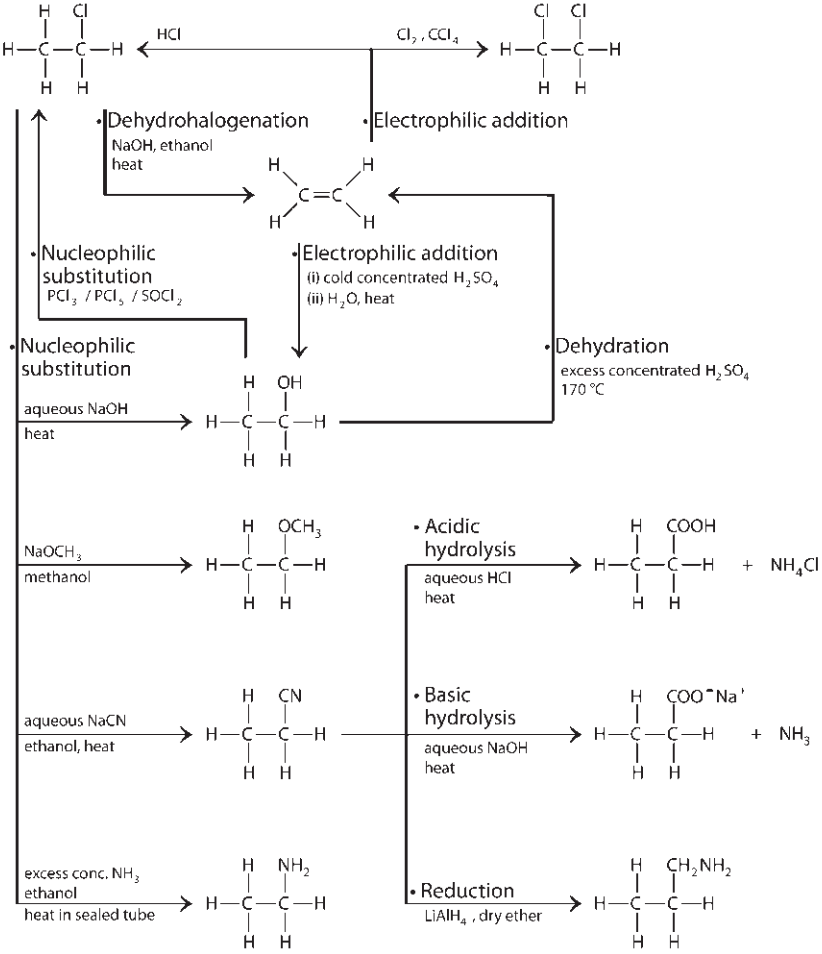
Although both *cis-trans*/geometrical isomers contain two chiral carbon atoms each, only the *trans*-1,2-dibromocyclobutane is optically active. This is because the *cis*-1,2-dibromocyclobutane is a *meso* compound as it contains an internal plane of symmetry. The pair of enantiomers for *trans*-1,2-dibromocyclobutane is shown below:



The enantiomers have different optical activities because they rotate plane-polarized light to the same extent but in opposite directions.

Do you know?

— A mind-map showing the important chemical reactions pertaining to chloroethane:



- Reaction that serves as a distinguishing test:
  - ○ The hydrolysis of the RX to form an alcohol releases the halide ion (Cl^-, Br^-, I^-), which can serve as a characteristic test for the identity of the halogenoalkane, by using $AgNO_3$(aq).

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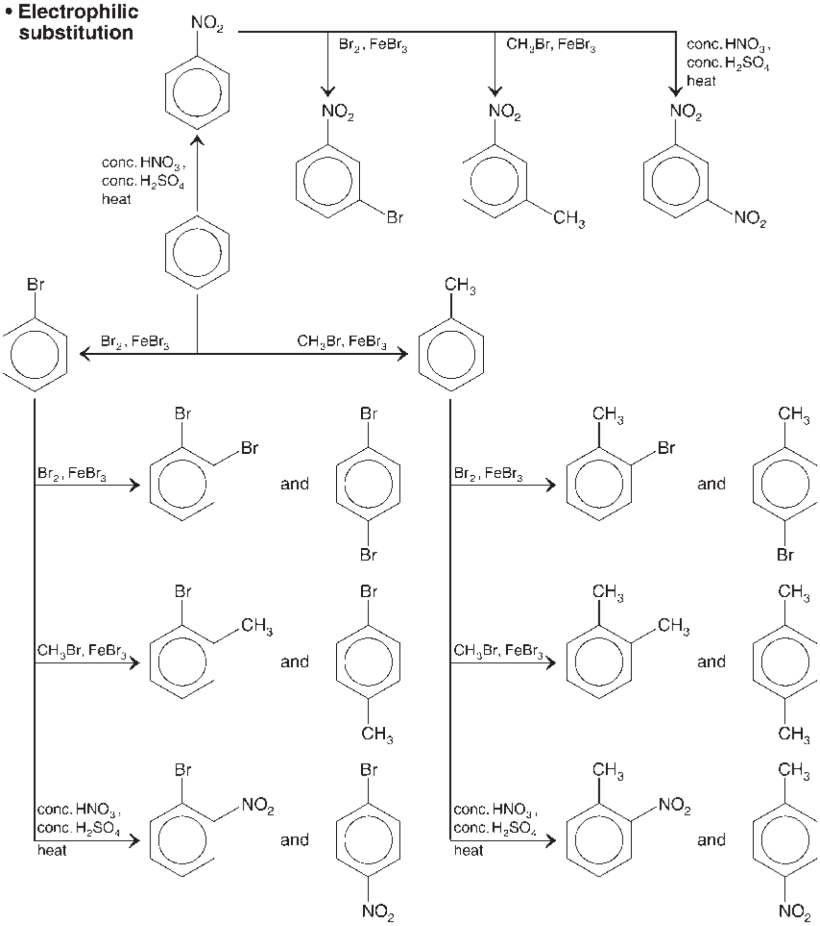
In addition, it can also distinguish between alkyl halides and halogenoarenes. The latter does not undergo hydrolysis easily.

— A mind-map showing the important chemical reactions pertaining to bromobenzene:



CHAPTER 8

ALCOHOLS AND PHENOL

Do you know?

Boiling point and solubility

- The boiling and melting points of alcohols increase with an increase in the carbon-chain length. This arises because of an increase in the number of electrons as the number of carbon atoms increases. Importantly, an alcohol's higher boiling point among most organic molecules of similar molecular weight, is due to the presence of strong hydrogen bonding. But as the carbon-chain length increases, the importance of hydrogen bonding diminishes as compared to the increase in the instantaneous dipole–induced dipole interaction due to increase in the number of electrons the higher molecular weight alcohol molecule has.
- The boiling point of low-molecular-weight alcohols, such as methanol and ethanol, is lower than that of water because alcohol molecules form less extensive hydrogen bonding than water. Alcohol molecules on the average only form one hydrogen bond per molecule, whereas water can form two hydrogen bonds per molecule.
- Due to its massive electron cloud, phenol is a solid at room temperature because of the strong id–id interaction arises from the large hydrophobic benzene ring, in addition to the hydrogen bonding.
- The solubilities of alcohols and phenol in water are much better than the non-polar hydrocarbon because of their ability to form hydrogen

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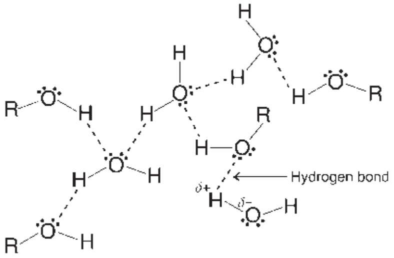
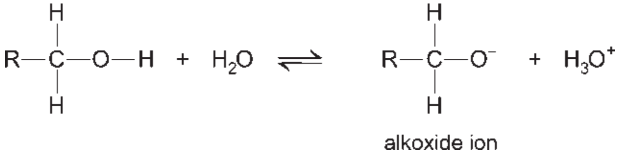
bonding with water molecules. But this does not mean that phenol is very soluble in water as it has a large hydrophobic benzene ring.



Acidity of alcohol

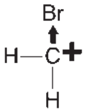
— Alcohols are the weakest organic acid among all because the conjugate base, RO^-, is the least stable.

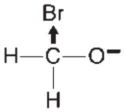


This is due to destabilization brought about by the intensification of electron density on the RO^- as a result of the electron-releasing effect (via inductive effect) of the alkyl group. Hence, the greater the number of alkyl groups that are present in the alcohol molecule, the less acidic is the alcohol.

Decreasing acid strength:
$RCH_2OH > R_2CHOH > R_3COH$

An electron-withdrawing group increases the acid strength as it disperses the electron density on the alkoxide conjugate base:





Compared to the carbocation, the electron-withdrawing effect has a destabilizing effect on the carbocation.

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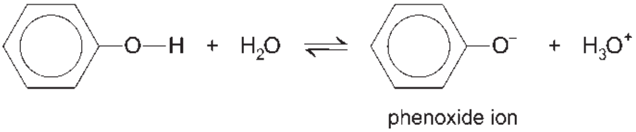
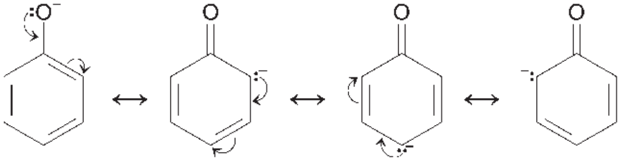
Acidity of phenol

— Phenol is a stronger acid than alcohols because the negative charge on the phenoxide ion can disperse into the benzene ring through resonance.



Thus, the phenoxide ion is resonance stabilized:



Therefore, like the –OH group in phenol, the negatively charged oxygen atom of the phenoxide is a 2,4-director, as can be seen from the accumulation of electron density on the 2- and 4-positions. In fact, the benzene ring of the phenoxide is much more electron-rich than the undissociated phenol.

— The electron-withdrawing group in a substituted phenol causes the molecule to be more acidic than an unsubstituted phenol as the electron density that is delocalized into the benzene ring of the phenoxide ion is further dispersed by the electron-withdrawing group, and vice versa.

— The electron-releasing group causes the molecule to be less acidic than an unsubstituted phenol.

Comparison of acidity of alcohol and phenol

— Increasing acid strength: ROH < H_2O < phenol.

— The relative acidities of these compounds can be observed from their reactions or non-reactions with the following bases and reactive metal:

	Na	NaOH	Na_2CO_3 or $NaHCO_3$
Phenol	☑ $H_2(g)$ + salt	☑ H_2O + salt	—
Water	☑ $H_2(g)$ + salt	—	—
ROH	☑ $H_2(g)$ + salt	—	—

(*Continued*)

(*Continued*)

Hydrolysis of the alkoxide and phenoxide conjugate bases

— Organic compounds that are formed from weak organic acids, such as alcohols and phenol, undergo alkaline hydrolysis in water. The hydrolytic product is actually the weak acid itself:

$$C_6H_5O^- + H_2O \rightleftharpoons C_6H_5OH + OH^-,$$
$$RO^- + H_2O \rightleftharpoons ROH + OH^-.$$

The weaker the weak acid, the stronger would the hydrolysis of its conjugate base be.

A: The strength of an acid depends on the extent of its dissociation in an aqueous solution and this extent of dissociation is indicated by the acid dissociation constant, K_a. Consider the partial dissociation of a weak acid, CH_3COOH:

$CH_3COOH(aq) + H_2O(l) \rightleftharpoons CH_3COO^-(aq) + H_3O^+ (aq)$.

$$\text{Acid dissociation constant, } K_a = \frac{[CH_3COO^-(aq)][H_3O^+(aq)]}{[CH_3COOH(aq)]}.$$

The magnitude of K_a is fixed at a particular temperature and is independent of the concentration of the weak acid. The greater the magnitude of K_a, the higher would the concentration of the H_3O^+ ions present at equilibrium be. Although the magnitude of K_a serves to measure the strength of acids, it is more convenient to use the corresponding pK_a value for comparison. The relationship between K_a and pK_a is given as follows:

$$pK_a = -\log K_a$$

The smaller the pK_a value, the stronger the acid.

Q What affects the stability of the conjugate bases of the weak acids?

A: Remember for a charged species, its stability depends on the extent of charge dispersal. For these anionic species, if the negative charge can be made less concentrated on the oxygen atom bearing it, there will be less tendency for it to be attacked by H_3O^+, rendering it to be more stable. We would then expect that electron-withdrawing groups could help to disperse this negative charge on the O atom and thus make the anion less basic and hence more stable. On the other hand, electron-donating groups would tend to destabilize the anion as these groups could increase the electron density on the O atom, making it more susceptible to attack by H_3O^+.

1. (a) The organic compound, **P**, is known to contain bromine and no other halogen. Describe how you would determine its percentage by mass of bromine.

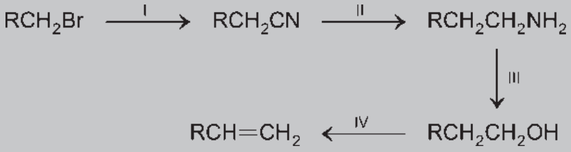
Explanation:

(i) Take a known mass of compound **P**, add NaOH(aq) to it and heat.
(ii) Next, cool the mixture before adding HNO_3(aq).
(iii) Add $AgNO_3$(aq) to precipitate out AgBr(s).
(iv) Filter the AgBr(s) and dry it to constant mass.
(v) Weigh and determine the mass of the Br in AgBr.
(vi) Calculate the percentage by mass of bromine in the mass of **P** used.

Q What would happen if the bromine atom is bonded to a benzene ring, would we still be able to "extract" the bromine atom?

A: Well, you need a more drastic condition to do so. In the above, we are assuming that compound **P** is a normal bromoalkane.

(b) The plan for a sequence of reactions is as follows:



(i) Describe briefly the reagents and conditions you would carry out for each of the conversions: I, II, III, and IV.

Explanation:

Step I:	NaCN(aq)/ethanol/heat	{Nucleophilic Substitution}
Step II:	(i) $LiAlH_4$/dry ether, (ii) H_2O/heat	{Reduction}
Step III:	$NaNO_2$/HCl(aq)/0^oC	{Diazotization followed by hydrolysis}
Step IV:	Excess conc. H_2SO_4/170^oC	{Dehydration/Elimination}

Do you know?

— When a primary amine, RNH_2, is treated with $NaNO_2$/HCl(aq)/0^oC, the nitrous acid or nitric(III) acid would convert the amine to a diazonium ion, $RN{\equiv}N^+$, which is highly unstable and decomposes spontaneously to the alcohol, ROH, and N_2 gas. Hence, using $NaNO_2$/HCl(aq) also serve as a characteristic test for the presence of a primary amine functional group.

(ii) When $RCH{=}CH_2$ was analyzed at r.t.p., 60 cm^3 of $RCH{=}CH_2$, weighing 0.14 g, were found to react with an equal volume of hydrogen gas. Determine the relative molecular mass and hence the constitutional/structural formula of $RCH{=}CH_2$.

Explanation:

$$RCH{=}CH_2(g) + H_2(g) \rightarrow RCH_2CH_3(g).$$

Assuming pV = nRT, under constant p and T, $n \propto V$.
Amount of H_2 in 60 cm^3 = 60/24000 = 2.50×10^{-3} mol.
Amount of $RCH{=}CH_2$ = Amount of H_2 in 60 cm^3 = 2.50×10^{-3} mol.
Molar mass of $RCH{=}CH_2$ = 0.14/2.50×10^{-3} = 56.0 g mol^{-1}.
Relative molecular mass of $RCH{=}CH_2$ = R + 13 + 14 = 56.0.

$$\Rightarrow \text{Relative molecular mass of R} = 29.0.$$

Therefore, R is likely to be CH_3CH_2, which has a relative molecular mass of 29.0.
Hence, $RCH{=}CH_2$ is $CH_3CH_2CH{=}CH_2$.

(iii) With appropriate reagents and conditions, describe a simple chemical test to differentiate the following pair of compounds:
(A) RCH_2Br and RCH_2CN;

Explanation:

Use NaOH(aq)/heat and test the gas with moist red litmus paper:

RCH_2Br: No alkaline gas evolved turned moist red litmus paper blue.
RCH_2CN: Alkaline gas evolved turned moist red litmus paper blue. Gas is NH_3.

$RCH_2CN + OH^- + H_2O \rightarrow RCH_2COO^- + NH_3(g)$. {Alkaline hydrolysis}

Q Can we use NaOH(aq)/heat, cooled, followed by $HNO_3(aq)$, and then add $AgNO_3(aq)$ to test for the cream ppt of AgBr?

A: Yes, but this is more troublesome than the given one-step test above. Remember 'simple chemical test.'

(B) RCH_2Br and RCH_2CH_2OH;

Explanation:

To differentiate between RCH_2Br and RCH_2CH_2OH, just use any one of the following tests:

(1) Use PCl_5 and test for HCl(g):

RCH_2Br: No white fumes of HCl(g).
RCH_2CH_2OH: White fumes of HCl(g) observed.
$RCH_2CH_2OH + PCl_5 \rightarrow RCH_2CH_2Cl + POCl_3 + HCl(g)$. {Nucleophilic Substitution}

(2) Use $SOCl_2$ and test for HCl(g):

RCH_2Br: No white fumes of HCl(g).
RCH_2CH_2OH: White fumes of HCl(g) observed.
$RCH_2CH_2OH + SOCl_2 \rightarrow RCH_2CH_2Cl + SO_2 + HCl(g)$. {Nucleophilic Substitution}

(3) Use $KMnO_4/H_2SO_4$/heat:

RCH_2Br: No decolorization of purple $KMnO_4$.
RCH_2CH_2OH: Purple $KMnO_4$ decolorized.
$RCH_2CH_2OH + 3[O] \rightarrow RCH_2COOH + H_2O$. {Oxidation}

(4) Use $KMnO_4$/NaOH/cold:

RCH_2Br: No decolorization of purple $KMnO_4$.
RCH_2CH_2OH: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.
$RCH_2CH_2OH + OH^- + 2[O] \rightarrow RCH_2COO^- + 2H_2O$. {Oxidation}

Q Can we use PCl_3 to test for the presence of an –OH functional group?

A: No, we cannot, because there is no evolution of gas, no formation of ppt, nor color change when PCl_3 reacts with an –OH group:

$$3ROH + PCl_3 \rightarrow 3RCl + H_3PO_3.$$

Q Can we convert the alcohol to an ester by reacting it with a carboxylic acid in the presence of conc. H_2SO_4 and then recognize the sweet-smelling ester evolved by smell?

A: Try not to use smell as a form of test as it is not very objective. And do not forget, not all esters are sweet-smelling.

(C) RCH_2Br and $RCH{=}CH_2$;

Explanation:

To differentiate between RCH_2Br and $RCH{=}CH_2$, just use any one of the following tests:

(1) Use Br_2/CCl_4/dark:

RCH_2Br: No decolorization of brown Br_2.
$RCH{=}CH_2$: Brown Br_2 decolorized.
$RCH{=}CH_2 + Br_2 \rightarrow RCHBrCH_2Br$. {Electrophilic Addition}

(2) Use $Br_2(aq)$/dark:

RCH_2Br: No decolorization of brown Br_2.
$RCH{=}CH_2$: Brown Br_2 decolorized.
$RCH{=}CH_2 + Br_2 + H_2O \rightarrow RCH(OH)CH_2Br + HBr$.
{Electrophilic Addition}

(3) Use $KMnO_4/H_2SO_4$/heat:

RCH_2Br: No decolorization of purple $KMnO_4$.
$RCH{=}CH_2$: Purple $KMnO_4$ decolorized.
$RCH{=}CH_2 + 5[O] \rightarrow RCOOH + CO_2 + H_2O$. {Oxidation}

(4) Use $KMnO_4$/NaOH/cold:

RCH_2Br: No decolorization of purple $KMnO_4$.
$RCH{=}CH_2$: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.
$RCH{=}CH_2 + [O] + H_2O \rightarrow RCH(OH)CH_2OH$. {Oxidation}

Q Can we use hydrogenation of alkenes to test for the presence of $C{=}C$ double bonds?

A: No! It is not easy to carry that out in the test tube. In addition, there is no visible observation that can be done.

(D) RCH_2CH_2OH and $RCH{=}CH_2$

Explanation:

To differentiate between RCH_2CH_2OH and $RCH{=}CH_2$, just use any one of the following tests:

(1) Use Br_2/CCl_4/dark:

RCH_2CH_2OH: No decolorization of brown Br_2.
$RCH{=}CH_2$: Brown Br_2 decolorized.
$RCH{=}CH_2 + Br_2 \rightarrow RCHBrCH_2Br$. {Electrophilic Addition}

(2) Use $Br_2(aq)$/dark:

RCH_2CH_2OH: No decolorization of brown Br_2.
$RCH{=}CH_2$: Brown Br_2 decolorized.
$RCH{=}CH_2 + Br_2 + H_2O \rightarrow RCH(OH)CH_2Br + HBr$. {Electrophilic Addition}

(3) Use PCl_5 and test for HCl(g):

$RCH{=}CH_2$: No white fumes of HCl(g).
RCH_2CH_2OH: White fumes of HCl(g) observed.
$RCH_2CH_2OH + PCl_5 \rightarrow RCH_2CH_2Cl + POCl_3 + HCl(g)$.
{Nucleophilic Substitution}

(4) Use $SOCl_2$ and test for HCl(g):

$RCH{=}CH_2$: No white fumes of HCl(g).
RCH_2CH_2OH: White fumes of HCl(g) observed.
$RCH_2CH_2OH + SOCl_2 \rightarrow RCH_2CH_2Cl + SO_2 + HCl(g)$.
{Nucleophilic Substitution}

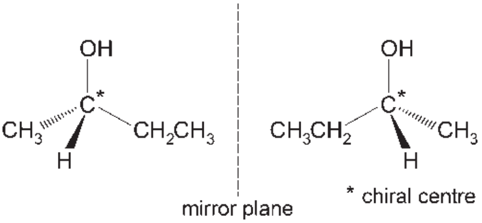
(c) An alcohol, C_4H_9OH, has two stereoisomers, **R** and **R**', which both have the same melting and boiling points. If **R** and **R**' are heated with concentrated sulfuric acid at 170°C, a hydrocarbon, C_4H_8, is produced, which can also exist as two stereoisomers, **S** and **S**'. Both **S** and **S**' have different melting and boiling points. Deduce the structures of the two stereoisomers and explain the type of isomerism illustrated by each pair.

Explanation:

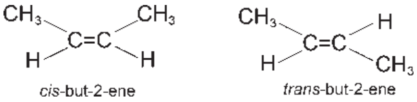
If C_4H_9OH, has two stereoisomers ⇒ the alcohol contains a chiral carbon and exhibits enantiomerism.

When an alcohol undergoes dehydration, it gives an alkene, C_4H_8. Since the alkene exhibits stereoisomerism ⇒ it must be *cis-trans*/geometrical isomerism ⇒ there are two different groups bonded to each of the carbon atoms of the C=C.

The two enantiomers, **R** and **R'**:



The two *cis-trans*/geometrical isomers, **S** and **S'**:



Do you know?

— In addition to *cis*- and *trans*-but-2-ene, but-1-ene can also be produced from the dehydration of butan-2-ol. So, there are a total of three isomers being formed when butan-2-ol undergoes dehydration.

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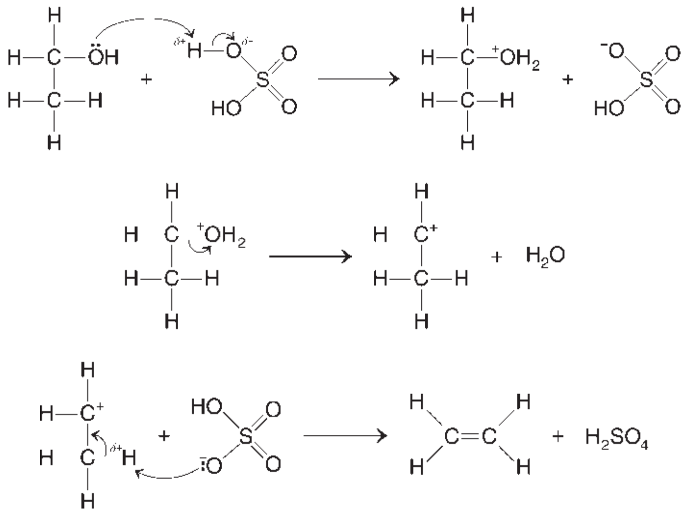
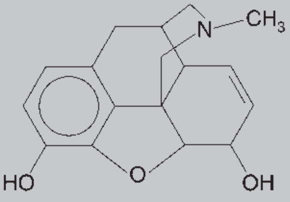
— The purpose of concentrated H_2SO_4 is to make the −OH group a better leaving group through protonation:

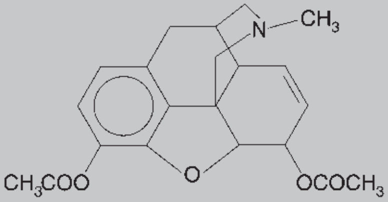


— Other than excess conc. H_2SO_4 at 170°C, we can also use solid AI_2O_3, at 400°C, or H_3PO_4 at 200–250°C to effect the dehydration of an alcohol.

(d) The two −OH groups in morphine are chemically different but both can be esterified in the same way to make heroin.



Morphine



Heroin

(i) Other than the −OH groups, name the other functional groups that are present in each of the above molecule.

Explanation:

Morphine: Ether (C–O–C), alkene, and tertiary amine.
Heroin: Ester, ether (C–O–C), alkene, and tertiary amine.

Do you know?

— A –OH group in an ROH should be named as 'alcohol functional group,' while if it is bonded to a benzene ring, then it should be labeled as 'phenol functional group.'

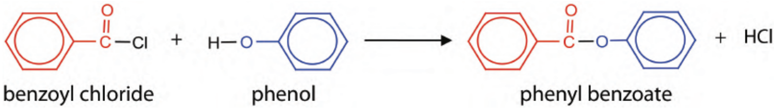
(ii) Explain, in terms of the structure of the –OH group and the surrounding molecule, why the two –OH groups in morphine show different chemical behaviors.

Explanation:

The lone pair of electrons of the –OH group that is bonded to a benzene ring can delocalize into the benzene ring. This thus makes the oxygen atom less nucleophilic. As for the –OH group of the alcohol, the electron-donating alkyl group intensifies the electron density on the oxygen atom. Hence, this makes the lone pair of electrons more nucleophilic. Thus, we can react an alcohol with a carboxylic acid to form an ester in the presence of some concentrated H_2SO_4 as the catalyst. But we can't do the same with phenol and carboxylic.

Do you know?

— In order to get the phenolic ester, we need to react a phenol with an acid chloride:



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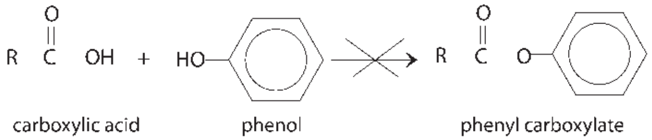
Reacting a phenol with a carboxylic acid will not work!



Converting the phenol to phenoxide to make it more reactive with the carboxylic acid will not work either because of the acid–base reaction between phenoxide and carboxylic acid:

$$RCOOH + C_6H_5O^- \rightarrow C_6H_5OH + RCOO^-.$$

Remember, carboxylic acid is a stronger acid than phenol. This would mean that a phenoxide ion is a stronger base than a carboxylate ion. Hence, instead of a nucleophilic reaction, we would have a acid–base reaction.

(iii) Give reagents and conditions as to how the two −OH groups in morphine could be esterified using the same method.

Explanation:

Use anhydrous CH_3COCl at room temperature.

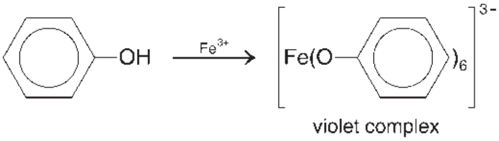
(iv) Suggest a simple chemical test to differentiate between morphine from heroin.

Explanation:

Use neutral aqueous iron (III) chloride:

Heroin: No formation of violet complex.

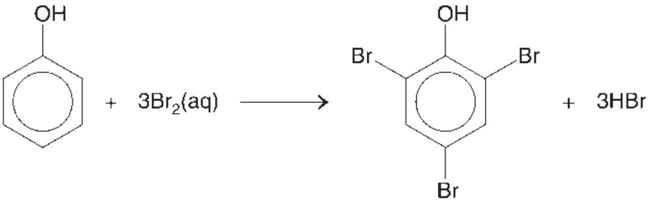
Morphine: Formation of violet complex.



{Complexation}

Do you know?

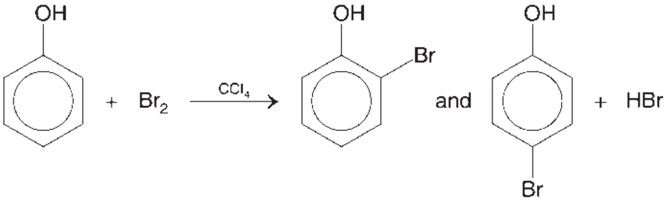
— Aqueous Br_2 not only can react with the C=C double bond, it can also react with the benzene ring of the phenol:



This is because the hydroxyl substituent is a strongly activating group that enhances the electron density in the benzene ring, making it more susceptible to electrophilic attack. As such, milder reaction conditions are required and even in such instances, polysubstitution is still observed.

Compared with the halogenation of methylbenzene or benzene, where both need the help of the $AlBr_3$ or $FeBr_3$ catalyst, the halogenation of phenol does not need it at all! Later, we are also going to see the same phenomenon for phenylamine, $C_6H_5NH_2$.

— Halogenation can also be carried out using Br_2 in a non-polar solvent such as CCl_4. However, only monosubstituted products will be obtained.



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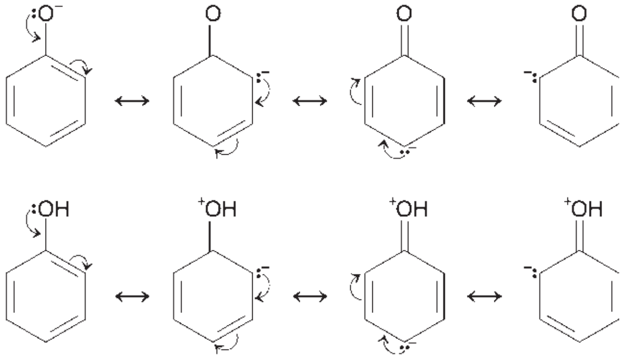
This is because in an aqueous medium, the phenol is partially ionized, generating the phenoxide ion, which is absent in the CCl_4 medium. The benzene ring of the phenoxide ion is much more electron-rich than a phenol molecule as shown below:



The more electron-rich the benzene ring, the more likely it will polarize the electron cloud of the Br─Br molecule, making the Br_2 molecule a better electrophile. The separation of charges during the delocalization of electrons in the phenol hinders the effectiveness of the delocalization. As a result, the benzene ring of phenol is not as electron-rich as that of the phenoxide ion, but note that it is still more electron-rich than an unsubstituted benzene. Hence, phenol becomes less susceptible to further electrophilic attack after the first halogenation process. Remember that a halogen group is a ring-deactivating group, it would thus oppose the ring-activating effect of the ─OH group.

— The phenolic ester functional group can also react with Br_2(aq), but only mono-substitution at the 2- or 4-position will take place. This is because the formation of the ester functional group diminishes the delocalization of electrons from the phenolic oxygen atom into the benzene ring; hence, this makes the benzene ring less electron-rich as compared to a phenoxide.

— To further demonstrate that the benzene ring of the phenol is so electron-rich, when phenol undergoes nitration with concentrated HNO_3,

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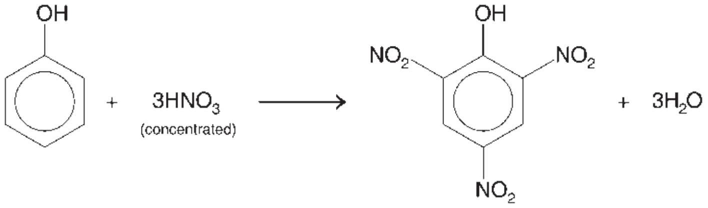
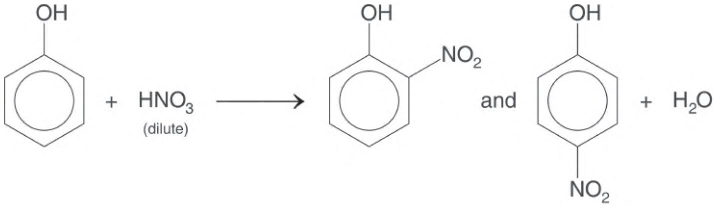
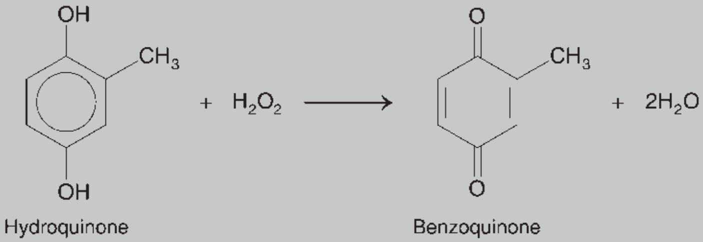
without the “help” of concentrated H_2SO_4 as needed in other nitrations, we get the tri-nitrated product easily:



Even if we use dilute HNO_3, we still can get the mono-nitrated product:



(e) Hydroquinone can be catalyzed to form benzoquinone by the enzyme peroxidase. The reaction is exothermic.



(i) Explain why the reaction is exothermic.

Explanation:

The reaction is exothermic because of the formation of two C=O double bonds in place of one O–O single bond in H–O–O–H. A C=O double bond ($740\,\mathrm{kJ\,mol^{-1}}$) is stronger than a O–O single bond ($150\,\mathrm{kJ\,mol^{-1}}$), hence there is an evolution of energy when the benzoquinone is formed.

Q But when the benzoquinone formed, the resonance stability in the hydroquinone is gone, isn't this a destabilization effect?

A: If you look at the benzoquinone, it is also resonance-stabilized.

(ii) Name the functional groups that are present in both hydroquinone and benzoquinone.

Explanation:

Hydroquinone: Phenol group.
Benzoquinone: Alkene and ketone.

(iii) Suggest a simple chemical test to differentiate between hydroquinone and benzoquinone.

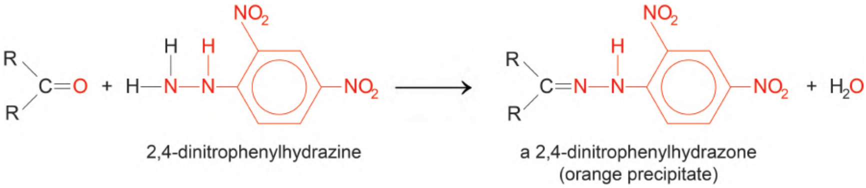
Explanation:

(1) Use neutral aqueous iron(III) chloride:

Benzoquinone: No formation of violet complex.
Hydroquinone: Formation of violet complex.

(2) Use 2,4-dinitrophenylhydrazine (2,4-DNPH):

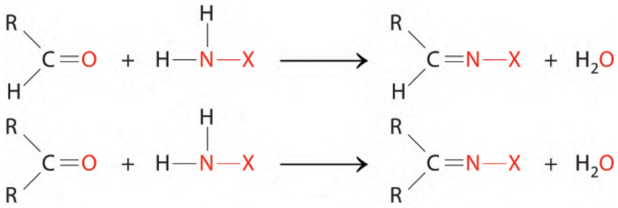
Hydroquinone: No formation of orange ppt.
Benzoquinone: Formation of orange ppt.



{Condensation/Addition–Elimination}

Do you know?

— Generally, an aldehyde or ketone can react with a compound, $H_2N–X$, that contains the $–NH_2$ group, where X = NH_2, OH, 2,4-dinitrophenylamine, or even the primary amine RNH_2.



(iv) Hydroquinone has K_a value that is smaller than 2-methylphenol. Explain.

Explanation:

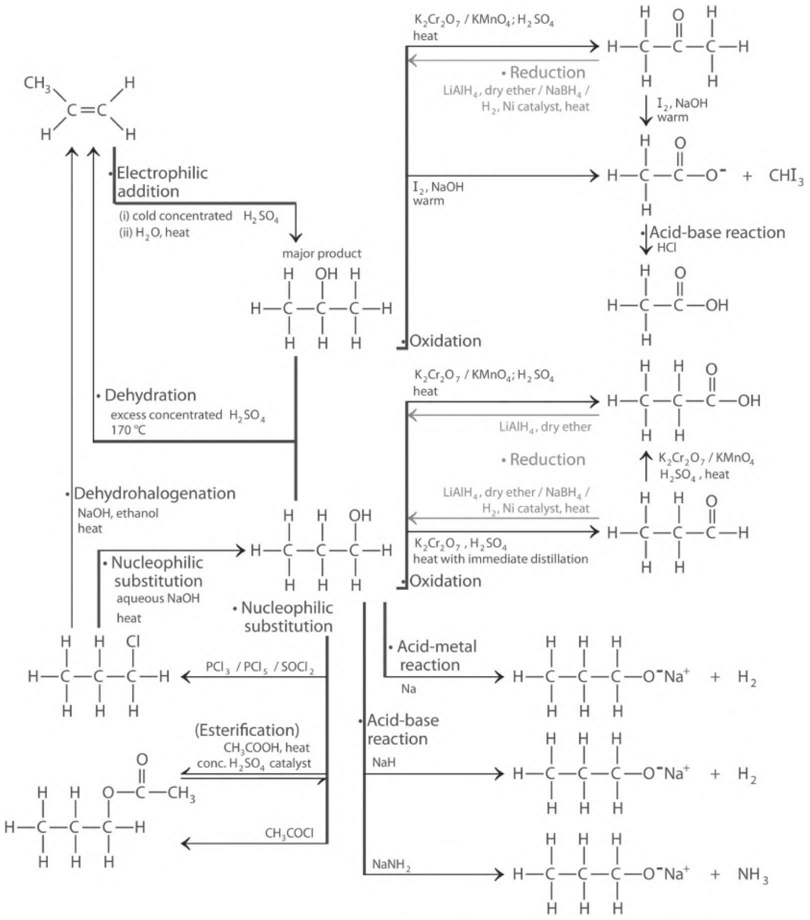
The smaller the K_a value, the weaker the acid. Hydroquinone has two –OH groups bonded to the benzene ring, as such, the lone pair of electrons on both –OH groups can delocalize into the benzene ring. Thus, the stability of the phenoxide would decrease as the negative charge on the oxygen atom of the phenoxide cannot effectively delocalize into the benzene ring due to the simultaneous delocalization of the lone pair of electrons into the ring from the other undissociated –OH group.

Q Isn't a $–CH_3$ group also electron-donating? Then, shouldn't it decrease the acidity of 2-methylphenol?

A: Indeed, if you compare the acidity of 2-methylphenol and unsubsituted phenol, the 2-methylphenol is indeed less acidic as the methyl group donates electron density into the ring via inductive effect and hence hinders the delocalization of the negative charge of the phenoxide. But obviously, this effect is not as significant as that of the additional —OH group on hydroquinone.

Do you know?

— A mind-map showing the important chemical reactions pertaining to propan-2-ol:



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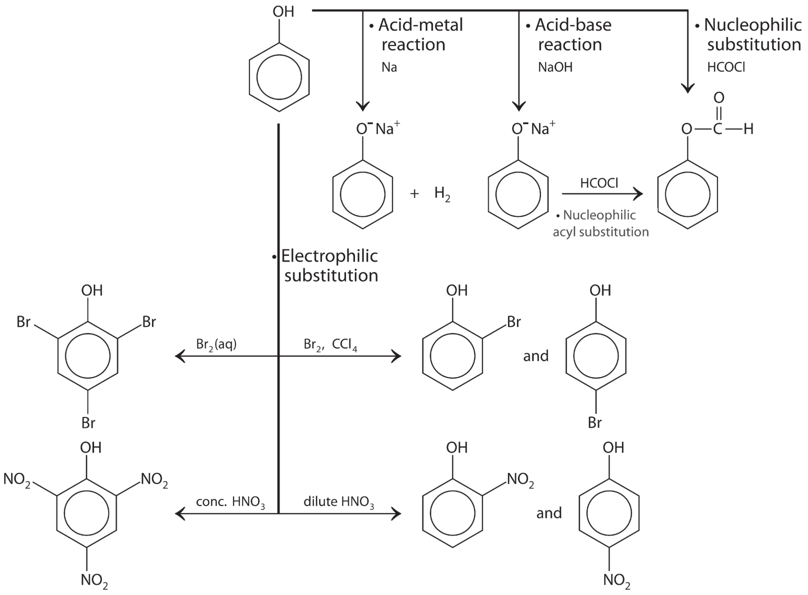
- Reactions that serve as distinguishing tests:
    - The oxidation of a primary or secondary alcohol by acidified $K_2Cr_2O_7$ would cause the orange $K_2Cr_2O_7$ to turn green (Cr^{3+}(aq)). This serves as a characteristic test for these two alcohols. Take note that a tertiary alcohol would not be oxidized.
    - The oxidation of a primary or secondary alcohol by acidified $KMnO_4$, would cause the purple $KMnO_4$ to turn colorless (Mn^{2+}(aq)). This serves as a characteristic test for these two alcohols. Take note that a tertiary alcohol would not be oxidized.
    - The oxidation of a secondary alcohol with the functional group, $-CH(OH)CH_3$, by I_2/NaOH would give a yellow ppt (CHI_3). This serves as a characteristic test for this particular functional group.
    - The reaction of an alcohol with PCl_5 and $SOCl_2$, generating HCl fumes, can serve as a characteristic test for alcohols.

— A mind-map showing the important chemical reactions pertaining to phenol:



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- Reactions that serve as a characteristic test for phenol:
  - The reaction of phenol with Br_2(aq), causing the brown Br_2 to decolorize with the formation of a white ppt (2,4,6-tribromophenol).
  - The reaction of phenol with NaOH(aq), causing two immiscible layers to become one layer as the phenoxide ion is more soluble in water than the un-ionized phenol due to the formation of ion-dipole interaction.
  - The reaction of phenol with $FeCl_3$(aq), generating a purple complex.

CHAPTER 9

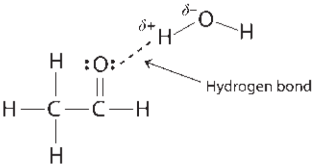
CARBONYL COMPOUNDS

Do you know?

— Both aldehydes and ketones are polar compounds, hence they have both instantaneous dipole–induced dipole and permanent dipole–permanent dipole interactions.

Generally, a ketone has a higher boiling point than an aldehyde of similar molecular weight because of its higher polarity, thus having stronger pd–pd interactions.

Low-molecular-weight carbonyl compounds are soluble in water because of the ability of the carbonyl molecule to form hydrogen bonding with the water molecule:



— Carbonyl compounds are polar molecules with the carbon atom of the –C=O group bearing the partial positive charge. As a result, nucleophiles are attracted to this electron-deficient site. But unlike halogenoalkanes and alcohols, carbonyl compounds do not undergo substitution reactions. Instead, they undergo Nucleophilic Addition reactions. A typical Nucleophilic Addition reaction is the addition of a

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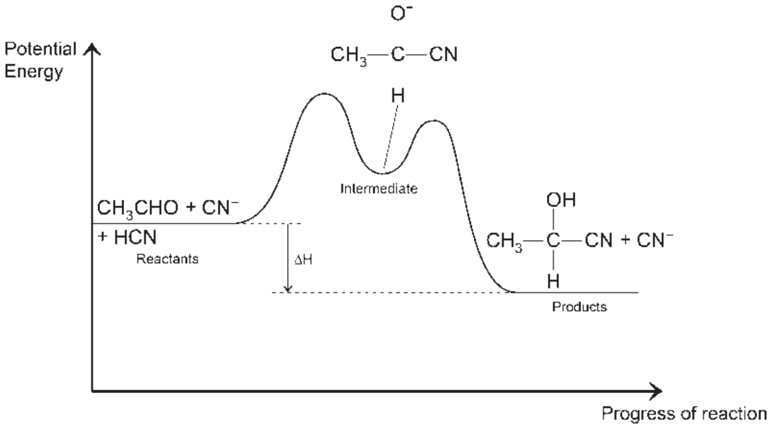
HCN molecule to the carbonyl functional group. The energy profile for the Nucleophilic Addition mechanism is shown below:



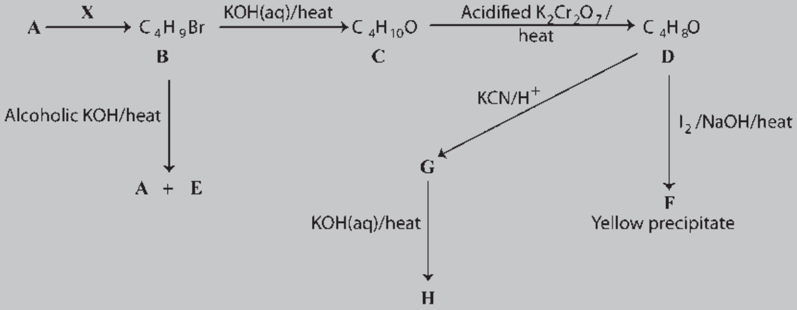
Q Why do carbonyl compounds not undergo Nucleophilic Substitution?

A: The carbonyl functional group is either bonded to two other carbon atoms (as in a ketone) or a carbon atom and a hydrogen atom (as in an aldehyde). Thus, if the carbonyl compound is to undergo Nucleophilic Substitution, then one of the C—C bond or the C—H bonds has to be broken. The breaking of these two types of bonds is energetically demanding. In addition, if the C—C bond or the C—H bond is broken, then we would have a leaving group such as a hydride ion (H^- for aldehyde) or a carbanion ion for ketone. These two leaving groups are themselves very strong nucleophiles and highly unstable.

Q Are aldehydes and ketones equally reactive to Nucleophilic Addition?

A: No. Generally, an aldehyde is more reactive than a ketone that has a similar number of carbon atoms. As an aldehyde has a H atom and an alkyl group bonded to the carbonyl functional group, a nucleophile would face less steric hindrance when approaching the carbonyl carbon of an aldehyde as compared to a ketone. There are two bulky electron-releasing alkyl groups bonded to the carbonyl group of ketone. As a result of this electronic effect, the carbonyl carbon atom of ketone is less electron-deficient than an aldehyde, thus being less susceptible to nucleophilic attack.

1. A hydrocarbon with a relative molecular mass of 56 and composition by mass 85.7% carbon and 14.3% hydrogen, undergoes the following reaction:



(a) Deduce the molecular formula of **A**. Draw all the possible constitutional/structural formulae for this molecular formula.

Explanation:

To calculate the empirical formula:

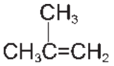
	C	H
Percentage by mass	85.7	14.3
No. of mole in 100 g	7.14	14.3
Mole ratio	1	2

The empirical formula of **A** is CH_2.
Now, molecular formula = n × empirical formula.
Therefore, $n \times (12 + 2) = 56 \Rightarrow n = 4$.
The molecular formula of **A** is C_4H_8.

Since the molecular formula C_4H_8 has two H atoms less than that of a four-carbon alkane (C_4H_{10}), compound **A** can be either an alkene or cycloalkane. Their possible constitutional/structural formulae are:

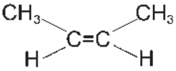
$CH_3CH_2CH{=}CH_2$

but-1-ene

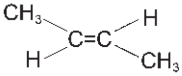


$CH_3C(CH_3){=}CH_2$

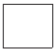
methylpropene



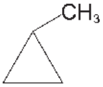
cis-but-2-ene



trans-but-2-ene



cyclobutane



methylcyclopropane

(b) Deduce the structures of compounds **A** to **H**. Hence, give the reagents and condition for Step **X**.

Explanation:

Compound **A** must be an alkene and this alkene reacts with **X** to give compound **B**, a bromoalkane.

When compound **B** undergoes dehydrohalogenation with alcoholic KOH and heat, we have two alkenes, **A** and **E**. This implies that the −Br group in compound **B** must not be at the end of the carbon chain.

Thus, compound **B**, a bromoalkane, must be $CH_3CH_2CHBrCH_3$.

Then, compound **A** has to be $CH_3CH{=}CHCH_3$:

A $CH_3CH{=}CHCH_3 + HBr \rightarrow CH_3CH_2CHBrCH_3$ **B** {Electrophilic Addition}

B $CH_3CH_2CHBrCH_3$ + alcoholic KOH/heat $\rightarrow CH_3CH{=}CHCH_3$ **A** {Elimination}

B $CH_3CH_2CHBrCH_3$ + alcoholic KOH/heat $\rightarrow CH_3CH_2CH{=}CH_2$ **E** {Elimination}

B $CH_3CH_2CHBrCH_3$ + KOH(aq)/heat $\rightarrow CH_3CH_2CH(OH)CH_3$ **C** {Nucleophilic Substitution}

C $CH_3CH_2CH(OH)CH_3$ + acidified $K_2Cr_2O_7$/heat $\rightarrow CH_3CH_2COCH_3$ **D** {Oxidation}

D $CH_3CH_2COCH_3 + I_2/NaOH/heat \rightarrow CH_3CH_2COO^- + CHI_3$ (yellow ppt) **F**
{Oxidation/Oxidative cleavage}

D $CH_3CH_2COCH_3 + KCN/H^+ \rightarrow CH_3CH_2C(OH)(CN)CH_3$ **G**
{Nucleophilic Addition}

G $CH_3CH_2C(OH)(CN)CH_3 + KOH(aq)/heat \rightarrow CH_3CH_2C(OH)(COOK)CH_3$ **H**
{Alkaline hydrolysis}

The reagents and conditions for Step **X** is HBr(g) at room temperature.

Q Why can't compound **A** be but-1-ene, $CH_3CH_2CH{=}CH_2$?

A: If compound **A** is $CH_3CH_2CH{=}CH_2$, then when it reacts with HBr(g), we would get two different bromoalkanes, $CH_3CH_2CHBrCH_3$ and $CH_3CH_2CH_2CH_2Br$. Then, there would be two possibilities for compound **B**. So, which one should we use to continue the story? Therefore, usually for structural elucidation questions, we would try to select an unambiguous compound so as to let the reaction scheme continue.

Q Then why can't compound **A** be methylpropene, $CH_3(CH_3)C{=}CH_2$?

A: We would get two different bromoalkanes, $CH_3(CH_3)CHCH_2Br$ and $CH_3(CH_3)CBrCH_3$.

(c) Using the constitutional/structural formulae, write balanced equations for the:

(i) conversion of **A** to **B**;

Explanation:

$CH_3CH{=}CHCH_3 + HBr \rightarrow CH_3CH_2CHBrCH_3$. {Electrophilic Addition}

(ii) conversion of **B** to **C**;

Explanation:

$CH_3CH_2CHBrCH_3 + KOH \rightarrow CH_3CH_2CH(OH)CH_3 + KBr.$
{Nucleophilic Substitution}

(iii) conversion of **C** to **D**;

Explanation:

$CH_3CH_2CH(OH)CH_3 + [O] \rightarrow CH_3CH_2COCH_3 + H_2O.$ {Oxidation}

(iv) conversion of **D** to **F**;

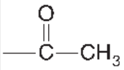
Explanation:

$CH_3CH_2COCH_3 + 3I_2 + 4OH^- \rightarrow CH_3CH_2COO^- + 3I^- + 3H_2O + CHI_3.$

Do you know?

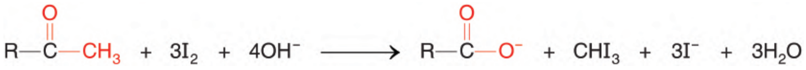
— Only carbonyl compounds containing the following bonding pattern can undergo this oxidation reaction. This group consists of ethanal and all methyl ketones.

The carbonyl carbon atom here must be bonded to either a H atom or another C atom.



$$—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3$$

When such carbonyl compounds are warmed with alkaline I_2(aq), a carboxylate salt will be obtained along with yellow crystals of tri-iodomethane:



$$R—\overset{\overset{\displaystyle O}{\|}}{C}—CH_3 + 3I_2 + 4OH^- \longrightarrow R—\overset{\overset{\displaystyle O}{\|}}{C}—O^- + CHI_3 + 3I^- + 3H_2O$$

Q It is difficult to memorize the stoichiometric coefficients for the balanced equation. Is there an easier way out?

A: Well, you can try to derive it as follows:

$RCOCH_3 \rightarrow RCOO^- + CHI_3$

$RCOCH_3 + H_2O \rightarrow RCOO^- + CHI_3$

$RCOCH_3 + H_2O + 3I_2 \rightarrow RCOO^- + CHI_3$

$RCOCH_3 + H_2O + 3I_2 \rightarrow RCOO^- + CHI_3 + 3I^-$

$RCOCH_3 + H_2O + 3I_2 \rightarrow RCOO^- + CHI_3 + 3I^- + 4H^+$

$RCOCH_3 + H_2O + 3I_2 + 4OH^- \rightarrow RCOO^- + CHI_3 + 3I^- + 4H^+ + 4OH^-$ (alkaline medium used)

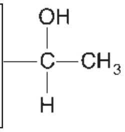
$\mathbf{RCOCH_3 + \underline{3}I_2 + \underline{4}OH^- \rightarrow RCOO^- + CHI_3 + \underline{3}I^- + \underline{3}H_2O}$

Another way to help remember this is that the $I_2 : OH^- : I^- : H_2O$ ratio is 3 : 4 : 3 : 3.

Q The methylketone group, $-COCH_3$, can be obtained by oxidizing an alcohol that contains a $-CH(OH)CH_3$ group. Can this same alcohol give CHI_3 when treated with I_2/NaOH(aq)/heat?

A: Yes, of course.Alcohols with the following bonding pattern also give the positive result for the tri-iodomethane test:

The carbonyl atom here must be bonded to either a H atom or another C atom.



Q Is there a way to derive the balanced equation from the basic?

A: Yes, take note that the alcohol is being oxidized to the methylketone first, as follows:

Oxidation half-equation:

$RCH(OH)CH_3 \rightarrow RCOCH_3$;

$RCH(OH)CH_3 \rightarrow RCOCH_3 + 2H^+$;

$RCH(OH)CH_3 + 2OH^- \rightarrow RCOCH_3 + 2H^+ + 2OH^-$ (alkaline medium used); and

$RCH(OH)CH_3 + 2OH^- \rightarrow RCOCH_3 + 2H_2O + 2e^-$.

Reduction half-equation:

$I_2 + 2e^- \rightarrow 2I^-$.

Overall:
$\mathbf{RCH(OH)CH_3 + 2OH^- + I_2 \rightarrow RCOCH_3 + 2H_2O + 2I^-}$. (Equation 1)
Then, adding Equation 1 with the following equation:
$\mathbf{RCOCH_3 + 3I_2 + 4OH^- \rightarrow RCOO^- + CHI_3 + 3I^- + 3H_2O}$.
$\Rightarrow \mathbf{RCH(OH)CH_3 + \underline{4}I_2 + \underline{6}OH^- \rightarrow RCOO^- + CHI_3 + \underline{5}I^- + \underline{5}H_2O}$.
Another way to help remember this is that the $I_2 : OH^- : I^- : H_2O$ ratio is 4 : 6 : 5 : 5.

(v) conversion of **D** to **G**;

Explanation:

$CH_3CH_2COCH_3 + HCN \rightarrow CH_3CH_2C(OH)(CN)CH_3$. {Nucleophilic Addition}

(vi) conversion of **G** to **H**; and

Explanation:

$CH_3CH_2C(OH)(CN)CH_3 + KOH + H_2O \rightarrow CH_3CH_2C(OH)(COOK)CH_3 + NH_3(g)$. {Alkaline hydrolysis}

(vii) conversion of **B** to **E**.

Explanation:

$CH_3CH_2CHBrCH_3 \rightarrow CH_3CH_2CH{=}CH_2 + HBr$. {Elimination}

Q What is the difference between elimination and dehydrohalogenation?

A: Elimination is the name of the mechanism while dehydrohalogenation informs us that the reaction is about the removal of a hydrogen and a halogen atom.

Q So, we would really get hydrogen bromide as the byproduct?

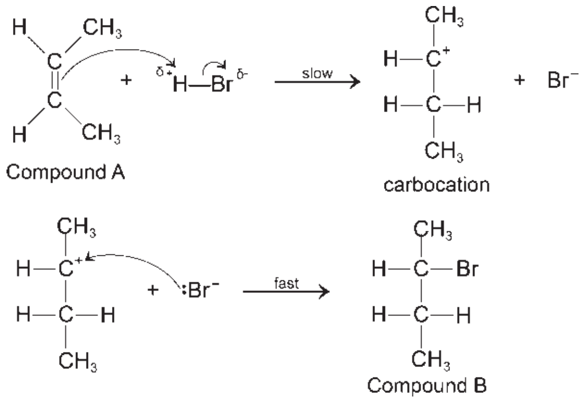
A: Actually we would not get HBr; the correct equation should be:

$$CH_3CH_2CHBrCH_3 + OH^- \rightarrow CH_3CH_2CH{=}CH_2 + H_2O + Br^-.$$

The hydrogen atom is "extracted" as H^+ by the base, OH^-. So, you won't get HBr.

(d) (i) Give the mechanism for the conversion of **A** to **B**.

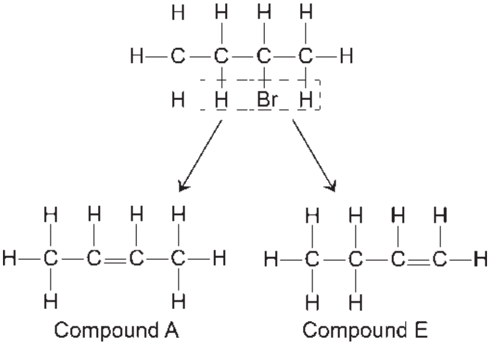
Explanation:



(ii) Give possible reasons why two products **A** and **E** are possibly formed when **B** is heated with alcoholic KOH solution.

Explanation:

There are two different types of β-hydrogen near the −Br group. As a result, the OH^- base is able to extract two different types of H^+, thus forming two different types of alkenes.



Q What is a β-hydrogen?

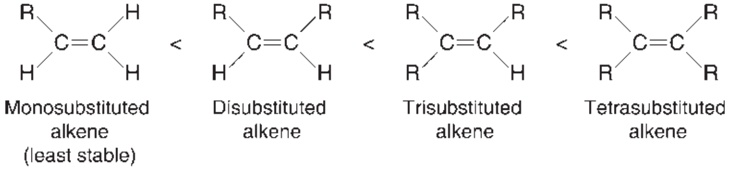
A: Now, α-carbon refers to the carbon atom which the functional group is bonded to. For example, in RCH_2Br, the carbon atom that the Br atom is bonded to is called α-carbon and the hydrogen atoms that are bonded to this α-carbon are known as α-hydrogen. The β-carbon is the next carbon atom that is bonded to the α-carbon; hence, its hydrogen atoms are known as β-hydrogen. But if the functional group is −COOH or −CO−, then the α-carbon is the carbon atom that is bonded to the −CO– group.

Q Why did the OH^- base extract the β-hydrogen and not the α-hydrogen or the γ-hydrogen?

A: If the OH^- base extracts the α-hydrogen, then the α-carbon would be negatively charged with the halogen atom attached to it; how would the alkene form? The γ-hydrogen is less acidic than the β-hydrogen because as the distance between the electron-withdrawing group increases, the inductive effect, which is mediated through the covalent, decreases.

Q Since there are two different types of alkenes being formed, does that mean they would form in equal proportions?

A: No. First, take note that there are three β-hydrogen to be extracted in order to form compound **E**, while there are only two β-hydrogen to be extracted in order to form compound **A**. Second, according to Saytzeff's rule, during an Elimination reaction, a more stable alkene is formed in larger proportions and greater stability is found in alkenes with more alkyl (R) groups attached to the doubly bonded carbons. Thus, in order of increasing stability, we have:



Q Why is a more-substituted alkene more stable than a less-substituted one?

A: Since alkyl groups are electron-releasing via inductive effect, they contribute electron density to the pi bond and thus strengthens it.

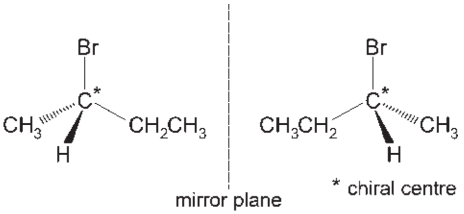
Q Why is the *trans* isomer more stable than the *cis* isomer even when they have the same numbers and types of substituents?

A: Here, we need to consider steric factor; alkyl groups are relatively bulky, and during the formation process, they are best placed opposite to each other diagonally across the C=C bond, so as to minimize inter-electronic repulsion. Thus, with the *trans* isomer being more stable, it is formed in greater quantity than the *cis* isomer.

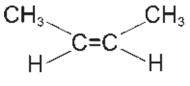
(iii) Both compounds **B** and **E** exhibit stereoisomerism. State the type of stereoisomerism in each of the compounds and draw the stereoisomers.

Explanation:

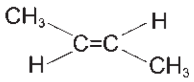
Compound **B** exhibits enantiomerism as there is a chiral carbon:



Compound **E** exhibits *cis-trans*/geometrical isomerism as there is a C=C double bond with two different groups of atoms bonded to each of the carbon atom of the C=C double bond:



cis-but-2-ene



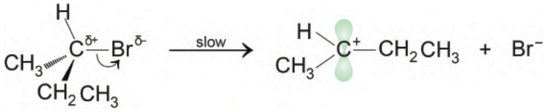
trans-but-2-ene

> (e) (i) If compound **B** is optically active but compound **C** is not, give the mechanism for the conversion of **B** to **C**.

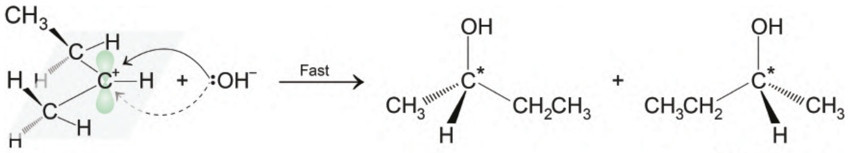
Explanation:

If compound **B** is optically active but compound **C** is not, the reaction mechanism is S_N1 because the intermediate is a trigonal planar sp^2 hybridized carbon atom and the product is a racemate or racemic mixture which is optically inactive.

Step 1: Formation of the carbocation.



Step 2: The nucleophhile attacks the carbocation to form the final product.



* chiral centre

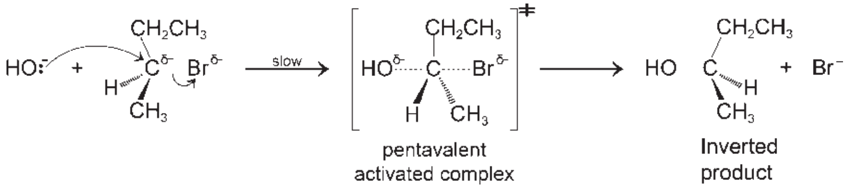
Q Why is the 1st step a slow step while the 2nd step a fast one?

A: The 1st step involves bond breaking, which needs energy, while the 2nd one involves bond forming, which releases energy.

(ii) Both compounds **B** and **C** are optically active. Give the mechanism for the conversion of **B** to **C**.

Explanation:

If both compounds **B** and **C** are optically active, the reaction mechanism is S_N2 because there is an inversion in the product:



(iii) Describe how the rate of each of the reactions in (*i*) and (*ii*) are affected when the concentration of KOH is doubled. Explain your answer.

Explanation:

Since the OH^- nucleophile is not involved in the slow step for the reaction in (*i*), doubling the concentration of KOH would not affect the rate. While for the reaction in (*ii*), doubling the concentration of KOH would double the rate as the reaction is first order with respect to $[OH^-]$.

(iv) By applying your understanding of the organic reaction mechanisms described in (*e*)(*i*) and (*e*)(*ii*), predict the organic products that you would expect when **B** reacts with potassium hydrogen sulfide, KHS.

Explanation:

Since HS^- is a bigger nucleophile than OH^-, we would expect the S_N2 mechanism to occur less likely as compared to S_N1 because of the greater steric effect faced by the HS^- nucleophile when doing the "back-side" attack. Hence, if the reaction mechanism is S_N1, then we would get a racemic mixture of products that is optically inactive.

(v) Explain briefly on the different roles played by KOH in the conversion of **B** into **C** as compared to the conversion of **B** into **A** and **E**.

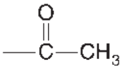
Explanation:

During the conversion of **B** into **C**, OH^- is acting as a nucleophile. On the other hand, during the conversion of **B** into **A** and **E**, it is acting as a base.

(f) (i) What structural features of **D** enables it to form **F**?

Explanation:

Compound **D** possesses the following structural features that enables it to form **F**:



$$-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

(ii) State the role played by iodine and sodium hydroxide.

Explanation:

The role played by iodine and sodium hydroxide is an oxidizing agent.

(iii) Give the name and constitutional/structural formula of the other organic product of this reaction.

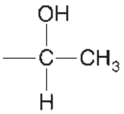
Explanation:

The other organic product formed in this reaction is CH_3CH_2COONa, sodium propanoate.

(iv) Compound **C** would also be able to form **F**. Give the structural feature of **C** that gives this possible result.

Explanation:

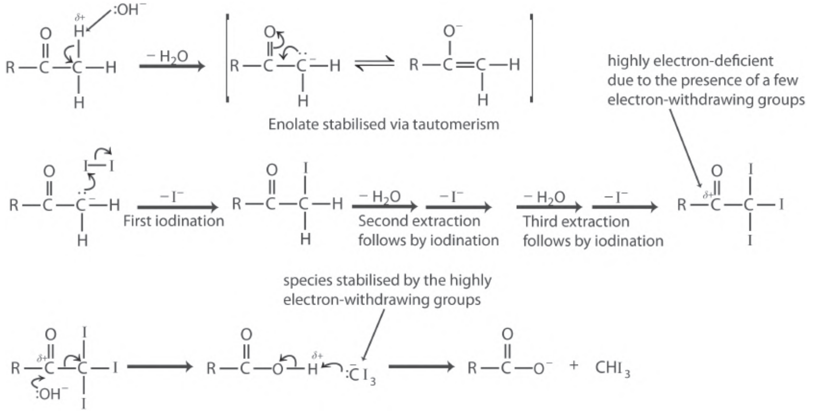
Compound **C** possesses the following structural feature that enables it to form **F**:



$$-\overset{OH}{\underset{H}{\overset{|}{\underset{|}{C}}}}-CH_3$$

Do you know?

— The $-CH(OH)CH_3$ group is oxidized to the $-COCH_3$ group before being oxidized to form CHI_3 as shown below:



Q How does I_2/NaOH oxidize the alcohol to a ketone?

A: From Group 17 chemistry, I_2 molecule disproportionates in NaOH to give the iodate(I) ion, IO^-, which is strong enough to oxidize the alcohol to a ketone:

$$I_2 + 2OH^- \rightarrow I^- + IO^- + H_2O.$$

(v) With appropriate reagents and conditions, describe a simple chemical test to differentiate **C** from **D**.

Explanation:

To differentiate between compound **C**, $CH_3CH_2CH(OH)CH_3$, and compound **D**, $CH_3CH_2COCH_3$, just use any of the following tests:

(1) Use $K_2Cr_2O_7/H_2SO_4$/heat:
$CH_3CH_2COCH_3$: Orange $K_2Cr_2O_7$ did not turn green.
$CH_3CH_2CH(OH)CH_3$: Orange $K_2Cr_2O_7$ turned green.
$CH_3CH_2CH(OH)CH_3 + [O] \rightarrow CH_3CH_2COCH_3 + H_2O.$ {Oxidation}

(2) Use $KMnO_4/H_2SO_4$/heat:
$CH_3CH_2COCH_3$: Purple $KMnO_4$ did not decolorize.
$CH_3CH_2CH(OH)CH_3$: Purple $KMnO_4$ decolorized.
$CH_3CH_2CH(OH)CH_3 + [O] \rightarrow CH_3CH_2COCH_3 + H_2O.$ {Oxidation}

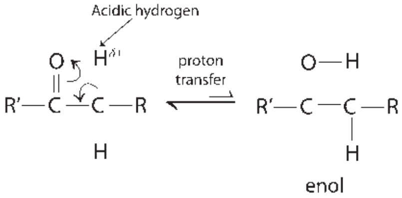
(3) Use $KMnO_4$/NaOH//heat:
$CH_3CH_2COCH_3$: Purple $KMnO_4$ did not decolorize.
$CH_3CH_2CH(OH)CH_3$: Purple $KMnO_4$ decolorized. Brown ppt of MnO_2 formed.
$CH_3CH_2CH(OH)CH_3 + [O] \rightarrow CH_3CH_2COCH_3 + H_2O.$ {Oxidation}

(4) Use PCl_5 and test for HCl(g):
$CH_3CH_2COCH_3$: No white fumes of HCl(g).
$CH_3CH_2CH(OH)CH_3$: White fumes of HCl(g) observed.
$CH_3CH_2CH(OH)CH_3 + PCl_5 \rightarrow CH_3CH_2CH(Cl)CH_3 + POCl_3 + HCl(g).$
{Nucleophilic Substitution}

(5) Use $SOCl_2$ and test for HCl(g):
$CH_3CH_2COCH_3$: No white fumes of HCl(g).
$CH_3CH_2CH(OH)CH_3$: White fumes of HCl(g) observed.
$CH_3CH_2CH(OH)CH_3 + SOCl_2 \rightarrow CH_3CH_2CH(Cl)CH_3 + SO_2 + HCl(g).$
{Nucleophilic Substitution}

Do you know?

— Ketones are considered non-oxidizable at the high-school level. In reality, if a very strong oxidizing agent is used, the ketone can still be oxidized but in a destructive way with the cleavage of C−C bonds. This is possible because of the phenomenon known as keto-enol tautomerism.



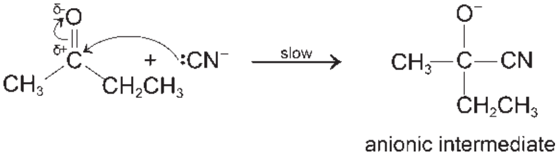
The two tautomers, ketone and enol, are functional group isomers, and tautomerism is an equilibrium process. Tautomerism arises because of the proximity of an acidic α-hydrogen to a lone pair of electrons on the carbonyl oxygen atom. The enol is known as such because there is an alkene functional group together with a hydroxyl group. The presence of this alkene functional group makes the enol susceptible to oxidative cleavage as what would happen to an alkene molecule. As the concentration of the enol is very minimal, indicated by a shorter forward half-arrow, the oxidation of ketone is not very prominent. But in the presence of a stronger oxidizing agent, the position of the equilibrium can be driven to the right.

(g) (i) Give the mechanism for the conversion of **D** to **G**. Hence, draw the stereoisomers formed in **G**.

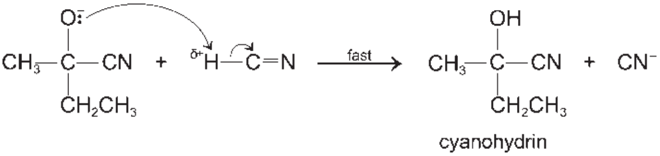
Explanation:

Compound **D** reacts with KCN/H^+ via the Nucleophilic Addition mechanism:

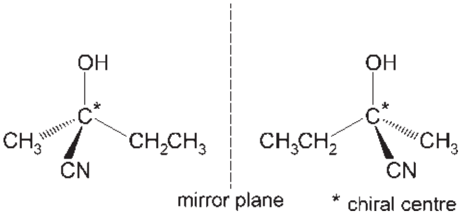
Step 1: The nucleophile attacks the electron-deficient carbonyl carbon to form an anionic intermediate.



Step 2: The anionic intermediate is protonated to form the final cyanohydrin product. A proton can be extracted from the undissociated HCN molecule.



The pair of enantiomers in compound G is:



Q Where does the HCN come from in the second step of the Nucleophilic Addition mechanism?

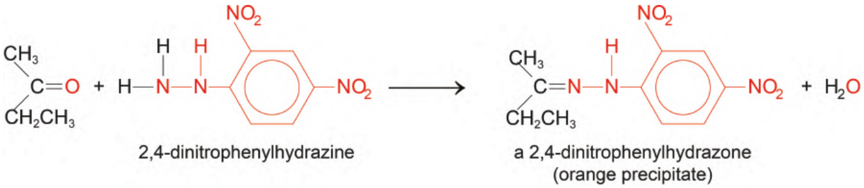
A: The H^+ protonates the CN^- to form HCN. Remember, HCN is a weak acid, hence its conjugate base, CN^-, is basic.

(ii) Compound **D** reacts with 2,4-DNPH to give its 2,4-dinitrophenylhydrazone derivatives.

(A) Write a balanced equation for the reaction between **D** and 2,4-DNPH.

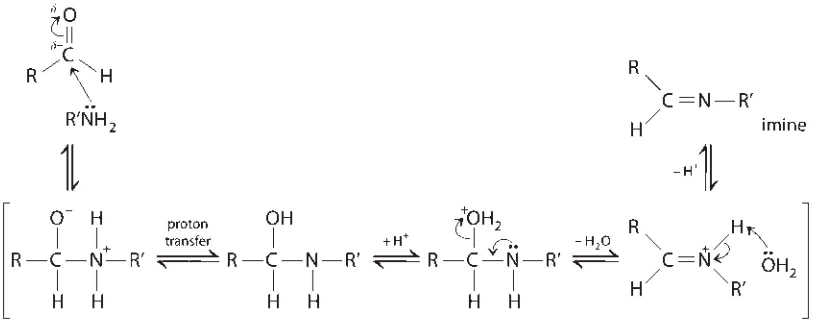
Explanation:

Compound **D** undergoes condensation or addition–elimination with 2,4-DNPH:



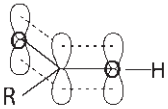
Do you know?

— The condensation reaction is also known as addition–elimination reaction. A simplified view of the mechanism consists firstly of a Nucleophilic Addition reaction, where the amine acts as a nucleophile attacking the electron-deficient carbonyl carbon atom. Subsequently, the elimination of water gives the iminium ion, which then undergoes deprotonation to form the neutral imine product.



Q There is also a carbonyl functional group in the −COOH group. Thus, can the carboxylic acid also undergo addition–elimination reaction with 2,4-DNPH?

A: No, it can't. This is because we would expect acid–base reaction between carboxylic acid and 2,4-DNPH instead, as the –NH_2 group of 2,4-DNPH is basic in nature. In addition, the lone pair of electrons of the −OH group of the −COOH functional group is delocalized into the C=O group; hence, the molecule would be relatively more stable. If addition–elimination reaction is to take place, the resonance stabilization effect would be lost.



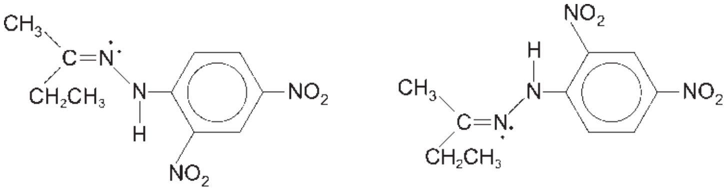
Q How about for functional groups such as esters, amides, and acyl halides?

A: No. There is a better leaving group such as −OR, $-NH_2$, and −Cl, bonded to the carbonyl carbon atom. Thus, the condensation mechanism won't work here, but Nucleophilic Acyl Substitution occurs instead. Similarly, if addition–elimination reaction is to take place, the resonance stabilization effect that is being mentioned above would be lost.

(B) The 2,4-dinitrophenylhydrazone derivative exhibits stereoisomerism. Draw the possible stereoisomers and name the type of stereoisomerism.

Explanation:

The derivative exhibits *cis-trans*/geometrical isomerism as shown below:



(C) Suggest why the two stereoisomers have different melting points.

Explanation:

Due to the different spatial orientations of the groups of atoms around the C=N double bond, the polarities of the two *cis-trans*/geometrical isomers are different. Hence, the strength of the permanent dipole–permanent dipole interaction for each of the isomer differs, which thus accounts for their different melting points.

(h) Heating of the organic content would usually be carried out in a water-bath rather than over a Bunsen burner. Give a possible reason for such a practice.

Explanation:

An organic compound can be flammable. Heating it over a Bunsen burner may be fire-hazardous, while heating over a water bath is not.

2. (a) 5 cm^3 of an alkene **P** was completely burned with 50 cm^3 of pure oxygen in a sealed vessel, and the resulting mixture showed a reduction in volume of 20 cm^3 when shaken with barium hydroxide solution, leaving a resultant volume of 20 cm^3.

P reacts with bromine water to give isomeric products **Q** and **R**. On treatment with concentrated sulfuric acid, **Q** does not react, but **R** is dehydrated to two isomeric bromoalkenes **S** and **T**. On oxidation at the double bond, **S** gives propanone among the products, while **T** gives methanal. Give the structural formulae of the compounds **P** to **T**. Write balanced equations for each of the reactions.

Explanation:

$$C_nH_{2n} + (n + \frac{n}{2})O_2 \rightarrow nCO_2 + nH_2O.$$

Using $pV = nRT$, under constant p and T, $n \propto V$.
Volume of $CO_2 = 20\ cm^3$.
Volume of O_2 used $= 50 - 20 = 30\ cm^3$.

Molar ratio of C_nH_{2n} : CO_2 = 5 : 20 = 1: n ⇒ n = 4.
Hence, the alkene **P** is C_4H_8.

Alkene **P** can be one of the following:

$$CH_3CH_2CH{=}CH_2 \quad / \quad CH_3CH{=}CHCH_3 \quad / \quad CH_3(CH_3)C{=}CH_2$$

Alkene **P** cannot be $CH_3CH{=}CHCH_3$ because when it reacts with bromine water, we only get one product: $CH_3CH(OH)CH(Br)CH_3$.

Alkene **P** is $CH_3(CH_3)C{=}CH_2$.

When alkene **P** reacts with bromine water via the Electrophilic Addition mechanism, we get:

$$\underset{\textbf{P}}{CH_3(CH_3)C{=}CH_2} + Br_2 + H_2O \rightarrow \underset{\textbf{Q}}{CH_3(CH_3)C(Br)CH_2(OH)} + HBr$$

$$\underset{\textbf{P}}{CH_3(CH_3)C{=}CH_2} + Br_2 + H_2O \rightarrow \underset{\textbf{R}}{CH_3(CH_3)C(OH)CH_2(Br)} + HBr$$

On treatment with concentrated sulfuric acid, **Q** does not react, but **R** is dehydrated to two isomeric bromoalkenes:

$$\underset{\textbf{R}}{CH_3(CH_3)C(OH)CH_2(Br)} \rightarrow \underset{\textbf{S}}{CH_3(CH_3)C{=}CH(Br)} + H_2O$$

$$\underset{\textbf{R}}{CH_3(CH_3)C(OH)CH_2(Br)} \rightarrow \underset{\textbf{T}}{CH_2{=}C(CH_3)CH_2(Br)} + H_2O$$

On oxidation at the double bond, **S** gives propanone among the products, while **T** gives methanal:

$$\underset{\textbf{S}}{CH_3(CH_3)C{=}CH(Br)} + [O] \rightarrow \underset{\textbf{propanone}}{CH_3COCH_3} + O{=}CH(Br)$$

$$\underset{\textbf{T}}{CH_2{=}C(CH_3)CH_2(Br)} + [O] \rightarrow \underset{\textbf{methanal}}{HCOH} + O{=}C(CH_3)CH_2(Br)$$

Q Why can't alkene **P** be but-1-ene, $CH_3CH_2CH{=}CH_2$?

A: If alkene **P** is but-1-ene, $CH_3CH_2CH{=}CH_2$:

When alkene **P** reacts with bromine water via the Electrophilic Addition mechanism, we get:

$$\underset{\textbf{P}}{CH_3CH_2CH{=}CH_2} + Br_2 + H_2O \rightarrow \underset{\textbf{Q}}{CH_3CH_2CH(Br)CH_2(OH)} + HBr$$

$$\underset{\textbf{P}}{CH_3CH_2CH{=}CH_2} + Br_2 + H_2O \rightarrow \underset{\textbf{R}}{CH_3CH_2CH(OH)CH_2(Br)} + HBr$$

On treatment with concentrated sulfuric acid, **Q** does react similarly as above, but **R** is dehydrated to two isomeric bromoalkenes:

$$\underset{\textbf{R}}{CH_3CH_2CH(OH)CH_2(Br)} \rightarrow \underset{\textbf{S}}{CH_3CH_2CH{=}CH(Br)} + H_2O$$

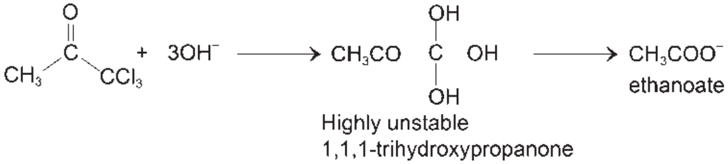
$$\underset{\textbf{R}}{CH_3CH_2CH(OH)CH_2(Br)} \rightarrow \underset{\textbf{T}}{CH_3CH{=}CH_2CH_2(Br)} + H_2O$$

The reaction scheme is discontinued here because compounds **S** and **T** would not give us propanone or methanal when we cleave at the double bond.

(b) Explain why propanone is not hydrolyzed to sodium ethanoate by aqueous barium hydroxide but 1,1,1-trichloropropanone is.

Explanation:

When 1,1,1-trichloropropanone reacts with barium hydroxide, we have Nucleophilic Substitution of the $-Cl$ groups taking place to generate the highly unstable 1,1,1-trihydroxypropanone:



It is highly unstable because there are three highly electron–withdrawing $-OH$ groups and another electron withdrawing $-CO-$ group bonded to the carbon atom. As such, the 1,1,1-trichloropropanone undergoes decarboxylation readily to give the ethanoate ion.

As for propanone, there is no good leaving group to be substituted, hence it doesn't form the ethanoate ion.

Q What is decarboxylation?

A: Decarboxylation refers to the process of removing a carbon atom in the form of CO_2.

(c) When 50 cm^3 of the gaseous CH_3COCH_3 were exploded with excess oxygen, there was an overall contraction of x cm^3. A further contraction of y cm^3 took place when excess calcium hydroxide was added. Deduce the values of x and y. (All measurements were done under r.t.p.)

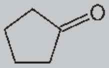
Explanation:

$$CH_3COCH_3 + 4O_2 \rightarrow 3CO_2 + 3H_2O.$$

Using pV = nRT, under constant p and T, $n \propto V$.
Molar ratio of $CH_3COCH_3 : CO_2 = 1:3 = 50 : y \Rightarrow y = 150$ cm^3.
Volume of O_2 needed $= 4 \times 50 = 200$ cm^3.
Initial volume of gases $= 50 + 200 +$ excess $O_2 = (250 +$ excess $O_2)$ cm^3.
After reaction, volume of gases $=$ (excess $O_2 + 150$) cm^3.
Amount of contraction, $x = (250 +$ excess $O_2) - ($excess $O_2 + 150) = 100$ cm^3.

(d) Account for why the reactivity of aldehydes and ketones towards nucleophiles falls along each of the series.

$$H_2CO > RCHO > R_2CO$$



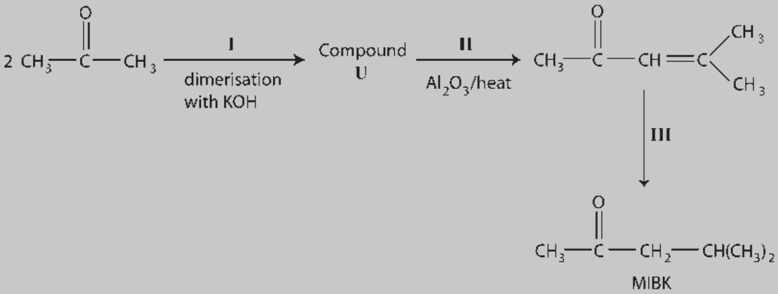
$> (CH_3CH_2)_2CO > ((CH_3)_2CH)_2CO$

Explanation:

Generally, toward nucleophiles, an aldehyde is more reactive than a ketone that has a similar number of carbon atoms. As an aldehyde has a H atom and an alkyl group bonded to the carbonyl functional group, a nucleophile would face less steric hindrance when approaching the carbonyl carbon of an aldehyde as compared to that of a ketone. In addition, there are two bulky electron-releasing alkyl groups bonded to the carbonyl group of a ketone. As a result of this electronic effect, the carbonyl carbon atom of a ketone is less electron-deficient than that of an aldehyde, thus making it less susceptible to nucleophilic attack.

An aldehyde that has a bulkier, −R group is less reactive because of greater steric effect, similarly for ketones that have more bulky R−groups.

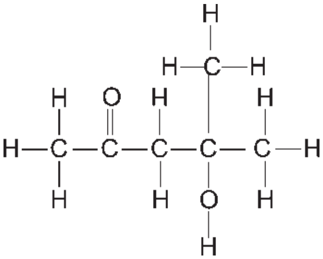
3. Propanone can be converted into MIBK, a solvent that is commonly used in adhesives, via the following synthetic pathway:



(a) Draw the displayed constitutional/structural formula of compound **U**.

Explanation:

The displayed constitutional/structural formula of compound **U** is:



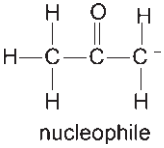
Do you know?

— ‘Displayed constitutional/structural formula’ and ‘full constitutional/structural formula’ mean the same!

(b) Suggest a name for the reaction in Step **I** and draw the species that reacts with propanone.

Explanation:

It is a Nucleophilic Addition reaction. The species that reacts with propanone is:



nucleophile

Do you know?

— The α-hydrogen of propanone is acidic due to the electron–withdrawing effect of the −CO group. Hence, in the presence of a strong base, the carbanion ion is generated, which can act as a nucleophile to attack the electron–deficient −CO group.

Q How can the carbanion ion be stable when the negative charge sits on a carbon atom?

A: The carbanion ion is resonance-stabilized through the delocalization of the negative charge into the highly electron–withdrawing −CO group.

Q So, can the remaining −CO group of compound **U** undergo further Nucleophilic Addition?

A: Yes, of course. Other carbanion ions can attack compound **U** and even compound **U** can be converted to another carbanion ion and act as a nucleophile. Thus, the reaction is quite complicated. You will get a lot of side products!

(c) What is the role played by Al_2O_3?

Explanation:

Since an alkene is formed with the elimination of a H_2O molecule, Al_2O_3 is acting as a dehydrating agent.

Q How does Al_2O_3 act as a dehydrating agent?

A: Recall from Chapter 9 of *Understanding Advanced Chemistry Through Problem Solving* Volume I, the Al^{3+} has a very high charge density, hence it is electron-deficient. It would be able to attract the electron cloud of the $-$OH group. At the same time, the O^{2-} in Al_2O_3 is highly electron–rich, so it would be able to extract a H^+ ion from the α-hydrogen.

(d) Suggest reagents and conditions for Step **III**.

Explanation:

We can use H_2/Pt/heat to convert the alkene functional group to the saturated molecule.

Q But wouldn't the carbonyl functional group be reduced too?

A: Well, we can adjust the temperature such that it would minimize the reduction of the carbonyl group.

(e) Suggest a simple chemical test to differentiate between propanone and compound U.

Explanation:

To differentiate between propanone and compound **U**, $R(CH_3)_2COH$, we can use any of the following tests:

(1) Use PCl_5 and test for HCl(g):
CH_3COCH_3: No white fumes of HCl(g).
Compound U: White fumes of HCl(g) observed.

$$R(CH_3)_2COH + PCl_5 \rightarrow R(CH_3)_2CCl + POCl_3 + HCl(g).$$

{Nucleophilic Substitution}

(2) Use $SOCl_2$ and test for HCl(g):
CH_3COCH_3: No white fumes of HCl(g).
Compound **U**: White fumes of HCl(g) observed.

$$R(CH_3)_2COH + SOCl_2 \rightarrow R(CH_3)_2CCl + SO_2 + HCl(g).$$

{Nucleophilic Substitution}

Do you know?

— $R(CH_3)_2COH$ is a tertiary alcohol which cannot be oxidized readily. Hence, we can't use an oxidizing agent such as $K_2Cr_2O_7$ or acidified $KMnO_4$, to differentiate a tertiary alcohol from a ketone.

— But this also means that we can differentiate a tertiary alcohol from primary or secondary alcohols through the use of these oxidizing agents.

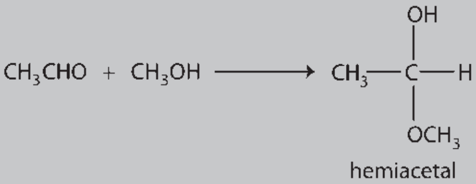
4. (a) Aldehydes and ketones both contain the carbonyl group, C=O, but differ in their positions in the hydrocarbon skeleton. The main reaction that these carbonyl compounds undergo is Nucleophilic Addition.

   (i) It is observed that aldehdyes are usually more reactive toward Nucleophilic Addition than ketones. State two reasons to account for this observation.

Explanation:

Generally, toward nucleophiles, an aldehyde is more reactive than a ketone that has a similar number of carbon atoms. As an aldehyde has a H atom and an alkyl group bonded to the carbonyl functional group, a nucleophile would face less steric hindrance when approaching the carbonyl carbon of an aldehyde as compared to that of a ketone. In addition, there are two bulky electron-releasing alkyl groups bonded to the carbonyl group of a ketone. As a result of this electronic effect, the carbonyl carbon atom of a ketone is less electron-deficient than that of an aldehyde, thus making it less susceptible to nucleophilic attack.

(ii) When heated with an alcohol (which serves as a nucleophile) in the presence of aqueous hydrochloric acid, an aldehyde produces a hemiacetal, a functional group consisting of one −OH and one −OR group bonded to the same carbon. For example, the reaction of methanol and ethanal produces the following hemiacetal:

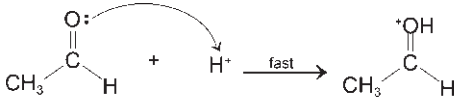


$$CH_3CHO + CH_3OH \longrightarrow CH_3-\overset{\displaystyle OH}{\underset{\displaystyle OCH_3}{C}}-H$$

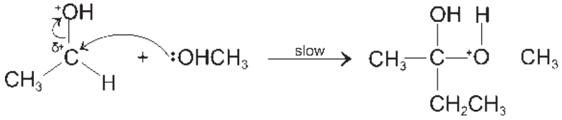
Propose the mechanism for the reaction described above.

Explanation:

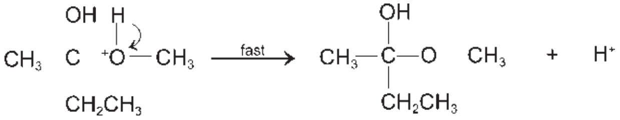
Step 1: The carbonyl oxygen is being protonated, as such the electron deficiency of the carbonyl carbon atom is much higher than that of the unprotonated aldehyde.



Step 2: The alcohol acts as a nucleophile attacking the carbonyl group, forming a protonated hemiacetal.



Step 3: The protonated hemiacetal lose a H^+.



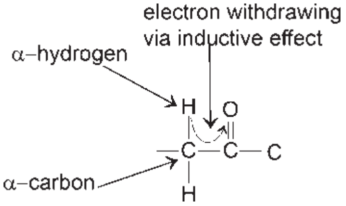
Q So HCl is acting as a catalyst?

A: Yes, indeed. The H^+ ion is regenerated, hence it is a catalyst.

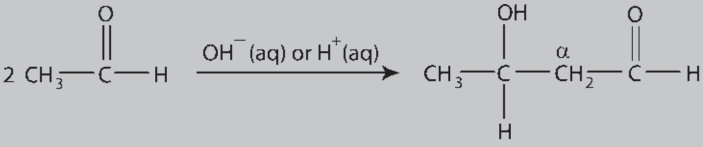
(b) In addition to Nucleophilic Addition, aldehydes and ketones can also undergo a condensation reaction due to the unusual acidity of the hydrogen atom attached to the carbon adjacent to the carbonyl group. Such a hydrogen atom is referred to as a α-hydrogen. With the aid of suitable diagrams, account for the unusual acidity of a α-hydrogen.

Explanation:

The oxygen atom of the carbonyl functional group is highly electronegative. It would pull electron density from the carbonyl carbon atom via inductive effect. This carbon atom would in turn withdraw electron density from the α-carbon and hence later from the α-hydrogen, making it electron-deficient, therefore acidic.



(c) Aldehydes that have a α-hydrogen can react with themselves or another carbonyl compound when mixed with an aqueous acid or base. Such a reaction is known as aldol condensation and the resulting compounds, β-hydroxyl aldehydes, are known as aldol compounds as they possess both an aldehyde and an alcohol functional group. For example:



3-hydroxybutanal

(i) Suggest a suitable aldehyde as the starting material for the synthesis of the compound **X**, $CH_3CH_2CH(CHO)CH(CH_2CH_2CH_3)OH$.

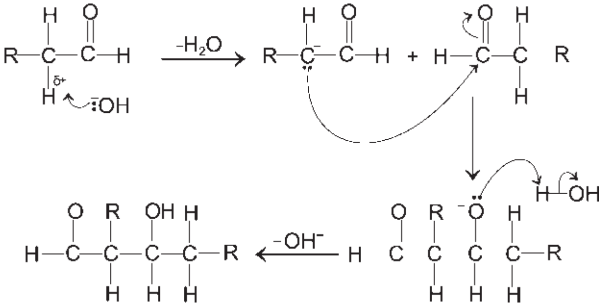
Explanation:

The position of the −OH group in compound **X** is the position of the −CHO functional group. Thus, a suitable aldehyde is $CH_3CH_2CH_2CHO$.

(ii) Hence, outline the reaction scheme for the conversion of the aldehyde in *c(i)* to compound **X**, stating clearly the reagents and conditions required and the structure of the intermediates formed.

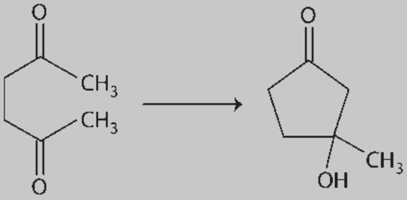
Explanation:

Let the $CH_3CH_2CH_2CHO$ be RCH_2CHO for simplicity. The $CH_3CH_2CH_2CHO$ is converted to compound **X** via the following Nucleophilic Addition mechanism:



Aqueous NaOH is used as the catalytic base with heating.

(d) When a dicarbonyl compound is treated with a base, intramolecular aldol condensation can occur, leading to the formation of cyclic products as exemplified by 2,5-hexanedione below:



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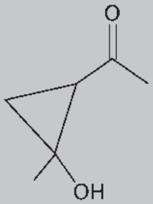
Another possible product of the aldol condensation of 2,5-hexanedione is



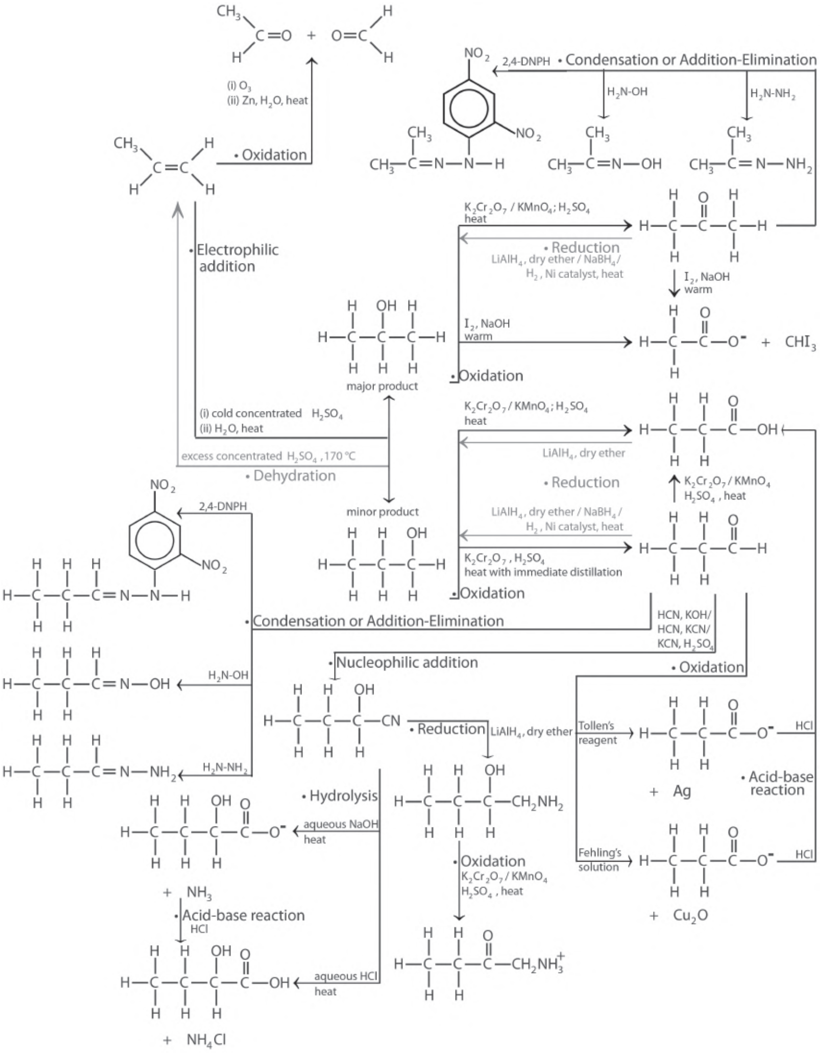
Suggest briefly why this compound is not formed.

Explanation:

The three-membered ring compound is not formed because there is too much ring strain. Hence, it would be unstable.

Do you know?

— A mind-map showing the important chemical reactions pertaining to propanal and propanone:



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- Reactions that serve as distinguishing tests:
  - The oxidation of an aldehyde by acidified $K_2Cr_2O_7$ would cause the orange $K_2Cr_2O_7$ to turn green (Cr^{3+}(aq)). This serves as a characteristic test for aldehydes.
  - The oxidation of an aldehyde by acidified $KMnO_4$ would cause the purple $KMnO_4$ to turn colorless (Mn^{2+}(aq)). This serves as a characteristic test for aldehydes.
  - The oxidation of an aldehyde by Tollens' reagent ($[Ag(NH_3)_2]^+$), generating a silver mirror (Ag(s)), can serve as a characteristic test for aldehydes.
  - The oxidation of an aliphatic aldehyde by Fehling's reagent, generating a red ppt (Cu_2O(s)), can serve as a characteristic test for aliphatic aldehydes.
  - The oxidation of a ketone with the methylketone functional group, $-COCH_3$, by I_2/NaOH would give the yellow ppt (CHI_3). This serves as a characteristic test for this particular functional group.
  - The reaction of an aldehyde or ketone with 2,4-DNPH, giving an orange ppt, can serve as a characteristic test for aldehydes and ketones.

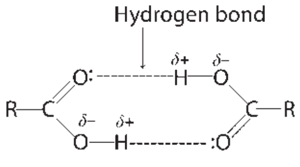
CHAPTER 10

CARBOXYLIC ACIDS AND THEIR DERIVATIVES

Do you know?

Boiling point and solubility of carboxylic acids and their derivatives

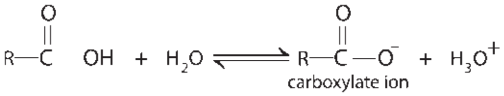
— A carboxylic acid has a higher boiling point than an alcohol of similar molecular weight. This is because of the stronger and more extensive hydrogen bonding between the carboxylic acid molecules:



A dimer

— The stronger hydrogen bonding arises because of the electron-withdrawing carbonyl functional group, which causes the O─H bond to be more polar. More extensive hydrogen bonding arises because of the presence of 4 lone pair of electrons and one H atom in the -COOH functional group. The strong and extensive hydrogen bonding even causes the carboxylic acid to form dimers.

— Low-molecular-weight carboxylic acids are highly soluble in water because of their ability to form strong and extensive hydrogen bonding with water molecules. Importantly, the partial dissociation of the weak acid in water further enhances the solubility of the acid due to the formation of ion–dipole interaction:



$$R{-}\overset{\displaystyle O}{\overset{\|}{C}}\ OH + H_2O \rightleftharpoons \underset{\text{carboxylate ion}}{R{-}\overset{\displaystyle O}{\overset{\|}{C}}{-}O^-} + H_3O^+$$

(*Continued*)

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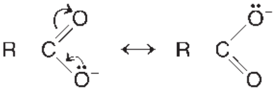
— Acyl chloride is more volatile than its corresponding carboxylic acid because of the weaker intermolecular forces of the permanent dipole-permanent dipole type as compared to the acid. It also hydrolyzes much more readily in water, releasing HCl a strong acid, which fully dissociates in water. Hence, the acidic nature of acid chloride in water in water arise mainly from the dissociated HCl.

— Esters are also polar analog molecules of the carboxylic acid, and are relatively soluble in water due to the ability of the ester functional group to form hydrogen bonding with the water molecules.

— Amides are solid at room temperature because of the stronger and more extensive hydrogen bonding made possible by the presence of the $-NH_2$ group (for primary amides) and the lone pair of electrons on the carbonyl ($C=O$) oxygen atom.

Acidity of carboxylic acids

— Carboxylic acids are the strongest organic acid. This is because, with the negative charge on the carboxylate ion being dispersed through resonance, two equivalent resonance structures are formed. In these two equivalent resonance structures, the negative charge "sits" on two highly electronegative oxygen atoms:

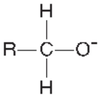


— The electron-withdrawing group in a substituted carboxylic acid causes the molecule to be more acidic than an unsubstituted carboxylic acid as the electron density that is delocalized into the $-CO-$ group is further dispersed by the electron-withdrawing group via inductive effect.

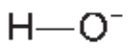
— The electron-releasing group causes the molecule to be less acidic than an unsubstituted carboxylic acid.

Comparison of acidities of alcohols, phenol, and carboxylic acids

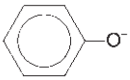
— Increasing acid strength: $ROH < H_2O < phenol < RCOOH$. The stability of the conjugate base increases from left to right:



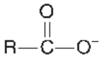
alkoxide ion



hydroxide ion



phenoxide ion



carboxylate ion

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— The relative acidities of these compounds can be observed from their reactions or non-reactions with the following bases and reactive metal:

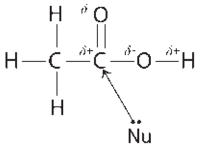
	Na	NaOH	Na_2CO_3 or $NaHCO_3$
RCOOH	☑ $H_2(g)$ + salt	☑ H_2O + salt	☑ $CO_2(g) + H_2O$ + salt
Phenol	☑ $H_2(g)$ + salt	☑ H_2O + salt	—
water	☑ $H_2(g)$ + salt	—	—
ROH	☑ $H_2(g)$ + salt	—	—

Between NaOH and Na_2CO_3, NaOH is the stronger base while Na_2CO_3 is the weaker one. Thus, the fact that only carboxylic acids can react with Na_2CO_3 indicates that it is the strongest acid in the above list. Hence, we can use Na_2CO_3 to differentiate the above acids.

Chemical properties of carboxylic acids

— The presence of the highly electron-deficient carbon atom of the carboxyl group makes it susceptible to nucleophilic attack, which is similar to that of aldehydes and ketones.

Ethanoic acid



In fact, the electron deficiency is even greater than that in aldehydes and ketones due to the presence of two highly electronegative O atoms. But, unlike aldehydes and ketones, carboxylic acids do not undergo addition reaction. In contrast, they prefer to undergo Nucleophilic Acyl Substitution due to the presence of the hydroxyl group, which is a better leaving group relative to the breaking of the C−C or C−H bonds, in ketones or aldehydes respectively, to generate carbanion (R^-) or hydride (H^-) ions as the leaving groups. The hydroxyl group can break off from the carboxyl functional group and exist “comfortably” as a hydroxide ion.

(*Continued*)

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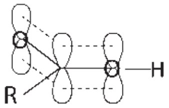
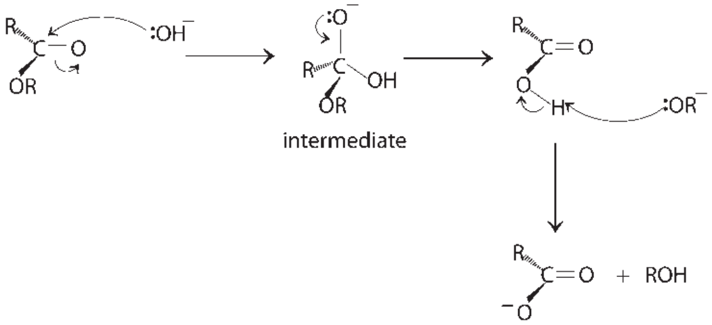
— With such close proximity, both the carbonyl and hydroxyl functional groups of the carboxyl actually alter each other's properties. The interaction of the *p* orbital of the hydroxyl O atom with that of the carbonyl group results in the delocalization of electrons into the carbonyl group. This thus leads to a partial double bond characteristic between the O atom of the hydroxyl group and the carbonyl carbon.

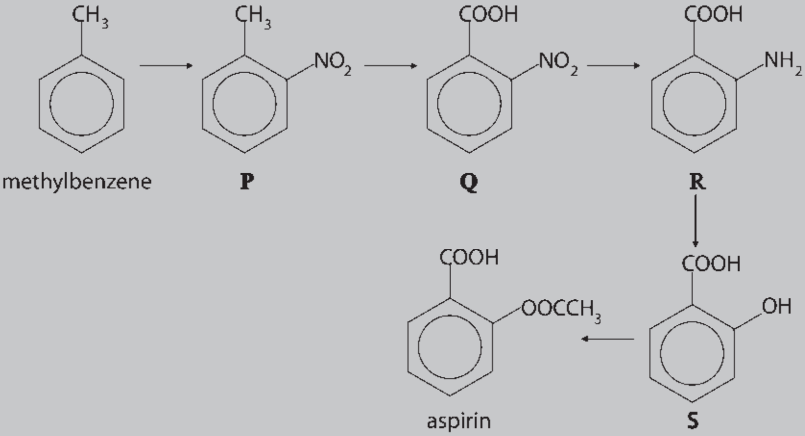


Q If there is a partial double bond characteristic between the O atom of the hydroxyl group and the carbonyl carbon, shouldn't this make the hydroxyl group unlikely to break away from the carbonyl group, as in the case of phenol or chlorobenzene?

A: Yes, indeed it would be more difficult to break the C−OH bond due to the partial double bond characteristic. But unlike the case of phenol or chlorobenzene, the carbonyl carbon atom is more susceptible to nucleophilic attack as its electron deficiency is increased due to the presence of another highly electron-withdrawing O atom. The latter factor is the more dominant one, thus resulting in the ease of substitution of the −OH group, forming other acid derivatives. In addition, one can look at the reaction from the mechanistic perspective. Overall, carboxylic acids undergo the Nucleophilic Acyl Substitution mechanism. But the mechanism is actually a Nucleophilic Addition followed by elimination type. During the addition stage, the intermediate has a tetrahedral configuration. At this stage, the partial double characteristic between the O atom of the hydroxyl group and the carbonyl carbon disappears. Hence, the C−OH bond becomes more susceptible to being broken during the elimination stage. The breakage of the C−OH bond would result in a re-establishment of the resonance stability in the acid derivatives.



1. Aspirin may be produced from methylbenzene via the following synthetic pathway:



   (a) Give the reagents and conditions required to convert:

      (i) methylbenzene to **P**;

Explanation:

Use concentrated HNO_3/concentrated H_2SO_4/heat. {Electrophilic Substitution}

(ii) **P** to **Q**;

Explanation:

Use $KMnO_4/H_2SO_4$/heat. {Oxidation}

(iii) **R** to **S**; and

Explanation:

Use (i) $NaNO_2$/HCl(aq)/0–5°C, (ii) water/heat. {Diazotization followed by hydrolysis}

Do you know?

— The purpose of $NaNO_2$/HCl(aq) is to generate the unstable HNO_2. When phenylamine, $C_6H_5NH_2$, reacts with HNO_2 at about 5°C, it will be converted to the highly unstable benzene diazonium ion, $C_6H_5{-}N{\equiv}N^+$. When heated with water, the benzene diazonium ion is converted to phenol, with the evolution of N_2 gas. Hence, nitrous acid can serve as test for phenylamine.

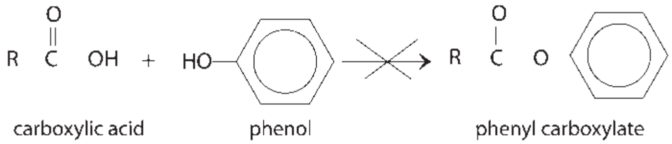
(iv) **S** to aspirin.

Explanation:

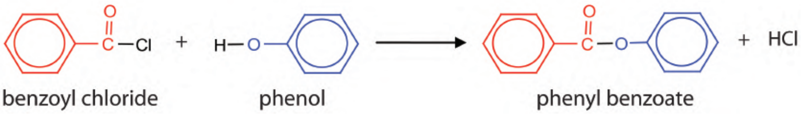
Use anhydrous CH_3COCl. {Nucleophilic Acyl Substitution}

Do you know?

— To get the phenolic ester, C_6H_5OCO-, we cannot use phenol to react with the carboxylic acid:

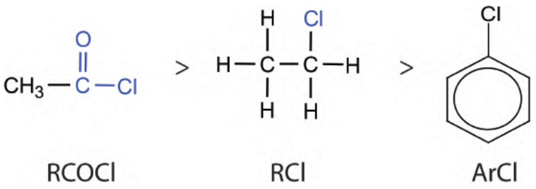


This is because the lone pair of electrons on the phenol would delocalize into the benzene ring, making phenol a weak nucleophile in the presence of the carboxylic acid. But if we use a more reactive acid chloride to react with the phenol, we would be able to get the phenolic ester:



Q Why do we need to use an anhydrous acid chloride?

A: Acid chlorides hydrolyze readily upon contact with water. Ethanoyl chloride even reacts rapidly with cold water. This is in contrast to the slow hydrolysis of halogenoalkanes that requires heating. This gives us the following trend of decreasing ease of hydrolysis:



Do you know?

The trend of the hydrolysis can be explained by the degree of susceptibility of these compounds toward nucleophilic attack, which is attributed to the following two factors:

1. *The electron density on the electron-deficient carbon atom of the C—Cl bond.*

   Nucleophiles are more likely to attack a highly electron-deficient site. The carbonyl carbon in RCOCl is the most electron-deficient as its electron density is drawn away by the more electronegative O atom of the carbonyl functional group and the electronegative Cl atom. Although there is a partial double bond characteristic in the C—Cl bond, this obviously does not decrease its susceptibility to hydrolysis.

   The carbon atom of the C—Cl bond in RCl is bonded to the electron-donating alkyl group that causes the C—Cl bond to be less polarized.

   As for ArCl, due to the extensive network of overlapping *p* orbitals, the C—Cl bond acquires some partial double bond characteristic, which also decreases the electron deficiency on the carbon atom, making it less susceptible to nucleophilic attack.

2. *The size and number of substituents bonded to the carbon atom of the C—Cl bond.*

   Nucelophiles are more likely to attack an electron-deficient site if there is less steric hindrance. The carbonyl C atom, in RCOCl, is sp^2 hybridized with three substituents attached to it in a trigonal planar geometry. This bonding structure poses less steric hindrance as compared to that of RCl wherein the sp^3 hybridized C atom of the C—Cl bond is bonded to four substituents in a tetrahedral geometry. Although the carbon atom of the C—Cl of ArCl is also trigonal planar, the steric hindrance is most significant for ArCl as it contains a bulky benzene ring.

(b) (i) Give a mechanistic account for the formation of **P** from methylbenzene.

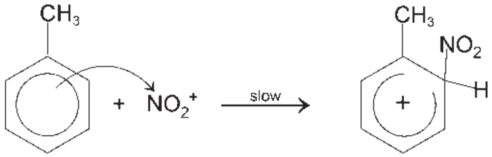
Explanation:

Methylbenzene is converted to 2-nitromethylbenzene via the Electrophilic Substitution mechanism:

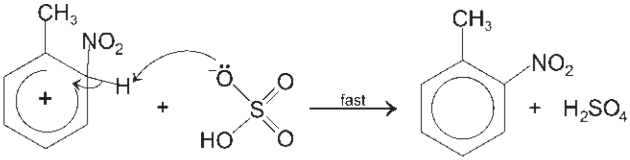
The electrophile NO_2^+ is generated in the acid–base reaction below:

$$\underset{\text{base}}{HNO_3} + \underset{\text{acid}}{2H_2SO_4} \rightleftharpoons NO_2^+ + H_3O^+ + 2HSO_4^-.$$

Step 1: The NO_2^+ electrophile attacks benzene to form a carbocation intermediate destroying the resonance stability.

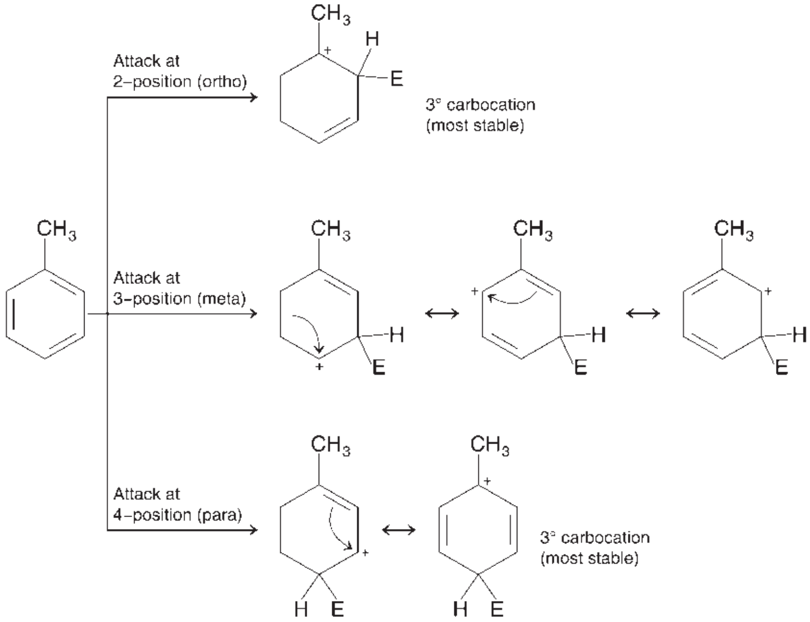


Step 2: Deprotonation of the carbocation to regenerate the resonance stability.



Do you know?

— An alkyl group is a 2,4-director due to the following reason:

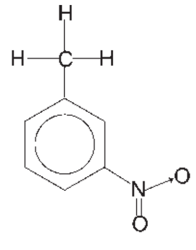


The carbocations that are formed during the attack at the 2- or 4-position are more stable due to the electron-releasing effect of the alkyl group.

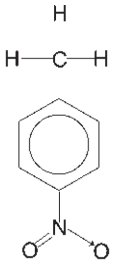
(ii) The reaction also produces two other isomers of **P**. Give the displayed formulae of these two isomers. What simple method could be used to show that the purified product is in fact **P**?

Explanation:

As all three compounds each has its unique melting point, we can determine the purity by using the melting point of **P**. If the melting point is very close to its theoretical one, then we have purified **P**. The two other isomers of **P** are:



3-nitromethylbenzene



4-nitromethylbenzene

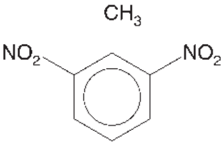
Do you know?

— For ring structures such as benzene and the cycloalkanes, it is alright to draw the skeletal form without showing any of carbon–carbon or carbon–hydrogen bonds for the displayed formula or full constitutional/structural formula.

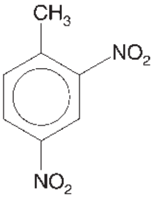
(iii) When the temperature of the reaction is raised above the optimum for the reaction, the overall yield of **P** and its isomers drops. Suggest two reasons for this.

Explanation:

At a higher temperature, further nitration can take place. This thus affects the yield of **P** and its isomers.



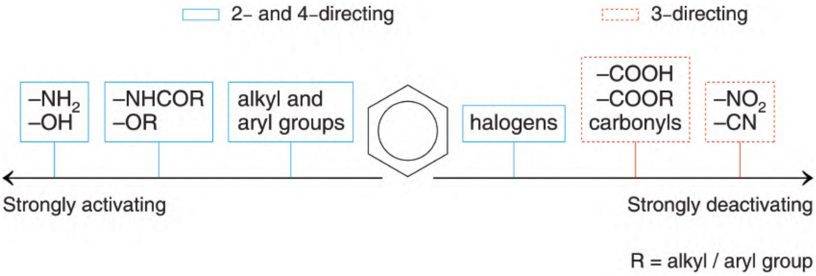
2,6-dinitromethylbenzene



2,4-dinitromethylbenzene

Do you know?

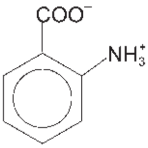
— In the situation where the directing properties of two groups do not complement each other, the more dominating group would dictate the preferential site of attack. A mixture of products of varying quantities would be formed. In the case between the $-CH_3$ and $-NO_2$ groups, the former is in dominance and Electrophilic Substitution takes place at positions 2, 4, and 6 rather than at position 3, with respect to the methyl group. The following figure shows the relative strengths of some activating and deactivating substituents.



(v) Account for why **R** has a higher boiling point than **Q**. Hence, suggest a simple way to separate a mixture of **R** and **Q**.

Explanation:

Compound **R** contains a $-NH_2$ and a $-COOH$ group, which are capable of undergoing intramolecular acid–base reaction to form the following zwitterion:



zwitterion

As a result, the ionic bonding present would cause compound **R** to have a higher boiling point than **Q**, which has hydrogen bonding. Making use of their different boiling points, we can separate compounds **R** and **Q** via fractional distillation.

Q Does the proximity of the $-COOH$ group and $-NO_2$ group in compound **Q** cause the formation of intramolecular hydrogen bonding?

A: Yes, of course. That is why we should expect the boiling point of 2-nitrobenzoic acid to be lower than that for 3-nitrobenzoic acid or 4-nitrobenzoic acid.

Do you know?

— A zwitterion is an electrically neutral species that contains an equal number of positive and negative charges.

(vi) The solubility of **Q** in water is low but is enhanced when aqueous sodium hydroxide is added. Explain the observation.

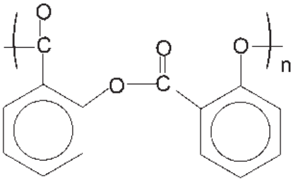
Explanation:

The proximity of the $-COOH$ group and $-NO_2$ group in compound **Q** causes the formation of intramolecular hydrogen bonding, which would hence limit sites available for intermolecular hydrogen bonding with the water molecules. In addition, the presence of the hydrophobic benzene ring also decreases the solubility of the molecule. But in the presence of aqueous NaOH, the acidic $-COOH$ group will react with the NaOH to generate the $-COO^-$. This anionic part enables the molecule to form stronger ion–dipole interaction with the water molecule, which releases a sufficient amount of energy to help dissolve compound **Q**.

(c) During the esterification process, traces of a polymeric by-product always form. Explain why it is formed and suggest a structure for it.

Explanation:

The −OH group of one molecule of **S** can undergo esterification with the −COOH group of another molecule of **S** and so forth to form a trace amount of polyester. One repeat unit is shown below:



Q So, the phenol can actually form an ester with a carboxylic acid after all?

A: Yes, as we have discussed before, the yield will not be good. That is why the phenolic ester polymer is formed in trace amounts.

(d) (i) **P** is a constitutional/structural isomer of **R**. State the type of structural isomerism.

Explanation:

P and **R** share the same molecular formula but different functional groups. Hence, they are functional group isomers.

(ii) Suggest with reasons, which of **P** and **R** would have the higher melting point.

Explanation:

In the solid state, compound **P** exists as a zwitterion with ionic bonding. Hence, its melting point is higher than that of **R**, which is polar with permanent dipole–permanent dipole interaction in addition to the instantaneous dipole–induced dipole interaction that the molecule has.

(iii) Suggest a simple chemical test to distinguish between **P** and **R**.

Explanation:

To differentiate between **P** and **R**, we can use anyone of the following tests:

(1) Use PCl_5 and test for HCl(g):

P: No white fumes of HCl(g).
R: White fumes of HCl(g) observed.
Compound **R** contains a −COOH group.
$-COOH + PCl_5 \rightarrow -COCl + POCl_3 + HCl(g)$. {Nucleophilic Acyl Substitution}

(2) Use $SOCl_2$ and test for HCl(g):

P: No white fumes of HCl(g).
R: White fumes of HCl(g) observed.
Compound **R** contains a –COOH group.
$-COOH + SOCl_2 \rightarrow -COCl + SO_2 + HCl(g)$. {Nucleophilic Acyl Substitution}

(3) Use $Na_2CO_3(s)$ and test for $CO_2(g)$:

P: No gas evolved gave white ppt with $Ca(OH)_2(aq)$.
R: Gas evolved gave white ppt with $Ca(OH)_2(aq)$.
Compound **R** contains a −COOH group.
$2-COOH + CO_3^{2-} \rightarrow 2-COO^- + CO_2 + H_2O$. {Acid–base reaction}

(4) Use $KMnO_4/H_2SO_4$/heat:

R: No decolorization of purple $KMnO_4$.
P: Purple $KMnO_4$ decolorized.
Compound **P** contains a $-CH_3$ group bonded to a benzene ring that is oxidizable.
$-CH_3 + 3[O] \rightarrow -COOH + H_2O$. {Oxidation}

(5) Use $KMnO_4$/NaOH/heat:

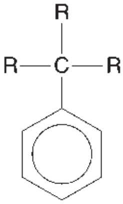
R: No decolorization of purple $KMnO_4$.
P: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.
Compound **P** contains a $-CH_3$ group bonded to benzene ring that is oxidizable.
$-CH_3 + OH^- + 3[O] \rightarrow -COO^- + 2H_2O$. {Oxidation}

(6) Use (i) $NaNO_2$/HCl(aq)/0–5°C, (ii) water/heat. {Diazotization followed by hydrolysis}

P: No evolution of N_2(g).
R: Evolution of N_2(g).
Compound **R** contains a $-NH_2$ group.

Do you know?

— An alkyl group that is bonded to a benzene ring can be completely oxidized to form benzoic acid by $KMnO_4/H_2SO_4$/heat, except the following type of molecule:



The absence of a hydrogen atom at the quarternary carbon atom prevents oxidation from taking place.

(iv) Suggest a different chemical test from (d)(iii) to distinguish between **R** and **S**.

Explanation:

To distinguish between **R** and **S**, just pick anyone of the following tests that you have not used in (*d*)(*iii*) above:

(1) Use (i) $NaNO_2/HCl(aq)/0–5°C$, (ii) water/heat. {Diazotization followed by hydrolysis}

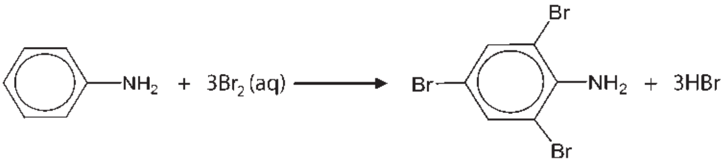
S: No evolution of $N_2(g)$.
R: Evolution of $N_2(g)$.
Compound **R** contains a $-NH_2$ group.

(2) Use neutral aqueous iron(III) chloride:

R: No formation of a violet complex.
S: Formation of a violet complex.
Compound **S** contain the phenol functional group that forms a violet complex with Fe^{3+}.

Q Can we use aqueous Br_2 to test for phenol?

A: No, because phenylamine also decolorizes aqueous Br_2 to form 2,4,6-tribromophenylamine.



2,4,6-tribromophenylamine
(a white ppt)

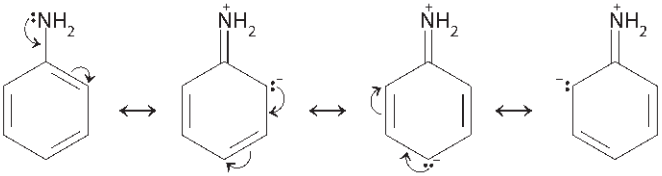
(e) (i) Suggest with reasons, which of **Q** and **R** would have a higher pK_a value.

Explanation:

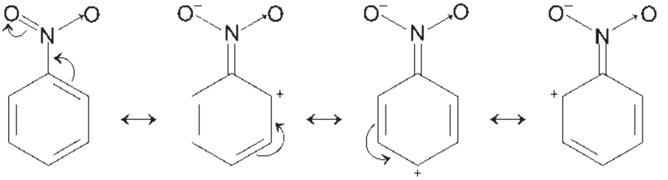
A higher pK_a value means a smaller K_a, which implies a weaker acid. The weaker the acid, the lower the stability of its conjugate base. Compound **R** will have a higher pK_a value than compound **Q**. This is because the lone pair of electrons of the $-NH_2$ group of compound **R** delocalizes into the benzene ring; as a result, the stability of the conjugate base of **R** is lowered as compared to the conjugate base of **Q**. For compound **Q**, the electron-withdrawing $-NO_2$ group could disperse the electron density of its conjugate base; this would help to stabilize it.

Do you know?

— The $-NH_2$ group is highly ring-activating due to the following resonance:



— The $-NO_2$ group is highly ring deactivating due to the following resonance:



(ii) Comparing benzoic acid with **Q**, explain why benzoic acid is less acidic than **Q**.

Explanation:

Benzoic acid is less acidic than **Q** due to the fact that the conjugate base of **Q** is more stable than the benzoate ion. This is because for compound **Q**, the electron-withdrawing $-NO_2$ group could disperse the electron density of its conjugate base; this would help to stabilize it.

(iii) Suggest with reasons how a mixture of **R** and **S** might be separated.

Explanation:

Both **R** and **S** have limited solubility in water because of the hydrophobic benzene ring. If aqueous HCl is added to a mixture of **R** and **S**, the basic $-NH_2$ group of compound **R** would be protonated. As a result, the cationic form of compound **R** would be more soluble in water due to its ability to form ion-dipole interaction with the water molecules. Now, when a non-polar organic solvent is added to the aqueous layer and shaken, compound **S** would dissolve in the non-polar solvent while the cationic form of **R** would stay in the aqueous acid. Both the aqueous and organic layers can then be separated using a separatory funnel. The cationic form of compound **R** is then regenerated by adding a base to neutralize it.

Q Can we use HNO_3(aq) for the above acid–base reaction?

A: You need to be extra careful when using HNO_3(aq), especially if phenylamine is involved. This is because the benzene ring of phenylamine is highly activated by the delocalization of electrons from the N atom. Moreover, HNO_3(aq) might nitrate the benzene ring by introducing a nitro group into the ring.

(f) The benzene rings of both **S** and **Q** can be further chlorinated with suitable reagents and conditions. Explain briefly why a higher temperature is required to effect the chlorination of **Q** than that of **S**. Give the appropriate reagents and conditions.

Explanation:

Compound **S** contains an –OH group on the benzoic acid while compound **Q** has a $-NO_2$ group. The benzene ring of compound **Q** is less electron-rich than that of compound **S** because of the electron-withdrawing $-NO_2$ group. In contrast, for compound **S**, the lone pair of electrons of the $-OH$ group can delocalize into the benzene ring. Hence, this makes the benzene ring of compound **S** more susceptible to electrophilic attack than that of compound **Q**. Thus, a higher temperature is required to effect the chlorination of **Q** than that of **S**. The chlorination reaction can be carried out with Cl_2/anhydrous $AlCl_3$/heat.

Q Why do we need the $AlCl_3$ to be anhydrous?

A: The Al atom of $AlCl_3$ is highly electron-deficient. If water is present, it undergoes hydrolysis, making it ineffective as a Lewis acid catalyst to generate an electrophile for the chlorination of benzene ring.

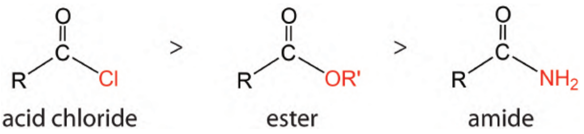
(g) Ketones and aspirin both have carbonyl groups, but only aspirin is hydrolyzed easily. Explain.

Explanation:

The carbon atom of the carbonyl group for aspirin is more electron-deficient because of the two electron-withdrawing oxygen atoms bonded to it as compared to a ketone, which only has one. Hence, a nucleophile, such as H_2O or OH^-, is more readily attracted to the carbon atom of the carbonyl group for aspirin. In addition, after hydrolysis of the ester in aspirin, the leaving group is an alcohol. But for a ketone, the leaving group is a negatively charged carbanion ion, which is less stable than the alcohol.

Do you know?

— The chemistry of the acid derivatives centers on Nucleophilic Acyl Substitution involving the replacement of good leaving groups such as $-Cl$, $-OR$, and $-NH_2$ by another nucleophile. These reactions mainly consist of the conversion of the more reactive acid derivative into a less reactive one, and also the conversion of these acid derivatives back into the parent carboxylic acid. The reactivities of these derivatives decrease in the order:



— The observed reactivity trend can be accounted for by considering the ease of the nucleophile carrying out the nucleophilic attack on the electron-deficient carbonyl carbon center. Based on the decreasing trend of electronegativity, O > N > Cl, we would expect the electron deficiency of the carbonyl carbon to be greatest for an ester, followed by an amide, and then an acid chloride. This obviously does not account for the observed trend of reactivity. So, what gives rise to the observed trend, especially since Cl atom is not the most electronegative atom among the three atoms?

— There are two different combinational factors, namely, the delocalization of the lone-pair of electrons of the $-Cl$, $-OR$, and $-NH_2$ groups into the carbonyl functional group and the difference in the electronegativities of the Cl, O, and N atoms:

(1) The delocalization of the lone pair of electrons from the Cl, O, and N atoms into the carbonyl functional group (via the overlap of two *p* orbitals), diminishes the electron deficiency on the carbonyl carbon. But the delocalization for an acid chloride is the least effective as it involves a 2*p*-3*p*-orbital overlap between the carbonyl carbon and the chlorine atom. Thus, the electron deficiency of the carbonyl carbon for an acid chloride is the highest among the three given derivatives. As for the higher reactivity of an ester as compared to an amide, the more electronegative O atom of the $-OR'$ group as compared to the N atom of $-NH_2$, results in a diminished effect of the delocalization. That is, the more electronegative O

(*Continued*)

(*Continued*)

atom would "pull back" more electron density that has been delocalized compared to the N atom, via inductive effect. Therefore, a higher level of electron deficiency would make the ester more susceptible to nucleophilic attack than the amide.

(2) In addition, the trend that arises from the susceptibility to nucleophilic attack also mirrors the decreasing ease of leaving for the corresponding leaving group:

$$-Cl \quad > \quad -OR \quad > \quad -NH_2$$

After the cleavage of the C–Y bond, where $Y = Cl$, OR, or NH_2, the stability of the species that is generated would decrease according to the following trend:

$$Cl^- \quad > \quad {}^-OR \quad > \quad {}^-NH_2$$

Q How is the reactivity of the carboxylic acid toward Nucleophilic Acyl Substitution like as compared to the trend for its derivatives in the above?

A: A carboxylic acid has the −OH group attached to the carbonyl group, whereas an ester has the −OR group bonded. Hence, both functional groups have the same O atom bonded to the carbonyl functional group. Considering the delocalization of electrons and electronegativity, we would expect both the ester and carboxylic acid to have the same reactivity. But we can rationalize the ester to be less reactive than the acid because due to the electron-releasing effect of the alkyl group from the alcohol group in ester, the electron-withdrawing effect of the O atom of the alcohol group that is bonded to the carbonyl carbon is less than the O atom of the −OH group that is attached to the carbonyl group for the carboxylic acid molecule. As a result, the delocalization of electrons into the carbonyl functional group in the ester functional group is more effective. This would diminish the electron deficiency of the carbonyl carbon atom to a greater extent for the ester functional group as compared to the carboxylic acid. In addition, from the leaving group perspective, –OH is a better leaving group than the −OR group as the stability of the ^-OH ion is higher than that of ^-OR. The latter is a stronger base due to the intensification of electron density on the atom brought about by the electron-donating alkyl group.

Q Can we say that the partial double bond characteristic for an acid chloride < a carboxylic acid < an ester < an amide?

A: Yes, you can. Basically, this trend can be accounted for by considering the same factors that affect the electron deficiency of the carbonyl carbon atom.

Q Can I say that the carboxylate ion is less reactive to Nucleophilic Acyl Substitution than the carboxylic acid molecule because the electron deficiency of the carbonyl carbon is lower for the carboxylate ion?

A: Yes. This is because in the carboxylate ion, the delocalization of the negative charge (which signifies an extra electron) into the carbonyl group decreases the electron deficiency of the carbon atom to a much greater extent than for carboxylic acid. In addition, the partial double characteristic is greater in the carboxylate ion than for the carboxylic acid molecule.

(h) The reaction of **S** to form aspirin does not proceed if CH_3COOH is used. Explain.

Explanation:

This is because the lone pair of electrons on the −OH group of compound **S** delocalizes into the benzene ring, thus making the −OH group a weak nucleophile in the presence of a carboxylic acid. But if we use a more reactive acid chloride to react with the phenol, we would be able to get the phenolic ester.

Q Since the negatively charged phenoxide ion is a better nucleophile than phenol, can we react the phenoxide with the carboxylic acid to obtain the ester then?

A: No, you can't. Remember, a carboxylic acid is a stronger acid than phenol. This would mean that the phenoxide ion is a stronger base than a carboxylate ion. Hence, instead of Nucleophilic Acyl Substitution, we would have an acid–base reaction:

$$RCOOH + C_6H_5O^- \rightarrow C_6H_5OH + RCOO^-.$$

2. Lactic acid, $CH_3CH(OH)COOH$, a compound that is produced during cell respiration from pyruvic acid, $CH_3COCOOH$, causes muscle fatigue.

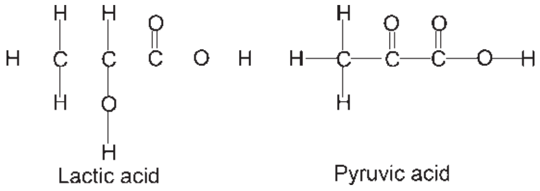
(a) (i) What type of chemical reaction has occurred when pyruvic acid is converted to lactic acid?

Explanation:

The ketone functional group of pyruvic acid is converted to a secondary alcohol in lactic acid, thus it is a reduction reaction.

(ii) Draw the displayed formulae for both pyruvic acid and lactic acid.

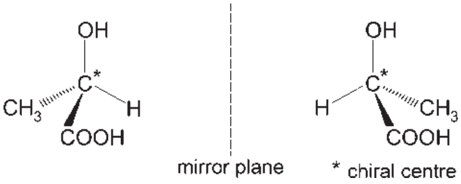
Explanation:



(iii) What type of isomerism is present in lactic acid? Draw the isomers.

Explanation:

Since there is a chiral carbon in lactic acid, it exhibits enantiomerism:



(iv) State with reasons, which of lactic acid or pyruvic acid would be more acidic.

Explanation:

The more acidic a molecule is, the more stable is its conjugate base. The carbon atom of the carbonyl functional group in pyruvic acid is more electron-deficient than the α-carbon of lactic acid, which has an electron-withdrawing −OH group on it. This is because the carbon atom of the carbonyl functional group is sp^2 hybridized while the α-carbon is sp^3 hybridized. Due to the greater percentage of *s* character in an sp^2 hybridized (about 33.3%) orbital than in an sp^3 hybridized (about 25%) orbital, the negative charge on the conjugate base of pyruvic acid is more dispersed; hence, it is more stabilized.

Q Can we say that pyruvic acid is more acidic because the conjugate base is resonance-stabilized?

A: No. This is because we can't draw a good resonance structure to show the dispersion of the negative charge on the $-COO^-$ group into the $C{=}O$ functional group. This is also similar to the case when you compare the acidity of benzoic acid to that of ethanoic acid. Benzoic acid is more acidic than ethanoic acid because the $-COO^-$ group of the benzoate ion is bonded to an sp^2 hybridized benzene ring. Hence, via inductive effect, the benzoate ion is more electronically stabilized.

Do you know?

— You can use the acronym A.R.I.O., from left to right, to help to pinpoint the contributing factor that stabilizes a species. 'A' stands for atom, 'R' for resonance, 'I' for induction, and 'O' for orbital. Take for instance, to account for the difference in the stabilities of the conjugate bases of pyruvic acid and lactic acid; both have a $-COO^-$ group bonded to a carbon atom, which thus is a constant for both. So, you can't use the atom factor. Next, is there any resonance for this carbon atom? Nope! So you can't use the resonance factor. If you now look at the type of carbon atom, it is sp^2 hybridized in pyruvic acid versus sp^3 hybridized in lactic acid; the inductive effect exerted by sp^2 hybridized is much greater. Hence, the 'I' factor accounts for the acidity.

Q How do you use the orbital factor, i.e., the 'O' factor?

A: If you consider the stability of CH_2^- versus that of CH_3^-, the negative charge, representing an extra electron, sits in an sp^2 hybridized atom in CH_2^- but an sp^3 hybridized atom in CH_3^-. As an *s* orbital is closer to the nucleus than a *p* orbital, having a higher percentage of *s* character in the hybrid orbital would mean that the electron in it would be more strongly attracted. This would help to stabilize the negative charge.

(v) Suggest two simple chemical tests to distinguish between lactic acid and pyruvic acid. Write balanced equations for the positive test.

Explanation:

To differentiate lactic acid, $CH_3CH(OH)COOH$, from pyruvic acid, $CH_3COCOOH$, just choose any of the following tests:

(1) Use $KMnO_4/H_2SO_4$/heat:

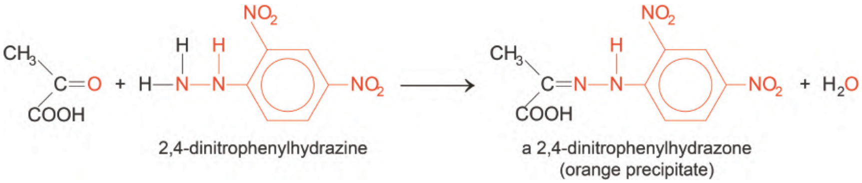
$CH_3COCOOH$: No decolorization of purple $KMnO_4$.
$CH_3CH(OH)COOH$: Purple $KMnO_4$ decolorized.
$CH_3CH(OH)COOH + [O] \rightarrow CH_3COCOOH + H_2O$. {Oxidation}

(2) Use $KMnO_4$/NaOH/heat:

$CH_3COCOOH$: No decolorization of purple $KMnO_4$.
$CH_3CH(OH)COOH$: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.
$CH_3CH(OH)COOH + OH^- + [O] \rightarrow CH_3COCOO^- + 2H_2O$. {Oxidation}

(3) Use 2,4-dinitrophenylhydrazine and heat:

$CH_3CH(OH)COOH$: No orange ppt formed.
$CH_3COCOOH$: Orange ppt formed.

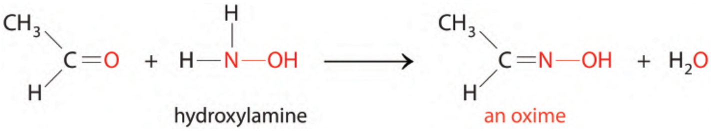


{Condensation/Addition–Elimination}

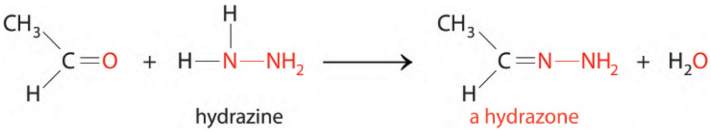
Do you know?

— Other than 2,4-DNPH, the aldehyde or ketone functional group can also react with:

Hydroxylamine to yield an oxime:



Hydrazine to yield a hydrazone:



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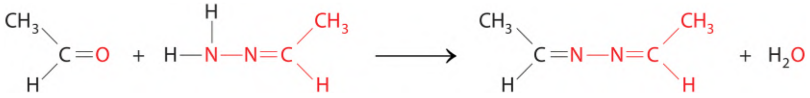
If there is an excess of a carbonyl compound, the hydrazone undergoes further condensation reaction:



Q There is also a carbonyl functional group in the –COOH group. Thus, can the carboxylic acid also undergoes addition–elimination reaction with 2,4-DNPH?

A: No, it can't. This is because we would expect an acid–base reaction between the carboxylic acid and 2,4-DNPH instead, as the $-NH_2$ group of 2,4-DNPH is basic in nature. In addition, the lone pair of electrons of the –OH group of the $-COOH$ functional group is delocalized into the $C{=}O$ group; hence, the molecule would be relatively more stable. If addition–elimination reaction were to take place, the resonance stabilization effect would be lost.

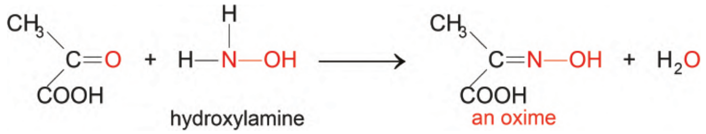
Q How about for functional groups such as esters, amides, and acyl halides?

A: No. There is a better leaving group such as $-OR$, $-NH_2$, or $-Cl$ being bonded to the carbonyl carbon atom. This also applies for the $-COOH$ group. Thus, the condensation mechanism won't work here, but Nucleophilic Acyl Substitution occurs instead. Similarly, if addition–elimination reaction were to take place, the resonance stabilization effect that is being mentioned above would be lost.

(vi) Pyruvic acid reacts with hydroxylamine (NH_2OH) to give a condensation product.

(A) Write a balanced equation for the reaction between pyruvic acid and hydroxylamine.

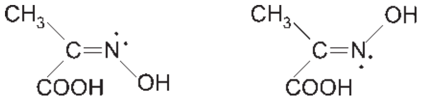
Explanation:



(B) The condensation product exhibits stereoisomerism. Draw the possible stereoisomers and name the type of stereoisomerism.

Explanation:

Since there is restricted rotation at the C=N double bond and there are two different groups of atoms bonded on each of the atoms in the C=N double bond, the molecule is able to exhibit *cis-trans*/geometrical isomerism:



(b) In the laboratory, lactic acid may be synthesized from ethanol via the following pathway:

$$CH_3CH_2OH \xrightarrow{\mathbf{P}} CH_3CHO \xrightarrow{\mathbf{Q}} CH_3CH(OH)CN \xrightarrow{\mathbf{R}} CH_3CH(OH)COOH$$

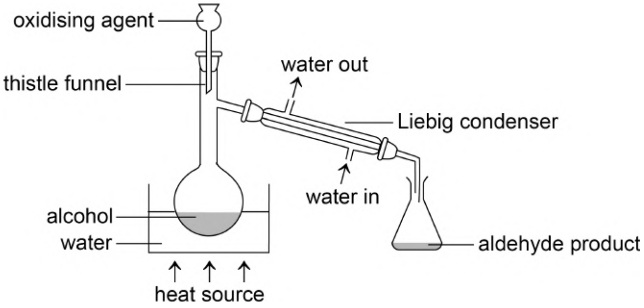
(i) Give the reagents and conditions for steps **P**, **Q**, and **R**.

Explanation:

Step **P**: Use $K_2Cr_2O_7/H_2SO_4$/immediate distillation.
Step **Q**: Use HCN/small amount of NaOH/cold or KCN/H_2SO_4 or HCN/NaCN.
Step **R**: Use H_2SO_4(aq)/heat or HCl(aq)/heat.

Q Why must we use immediate distillation when oxidizing the primary alcohol to an aldehyde?

A: Primary alcohols are readily oxidized to aldehydes which, in turn, are easily oxidized to carboxylic acids. Hence, if the desired product is an aldehyde, the milder oxidizing agent $K_2Cr_2O_7$ should be used and the aldehyde would be immediately distilled off from the reaction vessel to prevent it from being further oxidized to a carboxylic acid. It is also important to note that the oxidizing agent is added dropwise into the alcohol. This way of addition is to ensure that the added oxidizing agent is limiting with respect to the alcohol and is immediately being consumed once it comes in contact with the alcohol. There would not be any excess oxidizing agent present to further oxidize the aldehyde that is formed into the carboxylic acid. The set-up for the oxidation is shown below:



Q When we apply immediate distillation during the oxidation process, wouldn't this cause the alcohol to be distilled out too?

A: The aldehyde that is formed from the alcohol would have a lower boiling point than that of the alcohol, due to the stronger hydrogen bonding in alcohol. As for the aldehyde, it is polar and has permanent dipole–permanent dipole interaction in addition to the instantaneous dipole-induced dipole interaction the molecule has. Thus, heating at the boiling point of aldehyde would not distill the alcohol out.

Q Can we use acidified $KMnO_4$ with immediate distillation instead?

A: No, you can't. Acidified $KMnO_4$ is a much more powerful oxidizing agent than acidified $K_2Cr_2O_7$. The primary alcohol would be immediately oxidized to the carboxylic acid without any chance of isolating the aldehyde. Thus, immediate distillation would not help at all.

(ii) Give a mechanistic account for step **Q**.

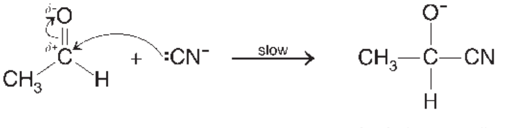
Explanation:

The aldehyde reacts with HCN/small amount of NaOH/cold via the Nucleophilic Addition mechanism.

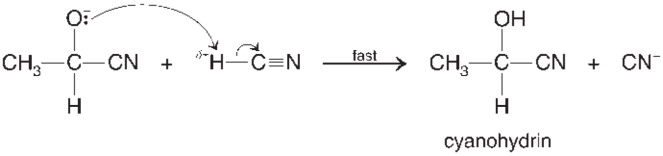
As HCN is a weak acid, $HCN \rightleftharpoons H^+ + CN^-$, the amount of CN^- is low. So, to increase the $[CN^-]$, NaOH(aq) as a catalyst is added:

$$HCN + OH^- \rightarrow H_2O + CN^-.$$

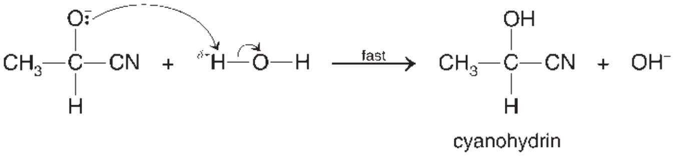
Step 1: The nucleophile attacks the electron-deficient carbonyl carbon to form an anionic intermediate.



Step 2: The anionic intermediate is protonated to form the final cyanohydrin product: a proton can be extracted from the undissociated HCN molecule; or



it can be extracted from the H_2O solvent molecule,



(iii) State with reasons, which of lactic acid or ethanol would be more acidic.

Explanation:

The stronger the acid, the more stable is its conjugate base. Lactic acid is more acidic than ethanol because the negative charge on the carboxylate ion is dispersed through resonance; two equivalent resonance structures are formed. In these two equivalent resonance structures, the negative charge "sits" on two highly electronegative oxygen atoms. In addition, since the -OH group in lactic acid is electron-withdrawing via inductive effect, it would further stabilized the conjugate base by dispersing electron density away from the carboxylate group.

As for ethanol, the ethyl group on the ethoxide ion ($CH_3CH_2O^-$) donates electron density to the oxygen atom. This intensifies the electron density on it and hence destabilizes it.

Q Lactic acid also contains an −OH group, so would it be able to reveal its acidity in the presence of the −COOH group?

A: No! This is because the dissociation from the stronger −COOH group would suppress the dissociation of the –OH group due to the common ion effect from the H^+ released from the dissociation of the stronger −COOH group.

Q So, would lactic acid be a stronger acid than propanoic acid, CH_3CH_2COOH?

A: Yes, lactic acid is stronger than propanoic acid. This is because the −OH group in lactic acid would help to disperse electron density from its conjugate base as the oxygen atom is electron-withdrawing via inductive effect. Hence, since the conjugate base of lactic acid is more stable than that of propanoic acid, it would be a stronger acid.

Q How about comparing 3-hydroxypropanoic acid, $HOCH_2CH_2COOH$, with lactic acid?

A: 3-hydroxypropanoic acid is a weaker acid than lactic acid because the –OH group is further away from the $-COO^-$ group. Hence, the effect of the dispersion of electron density on the $-COO^-$ group in 3-hydroxypropanoic acid via inductive effect is more inferior. Therefore, the conjugate base of 3-hydroxypropanoic acid is less stable than that of lactic acid.

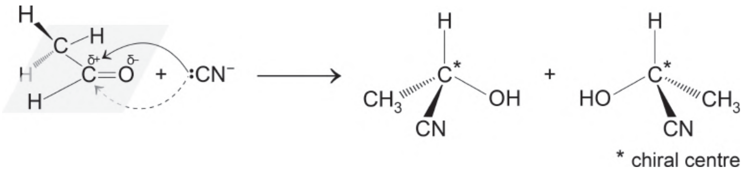
(v) What is the difference between lactic acid that is synthesized in the laboratory as compared to that formed in the cell?

Explanation:

Lactic acid that is synthesized in the laboratory is a racemic mixture or a racemate, i.e., optically inactive. This is because the carbonyl functional group in ethanal is trigonal planar in shape. As for lactic acid that is formed in the cell, as the enzymes that are involved are stereospecific, the lactic acid is optically active.

Do you know?

— Ethanal is an example of a prochiral molecule — an achiral molecule that can be transformed into a chiral molecule in one step. Just like a carbocation, the geometry around the sp^2 hybridized carbonyl carbon atom is trigonal planar. The nucleophile can attack the carbonyl carbon from either side of the plane to form a racemic mixture (or racemate) containing equal proportions of the two optically active isomers.



(vi) Suggest a simple chemical test to distinguish between each of the following pairs of compounds:

(A) CH_3CH_2OH and CH_3CHO;

Explanation:

To differentiate between CH_3CH_2OH and CH_3CHO, use anyone of the following tests:

(1) Use PCl_5 and test for HCl(g):

CH_3CHO: No white fumes of HCl(g).
CH_3CH_2OH: White fumes of HCl(g) observed.
$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl(g)$.
{Nucleophilic Substitution}

(2) Use $SOCl_2$ and test for HCl(g):

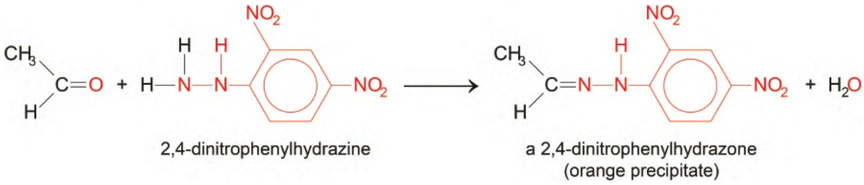
CH_3CHO: No white fumes of HCl(g).
CH_3CH_2OH: White fumes of HCl(g) observed.
$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl(g)$.
{Nucleophilic Substitution}

(3) Use sodium metal and test for $H_2(g)$:

CH_3CHO: No gas evolved that extinguished a lighted splint with a pop sound.
CH_3CH_2OH: Gas evolved that extinguished a lighted splint with a pop sound. Gas is $H_2(g)$
$CH_3CH_2OH + Na \rightarrow CH_3CH_2ONa + 1/2\ H_2(g)$.
{Acid–metal reaction}

(4) Use 2,4-dinitrophenylhydrazine and heat:

CH_3CH_2OH: No orange ppt formed.
CH_3CHO: Orange ppt formed.



{Condensation/Addition–Elimination}

(B) CH_3CH_2OH and $CH_3CH(OH)CN$; and

Explanation:

To differentiate between CH_3CH_2OH and $CH_3CH(OH)CN$, use the following test:

Use aqueous NaOH/heat and test for $NH_3(g)$:
CH_3CH_2OH: No gas evolved that turned moist red litmus paper blue.
$CH_3CH(OH)CN$: Gas evolved that turned moist red litmus paper blue.
Gas is $NH_3(g)$
$CH_3CH(OH)CN + OH^- + H_2O \rightarrow CH_3CH(OH)COO^- + NH_3(g)$.
{Alkaline hydrolysis}

Q Can we use aqueous HCl/heat and then test for $NH_3(g)$?

A: No! This is because the NH_3 that is formed would be immediately protonated by the HCl(aq), hence it would not be detected. Recall in the QA test that we add NaOH(aq)/heat when we want to test for the presence of NH_4^+.

(C) $CH_3CH(OH)CN$ and $CH_3CH(OH)COOH$.

Explanation:

To differentiate between $CH_3CH(OH)CN$ and $CH_3CH(OH)COOH$, use any of the following tests:

(1) Use aqueous NaOH/heat and test for $NH_3(g)$:

$CH_3CH(OH)COOH$: No gas evolved that turned moist red litmus paper blue.
$CH_3CH(OH)CN$: Gas evolved that turned moist red litmus paper blue. Gas is $NH_3(g)$.
$CH_3CH(OH)CN + OH^- + H_2O \rightarrow CH_3CH(OH)COO^- + NH_3(g)$.
{Alkaline hydrolysis}

(2) Use $Na_2CO_3(s)$ and test for $CO_2(g)$:

$CH_3CH(OH)CN$: No gas evolved gave white ppt with $Ca(OH)_2(aq)$.
$CH_3CH(OH)COOH$: Gas evolved gave white ppt with $Ca(OH)_2(aq)$.
$2CH_3CH(OH)COOH + CO_3^{2-} \rightarrow 2CH_3CH(OH)COO^- + CO_2 + H_2O$.
{Acid–base reaction}

(vii) State with reasons which of the following compounds would have a higher boiling point:

(A) CH_3CH_2OH and CH_3CHO; and

Explanation:

CH_3CH_2OH has a higher boiling point than CH_3CHO because the alcohol has hydrogen bonding, which is stronger than the permanent dipole–permanent dipole interaction in the polar CH_3CHO.

Do you know?

— A lot of students think that an aldehyde has hydrogen bonding just because of the molecular formula of an aldehyde is written as RCHO.

(B) CH_3CH_2OH and $CH_3CH(OH)COOH$.

Explanation:

$CH_3CH(OH)COOH$ has a higher boiling point than CH_3CH_2OH. This is because although both molecules have hydrogen bonding, the hydrogen bonding in the $CH_3CH(OH)COOH$ is more extensive because of the presence of a $-OH$ group and a $-COOH$ group. There are simply more hydrogen bonding sites available in $CH_3CH(OH)COOH$ than in CH_3CH_2OH due to the presence of greater number of lone pair of electrons and electron-deficient H atoms. In addition, the hydrogen bonds that are formed by the $-COOH$ group is stronger due to the presence of the electron-withdrawing $C{=}O$ group in the $-COOH$ group.

Q But since the $-OH$ group and $-COOH$ group are in close proximity in $CH_3CH(OH)COOH$, would the presence of intramolecular hydrogen bonding limit the sites available for intermolecular hydrogen bonding, hence making $CH_3CH(OH)COOH$ having a lower boiling point?

A: There is certainly a possibility of the presence of intramolecular hydrogen bonding limiting the sites available for intermolecular hydrogen bonding in $CH_3CH(OH)COOH$. But the data show that $CH_3CH(OH)COOH$ indeed has a higher boiling point than CH_3CH_2OH, so this factor is not predominant here.

3. An organic compound **Q**, of molecular formula $C_6H_{10}O_3$, reacted with calcium carbonate to give off carbon dioxide. **Q** formed $C_7H_{12}O_3$ with methanol, a sweet-smelling compound, when treated with concentrated sulfuric acid at 170°C. When 2,4-DNPH was added to **Q**, an orange precipitate was formed. **Q** also gave a positive result when treated with iodine in sodium hydroxide, forming a yellow precipitate.

   (a) (i) Deduce the constitutional/structural formula of **Q**.

Explanation:

With a six-carbon-atom molecular formula, the maximum number of H atoms should be 14. Hence, compound **Q** may have two double bonds!

As compound **Q** reacted with calcium carbonate to give off carbon dioxide ⇒ **Q** contains a −COOH group. This is an acid–base reaction.

Compound **Q** + CH_3OH → sweet-smelling compound, which is an ester ⇒ **Q** contains a –COOH group. This is an esterification/Nucleophilic Acyl Substitution.

Compound **Q** + 2,4-DNPH → orange ppt ⇒ **Q** is either an aldehyde or a ketone. This is a condensation/addition–elimination reaction.

Compound **Q** + I_2/NaOH → CHI_3 a yellow ppt ⇒ **Q** is a ketone with CH_3CO— group. This is an oxidation/oxidative cleavage reaction.

Compound **Q** can be $CH_3COCH_2CH_2CH_2COOH$.

(ii) Write a balanced equation for the reaction of **Q** with:

(A) calcium carbonate;

Explanation:

$2CH_3COCH_2CH_2CH_2COOH + CaCO_3(s) \rightarrow Ca(CH_3COCH_2CH_2CH_2COO)_2 + H_2O + CO_2(g)$.

(B) concentrated sulfuric acid with methanol;

Explanation:

$CH_3COCH_2CH_2CH_2COOH + CH_3OH \rightleftharpoons CH_3COCH_2CH_2CH_2COOCH_3 + H_2O$.

Q Why did you use a '⇌' for the above reaction?

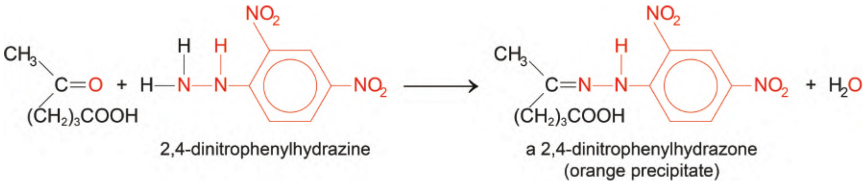
A: This is because the formation of an ester from a carboxylic acid and an alcohol will never go to completion, even if catalyzed by an acid. A dynamic equilibrium is established instead. Only if an acid chloride and alcohol, are used, then we would get a better yield of the ester.

Q But the HCl fumes that evolved when an acid chloride reacts with an alcohol is so corrosive, so how can we get a better yield of the ester if we want to use a carboxylic acid and an alcohol?

A: Well, we can evaporate away the water as the reaction is progressing. This would drive the position of equilibrium toward the right by Le Chatelier's Principle, hence enhancing the yield of the ester. This is how the industry produces polyesters from diacids and diols.

(C) 2,4-DNPH; and

Explanation:



(D) iodine in sodium hydroxide.

Explanation:

$CH_3COCH_2CH_2CH_2COOH + 3I_2 + 5OH^- \rightarrow {}^-OOCCH_2CH_2CH_2COO^- + CHI_3 + 3I^- + 4H_2O$.

(iii) State the role of concentrated sulfuric acid.

Explanation:

It acts as a catalyst that speeds up the esterification process.

Q How does the acid catalyze the reaction?

A: The acid protonates the C=O's oxygen atom of the –COOH group. This increases the electron deficiency of the C=O's carbon atom and makes it more susceptible to nucleophilic attack.

Q Why can't the O atom of the hydroxyl group (–OH) of the –COOH make a nucleophilic attack on the electron-deficient carbon atom of the alcohol molecule instead?

A: This is because the lone pair of electrons on the O atom of the hydroxyl group of the −COOH group delocalizes into the carbonyl group (C=O). As a result, it is less available to make a nucleophilic attack than the lone pair of electrons on the −OH group of the alcohol. In addition, the electron-donating effect of the alkyl group on the alcohol molecule intensifies the electron density on the −OH group of the alcohol, making it more nucleophilic in nature.

(b) **R** is an isomer of **Q** with the same molecular formula. **R** gave negative test when treated with iodine in sodium hydroxide, but responded positively with other tests. Give a possible constitutional/structural formula of **R**.

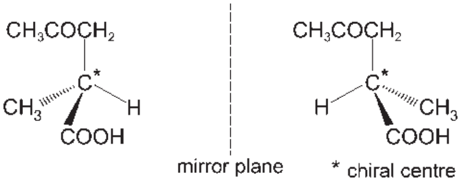
Explanation:

A possible constitutional/structural formula of **R** is $CH_3CH_2COCH_2CH_2COOH$.

(c) **S** is also isomer of **Q**, containing a chiral carbon. Give a possible constitutional/structural formula of **S** and draw the two stereoisomers.

Explanation:

A possible constitutional/structural formula of **S** is $CH_3COCH_2CH(CH_3)COOH$. The two enantiomers are:



(d) Write balanced equation when **S** reacts with the following reagents:

(i) $LiAlH_4$ in dry ether, followed by warming with water;

Explanation:

$CH_3COCH_2CH(CH_3)COOH + 4[H] \rightarrow CH_3CH(OH)CH_2CH(CH_3)CH_2OH$. {Reduction}

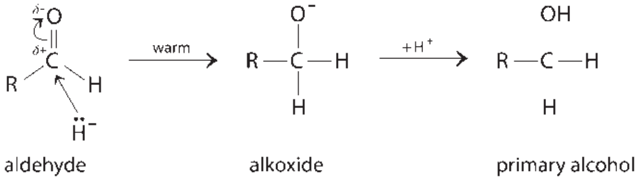
Do you know?

— $LiAlH_4$ does not affect both double and triple carbon–carbon bonds (i.e., C=C and C≡C) as it only attacks polar bonds. It is to be noted that the reduction cannot be carried out in the presence of water as $LiAlH_4$ reacts vigorously with it:

$$LiAlH_4 + 4H_2O \rightarrow LiOH + Al(OH)_3 + 4H_2.$$

— Reaction with $NaBH_4$ (sodium borohydride) can be carried out in an aqueous solution. Since it is a milder reducing agent than $LiAlH_4$ and less sensitive to water, $NaBH_4$ is commonly used as a laboratory reducing agent.

— The reduction mechanism, involving either $LiAlH_4$ or $NaBH_4$, is rather complex but it can be thought to proceed via the following mechanism:



In the first step, the reducing agent acts as a hydride ion donor (H^-), which attacks the electron-deficient carbonyl C atom in a Nucleophilic Addition reaction. Water or an aqueous acid is then added in the subsequent step to protonate the alkoxide intermediate to yield the alcohol. Hence, the hydrogen atom of the −OH group comes from H_2O and not from $LiAlH_4$.

(ii) ethylamine;

Explanation:

$CH_3COCH_2CH(CH_3)COOH + CH_3CH_2NH_2 \rightarrow CH_3COCH_2CH(CH_3)COO^-CH_3CH_2NH_3^+$.

{Acid–base reaction}

Q Since ethylamine also contains the $-NH_2$ group, can it undergo condensation reaction with the ketone functional group in **S**?

A: Yes, but this will not be covered here.

(iii) PCl_3;

Explanation:

$3CH_3COCH_2CH(CH_3)COOH + PCl_3 \rightarrow 3CH_3COCH_2CH(CH_3)COCl + H_3PO_3$.

{Nucleophilic Acyl Substitution}

(iv) KCN with HCN;

Explanation:

$CH_3COCH_2CH(CH_3)COOH + HCN \rightarrow CH_3C(OH)(CN)CH_2CH(CH_3)COOH$.

{Nucleophilic Addition}

(v) NH_2OH;

Explanation:

$CH_3COCH_2CH(CH_3)COOH + NH_2OH \rightarrow CH_3C{=}N(OH)CH_2CH(CH_3)COOH + H_2O$.

{Condensation/Addition–Elimination}

(vi) sodium phenoxide.

Explanation:

$CH_3COCH_2CH(CH_3)COOH$ + C_6H_5ONa → $CH_3COCH_2CH(CH_3)COONa$ + C_6H_5OH.

{Acid–base reaction}

Do you know?

— The above reaction demonstrates that a carboxylic acid is a stronger acid than phenol. In addition, the carboxylate is a more stable conjugate base than the phenoxide. This would mean that the following reaction would not happen:

$$C_6H_5OH + RCOONa \rightarrow RCOOH + C_6H_5ONa.$$

This is logical as a weaker acid, C_6H_5OH, cannot protonate a more stable base, $RCOO^-$.

4. (a) Ethanoyl chloride reacts far more rapidly with water than chloroethane. Explain.

Explanation:

The carbonyl carbon of the ethanoyl chloride is more electron-deficient than the α-carbon of chloroethane because it is bonded to an electronegative O atom and another electronegative Cl atom. In contrast, there is only one electronegative Cl atom on the α-carbon of chloroethane. As such, the carbonyl carbon of the ethanoyl chloride is more susceptible to nucleophilic attack. In addition, there is less steric effect when a nucleophile approaches the trigonal planar carbonyl carbon of the ethanoyl chloride than the tetrahedral α-carbon of chloroethane. These two factors cause ethanoyl chloride to react more readily with water than chloroethane.

(b) (i) Give the conditions and show the structure of the organic product formed when ammonia reacts with ethanoyl chloride.

Explanation:

Use $NH_3(g)$ in sealed tube at room temperature:

$$CH_3COCl + NH_3(g) \rightarrow CH_3CONH_2 + HCl(g).$$

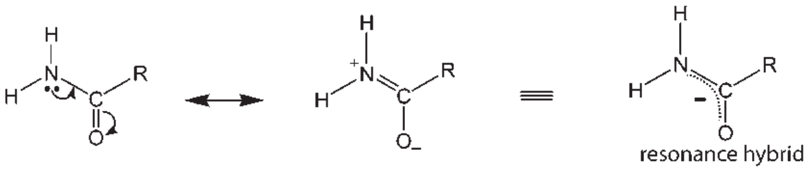
{Nucleophilic Acyl Substitution}

Q Wouldn't the $HCl(g)$ react with the $NH_3(g)$?

A: Yes, it will. Hence, we need to add excess $NH_3(g)$.

Q Would the $HCl(g)$ react with the amide formed, CH_3CONH_2?

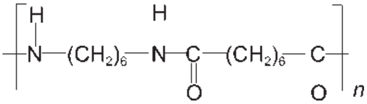
A: An amide is a neutral compound! This is because the lone pair of electrons on the nitrogen atom is delocalized into the carbonyl functional group, hence it is not available to act as a Lewis base.



(ii) Thus, give the structure of the organic product formed when an equimolar of $((CH_2)_3COCl)_2$ reacts with $H_2N(CH_2)_6NH_2$.

Explanation:

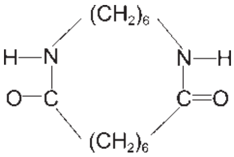
The reaction of the diacid chloride with the diamine would yield the polyamide:



(iii) Draw the structure of a possible side product that may be formed in *(b)(ii)*.

Explanation:

A cyclic amide may form:



(iv) The product formed in (*b*)(*i*) is readily hydrolyzed by an acid and a base. Write balanced equations to show the two hydrolysis processes. Explain the different roles played by the acid and the base.

Explanation:

In the presence of an acid and heat, the H^+ ion protonates the carbonyl oxygen atom and thus makes the carbonyl carbon atom more electron-deficient. This is because an oxygen atom possessing a positive charge is more electron-withdrawing than a neutral one:

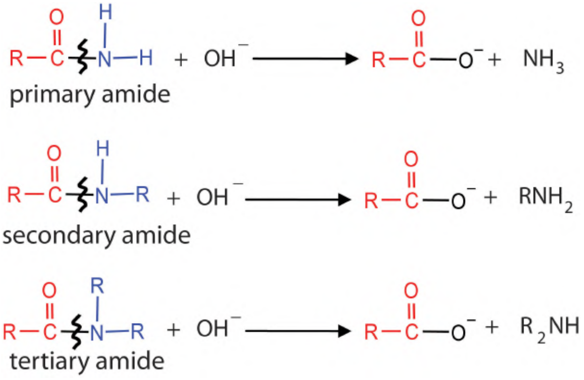
$$CH_3CONH_2 + H_2O + H^+ \rightarrow CH_3COOH + NH_4^+. \quad \{\text{Acidic hydrolysis}\}$$

In the presence of a base and heat, the OH^- acts as the nucleophile. A negatively charged OH^- is a stronger nucleophile than the neutral H_2O:

$$CH_3CONH_2 + OH^- \rightarrow CH_3COO^- + NH_3(g). \quad \{\text{Alkaline hydrolysis}\}$$

Do you know?

— The evolution of $NH_3(g)$ during the basic hydrolysis of a primary amide serves as a characteristic test for the presence of the primary amides. For secondary or tertiary amides, it would be the evolution of the basic amine gas.



(c) Carry out the following conversions:

(i) $RCH_2OH \rightarrow RCON(CH_3)_{2;}$

Explanation:

Step 1: $RCH_2OH \rightarrow RCOOH$. {Oxidation}

Use $KMnO_4/H_2SO_4$/heat or $K_2Cr_2O_7/ H_2SO_4$/heat.

Step 2: $RCOOH \rightarrow RCOCl$. {Nucleophilic Acyl Substitution}

Use $PCl_3/PCl_5/SOCl_2$.

Step 3: $RCOCl \rightarrow RCONH_2$. {Nucleophilic Acyl Substitution}

Use $NH_3(g)$/sealed tube.

(ii) $(CH_3)_3COH \rightarrow (CH_3)_3CCOOH$;

Explanation:

Step 1: $(CH_3)_3COH \rightarrow (CH_3)_3CCl$. {Nucleophilic Substitution}

Use $PCl_3/PCl_5/SOCl_2$/conc. HCl with $ZnCl_2$ as catalyst.

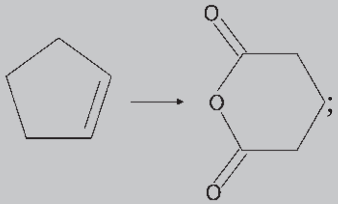
Step 2: $(CH_3)_3CCl \rightarrow (CH_3)_3CCN$. {Nucleophilic Substitution}

Use NaCN(aq)/ethanol/heat.

Step 3: $(CH_3)_3CCN \rightarrow (CH_3)_3CCOOH$. {Acidic hydrolysis}

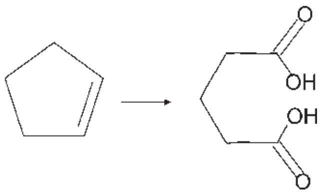
Use H_2SO_4(aq)/heat or HCl(aq)/heat.

(iii)



Explanantion:

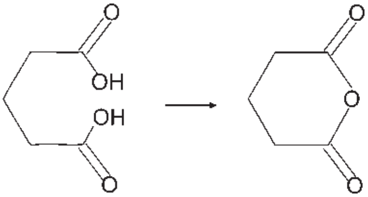
Step 1:



{Oxidation}

Use $KMnO_4/H_2SO_4$/heat.

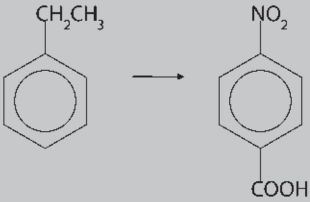
Step 2:



{Nucleophilic Acyl Substitution/Dehydration}

Use excess conc. H_2SO_4/heat.

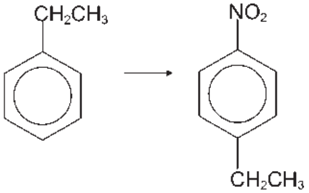
(iv)



; and

Explanation:

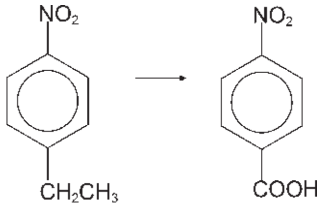
Step 1:



{Electrophilic Substitution}

Use conc. HNO_3/conc. H_2SO_4/heat.

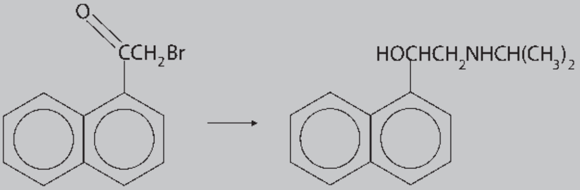
Step 2:



{Oxidation/Oxidative cleavage}

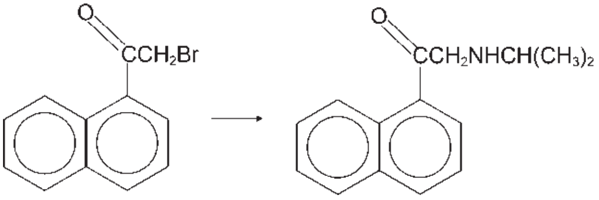
Use $KMnO_4/H_2SO_4$/heat.

(v)



Explanation:

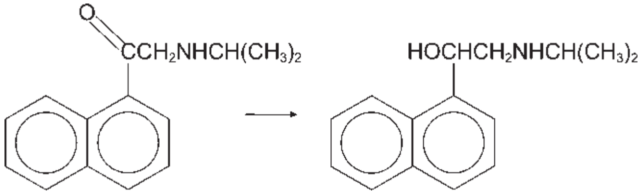
Step 1:



{Nucleophilic Substitution}

Use $(CH_3)_2CHNH_2$/sealed tube/heat.

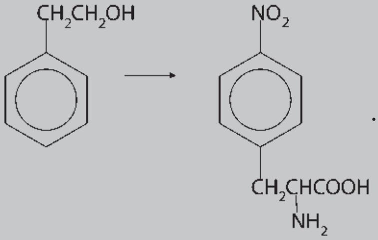
Step 2:



{Reduction}

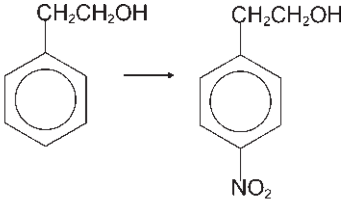
Use $LiAlH_4$ in dry ether, followed by warming with water.

(vi)



Explanation:

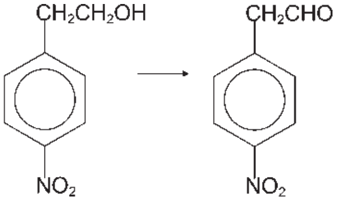
Step 1:



{Electrophilic Substitution}

Use conc. HNO_3/conc. H_2SO_4/heat.

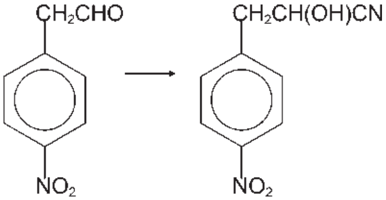
Step 2:



{Oxidation}

Use $K_2Cr_2O_7/H_2SO_4$/immediate distillation.

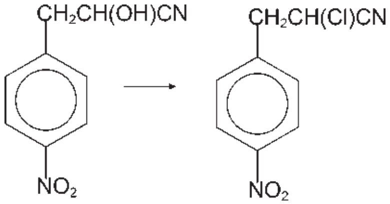
Step 3:



{Nucleophilic Addition}

Use HCN/small amount of NaOH/cold or KCN/H_2SO_4 or HCN/NaCN.

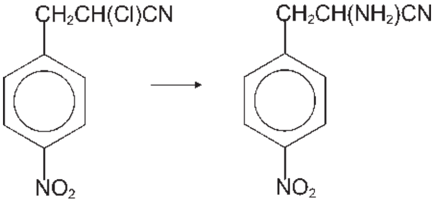
Step 4:



{Nucleophilic Substitution}

Use $PCl_3/PCl_5/SOCl_2$/conc. HCl with $ZnCl_2$ as catalyst.

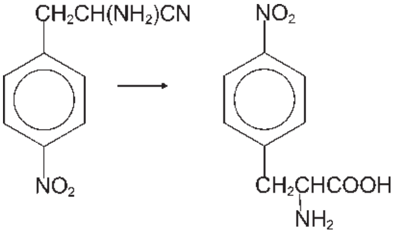
Step 5:



{Nucleophilic Substitution}

Use excess NH_3(g)/sealed tube.

Step 6:



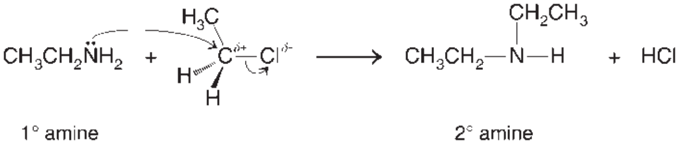
(Acidic hydrolysis)

Use H_2SO_4(aq)/heat or HCl(aq)/heat.

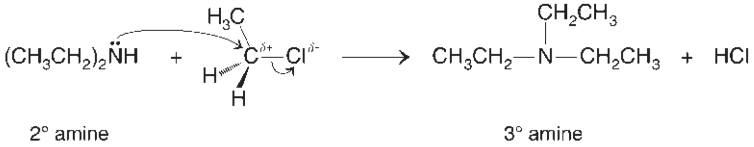
Q Why is excess NH_3 needed when converting the halogenoalkane to an amine in Step 5 above?

A: An amine is a weak base but a stronger base than NH_3. The primary amine product that is formed can also act as a nucleophile since there is a lone pair of electrons on the nitrogen atom of the amine molecule, readily available for dative bond formation. In fact, this lone pair of electrons is even more readily available than that of the N atom in NH_3, thanks to the attached electron-releasing alkyl group that enhance the electron density on the nitrogen atom. Therefore, the excess ammonia also serves to convert most of the halogenoalkane to the primary amine first, based on the statistical factor. Without excess ammonia, the primary amine that is formed initially would have the chance to react with other halogenoalkanes, resulting in the formation of the more highly substituted amines. The following shows how polyalkylation can take place.

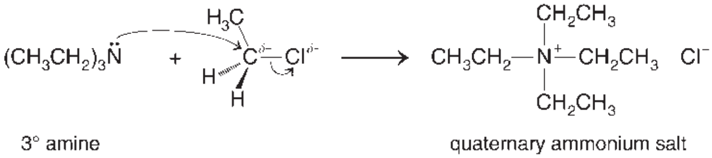
As soon as the primary amine is formed, it is drawn toward the halogenoalkane and Nucleophilic Substitution between these reactants results in the formation of a secondary amine:



With two electron-donating alkyl groups attached to the nitrogen atom, the 2° amine is a better nucleophile than both the 1° amine and NH_3. It reacts with the halogenoalkane to form yet another product, the 3° amine:



If you have noticed the trend by now, the much stronger nucleophilic 3° amine will be able to react with the same halogenoalkane. This time, a quaternary (4°) ammonium salt is formed:



Thus, if the desired product is the 1° amine, one must ensure that the halogenoalkane is a limiting reagent and there is excess NH_3 to limit the formation of the polysubstituted products. The higher concentration of NH_3 will ensure the faster depletion of the halogenoalkane and lowers the chance of the other nucleophiles attacking it.

(d) Explain the following observations:

  (i) $CH_3CH_2CO_2H$ is converted into $CH_3CH_2CO_2CH_2CH_3$ by ethanol, in the presence of concentrated sulfuric acid, faster than $H_2NCH_2CO_2H$ is converted to $H_2NCH_2CO_2CH_2CH_3$ under the same conditions;

Explanation:

When converting $CH_3CH_2CO_2H$ into $CH_3CH_2CO_2CH_2CH_3$ by ethanol, in the presence of concentrated sulfuric acid, the sulfuric acid protonates the carbonyl oxygen of the −COOH group, hence making the carbonyl carbon more susceptible to nucleophilic attack. But when concentrated sulfuric acid is added to $H_2NCH_2CO_2H$, the basic $–NH_2$ group would be protonated first. As such, it is more difficult to protonate the carbonyl oxygen of the $-COOH$ group as the species is already positively charged. Thus, the carbonyl carbon is less susceptible to nucleophilic attack, resulting in a slower reaction.

Q But wouldn't the positively charged group draw electron density away from the α-carbon, which would in turn draw electron density away from the carbonyl carbon atom? So, shouldn't this cause the carbonyl carbon to also be more electron-deficient and hence susceptible to nucleophilic attack?

A: You are right, this would indeed happen. But unfortunately, the inductive effect exerted by the $-NH_3^+$ group is smaller than if the carbonyl oxygen of the $-COOH$ group is being protonated. This is because the electron-withdrawing effect of the protonated oxygen acts immediately on the carbonyl carbon, while that of the $-NH_3^+$ group has to act through the α-carbon before reaching the carbonyl carbon.

(ii) CH_3CO_2H has a pK_a that is larger than that of $NCCH_2CO_2H$;

Explanation:

A smaller pK_a means a larger K_a value, which indicates that the conjugate base is more stable and hence the acid is more acidic. The $-CN$ group on $NCCH_2CO_2H$ exerts an electron-withdrawing effect on the $-COO^-$ group; as a result, the electron density on the negatively charged $-COO^-$ group is dispersed. This helps to stabilize the conjugate base and hence makes $NCCH_2CO_2H$ more acidic than CH_3CO_2H.

(iii) $CH_3CH_2NH_2$ is protonated by weak acids, whereas CH_3CONH_2 is difficult to protonate;

Explanation:

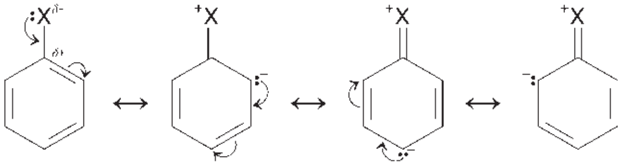
The greater the ease of protonation, the stronger the base. The lone pair of electrons on the N atom of $CH_3CH_2NH_2$ is more available as a Lewis base than that of CH_3CONH_2, because the lone pair of electrons on the nitrogen atom is delocalized into the carbonyl functional group, hence it is not available to act as a Lewis base.

(iv) CH_3COCl hydrolyzes much more readily than both CH_3CH_2Cl and C_6H_5Cl, whereas CH_3CH_2Cl hydrolyzes more readily than C_6H_5Cl; and

Explanation:

The carbonyl carbon of ethanoyl chloride is more electron-deficient than the α-carbon of chloroethane because it is bonded to an electronegative O atom and another electronegative Cl atom. In contrast, there is only one electronegative Cl atom on the α-carbon of chloroethane. As such, the carbonyl carbon of the ethanoyl chloride is more susceptible to nucleophilic attack. In addition, there is less steric effect when a nucleophile approaches the trigonal planar carbonyl carbon of ethanoyl chloride than the tetrahedral α-carbon of chloroethane. These two factors cause ethanoyl chloride to react more readily with water than chloroethane.

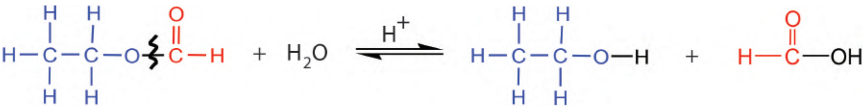
As for C_6H_5Cl, the lone pair of electrons on the Cl atom delocalizes into the benzene ring. As a result, there is a partial double bond characteristic between the carbon–chlorine bond, making the bond more difficult to break. In addition, the delocalization of electrons also diminishes the electron deficiency of the carbon atom. On top of these, the steric effect posed by the bulky benzene ring also hinders the approach of a nucleophile.



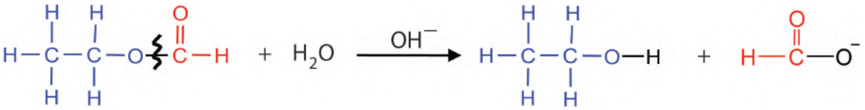
(v) The hydrolysis of a carboxylic ester using acid is reversible, but using alkali is not reversible.

Explanation:

In acidic hydrolysis, the products formed are a carboxylic acid and an alcohol. The reaction is reversible because the backward reaction is actually the esterification reaction:



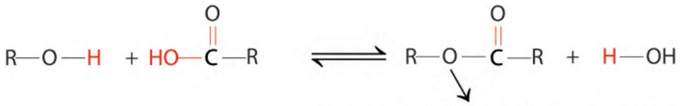
In alkaline hydrolysis, the presence of a base will cause the deprotonation of the acidic RCOOH after it has formed, generating the carboxylate salt.



Unlike acidic hydrolysis, alkaline hydrolysis is essentially irreversible since the carboxylate ion obtained is resonance-stabilized and exhibits little tendency to react with the alcohol to form back the ester.

Do you know?

— The oxygen atom of the ester functional group originates from the alcohol:

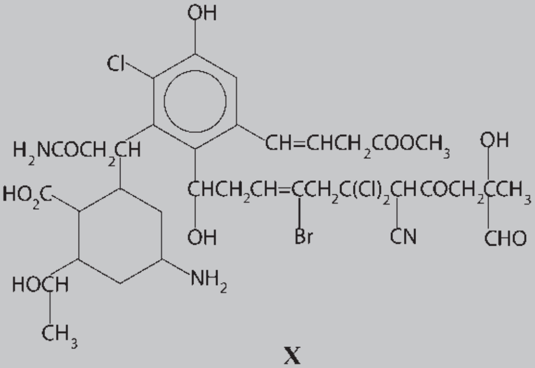


This oxygen atom originates from the alcohol, ROH

Q Why isn't the alcohol deprotonated by the OH^- since it is also a weak acid?

A: An alcohol is a weaker acid than water, which means that the alkoxide ion, RO^-, is a stronger base than OH^-. Thus, it is impossible for a OH^- ion to deprotonate a ROH generating H_2O and RO^-. The RO^- formed would instead be less stable than OH^-.

(e) Give the possible organic products formed when **X** reacts with each of the following reagent individually:

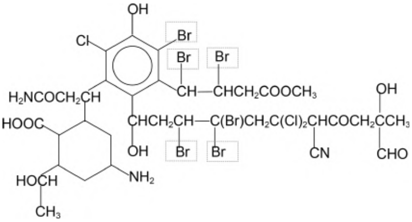


X

(i) Br_2/CCl_4; Br_2(aq); conc. NH_3/sealed tube; cold alkaline $KMnO_4$; hot acidified $KMnO_4$; cold conc. H_2SO_4; $Cl_2/AlCl_3$; $LiAlH_4$/dry ether; K(s); and dilute HNO_3;

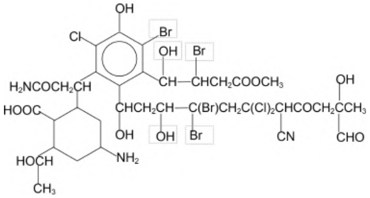
Explanation:

Br_2/CCl_4



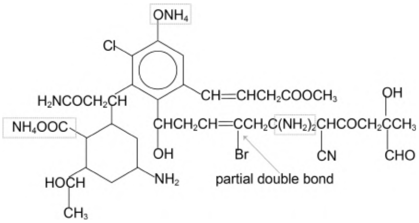
- Electrophilic Addition

$Br_2(aq)$



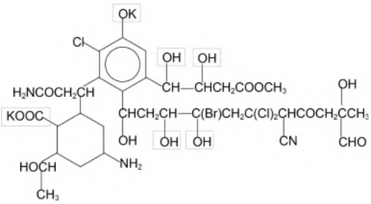
- Electrophilic Addition

Conc. NH_3/sealed tube



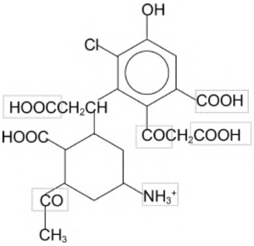
- Nucleophilic Substitution
- Acid–base reaction

Cold alkaline $KMnO_4$



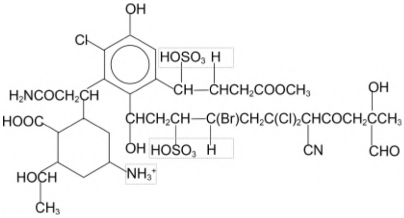
- Oxidation
- Acid–base reaction

Hot acidified $KMnO_4$



- Oxidation/Oxidative cleavage
- Acid–base reaction
- Acidic hydrolysis

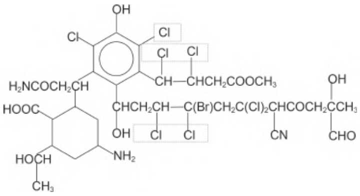
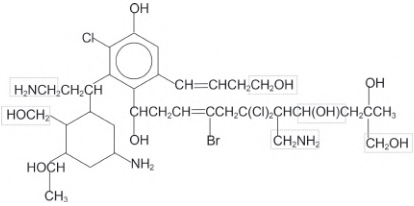
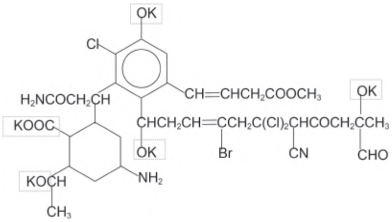
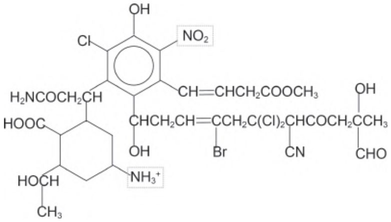
Cold conc. H_2SO_4



- Electrophilic Addition
- Acid–base reaction

(*Continued*)

(*Continued*)

$Cl_2/AlCl_3$	$LiAlH_4$/dry ether
	
• Electrophilic Substitution • Electrophilic Addition	• Reduction
K(s)	Dilute HNO_3
	
• Acid–metal reaction	• Electrophilic Substitution • Acid–base reaction

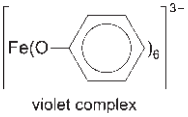
Do you know?

— Esters, amides, and nitrile (containing the –CN group) can only be hydrolyzed if there is heating!

(ii) $FeCl_3$(aq); $SOCl_2$; NaOH(aq)/heat; HCl(aq); H_2SO_4(aq)/heat; $BaCO_3$(s); Tollens’ reagent; Fehling’s reagent; and conc. H_2SO_4/conc. HNO_3; and

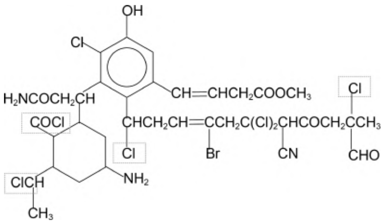
Explanation:

$FeCl_3(aq)$



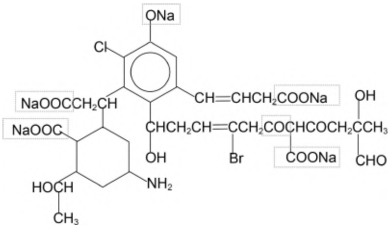
- Complexation

$SOCl_2$



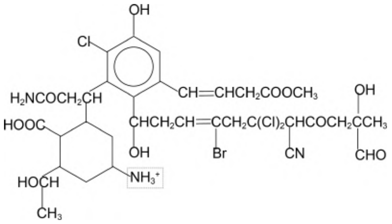
- Nucleophilic Substitution

NaOH(aq)/heat



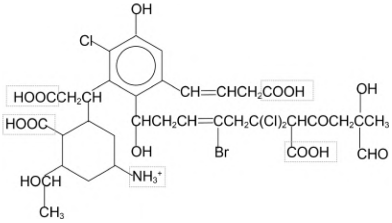
- Nucleophilic Substitution
- Acid–base reaction
- Alkaline hydrolysis

HCl(aq)



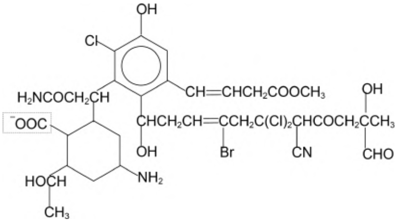
- Acid–base reaction

$H_2SO_4(aq)$/heat



- Acid–base reaction
- Acidic hydrolysis

$BaCO_3(s)$



- Acid–base reaction

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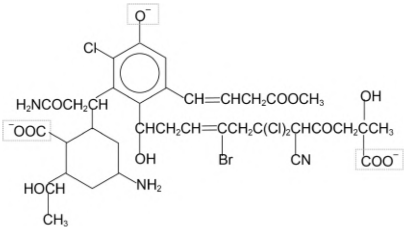
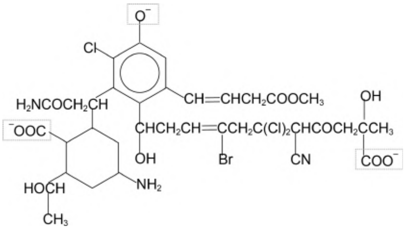
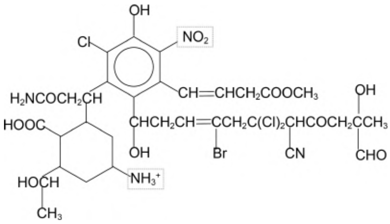
Tollens' reagent	Fehling's reagent
 • Oxidation • Acid–base reaction	 • Oxidation • Acid-base reaction
Conc. H_2SO_4/Conc. HNO_3	
 • Electrophilic Substitution • Acid-base reaction	

Q What would we get when CH_2Cl_2 reacts with NaOH(aq) with heating?

A: You won't get the germinal diol, $CH_2(OH)_2$. Instead, you would get the aldehyde, HCHO. This is because the germinal diol is a very highly unstable species due to two highly electronegative O atoms, withdrawing electron density away from the carbon. Hence, the germinal diol would undergo spontaneous intramolecular dehydration to form the aldehyde. Similarly, when $CHCl_3$ reacts with NaOH(aq) with heating, you would get HCOOH and not $CH(OH)_3$, a germinal triol.

Do you know?

— Tollens' reagent contains aqueous diamminesilver(I) ions, $[Ag(NH_3)_2]^+$, which function as an oxidizing agent in this redox reaction. The diamminesilver(I) ion oxidizes an aldehyde to a carboxylic acid while itself being reduced to silver metal. It should be noted that the actual organic product is the carboxylate ion since the carboxylic acid that is formed deprotonates in the alkaline medium. This reaction is also known as the 'silver mirror' test for a positive result would be the formation of a silver mirror achieved under carefully controlled conditions.

Q Is there a way to help us remember the balanced equation for the reaction of an aldehyde with Tollens' reagent?

A: Well, you can try formulating both the oxidation and reduction half-equations as follows:

Oxidation half-equation:

$RCHO \rightarrow RCOO^-$
$RCHO + H_2O \rightarrow RCOO^-$ (Add H_2O to balance O)
$RCHO + H_2O \rightarrow RCOO^- + 3H^+$ (Add H^+ to balance H)
$RCHO + H_2O + 3OH^- \rightarrow RCOO^- + 3H^+ + 3OH^-$ (Add OH^- to remove the H^+ as the solution is alkaline)
$RCHO + 3OH^- \rightarrow RCOO^- + 2H_2O$
$RCHO + 3OH^- \rightarrow RCOO^- + 2H_2O + 2e^-$ (Add electrons to balance charge)

Reduction half-equation:

$[Ag(NH_3)_2]^+ \rightarrow Ag$
$[Ag(NH_3)_2]^+ \rightarrow Ag + 2NH_3$
$[Ag(NH_3)_2]^+ + e^- \rightarrow Ag + 2NH_3$ (Add electrons to balance charge)

Overall balanced equation:

$$RCHO + 3OH^- + 2[Ag(NH_3)_2]^+ \rightarrow RCOO^- + 2H_2O + 2Ag + 4NH_3.$$

Do you know?

— The oxidizing agent in the alkaline Fehling's solution is a copper(II) complex. In this redox reaction, the aldehye is oxidized to the carboxylic acid. However, as the reaction occurs in an alkaline medium, the actual oxidation product obtained is the carboxylate ion. The copper(II) complex ion, in Fehling's solution, is reduced to the reddish-brown Cu_2O, which contains copper in the +1 oxidation state. This oxidative reaction is similar to the action of Benedict's solution on reducing sugars, which also contains a copper(II) complex but dissimilar to the one in Fehling's solution. The reducing sugar possesses an aldehydic functional group as well.

— Only aliphatic aldehydes give positive results. Aromatic aldehydes and ketones do not react with Fehling's solution. As such, this reaction can be used to tell an aliphatic aldehyde apart from the other two classes of carbonyl compounds.

— So, the fact that Tollens' reagent can oxidize aromatic aldehydes, while Fehling's solution cannot, is an indication that Tollens' reagent is a stronger oxidizing agent than Fehling's solution.

Q How does one formulate the balanced equation between Fehling's solution and aldehyde?

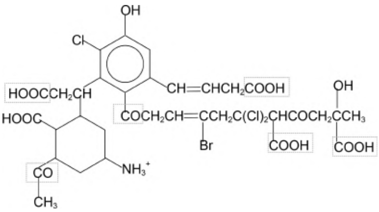
A: The oxidation equation would be the same as the one for Tollens' reagent. As for deriving the reduction half-equation, it would be as follow:

$2Cu^{2+} \rightarrow Cu_2O$
$2Cu^{2+} + H_2O \rightarrow Cu_2O$
$2Cu^{2+} + H_2O \rightarrow Cu_2O + 2H^+$
$2Cu^{2+} + H_2O + 2OH^- \rightarrow Cu_2O + 2H^+ + 2OH^-$
$2Cu^{2+} + 2OH^- \rightarrow Cu_2O + H_2O$
$2Cu^{2+} + 2OH^- + 2e^- \rightarrow Cu_2O + H_2O$ (Balanced reduction half-equation)

(iii) Acidified $K_2Cr_2O_7$(aq)/heat; acidified $K_2Cr_2O_7$(aq)/immediate distillation; I_2/NaOH(aq); HCN/NaOH; 2,4-DNPH; KCN(aq)/heat; NaOH/ethanol/heat; CH_3CH_2Br/ethanol/heat; $CH_3CH_2NH_2$/ethanol/heat; NH_2OH; CH_3COCl; and CH_3COOH/H_2SO_4/heat; H_2/Pt/heat.

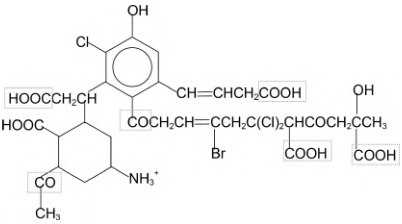
Explanation:

Acidified $K_2Cr_2O_7$(aq)/heat



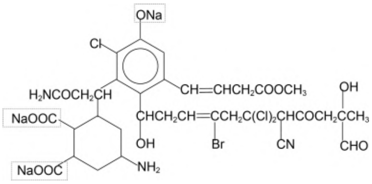
- Oxidation
- Acid–base reaction

Acidified $K_2Cr_2O_7$(aq)/immediate distillation



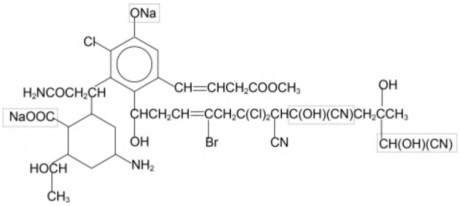
- Oxidation
- Acid–base reaction

I_2/NaOH(aq)



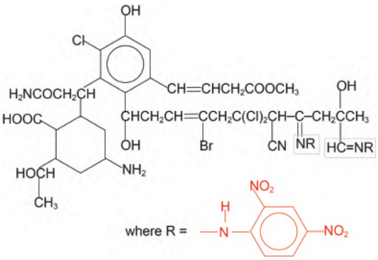
- Oxidation/Oxidative cleavage
- Acid–base reaction

HCN/NaOH



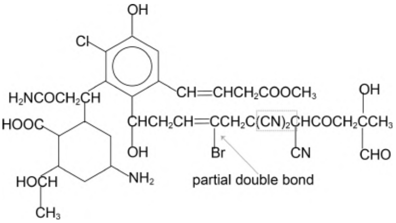
- Nucleophilic Addition
- Acid–base reaction

2,4-DNPH



- Condensation/
  Addition–Elimination

KCN(aq)/heat



- Nucleophilic Substitution

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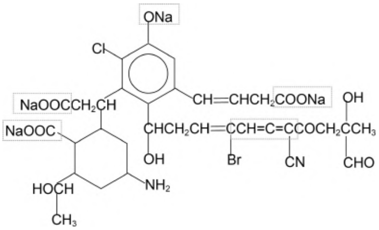
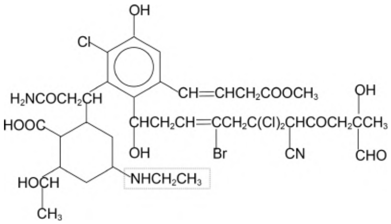
NaOH/ethanol/heat



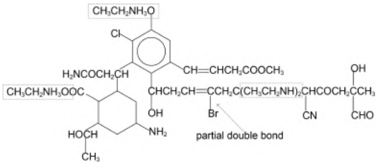
- Elimination
- Acid–base reaction

CH_3CH_2Br/ethanol/heat



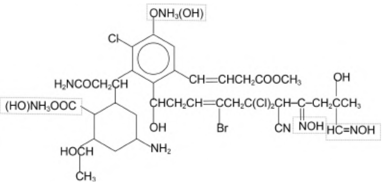
- Nucleophilic Substitution

$CH_3CH_2NH_2$/ethanol/heat



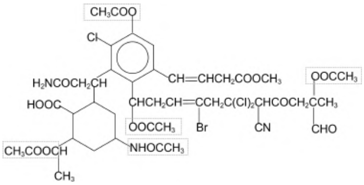
- Nucleophilic Substitution
- Acid–base reaction

NH_2OH



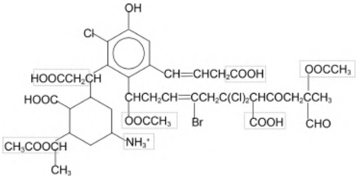
- Condensation/Addition–Elimination
- Acid–base reaction

CH_3COCl



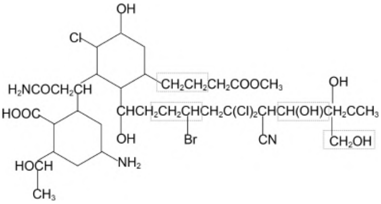
- Nucleophilic Substitution

CH_3COOH/H_2SO_4/heat



- Nucleophilic Substitution/Esterification
- Acid–base reaction
- Acidic hydrolysis

H_2/Pt/heat



- Reduction/Catalytic hydrogenation

Q Why is the aldehyde group converted to a carboxylic acid when you apply acidified $K_2Cr_2O_7$(aq)/immediate distillation?

A: You will get an aldehyde from a primary alcohol when you apply acidified $K_2Cr_2O_7$(aq)/immediate distillation. But now, since you started with an aldehyde instead of a primary alcohol, the aldehyde would likely be oxidized to a carboxylic acid.

Q Why is the alcohol functional group unable to undergo Nucleophilic Substitution with CH_3CH_2Br?

A: Unlike an amine, the lone pair of electrons of the alcohol is less available to make a nucleophilic attack on the CH_3CH_2Br. This is due to the fact that the oxygen atom is more electronegative than the nitrogen atom, hence it would attract its own lone pair of electrons more strongly. But if the alcohol is converted to the more electron rich RO^-, then the RO^- is a good nucleophile.

Q Then why can't the lone pair of electrons on the nitrogen atom of an amide make the nucleophilic attack on CH_3CH_2Br?

A: Remember that an amide is neutral because the lone pair of electrons delocalizes into the carbonyl functional group? It is this same reason that causes it to not be able to function as a nucleophile.

Q Why is hydroxylamine, NH_2OH, able to react with the phenolic $-OH$ group and $-COOH$ group?

A: The lone pair of electrons on the nitrogen atom of hydroxylamine is basic, just like in NH_3. Hence, it can react with weak acids.

Q So, is hydroxylamine more or less basic than NH_3?

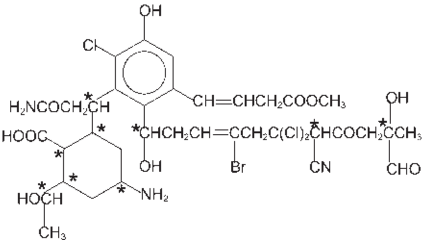
A: Hydroxylamine is less basic than NH_3 because of the presence of an electron–withdrawing $-OH$ group. This would make the lone pair of electrons on the nitrogen atom a weaker Lewis base.

Do you know?

— H_2/Pt/heat cannot reduce carboxylic acids, esters, amides and nitriles. But they can reduce aldehydes, ketones, alkenes and benzene.

(iv) * all the chiral carbons atom in **X**. How many stereoisomers are there in **X**?

Explanation:



There are nine chiral carbons and two C=C double bonds that can exhibit *cis-trans*/geometrical isomerism. Hence, there are a total of $2^{11} = 2048$ stereosiomers.

(f) There are three different straight-chain hydroxybutanoic acids with the molecular formula, $C_4H_8O_3$, **P**, **Q,** and **R**. Both **Q** and **R** can be isolated in optically active forms. When each of these three acids is heated, it loses water and forms a compound: **P** gives **S** ($C_4H_6O_2$), **Q** gives **T** ($C_4H_6O_2$), and **R** gives **U** ($C_8H_{12}O_4$). Compound **T** cannot be obtained in its optically pure form, even when made from optically active **Q**, but optically active **R** leads to optically active **U**.

S reacts with sodium hydroxide to form $C_4H_7O_3Na$, whereas **T** forms $C_4H_5O_2Na$. **T** decolorizes bromine water and reacts with calcium carbonate, whereas **S** and **U** have no effect on these reagents.

(i) Deduce the structures for **P** to **U**.

Explanation:

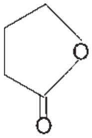
The three possible straight chain hydroxybutanoic acids are:

$CH_2(OH)CH_2CH_2COOH$, $CH_3CH(OH)CH_2COOH$, and $CH_3CH_2CH(OH)COOH$.

Since compound **P** does not contain a chiral carbon, it must be $CH_2(OH)CH_2CH_2COOH$.

When heated, each acid loses water. This loss of water can be due to (i) dehydration of an alcohol to form an alkene, or (ii) ester formation.

Compound **P** gave **S**:



S

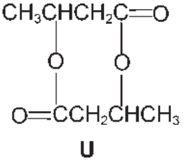
S has to be a cyclic ester because there is no alkene double bond and **S** does not react with calcium carbonate ⇒ it does not contain a −COOH group. In addition, when **S** ($C_4H_6O_2$) reacts with NaOH to form $C_4H_7O_3Na$, the number of O atoms increases by one. This shows the opening of the cyclic ester group.

Compound **Q** gave **T**, which is an alkene and contains a −COOH group as it "decolorizes bromine water" and "reacts with calcium carbonate." In addition, **T** is not optically active as it does not contain a chiral carbon. Compound **Q** is $CH_3CH_2CH(OH)COOH$:

Q $CH_3CH_2CH(OH)COOH \rightarrow$ **T** $CH_3CH{=}CHCOOH + H_2O$.
T $CH_3CH{=}CHCOOH + Br_2(aq) \rightarrow CH_3CH(OH)CH(Br)COOH + HBr$.
T $2CH_3CH{=}CHCOOH + CO_3^{2-}(aq) \rightarrow CH_3CH{=}CHCOO^- + CO_2 + H_2O$.

Compound **R** ($C_4H_8O_3$) gave **U** ($C_8H_{12}O_4$), where **U** is optically active; this means it contains a chiral carbon. **U** has to be a cyclic ester because there is no alkene double bond and **U** does not react with calcium carbonate ⇒ it does not contain −COOH group. **U** has two ester groups within the ring as two molecules of **R** gave one molecule of **U**.

R $2CH_3CH(OH)CH_2COOH \rightarrow$ **U** $+ 2H_2O$.



Q Can compound **Q** be $CH_3CH(OH)CH_2COOH$, while compound **R** is $CH_3CH_2CH(OH)COOH$?

A: If compound **Q** is $CH_3CH(OH)CH_2COOH$, then:

Q $CH_3CH(OH)CH_2COOH \rightarrow$ **T** $CH_3CH{=}CHCOOH$ or $CH_2{=}CHCH_2COOH + H_2O$.

T $CH_3CH{=}CHCOOH + Br_2(aq) \rightarrow CH_3CH(OH)CH(Br)COOH + HBr$ OR

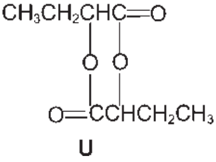
T $CH_2{=}CHCH_2COOH + Br_2(aq) \rightarrow CH_2(Br)CH(OH)CH_2COOH + HBr$.

T $2CH_3CH{=}CHCOOH + CO_3^{2-}(aq) \rightarrow CH_3CH{=}CHCOO^- + CO_2 + H_2O$ OR

T $2CH_2{=}CHCH_2COOH + CO_3^{2-}(aq) \rightarrow CH_2{=}CHCH_2COO^- + CO_2 + H_2O$.

If compound **R** is $CH_3CH_2CH(OH)COOH$, then:

R $2\ CH_3CH_2CH(OH)COOH \rightarrow$ **U** $+ 2H_2O$.



Compound **U** is a six-membered ring cyclic ester which is less stable than an eight-membered ring cyclic ester because of ring strain. But since there is no further information given, compound **Q** can be $CH_3CH(OH)CH_2COOH$, while compound **R** is $CH_3CH_2CH(OH)COOH$.

(ii) Given an unlabeled sample each of **P**, **Q**, and **R**, use chemical tests to identify each sample, without using the above-mentioned reactions.

Explanation:

If we take compounds **P**, **Q**, and **R** as follows:

P $CH_2(OH)CH_2CH_2COOH$, **R** $CH_3CH(OH)CH_2COOH$, and **Q** $CH_3CH_2CH(OH)COOH$

Step 1: Add I_2/NaOH(aq)/heat.

Only compound **R** will give a yellow ppt of CHI_3 as it contains the $CH_3CH(OH)$–functional group.

Step 2: Add $KMnO_4/H_2SO_4$/heat to the remaining two unknown compounds.

Both compounds would decolorize purple $KMnO_4$.
P $CH_2(OH)CH_2CH_2COOH + 2[O] \rightarrow HOOCCH_2CH_2COOH + H_2O$.
Q $CH_3CH_2CH(OH)COOH + [O] \rightarrow CH_3CH_2COCOOH + H_2O$.

Step 3: Add 2,4-DNPH to both the oxidized contents in Step 2.

Only $CH_3CH_2COCOOH$ will give an orange ppt as it contains the ketone functional group.

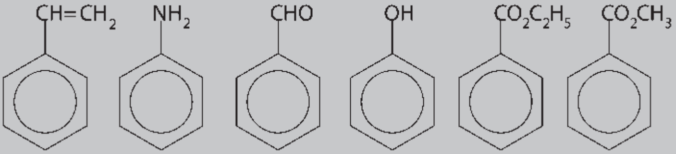
(g) Account for why 4-nitrophenyl ethanoate is hydrolyzed faster than phenyl ethanoate, which is in turn hydrolyzed faster than ethyl ethanoate.

Explanation:

The $-NO_2$ group in 4-nitrophenyl ethanoate is an electron–withdrawing group. This would help to withdraw electron density away from the benzene ring, which would in turn pull electron density away from the carbon atom of the ester functional group. Hence, due to its higher electron deficiency as compared to that in phenyl ethanoate, 4-nitrophenyl ethanoate is hydrolyzed faster than phenyl ethanoate.

In ethyl ethanoate, the ethyl group is electron–donating via inductive effect. This diminishs the electron deficiency on the carbon atom of the ester functional group. Hence, due to its lower electron deficiency as compared to that in phenyl ethanoate, phenyl ethanoate is hydrolyzed faster than ethyl ethanoate.

(h) The are seven unknown reagent bottles, each containing one of the following compounds:



Describe how you would identify each compound using appropriate reagent and conditions. You should not use more than seven positive tests.

Explanation:

Step 1: Add 2,4-DNPH; only C_6H_5CHO would give an orange ppt.

Step 2: Add neutral $FeCl_3(aq)$ to the remaining five unknowns; only C_6H_5OH would give a violet complex.

Step 3: Acid hot acidified $KMnO_4$ to the remaining four unknowns; only $C_6H_5CH{=}CH_2$ would decolorize purple $KMnO_4$.

Step 4: Add aqueous Br_2 to the remaining three unknowns; only $C_6H_5NH_2$ would decolorize brown aqueous Br_2 and form a white ppt.

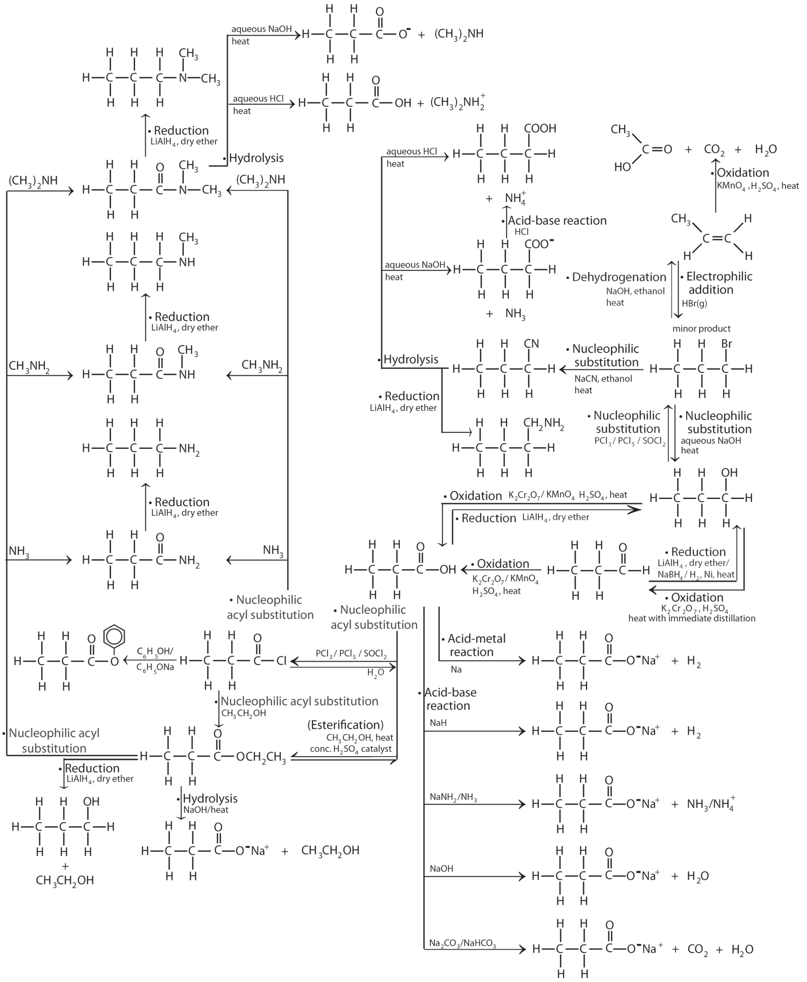
Step 5: Add dilute NaOH and heat. Both remaining esters would hydrolyze:

$$C_6H_5CO_2C_2H_5 + OH^- \rightarrow C_6H_5CO_2^- + C_2H_5OH\text{, and}$$
$$C_6H_5CO_2CH_3 + OH^- \rightarrow C_6H_5CO_2^- + CH_3OH.$$

Step 6: Add $I_2(aq)$/heat to the hydrolyzed content in Step 5; only the hydrolysis that produced C_2H_5OH would give a yellow ppt of CHI_3.

Do you know?

— A mind-map showing the important chemical reactions pertaining to propanoic acid and its derivatives:



- Reactions that serve as distinguishing tests:
  - o The reaction of a carboxylic acid with PCl_5 and $SOCl_2$, generating HCl fumes, can serve as a characteristic test for the acid.

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- The reaction of a carboxylic acid with Na_2CO_3(aq), generating CO_2(g), can serve as a characteristic test for the acid.
- The reaction of an acyl chloride with water, generating HCl fumes, can serve as a characteristic test for the acyl chloride.
- To test for the different types of acyl halides (RCOCl, RCOBr, and RCOI), aqueous $AgNO_3$ can be used. The color of the silver halide ppt serves as a characteristic test.
- To test for amides, the sample is heated with aqueous NaOH. An alkaline gas, which can be NH_3 or an amine, would turn moist red litmus paper blue.

CHAPTER 11

AMINES

Do you know?

Boiling point and solubility of amines

- Amine has a lower boiling point than an alcohol of similar molecular weight due to weaker hydrogen bonding as compared to the alcohol molecule. The weaker hydrogen bonding is due to the less polar N−H bond.
- Tertiary amines are more volatile than both the primary and secondary amines because of the lack of hydrogen bonding. Tertiary amines only have permanent dipole–permanent dipole and instantaneous dipole–induced dipole interactions.
- Amines are soluble in water because they can form hydrogen bonds with water molecules. Higher-molecular-weight amines are insoluble due to the presence of the large hydrophobic group.

Basicity of amines

- Organic bases that include amines, phenylamine, and amides are weak bases. They partially ionize in water. The strength of the base depends on the availability of the lone pair of electrons on the N atom of the base to be donated to the acidic H_2O molecule:

  $$\mathrm{B{-}N{:}(aq) + H_2O(l) \rightleftharpoons B{-}NH^+(aq) + OH^-(aq).}$$

  The strengths of different organic bases vary according to the following trend:

  Increasing basic strength: $RCONH_2$ < phenylamine < NH_3 < amine.
- Amines are the strongest organic base among all because the lone pair of electrons on the N atom is most available for donation. This is due to the intensification of electron density brought about by the electron-releasing effect (via inductive effect) of the alkyl group. Hence, the

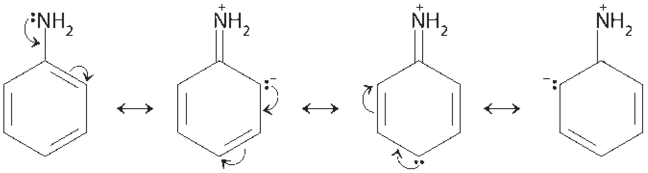
(*Continued*)

(*Continued*)

more alkyl groups that are present in the amine molecule, the more basic it is.

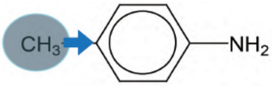
Decreasing basic strength: $R_3N > R_2NH > RNH_2$.

— Phenylamine is a weaker base than NH_3 because the lone pair of electrons on the N atom is less available for donation. This is due to the delocalization into the benzene ring through resonance:

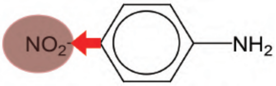


The electron-withdrawing group in a substituted phenylamine causes the molecule to be less basic than an unsubstituted phenylamine, as the electron density that is delocalized into the benzene ring is further dispersed by the electron-withdrawing group, and vice versa.

The electron-releasing group causes the molecule to be more basic than an unsubstituted phenylamine:

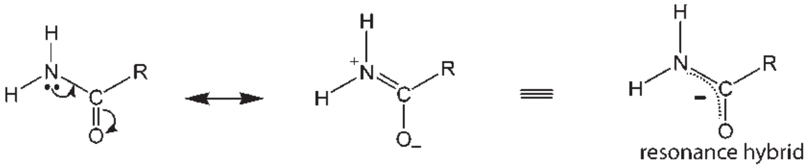


4-methylphenylamine
stronger base



4-nitrolphenylamine
weaker base

— An amide is a neutral organic compound! This is because the lone pair of electrons is delocalized into the carbonyl (C=O) functional group and is least available for donation.



1. Compounds **X**, **Y**, and **Z** are isomers with the molecular formula $C_5H_{11}NO$. **X**, **Y**, and **Z** contain a maximum of two functional groups each. Both **Y** and **Z** give a negative result when warmed with iodine in sodium hydroxide, whereas **X** gives a yellow precipitate. All three compounds give a negative test with sodium nitrate and hydrochloric acid at 0^oC.

   (a) (i) Identify the yellow precipitate that is formed.

Explanation:

The yellow ppt is CHI_3.

(ii) Name and give the constitutional/structural formula of the group identified with iodine in sodium hydroxide.

Explanation:

The group can be $CH_3CO–$ or $CH_3CH(OH)–$. But since compound **X** gives a negative result with sodium nitrate and hydrochloric acid, **X** does not contain a primary or secondary amine. Therefore, **X** is $CH_3COCH_2N(CH_3)_2$.

Q Why can't compound **X** be a primary or secondary amine?

A: This is because of the following reactions:

$RNH_2 + HNO_2 \rightarrow ROH + H_2O + N_2(g)$,

$R_2NH + HNO_2 \rightarrow R_2N\text{-}NO + H_2O$, and

$R_3N + HNO_2 \rightarrow R_3NH^+NO_2^-$.

For tertiary amines, the salt can be $R_3NH^+Cl^-$, as the chloride ion comes from the HCl used.

Q Why can't compound **X** contain the $CH_3CH(OH)$–group?

A: An amine has a molecular formula $C_nH_{2n+3}N$. An alcohol has a molecular formula $C_nH_{2n+2}O$. Hence, if **X** is an amine and alcohol without any double bonds then the number of H atoms should be 13 instead of 11.

If X has $CH_3CH(OH)$– group, and do not forget that **X** has to contain a double bond, then the various likely possibilities of **X** are:

$CH_3CH(OH)CH_2CH{=}CHNH_2$; $CH_3CH(OH)CH_2C(NH_2){=}CH_2$;
$CH_3CH(OH)CH(NH_2)CH{=}CH_2$; $CH_3CH(OH)CH{=}CHCH_2NH_2$;
$CH_3CH(OH)CH{=}C(NH_2)CH_3$; $CH_3CH(OH)C(NH_2){=}CHCH_3$;
$CH_3CH(OH)CH_2CH_2CH{=}NH$; and $CH_3CH(OH)C(CH_3){=}CH(NH_2)$.

Since none of the above is a non-tertiary amine, all of them will react with HNO_2 that is generated from sodium nitrate and hydrochloric acid at 0^oC. But the following two compounds would respond to I_2/NaOH but not to HNO_2:

$CH_3CH(OH)CH_2CH{=}NCH_3$ and $CH_3CH(OH)CH{=}NCH_2CH_3$.

This is because there are no hydrogen atoms attached to the N atom.

Q Is there a partial double bond characteristic between the N atoms and the C=C double bond?

A: Yes, it is just like in phenylamine, $C_6H_5NH_2$. The lone pair of electrons on the N atom can delocalize into the C=C double bond through *p–p* orbitals overlap, which is known as resonance.

Q Why can't the compound be a primary amide, $RCONH_2$?

A: There must be two different functional groups. There is only one $–CONH_2$ functional group in the amide, which is known as resonance. In addition, the primary amide can react with the nitric (III) acid to give nitrogen gas.

Do you know?

— Having a good understanding of the molecular formula of a compound gives us a glimpse of the possible constitutional/structural formula of the compound!

(b) (i) Write a formula for compound **X**.

Explanation:

X is $CH_3COCH_2N(CH_3)_2$.

(ii) Write the constitutional/structural formula of the organic product formed when **X** reacts with sodium nitrate and hydrochloric acid at 0°C.

Explanation:

Since **X** is a tertiary amine, the organic product formed when **X** reacts with sodium nitrate and hydrochloric acid at 0°C is either $CH_3COCH_2NH^+(CH_3)_2Cl^-$ or $CH_3COCH_2NH^+(CH_3)_2NO_2^-$.

(iii) Write the formula of a constitutional/structural isomer of **X** having the same functional groups, which would give a negative result with iodine in sodium hydroxide and a positive result with sodium nitrate and hydrochloric acid at 0°C.

Explanation:

The constitutional/structural isomer of **X** cannot contain CH_3CO– or $CH_3CH(OH)$–, but must contain a $–NH_2$ group, so a possible structure is $CH_3CH_2CH(OH)CH{=}CHNH_2$.

(c) **Y** is an isomer of **X**, containing the functional group of a primary amide, $–CONH_2$. **Y** is not chiral.

(i) State the type of isomerism that **X** and **Y** exhibit.

Explanation:

Since both **X** and **Y** have different functional groups, they exhibit functional group isomerism. Since **Y** is not chiral, a possible constitutional/structural formula is $CH_3CH_2CH_2CH_2CONH_2$.

(ii) State the physical state of **Y** and suggest reasons for it.

Explanation:

Compound **Y** is a solid at room temperature. This is because the stronger and more extensive hydrogen bonding that exists between the primary amide molecules makes them less volatile. A primary amide molecule has two electron-deficient H atoms and three lones pairs of electrons (two on the O atom and one on the N atom); like a water molecule, it is capable of forming two hydrogen bonds per amide molecule. In addition, the strength of the hydrogen bonding is made stronger due to the presence of the electron-withdrawing C=O group that make the H atoms of the $–NH_2$ group more electron-deficient.

Do you know?

— Unlike the primary amide, the secondary amide has only one electron-deficient hydrogen atom, thus the extensivity of the hydrogen bonding between the secondary amide molecules is less extensive than the primary amide.

— For polar tertiary amides, acid chlorides, and esters, only weak van der Waals attractive forces of the permanent dipole–permanent dipole type exist between their molecules. They are not able to form hydrogen bonds as they lack a H atom bonded to a small and highly electronegative atom such as O, F, or N. This also accounts for their higher volatility (relatively lower boiling point) as compared to the parent carboxylic acids, which of course, is capable of hydrogen bonding.

(iii) Suggest a structure for **Z**, which is a chiral isomer of **Y**, and mark the chiral center with an asterisk.

Explanation:

Z is $CH_3C^*H(CH_3CH_2)CONH_2$ where * indicates the chiral center.

(iv) Describe briefly how isomers **X** and **Z** might be distinguished.

Explanation:

To differentiate between **X**, $CH_3COCH_2N(CH_3)_2$, and **Z** $CH_3CH(CH_3CH_2)CONH_2$, we can use a piece of moist red litmus paper. Compound **X** is an amine; being basic, it would turn moist red litmus blue. But compound **Z** is a neutral amide, so it would not.

(d) (i) Describe a simple chemical test which would supply further evidence for the presence of *one* of the functional groups in **X**.

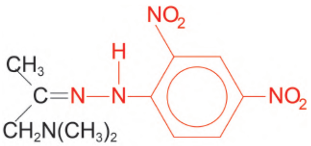
Explanation:

Use 2,4-DNPH and heat; **X**, $CH_3COCH_2N(CH_3)_2$, having a ketone functional group, would give an orange ppt with 2,4-DNPH. But **Z** would not.

(ii) Write the formula of the major organic product of the suggested test.

Explanation:

The constitutional/structural formula of the major organic product of the suggested test is shown below:



a 2,4-dinitrophenylhydrazone
(orange precipitate)

(iii) Explain how this test might be extended to allow the positive identification of compound **X**.

Explanation:

Compound **Z**, $CH_3CH(CH_3CH_2)CONH_2$, also contains the C=O group, but unlike ketones and aldehydes, the C=O functional group in an amide does not undergo condensation/addition–elimination reaction with 2,4-DNPH. Hence, the formation of the orange ppt is an indication of the presence of the ketone functional group in **X**.

Do you know?

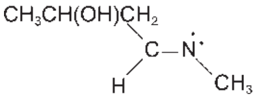
— In order to form an orange ppt with 2,4-DNPH, it has to be either C−CO−C or C−CO−H or H−CO−H.

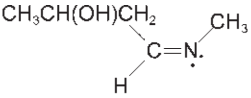
(e) Give the constitutional/structural formula of another isomer having the same molecular formula, which shows the same results as **X** for the tests of iodine in sodium hydroxide, and sodium nitrate and hydrochloric acid at 0^{o}C, but which would also exhibit *cis-trans*/geometric isomerism.

Explanation:

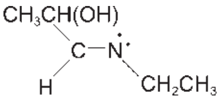
There are two possibilities:

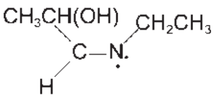
$CH_3CH(OH)CH_2CH{=}NCH_3$:





$CH_3CH(OH)CH{=}NCH_2CH_3$:





Q Is the lone pair of electrons on the N atom of –C=N more basic than that of C=C-NH_2?

A: The lone pair of electrons on the N atom of –C=N sits in an sp^2 hybridized orbital which is less available as compared to when the lone pair of electrons sits in a sp^3 hybridized orbital, while the lone pair of electrons on the N atom of C=C–NH_2 can delocalize into the C=C double bond. So, in order to know which is more basic, you need to look at the K_b value.

2. When a neutral compound **P**, $C_{10}H_{13}NO$, was refluxed with dilute acid, it formed two products **Q**, C_2H_7N, and **R**. On analysis, **R** was found to contain 70.59% carbon, 23.53% oxygen and 5.88% hydrogen by mass. The relative molecular mass of **R** was found to be 136 via mass spectrometry. On reaction with alkaline potassium manganate(VII) solution, **R** was oxidized to **S**, $C_8H_6O_4$.

   S, which was acidic, was readily dehydrated to the neutral compound **T**, $C_8H_4O_3$. **Q** reacted with gaseous hydrogen bromide to form an ionic solid, **U**, C_2H_8NBr. When **U** was dissolved in dilute hydrochloric acid and sodium nitrate(III) solution, a yellow oil, **V**, was formed and no effervescence occurred.

   (a) Determine the empirical and molecular formula of **R**.

Explanation:

To calculate the empirical formula of **R**:

	C	H	O
Percentage by mass	70.59	5.88	23.53
No. of mole in 100 g	5.88	5.88	1.47
Mole ratio	4	4	1

The empirical formula of **R** is C_4H_4O.
Now, molecular formula = $n \times$ empirical formula.
Therefore, $n \times (48 + 4 + 16) = 136 \Rightarrow n = 2$.
The molecular formula of **R** is $C_8H_2O_2$.

Do you know?

- — The molecular formula of **P**, $C_{10}H_{13}NO$, indicates the presence of a benzene ring since the C:H ratio is approximately 1:1. This information is useful as it allows us to solve the ambiguity of six carbon atoms out of a total of 10.
- — Since we are told that **P** is neutral, and from the molecular formula, we know that **P** contains an N and O atom, these would rule out the possibilities of the amine and phenol functional groups. Thus, a good guess is **P** has an amide functional group as an amide is neutral!

(b) Deduce the constitutional/structural formulae for compounds **P** to **V**.

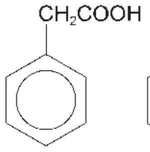
Explanation:

Since **Q** has a molecular formula of C_2H_7N, it is an amine as it reacts with hydrogen bromide to form an ionic solid, **U**, C_2H_8NBr via an acid-base reaction. This also indicates that **Q** is basic. But what kind of amine is **Q**? Is it $CH_3CH_2NH_2$ or $(CH_3)_2NH$?

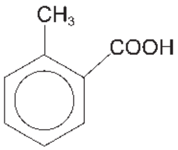
Q cannot be $CH_3CH_2NH_2$ as it would react with dilute hydrochloric acid and sodium nitrate(III) solution to give effervescence of N_2 gas (only a primary amine, RNH_2, would give N_2 gas). Thus, **Q** is $(CH_3)_2NH$.

Since **Q**, $(CH_3)_2NH$, is one of the hydrolyzed products of **P** after refluxing with dilute acid, then **P** must be an amide while **R**, $C_8H_2O_2$, is a carboxylic acid.

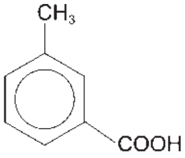
C:H ≈ 1:1 ⇒ **R**, $C_8H_2O_2$, has a benzene ring. But which of the following is **R**?



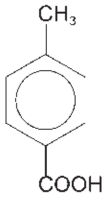
A



B



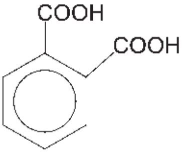
C



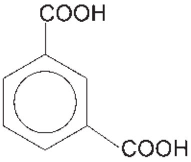
D

Structure **A** is out because we were told that on reaction with alkaline potassium manganate(VII) solution, **R** was oxidized to **S**, $C_8H_6O_4$. If **R** has structure **A**, upon oxidation, we would get benzoic acid, C_6H_5COOH. So, there is another carbon atom on **R** that can be converted to the carboxylic acid group.

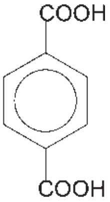
Hence, which of the following is **S**?



E



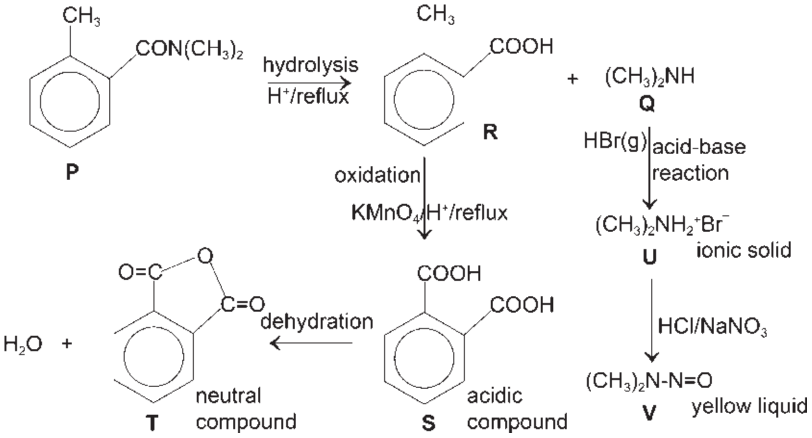
F



G

S has to be structure **E** as we were told that **S** was readily dehydrated to the neutral compound **T**, $C_8H_4O_3$. For structures **F** and **G**, the two –COOH groups are too far apart to effect intramolecular dehydration.

The constitutional/structural formulae for compounds **P** to **V** are shown below:



(c) Give the IUPAC names of compounds **Q, R**, and **U**.

Explanation:

Q is dimethylamine; **R** is 2-methylbenzoic acid; and **U** is dimethylammonium bromide.

3. (a) Explain why phenylamine is a weaker base than ethylamine.

Explanation:

The stronger the base, the more available is the lone pair of electrons for donation. For phenylamine, the lone pair of electrons on the N atom is delocalized into the benzene ring, hence it is less available for donation. As for ethylamine, the ethyl group is electron-donating. This intensifies the electron density on the N atom, making the lone pair of electrons more available for donation.

(b) Predict with reasons whether ethanol will be a weaker or stronger base than ethylamine.

Explanation:

The lone pair of electrons on the O atom of ethanol, CH_3CH_2OH, resides on a more electronegative atom than that of ethylamine, $CH_3CH_2NH_2$. This would thus make the lone pair of electrons on the O atom of ethanol less available for donation as a base.

Q Therefore, although the lone pair of phenylamine is delocalized, it does not mean that it is totally not available?

A: Absolutely right. Whether the lone pair of electrons is available is really very relative! Take for instance, the lone pair of electrons in an amide delocalizes into the C=O group, hence relative to phenylamine, which also has delocalization of lone pair, the delocalization of the lone pair in an amide causes it to be a neutral compound. But if there is a very strong acid that can protonate the lone pair of electrons on the N atom of the amide, then this lone pair can still act as a base! Take another example, many students think that ammonia is a base BUT in the presence of a reactive metal such as sodium, we still can get $Na + NH_3 \rightarrow NaNH_2 + H_2(g)$ — a demonstration of the acidic nature of ammonia!

(c) Both nitrobenzene and phenylamine contain a nitrogen atom, yet phenylamine is basic while nitrobenzene is not. Explain.

Explanation:

The nitrogen atom in nitrobenzene does not have a lone pair of electrons, hence it cannot act as a base. But the nitrogen atom in phenylamine does. So, although it is delocalized into the benzene ring, it is still available for donation.

Do you know?

— In a nutshell, the factors that determine basicity are:

(i) Is there a lone pair of electrons?

(ii) The charge on the atom. For example, O^{2-} is more basic than OH^- as it is doubly negatively charged, hence its lone pair of electrons would be more available for donation.

(iii) The electronegativity of the atom. For example, the lone pair of electrons on an O atom is less basic than that on the N atom.

(iv) Is there any electron-donating group? For example, the lone pair of electrons on ROH is more basic than H_2O as the alkyl group donates electron density onto the O atom, hence intensifying the electron density on the O atom, making it more available for donation.

(v) Is there any electron-withdrawing group? For example, the lone pair of electrons on $CH_2Cl(OH)$ is less basic than CH_3OH as the electron-withdrawing –Cl group withdraws electron density from the O atom, hence diminishes the electron density on the O atom, making it less available for donation.

(vi) The stability of the protonated species. The protonated species is positively charged. Thus, the electron-donating group would help disperse the electron deficiency on the positive-charge species, hence stabilizing it. In contrast, an electron-withdrawing group

(*Continued*)

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would further destabilize it by enhancing the electron deficiency on the positively charged species.

(vii) Is there an acid around? Without the presence of an acid, a base cannot "behave" as a base!

(viii) Last but not least, is the compound soluble? If it is an insoluble compound, then it would not dissolve to give us an alkaline solution. But take note, it is still basic! For example, MgO is basic but the solution is not alkaline in nature.

In conclusion, if there are more than two different factors involved, for example, comparing O^- and S^{2-}, to know which is the dominant factor, look at their K_b values. The greater the K_b value, the more basic is the species.

Q So, what are the factors that determine the strength of an acid?

A: The factors that determine acidity are:

(i) Using the Brϕnsted–Lowry definition, is there a H atom that can be donated as a proton?

(ii) How electron-deficient is this H atom? For example, the H atom of a –COOH group is more electron-deficient than that of an alcohol because of the electron-withdrawing effect of the C=O group. Or, the H atom of the –COOH group of an α-amino acid, $RCH(NH_2)COOH$, is more electron-deficient than that of RCOOH because of an electron-withdrawing $-NH_2$ group.

(iii) What is the bond strength of the H atom bonded to the parent molecule? For example, H–Cl bond is weaker than the H–O bond of an alcohol. The weaker the bond, the more likely it would break and hence the stronger is the acid.

(iv) How stable is the conjugate base that is formed? The more stable the conjugate base that is formed, the stronger is the acid. For example, phenoxide is more stable than an alcohol, thus making phenol a stronger acid. Moreover, the stability of this conjugate base may be enhanced if there are electron density dispersal groups or further destabilization if there are electron-donating groups.

(v) The charge density of a cation. For example, Al^{3+} is acidic in water because of the high charge density of the Al^{3+} ion, which distorts electron density on the H_2O molecule. This causes the O–H bond to weaken and hence it is able to release H^+ ion.

(vi) Is there a base around? Without the presence of a base, an acid cannot "behave" as an acid.

(vii) Last but not least, is the compound soluble?

(d) Describe briefly how a sample of phenylamine can be prepared by reducing nitrobenzene using an acid–metal reaction. Describe how you can isolate the phenylamine and give equations for the reactions.

Explanation:

Step 1: React nitrobenzene with conc. HCl/Sn metal/heat, resulting in the formation of the protonated phenylammonium cation:

$$C_6H_5NO_2 + 3Sn(s) + 7H^+ \rightarrow C_6H_5NH_3^+ + 2H_2O + 3Sn^{2+}.$$

Step 2: To recover the amine from its salt, a subsequent step involves adding NaOH(aq), which will react with the weakly acidic salt. At the same time, the tin would be precipitated out as $Sn(OH)_2$, which makes purification easier:

$$C_6H_5NH_3^+ + OH^- \rightarrow C_6H_5NH_2 + H_2O.$$

Q Can we use $LiAlH_4$ to reduce nitrobenzene to phenylamine?

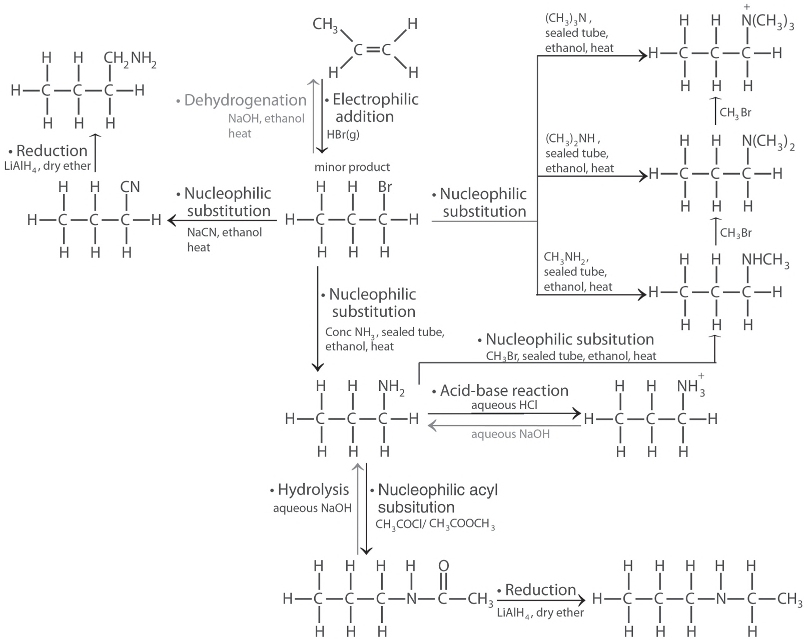
A: Yes, you can. But take note that if there are other functional groups that can be reduced by $LiAlH_4$ which you would like to preserve, then $LiAlH_4$ is not a good choice.

Q Can we use Na_2CO_3 as the base?

A: No, you can't. If $(NH_4)_2CO_3$ can exist, it just shows that ammonium, alkyl ammonium, and phenyl ammonium ions are not acidic enough to decompose the carbonate.

Do you know?

- To test for amines, moist red litmus paper is used as amines are basic.
- A mind-map showing the important chemical reactions pertaining to propylamine:



- The reaction of phenylamine with Br_2(aq) causes the brown Br_2 to decolorize with the formation of a white ppt (2,4,6-tribromophenylamine), serves as a characteristic test for phenylamine.

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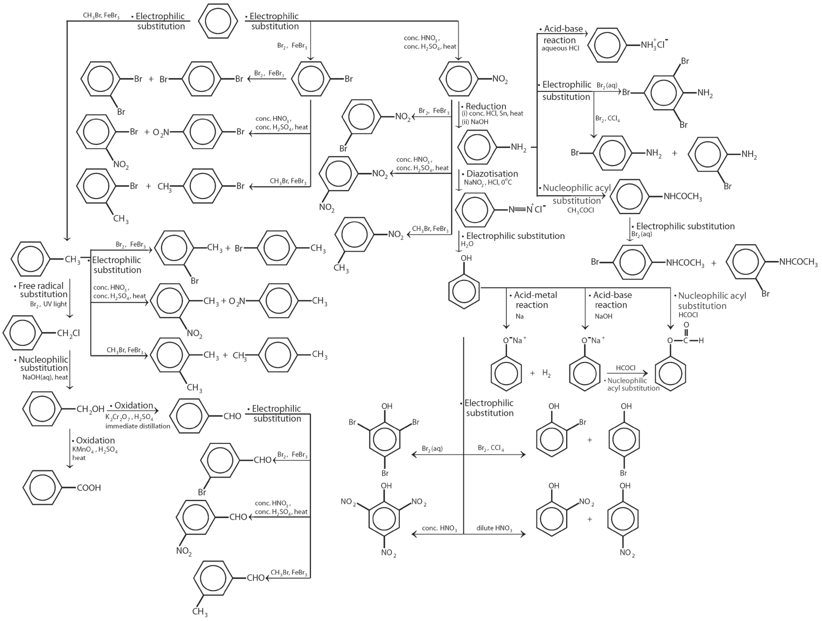
- A mind-map showing the important chemical reactions pertaining to phenylamine:



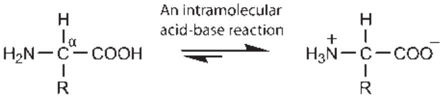
CHAPTER 12

AMINO ACIDS

Do you know?

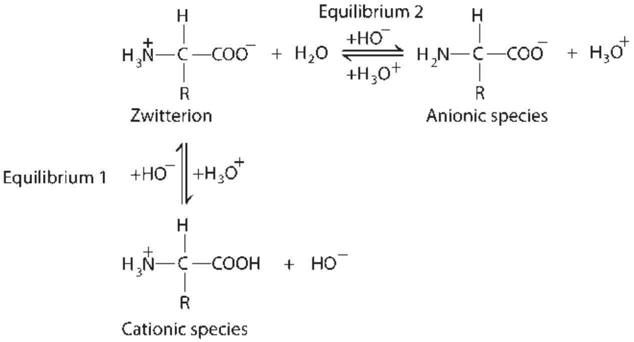
Physical properties of amino acids

— Amino acids are solid at room temperature because of the strong ionic bonds between the zwitterions. The zwitterion is formed through an intramolecular acid–base reaction:



— The solubility of amino acids in water is relatively low because of the close proximity of the two oppositely charged groups, which restricts the formation of the hydration sphere. As a result, the amount of energy that is released during the hydration process is insufficient to compensate for the energy that is required to overcome the strong ionic bonds in the solid state. Being in the zwitterionic form, the amino acids are even less soluble in non-polar solvents.

— The dominant species of the amino acid that is present in water depends very much on the pH of the solution:



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- If pH of the medium = p*I* (isoelectric point), the dominant species present are the zwitterions.

  In the presence of an applied electric field, the zwitterions would not migrate to any electrode.
- If the pH of the medium is lower than p*I* of an amino acid, the zwitterion's weakly basic $-COO^-$ group (along with basic –R group if any) will react with the H^+ ions in the medium, and the cationic form predominates under this type of acidic condition.

  In the presence of an applied electric field, the cationic species would thus migrate to the negatively charged electrode.
- If the pH of the medium is higher than p*I* of an amino acid, the zwitterion's weakly acidic $-NH_3^+$ group (along with acidic –R group if any) will react with the OH^- ions in the medium, and the anionic form predominates under this type of basic condition.

  In the presence of an applied electric field, the anionic species would thus migrate to the positively charged electrode.

— The pH of an amino acid dissolved in water depends very much on the K_a of the $-NH_3^+$ group and the K_b of the $-COO^-$ group. If the K_b of the $-COO^-$ is greater than the K_a of the $-NH_3^+$ group, then the predominant species that are present in the system would be both the zwitterions and the cationic species. Hence, an alkaline solution would be resulted as the hydrolysis of the $–COO^-$ group to form $-COOH$ and OH^- is more rampant than the dissociation of the $-NH_3^+$ group to form $-NH_2$ and H^+, as shown by Equilibrium I. An addition of H_3O^+ to Equilibrium 1 would "encourage" the formation of the cationic species in accordance to the prediction by Le Chatelier's Principle of equilibrium shift. In contrast, the addition of OH^- to Equilibrium 1 results in the formation of the zwitterion. An "over-addition" of OH^- to Equilibrium 1 would result in the formation of the anionic species.

— However, if the K_b of the $–COO^-$ is smaller than the K_a of the $-NH_3^+$ group, then the predominant species that are present in the system would be both the zwitterions and the anionic species, with an acidic solution being formed. This is because the dissociation of the $–NH_3^+$ group to form $-NH_2$ and H^+ is more rampant than the hydrolysis of the $-COO^-$ group to form $-COOH$ and OH^-. An addition of OH^- to Equilibrium 2 would "encourage" the formation of the anionic species in accordance to the prediction by Le Chatelier's Principle of

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equilibrium shift. In contrast, the addition of H_3O^+ to Equilibrium 2 results in the formation of the zwitterion. An “over-addition” of H_3O^+ to Equilibrium 2 would result in the formation of the cationic species.

— Hence, different types of amino acids would give rise to solutions of different pH values. One should take note that in the solid state, only the zwitterionic form exists! But in solution, there are the zwitterions, the cationic species, and the anionic species, each existing in different concentrations, and these concentrations in turn would depend on the nature of the amino acid itself and the pH of the solution.

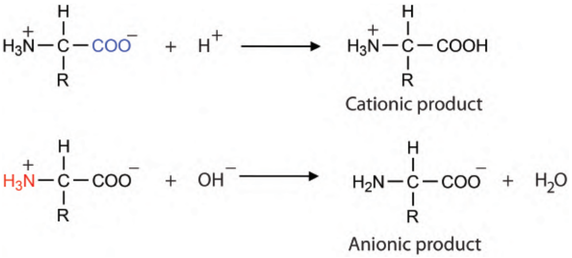
Q Given two different p*I* values, what information can we derive from them?

A: A lower p*I* value means that we need to create a more acidic pH (a higher concentration of H^+) to protonate the anionic form so as to convert all species into the zwitterionic form. This would mean that just by comparing the p*I* values, we can conclude which amino acid is more acidic in water. How does it go about? Recall that when $pH = pK_a$, the [weak acid] = [conjugate base]. So a stronger weak acid, which dissociates to a larger extent to form a larger [conjugate base], would need a lower pH to “force” a smaller [conjugate base] to a form. Hence, a smaller pK_a means a stronger acid! Likewise, p*I* is the pH when the zwitterion exists. The larger the extent of the dissociation of the $-NH_3^+$ group of the zwitterion, the more acidic is the zwitterion, and hence the lower the pH to make less zwitterion dissociates, leading to a smaller p*I*.

Do you know?

Chemical properties of amino acids

— Amino acids are amphoteric compounds, i.e., they able to react with both bases and acids. Hence, they can act as buffering agents:



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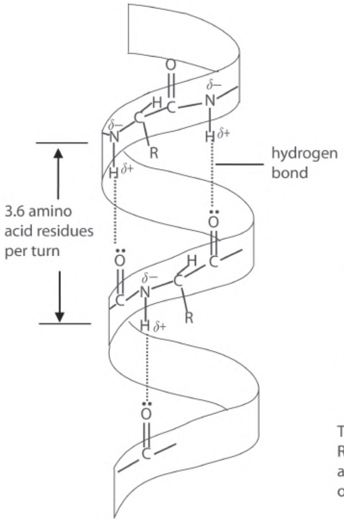
Polypeptides and proteins

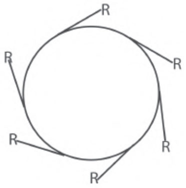
— Polypeptides and proteins consist of amino acids that have undergone condensation polymerization. There are four levels of protein structure: the primary structure, the secondary structure, the tertiary structure, and the quaternary structure.

- The primary structure of a protein is the sequence of amino acid residues in the linear protein chain. The primary structure is held together by strong covalent bonds (peptide/amide bonds) between adjacent amino acid residues.
- The secondary structure refers to the spatial orientation of the residues of the amino acids brought about by the hydrogen bonds that are formed between the peptide groups within the primary structure of the protein.

  These hydrogen bonds cause the backbone to adopt a highly regular pattern. There are two types of stable secondary structures, namely the α-helix and the β-pleated sheet structures.

α-*helix:*





Top-view showing all the R-groups of the amino acid residues pointing out fom the helix

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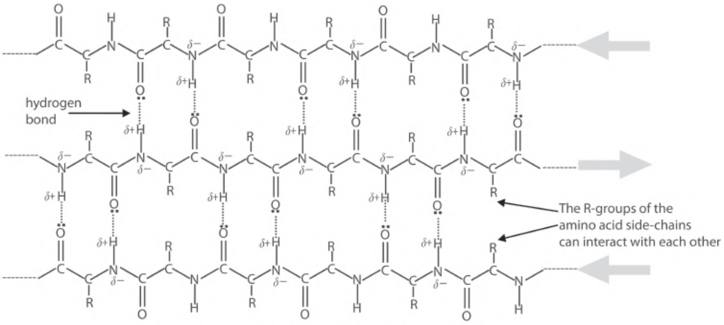
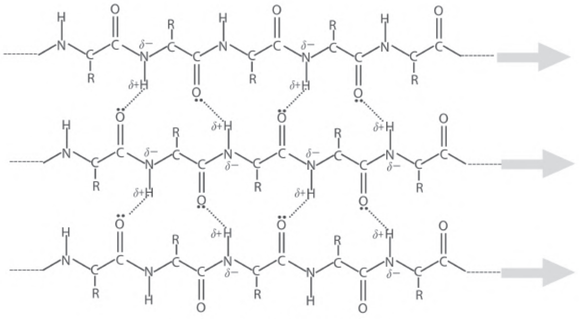
β-pleated sheet:



hydrogen bond

The R-groups of the amino acid side-chains can interact with each other

Anti-parallel pleated sheets



Parallel pleated sheets

- The tertiary structure of a protein refers to the three-dimensional structure of a single protein chain that arises from the folding of the secondary structures, i.e., the α-helix or β-pleated sheet, as a result of the interactions between the side chain –R groups.

  There are four types of –R group interactions that would stabilize the tertiary structure:
  - ○ ionic bonds between oppositely charged groups;
  - ○ hydrogen bonding between polar groups;
  - ○ van der Waals forces of attraction between uncharged groups; and
  - ○ disulfide bonds between the cysteine residues.
- The quaternary structure of a protein refers to the three-dimensional structure where more than one subunit of the protein cluster form a final specific shape.

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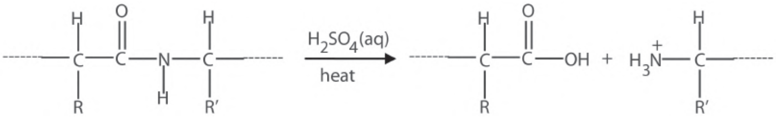
The types of interactions that hold these subunits together can be ionic interactions, hydrogen bonding, disulfide bridges, and van der Waals forces.

— Polypeptides and proteins can easily undergo denaturation due to *heat*, *pH*, *heavy metal ions*, *alcohols*, and *detergents*. The denaturation of proteins is the result of the disruption or possible destruction of both the secondary and tertiary structures. When the secondary or tertiary structures are affected, the interactions between the different side groups change. This causes the protein to change its conformation and hence unfold. The solubility of the protein would decrease, thus causing coagulation. Polypeptides and proteins are polyamides that undergo acidic hydrolysis similar to an amide:



1. (a) An organic compound has the following composition by mass: 61.3% carbon; 5.1% hydrogen; 10.2% nitrogen; and 23.4% oxygen. Determine the empirical formula of the compound.

Explanation:

To calculate the empirical formula:

	C	H	N	O
Percentage by mass	61.3	5.1	10.2	23.4
No. of mole in 100 g	5.11	5.1	0.73	1.46
Mole ratio	7	7	1	2

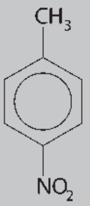
The empirical formula is $C_7H_7NO_2$.

(b) Given the relative molecular mass of the compound in (*a*) is 137, determine the molecular formula of the compound.

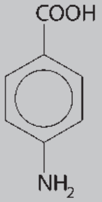
Explanation:

Now, molecular formula = $n \times$ empirical formula.
Therefore, $n \times (7 \times 12 + 7 + 14 + 32) = 137 \Rightarrow n = 1$.
The molecular formula is $C_7H_7NO_2$.

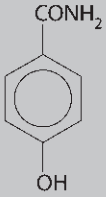
(c) The compound may be one of the following two isomers:



X



Y



Z

(i) Explain which isomer, **X** or **Y**, would have the higher boiling point.

Explanation:

Isomer **Y** has a $-$COOH and a $-NH_2$ group where the $-$COOH can protonate the $-NH_2$ group resulting in the formation of zwitterions. Hence, the ionic bonding between the zwitterions will cause isomer **Y** to have a higher boiling point than **X**. Isomer **X** has the $-NO_2$ group which causes **X** to be polar and hence possess permanent dipole–permanent dipole interaction in addition to instantaneous dipole–induced dipole interaction.

Q If we place the above zwitterionic form of the compound in water, would the zwitterion be acidic or basic in water? How would we know?

A: If the K_b of the $-COO^-$ group is greater than the K_a of the $-NH_3^+$ group, then the predominant species that are present in the system would be both the zwitterions and the cationic species. Hence, an alkaline solution would be resulted as the hydrolysis of the $-COO^-$ group to form $-COOH$ and OH^- is more rampant than the dissociation of the $-NH_3^+$ group to form $-NH_2$ and H^+. However, if the K_b of the $-COO^-$ is smaller than the K_a of the $-NH_3^+$ group, then the predominant species that are present in the system would be both the zwitterions and the anionic species, with an acidic solution being formed. This is because the dissociation of the $-NH_3^+$ group to form $-NH_2$ and H^+ is more rampant than the hydrolysis of the $-COO^-$ group to form $-COOH$ and OH^-. Hence, different types of amino acids would give rise to solutions of different pH values. One should take note that in the solid state, only the zwitterionic form exists! But in solution, there are the zwitterions, the cationic species, and the anionic species, each existing in different concentrations, and these concentrations in turn would depend on the nature of the amino acid itself and the pH of the solution.

Q If the $-COO^-$ group carries a negative charge, shouldn't it be a stronger base than the neutral $-NH_2$ group?

A: Good question! The negative charge (which means an extra electron) of the $-COO^-$ group is actually delocalized to the highly electron-withdrawing carbonyl group, and the negative charge is equally dispersed among two highly electronegative O atoms. As a result, the basicity of the $-COO^-$ group is lower than that of the neutral $-NH_2$ group. The K_b of CH_3COO^- is $\sim 5.6 \times 10^{-10}$ while the K_b of NH_3 is $\sim 1.8 \times 10^{-5}$. This is a good gauge to estimate the basicities of the $-COO^-$ and $-NH_2$ groups in the zwitterions. Thus, in conclusion, a negatively charged species may not necessarily be more basic than a neutral one. Take for example, Cl^- is negatively charged, but it is a very weak conjugate base of HCl.

(ii) With appropriate reagents and conditions, describe a simple chemical test to differentiate the following pair of compounds:

(A) **X** and **Y**;

Explanation:

To differentiate between **X** and **Y**, just use any of the following tests:

(1) Use sodium metal and test for $H_2(g)$:

X: No gas evolved that extinguished a lighted splint with a pop sound.

Y: Gas evolved that extinguished a lighted splint with a pop sound. Gas is $H_2(g)$.

Compound **Y** contains a -COOH group.

$-COOH + Na \rightarrow -COONa + ½ H_2(g)$. {Acid–metal reaction}

(2) Use PCl_5 and test for HCl(g):

X: No white fumes of HCl(g).

Y: White fumes of HCl(g) observed.

Compound **Y** contains a –COOH group.

$-COOH + PCl_5 \rightarrow -COCl + POCl_3 + HCl(g)$. {Nucleophilic Acyl Substitution}

(3) Use $SOCl_2$ and test for HCl(g):

X: No white fumes of HCl(g).

Y: White fumes of HCl(g) observed.

Compound **Y** contains a –COOH group.

$-COOH + SOCl_2 \rightarrow -COCl + SO_2 + HCl(g)$. {Nucleophilic Acyl Substitution}

(4) Use $Na_2CO_3(s)$ and test for $CO_2(g)$:

X: No gas evolved gave white ppt with $Ca(OH)_2(aq)$.

Y: Gas evolved gave white ppt with $Ca(OH)_2(aq)$.

Compound **Y** contains a −COOH group.

$2-COOH + CO_3^{2-} \rightarrow 2-COO^- + CO_2 + H_2O$. {Acid a base reaction}

(5) Use $KMnO_4/H_2SO_4$/heat:

Y: No decolorization of purple $KMnO_4$.

X: Purple $KMnO_4$ decolorized.

Compound **X** contains a $-CH_3$ group bonded to the benzene ring that is oxidizable.

$-CH_3 + 3[O] \rightarrow -COOH + H_2O$. {Oxidation}

(6) Use $KMnO_4$/NaOH/heat:

Y: No decolorization of purple $KMnO_4$.

X: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.

Compound **X** contains a $-CH_3$ group bonded to the benzene ring that is oxidizable.

$-CH_3 + OH^- + 3[O] \rightarrow -COO^- + 2H_2O$. {Oxidation}

(7) Use (i) $NaNO_2$/HCl(aq)/0-5°C, (ii) water/heat: {Diazotization followed by hydrolysis}

X: No evolution of $N_2(g)$.

Y: Evolution of $N_2(g)$.

Compound **Y** contains a $-NH_2$ group.

(8) Use $Br_2(aq)$:

X: No decolorization of brown Br_2.

Y: Brown Br_2 decolorized. White ppt formed. {Electrophilic Substitution}

Compound **Y** contains the phenylamine functional group.

(B) **X** and **Z**; and

Explanation:

To differentiate between **X** and **Z**, just use any of the following tests:

(1) Use sodium metal and test for $H_2(g)$:

X: No gas evolved that extinguished a lighted splint with a pop sound.

Z: Gas evolved that extinguished a lighted splint with a pop sound. Gas is $H_2(g)$.

Compound **Z** contains a $-OH$ group.

$-COOH + Na \rightarrow -COONa + \frac{1}{2} H_2(g)$. {Acid–metal reaction}

(2) Use $KMnO_4/H_2SO_4$/heat:

Z: No decolorization of purple $KMnO_4$.

X: Purple $KMnO_4$ decolorized.

Compound **X** contains a $-CH_3$ group bonded to the benzene ring that is oxidizable.

$-CH_3 + 3[O] \rightarrow -COOH + H_2O$. {Oxidation}

(3) Use $KMnO_4$/NaOH/heat:

Z: No decolorization of purple $KMnO_4$. But gas evolved turned moist red litmus paper blue. Gas is NH_3 which was formed due to alkaline hydrolysis of the primary amide functional group.

X: Purple $KMnO_4$ decolorized. Brown MnO_2 formed.

Compound **X** contains a $-CH_3$ group bonded to the benzene ring that is oxidizable.

$-CH_3 + OH^- + 3[O] \rightarrow -COO^- + 2H_2O$. {Oxidation}

(4) Use NaOH(aq)/heat:

X:No gas evolved that turned moist red litmus paper blue.

Z: Gas evolved that turned moist red litmus paper blue. Gas is NH_3.

Compound **Z** contains a $-CONH_2$ group.

$-CONH_2 + OH^- \rightarrow -COO^- + NH_3(g)$. {Alkaline hydrolysis}

(5) Use neutral aqueous iron(III) chloride: {Complexation}

X: No formation of a violet complex.

Z: Formation of a violet complex.

Compound **Z** contains the phenol functional group that formed a violet complex with Fe^{3+}.

(C) **Z** and **Y**.

Explanation:

To differentiate between **Z** and **Y**, just use any of the following tests:

(1) Use NaOH(aq)/heat:

Y: No gas evolved that turned moist red litmus paper blue.

Z: Gas evolved that turned moist red litmus paper blue. Gas is NH_3.

Compound **Z** contains a $-CONH_2$ group.

$-CONH_2 + OH^- \rightarrow -COO^- + NH_3(g)$. {Alkaline hydrolysis}

(2) Use PCl_5 and test for HCl(g):

Z: No white fumes of HCl(g).

Y: White fumes of HCl(g) observed.

Compound **Y** contains a -COOH group.

$-COOH + PCl_5 \rightarrow -COCl + POCl_3 + HCl(g)$. {Nucleophilic Acyl Substitution}

(3) Use $SOCl_2$ and test for HCl(g):
Z: No white fumes of HCl(g).
Y: White fumes of HCl(g) observed.
Compound **Y** contains a −COOH group.
$-COOH + SOCl_2 \rightarrow -COCl + SO_2 + HCl(g)$. {Nucleophilic Acyl Substitution}

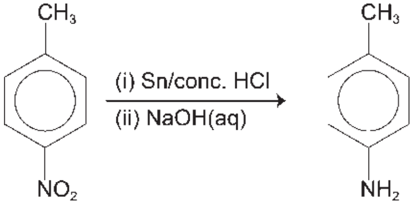
(4) Use $Na_2CO_3(s)$ and test for $CO_2(g)$:
Z: No gas evolved gave a white ppt with $Ca(OH)_2(aq)$.
Y: Gas evolved gave a white ppt with $Ca(OH)_2(aq)$.
Compound **Y** contains a −COOH group.
$2-COOH + CO_3^{2-} \rightarrow 2-COO^- + CO_2 + H_2O$. {Acid–base reaction}

(5) Use neutral aqueous iron(III) chloride: {Complexation}
Y: No formation of a violet complex.
Z: Formation of a violet complex.
Compound **Z** contains the phenol functional group that formed a violet complex with Fe^{3+}.

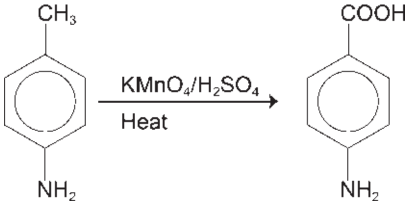
(iii) Compound **X** can be converted to compound **Y** via a two-step process. Give suitable reagents and conversions for each of the two steps.

Explanation:

Step 1: Use (i) conc. HCl/Sn metal/heat followed by (ii) NaOH(aq).



Step 2: Use $KMnO_4/H_2SO_4$/heat.



Q Can we use the following sequence: Step 1: Use $KMnO_4/H_2SO_4$/ heat, then Step 2: Use (i) conc. HCl/Sn metal/heat followed by (ii) NaOH(aq), instead?

A: If you oxidize the methyl group to the −COOH group first, followed by reduction, then there is a possibility that the reducing agent that you use may also reduce the −COOH group to the alcohol group. So, the yield of the product may not be good.

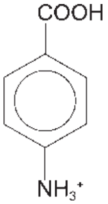
(d) Compound **Y** belongs to a class of compounds known as amino acids.

(i) Give the structures of **Y** which is present predominantly in each of the solution:

(A) pH 2;

Explanation:

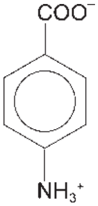
The predominant species at pH 2 is



(B) pH 7; and

Explanation:

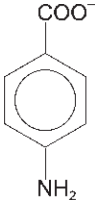
The predominant species at pH 7 is



(C) pH 10.

Explanation:

The predominant species at pH 10 is



Q How would we know what species to give at each of the pH?

A: Normally, if we are given the pK_a value, we should be able to determine what is the predominant species that will be present at that pH. This is because when an acid dissociates in water, the pH of the acid is roughly the same as the pK_a value. Of course, we know that the concentration of the acid does affect the actual pH. Hence, if the pH of the acid is roughly the same as the pK_a value, then at a pH value that is lower than the pK_a value, the acid would likely be in the protonated form. The same rule also applies to the base. At a pH that is smaller than the pK_b value, the base would be protonated. So, in order to know what species is present, just compare the pH of the solution against each of the pK_a or pK_b value. In this question, we roughly know that the pK_b value for a $-NH_2$ group is about 9, while the pK_a value for a $-COOH$ group is about 3.

Q Is there a pK_a value for a $-NH_2$ group?

A: When you are given a molecule that has a $-NH_2$ group and the question also gives you the pK_a value for this $-NH_2$ group, it is actually referring to the pK_a value for a $-NH_3^+$ group.

(ii) What key property does the presence of the amino acid confer on the solution? Suggest an important application of this solution.

Explanation:

The zwitterion of the amino acid is amphoteric in nature:

- The carboxylate group ($-COO^-$) is the conjugate base of the weakly acidic carboxyl group, and it is thus the species in the zwitterions that reacts with acids.
- The protonated amine group ($-NH_3^+$) is the conjugate acid of the weakly basic amine group, and it is thus the species in the zwitterions that reacts with bases.

We can use the amino acid solution as a buffer to maintain constant pH.

Q Is a zwitterion more acidic than a carboxylic acid? Can it liberate CO_2 from carbonate?

A: Although the zwitterionic form of the amino acid is amphoteric, it is generally less acidic than a carboxylic acid (using K_a of CH_3COOH which is ~ 1.8×10^{-5} as a guideline) and less basic than most amines (using K_b of NH_3which is ~1.8×10^{-5}, and that of $CH_3CH_2NH_2$ which is ~ 4.7×10^{-4} as a guideline). Why is it so? It is simply because $-NH_3^+$ is a weaker acid (K_a of $CH_3CH_2NH_3^+$ is ~ 2.1×10^{-11}) than a $-COOH$ group due to the stronger attractive force between the lone pair of electrons on the N atom and the H^+ ion, even though the $-NH_3^+$ is positively charged and thus more likely to be attracted by a base. The strong attractive force between the lone pair of electrons and the H^+ ion makes it less likely to be extracted, unless a stronger base such as OH^-, H^-, or NH_2^- is used.

Similarly, the basicity of the conjugate base, $-COO^-$ (using K_b of CH_3COO^- which is ~ 5.6×10^{-10} as a guideline), is not as high as that of a $-NH_2$ group, even though it contains a negative charge. This is because the negative charge is being dispersed into an electron-withdrawing carbonyl group through resonance. Hence, for an amino acid with an –R group that contains the $-COOH$ group, for example aspartic acid, the resultant acidity of the amino acid that has arisen is due to the more acidic $-COOH$ group on the –R group and not due to $-NH_3^+$ group. In addition, $-COOH$ being a stronger acid than $-NH_3^+$, the dissociation of the $-COOH$ would suppress the dissociation of the $-NH_3^+$. In a similar line of argument, for an amino acid with the basic $-NH_2$ group in the $-R$ group, the resultant basicity that has arisen is from the $-NH_2$ in the –R group and not the $-COO^-$ on the α-carbon. Just think logically: the fact that the zwitterions can be formed, means that $-COOH$ is a stronger acid than $-NH_3^+$, or else how is it able to protonate the $-NH_2$ group to create $-NH_3^+$? Similarly if $-COO^-$ is a stronger base than $-NH_2$ then it would be able to deprotonate the $-NH_3^+$ and exist as both $-NH_2$ and $-COOH$ instead, but it did not!

All these explanations can thus be used to account for the existence of $(NH_4)_2CO_3$, but not when a carboxylic acid and Na_2CO_3 are mixed. Usually, if we have two weak acids, HX and HY, and if HX is a stronger weak acid than HY, it would be indicated by a higher K_a value for HX. Then, the conjugate base of HX, which is X^-, would be a weaker base than Y^-, which is indicated by a higher K_b value for Y^-. Remember when the K_a of HX is multiplied by the K_b of X^-, it is equal to the K_w, which has a value of 1.0×10^{-14} mol^2 dm^{-6} at 25°C?

(e) (i) Rank the three compounds trimethylamine, aminoethanoic acid, and ethanamide in order of increasing melting points, give your reasons.

Explanation:

In the order of increasing melting points: trimethylamine $(CH_3)_3N$ < ethanamide CH_3CONH_2 < aminoethanoic acid $CH_2(NH_2)COOH$. Aminoethanoic acid has the highest melting point as it is present in the zwitterionic form with strong ionic bonding between the particles. As for ethanamide, it has strong and extensive hydrogen bonds that hold the molecules together. This is stronger than the permanent dipole–permanent dipole interaction between the molecules of the polar triethylamine.

(ii) Predict with reasons whether the ethyl ester of aminoethanoic acid will have a higher or lower melting point than that of aminoethanoic acid itself.

Explanation:

The ethyl ester of aminoethanoic acid will have a melting point lower than that of aminoethanoic acid. This is because aminoethanoic acid would be present in the zwitterionic form with strong ionic bonding, whereas the ethyl ester of aminoethanoic acid would only have hydrogen bonds resulted from the $-NH_2$ group and the lone pair of electrons on the ester, $-COO-$, functional group.

(f) Phenylalanine, $C_6H_5CH_2CH(NH_2)COOH$, is an amino acid that is commonly found in nature.

(i) Explain why the solubility of phenylalanine is low in water but the solubility increases when a base or an acid is added.

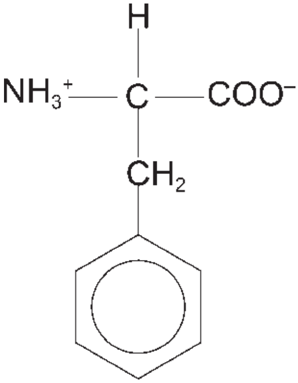
Explanation:

The solubility of phenylalanine in water is relatively low because of the close proximity of the two oppositely charged groups, which restricts the formation of the hydration sphere. As a result, the amount of energy that is released during the hydration process is insufficient to compensate for the energy that is required to overcome the strong ionic bonding between the zwitterions in the solid state. But when an acid or a base is added, the zwitterion is converted to the cationic and anionic form, respectively. Both the cationic and anionic form of phenylalanine are more soluble in water due to the ability of the species to undergo “more complete” hydration in water.

(ii) In a solution where the pH is about 7, there is very little movement of phenylalanine toward both the positive and negative electrodes. Draw the structure of the species that is present at this pH.

Explanation:

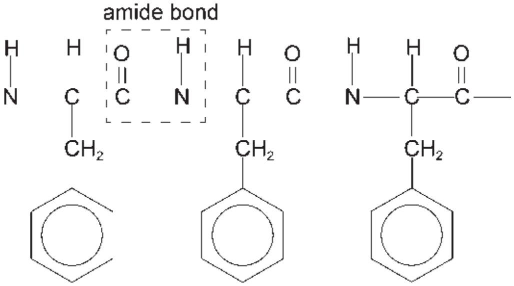
At pH 7, there is little movement of the species under the influence of an electric fields which is an indication of the presence of a zwitterion. The species is as follows:



(iii) Draw a polymeric section of poly(phenylalanine), showing three repeat units. Name the functional group that holds these monomers together.

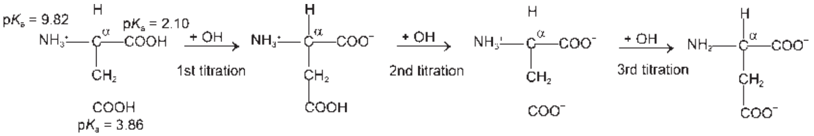
Explanation:

Phenylalanine undergoes condensation polymerization to form amide bonds that hold the monomers together in poly(phenylalanine):



Do you know?

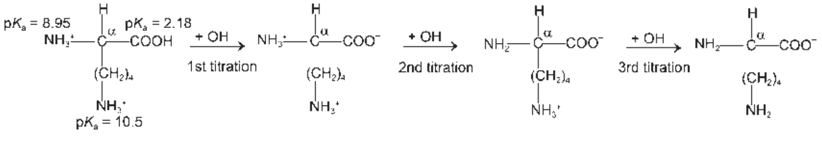
- When an amino acid with a $-\text{COOH}$ group in the –R group undergoes titration, for example aspartic acid, the first equivalence point corresponds to the neutralization of the $-\text{COOH}$ group at the a-carbon.



This is because between the two $-\text{COOH}$ groups, the one that is at the α-carbon is more acidic as it is near to an electron-withdrawing $-\text{NH}_3^+$ group, which helps to disperse the electron density of the conjugate base that form. Thus, being more acidic, the $-\text{COOH}$ group on the α-carbon would be more likely to dissociate and hence suppress the dissociation of the less acidic $-\text{COOH}$ in the –R group. In addition, the proximity of both groups on the α-carbon makes the deprotonation of the $-\text{COOH}$ group more favorable as the close proximity of the two oppositely charged groups that form, the $-\text{NH}_3^+$ and $-\text{COO}^-$ groups, allows intramolecular ionic interaction to take place.

The second equivalence point corresponds to the neutralization of the $-\text{COOH}$ group in the –R group, as a $-\text{COOH}$ group is more acidic than a $-\text{NH}_3^+$ group. Finally, the last equivalence point corresponds to the neutralization of the $-\text{NH}_3^+$ group.

- But when an amino acid with a $-\text{NH}_2$ group in the –R group undergoes titration, for example lysine, the first equivalence point corresponds to the neutralization of the $-\text{COOH}$ group at the α-carbon.



This is due to the $-\text{COOH}$ group being more acidic than the two $-\text{NH}_3^+$ groups. The second equivalence point corresponds to the neutralization of the $-\text{NH}_3^+$ group at the α-carbon. This is because the $-\text{NH}_3^+$ group at the α-carbon is more acidic as it is near an electron-withdrawing $-\text{COO}^-$ group, which increases the electron deficiency of the H atom of the $-\text{NH}_3^+$ group. Finally, the last equivalence point corresponds to the neutralization of the $-\text{NH}_3^+$ group.

Q Can we say that the $-NH_3^+$ group in the –R group of lysine is less acidic than the one at the α-carbon because it is bonded to an electron-releasing alkyl group?

A: No, you can't, as this same alkyl group is also bonded to the α-carbon.

Q How can we calculate the pK_a and pI from the titration curve?

A: Remember from Chapter 7 of *Understanding Advanced Chemistry Through Problem Solving* Volume I, the pK_a = pH at the mid-point of titration. As for the pI value, we can calculate it by using the following formula:

$$\mathrm{p}I = \frac{\mathrm{p}K_{a1} + \mathrm{p}K_{a2}}{2}.$$

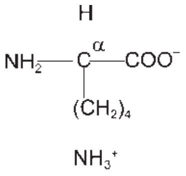
Hence, for aspartic acid, its pI = (2.10 + 3.86)/2 = 2.98. For lysine, its pI = (8.95 + 10.5)/2 = 9.73.

Q Why for lysine, the pI is calculated by using the pK_a values of the two $-NH_3^+$ groups?

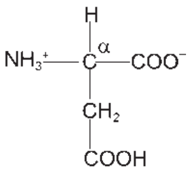
A: This is because the zwitterion is the intermediate between the second and third titrations, which corresponds to the neutralization of the two $-NH_3^+$ groups. So, the pI must be in between the pK_a values of the two $-NH_3^+$ groups. This is unlike aspartic acid, where its pI is between the first and second titration, which corresponds to the neutralization of the two $-COOH$ groups.

Q So, the zwitterion does not necessary need to have the charged groups, $-NH_3^+$ and -COO^-, on the α-carbon?

A: Of course not. If there is no additional acidic or basic group in the side chain of the amino acid, then the zwitterionic form of the amino acid would have both the $-NH_3^+$ and $-COO^-$ groups on the α-carbon. But if there is an acidic or basic group in the side chain, then they may not be at the α-carbon. As an example, the zwitterions of aspartic acid and lysine are shown below:



lysine



aspartic acid

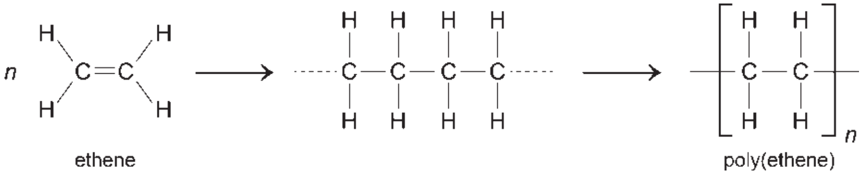
CHAPTER 13

POLYMERS

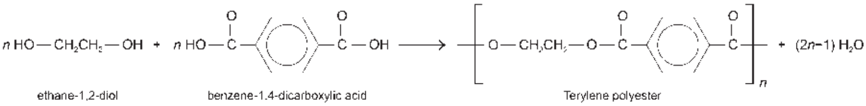
1. (a) (i) Explain the meaning of the terms *addition polymerization* and *condensation polymerization*, illustrating your answer with one example of each, their industrial importance.

Explanation:

Addition polymerization involves the breaking of the carbon–carbon pi bonds in monomers to form new sigma bonds between each other without the loss of any atom or molecule. An example is the formation of poly(ethene):



Condensation polymerization involves a condensation reaction in which monomers bind together with the elimination of small molecules such as water and ammonia. An example is the formation of the polyester Terylene:



Do you know?

- The molecular weight of the repeat unit is the same as the monomer in addition polymerization, but lower than that for the monomers in condensation polymerization because of the expulsion of small molecules.
- Addition polymerization is termed as such because the number of unsaturation within the molecules decreases when the monomer is converted to the polymer just like in the electrophilic addition of an alkene molecule with an electrophile.
- The mechanism for addition polymerization has three stages, namely: Initiation, Propagation, and Termination stages.

Q So, is addition polymerization electrophilic in nature just like that for alkene chemistry?

A: Addition polymerization can be initiated by a radical, a cation, or even an anion. Obviously, if the initiator is a cation, it must be electrophilic in nature, whereas if it is an anion-initiated reaction, it would be nucleophilic in nature.

Q I thought that the alkene is an electron-rich species, how can it be attacked by another electron-rich species?

A: Well, although the alkene is an electron-rich species, it can still be attacked by another electron-rich species that is more electron-rich than the alkene. Obviously, after the attack by the nucleophile, there are some stabilizing factors that would help to stabilize the carbanion intermediate that is formed. Such stabilizing factors may include the dispersion of the negatively charged particles through resonance.

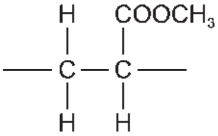
(ii) Draw the structure of the repeating unit in the polymer made from each of the following:

(A) $CH_2CHCOOCH_3$, and

(B) H_2NCH_2COOH.

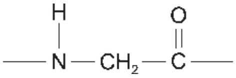
Explanation

(A) $CH_2CHCOOCH_3$ will form an addition polymer with the following repeat unit:



$$-\overset{\overset{\mathrm{H}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-\overset{\overset{\mathrm{COOCH_3}}{|}}{\underset{\underset{\mathrm{H}}{|}}{\mathrm{C}}}-$$

(B) H_2NCH_2COOH will form a condensation polymer with the following repeat unit:



$$-\overset{\overset{\mathrm{H}}{|}}{\mathrm{N}}-\mathrm{CH_2}-\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}-$$

(iii) Name the type of bond fission that is involved in both *(a)(ii)(A)* and *(a)(ii)(B)*.

Explanation:

During the formation of the polymer in *(a)(ii)(A)*, homolytic bond cleavage is involved, while during the formation of the polymer in *(a)(ii)(B)*, heterolytic bond cleavage is involved.

Do you know?

— A common method for addition polymerization involves free radical polymerization, which bears similarities to the Free Radical Substitution of alkanes. Thus, homolytic bond cleavage occurs to form the highly reactive free radicals.

— Condensation polymerization involves Nucleophilic Acyl Substitution where, in this case, the amine group acts as the nucleophile and attacks the electron-deficient carbon of the carboxylic acid group. Subsequently, heterolytic bond cleavage of the C−O bond occurs to form the amide linkage.

Q If the amino acid exists as a zwitterion, how is it possible for Nucleophilic Acyl Substitution to occur since the protonated amine group cannot serve as the nucleophile and the carboxylate group is also resonance-stabilized?

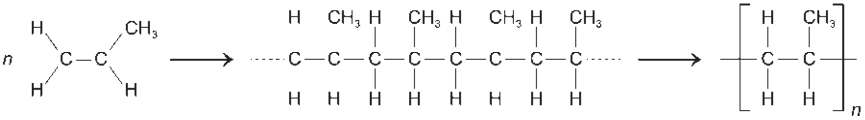
A: Although the predominant form of amino acids are zwitterions, there is actually an equilibrium being established between the unionized form of the amino acid and the zwitterion:

An acid–base reaction, be it between intramolecular or intermolecular molecules, will indeed occur. But since there are some unionized amino acid molecules, there is the possibility that Nucleophilic Acyl Substitution can occur. So, as time progresses, the formation of increasing numbers of the amide linkages between the monomer molecules would cause the above equilibrium position to shift to the left.

(b) Propene, $CH_3CH{=}CH_2$, a valuable chemical that is produced during the cracking of petroleum, is principally used for the manufacturing of poly(propene).

(i) Write an equation to show the polymerization of propene, representing the polymer with four repeat units.

Explanation:



(ii) Give the name of the catalyst that is used in the industrial polymerization of propene.

Explanation:

The catalyst is the Ziegler–Natta catalyst which consists of $AlCl_3$ as the active ingredient.

(iii) Explain how the use of this catalyst influences the structure of the polymer formed.

Explanation:

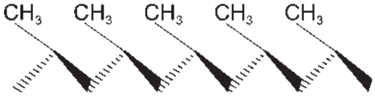
The Ziegler–Natta catalyst works by cationic polymerization. Hence, the type and stability of the momomeric carbocation that is generated by the catalyst would determine the type of polymer that is formed. In addition, because the monomer is anchored onto the catalyst in the initiation stage, the orientation of the first monomer would affect the orientation of subsequent monomers that are added on to this first monomer.

(iv) Draw three different types of poly(propene), explaining the differences between them.

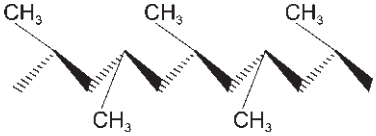
Explanation:

The three types of poly(propene) have different spatial orientation of the alkyl side groups.

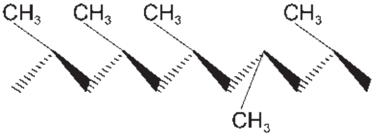
An isotactic poly(propene) has methyl groups on the same side of the carbon skeleton:



A syndiotactic poly(propene) has methyl groups on opposite sides of the carbon skeleton in an alternate fashion:



An atactic poly(propene) has methyl groups randomly distributed on both sides of the carbon skeleton:



Do you know?

— The different types of poly(propene) have different melting points: the isotactic poly(propene) melts at about 165^{o}C, the syndiotactic poly(propene) at about 128^{o}C, while the atactic poly(propene) melts below 0^{o}C. The higher melting point of the isotactice polymers arises because the electron cloud is more symmetrically distributed than the other two types of polymers. This allows for maximum surface area of contact between the isotactic polymer molecules. Different melting points result in different physical properties, hence leading to different applications.

(v) Poly(propene) is non-biodegradable. With reference to two different uses of poly(propene), suggest how this can both be an advantage and a disadvantage.

Explanation:

Poly(propene) is used to make stationery and packaging materials. The advantages of the use of poly(propene) for such items lie with its tough and flexible properties, along with its resistance to chemicals and heat, making the items durable and long-lasting. Nonetheless, the growing use of poly(propene) for such purposes, and many others, would pose a disposal problem if environmentally friendly practices such as recycling are not prevalent.

(vi) Poly(propene) is a popular material for the making of carpets. Suggest two advantages of using poly(propene) for carpets.

Explanation:

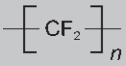
Poly(propene) is used for the making of carpets because its toughness makes it resistant to wear and tear chemicals, and heat. In addition, the hydrophobic nature of the polymer makes it less likely for polar molecules to be adsorbed on its surfaces.

(vii) When poly(propene) is heated, it softens over a range of temperatures rather than melting sharply at a particular temperature. Suggest reasons for the observed phenomenon.

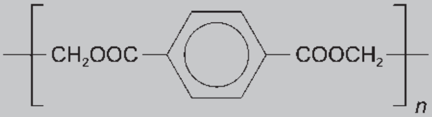
Explanation:

Poly(propene) is composed of many polymeric chains that have different molecular structures such as different chain lengths and degrees of branching. This gives rise to a different extent of van der Waals forces of attraction between the different polymeric chains throughout the polymer matrix. The different strengths of interactions require different amounts of energy to overcome. Hence, poly(propene) melts over a range of temperature.

(c) The structures of the repeating units of two polymers **P** and **Q** are given below:



P

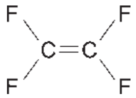


Q

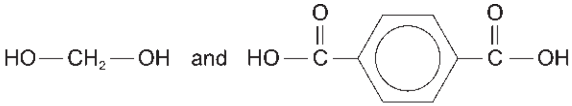
(i) Draw the constitutional/structural formulae of the monomers from which **P** and **Q** are synthesized.

Explanation:

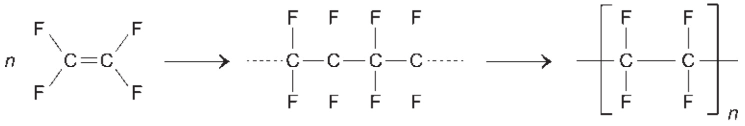
P is an addition polymer formed from the following alkene monomer:



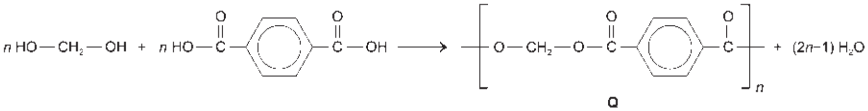
Q is a condensation polymer with ester linkages formed from the following diol and dicarboxylic acid monomers:



The following equations show the formation of **P** and **Q**, respectively.



P



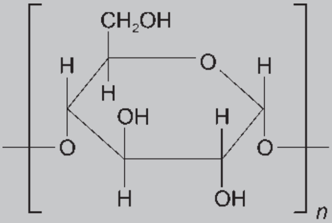
Q

(ii) Classify the type of polymerization and name the other compound produced when **Q** is made as in *(i)* above.

Explanation:

Polymer **Q** is produced from condensation polymerization and H_2O is formed as a byproduct.

(iii) Clothes that are made from polymer **Q** feel more comfortable than those made from poly(propene), but are not as comfortable as those that are made from cotton which is actually poly(glucose). Explain the observed phenomenon.

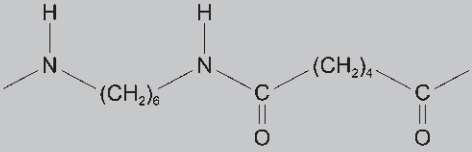


poly(glucose)

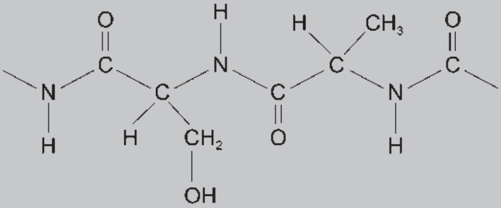
Explanation:

Clothing that is made from cotton is the most comfortable because cotton can remove moisture formed on the body due to perspiration. This is possible because there are many alcohol functional groups in poly(glucose) which can form extensive hydrogen bonds with the water molecules. Polymer **Q** has ester groups that can form hydrogen bonds with water molecules, but the hydrogen bonding are not extensive because the ester groups can only function as hydrogen bond acceptors. Hence, clothing made from polymer **Q** is not as comfortable as that made from cotton. Clothing made from poly(propene) is the least comfortable because the polymer is made up of non-polar hydrocarbon chains that cannot form strong attractive forces with water molecules.

(d) **R** and **S** represent the repeating unit of a synthetic polymer and a section of a natural material, respectively.



R



S

(i) State the type of compound represented by **R** and the type of compound represented by **S**.

Explanation:

Compound **R** is a synthetic polyamide, whereas **S** is a natural polyamide (or biological polyamide).

(ii) Name the polymerization process that results in **R** and **S**.

Explanation:

Both **R** and **S** are formed from condensation polymerization.

(iii) What is the name given to the unit that makes up **S**?

Explanation:

Compound **S** is formed from amino acid monomers, i.e.,

$HOOC-CH(CH_2OH)-NH_2$ and $HOOC-CH(CH_3)-NH_2$

(iv) Suggest two similarities and two differences between **R** and **S**.

Explanation:

Both polymers **R** and **S** have amide linkages that hold the monomeric units together. Consequently, they are both susceptible to hydrolysis in the presence of acids and alkalis. However, they will produce different hydrolyzed products. The hydrolysis of polymer **S** produces amino acids, whereas that of **R** produces two products — diamine and dicarboxylic acid molecules. For both polymers **R** and **S**, there are hydrogen bonds between the amide groups on different polymer chains. However, for polymer **S**, hydrogen bonds can also form between the alcohol side chains. In addition, polymer **S** contain chiral centers, while polymer **R** does not.

(v) Both the synthetic polymer **R** and the natural material **S** can be dyed to give a uniform color.

(A) Why do you think that the molecules of the two polymers might behave in the same way with the molecules of a dyestuff?

Explanation:

Dyes adhere to materials through different types of intermolecular forces of attractions which depend on the molecular structures of these substances. If the molecules of polymers **R** and **S** behave in the same way with the molecules of a dyestuff, it indicates that the molecules of these polymers form a similar type of attractive force with the molecules of the dyestuff.

(B) What type of bonding will be involved between the polymer and molecules of the dyestuff?

Explanation:

Since both polymers **R** and **S** have amide functional groups (and alcohol side chains in the latter), hydrogen bonding exists between the molecules of the polymers and the dyestuff.

(C) Suggest a disadvantage of making carpets with such a polymer.

Explanation:

Both polymers **R** and **S** are susceptible to hydrolysis of the amide linkages in the presence of acids and alkalis. Thus, long-term exposure to such chemicals can cause the carpet to be less wear-resistant. In addition, water molecules are able to form hydrogen bonds with the amide linkages of the polymer; this would make the carpet difficult to dry after it comes in contact with water.

(vi) Polymer **R** is known as nylon-6,6 in the industry and it is made by reacting a diacid chloride rather than the corresponding dicarboxylic acid with a diol. Suggest a reason why the dicarboxylic acid is not preferred.

Explanation:

A dicarboxylic acid is not preferred because it is less reactive than a diacid chloride. This is due to the fact that the carboxylic acid has a less electron-deficient carbonyl carbon, which is less susceptible to nucleophilic attack during the condensation reaction. Second, the –OH group is not as good a leaving group as compared to the –Cl substituent.

Q Since oxygen is more electronegative than chlorine, shouldn't the carbonyl carbon in a carboxylic acid be more electron-deficient as it is bonded to two oxygen atoms?

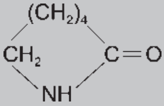
A: It is not wrong to make the above statement, but given the observed trends in reactivity (e.g., an acid chloride reacts with an alcohol at room temperature, whereas a carboxylic acid requires the use of a catalyst and heating), there must be other factors that come into play. In this case, we have to look at how the lone pair of electrons from the Cl and O atoms delocalize into the carbonyl functional group, thus affecting the electron deficiency of the carbonyl carbon. For such delocalization to take place in the acid chloride, the 3*p* orbital bearing the lone pair of electrons on chlorine has to overlap with the 2*p* orbital of the carbonyl carbon. This 2*p*–3*p* orbital overlap is less effective than the 2*p*–2*p* orbital overlap between oxygen and carbon atoms. Therefore, the delocalization of electron through resonance for the carboxylic acid is more effective, resulting in an increase in electron density on the carbonyl carbon, which thus makes it less electron-deficient.

(vii) Nylon-6,6 is almost twice as strong as poly(propene). Suggest possible explanations for the observed phenomenon.

Explanation:

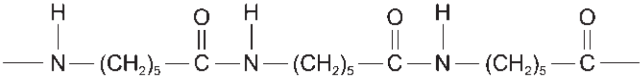
Nylon-6,6 is stronger than poly(propene) because of extensive intermolecular hydrogen bonding between the amide groups on the different polymer chains. These attractive forces are much stronger than the instantaneous dipole–induced dipole interaction present between the polymer chains in poly(propene).

(e) Nylon-6 is produced from caprolactam:



(i) Draw a section of the polymer showing three repeat units.

Explanation:



$$-N(H)-(CH_2)_5-C(=O)-N(H)-(CH_2)_5-C(=O)-N(H)-(CH_2)_5-C(=O)-$$

(ii) Name the functional group that is present in the polymer.

Explanation:

The amide functional group is present in the polymer.

(iii) Suggest what conditions might be required for the polymerization of caprolactam.

Explanation:

Since caprolactam is a cyclic amide, its polymerization involves ring-opening using hydrolysis and the subsequent removal of water at high temperatures.

(iv) Give a name for the mechanism responsible for the polymerization.

Explanation:

Condensation polymerization takes place to form the polymer.

(v) Suggest two uses of nylon-6.

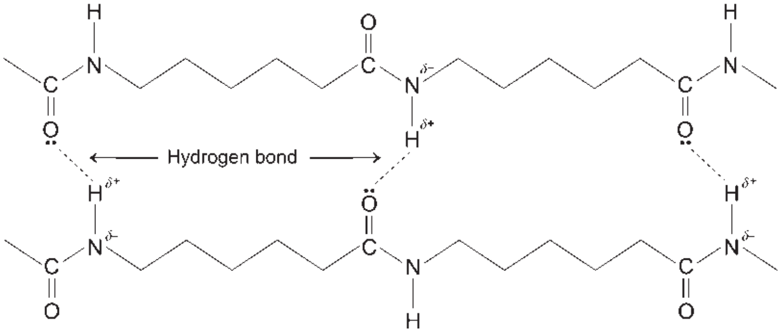
Explanation:

Nylon-6 is used as strings for musical instruments and also for gears and bearings in automobile and machine parts.

(vi) Explain, with the aid of a diagram, why nylon-6 has a high tensile strength when drawn into fibers.

Explanation:

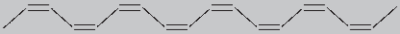
The extensive hydrogen bonding between polymer chains account for the high tensile strength of nylon-6.



Q What is tensile strength?

A: Tensile strength refers to the maximum stress that a material can withstand before it shows significant narrowing of its cross-sectional area or deformation of its body shape. The stress is measured by acting a force on a unit area of the material. It has a unit of force per area, which is N m^{-2}, same as that for pressure.

(vii) Although nylon is a good electrical insulator, there are polymers which are also good electrical conductors, such as the following:



(A) Identify the monomer.

Explanation:

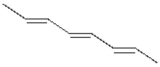
The polymer is an addition polymer formed from the ethyne monomer,

$$H—C\equiv C—H$$

(B) What type of stereoisomerism is exhibited by the above polymer? Draw a diagram of a section of the above polymer in the other stereoisomeric form.

Explanation:

The polymer exhibits *cis-trans*/geometrical isomerism. The question depicts the *cis* isomer since the H atoms that are attached to the doubly bonded carbon atoms are on the same side of the C=C double bond. Hence, the diagram to be drawn is that of the *trans* isomer as shown:



(C) Give a reason why the above polymer is able to conduct electricity and predict what will happen when the polymer is heated with buta-1,2-diene.

Explanation:

The *p* orbitals of the sp^2 hybridized C atoms can overlap side-on to form a continuous network of delocalized electrons. When a voltage is applied, these delocalized electrons are free to move along the polymeric chains to conduct electricity.

When the polymer is heated with buta-1,2-diene, sigma bonds can form between buta-1,2-diene and the different polymeric chains, utilizing the pi electrons that both molecules have. As a result, there may not be an extensive network of alternating C=C bonds, which would thus cause the polymer to lose its electrical conductivity.

Q So, if the buta-1,2-diene joins different polymeric chains together, would this increase the tensile strength and decrease the flexibility of the polymer?

A: Yes, it would. With different polymeric chains being connected, the intermolecular forces between these larger polymeric chains are stronger. In addition, the larger the polymeric chain, the more rigid it is as it is difficult for a larger molecule to "wriggle" around, hence the less flexible the polymer would be.

(D) What similar property does the polymer share with graphite?

Explanation:

Graphite has a giant layered structure made of sp^2 hybridized carbon atoms covalently bonded to three other carbon atoms within each layer and thus, there is a continuous network of delocalized electrons within each layer. Between the layers are weak van der Waals attractive forces.

The polymer has a similar structure in the sense that it has a continuous network of delocalized electrons within a polymer chain. Between them are also weak van der Waals' attractive forces.

Hence, both polymer and graphite can conduct electricity only when a voltage is applied along the chains or layers, but not when it is applied across the chains or layers, respectively.

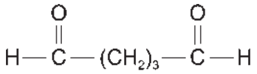
2. (a) Compound **T**, $C_5H_8O_2$, reacts with acidified potassium manganate(VII) to give **U** of molecular formula, $C_5H_8O_4$. Compound **T** also reacts with $LiAlH_4$ to form compound **V**, $C_5H_{12}O_2$. Both **U** and **V** react together with a catalyst to form a macromolecule.

   (i) Deduce the constitutional/structural formulae of **T** to **V**.

Explanation:

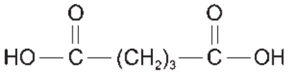
Compound **T** is oxidized by $KMnO_4$ to form **U**.	⇒	Since there is an increase of two O atoms, compound **U** is a dicarboxylic acid. Thus, compound **T** can contain a primary alcohol group and/or aldehyde group.
Compound **T** is reduced by $LiAlH_4$ to form **V**.	⇒	Since there is an increase of four H atoms, compound **T** must contain two aldehyde groups that are reduced to primary alcohols present in compound **V**.

Hence, compounds **T**, **U**, and **V** are deduced as shown:



$H-\overset{O}{\overset{\|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-H$

T



$HO-\overset{O}{\overset{\|}{C}}-(CH_2)_3-\overset{O}{\overset{\|}{C}}-OH$

U

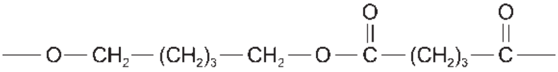
$HO-CH_2-(CH_2)_3-CH_2-OH$

V

(ii) Write a repeat unit of the macromolecule formed.

Explanation:

Compound **U** and **V** undergo condensation reaction to form a polyester with a repeat unit as shown below:



$$-O-CH_2-(CH_2)_3-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-(CH_2)_3-\overset{\overset{\displaystyle O}{\|}}{C}-$$

(iii) Suggest a suitable catalyst for the synthesis of the macromolecule.

Explanation:

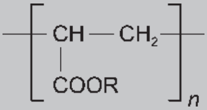
Since the condensation polymerization is actually an esterification reaction, concentrated sulfuric acid can be a suitable catalyst.

(iv) The macromolecular compound is not suitable to be made into a container to hold alkaline solutions. Suggest a reason for this.

Explanation:

The condensation polymer is unstable in the presence of alkalis (and acids) since hydrolysis of the ester linkages will occur. Prolonged exposure to alkalis (and acids) may cause degradation of the polyester since it is broken down into smaller molecules.

(b) A polymer represented by the following formula is obtained from a monomer of **W**:



$$-\!\!\left[\begin{array}{l} CH-CH_2 \\ | \\ COOR \end{array}\right]_n\!\!-$$

(i) What type of polymerization is taking place?

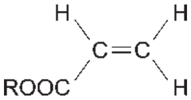
Explanation:

Addition polymerization is taking place.

(ii) Draw the constitutional/structural formula of monomer **W**.

Explanation:

The addition polymer is formed from the following monomer **W** that contains C=C bond:



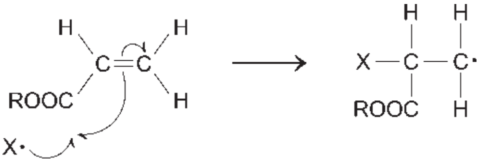
Q How can one identify the monomer/s that make up a polymer?

A: It is very simple. The polymer is usually presented in the head-to-tail or tail-to-head configuration. All you need to do is to move along the carbon backbone (from left to right) and identify the next repeat unit. The position where the head is bonded to the tail of the two repeat units would be the positions of the double bonds in the monomers. If there is a systematic occurrence of a double bond in the polymer, then the original monomer is likely to contain a 1,3-dienes group ($-C=C-C=C-$). If there are two double bonds that occur systematically in the polymer, then the monomer would contain the 1,3,5-trienes group ($-C=C-C=C-C=C-$).

(iii) The polymerization process is initiated by a radical X•. Write equations to show how the radical initiates the reaction, followed by another reaction with a second monomer.

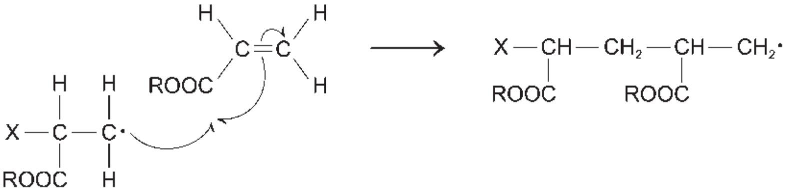
Explanation:

Step 1: Chain initiation.



The initiator X• attacks the alkene molecule to form a bond with one of the doubly bonded carbon atom, causing the pi bond to cleave homolytically and producing a new radical.

Step 2: Chain propagation.



The chain lengthens with each successive attack of the growing polymer chain radical on another monomer. Chain propagation ends when there are no more individual monomers or when chain termination occurs.

Q Would different amounts of initiators affect the type of polymers that we get?

A: The amount of initiator to the monomer would affect the molecular weight of the polymer obtained. If a larger amount of initiator is used, there would be a greater amount of the free radical monomer units created in the beginning, which would lead to a greater amount of monomers being added to the large number of different radical sites per unit time. This would cause a high depletion rate of the monomers, resulting in shorter polymer chains being formed.

(iv) If the R group in the monomer is a phenyl group, the polymer formed is less flexible, with a higher melting point than another similar polymer, where the R group is a $-CH_3$ group. Explain the differences in the physical properties observed.

Explanation:

The polymer containing phenyl groups as side chains is less flexible because the bulky benzene rings force the polymer molecules to adopt a particular spatial conformation that restricts their movement.

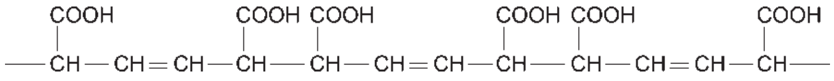
This polymer has a higher melting point because of stronger instantaneous dipole–induced dipole interactions attributed by the large electron cloud of the benzene rings.

(c) Muconic acid, HOOC−CH=CH−CH=CH−COOH, is capable of undergoing polymerization to produce a polymer with a high melting point.

(i) Draw a section of the polymer showing three repeat units.

Explanation:

Muconic acid undergoes addition polymerization to form the polymer with the following repeat units:



$$-\overset{\text{COOH}}{\overset{|}{\text{CH}}}-\text{CH}=\text{CH}-\overset{\text{COOH}}{\overset{|}{\text{CH}}}-\overset{\text{COOH}}{\overset{|}{\text{CH}}}-\text{CH}=\text{CH}-\overset{\text{COOH}}{\overset{|}{\text{CH}}}-\overset{\text{COOH}}{\overset{|}{\text{CH}}}-\text{CH}=\text{CH}-\overset{\text{COOH}}{\overset{|}{\text{CH}}}-$$

(ii) Suggest a reason why the melting point of the polymer is high.

Explanation:

The melting point of the polymer is high because of extensive hydrogen bonding between the carboxylic acid side chains on different polymer chains.

Do you know?

— The hydrogen bond that is formed between the −COOH groups is stronger than that formed between the alcohol molecules because of the greater electron deficiency of the H atom, as it is bonded to a highly electron-withdrawing −CO− group.

(iii) The polymer is likely to disintegrate under alkaline conditions. Suggest a reason for the phenomenon.

Explanation:

The carboxylic acid side chains will undergo an acid–base reaction in the alkaline medium. Consequently, the carboxylate side chains cannot form hydrogen bonds with each other and instead, the inter-electronic repulsion between the negatively charged $-COO^-$ groups would weaken the intermolecular forces between the polymeric chains. Hence, disintegration is resulted.

(iv) The polymer can be further hardened through heating with sulfur. Explain why it is possible for the hardening to take place.

Explanation:

The heating of the polymer with sulfur causes the polymer to undergo vulcanization which increases cross-linking between polymer chains through the formation of disulfide bonds. The high degree of cross-linking causes the polymer to be hard and rigid because it restricts the freedom of movement of individual chains.

(d) A bottle containing phenyl(ethene) turns cloudy with some white suspension when exposed to air. Account for the formation of the white solid.

Explanation:

When exposed to air, the radicals that are being generated in the air can initiate the free radical polymerization of phenyl(ethene). As the polymer grows in length with a high relative molecular mass, it becomes a dense white solid.

(e) Explain how ethene can produce both low-density and high-density polymers.

Explanation:

When subjected to the polymerization process, new covalent bonds form between the monomers, linking them up to form either long linear chains or an extensive three-dimensional structural network. When linear polymer chains stack on top of each other, they pack well together with extensive van der Waals forces of attraction between them. This leads to a linear polymer with high density of which high-density poly(ethene) is an example.

Low-density poly(ethene) is a branched-chain polymer. Branches are created during the free radical polymerization process, when there is no sequential attack of a growing polymer chain radical on a monomer but rather random attacks of any polymer chain radical on the carbon backbone. These branched chains tend to pack in an irregular manner, causing the polymer to have low density.

Q Why does branched-chain poly(ethene) have a lower density, melting point, and tensile strength?

A: The branches of branched-chain poly(ethene) prevent maximum surface area of contact between the polymeric molecules. As a result, the intermolecular forces between the molecules are not extensive, leading to a lower melting point and also a greater distance of separation between the molecules. The greater distance of separation results in a lower density as the mass per unit volume is smaller. The lower tensile strength arises because of the weaker intermolecular forces. Thus, take note that generally, branched-chain polymers would have a lower melting point, density, and tensile strength than linear-chain polymers of the same type.

(f) Explain the differences between thermosetting and thermoplastic materials, and give an example of each.

Explanation:

Thermosets and thermoplastics are affected in different ways by the action of heat. Thermoplastics soften when heated and harden again on cooling. An example of a thermoplastic is poly(styrene). Such materials can be melted and molded or reshaped into various useful products such as food packaging. On the other hand, thermosets harden when heated and do not soften again. An example of a thermoset is melamine, which is used in dinnerware. As they do not melt when heated, they are generally stronger than thermoplastics and are a suitable material for use in situations where strong heat (below the decomposition temperature) and abrasion are involved.

Q Why does heat have a different effect on thermoplastics and thermosets, causing them to exhibit different physical properties, and hence, uses?

A: Polymers are different because of the differences in the compositions and molecular structures. These differences in the compositions and molecular structures cause the bonding between the polymeric molecules to be different, hence resulting in different physical and chemical properties.

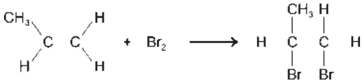
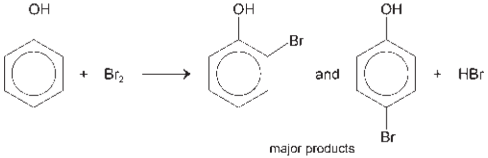
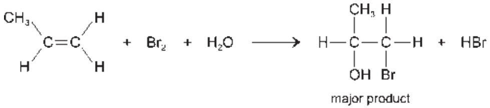
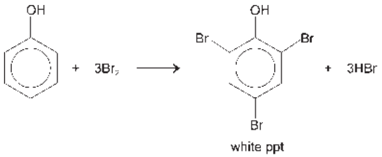
Q How can the thermoset further harden on heating? Does that mean more bonds are being formed during the heating process?

A: For thermoset polymers, once the polymer is synthesized, cross-linking is not completed, which means there are still cross-linking sites available but they are not in close proximity. When we heat the polymer again, the heating would cause the molecules to be more mobile due to a greater amount of vibrational and rotational energies. These would allow the molecules to re-orientate themselves, resulting in the cross-linking sites to be in close proximity.

CHAPTER 14

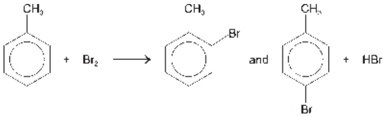
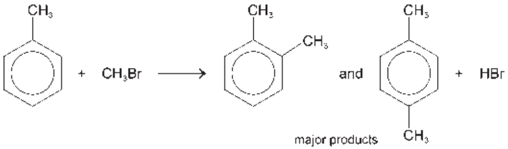
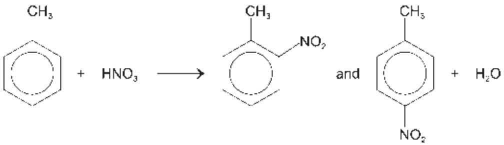
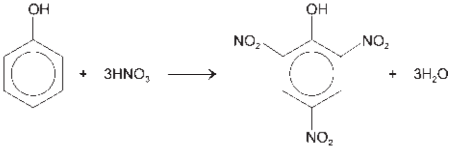
SUMMARY OF IMPORTANT ORGANIC REACTIONS

ELECTROPHILE: Electron-deficient species (Lewis acid) that accepts a lone pair of electrons in forming a bond with an electron-rich species (Lewis base).

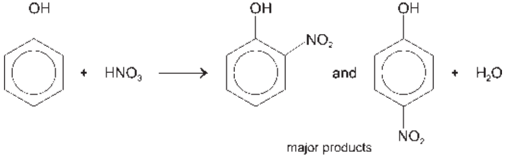
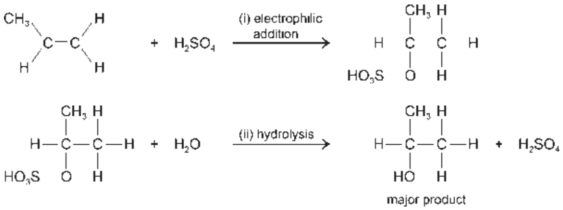
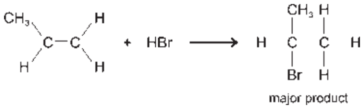
Reagent*	Conditions	Reactive Group	Type of Reaction	Equation
Br_2/Cl_2	CCl_4 r.t.p.	Alkene	Electrophilic Addition	
		Phenol & Phenylamine[#]	Electrophilic Substitution	
$Br_2(aq)/Cl_2(aq)$	r.t.p.	Alkene	Electrophilic Addition	
		Phenol & Phenylamine [#]Note: Phenylamine gives trisubstituted product with Br_2/Cl_2 in CCl_4.	Electrophilic Substitution	

*Decolourisation of reddish-brown Br_2 (org) / yellowish-brown Br_2 (aq)

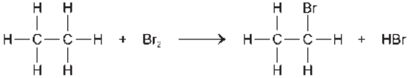
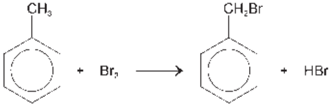
A LEWIS ACID, such as $AlBr_3$ and $FeBr_3$, is an electron-deficient species which can function as an electron-pair acceptor to generate a stronger electrophile.

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
Br_2	anhydrous $AlBr_3$/ $FeBr_3$ r.t.p.	Arene	Electrophilic Substitution	 Decolourisation of reddish-brown Br_2 (l)
Cl_2	anhydrous $AlCl_3$/ $FeCl_3$ r.t.p.			
RBr e.g. CH_3Br RCl e.g. CH_3Cl	anhydrous $AlBr_3$/ $FeBr_3$ r.t.p. anhydrous $AlCl_3$/ $FeCl_3$ r.t.p.	Arene	Electrophilic Substitution	
Concentrated HNO_3	concentrated H_2SO_4 reflux at 30ºC	Arene	Electrophilic Substitution	
Concentrated HNO_3	r.t.p.	Phenol	Electrophilic Substitution	

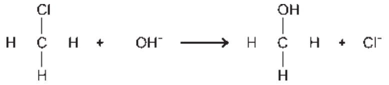
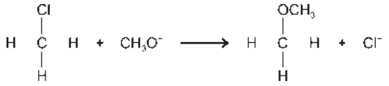
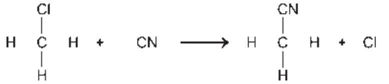
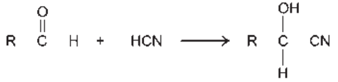
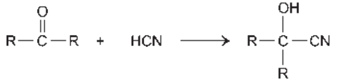
ELECTROPHILE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
Dilute $HNO_3(aq)$	r.t.p.	Phenol Note: Phenylamine undergoes acid-base reaction with $HNO_3(aq)$.	Electrophilic Substitution	
Step (i): Concentrated H_2SO_4	Step (i): cold temp.	Alkene	Electrophilic Addition	
Step (ii): H_2O	Step (ii): heat			
$H_2O(g)$	H_3PO_4 on celite, 60 atm, 330ºC			
dry HBr(g)/ HCl(g)/ HI(g)	r.t.p.	Alkene	Electrophilic Addition	

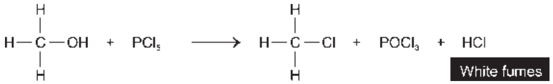
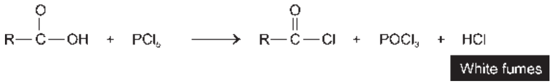
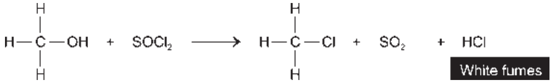
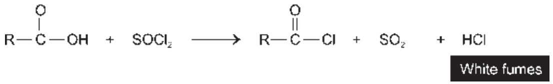
FREE RADICAL: Electron-deficient species with an unpaired electron that seeks another unpaired electron by forming a bond.

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
$Br_2/Cl_2/F_2$	UV light/heat	Alkane	Free Radical Substitution	  Decolourisation of reddish-brown Br_2 (l) Note: Polysubstitution is inevitable but yield of desired product can be managed to a certain degree. Use excess alkane to obtain mono-substituted compound as the main product.

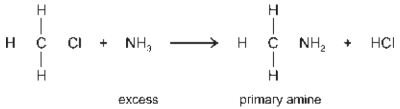
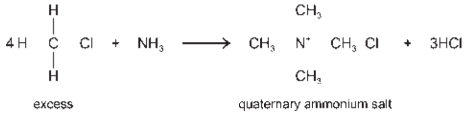
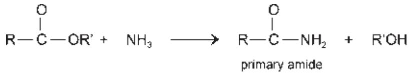
NUCLEOPHILES: Electron-rich species (Lewis base) that donates a lone pair of electrons in forming a bond with an electron-deficient species (Lewis acid).

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
NaOH(aq)/ KOH(aq)	heat	Halogenoalkane	Nucleophilic Substitution $RX \rightarrow ROH$	
$RO^{-}Na^{+}$ e.g. $CH_3O^{-}Na^{+}$	alcohol, ROH e.g. CH_3OH r.t.p.	Halogenoalkane	Nucleophilic Substitution $RX \rightarrow ROR'$	
NaCN(aq) / KCN(aq)	ethanol heat	Halogenoalkane	Nucleophilic Substitution $RX \rightarrow RCN$ Nitrile formed has 1 more C atom	 Note: Halogenoarene does not undergo nucleophilic substitution because the C–X bond has partial double bond character and is harder to cleave than the C–X bond in halogenoalkane.
HCN	small amount of NaOH/ KOH/ NaCN/ KCN 10–20ºC	Aldehydes & Ketones	Nucleophilic Addition Cyanohydrin formed has 1 more C atom	 

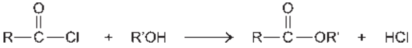
NUCLEOPHILE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
PCl_5	r.t.p.	Aliphatic alcohol	Nucleophilic Substitution ROH → RCl	 $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}OH + PCl_5 \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}Cl + POCl_3 + HCl}$
		Carboxylic acid	Nucleophilic Acyl Substitution RCOOH → RCOCl	 $\mathrm{R{-}\overset{O}{\overset{\Vert}{C}}{-}OH + PCl_5 \longrightarrow R{-}\overset{O}{\overset{\Vert}{C}}{-}Cl + POCl_3 + HCl}$
$SOCl_2$	r.t.p.	Aliphatic alcohol	Nucleophilic Substitution ROH → RCl	 $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}OH + SOCl_2 \longrightarrow H{-}\overset{H}{\underset{H}{C}}{-}Cl + SO_2 + HCl}$
		Carboxylic acid	Nucleophilic Acyl Substitution RCOOH → RCOCl	 $\mathrm{R{-}\overset{O}{\overset{\Vert}{C}}{-}OH + SOCl_2 \longrightarrow R{-}\overset{O}{\overset{\Vert}{C}}{-}Cl + SO_2 + HCl}$
$PCl_3/PBr_3/$ red P + I_2	r.t.p.	Aliphatic alcohol Carboxylic acid	Nucleophilic Substitution ROH → RX RCOOH → RCOX	$3ROH + PCl_3 \longrightarrow 3RCl + H_3PO_3$ $3RCOOH + PCl_3 \longrightarrow 3ROCl + H_3PO_3$ Note: Phenol does not undergo Nucleophilic Substitution because the C–O bond has partial double bond character and is harder to cleave than the C–O bond in aliphatic alcohols.

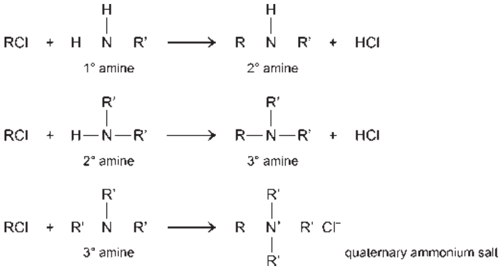
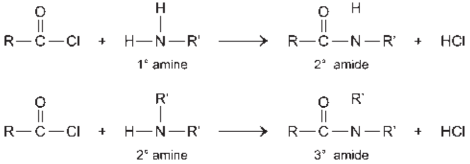
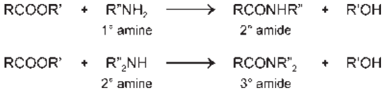
NUCLEOPHILE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
NH_3	excess conc. NH_3 ethanol heat in sealed tube	Halogenoalkane	Nucleophilic Substitution $RX \rightarrow RNH_2$	 Note: In reality, $NH_4^+Cl^-$ is formed instead of HCl as the latter undergoes acid–base reaction with NH_3.
	limited conc. NH_3 ethanol heat in sealed tube	Halogenoalkane	Nucleophilic Substitution $RX \rightarrow R_4N^+X^-$ Polysubstitution favoured	
	excess NH_3 r.t.p. sealed tube	Acid halide (Acyl halide)	Nucleophilic Acyl Substitution $RCOX \rightarrow RCONH_2$	
	excess NH_3 heat in sealed tube	Ester	Nucleophilic Acyl Substitution $RCOOR \rightarrow RCONH_2$	 Note: NH_3 undergoes an acid–base reaction with carboxylic acid instead of amide formation.

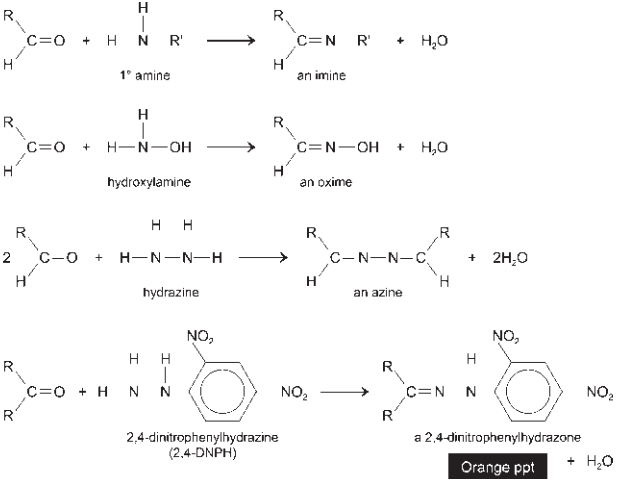
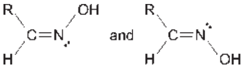
NUCLEOPHILE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
Aliphatic alcohol e.g. CH_3OH	conc. H_2SO_4 catalyst heat	Carboxylic acid	Nucleophilic Acyl Substitution	 $\mathrm{R-C(=O)-OH + R'OH \rightleftharpoons R-C(=O)-OR' + H_2O}$
	anhydrous reagents r.t.p.	Acid halide (Acyl halide)	Nucleophilic Acyl Substitution	 $\mathrm{R-C(=O)-Cl + R'OH \longrightarrow R-C(=O)-OR' + HCl}$
Phenol	anhydrous reagents r.t.p.	Acid halide (Acyl halide)	Nucleophilic Acyl Substitution	 Note: Phenol can be treated with NaOH(aq) to form the phenoxide ion that is a stronger nucleophile. Both phenol and the phenoxide ion will form the same ester with a given acid halide. However, both phenol and the phenoxide ion do not react with a carboxylic acid to form an ester. Phenol is a weaker nuclephile than aliphatic alcohols and carboxylic acids are less reactive than acid halides, Hence, phenol and carboxylic acids do not react together. As for the phenoxide ion, it undergoes an acid–base reaction with carboxylic acids.

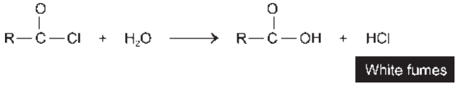
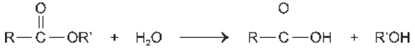
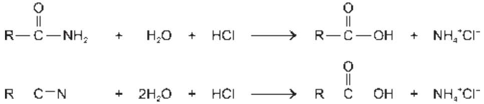
NUCLEOPHILE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
1° amine/ 2° amine/ 3° amine	excess amine ethanol heat in sealed tube	Halogenoalkane	Nucleophilic Substitution	 Note: Excess halogenoalkane will favor the formation of polysubstituted products.
1° amine/ 2° amine	excess amine r.t.p. sealed tube	Acid halide (Acyl halide)	Nucleophilic Acyl Substitution	
	excess amine heat in sealed tube	Ester	Nucleophilic Acyl Substitution	 $RCOOR' + \underset{1^\circ\ \text{amine}}{R''NH_2} \longrightarrow \underset{2^\circ\ \text{amide}}{RCONHR''} + R'OH$ $RCOOR' + \underset{2^\circ\ \text{amine}}{R''_2NH} \longrightarrow \underset{3^\circ\ \text{amide}}{RCONR''_2} + R'OH$ Note: Amines undergo an acid–base reaction with carboxylic acids instead of amide formation.

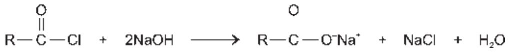
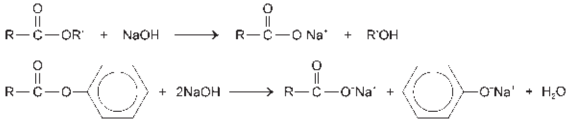
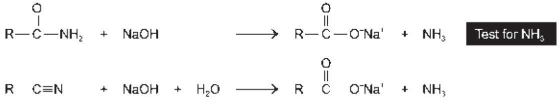
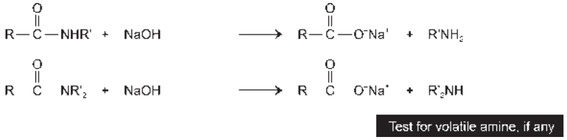
NUCLEOPHILE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
1° amine/ 2,4-DNPH or compounds with –NH_2 group e.g. NH_2OH & NH_2NH_2	r.t.p.	Aldehyde & Ketone	Condensation/ Addition–Elimination	 Note: Geometrical isomerism is exhibited by compounds containing the C=N bond, provided that there are different substituents bonded to the C atom of the C=N bond. E.g. are a pair of geometrical isomers.

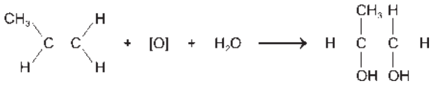
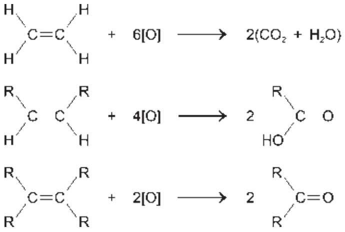
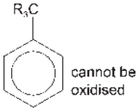
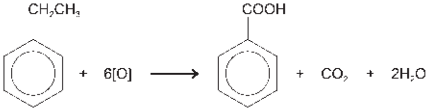
NUCLEOPHILE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
H_2O	Note: reaction occurs rapidly with cold H_2O	Acid halide (Acyl halide)	Hydrolysis $RCOX \rightarrow RCOOH + HX$	 $RCOCl + H_2O \longrightarrow RCOOH + HCl$ Note: - RCOX hydrolyzed readily upon contact with water to produce white fumes of HX. - When $AgNo_3(aq)$ is added to RCOX, AgX(s) ppt is seen immediately. This test thus serves to distinguish between RCOX and RX. The latter products ppt only upon heating.
HCl(aq)/ $H_2SO_4(aq)$ Note: H_2O is the nucleophile. Acid is added as a catalyst.	heat	Ester	Acidic Hydrolysis $RCOOR' \rightarrow RCOOH + R'OH$	 $RCOOR' + H_2O \longrightarrow RCOOH + R'OH$
		1º Amide & Nitrile	Acidic Hydrolysis $RCONH_2$ or $RCN \rightarrow RCOOH + NH_4^+$	 $RCONH_2 + H_2O + HCl \longrightarrow RCOOH + NH_4^+Cl^-$ $RCN + 2H_2O + HCl \longrightarrow RCOOH + NH_4^+Cl^-$
		2º & 3º Amide	Acidic Hydrolysis $RCONHR' \rightarrow RCOOH + R'NH_3^+$ $RCONR'_2 \rightarrow RCOOH + R'_2NH_2^+$	 $RCONHR' + H_2O + HCl \longrightarrow RCOOH + R'NH_3^+Cl^-$ $RCONR'_2 + H_2O + HCl \longrightarrow RCOOH + R'_2NH_2^+Cl^-$

NUCLEOPHILE

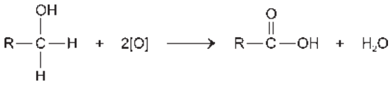
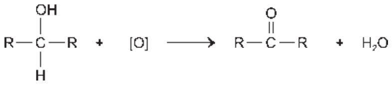
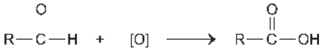
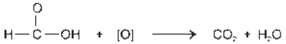
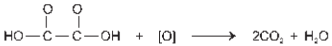
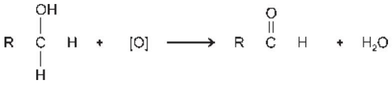
Reagent	Conditions	Reactive Group	Type of Reaction	Equation
NaOH(aq) / KOH(aq)	Note: Reaction occurs rapidly with cold solution	Acid halide (Acyl halide)	Alkaline Hydrolysis $RCOX \rightarrow RCOO^- + X^-$	 $RCOCl + 2NaOH \longrightarrow RCOO^-Na^+ + NaCl + H_2O$
	heat	Ester	Alkaline Hydrolysis $RCOOR' \rightarrow RCOO^- + R'OH$	 $RCOOR' + NaOH \longrightarrow RCOO^-Na^+ + R'OH$ Note: In alkaline hydrolysis, both the carboxylic acid and acidic phenol will undergo an acid–base reaction. Hence, carboxylate and phenoxide ions are obtained instead.
		1° Amide & Nitrile	Alkaline Hydrolysis $RCONH_2$ or $RCN \rightarrow RCOO^- + NH_3$	 $RCONH_2 + NaOH \longrightarrow RCOO^-Na^+ + NH_3$ $RC{\equiv}N + NaOH + H_2O \longrightarrow RCOO^-Na^+ + NH_3$
		2° & 3° Amide	Alkaline Hydrolysis $RCONHR' \rightarrow RCOO^- + R'NH_2$ $RCONR'_2 \rightarrow RCOO^- + R'_2NH$	 $RCONHR' + NaOH \longrightarrow RCOO^-Na^+ + R'NH_2$ $RCONR'_2 + NaOH \longrightarrow RCOO^-Na^+ + R'_2NH$

OXIDISING AGENT: It oxidizes another compound and is itself reduced in the process.

Reagent*	Conditions	Reactive Group	Type of Reaction	Equation
$KMnO_4$(aq)	NaOH(aq)/ KOH(aq) cold temp.	Alkene	Oxidation (breaking of pi bond)	
$KMnO_4$(aq)	H_2SO_4(aq) heat	Alkene	Oxidative cleavage of C=C bond	 Test for CO_2 Note: If hot alkaline $KMnO_4$ is used, cleavage of the C=C bond would occur. However, CO_2 is not evolved as it undergoes an acid–base reaction in the alkaline medium. Likewise, a carboxylate salt is formed instead of the carboxylic acid due to neutralization of the latter.
		Alkylbenzene 	Oxidation of alkyl side-chain on benzene	 Test for CO_2 Note: Benzoic acid is a white solid which is insoluble in cold water, becomes soluble on warming and reappears as a white solid on cooling.

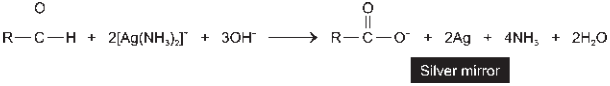
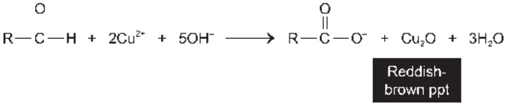
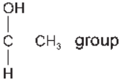
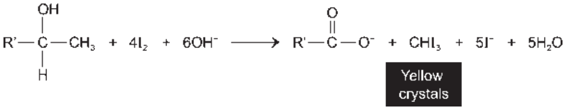
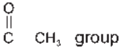
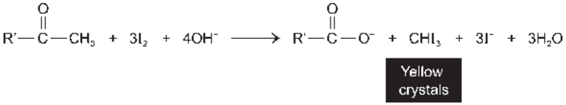
*Decolourisation of purple aq. $KMnO_4$ (and brown ppt of MnO_2 if alkali is used)

OXIDISING AGENT

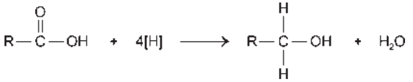
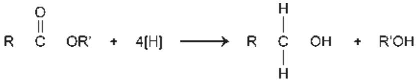
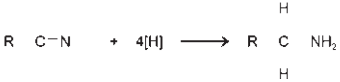
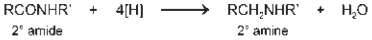
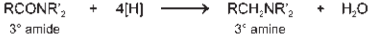
Reagent*	Conditions	Reactive Group	Type of Reaction	Equation
$KMnO_4$(aq) / $K_2Cr_2O_7$(aq)	H_2SO_4(aq) heat	Alcohol: Only 1° ROH & 2° ROH	1° ROH → RCOOH	 $R-\overset{OH}{\underset{H}{\overset{\vert}{\underset{\vert}{C}}}}-H + 2[O] \longrightarrow R-\overset{O}{\overset{\Vert}{C}}-OH + H_2O$
			2° ROH → ketone	 $R-\overset{OH}{\underset{H}{\overset{\vert}{\underset{\vert}{C}}}}-R + [O] \longrightarrow R-\overset{O}{\overset{\Vert}{C}}-R + H_2O$
		Aldehyde	RCHO → RCOOH	 $R-\overset{O}{C}-H + [O] \longrightarrow R-\overset{O}{\overset{\Vert}{C}}-OH$
$KMnO_4$(aq)	H_2SO_4(aq) heat	HCOOH & $(COOH)_2$	Both acids → CO_2	 $H-\overset{O}{\overset{\vert}{C}}-OH + [O] \longrightarrow CO_2 + H_2O$ Test for CO_2  $HO-\overset{O}{\overset{\vert}{C}}-\overset{O}{\overset{\vert}{C}}-OH + [O] \longrightarrow 2CO_2 + H_2O$
$K_2Cr_2O_7$(aq)	H_2SO_4(aq) heat with immediate distillation	Alcohol: only 1° ROH & 2° ROH Aldehyde	1° ROH → aldehyde 2° ROH → ketone RCHO → RCOOH	 $R\ \overset{OH}{\underset{H}{\overset{\vert}{\underset{\vert}{C}}}}\ H + [O] \longrightarrow R\ \overset{O}{\overset{\Vert}{C}}\ H + H_2O$ Note: The aldehyde formed is immediately distilled off from the reaction vessel to prevent it from being further oxidized.

*Decolourisation of purple $KMnO_4$(aq) / Orange $K_2Cr_2O_7$(aq) turns green

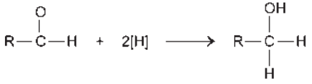
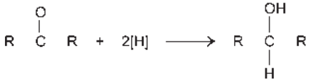
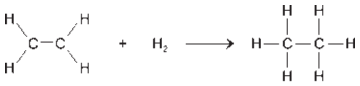
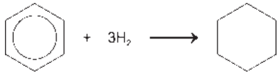
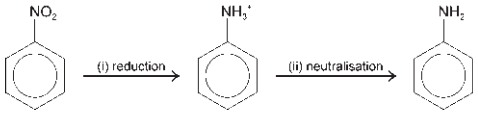
OXIDISING AGENT

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
Tollens' reagent	heat	Aldehyde: Both aliphatic & aromatic RCHO	$RCHO \rightarrow RCOO^-$ Reaction occurs in alkaline medium	 $R-\overset{O}{C}-H + 2[Ag(NH_3)_2]^+ + 3OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + 2Ag + 4NH_3 + 2H_2O$
Fehling's solution	heat	Aliphatic aldehyde	$RCHO \rightarrow RCOO^-$ Reaction occurs in alkaline medium	 $R-\overset{O}{C}-H + 2Cu^{2+} + 5OH^- \longrightarrow R-\overset{O}{\overset{\|}{C}}-O^- + Cu_2O + 3H_2O$
$I_2(aq)$	NaOH(aq)/ KOH(aq) warm	Alcohol that has  $\underset{H}{\overset{OH}{C}}$ CH_3 group	Oxidation to give $RCOO^-$ with 1 less C atom	 $R'-\underset{H}{\overset{OH}{C}}-CH_3 + 4I_2 + 6OH^- \longrightarrow R'-\overset{O}{\overset{\|}{C}}-O^- + CHI_3 + 5I^- + 5H_2O$ Note: R′ must be either a H atom or another C atom.
		Ketone that has  $\overset{O}{\overset{\|}{C}}$ CH_3 group	Oxidation to give $RCOO^-$ with 1 less C atom	 $R'-\overset{O}{\overset{\|}{C}}-CH_3 + 3I_2 + 4OH^- \longrightarrow R'-\overset{O}{\overset{\|}{C}}-O^- + CHI_3 + 3I^- + 3H_2O$ Note: R′ must be either a H atom or another C atom.

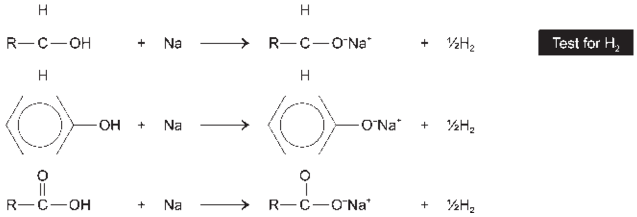
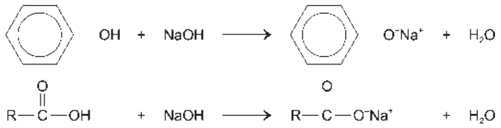
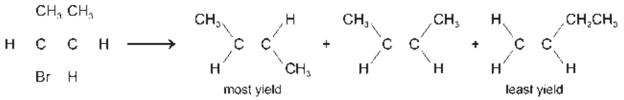
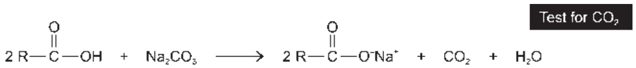
REDUCING AGENT: It reduces another compound and is itself oxidized in the process.

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
Step (i): $LiAIH_4$ Step (ii): H_2O	Step (i): dry ether r.t.p. Step (ii): heat	Carboxylic acid	Reduction $RCOOH \rightarrow 1^{o}$ ROH	
		Ester	$RCOOR' \rightarrow 1^{o}$ ROH + R'OH	
		1^{o} Amide & Nitrile	$RCONH_2$ or RCN $\rightarrow RCH_2NH_2$	 
		2^{o} & 3^{o} Amide	$RCONHR' \rightarrow RCH_2NHR'$ $RCONR'_2 \rightarrow RCH_2NR'_2$	 $\underset{2^{\circ}\text{ amide}}{RCONHR'} + 4[H] \longrightarrow \underset{2^{\circ}\text{ amine}}{RCH_2NHR'} + H_2O$  $\underset{3^{\circ}\text{ amide}}{RCONR'_2} + 4[H] \longrightarrow \underset{3^{\circ}\text{ amine}}{RCH_2NR'_2} + H_2O$

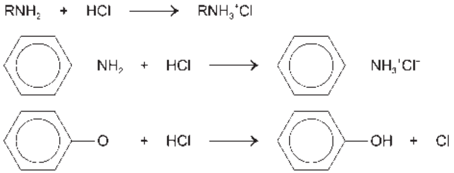
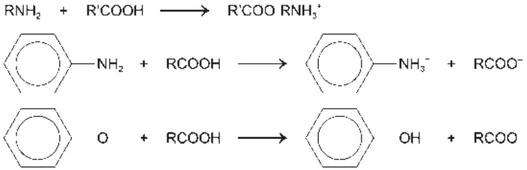
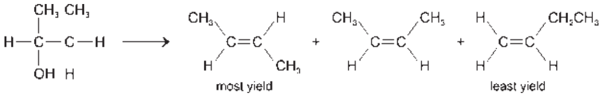
REDUCING AGENT

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
Step (i): $LiAlH_4$	Step (i) dry ether r.t.p.	Aldehyde & Ketone	Reduction RCHO → 1° ROH RCOR → 2° ROH	
Step (ii): H_2O	Step (ii): heat			
$NaBH_4$ (aq)	r.t.p.			
H_2(g)	Ni/Pt/Pd (s) catalyst heat	Alkene & Alkyne	Reduction / Catalytic Hydrogenation	 $H{-}C{\equiv}C{-}H + 2H_2 \longrightarrow CH_3CH_3$
	Ni/Pt/Pd (s) catalyst heat under high temp. & pressure	Arene	Reduction / Catalytic Hydrogenation	
Step (i): Sn	Step (i): conc. HCl heat	Nitrobenzene	Reduction	
Step (ii): NaOH(aq)	Step (ii): r.t.p.			

ACID & BASE: Based on Brϕnsted–Lowry theory, an acid is a proton donor and a base is a proton acceptor.

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
Na(s)/K(s)	r.t.p.	Alcohol, Phenol & Carboxylic acid	Acid–metal reaction / Redox reaction	
NaOH(aq) / KOH(aq)	r.t.p.	Phenol & Carboxylic acid	Acid–base reaction / Neutralization	
NaOH/ KOH	ethanol heat	Halogenoalkane	Elimination	 Note: The electronegative Br atom withdraws electron density from neighboring bonds. Pertaining to the mechanism, the H atom on the carbon adjacent to the C–Br bond is electron-deficient and is easily extracted by a strong base.
Na_2CO_3(aq)/ $NaHCO_3$(aq)	r.t.p.	Carboxylic acid	Acid-base reaction/ Neutralization	

ACID & BASE

Reagent	Conditions	Reactive Group	Type of Reaction	Equation
HCI(aq)/ H_2SO_4(aq)	r.t.p.	Amine, Phenylamine, & Phenoxide ion	Acid–base reaction/ Neutralization	 Note: Amides are not basic as the lone pair of electrons on the N atom delocalizes into the electron-withdrawing carbonyl group and is thus less readily available for bonding with a proton.
Carboxylic acid	r.t.p.	Amine, Phenylamine, & Phenoxide ion	Acid–base reaction / Neutralization	
Concentrated H_2SO_4	excess acid heat, 170ºC	Alcohol	Dehydration / Elimination	
Al_2O_3	heat, 400ºC			Note: Pertaining to the mechanism, the acid serves as a catalyst by protonating the –OH group of the alcohol. The electronegative O atom which now possesses a positive charge is highly electron-withdrawing. This weakens the C–O bond and makes it more susceptible to breakage.

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