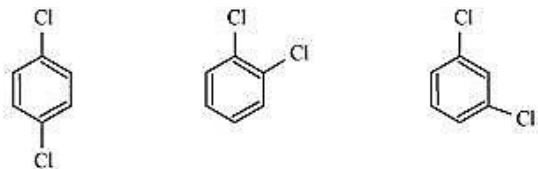


REASONING BASED

Q1 *p*-Dichlorobenzene has higher m.p. and lower solubility than those of *o*- and *m*-isomers. Discuss.



p-Dichlorobenzene *o*-Dichlorobenzene *m*-Dichlorobenzene

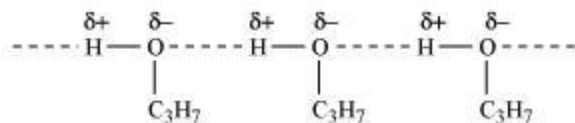
A *p*-Dichlorobenzene is more symmetrical than *o*- and *m*-isomers. For this reason, it fits more closely than *o*- and *m*-isomers in the crystal lattice. Therefore, more energy is required to break the crystal lattice of *p*-dichlorobenzene. As a result, *p*-dichlorobenzene has a higher melting point and lower solubility than *o*- and *m*-isomers.

Q2 Why C-Cl bond is more polar than C-F bond?

A2 Higher bond length of C-Cl

Q3 Explain why propanol has higher boiling point than that of the hydrocarbon, butane?

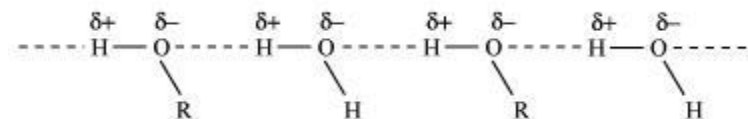
A3 Propanol undergoes intermolecular H-bonding because of the presence of -OH group. On the other hand, butane does not



Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

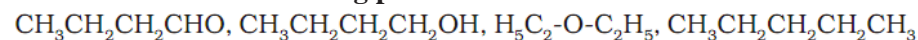
Q4 Alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses. Explain this fact.

A4 Alcohols form H-bonds with water due to the presence of -OH group. However, hydrocarbons cannot form H-bonds with water.

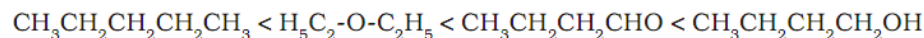


As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

Q5 Arrange the following compounds in the increasing order of their boiling points:

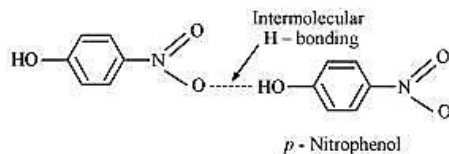
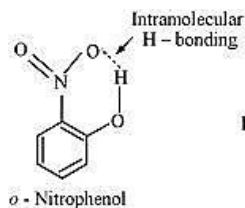


A 6 The molecular masses of these compounds are in the range of 72 to 74. Since only butan-1-ol molecules are associated due to extensive intermolecular hydrogen bonding, therefore, the boiling point of butan-1-ol would be the highest. Butanal is more polar than ethoxyethane. Therefore, the intermolecular dipole-dipole attraction is stronger in the former. n-Pentane molecules have only weak van der Waals forces. Hence, increasing order of boiling points of the given compounds is as follows:



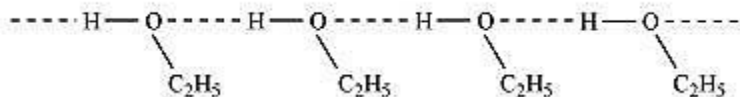
Q6 While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

A6 Intramolecular H-bonding is present in *o*-nitrophenol and *p*-nitrophenol. In *p*-nitrophenol, the molecules are strongly associated due to the presence of intermolecular bonding. Hence, *o*-nitrophenol is steam volatile.



Q7 Give reason for the higher boiling point of ethanol in comparison to methoxymethane.

A7 Ethanol undergoes intermolecular H-bonding due to the presence of –OH group, resulting in the association of molecules. Extra energy is required to break these hydrogen bonds. On the other hand, methoxymethane does not undergo H-bonding. Hence, the boiling point of ethanol is higher than that of methoxymethane.



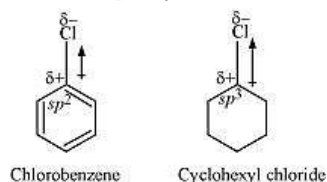
Q8 Explain why

(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

(ii) alkyl halides, though polar, are immiscible with water?

(iii) Grignard reagents should be prepared under anhydrous conditions?

A8 (i) In chlorobenzene, the Cl-atom is linked to a sp^2 hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a sp^3 hybridized carbon atom. Now, sp^2 hybridized carbon has more s-character than sp^3 hybridized carbon atom. Therefore, the former is more electronegative than the latter. Therefore, the density of

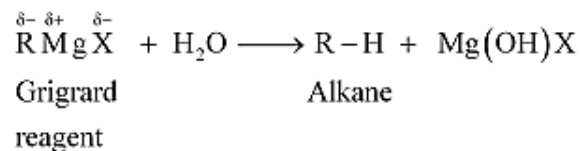


electrons of C–Cl bond near the Cl-atom is less in chlorobenzene than in cyclohexyl chloride.

Moreover, the –R effect of the benzene ring of chlorobenzene decreases the electron density of the C–Cl bond near the Cl-atom. As a result, the polarity of the C–Cl bond in chlorobenzene decreases. Hence, the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride.

(ii) To be miscible with water, the solute-water force of attraction must be stronger than the solute-solute and water-water forces of attraction. Alkyl halides are polar molecules and so held together by dipole-dipole interactions. Similarly, strong H-bonds exist between the water molecules. The new force of attraction between the alkyl halides and water molecules is weaker than the alkyl halide-alkyl halide and water-water forces of attraction. Hence, alkyl halides (though polar) are immiscible with water.

(iii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes.



Therefore, Grignard reagents should be prepared under anhydrous conditions.

Q9 Arrange the following sets of compounds in order of their increasing boiling points:

(a) Pentan-1-ol, butan-1-ol, butan-2-ol, ethanol, propan-1-ol, methanol.

(b) Pentan-1-ol, n-butane, pentanal, ethoxyethane.

A 9 (a) Methanol, ethanol, propan-1-ol, butan-2-ol, butan-1-ol, pentan-1-ol.

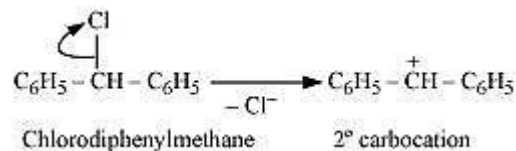
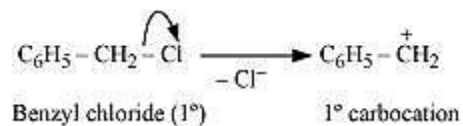
(b) n-Butane, ethoxyethane, pentanal and pentan-1-ol

Q10 Arrange the following compounds in increasing order of their boiling points.

CH₃CHO, CH₃CH₂OH, CH₃OCH₃, CH₃CH₂CH₃

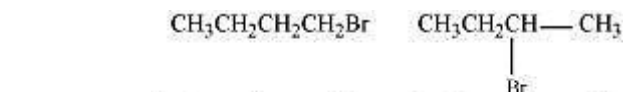
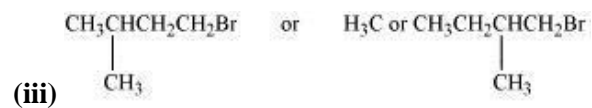
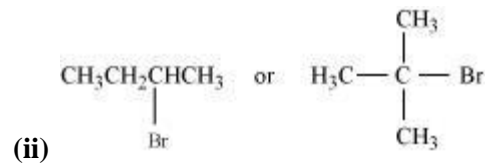
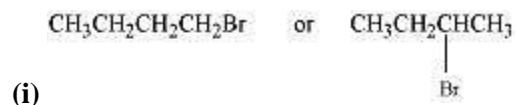
A10 CH₃CH₂CH₃ < CH₃OCH₃ < CH₃CHO < CH₃CH₂OH

Q11 Out of C₆H₅CH₂Cl and C₆H₅CHClC₆H₅, which is more easily hydrolysed by aqueous KOH?

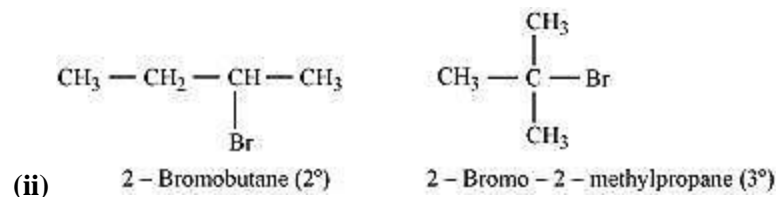


A11 Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now, C₆H₅CH₂Cl forms 1°-carbocation, while C₆H₅CHClC₆H₅ forms 2°-carbocation, which is more stable than 1°-carbocation. Hence, C₆H₅CHClC₆H₅ is hydrolyzed more easily than C₆H₅CH₂Cl by aqueous KOH.

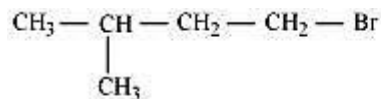
Q12 Which alkyl halide from the following pairs would you expect to react more rapidly by an S_N2 mechanism? Explain your answer.



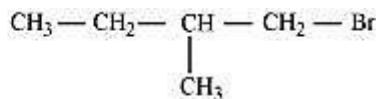
A12 (i) 1-Bromobutane (1°) 2-Bromobutane (2°) 2-bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.



2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2 mechanism.



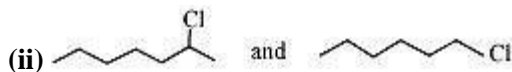
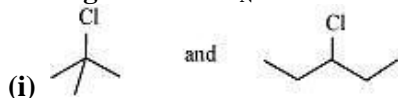
(iii) 1-Bromo-3-methylbutane (1°)



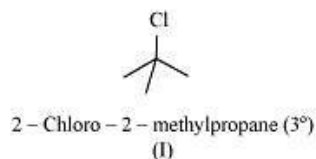
1-Bromo-2-methylbutane (1°)

Both the alkyl halides are primary. However, the substituent $-\text{CH}_3$ is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by $\text{S}_\text{N}2$ mechanism.

Q13 In the following pairs of halogen compounds, which compound undergoes faster $\text{S}_\text{N}1$ reaction?



A13 (i)



$\text{S}_\text{N}1$ reaction proceeds via the formation of carbocation. The alkyl halide (I) is 3° while (II) is 2° . Therefore, (I) forms 3° carbocation while (II) forms 2° carbocation. Greater the stability of the carbocation, faster is the rate of $\text{S}_\text{N}1$ reaction. Since 3° carbocation is more stable than 2° carbocation, (I), i.e., 2-chloro-2-methylpropane, undergoes faster $\text{S}_\text{N}1$ reaction than (II) i.e., 3-chloropentane.



2-chloroheptane (2°)

(ii)

(I)



1-chlorohexane (1°)

(II)

The alkyl halide (I) is 2° while (II) is 1° . 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2-chloroheptane, undergoes faster $\text{S}_\text{N}1$ reaction than (II), 1-chlorohexane.

Q14 Haloalkanes react with KCN to form alkyl cyanides as main product while AgCN forms isocyanides as the chief product. Explain.

A14 KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

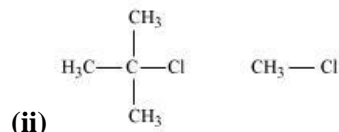
Q15 Which compound in each of the following pairs will react faster in $\text{S}_\text{N}2$ reaction with OH^- ?

(i) CH_3Br or CH_3I (ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

A15 (i) In the $\text{S}_\text{N}2$ mechanism, the reactivity of halides for the same alkyl group increases in the order. This happens because as the size increases, the halide ion becomes a better leaving group.

$\text{R-F} \ll \text{R-Cl} < \text{R-Br} < \text{R-I}$

Therefore, CH_3I will react faster than CH_3Br in $\text{S}_\text{N}2$ reactions with OH^- .



The $\text{S}_\text{N}2$ mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(\text{CH}_3)_3\text{CCl}$, the attack of the nucleophile at the carbon atom is hindered because of the presence of bulky substituents on that carbon atom bearing the leaving group. On the other hand, there are no bulky substituents on the carbon atom bearing the leaving

group in CH_3Cl . Hence, CH_3Cl reacts faster than $(\text{CH}_3)_3\text{CCl}$ in $\text{S}_\text{N}2$ reaction with OH^- .

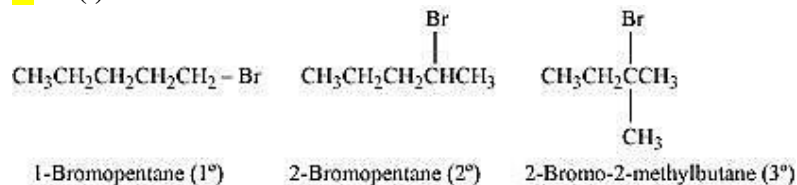
Q16 Arrange the compounds of each set in order of reactivity towards $\text{S}_\text{N}2$ displacement:

(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

(iii) 1-Bromobutane, 1-Bromo-2,2-dimethylpropane, 1-Bromo-2-methylbutane, 1-Bromo-3-methylbutane.

A 16 (i)



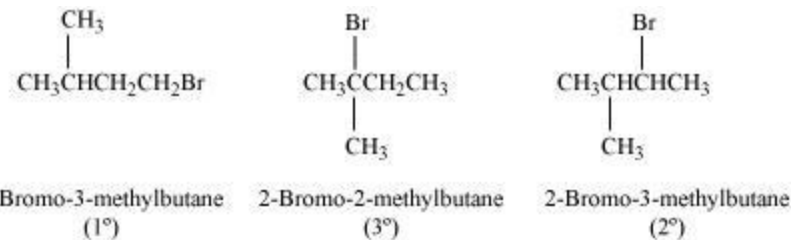
An $\text{S}_\text{N}2$ reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards $\text{S}_\text{N}2$ displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

1-Bromopentane < 2-bromopentane < 2-Bromo-2-methylbutane

Hence, the increasing order of reactivity towards $\text{S}_\text{N}2$ displacement is:

2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

(ii)



Since steric hindrance in alkyl halides increases in the order of $1^\circ < 2^\circ < 3^\circ$, the increasing order of reactivity towards $\text{S}_\text{N}2$ displacement is

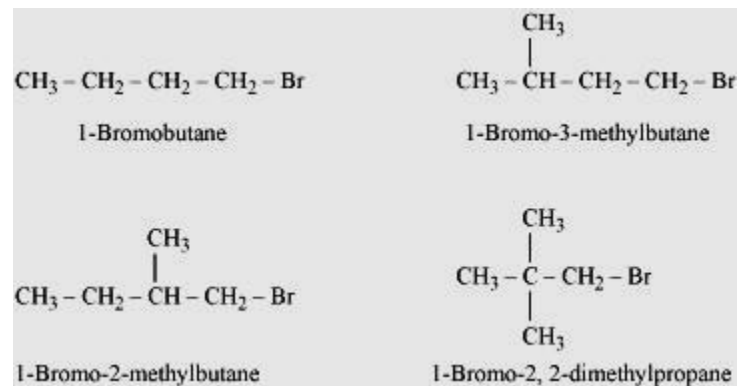
$3^\circ < 2^\circ < 1^\circ$.

Hence, the given set of compounds can be arranged in the increasing order of their reactivity towards $\text{S}_\text{N}2$ displacement as:

2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane

[2-Bromo-3-methylbutane is incorrectly given in NCERT]

(iii)



The steric hindrance to the nucleophile in the $\text{S}_\text{N}2$ mechanism increases with a decrease in the distance of the substituents from the atom containing the leaving group. Further, the steric hindrance increases with an increase in the

number of substituents. Therefore, the increasing order of steric hindrances in the given compounds is as below:

1-Bromobutane < 1-Bromo-3-methylbutane < 1-Bromo-2-methylbutane

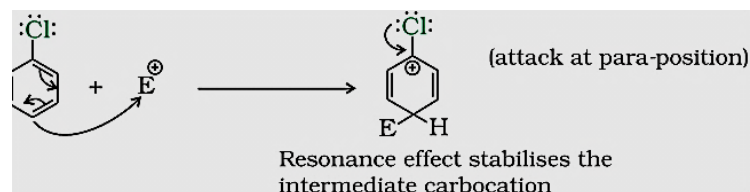
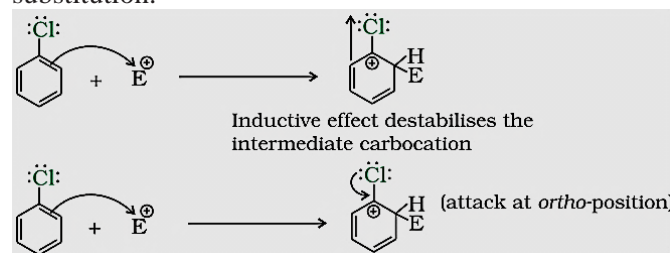
< 1-Bromo-2, 2-dimethylpropane

Hence, the increasing order of reactivity of the given compounds towards S_N2 displacement is:

1-Bromo-2, 2-dimethylpropane < 1-Bromo-2-methylbutane < 1-Bromo-3-methylbutane < 1-Bromobutane

Q17 Although chlorine is an electron withdrawing group, yet it is ortho-, para- directing in electrophilic aromatic substitution reactions. Why?

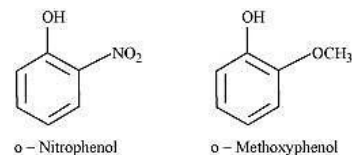
A17 Chlorine withdraws electrons through inductive effect and releases electrons through resonance. Through inductive effect, chlorine destabilises the intermediate carbocation formed during the electrophilic substitution.



Through resonance, halogen tends to stabilise the carbocation and the effect is more pronounced at ortho- and para- positions. The inductive effect is stronger than resonance and causes net electron withdrawal and thus causes net deactivation. The resonance effect

tends to oppose the inductive effect for the attack at ortho- and parapositions and hence makes the deactivation less for ortho- and paraattack. Reactivity is thus controlled by the stronger inductive effect and orientation is controlled by resonance effect

Q18 Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol?



A18 The nitro-group is an electron-withdrawing group. The presence of this group in the ortho position decreases the electron density in the O-H bond. As a result, it is easier to lose a proton. Also, the *o*-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, *ortho* nitrophenol is a stronger acid.


On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O-H bond and hence, the proton cannot be given out easily.

For this reason, *ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol.

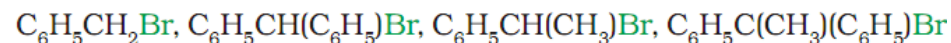
Q19 In the following pairs of halogen compounds, which would undergo S_N2 reaction faster?



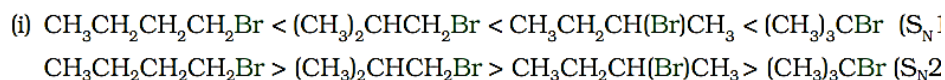
A19 In 1st pair is primary halide and therefore undergoes S_N2 reaction faster.

In 2nd  As iodine is a better leaving group because of its large size, it will be released at a faster rate in the presence of incoming nucleophile.

Q20 Predict the order of reactivity of the following compounds in S_N1 and S_N2 reactions:



A21

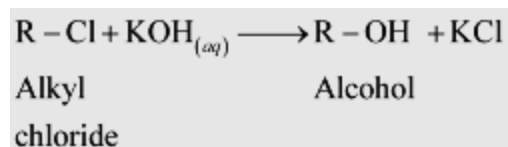


Q22 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

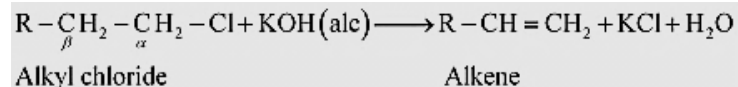
A22 The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed.

Q23 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

A23 In an aqueous solution, KOH almost completely ionizes to give OH⁻ ions. OH⁻ ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

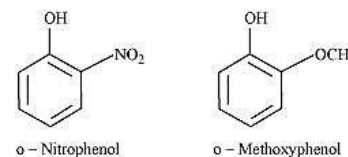


On the other hand, an alcoholic solution of KOH contains alkoxide (RO⁻) ion, which is a strong base. Thus, it can abstract a hydrogen from the β-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.



OH⁻ ion is a much weaker base than RO⁻ ion. Also, OH⁻ ion is highly solvated in an aqueous solution and as a result, the basic character of OH⁻ ion decreases. Therefore, it cannot abstract a hydrogen from the β-carbon.

Q 24 Explain why is *ortho* nitrophenol more acidic than *ortho* methoxyphenol?



A24 The nitro-group is an electron-withdrawing group. The presence of this group in the *ortho* position decreases the electron density in the O-H bond. As a result, it is easier to lose a proton. Also, the *o*-nitrophenoxide ion formed after the loss of protons is stabilized by resonance. Hence, *ortho* nitrophenol is a stronger acid.

On the other hand, methoxy group is an electron-releasing group. Thus, it increases the electron density in the O-H bond and hence, the proton cannot be given out easily.

For this reason, *ortho*-nitrophenol is more acidic than *ortho*-methoxyphenol.

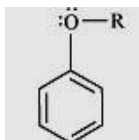
Q25 Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method. Give reason.

A25 The formation of ethers by dehydration of alcohol is a bimolecular reaction (S_N2) involving the attack of an alcohol molecule on a protonated alcohol molecule. In the method, the alkyl group should be unhindered. In case of secondary or tertiary alcohols, the alkyl group is hindered. As a result, elimination dominates substitution. Hence, in place of ethers, alkenes are formed.

Q26 Explain the fact that in aryl alkyl ethers

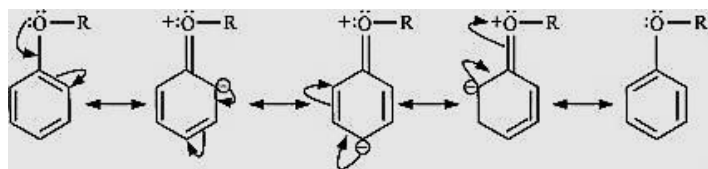
(i) The alkoxy group activates the benzene ring towards electrophilic substitution and

(ii) It directs the incoming substituents to ortho and para positions in benzene ring.



A26 (i) Aryl alkyl ether

In aryl alkyl ethers, due to the +R effect of the alkoxy group, the electron density in the benzene ring increases as shown in the following resonance structure.

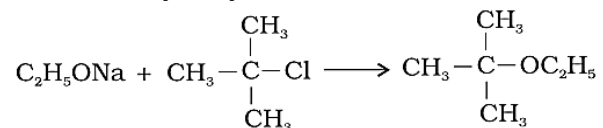


Thus, benzene is activated towards electrophilic substitution by the alkoxy group.

(ii) It can also be observed from the resonance structures that the electron density increases more at the ortho and para positions than at the meta position. As a result, the incoming substituents are directed to the ortho and para positions in the benzene ring.

Q27 The following is not an appropriate reaction for the preparation of

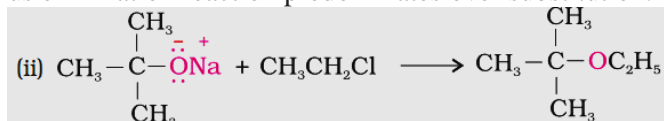
t-butyl ethyl ether.



(i) What would be the major product of this reaction ?

(ii) Write a suitable reaction for the preparation of t-butylethyl ether.

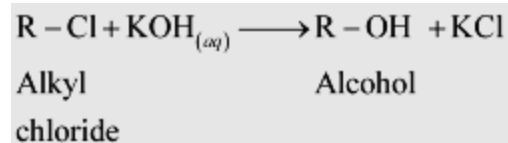
A27 (i) The major product of the given reaction is 2-methylprop-1-ene. It is because sodium ethoxide is a strong nucleophile as well as a strong base. Thus elimination reaction predominates over substitution.



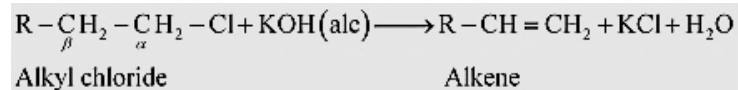
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Q28 The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

A28 In an aqueous solution, KOH almost completely ionizes to give OH^- ions. OH^- ion is a strong nucleophile, which leads the alkyl chloride to undergo a substitution reaction to form alcohol.

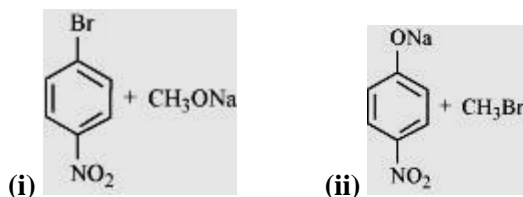


On the other hand, an alcoholic solution of KOH contains alkoxide (RO^-) ion, which is a strong base. Thus, it can abstract a hydrogen from the β -carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.

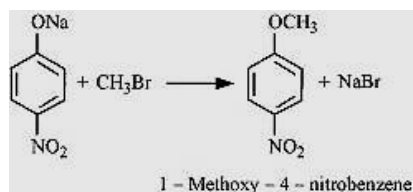


OH^- ion is a much weaker base than RO^- ion. Also, OH^- ion is highly solvated in an aqueous solution and as a result, the basic character of OH^- ion decreases. Therefore, it cannot abstract a hydrogen from the β -carbon.

Q29 Which of the following is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene and why?



A29 Set (ii) is an appropriate set of reactants for the preparation of 1-methoxy-4-nitrobenzene.

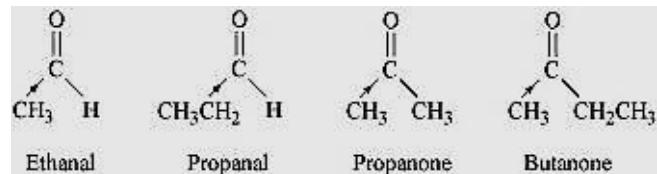


In set (i), sodium methoxide (CH_3ONa) is a strong nucleophile as well as a strong base. Hence, an elimination reaction predominates over a substitution reaction.

Q30 Arrange the following compounds in increasing order of their reactivity in nucleophilic addition reactions.

- (i) Ethanal, Propanal, Propanone, Butanone.
 (ii) Benzaldehyde, *p*-Tolualdehyde,
p Nitrobenzaldehyde, Acetophenone.

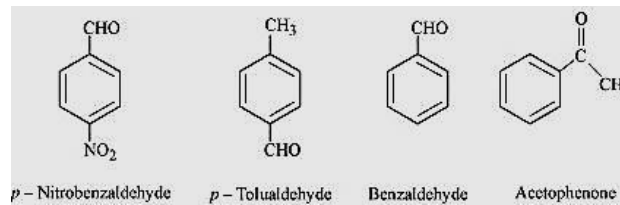
A30 (i)



The +I effect of the alkyl group increases in the order: Ethanal < Propanal < Propanone < Butanone

The electron density at the carbonyl carbon increases with the increase in the +I effect. As a result, the chances of attack by a nucleophile decrease. Hence, the increasing order of the reactivities of the given carbonyl compounds in nucleophilic addition reactions is:

Butanone < Propanone < Propanal < Ethanal
 (ii)



The +I effect is more in ketone than in aldehyde. Hence, acetophenone is the least reactive in nucleophilic addition reactions. Among aldehydes, the +I effect is the highest in *p*-tolualdehyde because of the presence of the electron-donating $-\text{CH}_3$ group and the lowest in *p*-nitrobenzaldehyde because of the presence of the electron-withdrawing $-\text{NO}_2$ group. Hence, the increasing order of the reactivities of the given compounds is:

Acetophenone < *p*-tolualdehyde < Benzaldehyde
 < *p*-Nitrobenzaldehyde

Q31 Would you expect benzaldehyde to be more reactive or less reactive in nucleophilic addition reactions than propanal? Explain your answer.

A32 The carbon atom of the carbonyl group of benzaldehyde is less electrophilic than carbon atom of the carbonyl group present in propanal. The polarity of the carbonyl group is reduced in benzaldehyde due to resonance as shown below and hence it is less reactive than propanal.

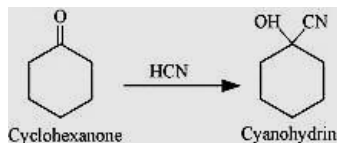
Q33 Give plausible explanation for each of the following:

(i) Cyclohexanone forms cyanohydrin in good yield but 2, 2, 6 trimethylcyclohexanone does not.

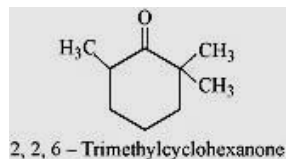
(ii) There are two $-NH_2$ groups in semicarbazide. However, only one is involved in the formation of semicarbazones.

(iii) During the preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, the water or the ester should be removed as soon as it is formed.

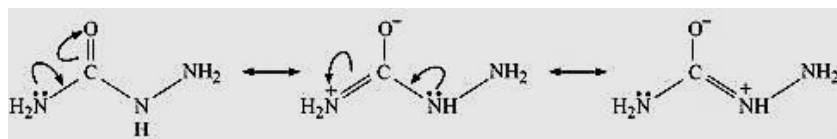
A33 (i) Cyclohexanones form cyanohydrins according to the following equation.



In this case, the nucleophile CN^- can easily attack without any steric hindrance. However, in the case of 2, 2, 6 trimethylcyclohexanone, methyl groups at α -positions offer steric hindrances and as a result, CN^- cannot attack effectively. For this reason, it does not form a cyanohydrin.



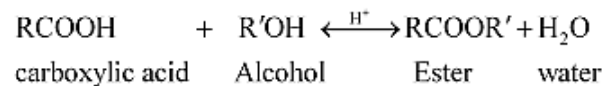
(ii) Semicarbazide undergoes resonance involving only one of the two $-NH_2$ groups, which is attached directly to the carbonyl-carbon atom.



Therefore, the electron density on $-NH_2$ group involved in the resonance also decreases. As a result, it cannot act as a nucleophile. Since the other $-NH_2$

group is not involved in resonance; it can act as a nucleophile and can attack carbonyl-carbon atoms of aldehydes and ketones to produce semicarbazones.

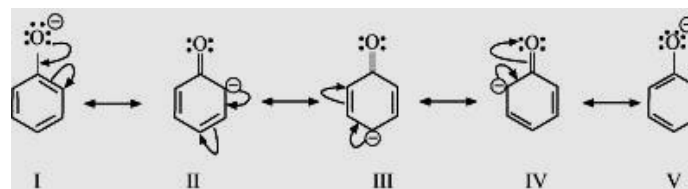
(iii) Ester along with water is formed reversibly from a carboxylic acid and an alcohol in presence of an acid.



If either water or ester is not removed as soon as it is formed, then it reacts to give back the reactants as the reaction is reversible. Therefore, to shift the equilibrium in the forward direction i.e., to produce more ester, either of the two should be removed.

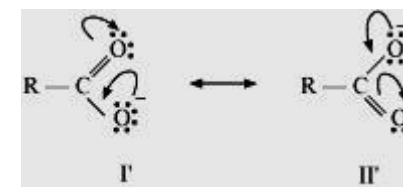
Q34 Although phenoxide ion has more number of resonating structures than carboxylate ion, carboxylic acid is a stronger acid than phenol. Why?

A34 Resonance structures of phenoxide ion are:



It can be observed from the resonance structures of phenoxide ion that in II, III and IV, less eliminated. Only structures I and V carry a negative charge on the more electronegative oxygen atom.

Resonance structures of carboxylate ion are: Structure of arboxylate ion are exactly equivalent which make the hybrid [conjugate base] more stable than phenoxide ion



Q35 Arrange the following compounds in increasing order of their acid strength:

Propan-1-ol, 2,4,6-trinitrophenol, 3-nitrophenol, 3,5-dinitrophenol, phenol, 4-methylphenol.

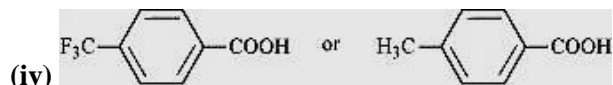
A35 Propan-1-ol, 4-methylphenol, phenol, 3-nitrophenol, 3,5-dinitrophenol, 2,4, 6-trinitrophenol.

Q36 Which acid of each pair shown here would you expect to be stronger?

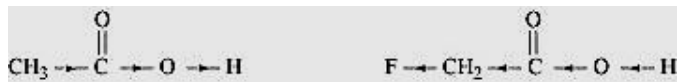
(i) $\text{CH}_3\text{CO}_2\text{H}$ or $\text{CH}_2\text{FCO}_2\text{H}$

(ii) $\text{CH}_2\text{FCO}_2\text{H}$ or $\text{CH}_2\text{ClCO}_2\text{H}$

(iii) $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$ or $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$



A36 (i)



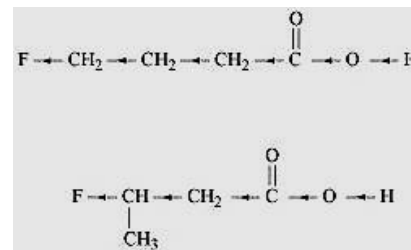
The +I effect of $-\text{CH}_3$ group increases the electron density on the O–H bond. Therefore, release of proton becomes difficult. On the other hand, the –I effect of F decreases the electron density on the O–H bond. Therefore, proton can be released easily. Hence, $\text{CH}_2\text{FCO}_2\text{H}$ is a stronger acid than $\text{CH}_3\text{CO}_2\text{H}$.

(ii)



F has stronger –I effect than Cl. Therefore, $\text{CH}_2\text{FCO}_2\text{H}$ can release proton more easily than $\text{CH}_2\text{ClCO}_2\text{H}$. Hence, $\text{CH}_2\text{FCO}_2\text{H}$ is stronger acid than $\text{CH}_2\text{ClCO}_2\text{H}$.

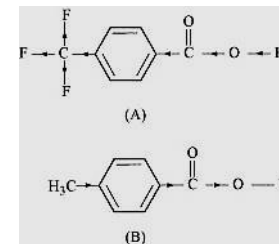
(iii)



Inductive effect decreases with increase in distance. Hence, the +I effect of F in $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$ is more than it is in $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$. Hence, $\text{CH}_3\text{CHFCH}_2\text{CO}_2\text{H}$ is stronger acid than $\text{CH}_2\text{FCH}_2\text{CH}_2\text{CO}_2\text{H}$.

(iv)

Due to the –I effect of F, it is easier to release proton in the case of compound (A). However, in the case of compound (B), release of proton is difficult due to the +I effect of $-\text{CH}_3$ group. Hence, (A) is a stronger acid than (B).



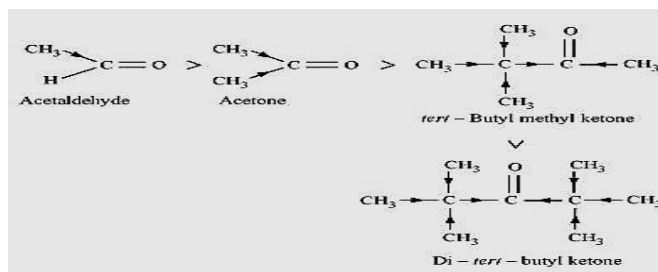
Q37 Arrange the following compounds in increasing order of their property as indicated:

(i) Acetaldehyde, Acetone, Di-*tert*-butyl ketone, Methyl *tert*-butyl ketone (reactivity towards HCN)

(ii) $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}_2\text{COOH}$ (acid strength)

(iii) Benzoic acid, 4-Nitrobenzoic acid, 3,4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)

A37



(i) In the given compounds, the +I effect increases as shown below. It can be observed that steric hindrance also increases in the same. Hence, the given compounds can be arranged according to their increasing reactivities toward HCN as:

Di-*tert*-butyl ketone < Methyl *tert*-butyl ketone < Acetone < Acetaldehyde

(ii) After losing a proton, carboxylic acids gain a negative charge as shown:

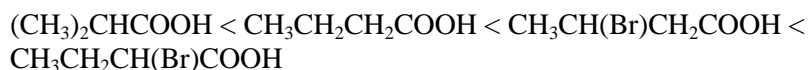


Now, any group that will help stabilise the negative charge will increase the stability of the carboxyl ion and as a result, will increase the strength of the acid. Thus, groups having +I effect will decrease the strength of the acids and groups having -I effect will increase the strength of the acids. In the given compounds, -CH₃ group has +I effect and Br⁻ group has -I effect. Thus, acids containing Br⁻ are stronger.

Now, the +I effect of isopropyl group is more than that of *n*-propyl group. Hence, (CH₃)₂CHCOOH is a weaker acid than CH₃CH₂CH₂COOH.

Also, the -I effect grows weaker as distance increases. Hence, CH₃CH(Br)CH₂COOH is a weaker acid than CH₃CH₂CH(Br)COOH.

Hence, the strengths of the given acids increase as:



(iii) As we have seen in the previous case, electron-donating groups decrease the strengths of acids, while electron-withdrawing groups increase the strengths of acids. As methoxy group is an electron-donating group, 4-methoxybenzoic acid is a weaker acid than benzoic acid. Nitro group is an electron-withdrawing group and will increase the strengths of acids. As 3,4-dinitrobenzoic acid contains two nitro groups, it is a slightly stronger acid than

nitrobenzoic acid. Hence, the strengths of the given acids increase as:

4-Methoxybenzoic acid < Benzoic acid < 4-Nitrobenzoic acid < 3,4-Dinitrobenzoic acid

Q38 Account for the following:

(i) pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not.

(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide.

(iv) Although amino group is *o*, *p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline.

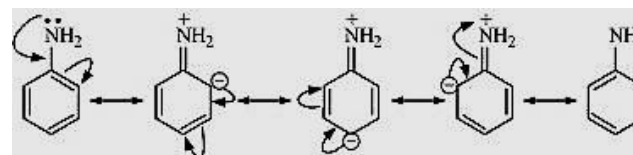
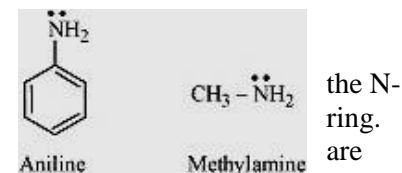
(v) Aniline does not undergo Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines.

A38

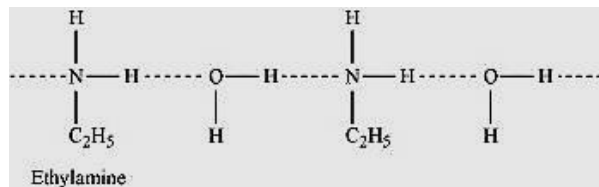
(i) pK_b of aniline is more than that of methylamine: Aniline undergoes resonance and as a result, the electrons on the atom are delocalized over the benzene ring. Therefore, the electrons on the N-atom are less available to donate.



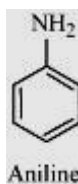
On the other hand, in case of methylamine (due to the +I effect of methyl group), the electron density on the N-atom is increased. As a result, aniline is less basic than methylamine. Thus, pK_b of aniline is more than that of methylamine.

(ii) Ethylamine is soluble in water whereas aniline is not:

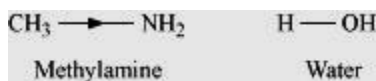
Ethylamine when added to water forms intermolecular H-bonds with water. Hence, it is soluble in water.



But aniline does not undergo H-bonding with water to a very large extent due to the presence of a large hydrophobic $-C_6H_5$ group. Hence, aniline is insoluble in water.



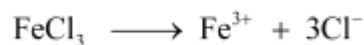
(iii) Methylamine in water reacts with ferric chloride to precipitate hydrated ferric oxide:



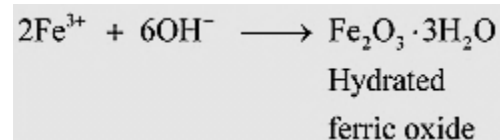
Due to the +I effect of $-CH_3$ group, methylamine is more basic than water. Therefore, in water, methylamine produces OH^- ions by accepting H^+ ions from water.



Ferric chloride (FeCl_3) dissociates in water to form Fe^{3+} and Cl^- ions.

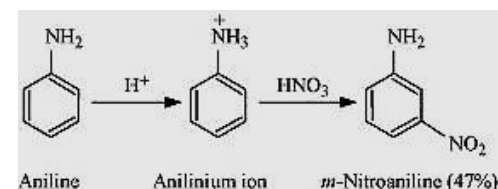


Then, OH^- ion reacts with Fe^{3+} ion to form a precipitate of hydrated ferric oxide.



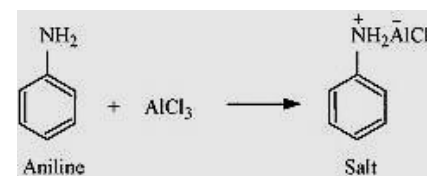
(iv) Although amino group is *o,p*- directing in aromatic electrophilic substitution reactions, aniline on nitration gives a substantial amount of *m*-nitroaniline:

Nitration is carried out in an acidic medium. In an acidic medium, aniline is protonated to give anilinium ion (which is meta-directing). For this reason, aniline on nitration gives a substantial amount of *m*-nitroaniline.



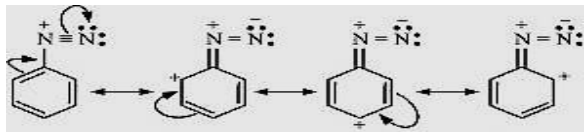
(v) Aniline does not undergo Friedel-Crafts reaction:

A Friedel-Crafts reaction is carried out in the presence of AlCl_3 . But AlCl_3 is acidic in nature, while aniline is a strong base. Thus, aniline reacts with AlCl_3 to form a salt (as shown in the following equation).



Due to the positive charge on the N-atom, electrophilic substitution in the benzene ring is deactivated. Hence, aniline does not undergo the Friedel-Crafts reaction.

(vi) Diazonium salts of aromatic amines are more stable than those of aliphatic amines:



The diazonium ion undergoes resonance as shown below:

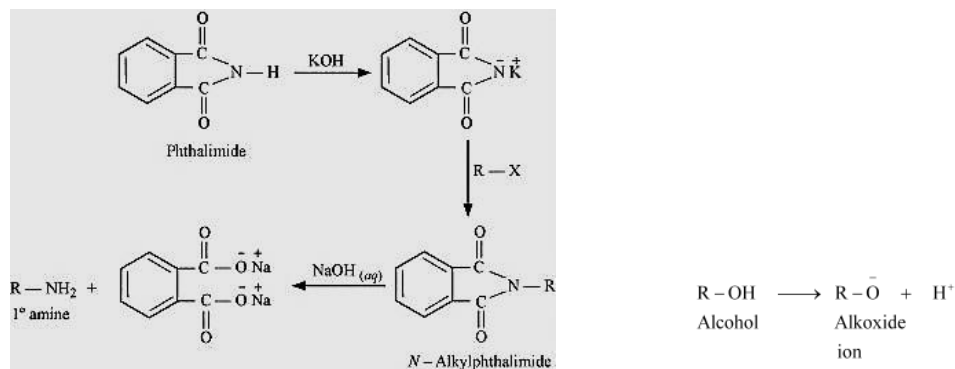
This resonance accounts for the stability of the diazonium ion. Hence, diazonium salts of aromatic amines are more stable than those of aliphatic amines.

(vii) Gabriel phthalimide synthesis is preferred for synthesising primary amines:

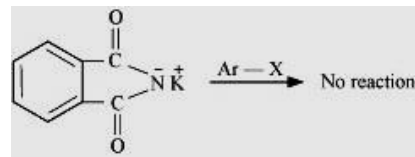
Gabriel phthalimide synthesis results in the formation of 1° amine only. 2° or 3° amines are not formed in this synthesis. Thus, a pure 1° amine can be obtained. Therefore, Gabriel phthalimide synthesis is preferred for synthesising primary amines.

Q39 Why cannot aromatic primary amines be prepared by Gabriel phthalimide synthesis?

A39 Gabriel phthalimide synthesis is used for the preparation of aliphatic primary amines. It involves nucleophilic substitution (S_N2) of alkyl halides by the anion formed by the phthalimide.



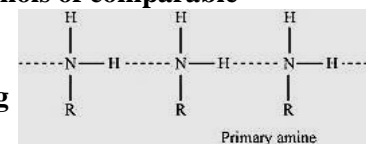
But aryl halides do not undergo nucleophilic substitution with the anion formed by the phthalimide.



Hence, aromatic primary amines cannot be prepared by this process.

Q40 Give plausible explanation for each of the following:

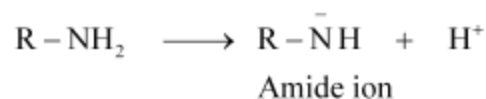
A40 (i) Why are amines less acidic than alcohols of comparable molecular masses?



(ii) Why do primary amines have higher boiling point than tertiary amines?

(iii) Why are aliphatic amines stronger bases than aromatic amines?

(i) Amines undergo protonation to give amide ion.

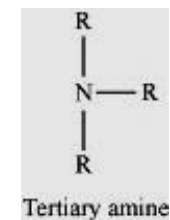


Similarly, alcohol loses a proton to give alkoxide ion.

In an amide ion, the negative charge is on the N-atom whereas in alkoxide ion, the negative charge is on the O-atom. Since O is more electronegative than N, O can accommodate the negative charge more easily than N. As a result, the amide ion is less stable than the alkoxide ion. Hence, amines are less acidic than alcohols of comparable molecular masses.

(ii) In a molecule of tertiary amine, there are no H-atoms whereas in primary amines, two hydrogen atoms are present. Due to the presence of H-atoms, primary amines undergo extensive intermolecular H-bonding.

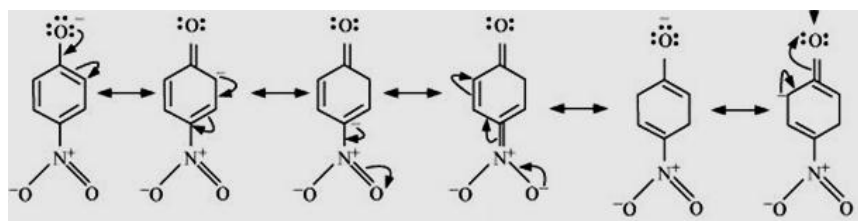
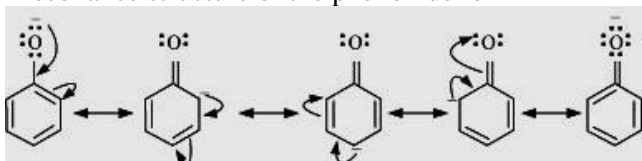
As a result, extra energy is required to separate the molecules of primary amines. Hence, primary amines have higher boiling points than tertiary amines.



(iii) Due to the $-R$ effect of the benzene ring, the electrons on the N-atom are less available in case of aromatic amines. Therefore, the electrons on the N-atom in aromatic amines cannot be donated easily. This explains why aliphatic amines are stronger bases than aromatic amines.

Q 41 *Ortho* and *para* nitrophenols are more acidic than phenol. Draw the resonance structures of the corresponding phenoxide ions.

A41 Resonance structure of the phenoxide ion



Q42 Arrange the following:

(i) In decreasing order of the pK_b values:

$C_2H_5NH_2$, $C_6H_5NHCH_3$, $(C_2H_5)_2NH$ and $C_6H_5NH_2$

(ii) In increasing order of basic strength:

$C_6H_5NH_2$, $C_6H_5N(CH_3)_2$, $(C_2H_5)_2NH$ and CH_3NH_2

(iii) In increasing order of basic strength:

(a) Aniline, *p*-nitroaniline and *p*-toluidine

(b) $C_6H_5NH_2$, $C_6H_5NHCH_3$, $C_6H_5CH_2NH_2$.

(iv) In decreasing order of basic strength in gas phase:

$C_2H_5NH_2$, $(C_2H_5)_2NH$, $(C_2H_5)_3N$ and NH_3

(v) In increasing order of boiling point:

C_2H_5OH , $(CH_3)_2NH$, $C_2H_5NH_2$

(vi) In increasing order of solubility in water:

$C_6H_5NH_2$, $(C_2H_5)_2NH$, $C_2H_5NH_2$.

A42 (i) In $C_2H_5NH_2$, only one $-C_2H_5$ group is present while in $(C_2H_5)_2NH$, two $-C_2H_5$ groups are present. Thus, the $+I$ effect is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Therefore, the electron density over the N-atom is more in $(C_2H_5)_2NH$ than in $C_2H_5NH_2$. Hence, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

Also, both $C_6H_5NHCH_3$ and $C_6H_5NH_2$ are less basic than $(C_2H_5)_2NH$ and $C_2H_5NH_2$ due to the delocalization of the lone pair in the former two. Further, among $C_6H_5NHCH_3$ and $C_6H_5NH_2$, the former will be more basic due to the $+T$ effect of $-CH_3$ group. Hence, the order of increasing basicity of the given compounds is as follows:

$C_6H_5NH_2 < C_6H_5NHCH_3 < C_2H_5NH_2 < (C_2H_5)_2NH$

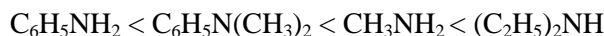
We know that the higher the basic strength, the lower is the pK_b values.

$C_6H_5NH_2 > C_6H_5NHCH_3 > C_2H_5NH_2 > (C_2H_5)_2NH$

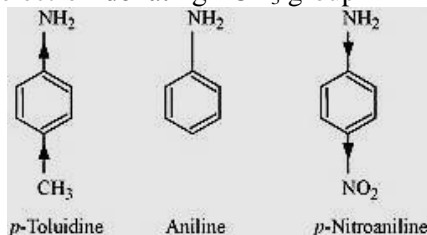
(ii) $C_6H_5N(CH_3)_2$ is more basic than $C_6H_5NH_2$ due to the presence of the $+I$ effect of two $-CH_3$ groups in $C_6H_5N(CH_3)_2$. Further, CH_3NH_2 contains one $-CH_3$ group while $(C_2H_5)_2NH$ contains two $-C_2H_5$ groups. Thus, $(C_2H_5)_2NH$ is more basic than $C_2H_5NH_2$.

Now, $C_6H_5N(CH_3)_2$ is less basic than CH_3NH_2 because of the $-R$ effect of $-C_6H_5$ group.

Hence, the increasing order of the basic strengths of the given compounds is as follows:



(iii) (a) In *p*-toluidine, the presence of electron-donating $-\text{CH}_3$ group increases the electron density on the N-atom. Thus, *p*-toluidine is more basic than aniline.



On the other hand, the presence of electron-withdrawing

$-\text{NO}_2$ group decreases the electron density over the N-atom in *p*-nitroaniline. Thus, *p*-nitroaniline is less basic than aniline.

Hence, the increasing order of the basic strengths of the given compounds is as follows:



(b) $\text{C}_6\text{H}_5\text{NHCH}_3$ is more basic than $\text{C}_6\text{H}_5\text{NH}_2$ due to the presence of electron-donating $-\text{CH}_3$ group in $\text{C}_6\text{H}_5\text{NHCH}_3$.

Again, in $\text{C}_6\text{H}_5\text{NHCH}_3$, $-\text{C}_6\text{H}_5$ group is directly attached to the N-atom. However, it is not so in $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$. Thus, in $\text{C}_6\text{H}_5\text{NHCH}_3$, the $-\text{R}$ effect of $-\text{C}_6\text{H}_5$ group decreases the electron density over the N-atom. Therefore, $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$ is more basic than $\text{C}_6\text{H}_5\text{NHCH}_3$.

Hence, the increasing order of the basic strengths of the given compounds is as follows:



(iv) In the gas phase, there is no solvation effect. As a result, the basic strength mainly depends upon the +I effect. The higher the +I effect, the stronger is the base. Also, the greater the number of alkyl groups, the higher

is the +I effect. Therefore, the given compounds can be arranged in the decreasing order of their basic strengths in the gas phase as follows:



(v) The boiling points of compounds depend on the extent of H-bonding present in that compound. The more extensive the H-bonding in the compound, the higher is the boiling point. $(\text{CH}_3)_2\text{NH}$ contains only one H-atom whereas $\text{C}_2\text{H}_5\text{NH}_2$ contains two H-atoms. Then, $\text{C}_2\text{H}_5\text{NH}_2$ undergoes more extensive H-bonding than $(\text{CH}_3)_2\text{NH}$. Hence, the boiling point of $\text{C}_2\text{H}_5\text{NH}_2$ is higher than that of $(\text{CH}_3)_2\text{NH}$.

Further, O is more electronegative than N. Thus, $\text{C}_2\text{H}_5\text{OH}$ forms stronger H-bonds than $\text{C}_2\text{H}_5\text{NH}_2$. As a result, the boiling point of $\text{C}_2\text{H}_5\text{OH}$ is higher than that of $\text{C}_2\text{H}_5\text{NH}_2$ and $(\text{CH}_3)_2\text{NH}$.

Now, the given compounds can be arranged in the increasing order of their boiling points as follows:



(vi) The more extensive the H-bonding, the higher is the solubility. $\text{C}_2\text{H}_5\text{NH}_2$ contains two H-atoms whereas $(\text{C}_2\text{H}_5)_2\text{NH}$ contains only one H-atom. Thus, $\text{C}_2\text{H}_5\text{NH}_2$ undergoes more extensive H-bonding than $(\text{C}_2\text{H}_5)_2\text{NH}$. Hence, the solubility in water of $\text{C}_2\text{H}_5\text{NH}_2$ is more than that of $(\text{C}_2\text{H}_5)_2\text{NH}$.

Further, the solubility of amines decreases with increase in the molecular mass. This is because the molecular mass of amines increases with an increase in the size of the hydrophobic part. The molecular mass of $\text{C}_6\text{H}_5\text{NH}_2$ is greater than that of $\text{C}_2\text{H}_5\text{NH}_2$ and $(\text{C}_2\text{H}_5)_2\text{NH}$.

Hence, the increasing order of their solubility in water is as follows:

