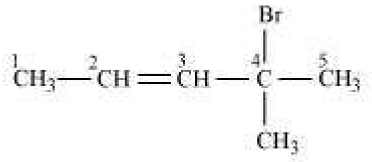
3−Chloro−5−methylhex−2−ene

(Vinyl halide)

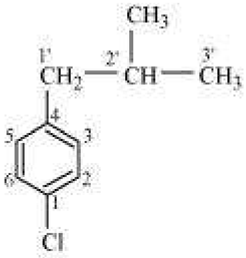
(ix)



4−Bromo−4−methylpent−2−ene

(Allyl halide)

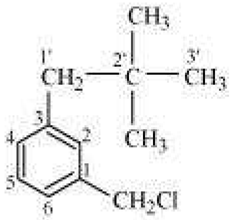
(x)



1−Chloro−4−(2−methylpropyl) benzene

(Aryl halide)

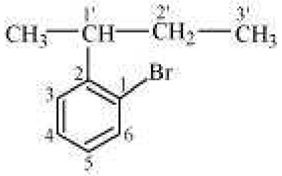
(xi)



1−Chloromethyl−3−(2, 2−dimethylpropyl) benzene

(Primary benzyl halide)

(xii)



1−Bromo−2−(1−methylpropyl) benzene

(Aryl halide)

Question 10.2:

Give the IUPAC names of the following compounds:

(i) $CH_3CH(Cl)CH(Br)CH_3$

(ii) $CHF_2CBrClF$

(iii) $ClCH_2C{\equiv}CCH_2Br$

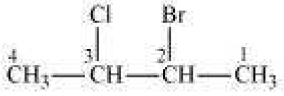
(iv) $(CCl_3)_3CCl$

(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$

(vi) $(CH_3)_3CCH{=}CClC_6H_4I\text{-}p$

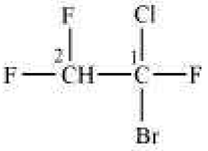
Answer

(i)



2−Bromo−3−chlorobutane

(ii)

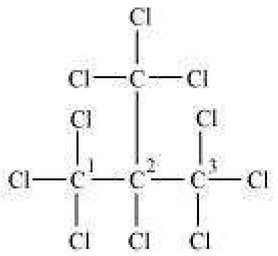


1−Bromo−1−chloro−1, 2, 2−trifluoroethane

(iii)

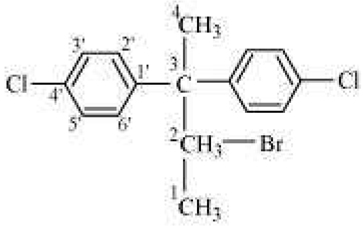
1−Bromo−4−chlorobut−2−yne

(iv)



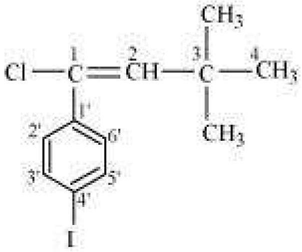
2−(Trichloromethyl)−1,1,1,2,3,3,3−heptachloropropane

(v)



2−Bromo−3, 3−bis(4−chlorophenyl) butane

(vi)



1−chloro−1−(4−iodophenyl)−3, 3−dimethylbut−1−ene

Question 10.3:

Write the structures of the following organic halogen compounds.

(i) 2-Chloro-3-methylpentane

(ii) *p*-Bromochlorobenzene

(iii) 1-Chloro-4-ethylcyclohexane

(iv) 2-(2-Chlorophenyl)-1-iodooctane

(v) Perfluorobenzene

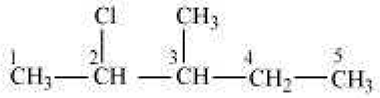
(vi) 4-tert-Butyl-3-iodoheptane

(vii) 1-Bromo-4-sec-butyl-2-methylbenzene

(viii) 1,4-Dibromobut-2-ene

Answer

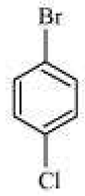
(i)



$$\overset{1}{CH_3}-\overset{\overset{Cl}{|}}{\overset{2}{CH}}-\overset{\overset{CH_3}{|}}{\overset{3}{CH}}-\overset{4}{CH_2}-\overset{5}{CH_3}$$

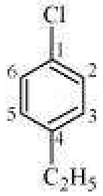
2-Chloro-3-methylpentane

(ii)



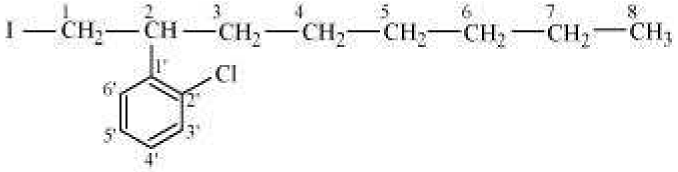
p-Bromochlorobenzene

(iii)



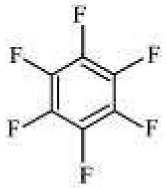
1-Chloro-4-ethylcyclohexane

(iv)



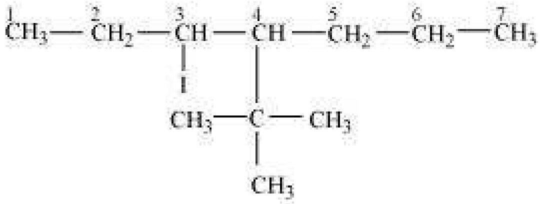
2-(2-Chlorophenyl)-1-iodooctane

(v)



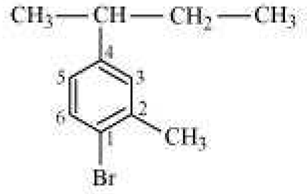
Perfluorobenzene

(vi)



4-Tert-Butyl-3-iodoheptane

(vii)



1-Bromo-4-sec-butyl-2-methylbenzene

(viii)

$Br-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-Br$

1,4-Dibromobut-2-ene

Question 10.4:

Which one of the following has the highest dipole moment?

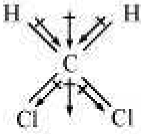
(i) CH_2Cl_2

(ii) $CHCl_3$

(iii) CCl_4

Answer

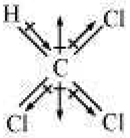
(i)



Dichlormethane (CH_2Cl_2)

μ = 1.60D

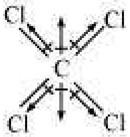
(ii)



Chloroform ($CHCl_3$)

μ = 1.08D

(iii)



Carbon tetrachloride (CCl_4)

$\mu = 0D$

CCl_4 is a symmetrical molecule. Therefore, the dipole moments of all four C−Cl bonds cancel each other. Hence, its resultant dipole moment is zero.

As shown in the above figure, in $CHCl_3$, the resultant of dipole moments of two C−Cl bonds is opposed by the resultant of dipole moments of one C−H bond and one C−Cl bond. Since the resultant of one C−H bond and one C−Cl bond dipole moments is smaller than two C−Cl bonds, the opposition is to a small extent. As a result, $CHCl_3$ has a small dipole moment of 1.08 D.

On the other hand, in case of CH_2Cl_2, the resultant of the dipole moments of two C−Cl bonds is strengthened by the resultant of the dipole moments of two C−H bonds. As a result, CH_2Cl_2 has a higher dipole moment of 1.60 D than $CHCl_3$ i.e., CH_2Cl_2 has the highest dipole moment.

Hence, the given compounds can be arranged in the increasing order of their dipole moments as:

$CCl_4 < CHCl_3 < CH_2Cl_2$

Question 10.5:

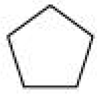
A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

Answer

A hydrocarbon with the molecular formula, C_5H_{10} belongs to the group with a general molecular formula C_nH_{2n}. Therefore, it may either be an alkene or a cycloalkane.

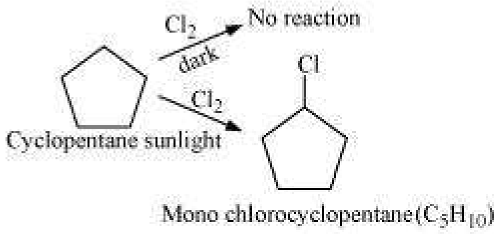
Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane.

Further, the hydrocarbon gives a single monochloro compound, C_5H_9Cl by reacting with chlorine in bright sunlight. Since a single monochloro compound is formed, the hydrocarbon must contain H−atoms that are all equivalent. Also, as all H−atoms of a cycloalkane are equivalent, the hydrocarbon must be a cycloalkane. Hence, the said compound is cyclopentane.



Cyclopentane (C_5H_{10})

The reactions involved in the question are:



Question 10.6:

Write the isomers of the compound having formula C_4H_9Br.

Answer

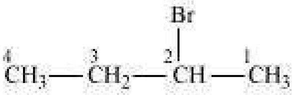
There are four isomers of the compound having the formula C_4H_9Br. These isomers are given below.

(a)

$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{2}{C}H_2-\overset{1}{C}H_2-Br$

1−Bromobutane

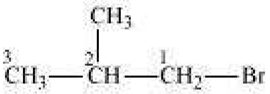
(b)



$\overset{4}{C}H_3-\overset{3}{C}H_2-\overset{\overset{Br}{|}}{\overset{2}{C}H}-\overset{1}{C}H_3$

2−Bromobutane

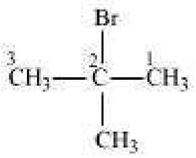
(c)



$\overset{3}{C}H_3-\overset{\overset{CH_3}{|}}{\overset{2}{C}H}-\overset{1}{C}H_2-Br$

1−Bromo−2−methylpropane

(d)



$\overset{3}{C}H_3-\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{\overset{2}{C}}}-\overset{1}{C}H_3$

2−Bromo−2−methylpropane

Question 10.7:

Write the equations for the preparation of 1−iodobutane from

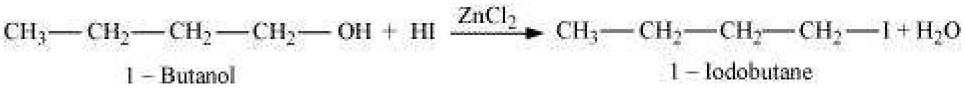
(i) 1-butanol

(ii) 1-chlorobutane

(iii) but-1-ene.

Answer

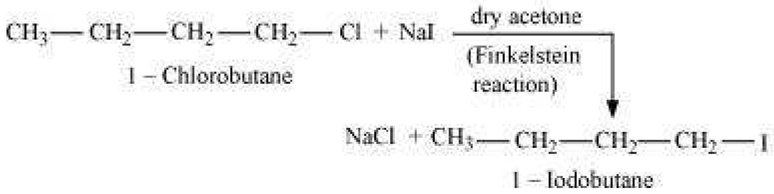
(i)



$$CH_3-CH_2-CH_2-CH_2-OH + HI \xrightarrow{ZnCl_2} CH_3-CH_2-CH_2-CH_2-I + H_2O$$

1 – Butanol; 1 – Iodobutane

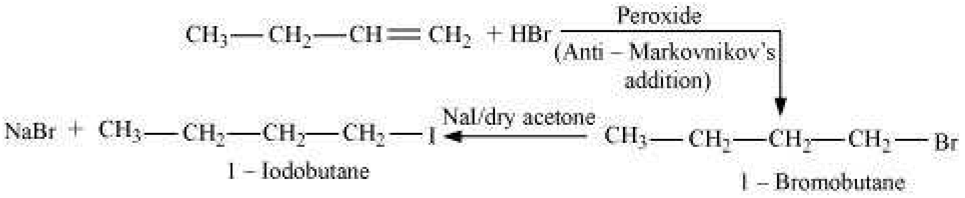
(ii)



$$CH_3-CH_2-CH_2-CH_2-Cl + NaI \xrightarrow[\text{(Finkelstein reaction)}]{\text{dry acetone}} NaCl + CH_3-CH_2-CH_2-CH_2-I$$

1 – Chlorobutane; 1 – Iodobutane

(iii)



$$CH_3-CH_2-CH=CH_2 + HBr \xrightarrow[\text{(Anti – Markovnikov's addition)}]{\text{Peroxide}} CH_3-CH_2-CH_2-CH_2-Br$$

1 – Bromobutane

$$CH_3-CH_2-CH_2-CH_2-Br \xrightarrow{\text{NaI/dry acetone}} NaBr + CH_3-CH_2-CH_2-CH_2-I$$

1 – Iodobutane

Question 10.8:

What are ambident nucleophiles? Explain with an example.

Answer

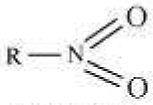
Ambident nucleophiles are nucleophiles having two nucleophilic sites. Thus, ambident nucleophiles have two sites through which they can attack.

For example, nitrite ion is an ambident nucleophile.

$$[\bar{O}-\ddot{N}=O]$$

Nitrite ion can attack through oxygen resulting in the formation of alkyl nitrites. Also, it can attack through nitrogen resulting in the formation of nitroalkanes.

Alkylnitrite



Nitroalkane

Question 10.9:

Which compound in each of the following pairs will react faster in S_N2 reaction with OH^-?

(i) CH_3Br or CH_3I

(ii) $(CH_3)_3CCl$ or CH_3Cl

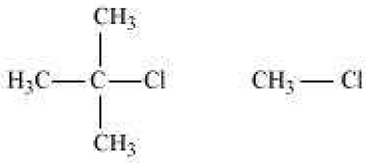
Answer

(i) In the S_N2 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.

R−F << R−Cl < R−Br < R−I

Therefore, CH_3I will react faster than CH_3Br in S_N2 reactions with OH^-.

(ii)



The S_N2 mechanism involves the attack of the nucleophile at the atom bearing the leaving group. But, in case of $(CH_3)_3CCl$, 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 $(CH_3)_3CCl$ in S_N2 reaction with OH^-.

Question 10.10:

Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

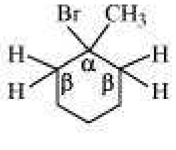
(i) 1-Bromo-1-methylcyclohexane

(ii) 2-Chloro-2-methylbutane

(iii) 2,2,3-Trimethyl-3-bromopentane.

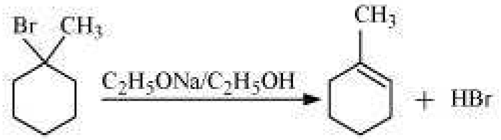
Answer

(i)

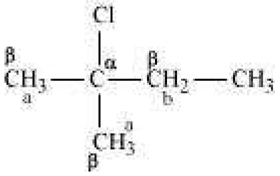


1−bromo−1−methylcyclohexane

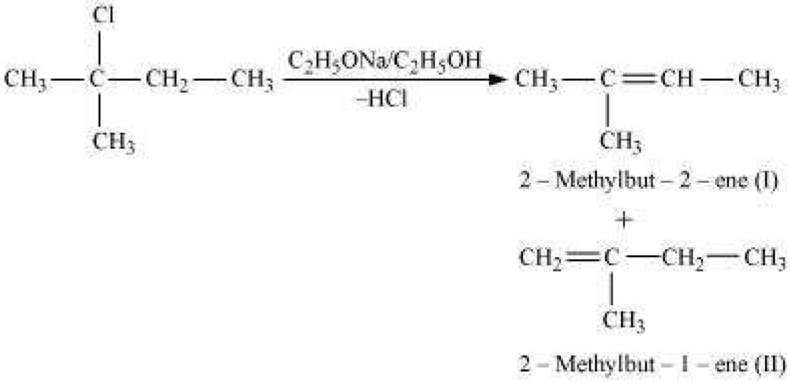
In the given compound, all β-hydrogen atoms are equivalent. Thus, dehydrohalogenation of this compound gives only one alkene.



(ii)



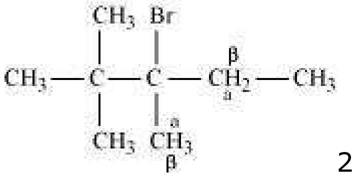
In the given compound, there are two different sets of equivalent β-hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.



Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced.

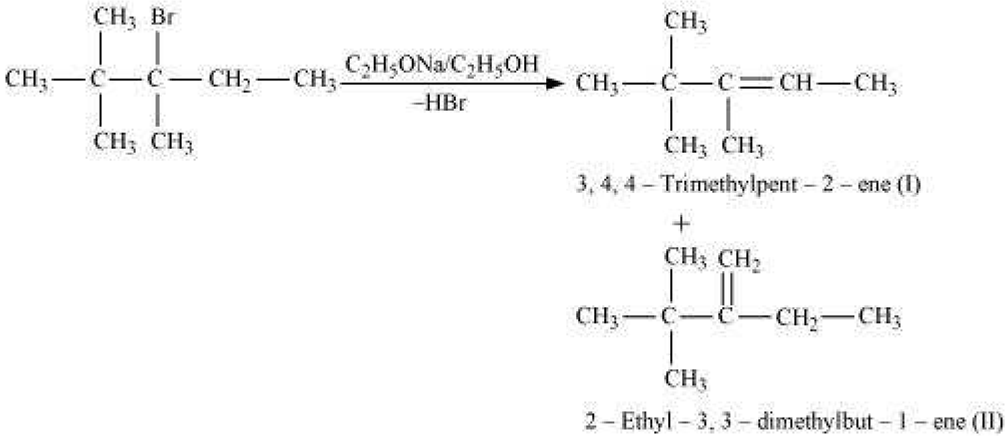
Therefore, alkene (I) i.e., 2-methylbut-2-ene is the major product in this reaction.

(iii)



2,2,3-Trimethyl-3-bromopentane

In the given compound, there are two different sets of equivalent β-hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.



According to Saytzeff's rule, in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to the doubly bonded carbon atom is preferably formed.

Hence, alkene (I) i.e., 3,4,4-trimethylpent-2-ene is the major product in this reaction.

Question 10.11:

How will you bring about the following conversions?

(i) Ethanol to but-1-yne

(ii) Ethane to bromoethene

(iii) Propene to 1-nitropropane

(iv) Toluene to benzyl alcohol

(v) Propene to propyne

(vi) Ethanol to ethyl fluoride

(vii) Bromomethane to propanone

(viii) But-1-ene to but-2-ene

(ix) 1-Chlorobutane to n-octane

(x) Benzene to biphenyl.

Answer

(i)

$$\mathrm{CH_3CH_2OH \xrightarrow{SOCl_2\,,\ Pyridine} CH_3CH_2Cl\ + SO_2\ + HCl}$$

Ethanol Chloroethane

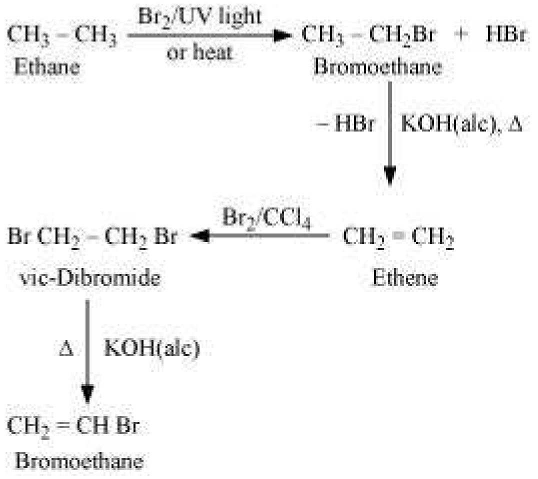
$$\mathrm{HC \equiv CH + NaNH_2 \xrightarrow{Liq.\ NH_3} HC \equiv \overset{-}{C}\overset{+}{N}a}$$

Ethyne Sodium acetylide

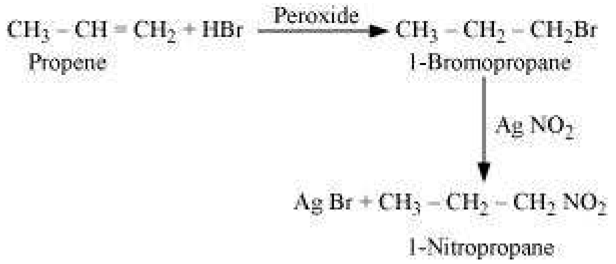
$$\mathrm{CH_3CH_2 - Cl + HC \equiv \overset{-}{C}\overset{+}{N}a \longrightarrow CH_3CH_2C \equiv CH + NaCl}$$

Chloroethane But – 1 – yne

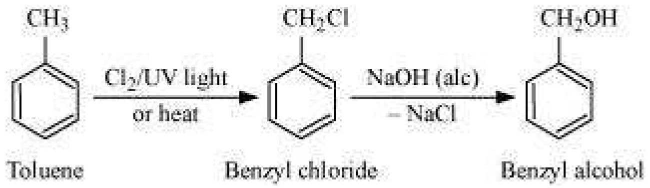
(ii)



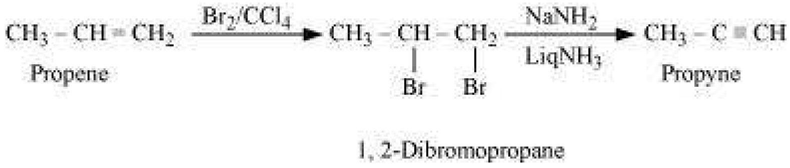
(iii)



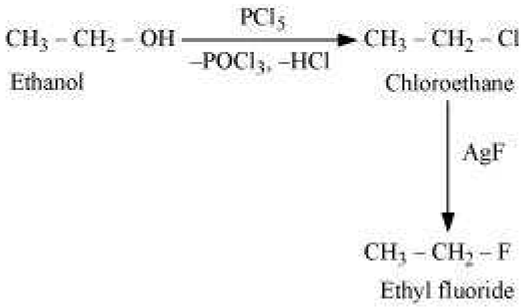
(iv)



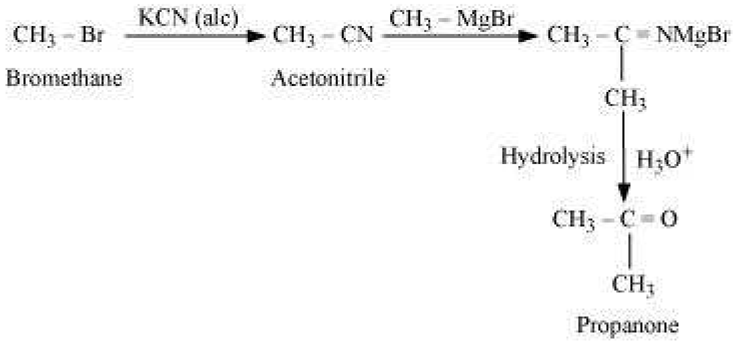
(v)



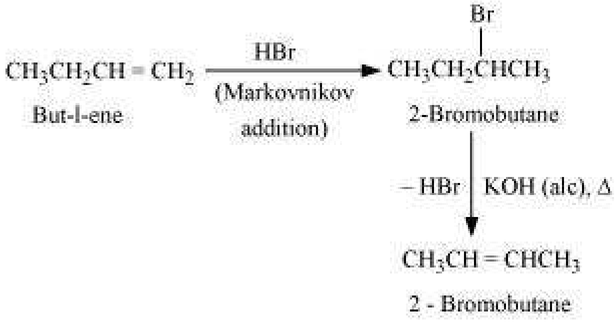
(vi)



(vii)



(viii)



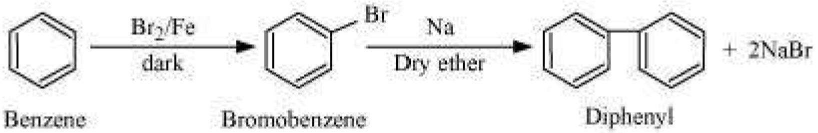
(ix)

$$2CH_3CH_2CH_2CH_2-Cl+2Na \xrightarrow[-2NaCl]{dry\ ether} CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$

1 – Chlordrutane

n – Octane

(x)



Question 10.12:

Explain why

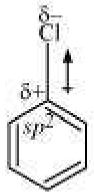
(i) the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

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

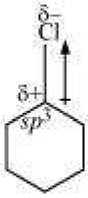
(iii) Grignard reagents should be prepared under anhydrous conditions?

Answer

(i)



Chlorobenzene



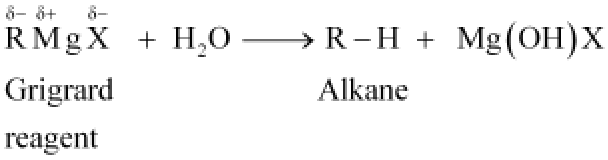
Cyclohexyl chloride

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 cydohexyl 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.



$$\underset{\text{Grigrard reagent}}{\overset{\delta-}{R}\overset{\delta+}{Mg}\overset{\delta-}{X}} + H_2O \longrightarrow \underset{\text{Alkane}}{R-H} + Mg(OH)X$$

Therefore, Grignard reagents should be prepared under anhydrous conditions.

Question 10.13:

Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

Answer

Uses of Freon – 12

Freon-12 (dichlorodifluoromethane, CF_2Cl_2) is commonly known as CFC. It is used as a refrigerant in refrigerators and air conditioners. It is also used in aerosol spray propellants such as body sprays, hair sprays, etc. However, it damages the ozone layer. Hence, its manufacture was banned in the United States and many other countries in 1994.

Uses of DDT

DDT (*p, p*−dichlorodiphenyltrichloroethane) is one of the best known insecticides. It is very effective against mosquitoes and lice. But due its harmful effects, it was banned in the United States in 1973.

Uses of carbontetrachloride (CCl_4)

(i) It is used for manufacturing refrigerants and propellants for aerosol cans.

(ii) It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

(iii) It is used as a solvent in the manufacture of pharmaceutical products.

(iv) Until the mid 1960's, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot reamer in homes, and a fire extinguisher.

Uses of iodoform (CHI_3)

Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations-containing iodine-due to its objectionable smell. The antiseptic property of iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

Question 10.14:

Write the structure of the major organic product in each of the following reactions:

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}}$

(ii) $(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}}$

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}}$

(iv) $CH_3CH_2Br + KCN \xrightarrow{\text{aq.ethanol}}$

(v) $C_6H_5ONa + C_2H_5Cl \longrightarrow$

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow$

(vii) $CH_3CH_2CH = CH_2 + HBr \xrightarrow{\text{Peroxide}}$

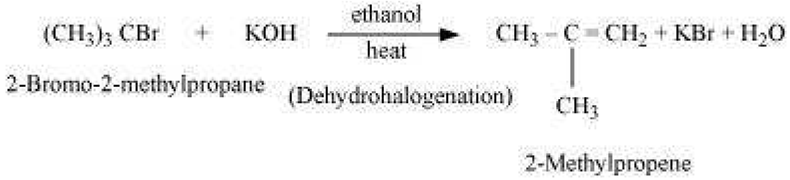
(viii) $CH_3CH = C(CH_3)_2 + HBr \longrightarrow$

Answer

(i) $CH_3CH_2CH_2Cl + NaI \xrightarrow[\text{heat}]{\text{acetone}} CH_3CH_2CH_2I + NaCl$

1 – Chloropropane (Finkelstein reaction) 1 – Iodopropane

(ii)



$$(CH_3)_3CBr + KOH \xrightarrow[\text{heat}]{\text{ethanol}} CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + KBr + H_2O$$

2-Bromo-2-methylpropane (Dehydrohalogenation) 2-Methylpropene

(iii) $CH_3CH(Br)CH_2CH_3 + NaOH \xrightarrow{\text{water}} CH_3CH(OH)CH_2CH_3 + NaBr$

2 – Bromobutane Butan – 2 – ol

(iv) $CH_3CH_2Br + KCN \xrightarrow[\text{(Nucleophilic substitution)}]{\text{aq. ethanol}} CH_3CH_2CN + KBr$

Bromobutane Cyanoethane

(v) $C_6H_5ONa + C_2H_5Cl \xrightarrow[\text{(Williamson synthesis)}]{} C_6H_5-O-C_2H_5 + NaCl$

Sodium phenoxide Chloroethane Phenetole

(vi) $CH_3CH_2CH_2OH + SOCl_2 \longrightarrow CH_3CH_2CH_2Cl + SO_2 + HCl$

1 – Propanol 1 – Chloropropane

(vii) $$\underset{\text{But}-1-\text{ene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow[\left(\text{Anti}-\text{Markovnikov's addition}\right)]{\text{Peroxide}} \underset{1-\text{Bromobutane}}{CH_3CH_2CH_2CH_2-Br}$$

(viii)

$$\underset{\text{2-Methylbut-2-ene}}{CH_3CH=C(CH_3)_2} + HBr \xrightarrow[\text{addition)}]{\text{(Markovnikov}} \underset{\text{2-Bromo-2-methylbutane}}{CH_3-CH_2-\overset{\overset{Br}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3}$$

Question 10.15:

Write the mechanism of the following reaction:

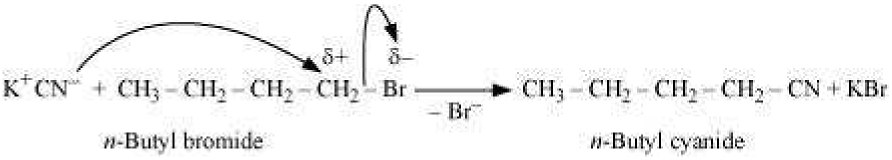
$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

Answer

The given reaction is:

$$nBuBr + KCN \xrightarrow{EtOH-H_2O} nBuCN$$

The given reaction is an S_N2 reaction. In this reaction, CN^- acts as the nucleophile and attacks the carbon atom to which Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



Question 10.16:

Arrange the compounds of each set in order of reactivity towards S_N2 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.

Answer

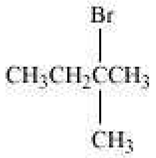
(i)

$CH_3CH_2CH_2CH_2CH_2-Br$

1-Bromopentane (1°)

$CH_3CH_2CH_2\overset{\mathrm{Br}}{\overset{|}{C}}HCH_3$

2-Bromopentane (2°)



$CH_3CH_2\overset{\mathrm{Br}}{\overset{|}{\underset{\underset{\mathrm{CH_3}}{|}}{C}}}CH_3$

2-Bromo-2-methylbutane (3°)

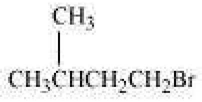
An S_N2 reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards S_N2 displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile increases in the following order.

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

Hence, the increasing order of reactivity towards S_N^2 displacement is:

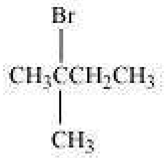
2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

(ii)



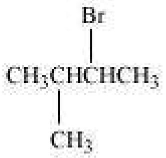
$CH_3\overset{\mathrm{CH_3}}{\overset{|}{C}}HCH_2CH_2Br$

1-Bromo-3-methylbutane (1°)



$CH_3\overset{\mathrm{Br}}{\overset{|}{\underset{\underset{\mathrm{CH_3}}{|}}{C}}}CH_2CH_3$

2-Bromo-2-methylbutane (3°)



$CH_3CH\overset{\mathrm{Br}}{\overset{|}{C}}HCH_3$ with $\underset{\mathrm{CH_3}}{|}$ on the second carbon: $CH_3\underset{\underset{\mathrm{CH_3}}{|}}{C}H\overset{\mathrm{Br}}{\overset{|}{C}}HCH_3$

2-Bromo-3-methylbutane (2°)

Since steric hindrance in alkyl halides increases in the order of 1° < 2° < 3°, the increasing order of reactivity towards S_N2 displacement is

3° < 2° < 1°.

Hence, the given set of compounds can be arranged in the increasing order of their reactivity towards S_N^2 displacement as:

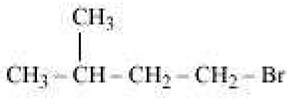
2-Bromo-2-methylbutane < 2-Bromo-3-methylbutane < 1-Bromo-3-methylbutane

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

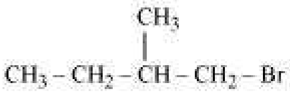
(iii)

$CH_3-CH_2-CH_2-CH_2-Br$

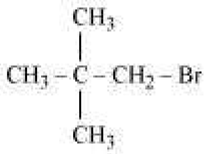
1-Bromobutane


$CH_3-\overset{CH_3}{\overset{|}{C}}H-CH_2-CH_2-Br$

1-Bromo-3-methylbutane


$CH_3-CH_2-\overset{CH_3}{\overset{|}{C}}H-CH_2-Br$

1-Bromo-2-methylbutane


$CH_3-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{C}}}}-CH_2-Br$

1-Bromo-2, 2-dimethylpropane

The steric hindrance to the nucleophile in the S_N2 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

Question 10.17:

Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

Answer

Benzyl chloride (1°) 1° carbocation

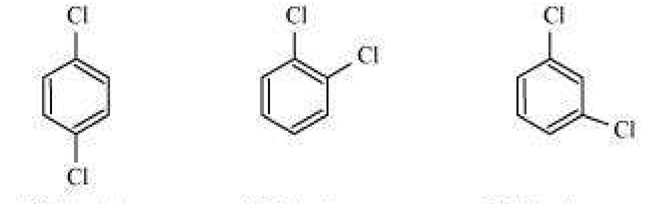
Chlorodiphenylmethane 2° carbocation

Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now, $C_6H_5CH_2Cl$ forms 1°-carbocation, while $C_6H_5CHCLC_6H_5$ forms 2°-carbocation, which is more stable than 1°-carbocation. Hence, $C_6H_5CHClC_6H_5$ is hydrolyzed more easily than $C_6H_5CH_2Cl$ by aqueous KOH.

Question 10.18:

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

Answer



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

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.

Question 10.19:

How the following conversions can be carried out?

(i) Propene to propan-1-ol

(ii) Ethanol to but-1-yne

(iii) 1-Bromopropane to 2-bromopropane

(iv) Toluene to benzyl alcohol

(v) Benzene to 4-bromonitrobenzene

(vi) Benzyl alcohol to 2-phenylethanoic acid

(vii) Ethanol to propanenitrile

(viii) Aniline to chlorobenzene

(ix) 2-Chlorobutane to 3, 4-dimethylhexane

(x) 2-Methyl-1-propene to 2-chloro-2-methylpropane

(xi) Ethyl chloride to propanoic acid

(xii) But-1-ene to n-butyliodide

(xiii) 2-Chloropropane to 1-propanol

(xiv) Isopropyl alcohol to iodoform

(xv) Chlorobenzene to *p*-nitrophenol

(xvi) 2-Bromopropane to 1-bromopropane

(xvii) Chloroethane to butane

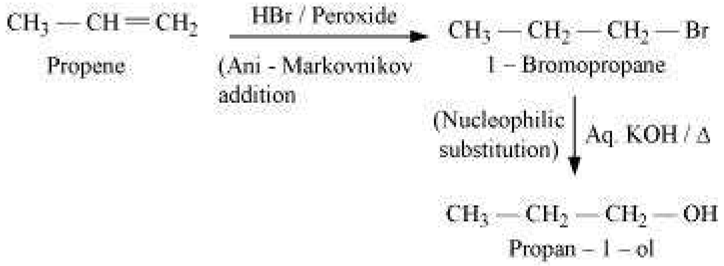
(xviii) Benzene to diphenyl

(xix) *tert*-Butyl bromide to isobutyl bromide

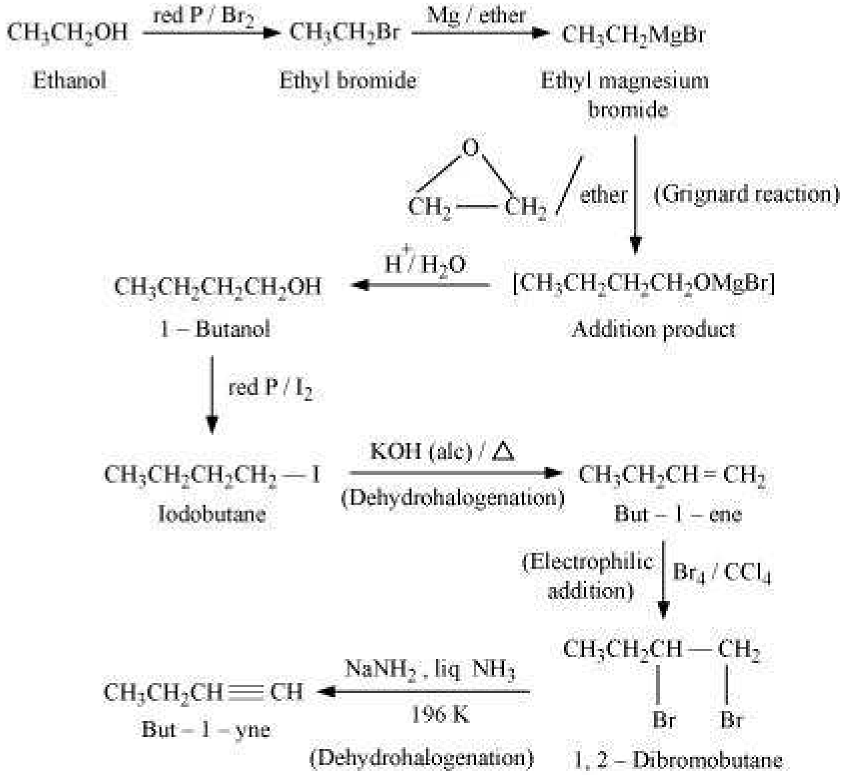
(xx) Aniline to phenylisocyanide

Answer

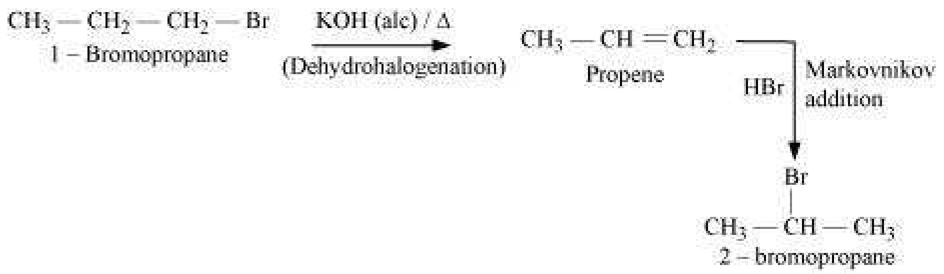
(i)



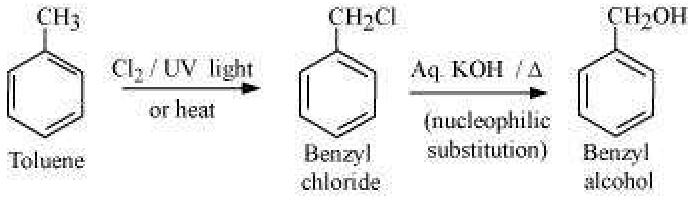
(ii)



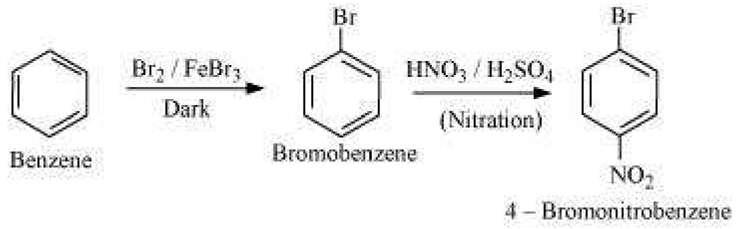
(iii)



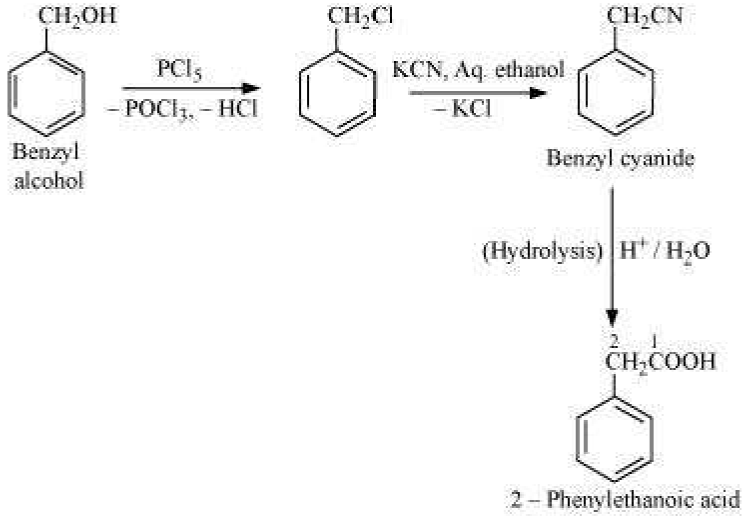
(iv)



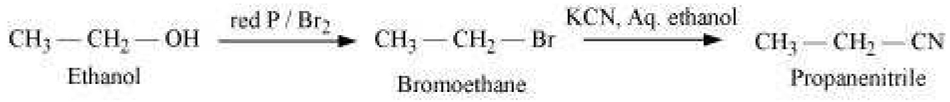
(v)



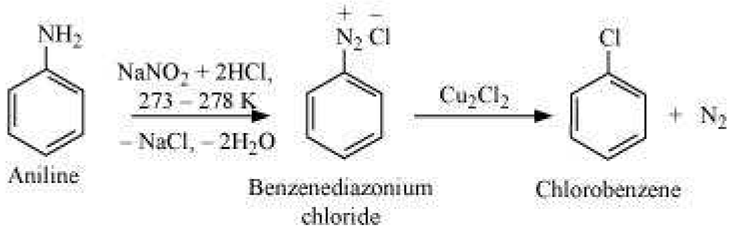
(vi)



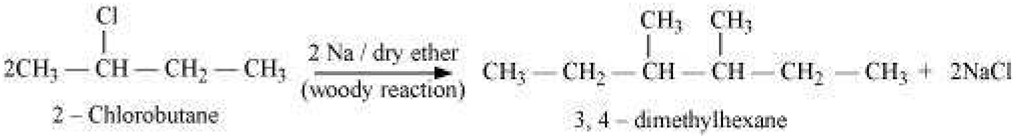
(vii)



(viii)



(ix)

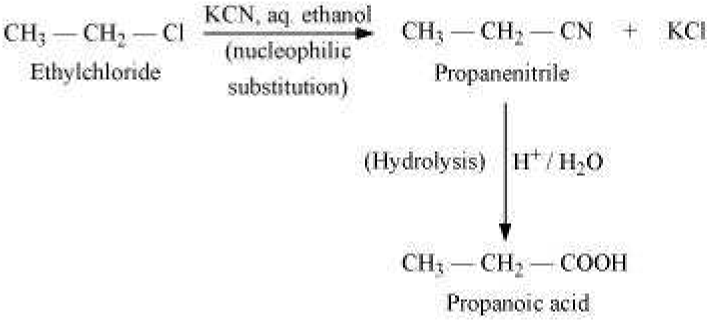


$$2CH_3-\underset{\text{2 – Chlorobutane}}{\overset{Cl}{\overset{|}{CH}}-CH_2-CH_3} \xrightarrow[\text{(woody reaction)}]{\text{2 Na / dry ether}} \underset{\text{3, 4 – dimethylhexane}}{CH_3-CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3} + 2NaCl$$

(x)

$$\underset{\text{2 – Methyl – 1 – propene}}{CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2} \xrightarrow[\text{(Markovnikov addition)}]{HCl} \underset{\text{2-chloro-2-methylpropane}}{CH_3-\overset{CH_3}{\overset{|}{\underset{Cl}{\underset{|}{C}}}}-CH_3}$$

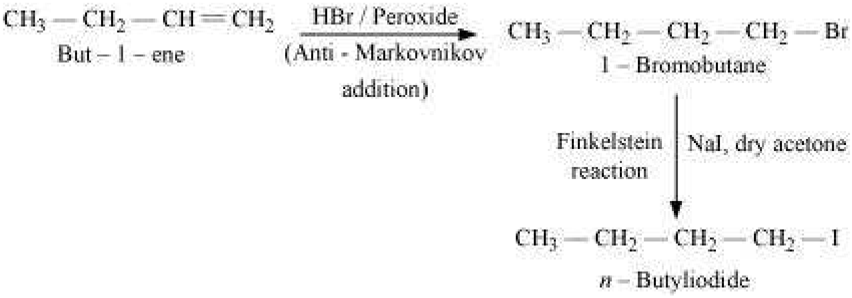
(xi)



$$\underset{\text{Ethylchloride}}{CH_3-CH_2-Cl} \xrightarrow[\text{(nucleophilic substitution)}]{\text{KCN, aq. ethanol}} \underset{\text{Propanenitrile}}{CH_3-CH_2-CN} + KCl$$

$$\xrightarrow[\text{(Hydrolysis)}]{H^+ / H_2O} \underset{\text{Propanoic acid}}{CH_3-CH_2-COOH}$$

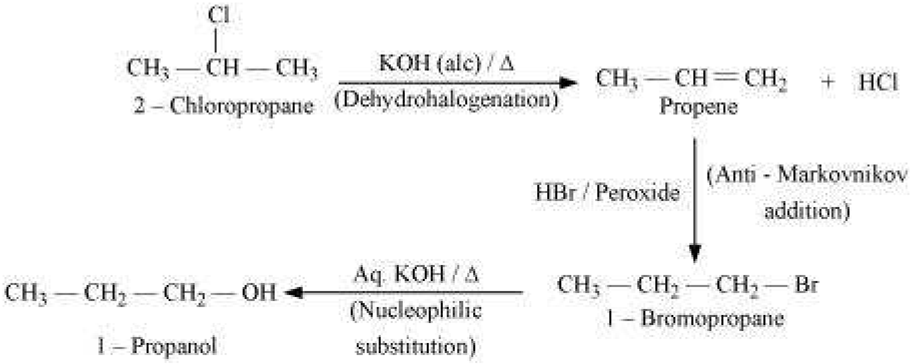
(xii)



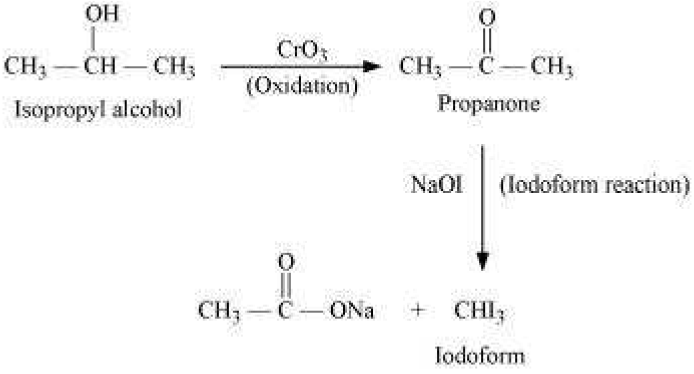
$$\underset{\text{But – 1 – ene}}{CH_3-CH_2-CH=CH_2} \xrightarrow[\text{(Anti - Markovnikov addition)}]{\text{HBr / Peroxide}} \underset{\text{1 – Bromobutane}}{CH_3-CH_2-CH_2-CH_2-Br}$$

$$\xrightarrow[\text{Finkelstein reaction}]{\text{NaI, dry acetone}} \underset{n\text{ – Butyliodide}}{CH_3-CH_2-CH_2-CH_2-I}$$

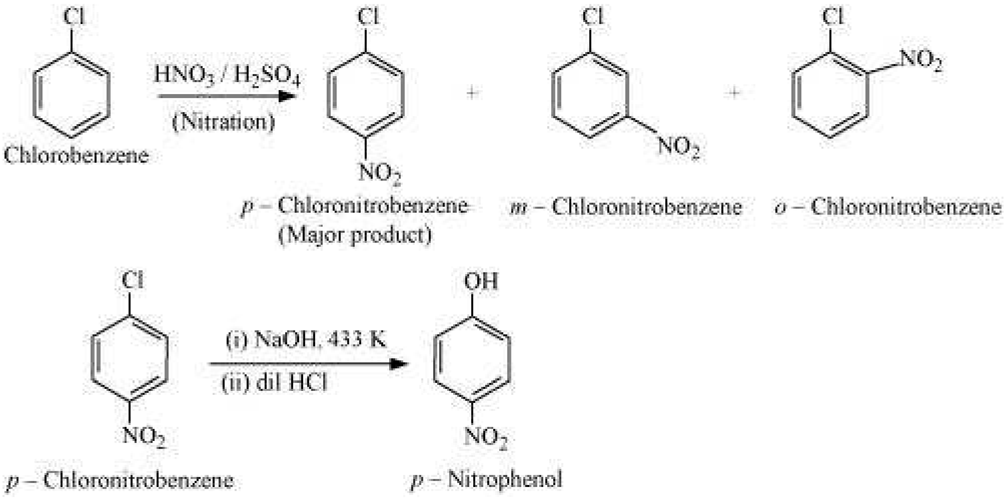
(xiii)


2 – Chloropropane
KOH (alc) / Δ
(Dehydrohalogenation)
Propene
+ HCl
HBr / Peroxide
(Anti - Markovnikov addition)
1 – Bromopropane
Aq. KOH / Δ
(Nucleophilic substitution)
1 – Propanol

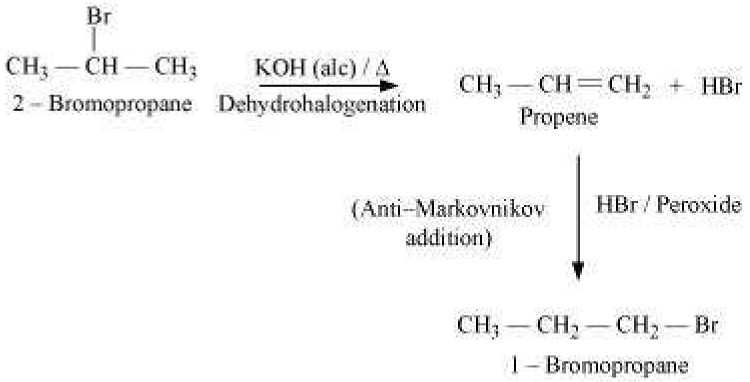
(xiv)


Isopropyl alcohol
CrO$_3$
(Oxidation)
Propanone
NaOI
(Iodoform reaction)
Iodoform

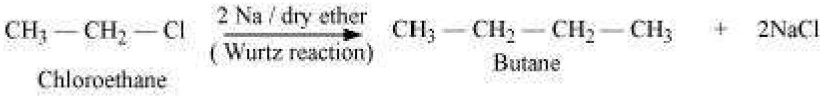
(xv)


Chlorobenzene
HNO$_3$ / H$_2$SO$_4$
(Nitration)
p – Chloronitrobenzene
(Major product)
m – Chloronitrobenzene
o – Chloronitrobenzene
(i) NaOH, 433 K
(ii) dil HCl
p – Chloronitrobenzene
p – Nitrophenol

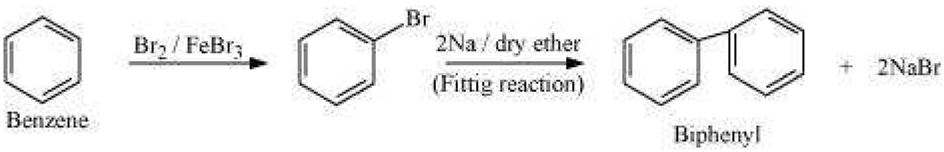
(xvi)



(xvii)



(xviii)



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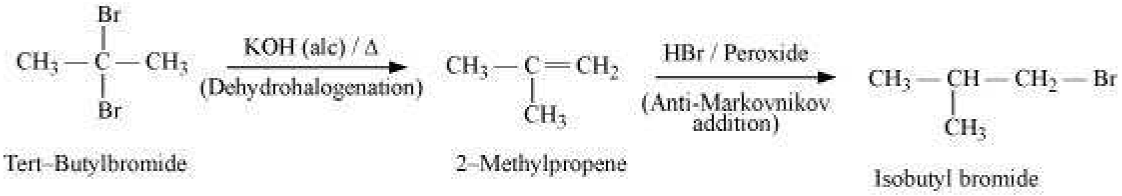

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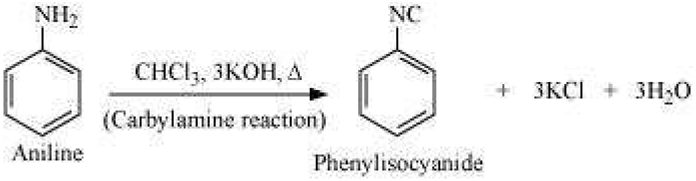


Question 10.20:

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.

Answer

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.

$$R-Cl+KOH_{(aq)}\longrightarrow R-OH\ +KCl$$

Alkyl chloride — 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.

$$R-\underset{\beta}{C}H_2-\underset{\alpha}{C}H_2-Cl+KOH(alc)\longrightarrow R-CH=CH_2+KCl+H_2O$$

Alkyl chloride — Alkene

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.

Question 10.21:

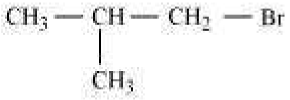
Primary alkyl halide C_4H_9Br (a) reacted with alcoholic KOH to give compound (b).Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C_8H_{18} which is different from the compound formed when n-butyl bromide is reacted with sodium. Give the structural formula of (a) and write the equations for all the reactions.

Answer

There are two primary alkyl halides having the formula, C_4H_9Br. They are *n* − bulyl bromide and isobutyl bromide.

$$CH_3-CH_2-CH_2-CH_2-Br$$

n – Butyl bromide

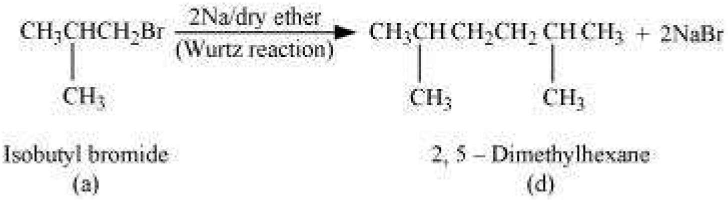


$$CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br$$

Isobutyl bromide

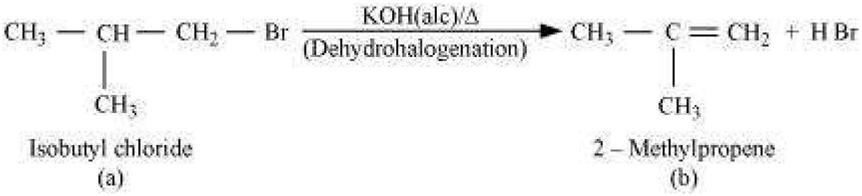
Therefore, compound (a) is either *n*−butyl bromide or isobutyl bromide.

Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, $C_8H_{18,}$ which is different from the compound formed when *n*−butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

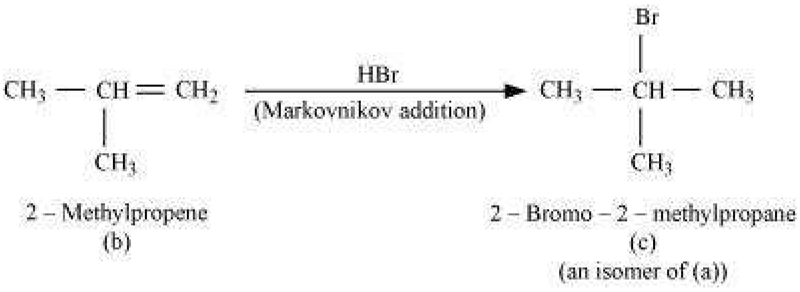


Thus, compound (d) is 2, 5−dimethylhexane.

It is given that compound (a) reacts with alcoholic KOH to give compound (b). Hence, compound (b) is 2−methylpropene.



Also, compound (b) reacts with HBr to give compound (c) which is an isomer of (a). Hence, compound (c) is 2−bromo−2−methylpropane.



Question 10.22:

What happens when

(i) n-butyl chloride is treated with alcoholic KOH,

(ii) bromobenzene is treated with Mg in the presence of dry ether,

(iii) chlorobenzene is subjected to hydrolysis,

(iv) ethyl chloride is treated with aqueous KOH,

(v) methyl bromide is treated with sodium in the presence of dry ether,

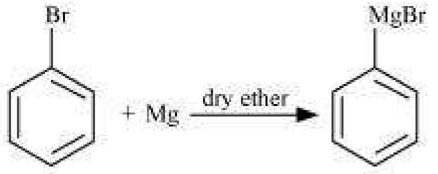
(vi) methyl chloride is treated with KCN.

Answer

(i) When n−butyl chloride is treated with alcoholic KOH, the formation of but−l−ene takes place. This reaction is a dehydrohalogenation reaction.

$$\underset{n-\text{Butyl chloride}}{CH_3-CH_2-CH_2-CH_2-Cl} \xrightarrow[\text{(Dehydrohalogenation)}]{KOH(alc)/\Delta} \underset{\text{But-l-ene}}{CH_3-CH_2-CH=CH_2} + KCl + H_2O$$

(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



Bromobenzene Phenylmagensium bromide

(iii) Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.

Chlorobenzene Phenol

(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.

$$\underset{\text{Ethyl chloride}}{CH_3-CH_2-Cl} \xrightarrow[\text{(Hydrolysis)}]{KOH_{(aq)}} \underset{\text{Ethanol}}{CH_3-CH_2-OH} + KCl$$

(v) When methyl bromide is treated with sodium in the presence of dry ether, ethane is formed. This reaction is known as the Wurtz reaction.

$$\underset{\text{Methyl bromide}}{2\,CH_3-Br} + 2\,Na \xrightarrow[\text{(Wurtz reaction)}]{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + 2NaBr$$

(vi) When methyl chloride is treated with KCN, it undergoes a substitution reaction to give methyl cyanide.

$$\underset{\text{Methyl chloride}}{CH_3-Cl} + KCN \xrightarrow[\text{Nucleophilic substitution}]{} \underset{\text{Methyl cyanide}}{CH_3-CN} + KCl$$

Text solution

Question 10.1:

Write structures of the following compounds:

(i) 2-Chloro-3-methylpentane

(ii) 1-Chloro-4-ethylcyclohexane

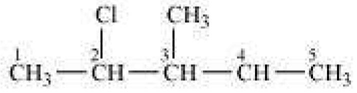
(iii) 4-tert. Butyl-3-iodoheptane

(iv) 1,4-Dibromobut-2-ene

(v) 1-Bromo-4-sec. butyl-2-methylbenzene

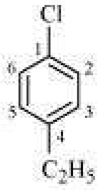
Answer

(i)



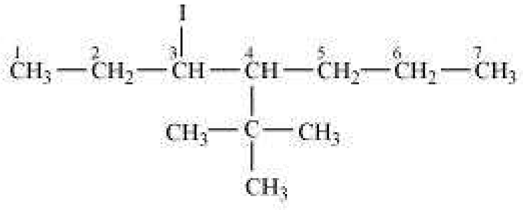
2-Chloro-3-methyl pentane

(ii)



1-Chloro-4-ethylcyclohexane

(iii)



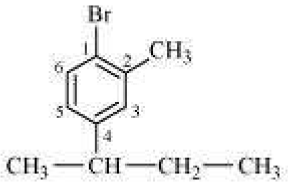
4- tert-Butyl-3-iodoheptane

(iv)

$$Br-\overset{1}{C}H_2-\overset{2}{C}H=\overset{3}{C}H-\overset{4}{C}H_2-Br$$

1, 4-Dibromobut-2-ene

(v)



1-Bromo-4-sec-butyl-2-methylbenzene

Question 10.2:

Why is sulphuric acid not used during the reaction of alcohols with KI?

Answer

In the presence of sulphuric acid (H_2SO_4), KI produces HI

$$2KI + H_2SO_4 \longrightarrow 2KHSO_4 + 2HI$$

Since H_2SO_4 is an oxidizing agent, it oxidizes HI (produced in the reaction to $I_{2)}$.

$$2HI + H_2SO_4 \longrightarrow I_2 + SO_2 + H_2O$$

As a result, the reaction between alcohol and HI to produce alkyl iodide cannot occur. Therefore, sulphuric acid is not used during the reaction of alcohols with KI. Instead, a non-oxidizing acid such as H_3PO_4 is used.

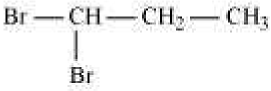
Question 10.3:

Write structures of different dihalogen derivatives of propane.

Answer

There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

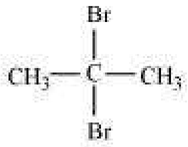
(i)



$$Br-\underset{\displaystyle Br}{\underset{|}{C}H}-CH_2-CH_3$$

1, 1-Dibromopropane

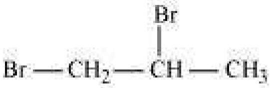
(ii)



$CH_3-\overset{\displaystyle Br}{\underset{\displaystyle Br}{C}}-CH_3$

2, 2-Dibromopropane

(iii)



$Br-CH_2-\overset{\displaystyle Br}{CH}-CH_3$

1, 2-Dibromopropane

(iv)

$Br-CH_2-CH_2-CH_2-Br$

1, 3-Dibromopropane

Question 10.4:

Among the isomeric alkanes of molecular formula C_5H_{12}, identify the one that on photochemical chlorination yields

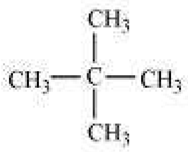
(i) A single monochloride.

(ii) Three isomeric monochlorides.

(iii) Four isomeric monochlorides.

Answer

(i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula C_5H_{12}. This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.

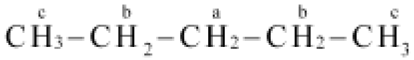


$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3$

Neopentane

(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain three different types of H-atoms.

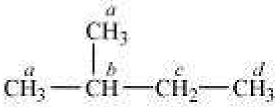
Therefore, the isomer is *n*-pentane. It can be observed that there are three types of H atoms labelled as *a*, *b* and *c* in *n*-pentane.



$C\overset{c}{H}_3-C\overset{b}{H}_2-C\overset{a}{H}_2-C\overset{b}{H}_2-C\overset{c}{H}_3$

n-Pentane

(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula C_5H_{12} should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c,* and *d* in 2-methylbutane.



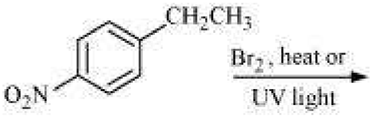
$\overset{a}{C}H_3-\overset{\overset{\overset{a}{CH_3}}{|}}{\overset{b}{C}H}-\overset{c}{C}H_2-\overset{d}{C}H_3$

Question 10.5:

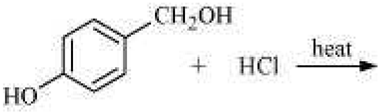
Draw the structures of major monohalo products in each of the following reactions:

(i)

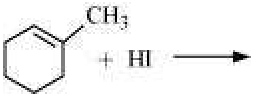
(ii)



(iii)



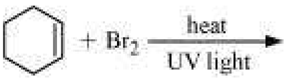
(iv)



(v)

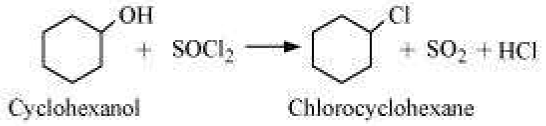
$CH_3CH_2Br + NaI \longrightarrow$

(vi)

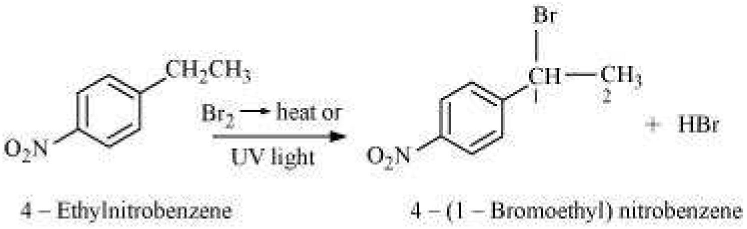


Answer

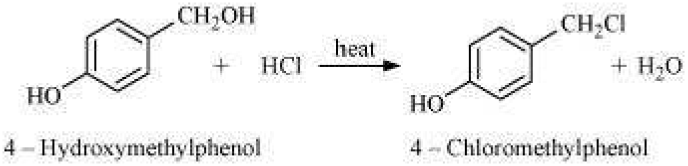
(i)



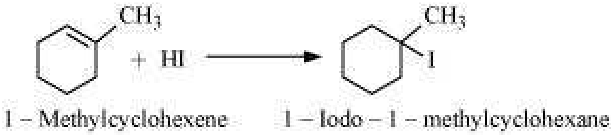
(ii)



(iii)



(iv)

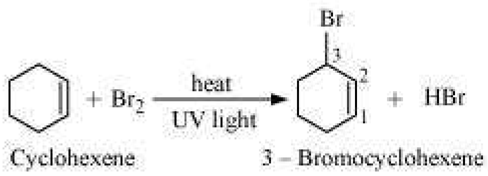


(v)

$CH_3CH_2Br + NaI \longrightarrow CH_3CH_2I + NaBr$

Bromoethane Iodoethane

(vi)



Question 10.6:

Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

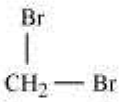
(ii) 1-Chloropropane, Isopropyl chloride, 1-Chlorobutane.

Answer

(i)

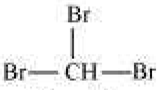
$CH_3—Cl$
Chloromethane

$CH_3—Br$
Bromomethane



$Br—CH_2—Br$

Dibromomethane



$Br—\overset{Br}{CH}—Br$

Bromoform

For alkyl halides containing the same alkyl group, the boiling point increases with an increase in the atomic mass of the halogen atom.

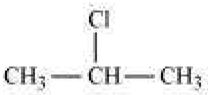
Since the atomic mass of Br is greater than that of Cl, the boiling point of bromomethane is higher than that of chloromethane.

Further, for alkyl halides containing the same alkyl group, the boiling point increases with an increase in the number of halides. Therefore, the boiling point of Dibromomethane is higher than that of chloromethane and bromomethane, but lower than that of bromoform.

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

Chloromethane < Bromomethane < Dibromomethane < Bromoform.

(ii)



$CH_3—\overset{Cl}{CH}—CH_3$

Isopropyl chloride

$Cl—CH_2—CH_2—CH_3$
1 – Chloropropane

$Cl—CH_2—CH_2—CH_2—CH_3$
1 – Chlorobutane

For alkyl halides containing the same halide, the boiling point increases with an increase in the size of the alkyl group. Thus, the boiling point of 1-chlorobutane is higher than that of isopropyl chloride and 1-chloropropane.

Further, the boiling point decreases with an increase in branching in the chain. Thus, the boiling point of isopropyl alcohol is lower than that of 1-chloropropane.

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

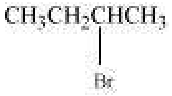
Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

Question 10.7:

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

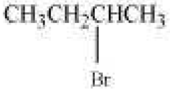
(i)

$CH_3CH_2CH_2CH_2Br$ or



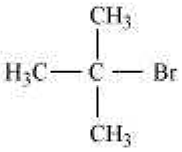
$CH_3CH_2CH(Br)CH_3$

(ii)



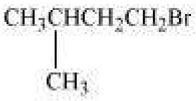
$CH_3CH_2CH(Br)CH_3$

or



$H_3C-C(CH_3)_2-Br$

(iii)



$CH_3CH(CH_3)CH_2CH_2Br$

or

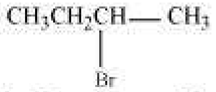
H_3C or $CH_3CH_2CH(CH_3)CH_2Br$

Answer

(i)

$CH_3CH_2CH_2CH_2Br$

1 – Bromobutane (1°)

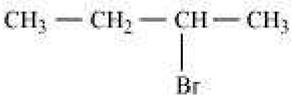


$CH_3CH_2CH(Br)-CH_3$

2 – Bromobutane (2°)

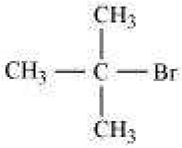
2-bromobutane is a 2° alkylhalide whereas 1-bromobutane is a 1° alkyl halide. The approaching of nucleophile is more hindered in 2-bromobutane than in 1-bromobutane. Therefore, 1-bromobutane reacts more rapidly than 2-bromobutane by an S_N2 mechanism.

(ii)



$CH_3-CH_2-CH(Br)-CH_3$

2 – Bromobutane (2°)

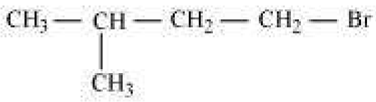


$CH_3-C(CH_3)_2-Br$

2 – Bromo – 2 – methylpropane (3°)

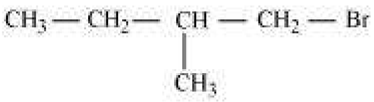
2-Bromobutane is 2° alkylhalide whereas 2-bromo-2-methylpropane is 3° alkyl halide. Therefore, greater numbers of substituents are present in 3° alkyl halide than in 2° alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than 2-bromo-2-methylpropane by an S_N2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

(iii)



$CH_3-CH(CH_3)-CH_2-CH_2-Br$

1 – Bromo – 3 – methylbutane (1°)



$CH_3-CH_2-CH(CH_3)-CH_2-Br$

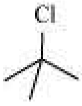
1 – Bromo – 2 – methylbutane (1°)

Both the alkyl halides are primary. However, the substituent $-CH_3$ 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 S_N2 mechanism.

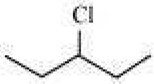
Question 10.8:

In the following pairs of halogen compounds, which compound undergoes faster S_N1 reaction?

(i)



and

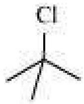


(ii)

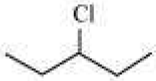
and

Answer

(i)



2 – Chloro – 2 – methylpropane (3°)
(I)



3 – chloropentane (2°)
(II)

S_N1 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 S_N1 reaction. Since 3° carbocation is more stable than 2° carbocation. (I), i.e. 2−chloro-2-methylpropane, undergoes faster S_N1 reaction than (II) i.e., 3-chloropentane.

(ii)

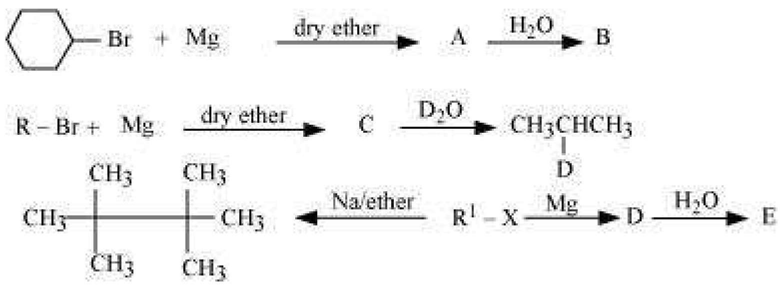
2 – chloroheptane (2°)
(I)

1 – chlorohexane (1°)
(II)

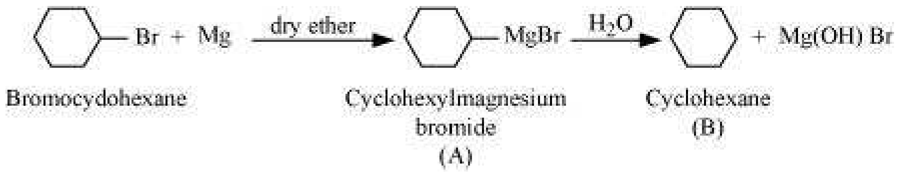
The alkyl halide (I) is 2° while (II) is 1°. 2° carbocation is more stable than 1° carbocation. Therefore, (I), 2−chloroheptane, undergoes faster S_N1 reaction than (II), 1-chlorohexane.

Question 10.9:

Identify A, B, C, D, E, R and R^1 in the following:



Answer

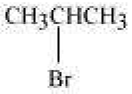


Since D of D_2O gets attached to the carbon atom to which MgBr is attached, C is

$$\underset{\substack{|\\ MgBr}}{CH_3CHCH_3}$$

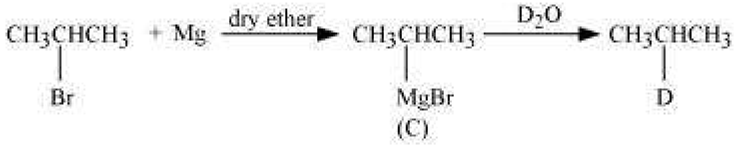
Isopropylmagnesium bromide

Therefore, the compound R − Br is

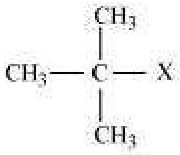


$$\underset{\substack{|\\ Br}}{CH_3CHCH_3}$$

2 – Bromopropane



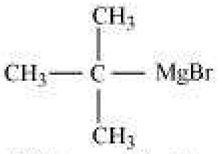
When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product. This is known as Wurtz reaction. Therefore, the halide, R^1−X, is



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-X$

tert – Butylhalide

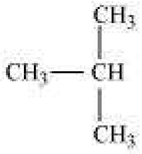
Therefore, compound D is



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-MgBr$

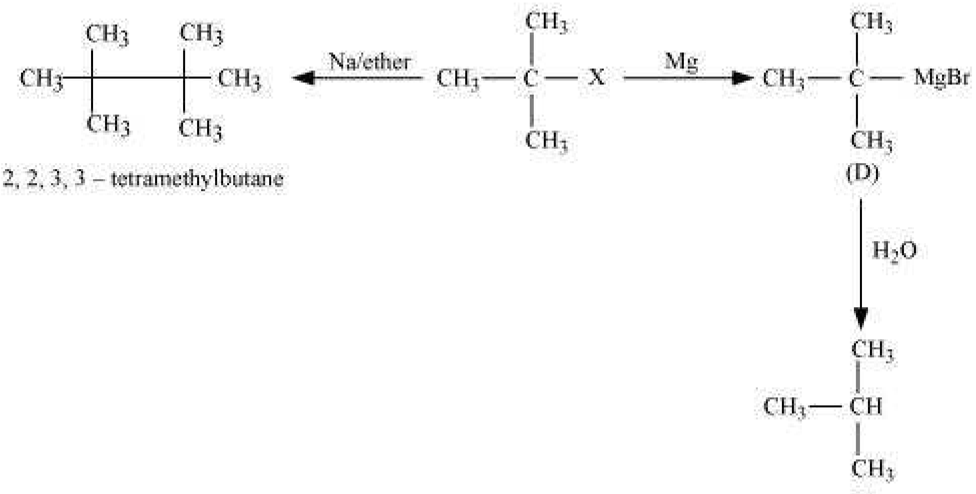
tert – Bulytmagnesiumbromide

And, compound E is



$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{CH}}$

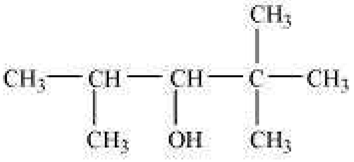
2 – Methylpropane



Question 11.1:

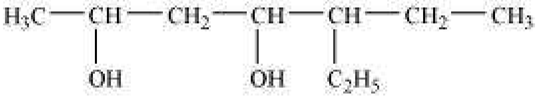
Write IUPAC names of the following compounds:

(i)



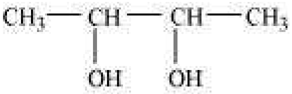
$CH_3-CH(CH_3)-CH(OH)-C(CH_3)_2-CH_3$

(ii)



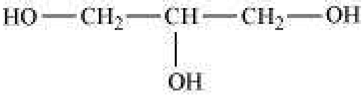
$H_3C-CH(OH)-CH_2-CH(OH)-CH(C_2H_5)-CH_2-CH_3$

(iii)



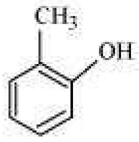
$CH_3-CH(OH)-CH(OH)-CH_3$

(iv)

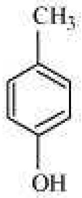


$HO-CH_2-CH(OH)-CH_2-OH$

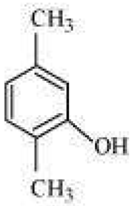
(v)



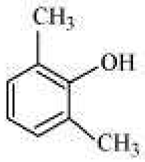
(vi)



(vii)



(viii)



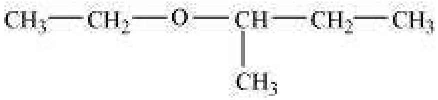
(ix)

$CH_3-O-CH_2-\underset{\underset{CH_3}{|}}{CH}-CH_3$

(x) $C_6H_5-O-C_2H_5$

(xi) $C_6H_5-O-C_7H_{15}(n-)$

(xii)



$CH_3-CH_2-O-\underset{\underset{CH_3}{|}}{CH}-CH_2-CH_3$

Answer

(i) 2, 2, 4-Trimethylpentan-3-ol

(ii) 5-Ethylheptane-2, 4-diol

(iii) Butane-2, 3-diol

(iv) Propane-1, 2, 3-triol

(v) 2-Methylphenol

(vi) 4-Methylphenol

(vii) 2, 5-Dimethylphenol

(viii) 2, 6-Dimethylphenol

(ix) 1-Methoxy-2-methylpropane

(x) Ethoxybenzene

(xi) 1-Phenoxyheptane

(xii) 2-Ethoxybutane

Question 11.2:

Write structures of the compounds whose IUPAC names are as follows:

(i) 2-Methylbutan-2-ol

(ii) 1-Phenylpropan-2-ol

(iii) 3,5-Dimethylhexane −1, 3, 5-triol

(iv) 2,3 − Diethylphenol

(v) 1 − Ethoxypropane

(vi) 2-Ethoxy-3-methylpentane

(vii) Cyclohexylmethanol

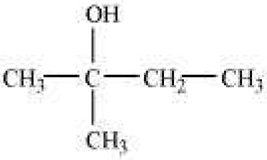
(viii) 3-Cyclohexylpentan-3-ol

(ix) Cyclopent-3-en-1-ol

(x) 3-Chloromethylpentan-1-ol.

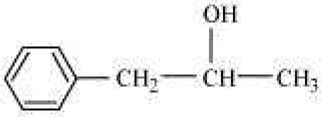
Answer

(i)

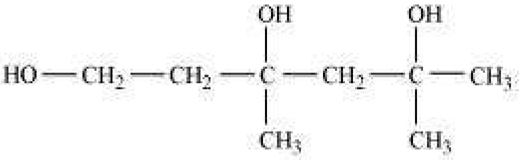


$$CH_3-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-CH_3$$

(ii)

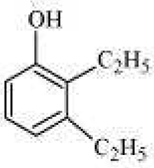


(iii)



$$HO-CH_2-CH_2-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle OH}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3$$

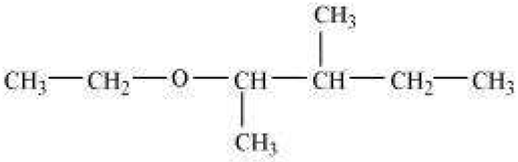
(iv)



(v)

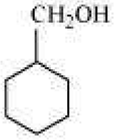
$$CH_3-CH_2-O-CH_2-CH_2-CH_3$$

(vi)

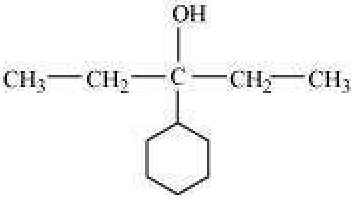


$CH_3-CH_2-O-\underset{CH_3}{\underset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_3$

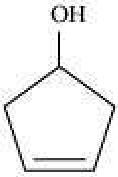
(vii)



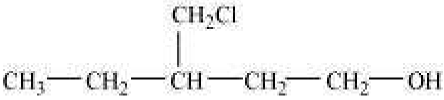
(viii)



(ix)



(x)



$CH_3-CH_2-\overset{CH_2Cl}{\overset{|}{CH}}-CH_2-CH_2-OH$

Question 11.3:

(i) Draw the structures of all isomeric alcohols of molecular formula $C_5H_{12}O$ and give their IUPAC names.

(ii) Classify the isomers of alcohols in question 11.3 (i) as primary, secondary and tertiary alcohols.

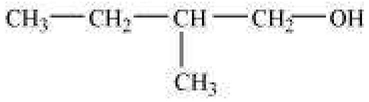
Answer

(i) The structures of all isomeric alcohols of molecular formula, $C_5H_{12}O$ are shown below:

(a) $CH_3-CH_2-CH_2-CH_2-CH_2-OH$

Pentan-1-ol (1°)

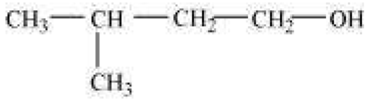
(b)



$CH_3-CH_2-\underset{\substack{|\\ CH_3}}{CH}-CH_2-OH$

2-Methylbutan-1-ol (1°)

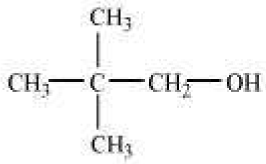
(c)



$CH_3-\underset{\substack{|\\ CH_3}}{CH}-CH_2-CH_2-OH$

3-Methylbutan-1-ol (1°)

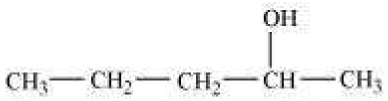
(d)



$CH_3-\overset{\substack{CH_3\\ |}}{\underset{\substack{|\\ CH_3}}{C}}-CH_2-OH$

2, 2-Dimethylpropan-1-ol (1°)

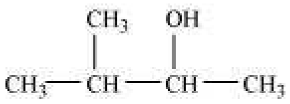
(e)



$CH_3-CH_2-CH_2-\overset{\substack{OH\\ |}}{CH}-CH_3$

Pentan-2-ol (2°)

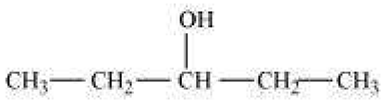
(f)



$CH_3-\overset{\substack{CH_3\\ |}}{CH}-\overset{\substack{OH\\ |}}{CH}-CH_3$

3-Methylbutan-2-ol (2°)

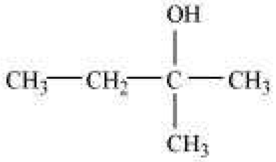
(g)



$CH_3-CH_2-\overset{\substack{OH\\ |}}{CH}-CH_2-CH_3$

Pentan-3-ol (2°)

(h)



2-Methylbutan-2-ol (3°)

(ii) Primary alcohol: Pentan-1-ol; 2-Methylbutan-1-ol;

3-Methylbutan-1-ol; 2, 2−Dimethylpropan-1-ol

Secondary alcohol: Pentan-2-ol; 3-Methylbutan-2-ol;

Pentan-3-ol

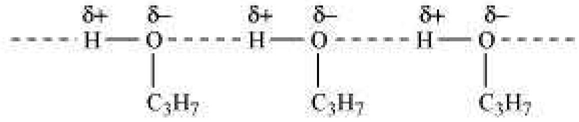
Tertiary alcohol: 2-methylbutan-2-ol

Question 11.4:

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

Answer

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



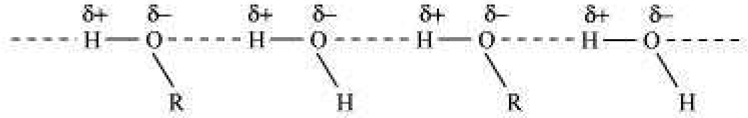
Therefore, extra energy is required to break hydrogen bonds. For this reason, propanol has a higher boiling point than hydrocarbon butane.

Question 11.5:

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

Answer

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



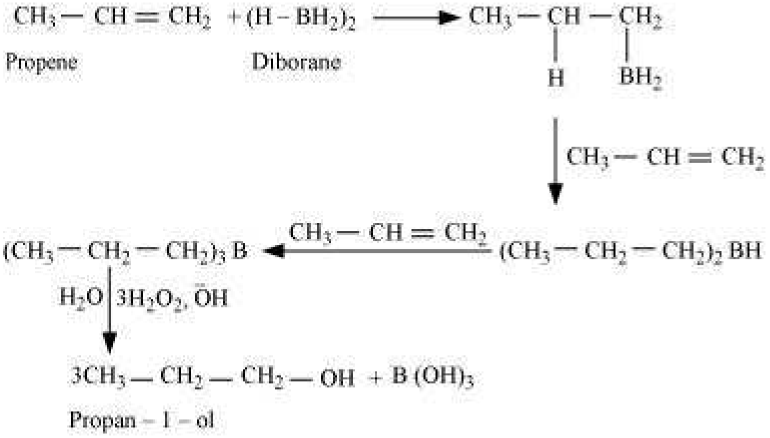
As a result, alcohols are comparatively more soluble in water than hydrocarbons of comparable molecular masses.

Question 11.6:

What is meant by hydroboration-oxidation reaction? Illustrate it with an example.

Answer

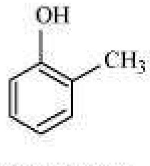
The addition of borane followed by oxidation is known as the hydroboration-oxidation reaction. For example, propan-1-ol is produced by the hydroboration-oxidation reaction of propene. In this reaction, propene reacts with diborane $(BH_3)_2$ to form trialkyl borane as an addition product. This addition product is oxidized to alcohol by hydrogen peroxide in the presence of aqueous sodium hydroxide.



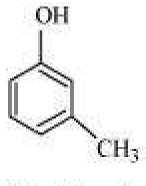
Question 11.7:

Give the structures and IUPAC names of monohydric phenols of molecular formula, C_7H_8O.

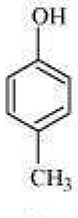
Answer



2 – Methylphenol
(*o* – Cresol)



3 – Methylphenol
(*m* – Cresol)



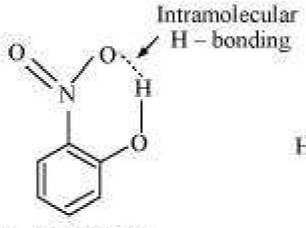
4 – Methylphenol
(*p* – Cresol)

Question 11.8:

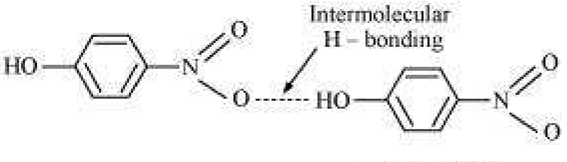
While separating a mixture of *ortho* and *para* nitrophenols by steam distillation, name the isomer which will be steam volatile. Give reason.

Answer

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.



o - Nitrophenol



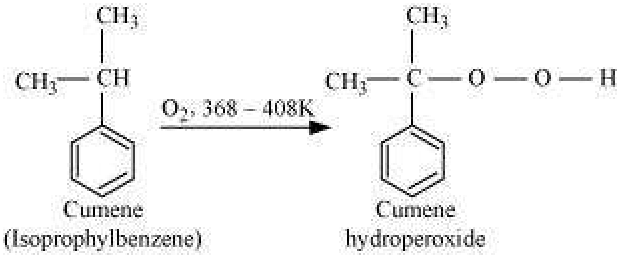
p - Nitrophenol

Question 11.9:

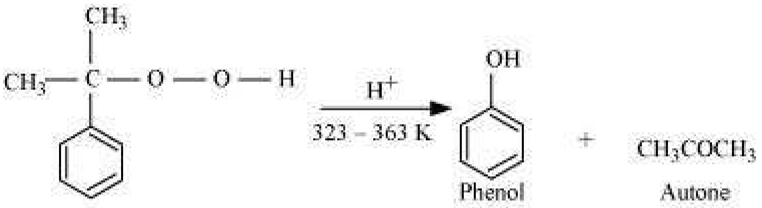
Give the equations of reactions for the preparation of phenol from cumene.

Answer

To prepare phenol, cumene is first oxidized in the presence of air of cumene hydroperoxide.



Then, cumene hydroxide is treated with dilute acid to prepare phenol and acetone as by-products.

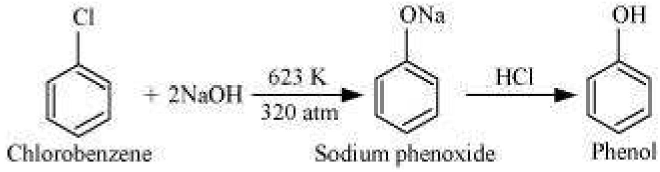


Question 11.10:

Write chemical reaction for the preparation of phenol from chlorobenzene.

Answer

Chlorobenzene is fused with NaOH (at 623 K and 320 atm pressure) to produce sodium phenoxide, which gives phenol on acidification.



Question 11.11:

Write the mechanism of hydration of ethene to yield ethanol.

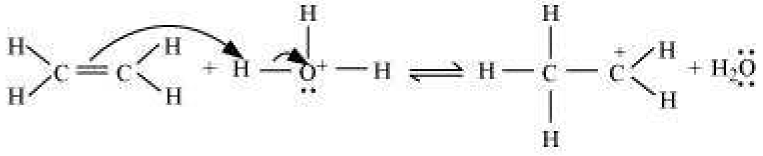
Answer

The mechanism of hydration of ethene to form ethanol involves three steps.

Step 1:

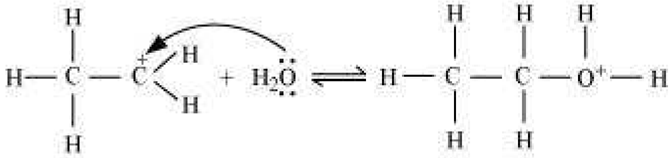
Protonation of ethene to form carbocation by electrophilic attack of H_3O^+:

$H_2O + H^+ \longrightarrow H_3O^+$



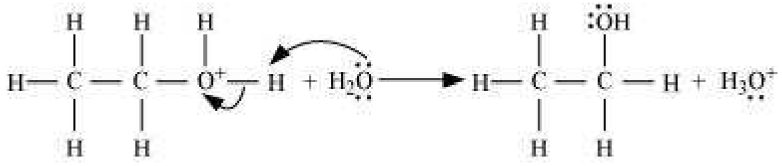
Step 2:

Nucleophilic attack of water on carbocation:



Step 3:

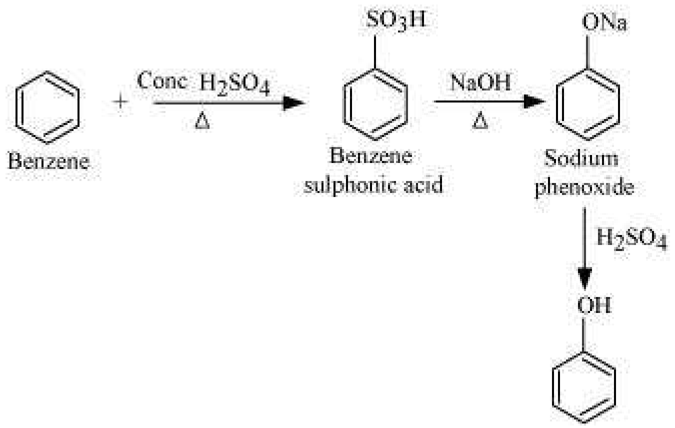
Deprotonation to form ethanol:



Question 11.12:

You are given benzene, conc. H_2SO_4 and NaOH. Write the equations for the preparation of phenol using these reagents.

Answer



Question 11.13:

Show how will you synthesize:

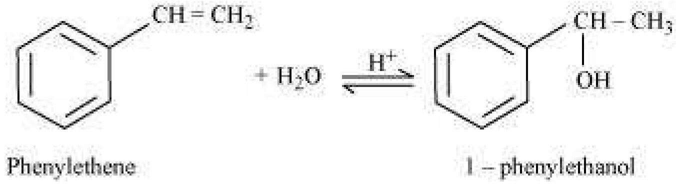
(i) 1-phenylethanol from a suitable alkene.

(ii) cyclohexylmethanol using an alkyl halide by an S_N2 reaction.

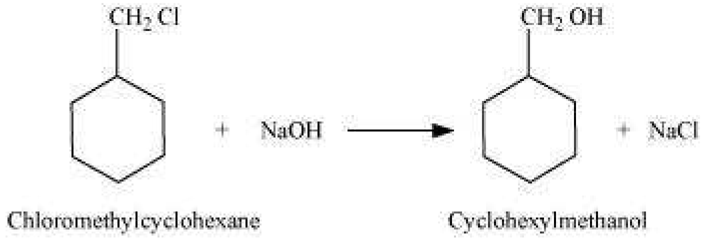
(iii) pentan-1-ol using a suitable alkyl halide?

Answer

(i) By acid-catalyzed hydration of ethylbenzene (styrene), 1-phenylethanol can be synthesized.



(ii) When chloromethylcyclohexane is treated with sodium hydroxide, cyclohexylmethanol is obtained.



(iii) When 1-chloropentane is treated with NaOH, pentan-1-ol is produced.

$$\underset{\text{1-Chloropentane}}{CH_3CH_2CH_2CH_2CH_2Cl} + NaOH \longrightarrow \underset{\text{Pantan-1-ol}}{CH_3CH_2CH_2CH_2CH_2OH} + NaCl$$

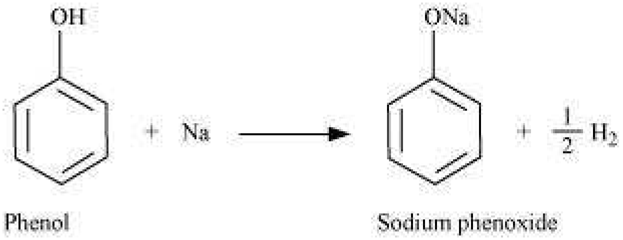
Question 11.14:

Give two reactions that show the acidic nature of phenol. Compare acidity of phenol with that of ethanol.

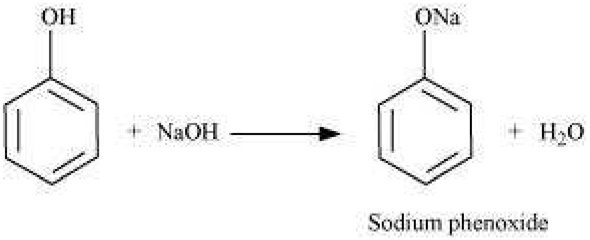
Answer

The acidic nature of phenol can be represented by the following two reactions:

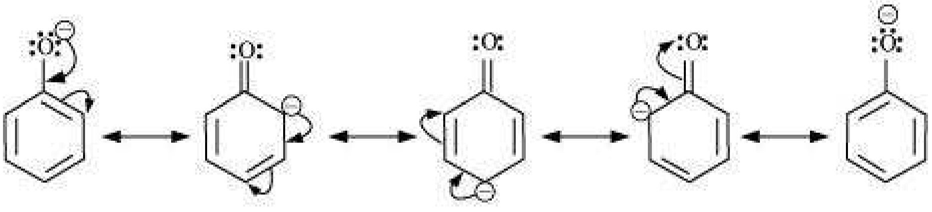
(i) Phenol reacts with sodium to give sodium phenoxide, liberating H_2.



(ii) Phenol reacts with sodium hydroxide to give sodium phenoxide and water as by-products.



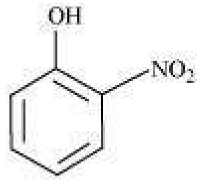
The acidity of phenol is more than that of ethanol. This is because after losing a proton, the phenoxide ion undergoes resonance and gets stabilized whereas ethoxide ion does not.



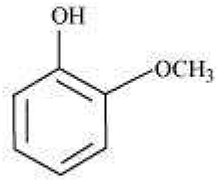
Question 11.15:

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

Answer



o – Nitrophenol



o – Methoxyphenol

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.

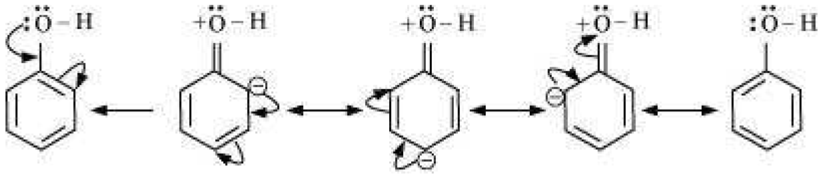
For this reason, ortho-nitrophenol is more acidic than ortho-methoxyphenol.

Question 11.16:

Explain how does the −OH group attached to a carbon of benzene ring activate it towards electrophilic substitution?

Answer

The −OH group is an electron-donating group. Thus, it increases the electron density in the benzene ring as shown in the given resonance structure of phenol.



As a result, the benzene ring is activated towards electrophilic substitution.

Question 11.17:

Give equations of the following reactions:

(i) Oxidation of propan-1-ol with alkaline $KMnO_4$ solution.

(ii) Bromine in CS_2 with phenol.

(iii) Dilute HNO_3 with phenol.

(iv) Treating phenol with chloroform in presence of aqueous NaOH.

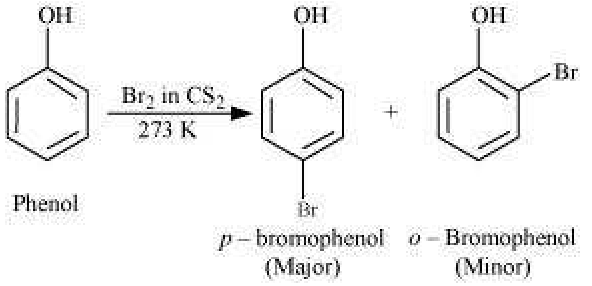
Answer

(i)

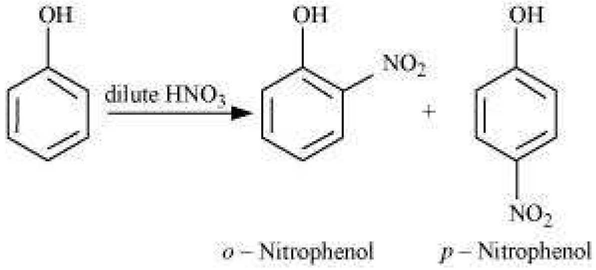
$$CH_3CH_2CH_2OH \xrightarrow{\text{alk KmnO}_4} CH_3CH_2COOH$$

Propan-1-ol Propanoic acid

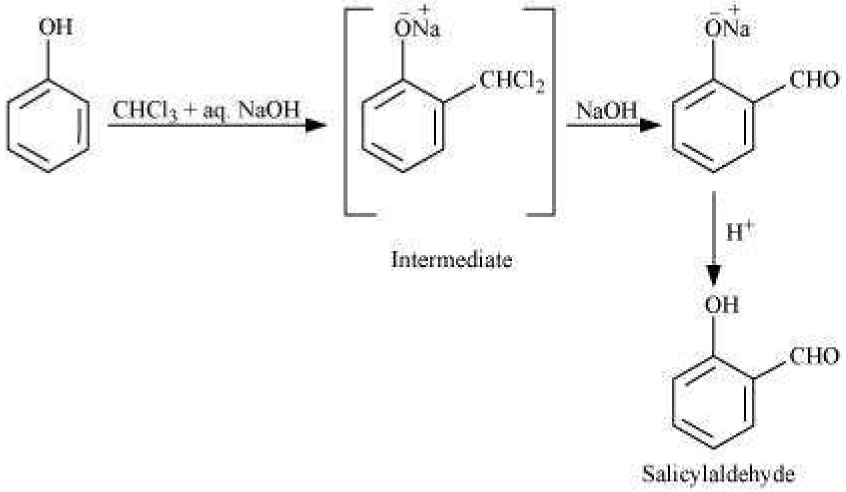
(ii)



(iii)



(iv)



Question 11.18:

Explain the following with an example.

(i) Kolbe’s reaction.

(ii) Reimer-Tiemann reaction.

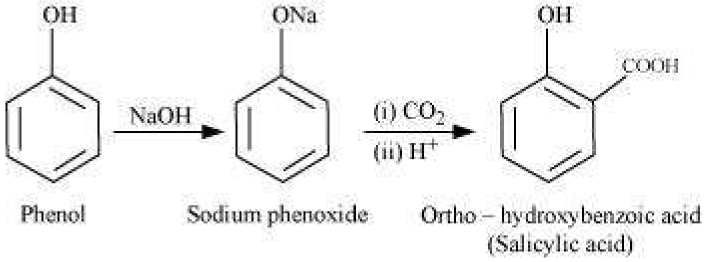
(iii) Williamson ether synthesis.

(iv) Unsymmetrical ether.

Answer

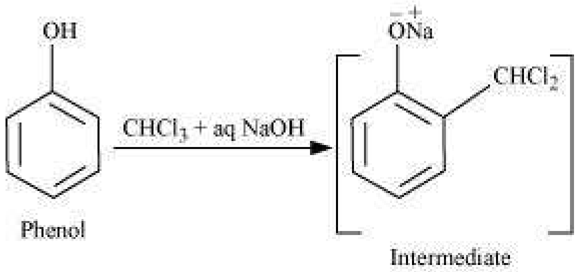
(i) Kolbe's reaction:

When phenol is treated with sodium hydroxide, sodium phenoxide is produced. This sodium phenoxide when treated with carbon dioxide, followed by acidification, undergoes electrophilic substitution to give ortho-hydroxybenzoic acid as the main product. This reaction is known as Kolbe's reaction.



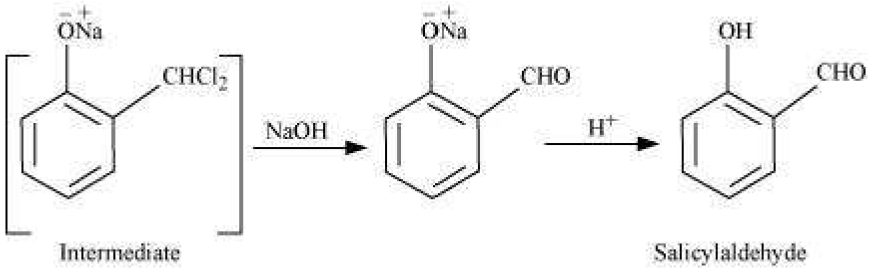
(ii) Reimer-Tiemann reaction:

When phenol is treated with chloroform ($CHCl_3$) in the presence of sodium hydroxide, a −CHO group is introduced at the ortho position of the benzene ring.



This reaction is known as the Reimer-Tiemann reaction.

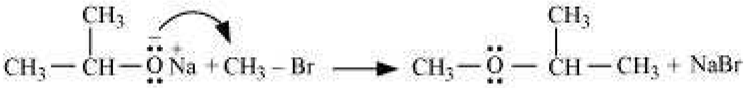
The intermediate is hydrolyzed in the presence of alkalis to produce salicyclaldehyde.



(iii) Williamson ether synthesis:

Williamson ether synthesis is a laboratory method to prepare symmetrical and unsymmetrical ethers by allowing alkyl halides to react with sodium alkoxides.

This reaction involves S_N2 attack of the alkoxide ion on the alkyl halide. Better results are obtained in case of primary alkyl halides.



If the alkyl halide is secondary or tertiary, then elimination competes over substitution.

(iv) Unsymmetrical ether:

An unsymmetrical ether is an ether where two groups on the two sides of an oxygen atom differ (i.e., have an unequal number of carbon atoms). For example: ethyl methyl ether ($CH_3-O-CH_2CH_3$).

Question 11.19:

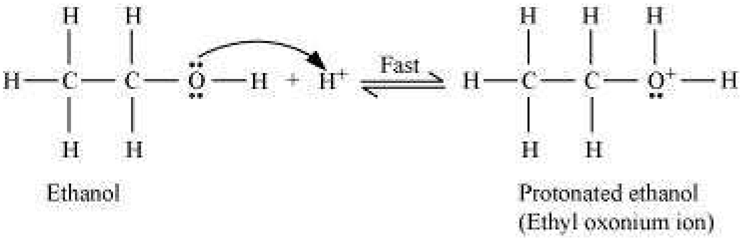
Write the mechanism of acid-catalysed dehydration of ethanol to yield ethene.

Answer

The mechanism of acid dehydration of ethanol to yield ethene involves the following three steps:

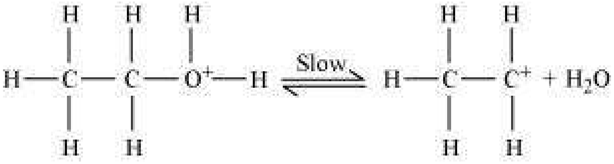
Step 1:

Protonation of ethanol to form ethyl oxonium ion:



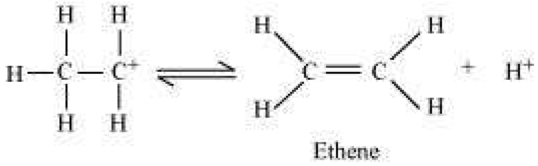
Step 2:

Formation of carbocation (rate determining step):



Step 3:

Elimination of a proton to form ethene:



The acid consumed in step 1 is released in Step 3. After the formation of ethene, it is removed to shift the equilibrium in a forward direction.

Question 11.20:

How are the following conversions carried out?

(i) Propene → Propan-2-ol

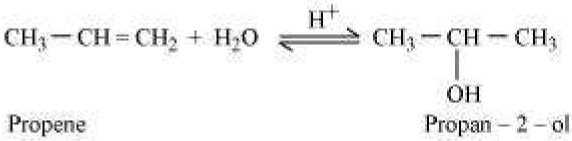
(ii) Benzyl chloride → Benzyl alcohol

(iii) Ethyl magnesium chloride → Propan-1-ol.

(iv) Methyl magnesium bromide → 2-Methylpropan-2-ol.

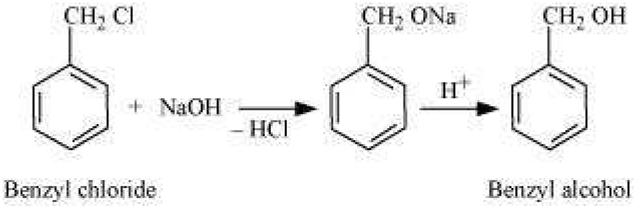
Answer

(i) If propene is allowed to react with water in the presence of an acid as a catalyst, then propan-2-ol is obtained.

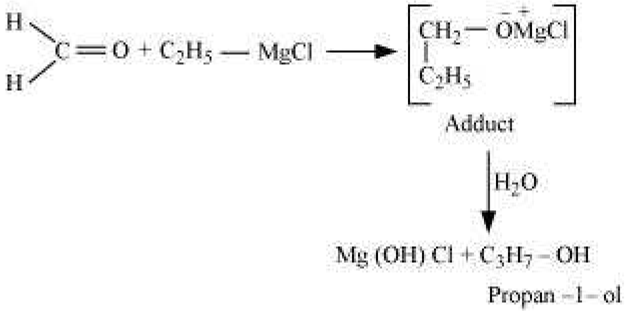


$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2O \overset{H^+}{\rightleftharpoons} \underset{\text{Propan}-2-\text{ol}}{CH_3-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3}$$

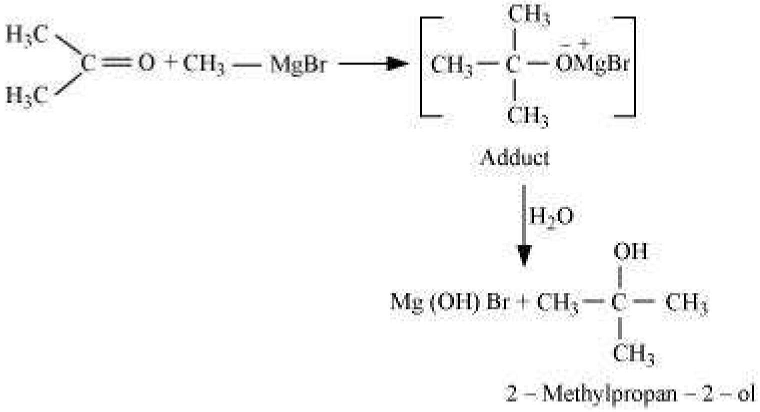
(ii) If benzyl chloride is treated with NaOH (followed by acidification) then benzyl alcohol is produced.



(iii) When ethyl magnesium chloride is treated with methanal, an adduct is the produced which gives propan-1-ol on hydrolysis.



(iv) When methyl magnesium bromide is treated with propane, an adduct is the product which gives 2-methylpropane-2-ol on hydrolysis.



Question 11.21:

Name the reagents used in the following reactions:

(i) Oxidation of a primary alcohol to carboxylic acid.

(ii) Oxidation of a primary alcohol to aldehyde.

(iii) Bromination of phenol to 2,4,6-tribromophenol.

(iv) Benzyl alcohol to benzoic acid.

(v) Dehydration of propan-2-ol to propene.

(vi) Butan-2-one to butan-2-ol.

Answer

(i) Acidified potassium permanganate

(ii) Pyridinium chlorochromate (PCC)

(iii) Bromine water

(iv) Acidified potassium permanganate

(v) 85% phosphoric acid

(vi) $NaBH_4$ or $LiAlH_4$

Question 11.22:

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

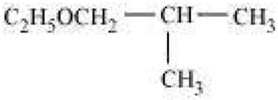
Answer

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.

Question 11.23:

Give IUPAC names of the following ethers:

(i)



$C_2H_5OCH_2-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_3$

(ii)

$CH_3OCH_2CH_2Cl$

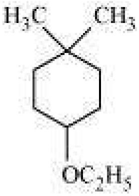
(iii)

$O_2N-C_6H_4-OCH_3(p)$

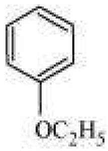
(iv)

$CH_3CH_2CH_2OCH_3$

(v)



(vi)



Answer

(i) 1-Ethoxy-2-methylpropane

(ii) 2-Chloro-1-methoxyethane

(iii) 4-Nitroanisole

(iv) 1-Methoxypropane

(v) 1-Ethoxy-4, 4-dimethylcyclohexane

(vi) Ethoxybenzene

Question 11.24:

Write the names of reagents and equations for the preparation of the following ethers by Williamson’s synthesis:

(i) 1-Propoxypropane

(ii) Ethoxybenzene

(iii) 2-Methoxy-2-methylpropane

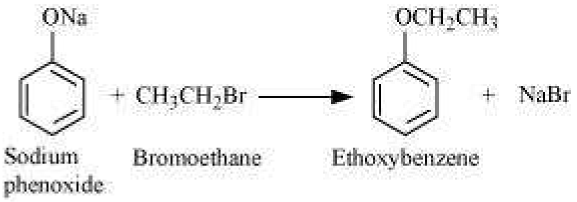
(iv) 1-Methoxyethane

Answer

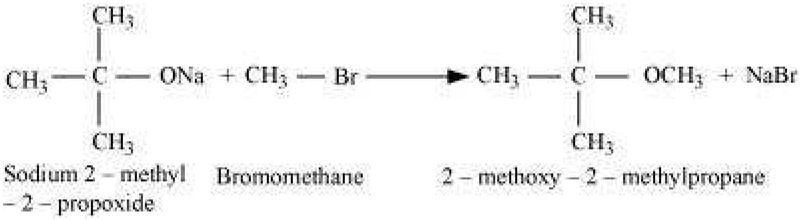
$$\underset{\text{Sodium propoxide}}{CH_3CH_2CHONa} + \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \longrightarrow \underset{\text{1- Propoxypropane}}{C_2H_5CH_2-O-CH_2C_2H_5} + NaBr$$

(i)

(ii)



(iii)



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-ONa + CH_3-Br \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-OCH_3 + NaBr$$