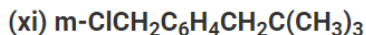
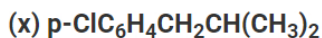
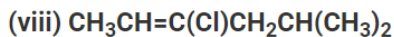
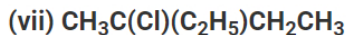
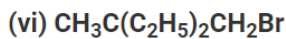
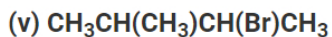
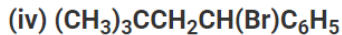
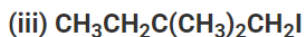
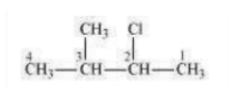


Question 10.1: Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides :



Soln:

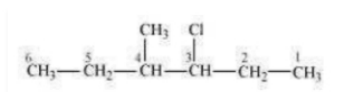
(i)



2 - Chloro - 3 - methylbutane

(Secondary alkyl halide)

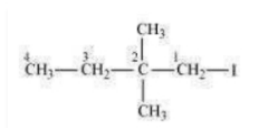
(ii)



3 - Chloro - 4 - methylhexane

(Secondary alkyl halide)

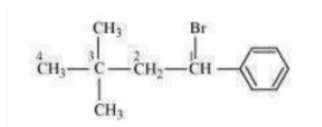
(iii)



1 - Iodo - 2, 2 - dimethylbutane

(Primary alkyl halide)

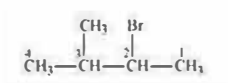
(iv)



1 - Bromo - 3, 3 - dimethyl - 1 - phenylbutane

(Secondary benzyl halide)

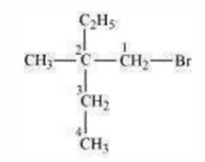
(v)



2 - Bromo - 3 - methylbutane

(Secondary alkyl halide)

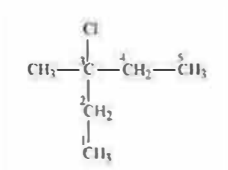
(vi)



1 - Bromo - 2 - ethyl - 2 - methylbutane

(Primary alkyl halide)

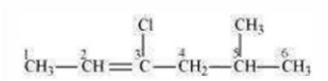
(vii)



3 - Chloro - 3 - methylpentane

(Tertiary alkyl halide)

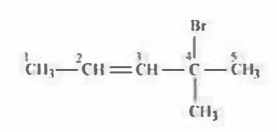
(viii)



3-Chloro-5-methylhex-2-ene

(Vinyl halide)

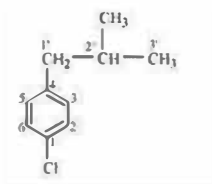
(ix)



4 - Bromo - 4 - methylpent - 2 - ene

(Allyl halide)

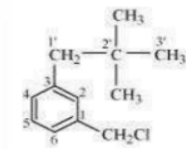
(x)



1 - Chloro - 4 - (2 - methylpropyl) benzene

(Aryl halide)

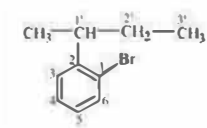
(xi)



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) $\text{CH}_3 \text{CH}(\text{Cl}) \text{CH}(\text{Br}) \text{CH}_3$

(ii) $\text{CH F}_2 \text{CBr ClF}$

(iii) $\text{Cl CH}_2 \text{C} \equiv \text{C CH}_2 \text{Br}$

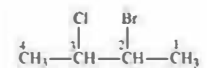
(iv) $(\text{CCl}_3)_3 \text{CCl}$

(v) $\text{CH}_3 \text{C} (p - \text{Cl C}_6 \text{H}_4)_2 \text{CH}(\text{Br}) \text{CH}_3$

(vi) $(\text{CH}_3)_3 \text{C CH} = \text{C Cl C}_6 \text{H}_4 \text{I} - p$

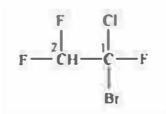
Soln :

(i)



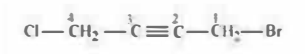
2-Bromo-3-chlorobutane

(ii)



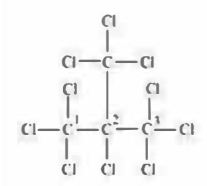
1-Bromo-1-chloro-1, 2, 2-trifluoroethane

(iii)



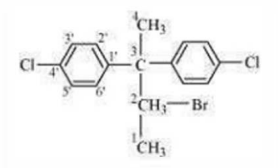
1 - Bromo - 4 - chlorobut - 2 - yne

(iv)



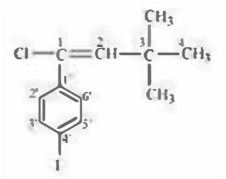
2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

(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) 2-Bromobutane

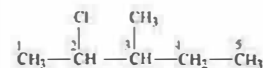
(vi) 4-tert-Butyl-3-iodoheptane

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

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

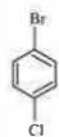
Soln:

(i)



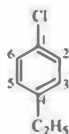
2-Chloro-3-methylpentane

(ii)



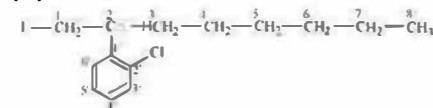
p-Bromochlorobenzene

(iii)



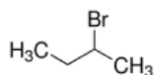
1-Chloro-4-ethylcyclohexane

(iv)



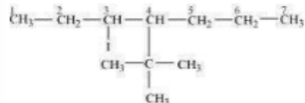
2-(2-Chlorophenyl)-1-iodooctane

(v)



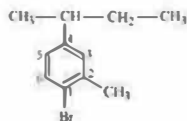
2-bromobutane

(vi)



4-Tert-Butyl-3-iodoheptane

(vii)



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

(viii)



1,4-Dibromobut-2-ene

Question 10.4:**Which one of the following has the highest dipole moment?****(i) CH₂Cl₂ (ii) CHCl₃ (iii) CCl₄****Soln :**

CCl₄ 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 CHCl₃, 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, CHCl₃ has a small dipole moment of 1.08 D.

On the other hand, in case of CH₂Cl₂, 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.

result, CH₂Cl₂ has a higher dipole moment of 1.60 D than CHCl₃ i.e., CH₂Cl₂ has the highest dipole moment.

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



Question 10.5: A hydrocarbon C₅H₁₀ does not react with chlorine in dark but gives a single monochloro compound C₅H₉Cl in bright sunlight. Identify the hydrocarbon.

Soln: A hydrocarbon with the molecular formula, C₅H₁₀ 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, C₅H₉Cl 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.

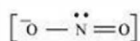
Cyclopentane (C₅H₁₀)

The reactions involved in the question are:

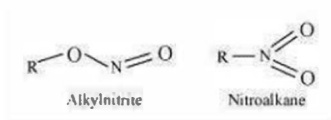
Question 10.8: What are ambident nucleophiles? Explain with an example.

Soln: When there are two nucleophilic sites in a nucleophile, they are called ambident nucleophile. These nucleophilic sites are sites through which they can attack.

For ex- Nitrite ion



Alkyl nitrites are formed when nitrite ion can attack through oxygen. And, nitroalkanes are formed when it can attack through nitrogen.

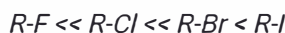


Question 10.9: Which compound in each of the following pairs will react faster in $\text{S}_{\text{N}}2$ reaction with OH^- ?

(i) CH_3Br or CH_3I

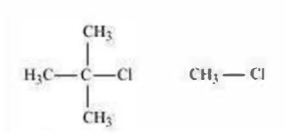
(ii) $(\text{CH}_3)_3\text{CCl}$ or CH_3Cl

Soln: (i) In $\text{S}_{\text{N}}2$ mechanism, the order in which the halides react to some alkyl group is constant. This is because the halide ion becomes a better leaving group when the size of the ion increases.



Hence, the reactivity of CH_3I is faster as compared to CH_3Br in $\text{S}_{\text{N}}2$ reactions with OH^- .

(ii)



In $\text{S}_{\text{N}}2$ mechanism, the nucleophile attacks at the atom bearing the leaving group. The attack of nucleophile in $(\text{CH}_3)_3\text{CCl}$ at the carbon atom is hindered as the carbon atom (bearing the leaving group) contains bulky substituents.

However, CH_3Cl does not consist of bulky substituents on the carbon atom bearing the leaving group.

Hence, the reactivity of CH_3Cl is faster as compared to $(\text{CH}_3)_3\text{CCl}$ in $\text{S}_{\text{N}}2$ reaction with OH^- .

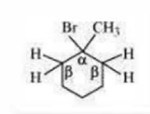
Question 10.10: Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

(i) 1-Bromo-1-methylcyclohexane

(ii) 2-Chloro-2-methylbutane

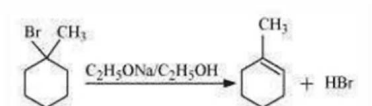
(iii) 2,2,3-Trimethyl-3-bromopentane.

Soln: (i)

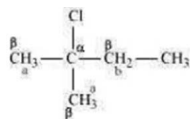


1-bromo-1-methylcyclohexane

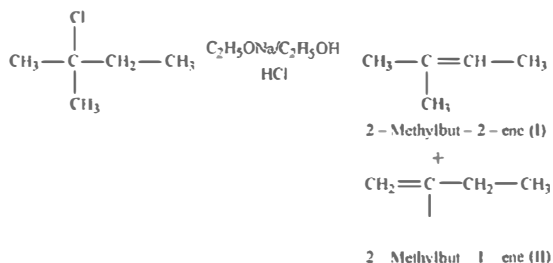
All the β -hydrogen are equal in the given compound. Hence, dehydrohalogenation of the given compound gives only one alkene.



(ii)



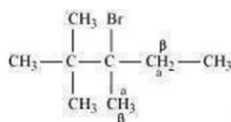
a and *b* are different sets of equivalent β -hydrogen atoms. Dehydrohalogenation of this compound gives two alkenes.



The alkene with more number of alkyl groups attached to a doubly bonded carbon atoms is preferable, according to Saytzeff's rule in dehydrohalogenation reactions.

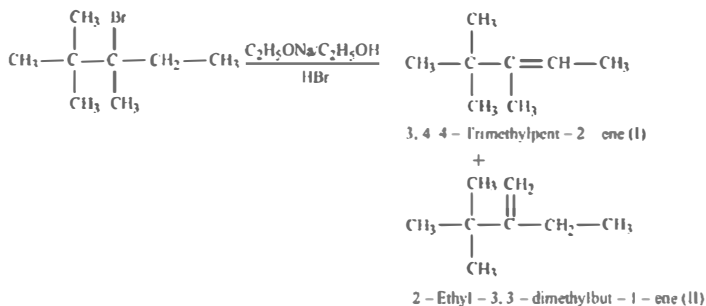
Hence, major product in this reaction is 2-methylbut-2-ene.

(iii)



2,2,3-Trimethyl-3-bromopentane

a and *b* are different sets of equivalent β -hydrogen atoms. Dehydrohalogenation of this compound gives two alkenes.



The alkene with more number of alkyl groups attached to a doubly bonded carbon atoms is preferable, according to Saytzeff's rule in dehydrohalogenation reactions.

Hence, 3,4,4-trimethylpent-2-ene is the major product.

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**

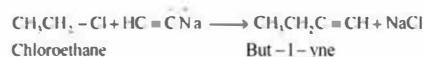
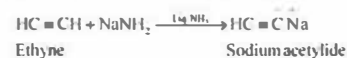
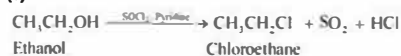
(viii) **But-1-ene to but-2-ene**

(ix) **1-Chlorobutane to n-octane**

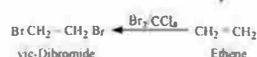
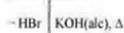
(x) **Benzene to biphenyl.**

Soln:

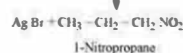
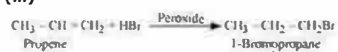
(i)



(ii)



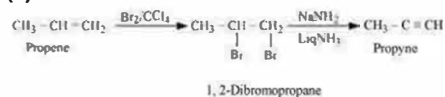
(iii)



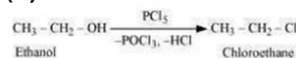
(iv)



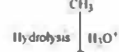
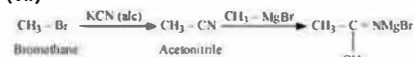
(v)



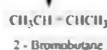
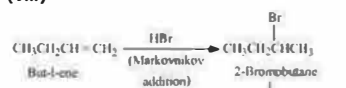
(vi)



(vii)

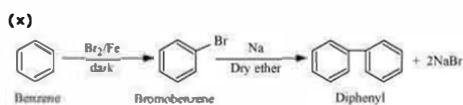


(viii)



(ix)

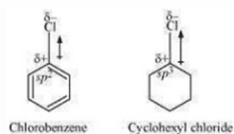




Question 10.12: Explain why

- (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?

Soln: (i)

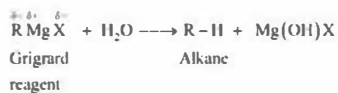


The Cl-atom in chlorobenzene is linked to sp^2 hybridized carbon atom, whereas in cyclohexyl chloride it is linked to sp^3 hybridized carbon atom. Now, as sp^2 hybridized carbon has more s-character, it is more electronegative than sp^3 hybridized carbon atom. Hence, the density of electrons of C-Cl bond near the Cl atom is less in chlorobenzene than in cyclohexyl chloride.

Moreover, the electron density is reduced by the $-R$ effect of the benzene ring of chlorobenzene. Hence, chlorobenzene has a decreased polarity of C-Cl bond, also the dipole moment is lower than that of cyclohexyl chloride.

(ii) When the solute-water force of attraction is stronger than solute-solute and water-water force of attraction, it determines the miscibility with water. Dipole-dipole interactions hold the polar molecules of alkyl halides together. Now, the alkyl halide-alkyl halide and water-water forces of attraction are stronger than the new force of attraction between alkyl halides and water molecules. As a result, 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.

Question 10.13: Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.

Soln: **Uses of Freon -12**

Common name given to Freon-12 (dichlorodifluoromethane, CF_2Cl_2) is CFC. It is used in aerosol spray propellants such as deodorants, hair sprays etc. It is also used in refrigerators and air-conditioners as a refrigerant. Its manufacturing was banned in United States and many other countries in 1994 as it was severely damaging ozone layer.

Uses of DDT

The most commonly used insecticide is DDT (*p,p*-dichlorodiphenyltrichloroethane). It has various harmful effects due to which it was banned in United States in 1973, though it is very effective against mosquitoes and lice.

Uses of carbontetrachloride (CCl_4)

- (i) Refrigerants and propellant for aerosol cans are manufactured using CCl_4 .
- (ii) Chlorofluorocarbons and other chemicals are synthesized.
- (iii) Used as a solvent in the manufacture of pharmaceutical products.
- (iv) Used as cleaning fluid, a spot remover in homes and a fire extinguisher during the mid 1960s.

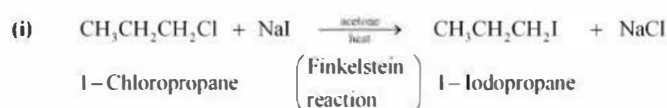
Uses of Iodoform (CHI_3)

Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations containing iodine due to its objectionable smell.

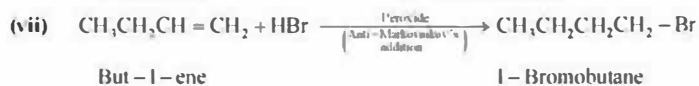
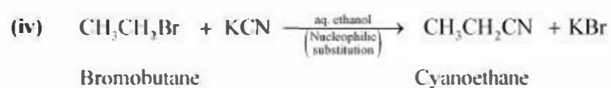
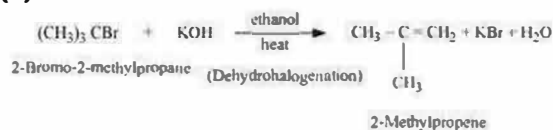
Question 10.14: Write the structure of the major organic product in each of the following reactions:

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl} + \text{NaI} \xrightarrow[\text{-heat-}]{\text{acetone}}$
- (ii) $(\text{CH}_3)_3\text{CBr} + \text{KOH} \xrightarrow[\text{heat}]{\text{ethanol}}$
- (iii) $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3 + \text{NaOH} \xrightarrow{\text{water}}$
- (iv) $\text{CH}_3\text{CH}_2\text{Br} + \text{KCN} \xrightarrow{\text{aq. ethanol}}$
- (v) $\text{C}_6\text{H}_5\text{ONa} + \text{C}_2\text{H}_5\text{Cl} \longrightarrow$
- (vi) $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{SOCl}_2 \longrightarrow$
- (vii) $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 + \text{HBr} \xrightarrow{\text{Peroxide}}$
- (viii) $\text{CH}_3\text{CH}=\text{C}(\text{CH}_3)_2 + \text{HBr} \longrightarrow$

Soln:



(ii)



(viii)



Question 10.15: What will be the mechanism for the following reaction?

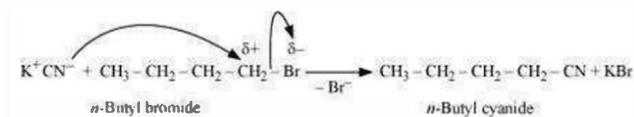


Soln: The given reaction is



CN^- acts as the nucleophile and attacks the carbon atom on which the Br is attached. CN^- ion is an ambident nucleophile and can attack through both C and N positions. It attacks through C atom, in this

case.



Question 10.16: Arrange the compounds of each set in order of reactivity towards $\text{S}_{\text{N}}2$ displacement:

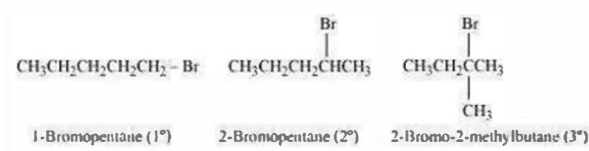
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

(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.

Soln:

(i)



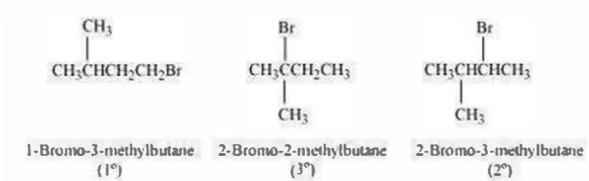
An $\text{S}_{\text{N}}2$ reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards $\text{S}_{\text{N}}2$ displacement decreases. Due to the presence of substituents, hindrance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

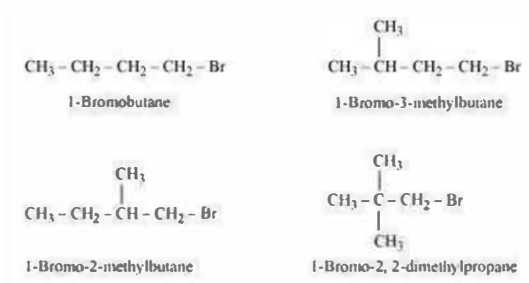


Since steric hindrance in alkyl halides increases in the order of $1^\circ < 2^\circ < 3^\circ$, the increasing order of reactivity towards $\text{S}_{\text{N}}2$ displacement is $3^\circ < 2^\circ < 1^\circ$.

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

(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:

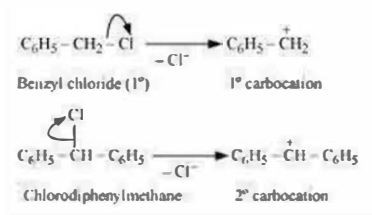
1-Bromobutane < 1-Bromo-3-methylbutane < 1-Bromo-2-methylbutane < 1-Bromo-2, 2-dimethylpropane

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

Question 10.17: Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

Soln:

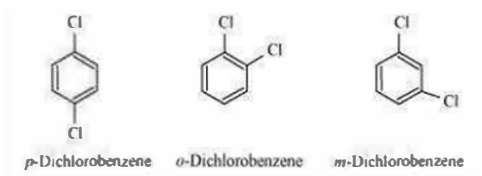


Hydrolysis by aqueous KOH proceeds through the formation of carbocation. If carbocation is stable, then the compound is easily hydrolyzed by aqueous KOH. Now,

$C_6H_5CH_2Cl$ 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.

Soln:



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

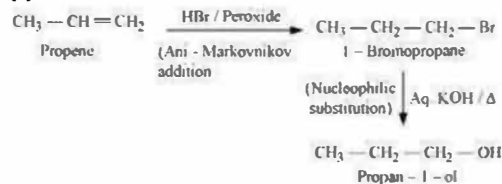
(xviii) Benzene to diphenyl

(xix) tert-Butyl bromide to isobutyl bromide

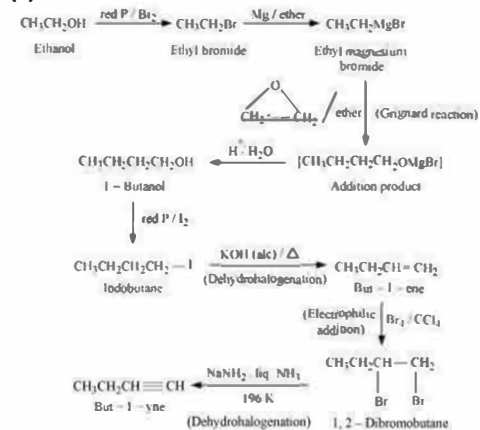
(xx) Aniline to phenylisocyanide

Soln:

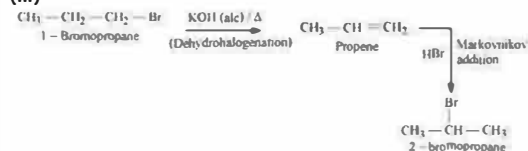
(i)



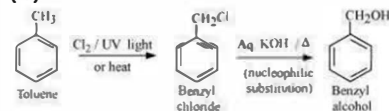
(ii)



(iii)



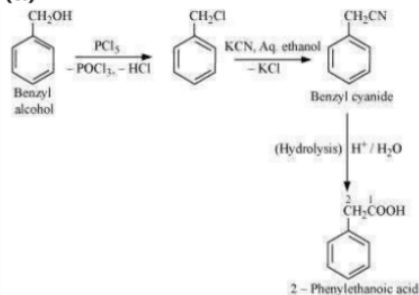
(iv)



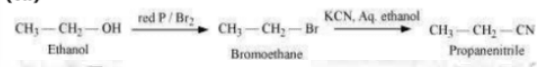
(v)



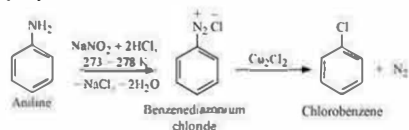
(vi)



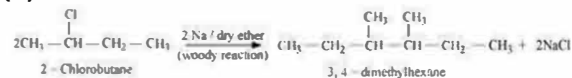
(vii)



(viii)



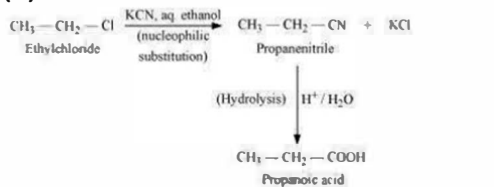
(ix)



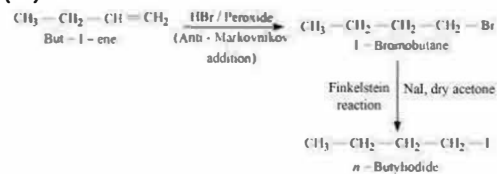
(x)



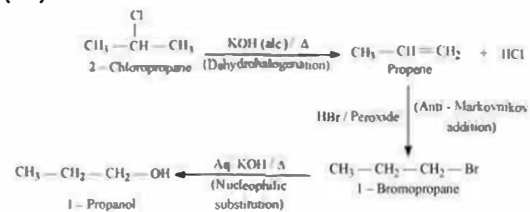
(xi)



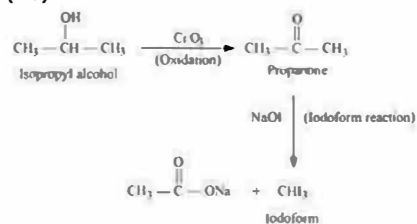
(xii)



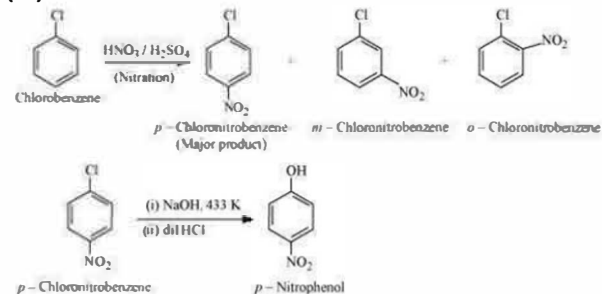
(xiii)



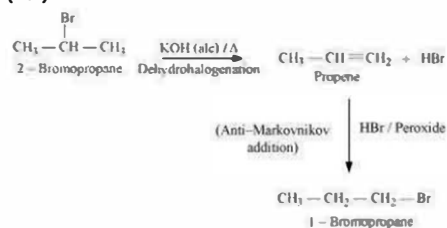
(xiv)

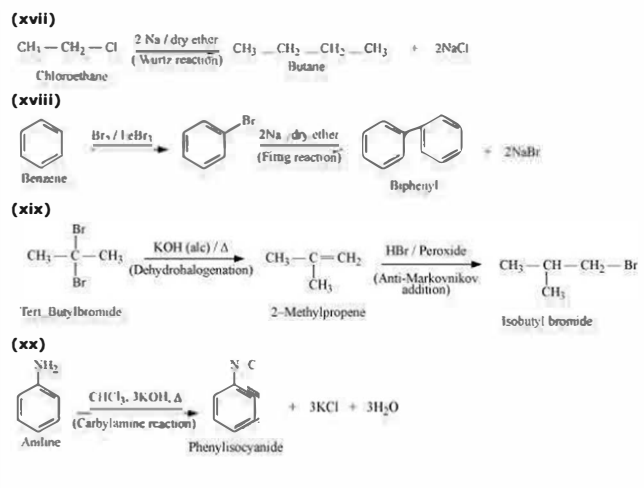


(xv)



(xvi)

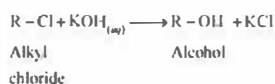




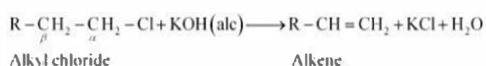
Question 10.20: The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Soln:

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.



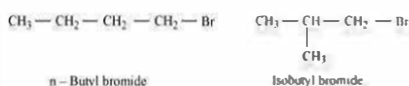
On the other hand, an alcoholic solution of KOH contains alkoxide (RO⁻) ion, which is a strong base. Thus, it can abstract a hydrogen from the β-carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.



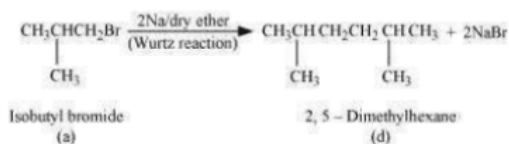
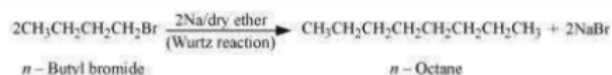
OH⁻ ion is a much weaker base than RO⁻ ion. Also, OH⁻ ion is highly solvated in an aqueous solution and as a result, the basic character of OH⁻ ion decreases. Therefore, it cannot abstract a hydrogen from the β-carbon.

Question 10.21: Primary alkyl halide C₄H₉Br (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), C₈H₁₈ 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.

Soln: There are two primary alkyl halides having the formula, C₄H₉Br. They are n-butyl bromide and isobutyl bromide.

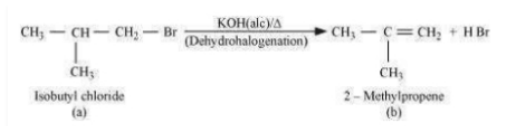


Therefore, compound (a) is either n-butyl bromide or isobutyl bromide. Now, compound (a) reacts with Na metal to give compound (b) of molecular formula, C₈H₁₈, which is different from the compound formed when n-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

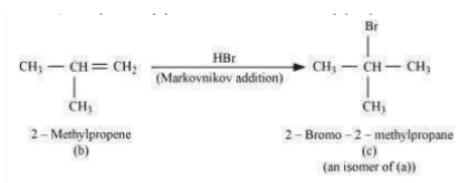


Thus, compound (d) is 2, 5-dimethylhexane.

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.

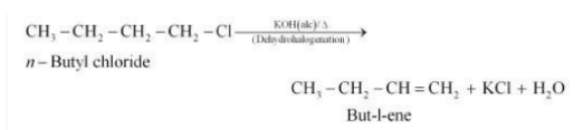


Question 10.22: What happens when

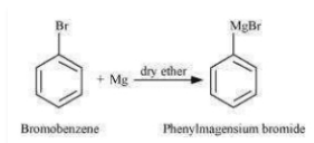
- (i) *n*-butyl chloride is treated with alcoholic KOH,
- (ii) bromobenzene is treated with Mg in the presence of dry ether,
- (iii) chlorobenzene is subjected to hydrolysis,
- (iv) ethyl chloride is treated with aqueous KOH,
- (v) methyl bromide is treated with sodium in the presence of dry ether,
- (vi) methylchloride is treated with KCN.

Soln:

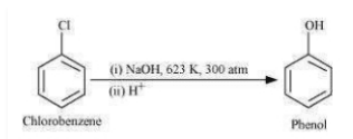
(i) When *n*-butyl chloride is treated with alcoholic KOH, the formation of but-1-ene takes place. This reaction is a dehydrohalogenation reaction.



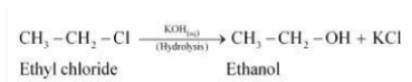
(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



(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.

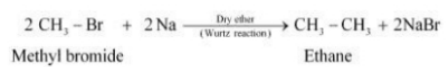


(iv) When ethyl chloride is treated with aqueous KOH, it undergoes hydrolysis to form ethanol.



(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.



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

