

## Chapter 6 - Haloalkanes and Haloarenes XII

### Intext Questions

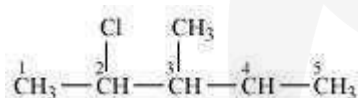
#### Question 6.1:

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

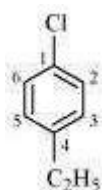
Answer

(i)



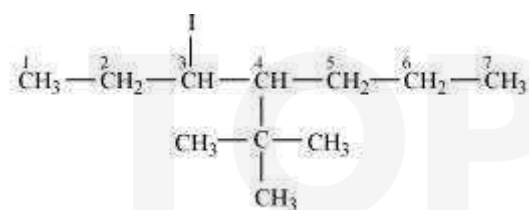
2-Chloro-3-methyl pentane

(ii)



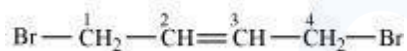
1-Chloro-4-ethylcyclohexane

(iii)



4- tert-Butyl-3-iodoheptane

(iv)



1, 4-Dibromobut-2-ene

(v)



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

**Question 6.2:**

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

Answer

In the presence of sulphuric acid ( $\text{H}_2\text{SO}_4$ ), KI produces HI



Since  $\text{H}_2\text{SO}_4$  is an oxidizing agent, it oxidizes HI (produced in the reaction to  $\text{I}_2$ ).



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  $\text{H}_3\text{PO}_4$  is used.

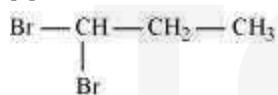
**Question 6.3:**

Write structures of different dihalogen derivatives of propane.

Answer

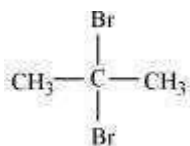
There are four different dihalogen derivatives of propane. The structures of these derivatives are shown below.

(i)



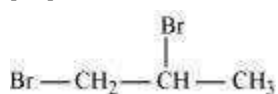
1, 1-Dibromopropane

(ii)



2, 2-Dibromopropane

(iii)



1, 2-Dibromopropane

(iv)



1, 3-Dibromopropane

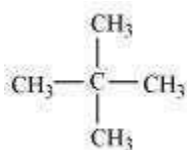
**Question 6.4:**

Among the isomeric alkanes of molecular formula  $\text{C}_5\text{H}_{12}$ , identify the one that on photochemical chlorination yields

- (i) A single monochloride.
- (ii) Three isomeric monochlorides.
- (iii) Four isomeric monochlorides.

Answer

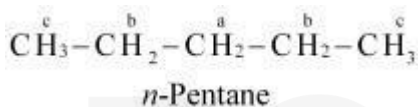
(i) To have a single monochloride, there should be only one type of H-atom in the isomer of the alkane of the molecular formula  $\text{C}_5\text{H}_{12}$ . This is because, replacement of any H-atom leads to the formation of the same product. The isomer is neopentane.



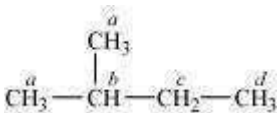
Neopentane

(ii) To have three isomeric monochlorides, the isomer of the alkane of the molecular formula  $\text{C}_5\text{H}_{12}$  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.

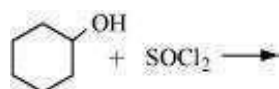
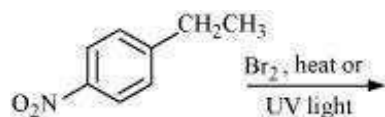
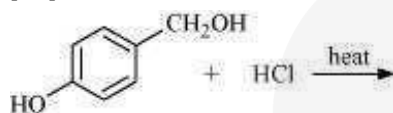
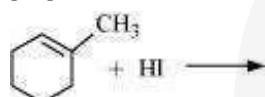
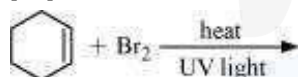


(iii) To have four isomeric monochlorides, the isomer of the alkane of the molecular formula  $\text{C}_5\text{H}_{12}$  should contain four different types of H-atoms. Therefore, the isomer is 2-methylbutane. It can be observed that there are four types of H-atoms labelled as *a*, *b*, *c*, and *d* in 2-methylbutane.

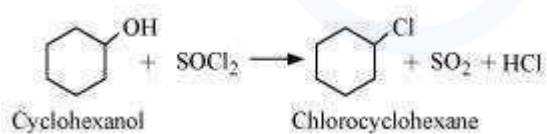
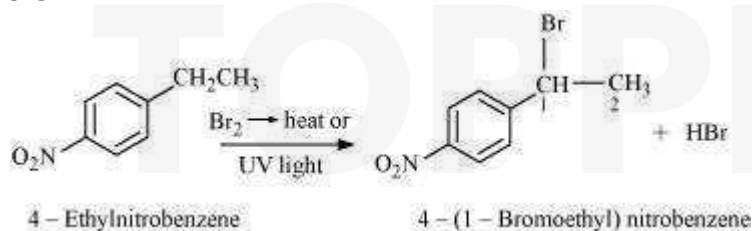
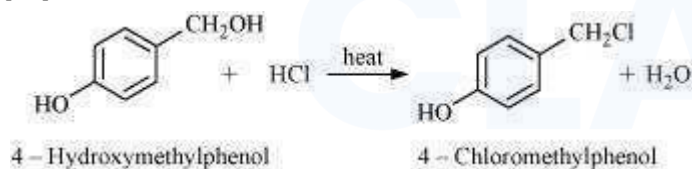
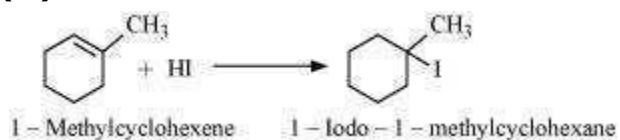


**Question 6.5:**

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

**(i)****(ii)****(iii)****(iv)****(v)****(vi)**

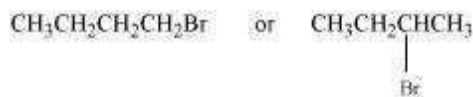
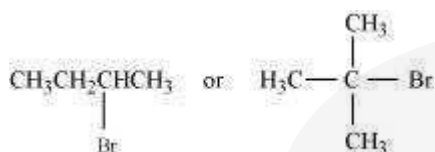
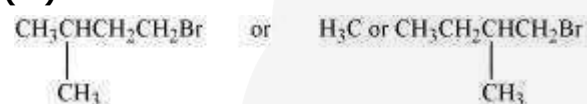
Answer

**(i)****(ii)****(iii)****(iv)**



**Question 6.7:**

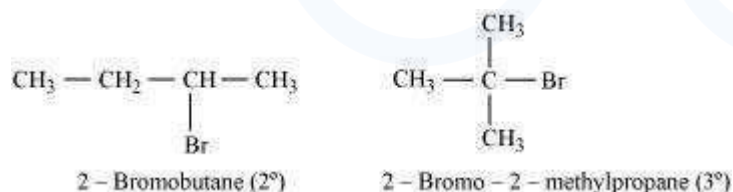
Which alkyl halide from the following pairs would you expect to react more rapidly by an  $S_N2$  mechanism? Explain your answer.

**(i)****(ii)****(iii)**

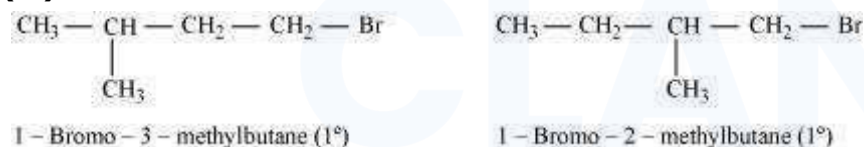
Answer

**(i)**1 - Bromobutane ( $1^\circ$ )      2 - Bromobutane ( $2^\circ$ )

2-bromobutane is a  $2^\circ$  alkylhalide whereas 1-bromobutane is a  $1^\circ$  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)**

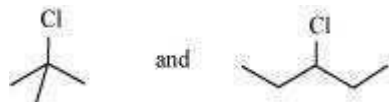
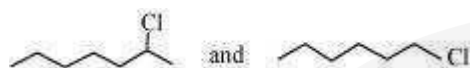
2-Bromobutane is  $2^\circ$  alkylhalide whereas 2-bromo-2-methylpropane is  $3^\circ$  alkyl halide. Therefore, greater numbers of substituents are present in  $3^\circ$  alkyl halide than in  $2^\circ$  alkyl halide to hinder the approaching nucleophile. Hence, 2-bromobutane reacts more rapidly than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

**(iii)**

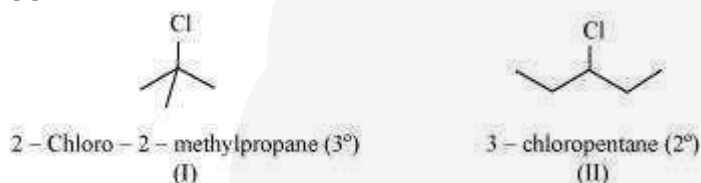
Both the alkyl halides are primary. However, the substituent  $-\text{CH}_3$  is at a greater distance to the carbon atom linked to Br in 1-bromo-3-methylbutane than in 1-bromo-2-methylbutane. Therefore, the approaching nucleophile is less hindered in case of the former than in case of the latter. Hence, the former reacts faster than the latter by  $S_N2$  mechanism.

**Question 6.8:**

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

**(i)****(ii)**

Answer

**(i)**

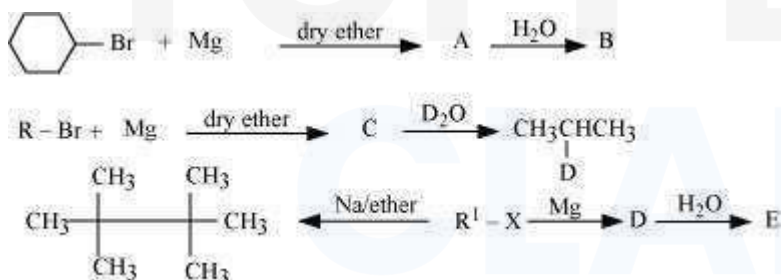
$S_N1$  reaction proceeds via the formation of carbocation. The alkyl halide (I) is  $3^\circ$  while (II) is  $2^\circ$ . Therefore, (I) forms  $3^\circ$  carbocation while (II) forms  $2^\circ$  carbocation. Greater the stability of the carbocation, faster is the rate of  $S_N1$  reaction. Since  $3^\circ$  carbocation is more stable than  $2^\circ$  carbocation. (I), i.e., 2-chloro-2-methylpropane, undergoes faster  $S_N1$  reaction than (II) i.e., 3-chloropentane.

**(ii)**

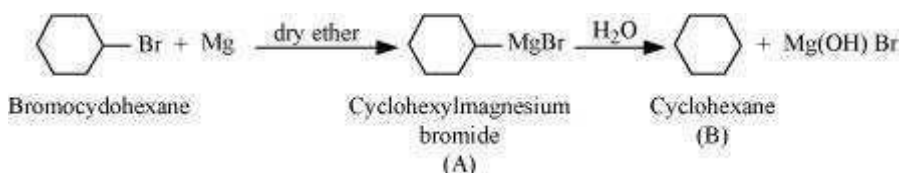
The alkyl halide (I) is  $2^\circ$  while (II) is  $1^\circ$ .  $2^\circ$  carbocation is more stable than  $1^\circ$  carbocation. Therefore, (I), 2-chloroheptane, undergoes faster  $S_N1$  reaction than (II), 1-chlorohexane.

**Question 6.9:**

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



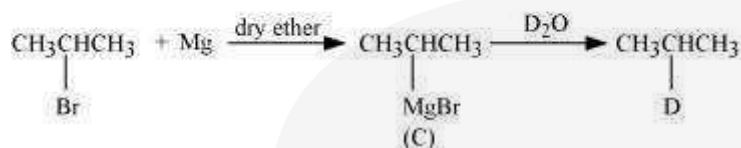
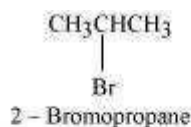
Answer



Since D of D<sub>2</sub>O gets attached to the carbon atom to which MgBr is attached, C is

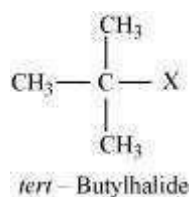


Therefore, the compound R – Br is

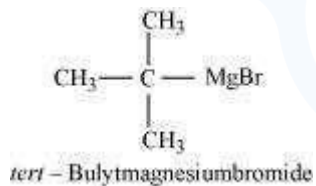


When an alkyl halide is treated with Na in the presence of ether, a hydrocarbon containing double the number of carbon atoms as present in the original halide is obtained as product.

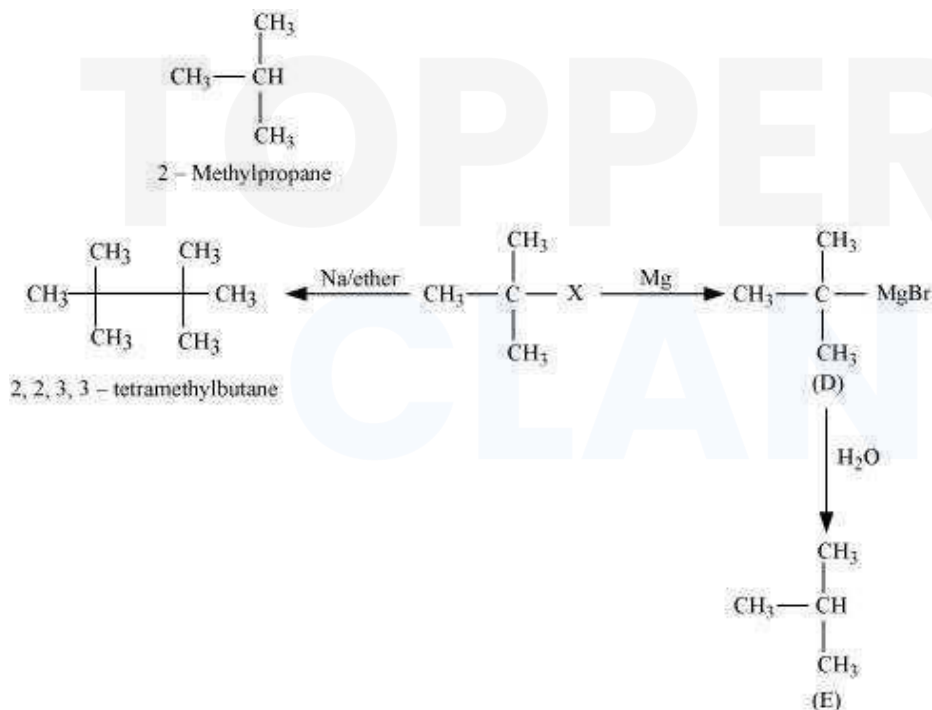
This is known as Wurtz reaction. Therefore, the halide, R<sup>1</sup>-X, is



Therefore, compound D is



And, compound E is



## Exercises

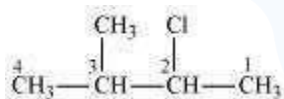
### Question 6.1:

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

- (i)  $(\text{CH}_3)_2\text{CHCH}(\text{Cl})\text{CH}_3$
- (ii)  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}(\text{C}_2\text{H}_5)\text{Cl}$
- (iii)  $\text{CH}_3\text{CH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{I}$
- (iv)  $(\text{CH}_3)_3\text{CCH}_2\text{CH}(\text{Br})\text{C}_6\text{H}_5$
- (v)  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}(\text{Br})\text{CH}_3$
- (vi)  $\text{CH}_3\text{C}(\text{C}_2\text{H}_5)_2\text{CH}_2\text{Br}$
- (vii)  $\text{CH}_3\text{C}(\text{Cl})(\text{C}_2\text{H}_5)\text{CH}_2\text{CH}_3$
- (viii)  $\text{CH}_3\text{CH}=\text{C}(\text{Cl})\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (ix)  $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$
- (x)  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (xi)  $m\text{-ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_3$
- (xii)  $o\text{-Br-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

Answer

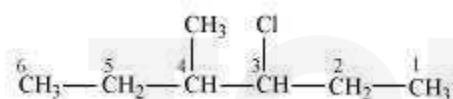
(i)



2-Chloro-3-methylbutane

(Secondary alkyl halide)

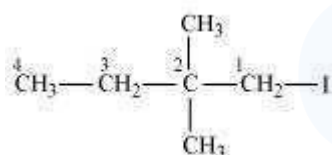
(ii)



3-Chloro-4-methylhexane

(Secondary alkyl halide)

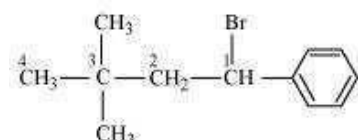
(iii)



1-Iodo-2, 2 -dimethylbutane

(Primary alkyl halide)

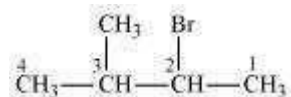
(iv)



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

(Secondary benzyl halide)

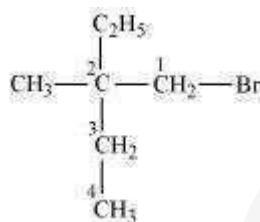
(v)



2-Bromo-3-methylbutane

(Secondary alkyl halide)

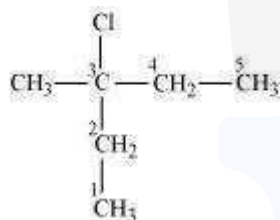
(vi)



1-Bromo-2-ethyl-2-methylbutane

(Primary alkyl halide)

(vii)



3-Chloro-3-methylpentane

(Tertiary alkyl halide)

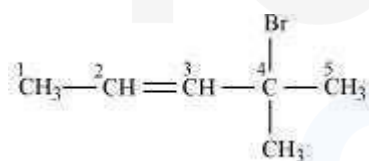
(viii)



3-Chloro-5-methylhex-2-ene

(Vinyl halide)

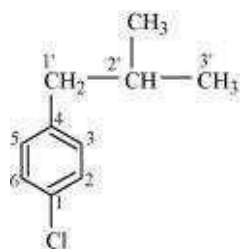
(ix)



4-Bromo-4-methylpent-2-ene

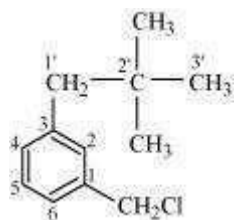
(Allyl halide)

(x)



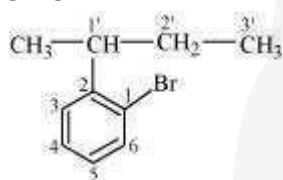
1-Chloro-4-(2-methylpropyl) benzene  
(Aryl halide)

(xi)



1-Chloromethyl-3-(2, 2-dimethylpropyl) benzene  
(Primary benzyl halide)

(xii)



1-Bromo-2-(1-methylpropyl) benzene  
(Aryl halide)

### Question 6.2:

Give the IUPAC names of the following compounds:

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

(ii)  $\text{CHF}_2\text{CBrClF}$

(iii)  $\text{ClCH}_2\text{C}\equiv\text{CCH}_2\text{Br}$

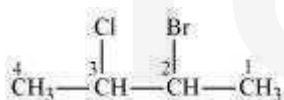
(iv)  $(\text{CCl}_3)_3\text{CCl}$

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

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

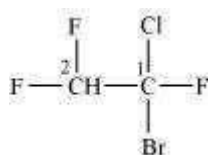
Answer

(i)



2-Bromo-3-chlorobutane

(ii)



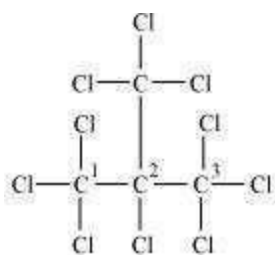
1-Bromo-1-chloro-1, 2, 2-trifluoroethane

(iii)



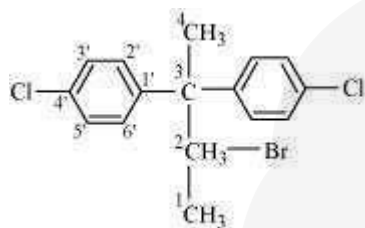
1-Bromo-4-chlorobut-2-yne

(iv)



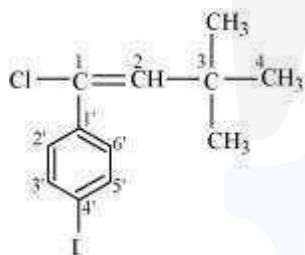
2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

(v)



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

(vi)



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

### Question 6.3:

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

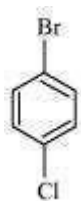
Answer

(i)



2-Chloro-3-methylpentane

(ii)



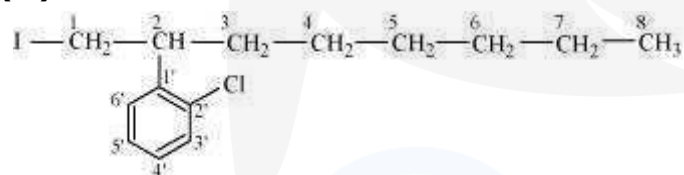
*p*-Bromochlorobenzene

(iii)



1-Chloro-4-ethylcyclohexane

(iv)

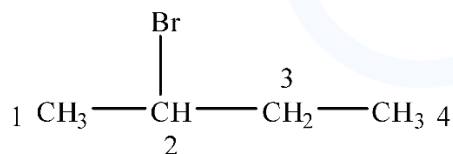


2-(2-Chlorophenyl)-1-iodooctane

(v)

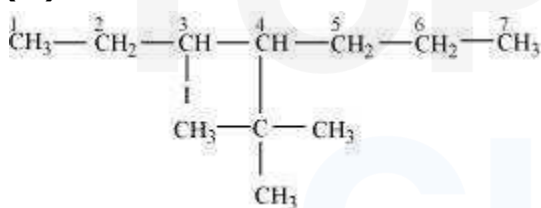
2-Bromobutane

Br is attached to a four carbon chain at 2-position.



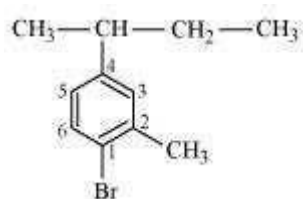
2-bromobutane

(vi)



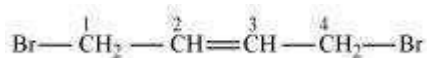
4-Tert-Butyl-3-iodoheptane

(vii)



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

(viii)



1,4-Dibromobut-2-ene

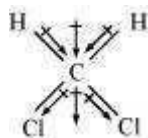
**Question 6.4:**

Which one of the following has the highest dipole moment?

- (i)  $\text{CH}_2\text{Cl}_2$
- (ii)  $\text{CHCl}_3$
- (iii)  $\text{CCl}_4$

Answer

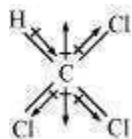
(i)



Dichloromethane ( $\text{CH}_2\text{Cl}_2$ )

$$\mu = 1.60\text{D}$$

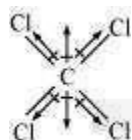
(ii)



Chloroform ( $\text{CHCl}_3$ )

$$\mu = 1.08\text{D}$$

(iii)



Carbon tetrachloride ( $\text{CCl}_4$ )

$$\mu = 0\text{D}$$

$\text{CCl}_4$  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  $\text{CHCl}_3$ , 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,  $\text{CHCl}_3$  has a small dipole moment of 1.08 D.

On the other hand, in case of  $\text{CH}_2\text{Cl}_2$ , 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,  $\text{CH}_2\text{Cl}_2$  has a higher dipole moment of 1.60 D than  $\text{CHCl}_3$  i.e.,  $\text{CH}_2\text{Cl}_2$  has the highest dipole moment.

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



### Question 6.5:

A hydrocarbon  $\text{C}_5\text{H}_{10}$  does not react with chlorine in dark but gives a single monochloro compound  $\text{C}_5\text{H}_9\text{Cl}$  in bright sunlight. Identify the hydrocarbon.

Answer

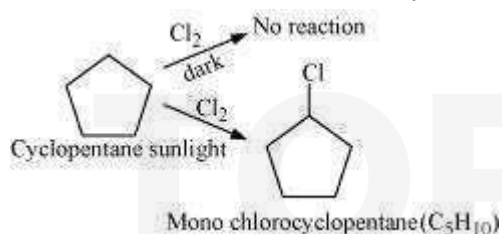
A hydrocarbon with the molecular formula,  $\text{C}_5\text{H}_{10}$  belongs to the group with a general molecular formula  $\text{C}_n\text{H}_{2n}$ . Therefore, it may either be an alkene or a cycloalkane. Since hydrocarbon does not react with chlorine in the dark, it cannot be an alkene. Thus, it should be a cycloalkane.

Further, the hydrocarbon gives a single monochloro compound,  $\text{C}_5\text{H}_9\text{Cl}$  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 ( $\text{C}_5\text{H}_{10}$ )

The reactions involved in the question are:



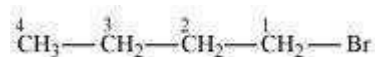
### Question 6.6:

Write the isomers of the compound having formula  $\text{C}_4\text{H}_9\text{Br}$ .

Answer

There are four isomers of the compound having the formula  $\text{C}_4\text{H}_9\text{Br}$ . These isomers are given below.

(a)



1-Bromobutane



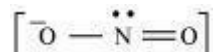
**Question 6.8:**

What are ambident nucleophiles? Explain with an example.

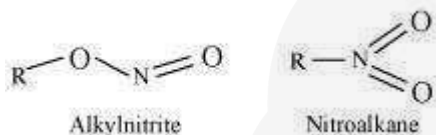
Answer

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.



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.

**Question 6.9:**

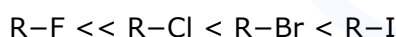
Which compound in each of the following pairs will react faster in  $\text{S}_{\text{N}}2$  reaction with  $\text{OH}^-$ ?

(i)  $\text{CH}_3\text{Br}$  or  $\text{CH}_3\text{I}$

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

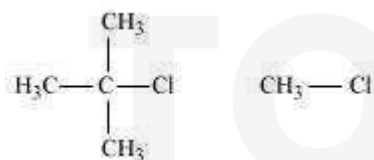
Answer

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



Therefore,  $\text{CH}_3\text{I}$  will react faster than  $\text{CH}_3\text{Br}$  in  $\text{S}_{\text{N}}2$  reactions with  $\text{OH}^-$ .

(ii)



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

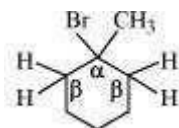
**Question 6.10:**

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.

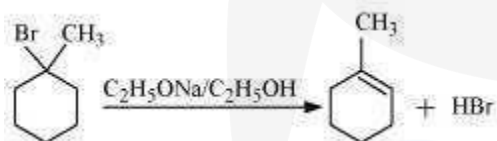
Answer

(i)

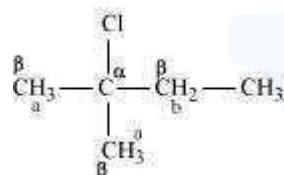


1-bromo-1-methylcyclohexane

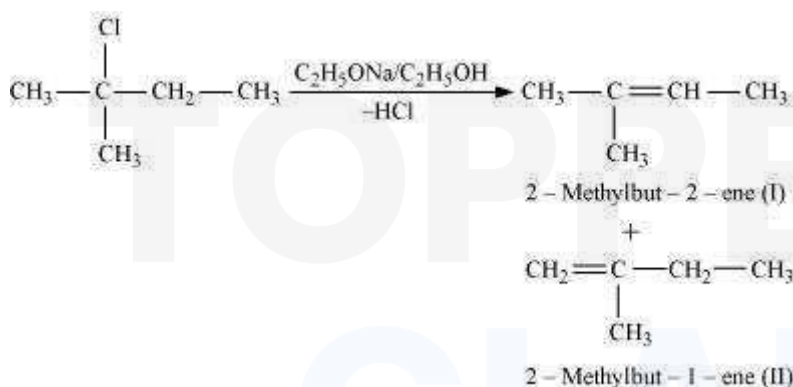
In the given compound, all  $\beta$ -hydrogen atoms are equivalent. Thus, dehydrohalogenation of this compound gives only one alkene.



(ii)

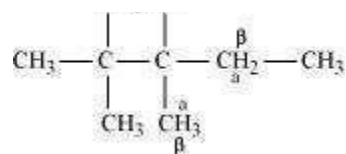


In the given compound, there are two different sets of equivalent  $\beta$ -hydrogen atoms labelled as *a* and *b*. Thus, dehydrohalogenation of the compound yields two alkenes.



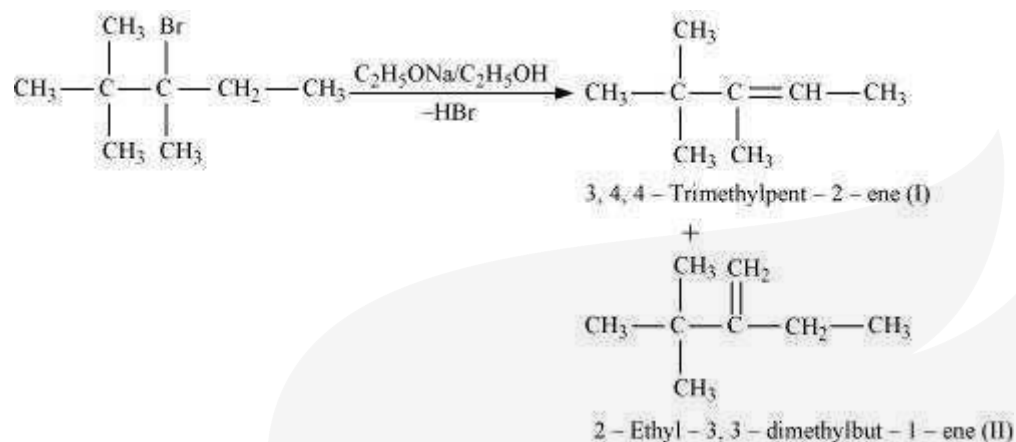
Saytzeff's rule implies that in dehydrohalogenation reactions, the alkene having a greater number of alkyl groups attached to a doubly bonded carbon atoms is preferably produced. Therefore, alkene (I) i.e., 2-methylbut-2-ene is the major product in this reaction.

(iii)



2,2,3-Trimethyl-3-bromopentane

In the given compound, there are two different sets of equivalent  $\beta$ -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.

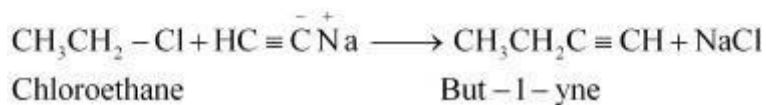
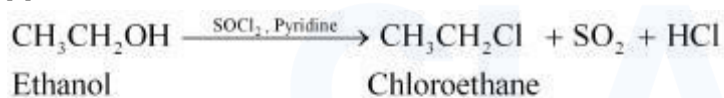
#### Question 6.11:

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)





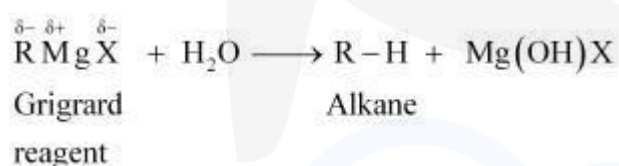


electronegative than the latter. Therefore, the density of electrons of C–Cl bond near the Cl-atom is less in chlorobenzene than in cyclohexyl chloride.

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

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

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



Therefore, Grignard reagents should be prepared under anhydrous conditions.

#### Question 6.13:

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

Answer

#### Uses of Freon – 12

Freon-12 (dichlorodifluoromethane,  $\text{CF}_2\text{Cl}_2$ ) 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 ( $\text{CCl}_4$ )

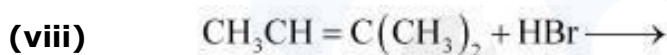
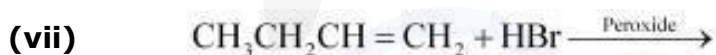
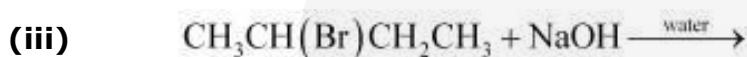
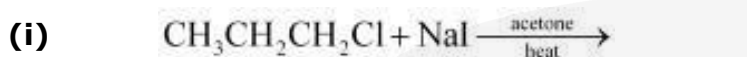
- (i)** It is used for manufacturing refrigerants and propellants for aerosol cans.
- (ii)** It is used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.
- (iii)** It is used as a solvent in the manufacture of pharmaceutical products.
- (iv)** Until the mid 1960's, carbon tetrachloride was widely used as a cleaning fluid, a degreasing agent in industries, a spot remover in homes, and a fire extinguisher.

### Uses of iodoform (CHI<sub>3</sub>)

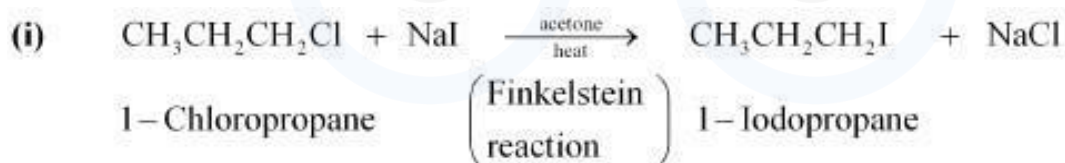
Iodoform was used earlier as an antiseptic, but now it has been replaced by other formulations-containing iodine-due to its objectionable smell. The antiseptic property of iodoform is only due to the liberation of free iodine when it comes in contact with the skin.

### Question 6.14:

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

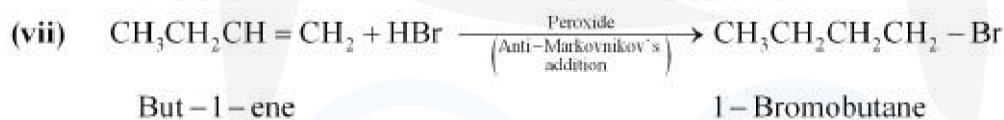
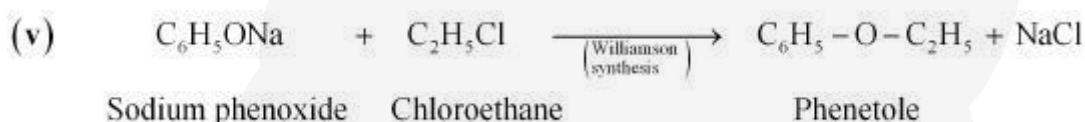
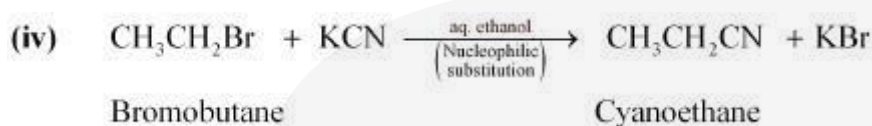
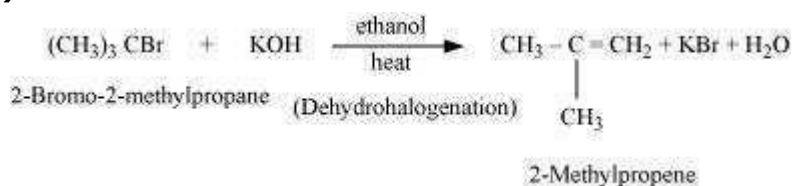


Answer



TOPPERS  
CLAN

(ii)



(viii)



### Question 6.15:

Write the mechanism of the following reaction:

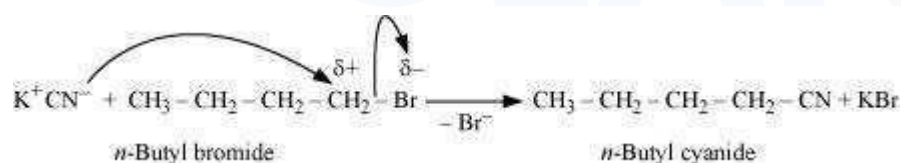


Answer

The given reaction is:



The given reaction is an  $\text{S}_{\text{N}}2$  reaction. In this reaction,  $\text{CN}^-$  acts as the nucleophile and attacks the carbon atom to which Br is attached.  $\text{CN}^-$  ion is an ambident nucleophile and can attack through both C and N. In this case, it attacks through the C-atom.



**Question 6.16:**

Arrange the compounds of each set in order of reactivity towards  $S_N2$  displacement:

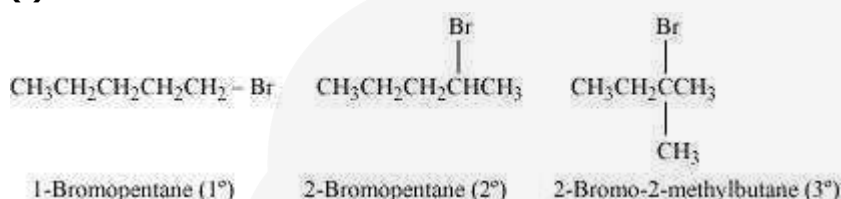
(i) 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

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

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

Answer

(i)



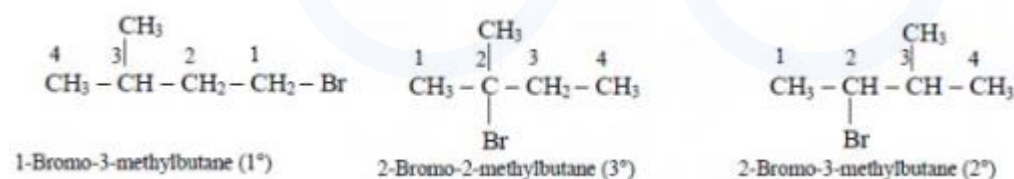
An  $S_N2$  reaction involves the approaching of the nucleophile to the carbon atom to which the leaving group is attached. When the nucleophile is sterically hindered, then the reactivity towards  $S_N2$  displacement decreases. Due to the presence of substituents, hindrance to the approaching nucleophile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

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

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

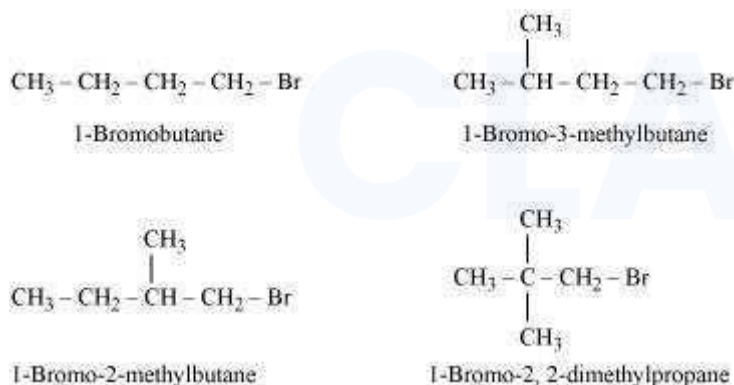
2-Bromo-2-methylbutane < 2-Bromopentane < 1-Bromopentane

(ii)



Since, due to steric reasons, the order of reactivity of alkyl halides in  $S_N2$  reaction follows the order:  $1^\circ > 2^\circ > 3^\circ$ , therefore, the order of reactivity of the given alkyl bromides is 1-Bromo-3-methylbutane ( $1^\circ$ ) > 2-Bromo-3-methylbutane ( $2^\circ$ ) > 2-Bromo-2-methylbutane ( $3^\circ$ ).

(iii)



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

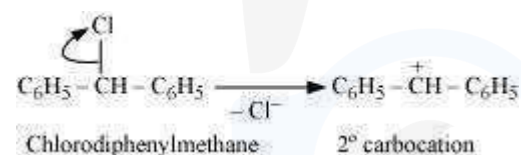
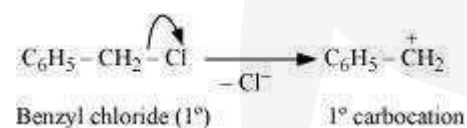
Hence, the increasing order of reactivity of the given compounds towards  $S_N2$  displacement is:

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

#### Question 6.17:

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

Answer



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  $1^\circ$ -carbocation, while  $C_6H_5CHClC_6H_5$  forms  $2^\circ$ -carbocation, which is more stable than  $1^\circ$ -carbocation. Hence,  $C_6H_5CHClC_6H_5$  is hydrolyzed more easily than  $C_6H_5CH_2Cl$  by aqueous KOH.

**Question 6.18:** *p*-Dichlorobenzene has higher m.p. than those of *o*- and *m*-isomers. Discuss.

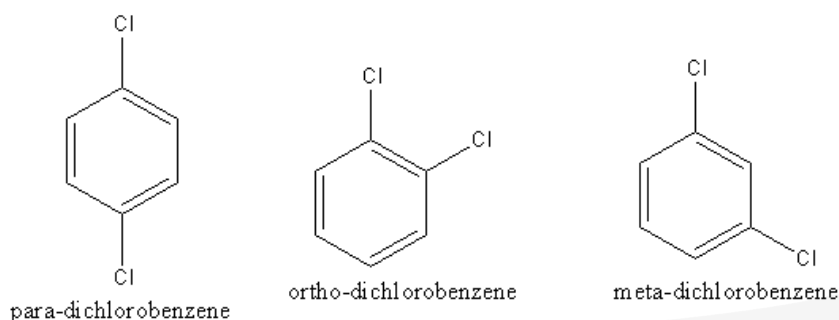
Answer

The melting point of *p*-, *o*- and *m*-isomers of dichlorobenzene is decided on the basis of lattice energy. The compounds having a close packed structure are most stable. High lattice energy leads to a higher melting point. Lattice energy is directly proportional to the melting point.

#### Complete step-by-step solution

The temperature at which the solid and liquid phases coexist in equilibrium is known as the melting point. As the phase is changing and the solid phase has a higher force of attraction than the liquid phase, heat is required to break the force of attraction.

The structure of *p*-, *o*-, and *m*-isomers of dichlorobenzene are as follows:



The structure of p-dichlorobenzene is symmetrical rather than Ortho and Meta isomer. So, p- dichlorobenzene forms a closed packed crystal. Due to close packing, the intermolecular forces are very strong. The force which binds molecules is known as intermolecular force. Strong intermolecular force leads to a stable crystal. The stability of the p- dichlorobenzene leads to high lattice energy.

So, the breaking of p- dichlorobenzene crystal requires high energy. High energy requirements lead to a high melting point. Whereas o- and m-isomers are unsymmetrical structures. Their crystal is not as stable as p-dichlorobenzene. Thus less energy is required for the breaking of o- and m-isomers.

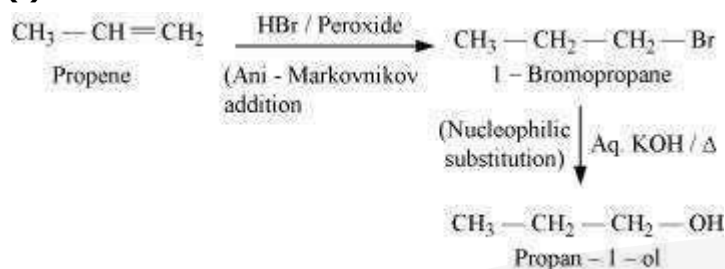
#### Question 6.19:

How the following conversions can be carried out?

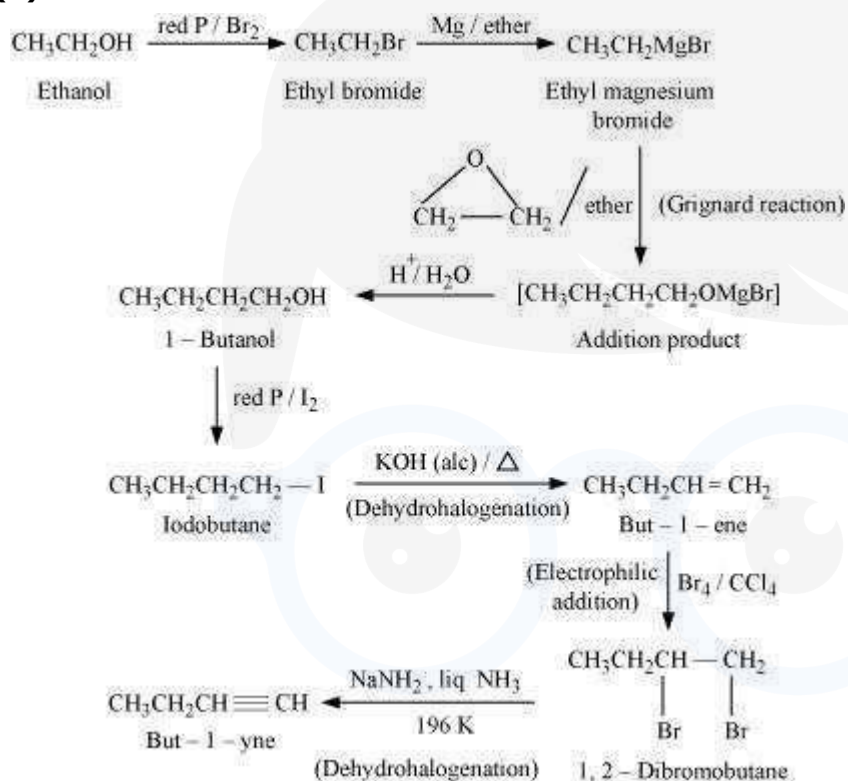
- (i) Propene to propan-1-ol
- (ii) Ethanol to but-1-yne
- (iii) 1-Bromopropane to 2-bromopropane
- (iv) Toluene to benzyl alcohol
- (v) Benzene to 4-bromonitrobenzene
- (vi) Benzyl alcohol to 2-phenylethanoic acid
- (vii) Ethanol to propanenitrile
- (viii) Aniline to chlorobenzene
- (ix) 2-Chlorobutane 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

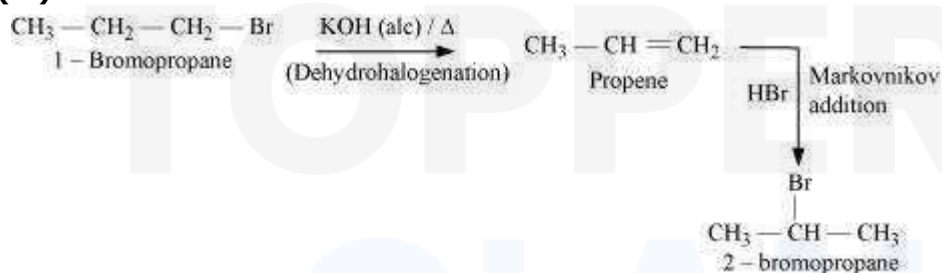
(i)



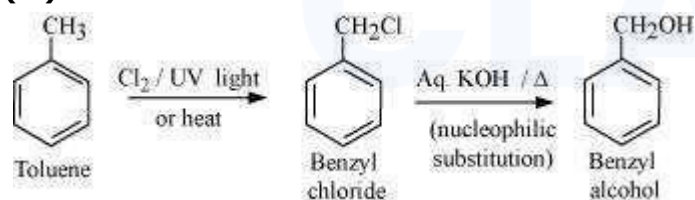
(ii)



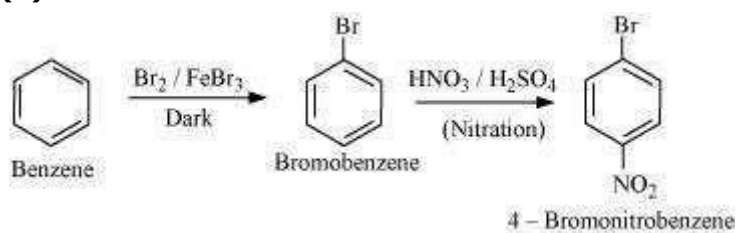
(iii)



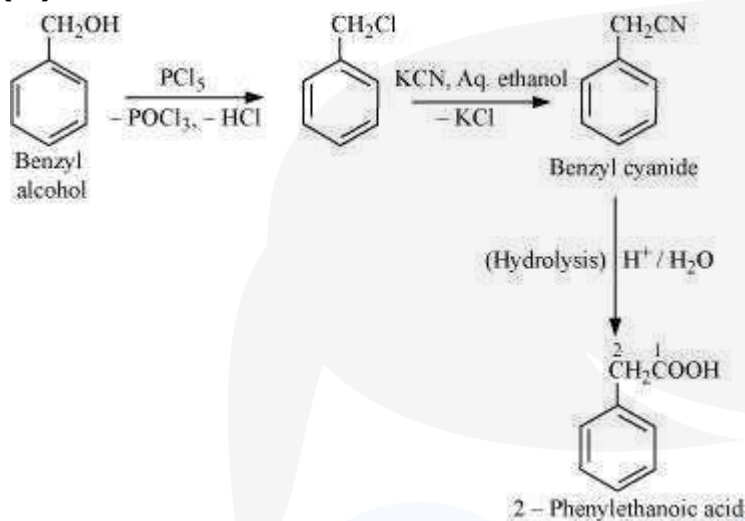
(iv)



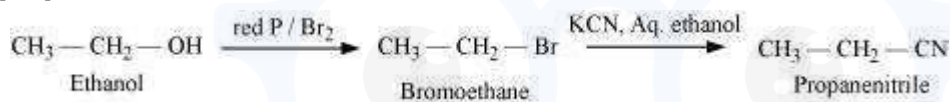
(v)



(vi)



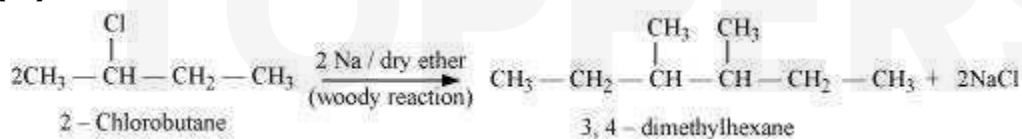
(vii)



(viii)



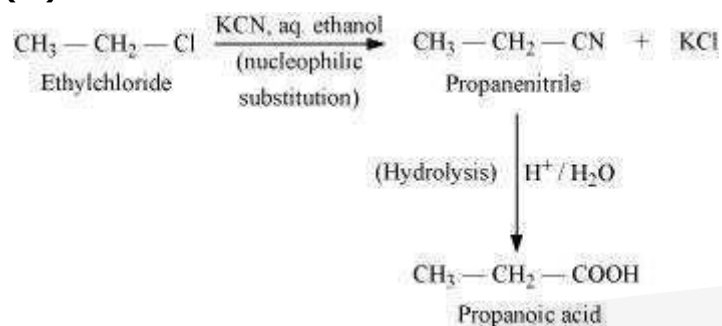
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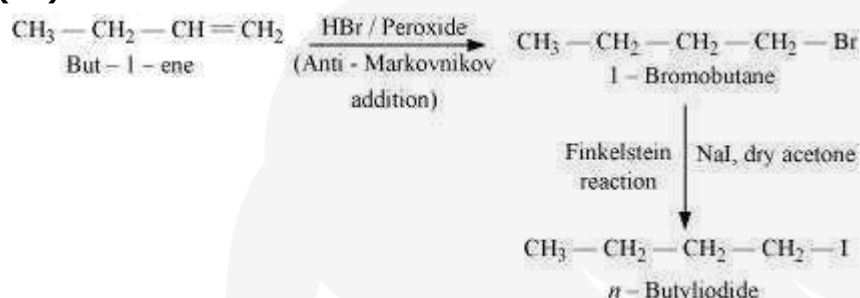
(x)



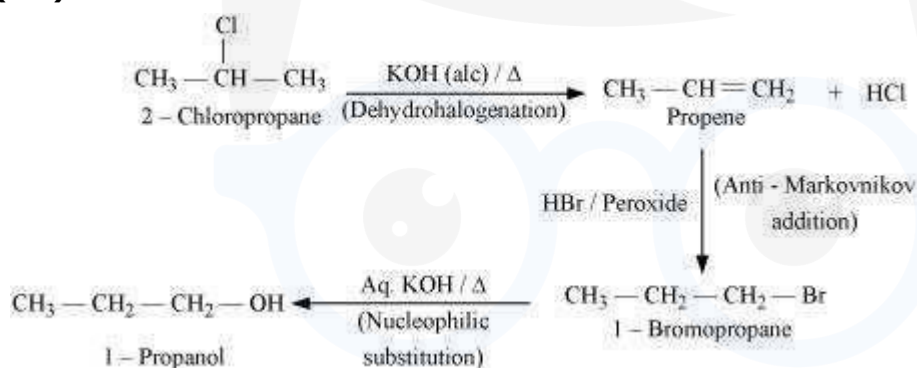
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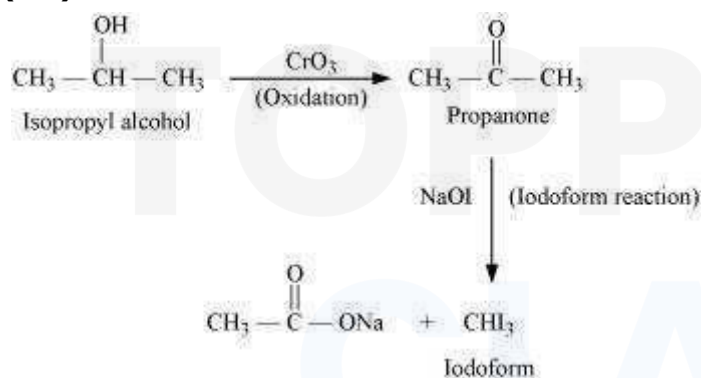
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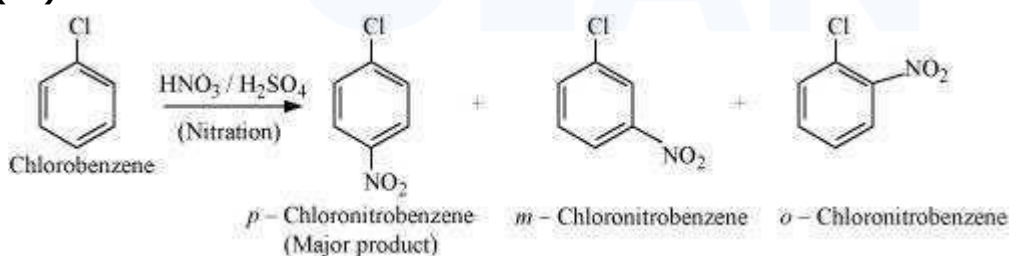
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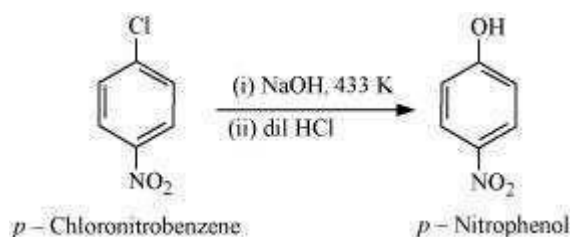


(xiv)

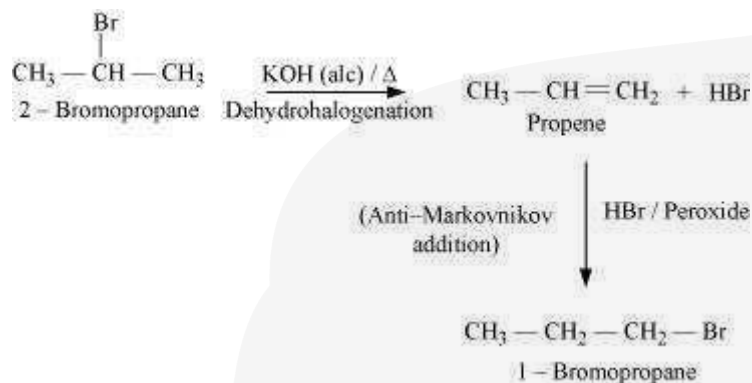


(xv)

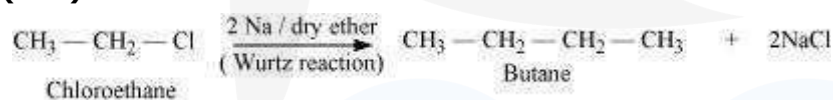




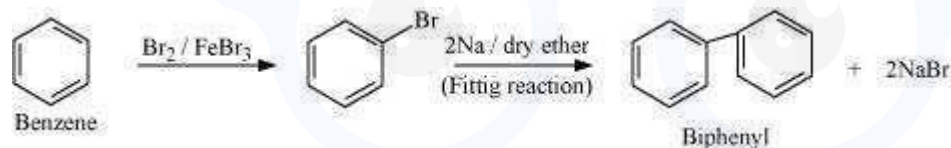
(xvi)



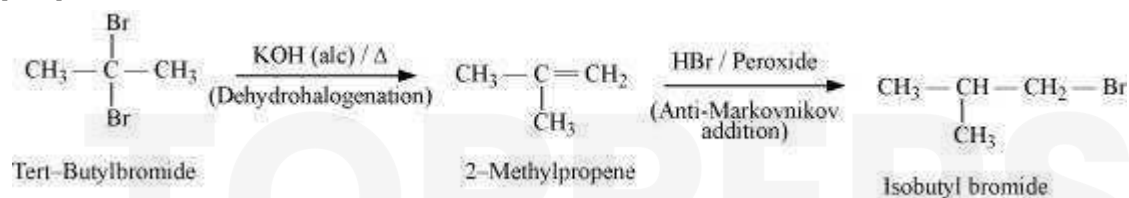
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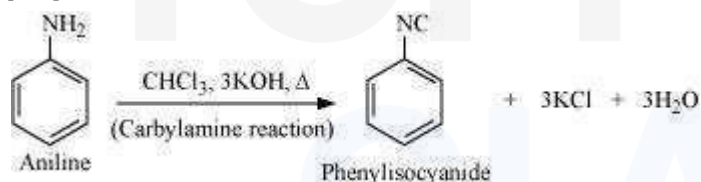
(xviii)



(xix)



(xx)

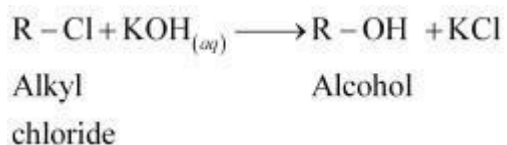


### Question 6.20:

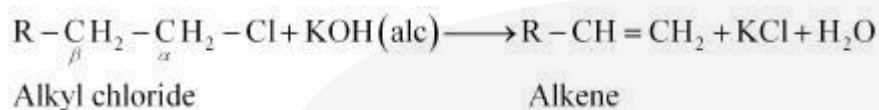
The treatment of alkyl chlorides with aqueous KOH leads to the formation of alcohols but in the presence of alcoholic KOH, alkenes are major products. Explain.

Answer

In an aqueous solution, KOH almost completely ionizes to give OH<sup>-</sup> ions. OH<sup>-</sup> 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 ( $\text{RO}^-$ ) ion, which is a strong base. Thus, it can abstract a hydrogen from the  $\beta$ -carbon of the alkyl chloride and form an alkene by eliminating a molecule of HCl.



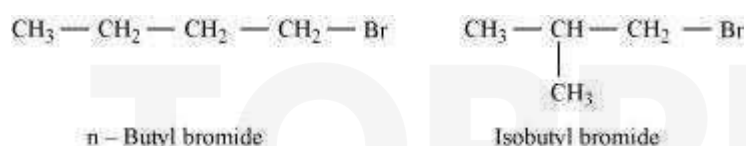
$\text{OH}^-$  ion is a much weaker base than  $\text{RO}^-$  ion. Also,  $\text{OH}^-$  ion is highly solvated in an aqueous solution and as a result, the basic character of  $\text{OH}^-$  ion decreases. Therefore, it cannot abstract a hydrogen from the  $\beta$ -carbon.

#### Question 6.21:

Primary alkyl halide  $\text{C}_4\text{H}_9\text{Br}$  (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),  $\text{C}_8\text{H}_{18}$  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.

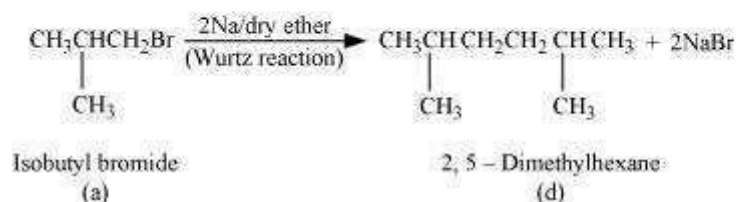
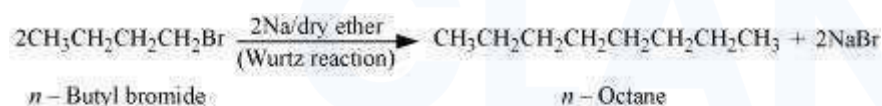
Answer

There are two primary alkyl halides having the formula,  $\text{C}_4\text{H}_9\text{Br}$ . They are *n*-butyl bromide and isobutyl bromide.



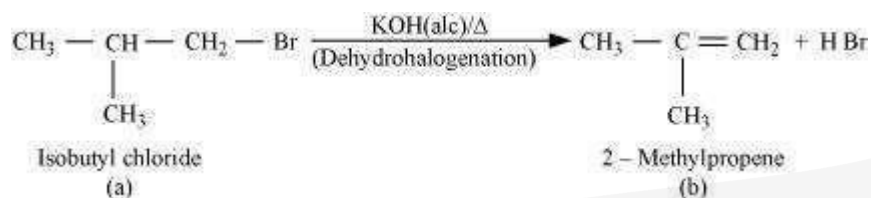
Therefore, compound (a) is either *n*-butyl bromide or isobutyl bromide.

Now, compound (a) reacts with Na metal to give compound (b) of molecular formula,  $\text{C}_8\text{H}_{18}$ , which is different from the compound formed when *n*-butyl bromide reacts with Na metal. Hence, compound (a) must be isobutyl bromide.

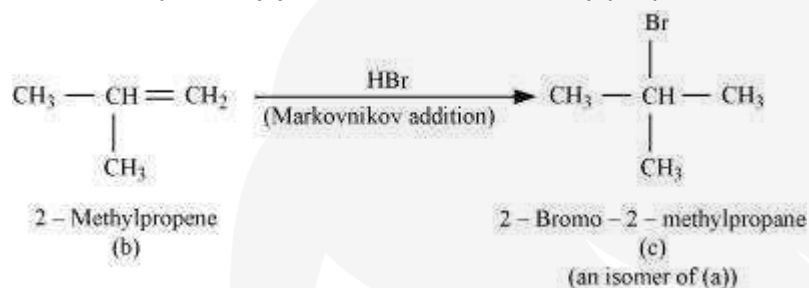


Thus, compound (d) is 2, 5–dimethylhexane.

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.



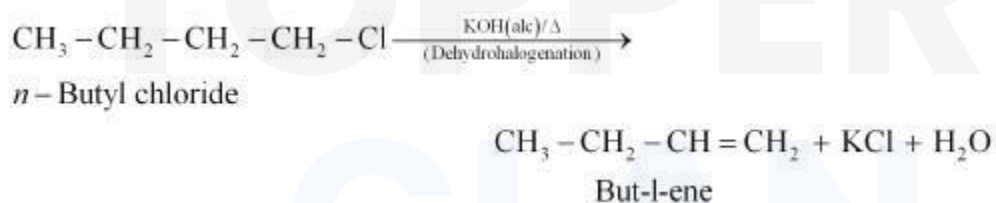
#### Question 6.22:

What happens when

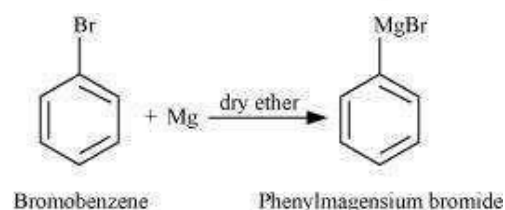
- (i) n-butyl chloride is treated with alcoholic KOH,
- (ii) bromobenzene is treated with Mg in the presence of dry ether,
- (iii) chlorobenzene is subjected to hydrolysis,
- (iv) ethyl chloride is treated with aqueous KOH,
- (v) methyl bromide is treated with sodium in the presence of dry ether,
- (vi)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

Answer

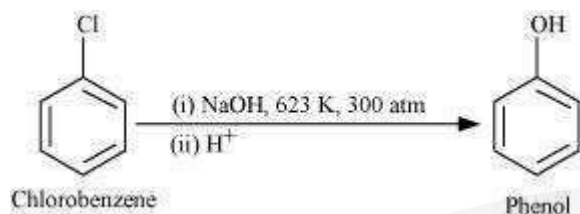
(i) When n-butyl chloride is treated with alcoholic KOH, the formation of but-1-ene takes place. This reaction is a dehydrohalogenation reaction.



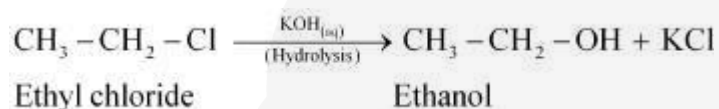
(ii) When bromobenzene is treated with Mg in the presence of dry ether, phenylmagnesium bromide is formed.



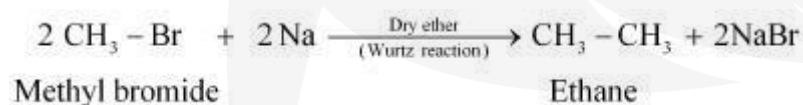
**(iii)** Chlorobenzene does not undergo hydrolysis under normal conditions. However, it undergoes hydrolysis when heated in an aqueous sodium hydroxide solution at a temperature of 623 K and a pressure of 300 atm to form phenol.



**(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.



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