

## CHAPTER 6 Haloalkanes and Haloarenes

### INTEXT QUESTIONS

PAGE NO: 163

Question 1. Write structures of the following compounds:

(i) 2-Chloro-3-methylpentane

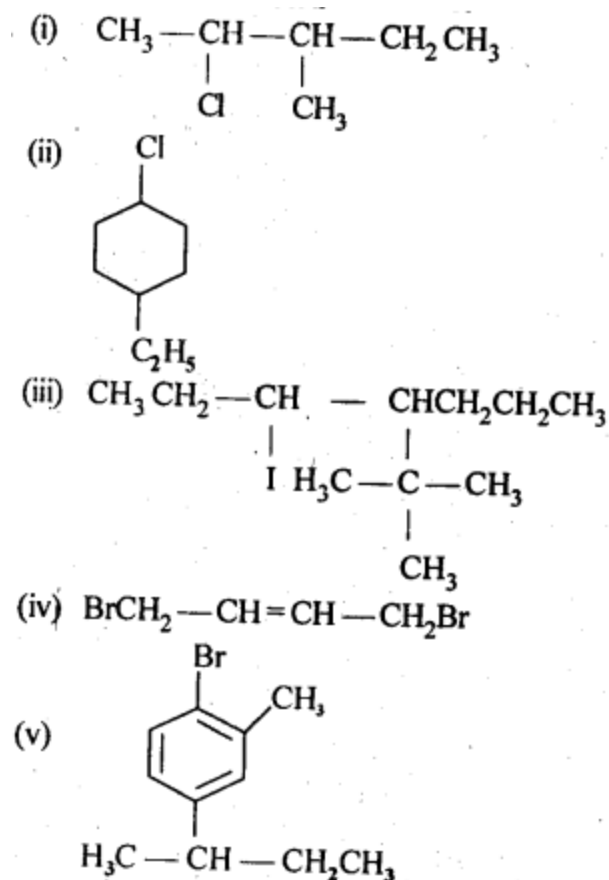
(ii) 1-Chloro-4-ethylcyclohexane

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

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

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

Solution :



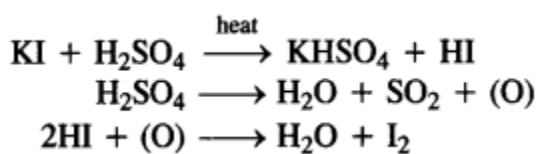
## INTEXT QUESTIONS

PAGE NO: 167

Question2. Why is sulphuric acid not used during the reaction of alcohols with KI?

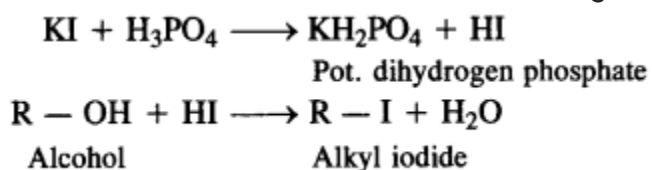
### Solution

KI is expected to give HI on reacting with  $\text{H}_2\text{SO}_4$  which will convert alcohols ( $\text{R}-\text{OH}$ ) to alkyl iodides ( $\text{R}-\text{I}$ ). However,  $\text{H}_2\text{SO}_4$  is a strong oxidising agent and it oxidises HI formed during the reaction to  $\text{I}_2$  which does not react with alcohol.



To solve the problem,  $\text{H}_2\text{SO}_4$  is replaced by phosphoric acid ( $\text{H}_3\text{PO}_4$ ) which provides HI

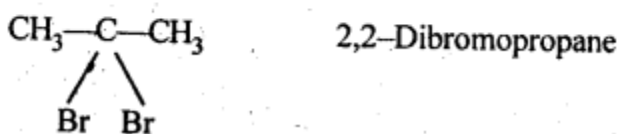
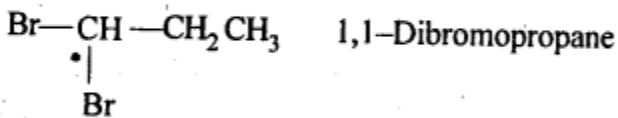
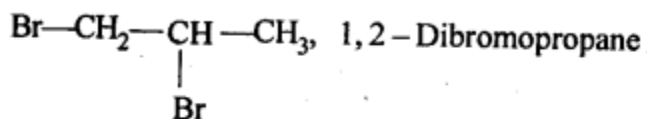
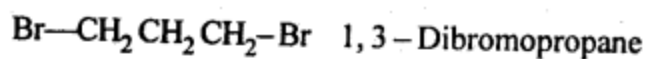
for the reaction and does not give I<sub>2</sub> as is done by H<sub>2</sub>SO<sub>4</sub>.



**Question3. Write structures of different dihalogen derivatives of propane.**

**Solution**

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



**Question4. Among the isomeric alkanes of molecular formula C<sub>5</sub>H<sub>12</sub>, identify the one that on photochemical chlorination yields**

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

Solution

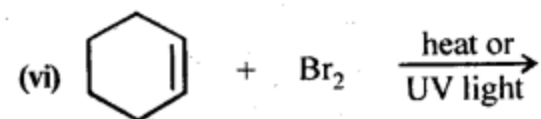
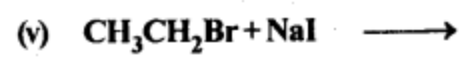
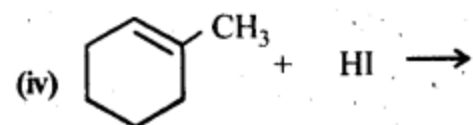
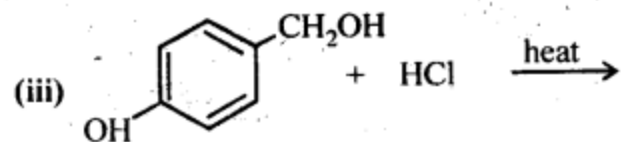
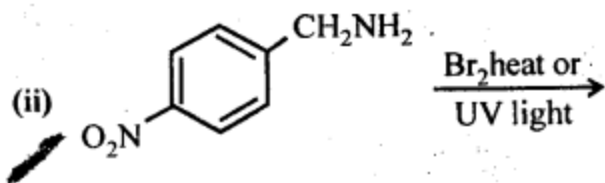
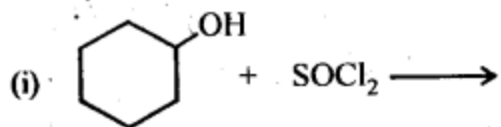
(i) Neopentane  $\begin{array}{c} \text{CH}_3 \\ | \\ \text{H}_3\text{C}-\text{C}-\text{CH}_3 \\ | \\ \text{CH}_3 \end{array}$ . As all the H-atoms are equivalent, the replacement of any one of them gives the same product.

(ii)  $\overset{a}{\text{CH}_3}\overset{b}{\text{CH}_2}\overset{c}{\text{CH}_2}\overset{b}{\text{CH}_2}\overset{a}{\text{CH}_3}$  *n*-pentane. *a*, *b*, *c* are the three sets of equivalent hydrogens. Therefore, three isomeric monochlorides are possible.

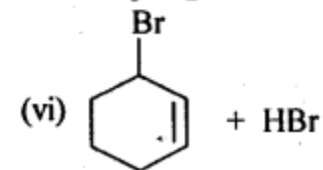
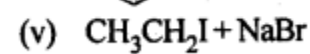
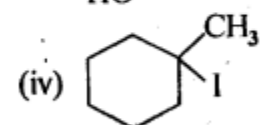
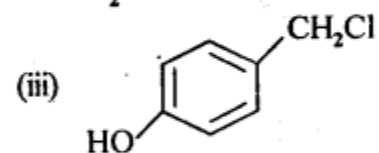
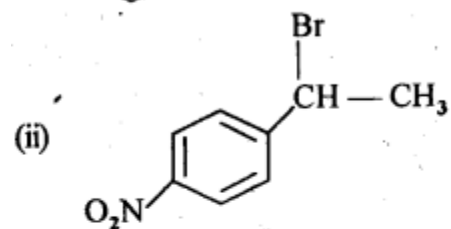
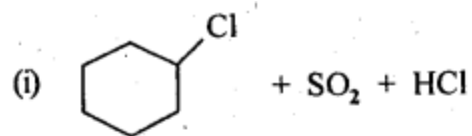
(ii)  $\overset{a}{\text{CH}_3}-\overset{b}{\underset{\text{CH}_3}{\text{C}}}-\overset{c}{\text{CH}_2}-\overset{d}{\text{CH}_3}$  iso-pentane.

there are four sets of equivalent hydrogens Designated as *a*, *b*, *c*, *d*. Thus, four isomeric monochlorides are possible.

Question5. Draw the structures of major monohalo products in each of the following reactions:



Solution :



## INTEXT QUESTIONS

PAGE NO: 169

Question 28. Arrange each set of compounds in order of increasing boiling points.

(i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.

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

Solution :

(i) 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)

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.

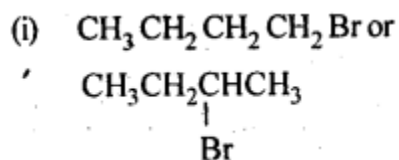
Hence, the given set of compounds can be arranged in the increasing order of their boiling points as:

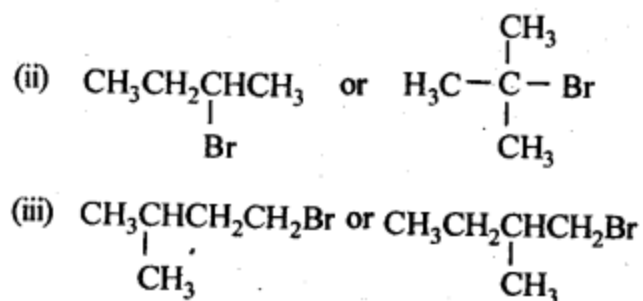
Isopropyl chloride < 1-Chloropropane < 1-Chlorobutane

## INTEXT QUESTIONS

PAGE NO: 186

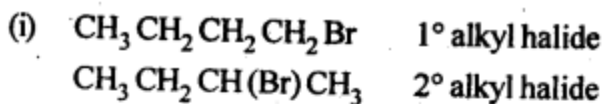
**Question 7. Which alkyl halide from the following pairs would you expect to react more rapidly by an SN2 mechanism? Explain your answer.**



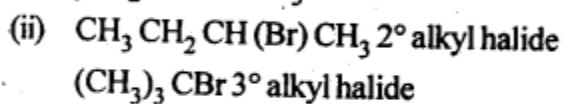


### Solution

In  $\text{S}_{\text{N}}2$  mechanism, reactivity depends upon the steric hindrance around the C-atom carrying the halogen. Lesser the steric hindrance, faster the reaction.



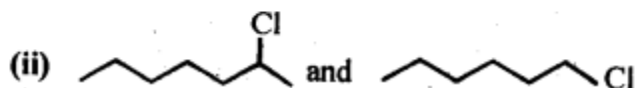
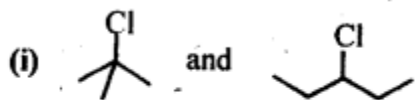
As steric hindrance in  $2^\circ$  alkyl halide is more, thus reactivity of  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{Br} > \text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$



As steric hindrance in  $(\text{CH}_3)_3\text{CBr}$  is more, thus it is less reactive than  $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{CH}_3$

(iii) Both are  $2^\circ$  alkyl halides but  $\text{CH}_3$  group at  $\text{C}_2$  is closer to Br atom than  $-\text{CH}_3$  group at  $\text{C}_3$ . As a result  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}_2\text{Br}$  suffers greater steric hindrance than  $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{Br}$  and will thus be less reactive in  $\text{S}_{\text{N}}2$ .

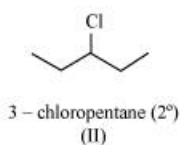
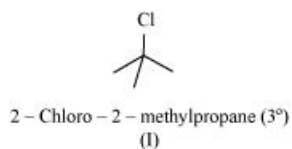
Question 8. In the following pairs of halogen compounds, which compound undergoes faster  $\text{S}_{\text{N}}1$  reaction?





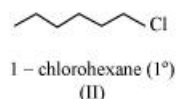
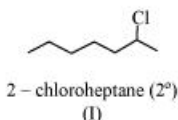
## Solution

(i)



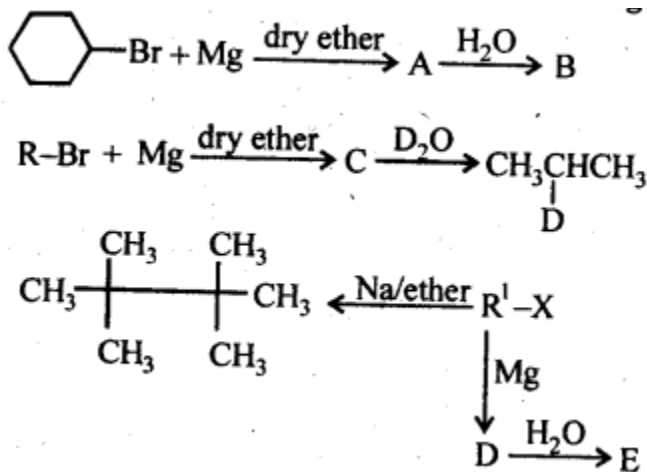
$S_N1$  reaction proceeds via the formation of carbocation. The alkyl halide (I) is  $3^\circ$  while (II) is  $2^\circ$ . Therefore, (I) forms  $3^\circ$  carbocation while (II) forms  $2^\circ$  carbocation. Greater the stability of the carbocation, faster is the rate of  $S_N1$  reaction. Since  $3^\circ$  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)



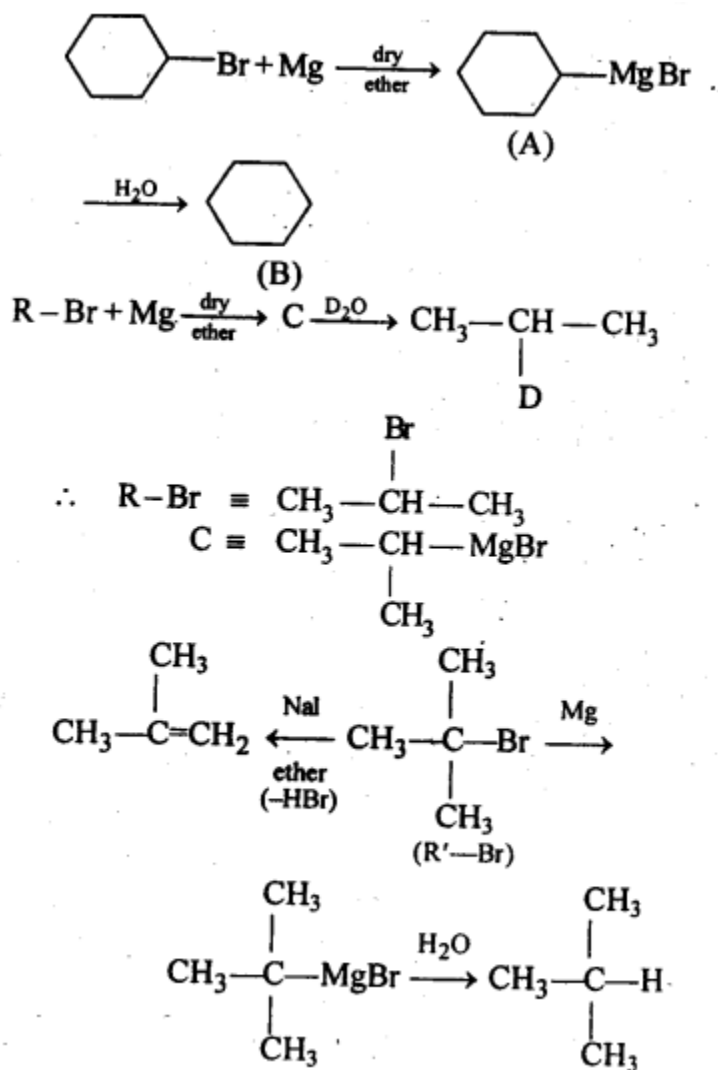
The alkyl halide (I) is  $2^\circ$  while (II) is  $1^\circ$ .  $2^\circ$  carbocation is more stable than  $1^\circ$  carbocation. Therefore, (I), 2-chloroheptane, undergoes faster  $S_N1$  reaction than (II), 1-chlorohexane.

**Question9. Identify A, B, C, D, E, R and R1 in the following:**



Solution

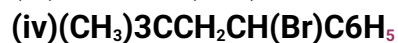
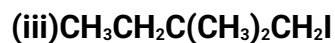
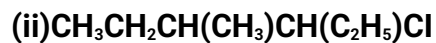
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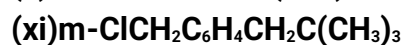
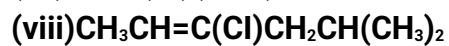
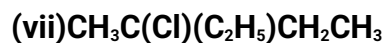


## EXERCISES

PAGE NO: 189

Question 1. Name the following halides according to IUPAC system and classify them as alkyl, allyl, benzyl (primary, secondary, tertiary), vinyl or aryl halides:





### Solution

(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 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)  $\text{ClCH}_2\text{C}=\text{CCH}_2\text{Br}$  (iv)  $(\text{CCl}_3)_3\text{CCl}$   
(v)  $\text{CH}_3\text{C}(\text{p-ClC}_6\text{H}_4)_2\text{CH}(\text{Br})\text{CH}_3$  (vi)  $(\text{CH}_3)_3\text{CCH}=\text{C}(\text{Cl})\text{C}_6\text{H}_4\text{I-p}$

**Solution**

(i) 2-Bromo-3-chlorobutane  
(ii) 1-bromo-1,1,2,2,2-pentafluoroethane  
(iii) 1-bromo-4-chlorobut-2-yne  
(iv) 2-(Trichloromethyl)-1,1,2,3,3,3-hexachloropropane  
(v) 2-bromo-3,3-bis(4-chlorophenyl)butane  
(vi) 1-chloro-1-(4-iodophenyl)-3,3-dimethylbut-1-ene.

**Question3. 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**

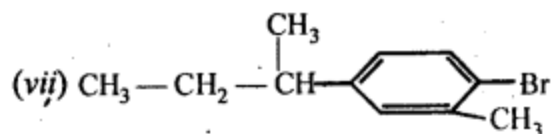
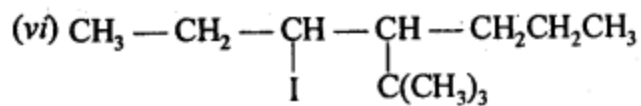
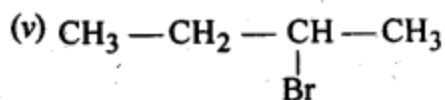
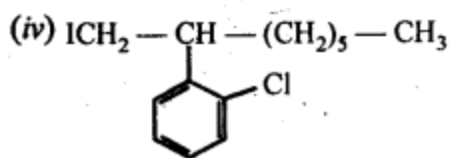
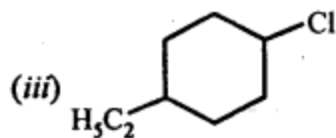
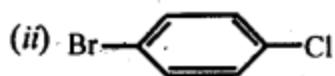
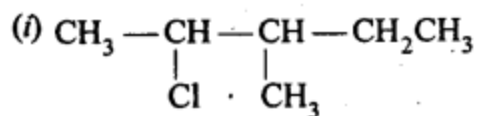
**(v) Perfluorobenzene**

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

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

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

**Solution:**

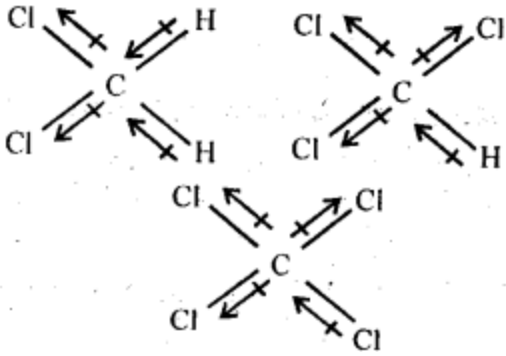


Question 4. Which one of the following has the highest dipole moment?

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

Solution :

The three dimensional structures of the three compounds along with the direction of dipole moment in each of their bonds are given below:



$\text{CCl}_4$  being symmetrical has zero dipole moment. In  $\text{CHCl}_3$ , the resultant of two C – Cl dipole moments is opposed by the resultant of C – H and C – Cl bonds. Since the dipole moment of latter resultant is expected to be smaller than the former,  $\text{CHCl}_3$  has a finite dipole moment (1.03 D). In  $\text{CH}_2\text{Cl}_2$ , the resultant of two C – Cl dipole moments is reinforced by resultant of two C – H dipoles, therefore,  $\text{CH}_2\text{Cl}_2$  (1.62 D) has a dipole moment higher than that of  $\text{CHCl}_3$ . Thus,  $\text{CH}_2\text{Cl}_2$  has highest dipole moment.

**Question5. 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.**

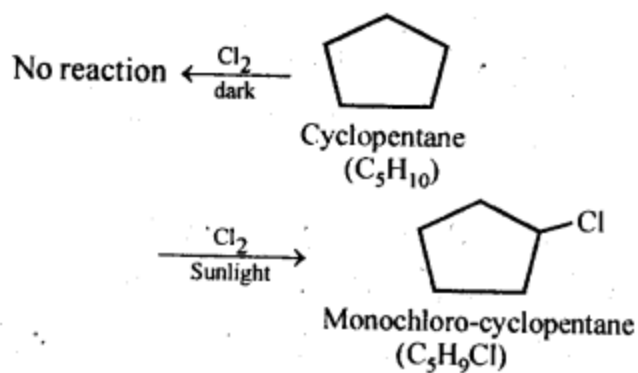
**Solution :**

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.

The reactions involved in the question are:



**Question6.** Write the isomers of the compound having formula C<sub>4</sub>H<sub>9</sub>Br.

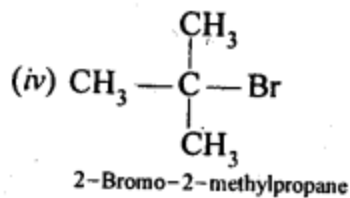
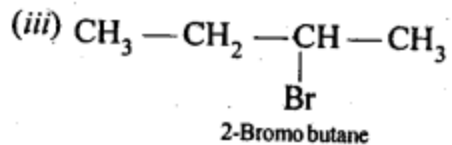
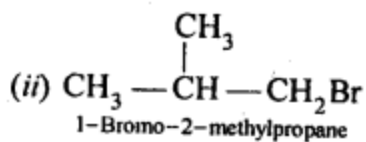
**Solution**

There are four isomers of the compound having the formula C<sub>4</sub>H<sub>9</sub>Br. These isomers are given below.

**Double bond equivalent (DBE) for C<sub>4</sub>H<sub>9</sub>Br**

$$= \frac{4(4-2) + 9(1-2) + 1(1-2)}{2} + 1 = 0$$

So none of the isomer has a ring or unsaturation, so the isomers are position or chain isomers





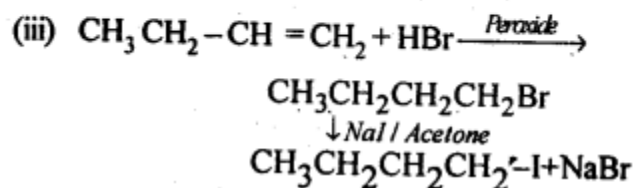
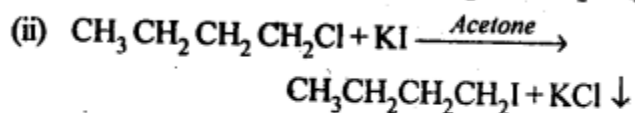
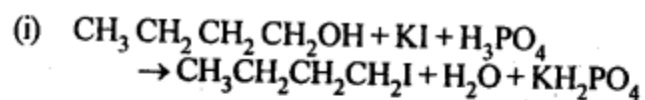
Question7. Write the equations for the preparation of 1-iodobutane from

(i) 1-butanol

(ii) 1-chlorobutane

(iii) but-1-ene.

Solution :



Question8. What are ambident nucleophiles? Explain with an example.

Solution :

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

For example, cyanide ion is a resonance hybrid of the following two structures:



It can attack through carbon to form cyanide and through N to form is O cyanide.

Question9. Which compound in each of the following pairs will react faster in SN2 reaction with OH<sup>-</sup>?

(i) CH<sub>3</sub>Br

or

CH<sub>3</sub>I

(ii) (CH<sub>3</sub>)<sub>3</sub>CCl or CH<sub>3</sub>Cl

**Solution**

(i) Since I<sup>-</sup> ion is a better leaving group than Br<sup>-</sup> ion, therefore, CH<sub>3</sub>I reacts faster than CH<sub>3</sub>Br in S<sub>N</sub>2 reaction with OH<sup>-</sup> ion.

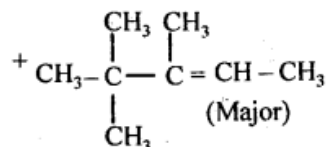
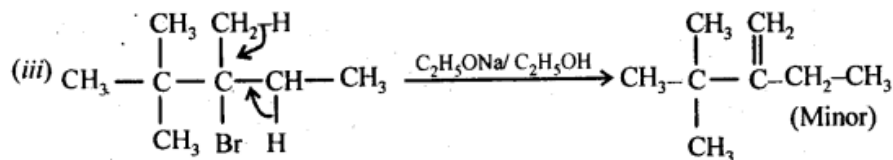
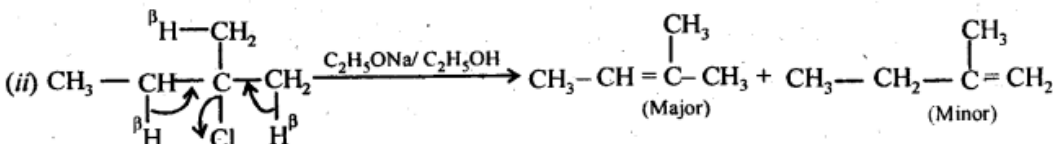
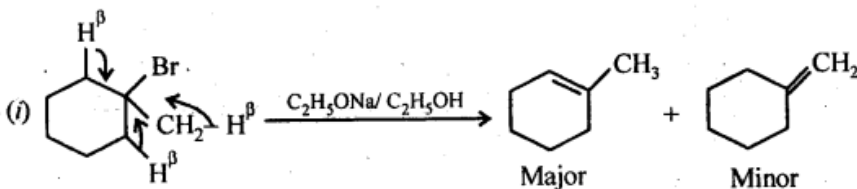
(ii) On steric grounds, 1° alkyl halides are more reactive than tert-alkyl halides in S<sub>N</sub>2 reactions. Therefore, CH<sub>3</sub>Cl will react at a faster rate than (CH<sub>3</sub>)<sub>3</sub>CCl in a S<sub>N</sub>2 reaction with OH<sup>-</sup> ion.

**Question 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.

**Solution**

**Question 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

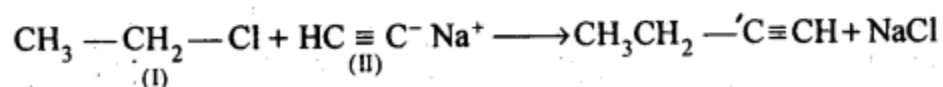
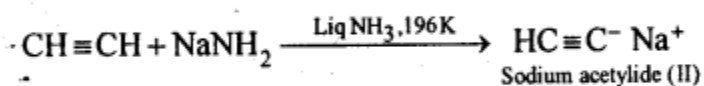
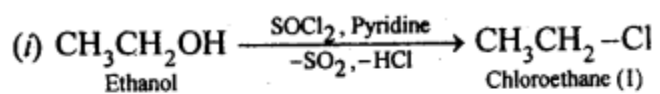
(vii) Bromomethane to propanone

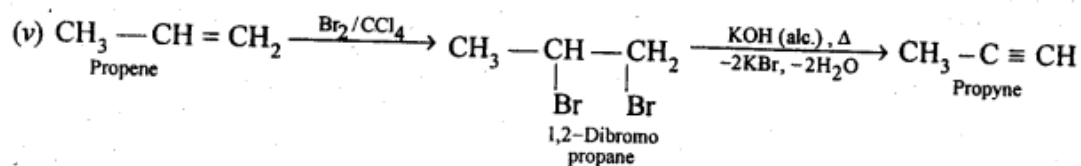
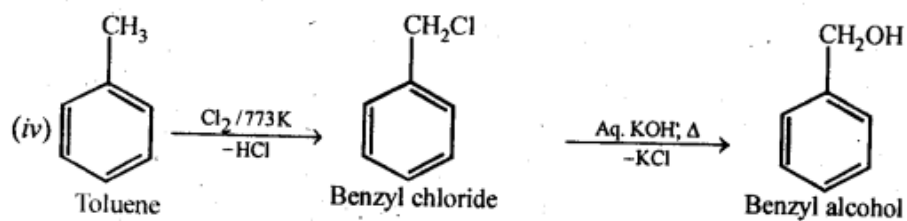
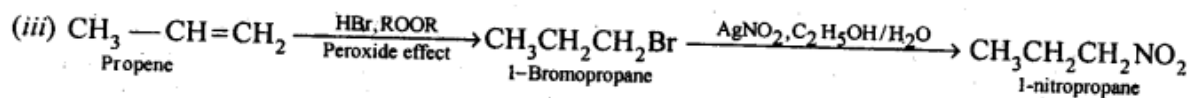
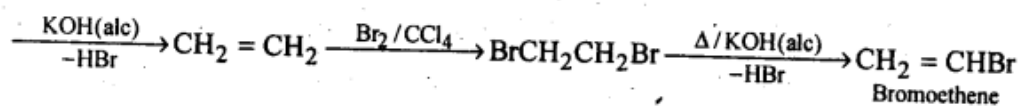
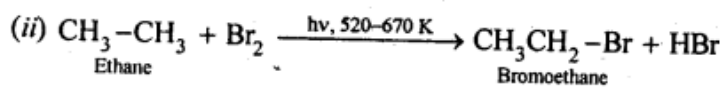
(viii) But-1-ene to but-2-ene

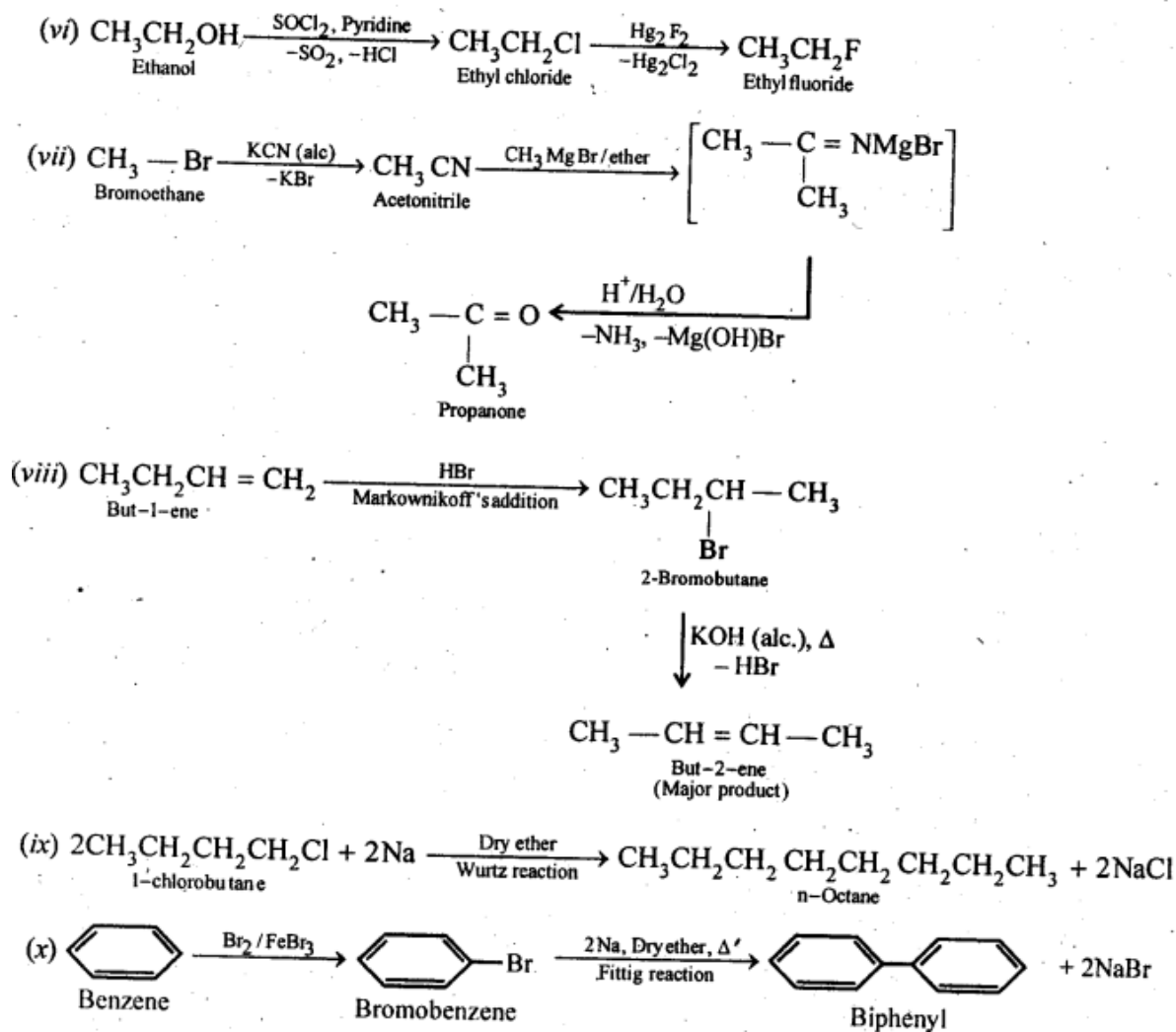
(ix) 1-Chlorobutane to n-octane

(x) Benzene to biphenyl.

Solution







Question 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?

**Solution**

(i) In chlorobenzene, the Cl-atom is linked to a  $\text{sp}^2$  hybridized carbon atom. In cyclohexyl chloride, the Cl-atom is linked to a  $\text{sp}^3$  hybridized carbon atom. Now,  $\text{sp}^2$  hybridized carbon has more s-character than  $\text{sp}^3$  hybridized carbon atom. Therefore, the former is more

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

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

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

(iii) Grignard reagents are very reactive. In the presence of moisture, they react to give alkanes. Therefore, Grignard reagents should be prepared under anhydrous conditions.

**Question 13. Give the uses of freon 12, DDT, carbon tetrachloride and iodoform.**

**Solution**

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 to its harmful effects, it was banned in the United States in 1973.

Uses of carbon tetrachloride ( $\text{CCl}_4$ )

(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.

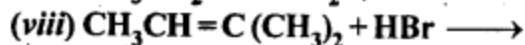
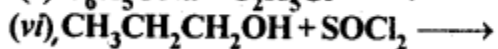
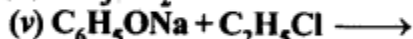
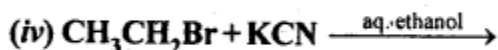
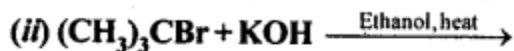
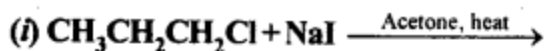
(iii) It is used as a solvent in the manufacture of pharmaceutical products.

(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.

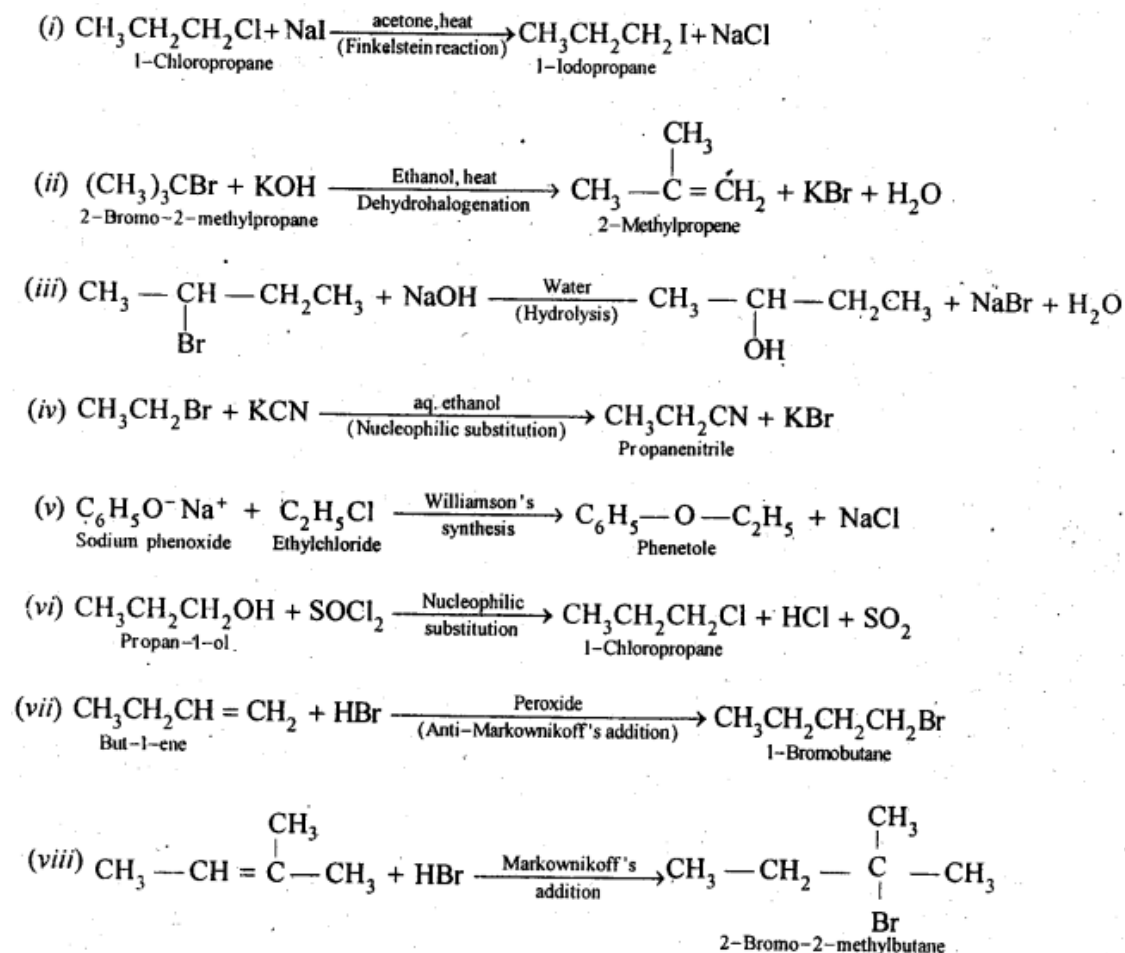
Uses of iodoform (CHI<sub>3</sub>)

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.

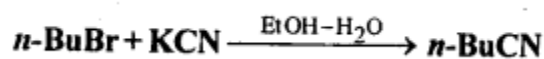
**Question 14. Write the structure of the major organic product in each of the following reactions:**



### Solution

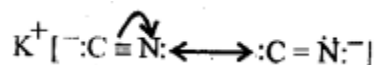


Question 15. Write the mechanism of the following reaction:



### Solution

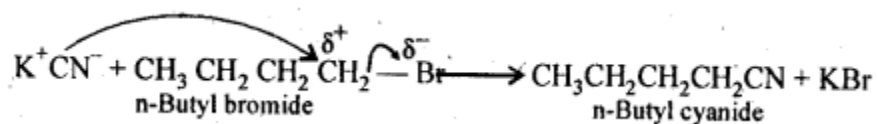
KCN is a resonance hybrid of the following two contributing structures:



Thus, CN<sup>-</sup> ion is an ambident nucleophile. Therefore, it can attack the "carbon atom of C-Br bond in n-BuBr either through C or N. Since C - C bond is stronger than C - N bond,



therefore, attack occurs through C to form n-butyl cyanide.



**Question16.** Arrange the compounds of each set in order of reactivity towards SN2 displacement:

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

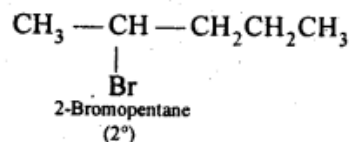
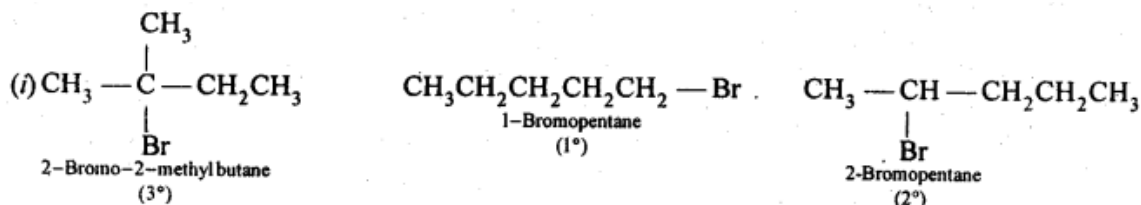
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane

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

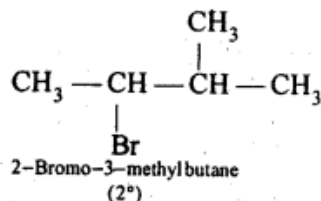
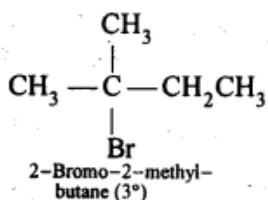
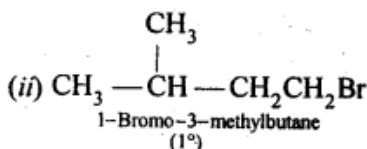
**Solution**

:

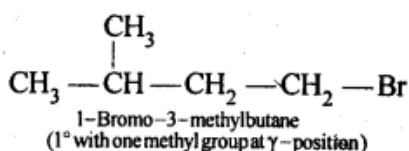
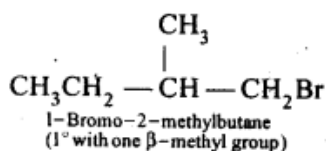
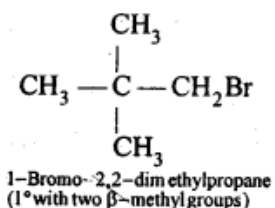
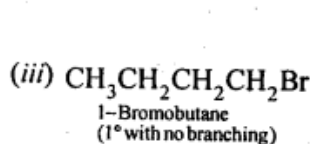
The S<sub>N</sub>2 reactions reactivity depends upon steric hindrance. More the steric hindrance slower the reaction. Thus the order of reactivity will be 1° > 2° > 3°



1-Bromopentane > 2-Bromopentane > 2-Bromo-2-methylbutane



1-Bromo-3-methylbutane > 2-Bromo-3-methylbutane > 2-Bromo-2-methylbutane

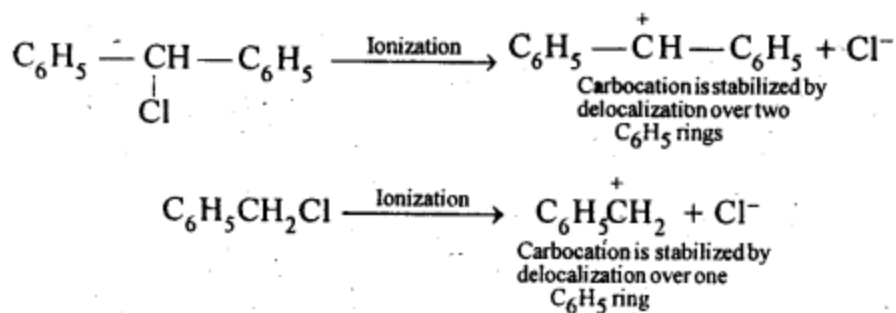


Since in case of 1° alkyl halides steric hindrance increases in the order) n-alkyl halides, alkyl halides with a substituent at any position other than the β-position, one substituent at the β-position, two substituents at the β-position, therefore, the reactivity decreases in the same order. Thus, the reactivity of the given alkyl bromides decreases in the order: 1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane.

**Question 17.** Out of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and  $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$ , which is more easily hydrolysed by aqueous KOH?

**Solution**

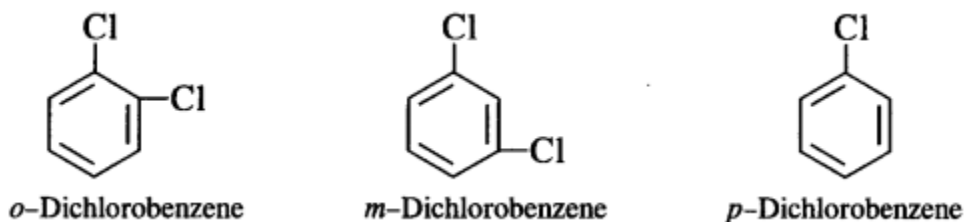
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  is 1° aryl halide while  $\text{C}_6\text{H}_5\text{CH}(\text{Cl})\text{C}_6\text{H}_5$  is a 2° aryl halide. In  $\text{S}_\text{N}1$  reactions, the reactivity depends upon the stability of carbocations.



Since the  $\text{C}_6\text{H}_5\text{CHC}_6\text{H}_5$  carbocation is more stable than  $\text{C}_6\text{H}_5\text{CH}_2$  carbocation, therefore,  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  gets hydrolysed more easily than  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  under  $\text{S}_{\text{N}}1$  conditions. However, under  $\text{S}_{\text{N}}2$  conditions, the reactivity depends on steric hindrance, therefore, under  $\text{S}_{\text{N}}2$  conditions,  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  gets hydrolysed more easily than  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ .

**Question 18.** *p*-Dichlorobenzene has higher m.p. and lower solubility than those of *o*- and *m*-isomers. Discuss.

**Solution**



*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 19.** How the following conversions can be carried out?

(i) Propene to propan-1-ol

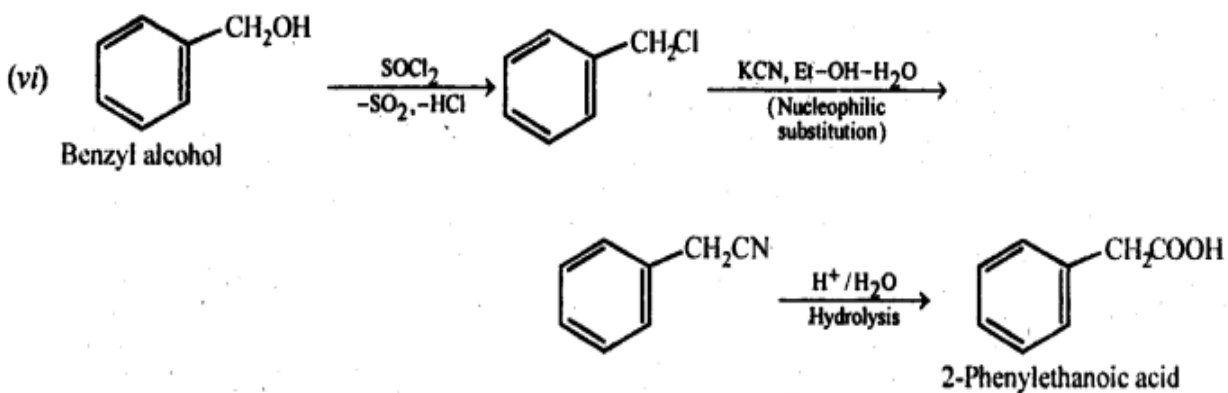
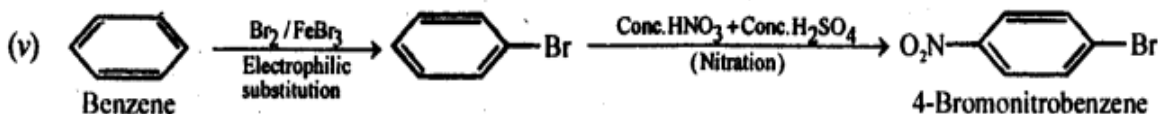
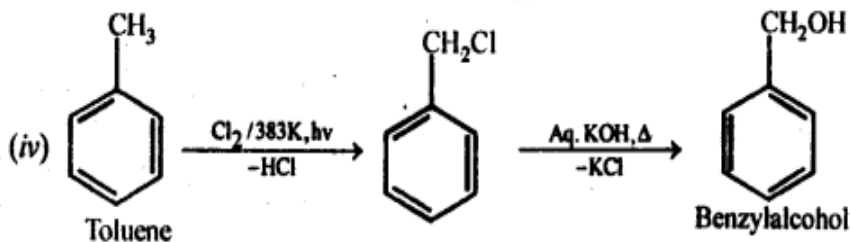
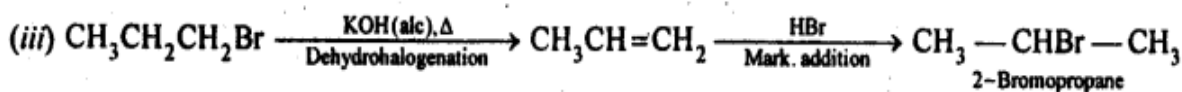
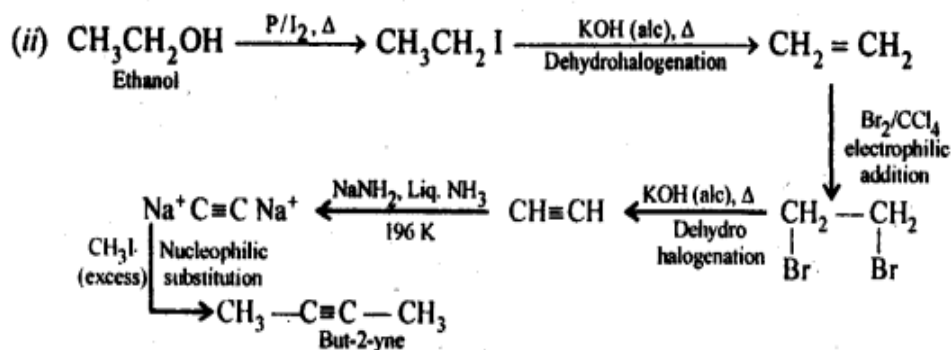
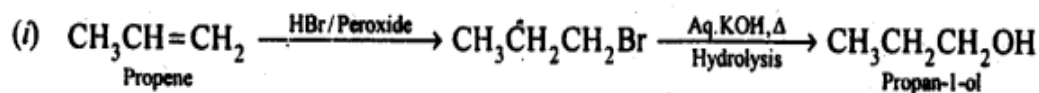
(ii) Ethanol to but-1-yne

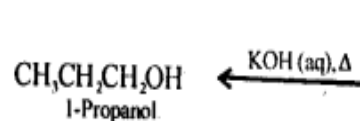
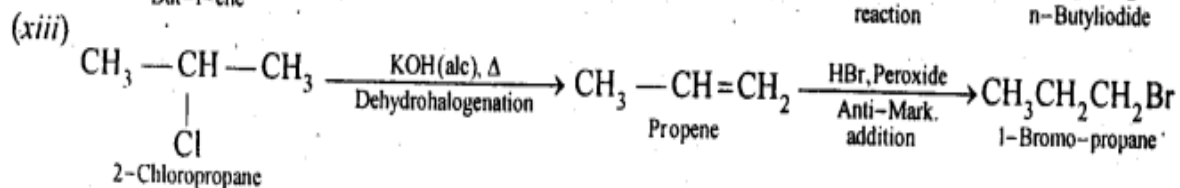
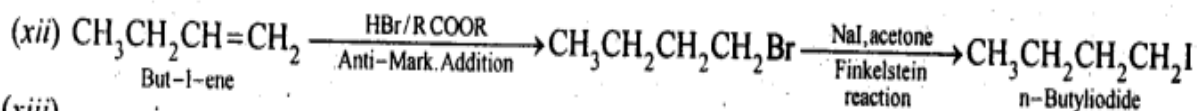
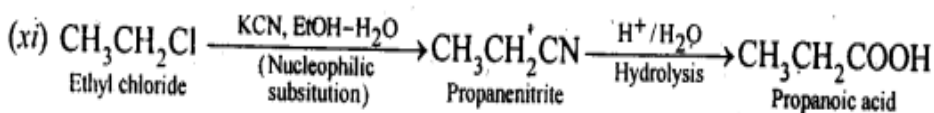
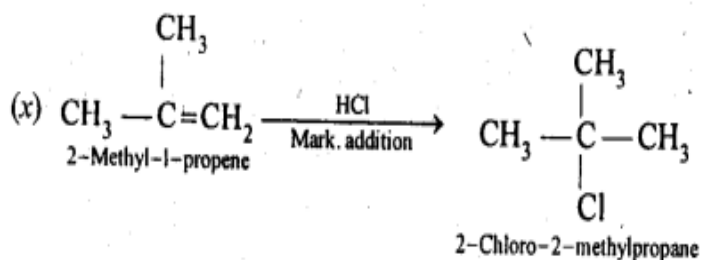
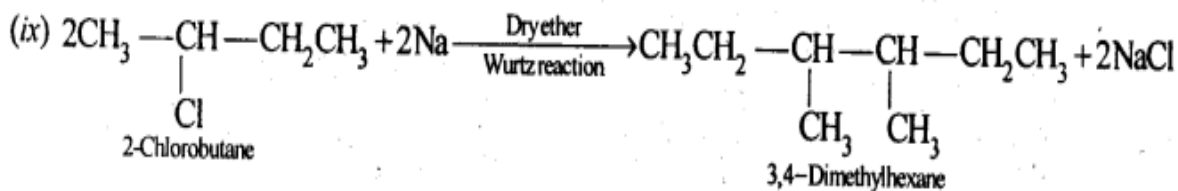
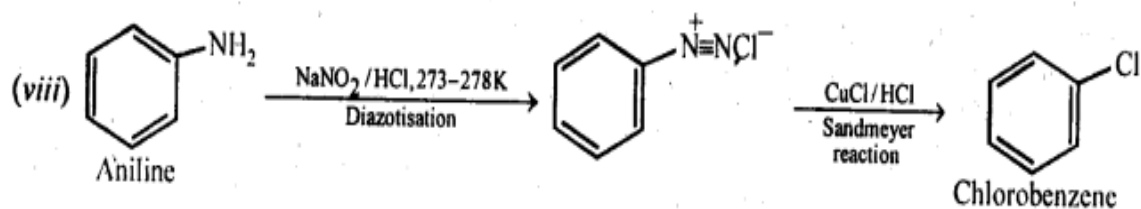
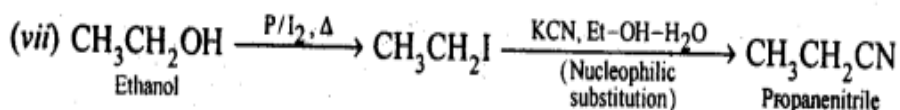
(iii) 1-Bromopropane to 2-bromopropane

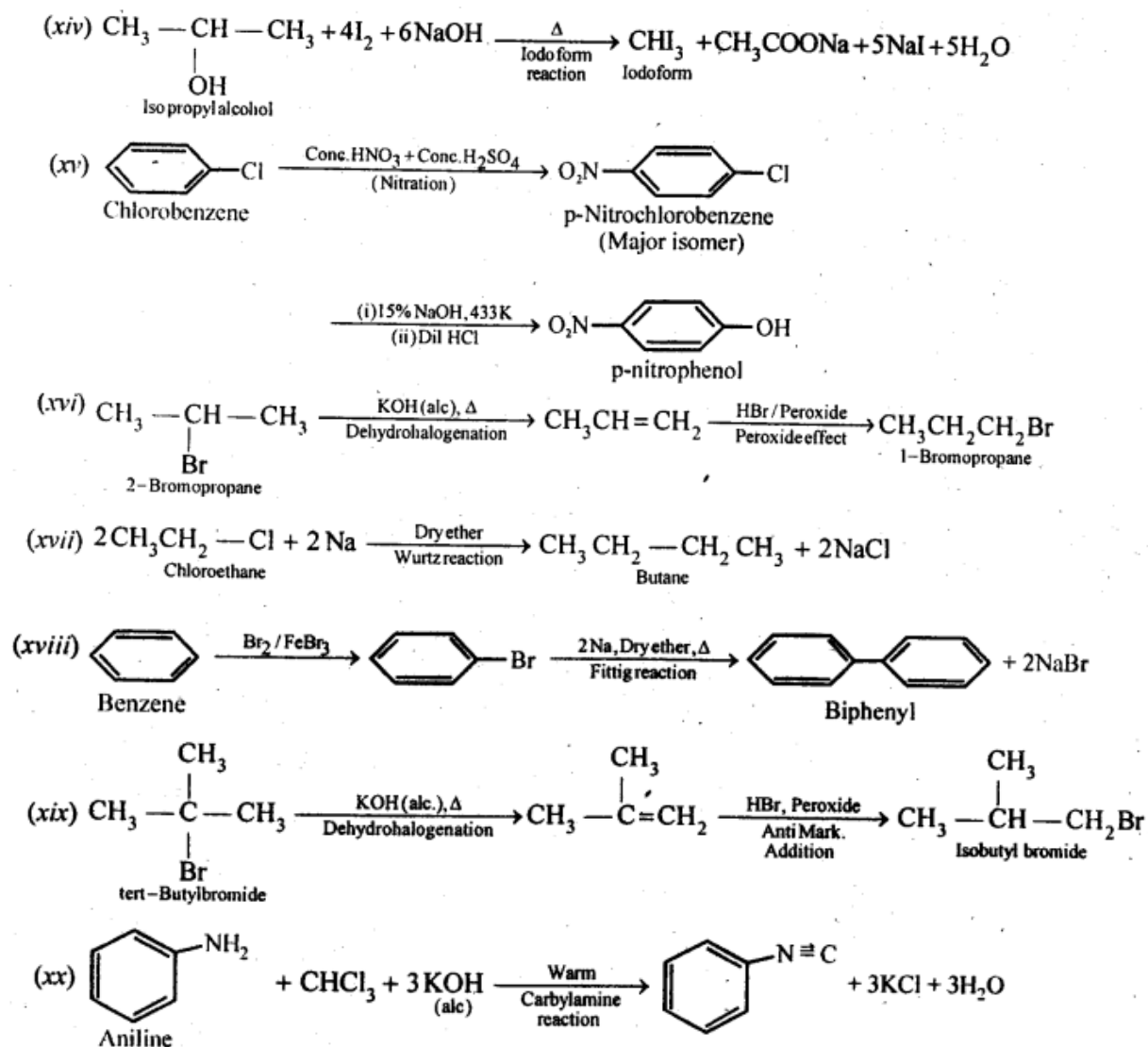
(iv) Toluene to benzyl alcohol

- (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**

Solution







**Question 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.

**Solution :**

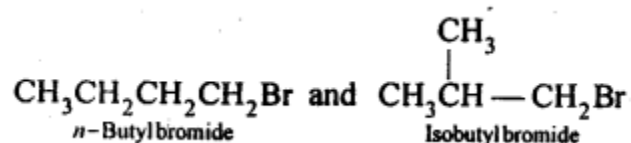
In aqueous medium i.e., water, KOH will be completely dissociated to give  $\text{OH}^-$  ions. They being a strong nucleophile, will bring about the substitution of alkyl halides to form alcohols. At the same time, the  $\text{OH}^-$  ions will be highly hydrated also. They will not be able to abstract a proton ( $\text{H}^+$ ) from the  $\beta$ -carbon atom to form alkenes. In other words, in aqueous medium,  $\text{OH}^-$  ions will behave as weak base and elimination leading to alkenes will not be feasible. In alcoholic KOH, the solution will also contain ethoxide ions ( $\text{C}_2\text{H}_5\text{O}^-$ ) in addition to  $\text{OH}^-$

ions. They being a stronger base than OH<sup>-</sup> ions, will abstract a H<sup>+</sup> ion from the β-carbon atom giving alkene as the product as a result of dehydrohalogenation.

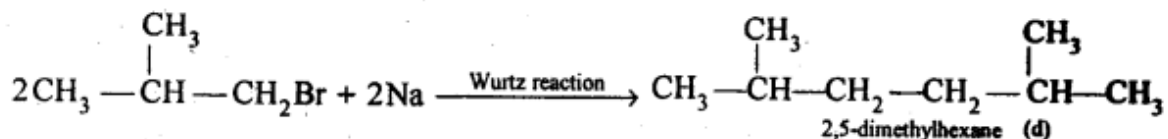
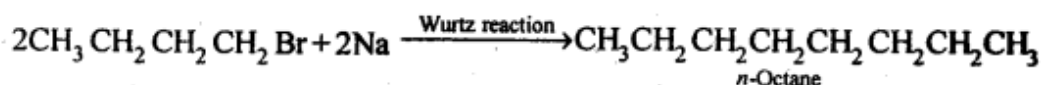
**Question 21.** Primary alkyl halide C<sub>4</sub>H<sub>9</sub>Br (a) reacted with alcoholic KOH to give compound (b). Compound (b) is reacted with HBr to give (c) which is an isomer of (a). When (a) is reacted with sodium metal it gives compound (d), C<sub>8</sub>H<sub>18</sub> which is different from 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.

**Solution**

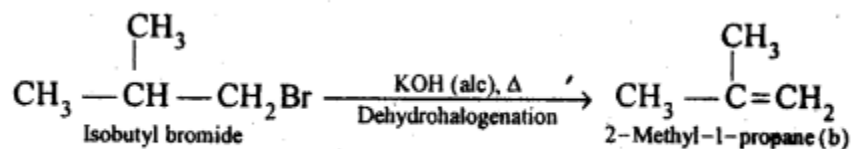
(i) There are two primary alkyl halides having the molecular formula, C<sub>4</sub>H<sub>9</sub>Br.



(ii) Since compound (a) when reacted with Na metal gave a compound (d) with molecular formula C<sub>8</sub>H<sub>18</sub> which was different from the compound obtained when n-butyl bromide was reacted with Na metal, therefore, (a) must be isobutyl bromide and compound (d) must be 2,3-dimethylhexane.

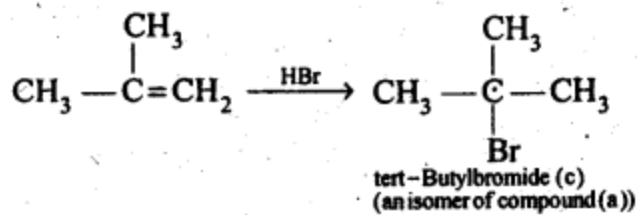


(iii) If compound (a) is isobutyl bromide, then the compound (b) which it gives on treatment with alcoholic KOH must be 2-methyl-1-propane.



(iv) The compound (b) on treatment with HBr gives compound (c) in accordance with Markownikoff rule. Therefore, compound (c) is tert-butyl bromide which is an isomer of compound (a), i.e., isobutyl bromide.





Thus

- |        |                     |           |
|--------|---------------------|-----------|
| (a) is | isobutyl            | bromide,  |
| (b) is | 2-methyl-1          | -propane, |
| (c) is | tert-butylbromide,  | and       |
| (d) is | 2,5-dimethylhexane. |           |

**Question 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.

