

## PART-2

### CHAPTER 6

## HALOALKANES & HALOARENES

### QUESTION AND ANSWERS

#### 2MARKS

1. Name the following halides according to the 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)  $\text{p-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (xi)  $\text{m-ClCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{C}(\text{CH}_3)_3$
- (xii)  $\text{o-Br-C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$

- Ans:** (i) 2-Chloro-3methylbutane, 2° alkyl halide  
(ii) 3-Chloro-4methyl hexane, 2° alkyl halide  
(iii) 1 -Iodo-2,2-dimethylbutane, 1 ° alkyl halide  
(iv) 1-Bromo-3, 3-dimethyl -1-phenylbutane, 2° benzylic halide  
(v) 2-Bromo-3-methylbutane, 2° alkyl halide  
(vi) 1-Bromo-2-ethyl-2-methylbutane, 1° alkyl halide  
(vii) 3-Chloro-3-methylpentane, 3° alkyl halide  
(viii) 3-Chloro-5-methylhex-2-ene, vinylic halide  
(ix) 4-Bromo-4-methylpent-2-ene, allylic halide  
(x) 1-Chloro-4-(2-methylpropyl) benzene, aryl halide

(xi) 1-Chloromethyl-3- (2,2-dimethylpropyl) benzene, 1 ° benzylic halide.

(xii) 1-Bromo-2-(1-methylpropyl) benzene, aryl halide.

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

**Ans:** (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.

**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- iodo-octane

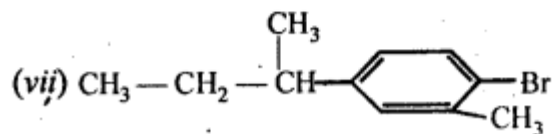
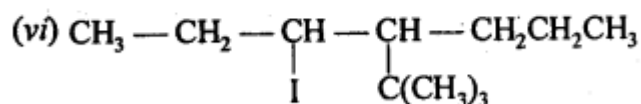
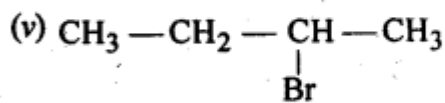
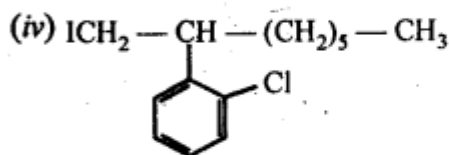
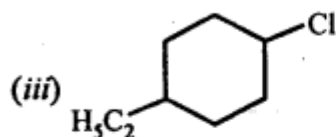
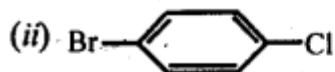
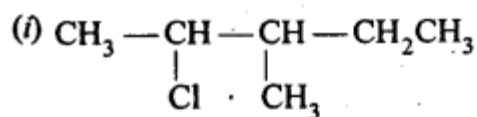
(v) 2-Bromobutane

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

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

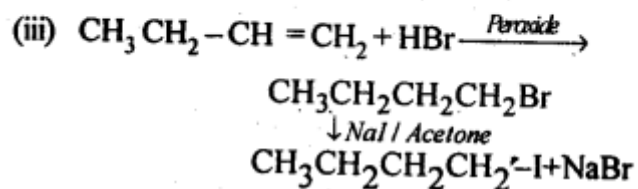
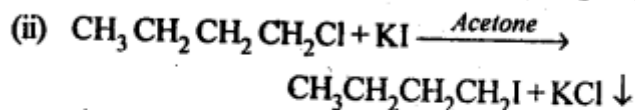
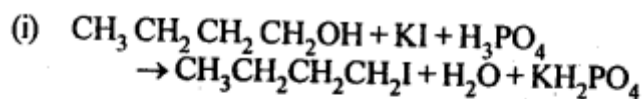
(viii) 1,4-Dibromobut-2-ene

Ans:



4. Write the equations for the preparation of 1-iodobutane from (i) 1-butanol (ii) 1-chlorobutane (iii) but-1-ene.

Ans:



**5. What are ambident nucleophiles ? Explain with an example.**

**Ans:** Nucleophiles which can attack through two different sites are called ambident nucleophiles. 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.

**6. 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  $\text{CH}_3\text{Cl}$**

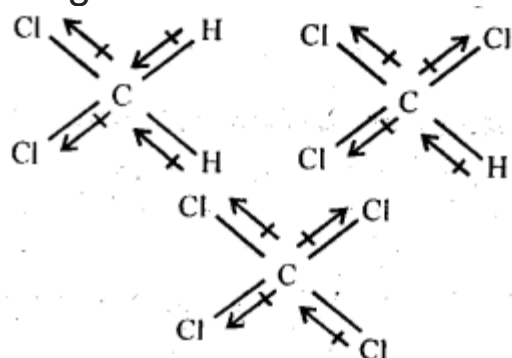
**Ans:** (i) Since  $\text{I}^-$  ion is a better leaving group than  $\text{Br}^-$  ion, therefore,  $\text{CH}_3\text{I}$  reacts faster  $\text{CH}_3\text{Br}$  in  $\text{S}_{\text{N}}2$  reaction with  $\text{OH}^-$  ion.  
(ii) On steric grounds,  $1^\circ$  alkyl halides are more reactive than tert-alkyl halides in  $\text{S}_{\text{N}}2$  reactions. Therefore,  $\text{CH}_3\text{Cl}$  will react at a faster rate than  $(\text{CH}_3)_3\text{CCl}$  in a  $\text{S}_{\text{N}}2$  reaction with  $\text{OH}^-$  ion.

**5MARKS**

**1. Which one of the following has the highest dipole moment?**

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

**Ans:** 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

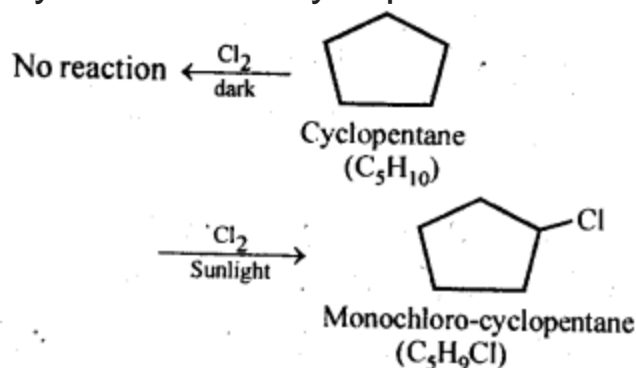
resultant of two C – Cl dipole moments is opposed by the resultant of C – H and C – Cl bonds. Since the dipole moment of latter resultant is expected to be smaller than the former,  $\text{CHCl}_3$  has a finite dipole (1.03 D) moment.

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.

**2. 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.**

**Ans:** The hydrocarbon with molecular formula  $\text{C}_5\text{H}_{10}$  can either be a cycloalkane or an alkene.

Since the compound does not react with  $\text{Cl}_2$  in the dark, therefore it cannot be an alkene but must be a cycloalkane. Since the cycloalkane reacts with  $\text{Cl}_2$  in the presence of bright sunlight to give a single monochloro compound,  $\text{C}_5\text{H}_9\text{Cl}$ , therefore, all the ten hydrogen atoms of the cycloalkanes must be equivalent. Thus, the cycloalkane is cyclopentane.



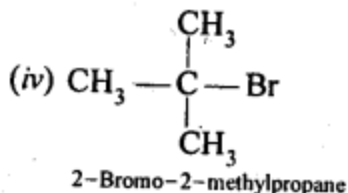
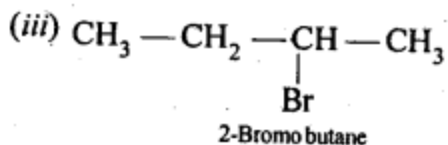
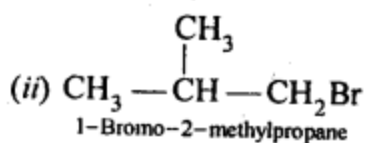
3. Write the isomers of the compound having formula  $C_4H_9Br$ .

Ans:

Double bond equivalent (DBE) for  $C_4H_9Br$

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

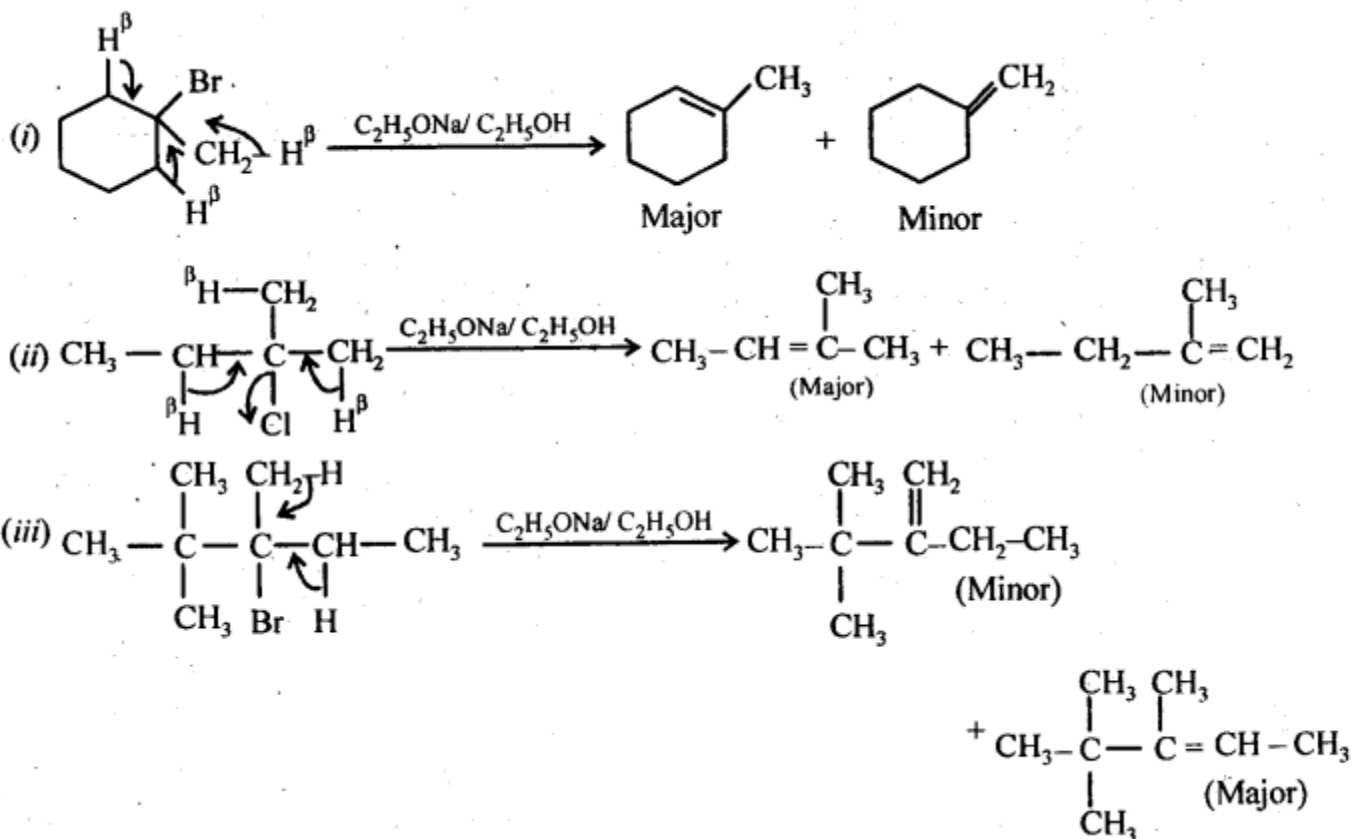
So none of the isomer has a ring or unsaturation, so the isomers are position or chain isomers



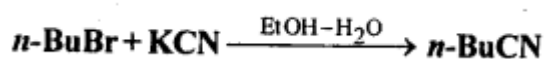
4. Predict all the alkenes that would be formed by dehydrohalogenation of the following halides with sodium ethoxide in ethanol and identify the major alkene:

- (i) 1-Bromo-1-methylcyclohexane
- (ii) 2-Chloro-2-methylbutane.
- (iii) 2,2,3-Trimethyl-3-bromopentane.

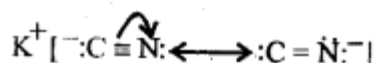
Ans:



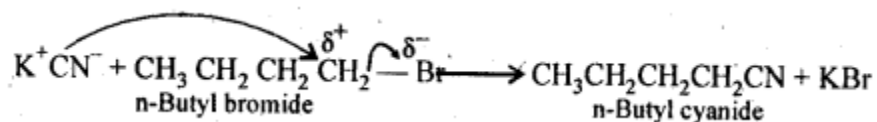
5. Write the mechanism of the following reaction:



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

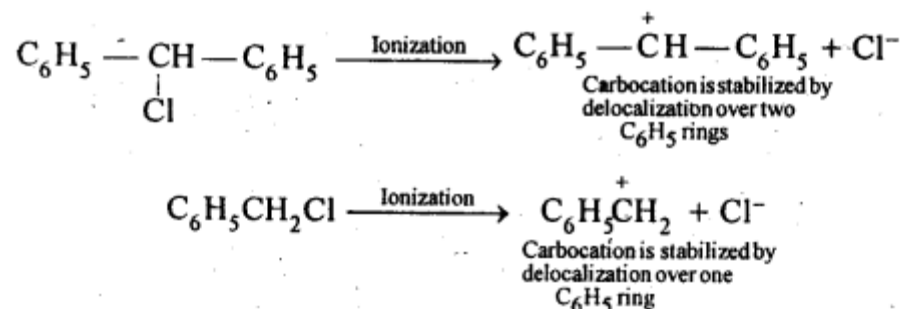


Thus,  $\text{CN}^-$  ion is an ambident nucleophile. Therefore, it can attack the "carbon atom of C-Br bond in n-BuBr either through C or N. Since C – C bond is stronger than C – N bond, therefore, attack occurs through C to form n-butyl cyanide.



**6. Out of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  which is more easily hydrolysed by aqueous KOH.**

**Ans:**  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  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  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ .

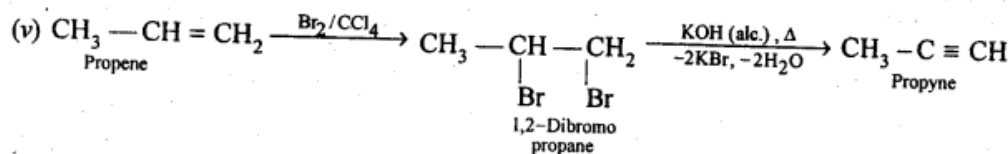
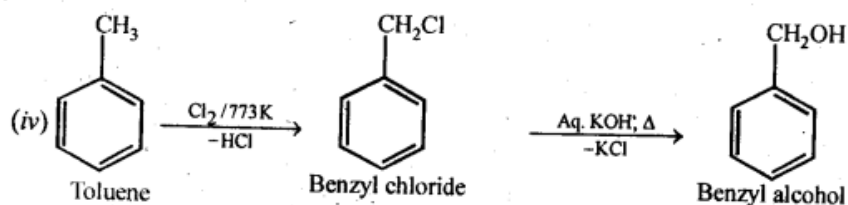
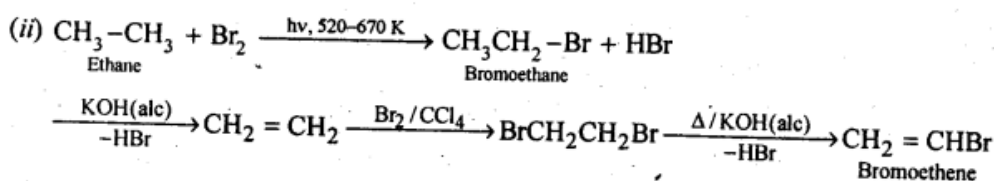
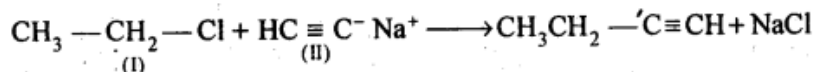
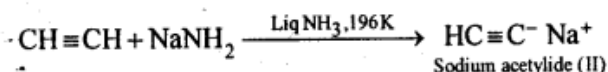
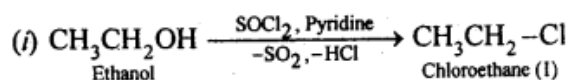


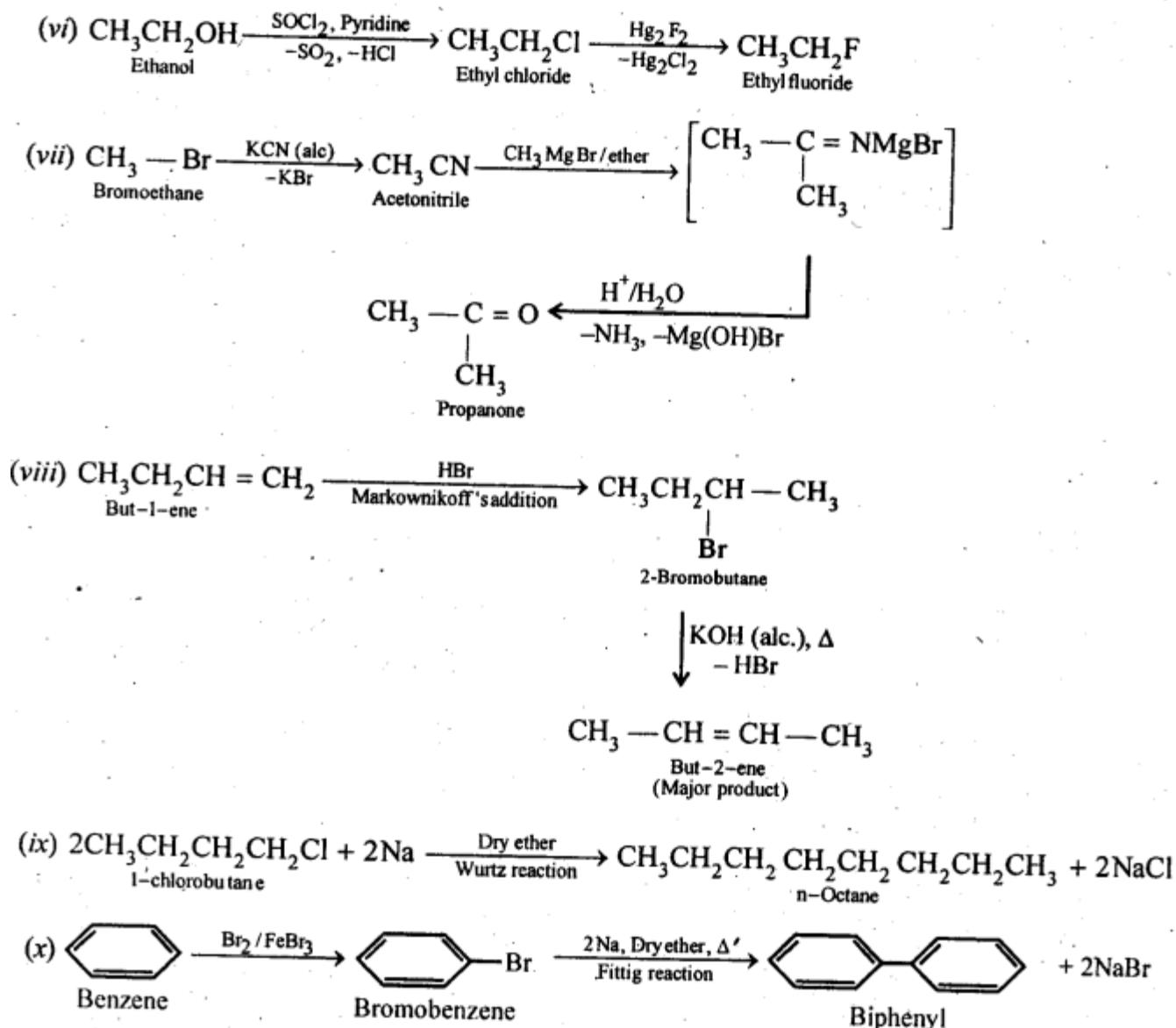
## 7MARKS

1. 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

Ans:





## 2. 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?

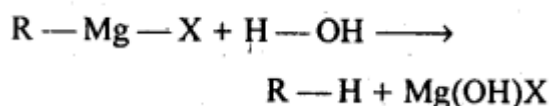
**Ans:** (i)  $\text{sp}^2$ -hybrid carbon in chlorobenzene is more electronegative than a  $\text{sp}^3$ -hybrid carbon in cyclohexylchloride, due to greater s-character. Thus, C atom of chlorobenzene has

less tendency to release electrons to Cl than carbon atom of cyclohexylchloride.

As a result, C – Cl bond in chlorobenzene is less polar than in cyclohexylchloride. Further, due to delocalization of lone pairs of electrons of the Cl atom over the benzene ring, C-Cl bond in chlorobenzene acquires some double bond character while the C – Cl in cyclohexyl chloride is a pure single bond. In other words, C-Cl bond in chlorobenzene is shorter than in cyclohexyl chloride. Since dipole moment is a product of charge and distance, therefore, chlorobenzene has lower dipole moment than cyclohexylchloride due to lower magnitude of negative charge on the Cl atom and shorter C-Cl distance.

(ii) Alkyl halides are polar molecules, therefore, their molecules are held together by dipole-dipole attraction. The molecules of H<sub>2</sub>O are held together by H-bonds. Since the new forces of attraction between water and alkyl halide molecules are weaker than the forces of attraction already existing between alkyl halide – alkyl halide molecules and water-water molecules, therefore, alkyl halides are immiscible (not soluble) in water. Alkyl halides are neither able to form H-bonds with water nor are able to break the H-bonding network of water.

(iii) Grignard reagents are very reactive. They react with moisture present in the apparatus to form alkanes



Thus, Grignard reagents must be prepared under anhydrous conditions.

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

**Ans:** Iodoform: It was earlier used as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself. Due to its objectionable smell, it has been replaced by other formulations containing iodine.

#### **Carbon tetrachloride:**

##### **Uses:**

- (i) As an industrial solvent for oil, fats, resins etc. and also in dry cleaning.
- (ii)  $\text{CCl}_4$  vapours are highly non-inflammable, thus  $\text{CCl}_4$  is used as a fire extinguisher under the name pyrene.
- (iii) Used in the manufacture of refrigerants and propellants for aerosol cans.

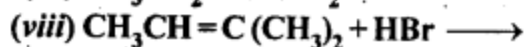
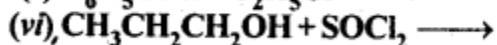
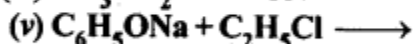
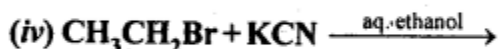
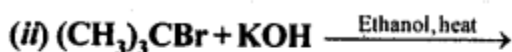
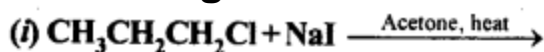
**Freons:** Freon-12 ( $\text{CCl}_2\text{F}_2$ ) is most common freons in industrial use.

Uses: For aerosol propellants, refrigeration, and air conditioning purposes.

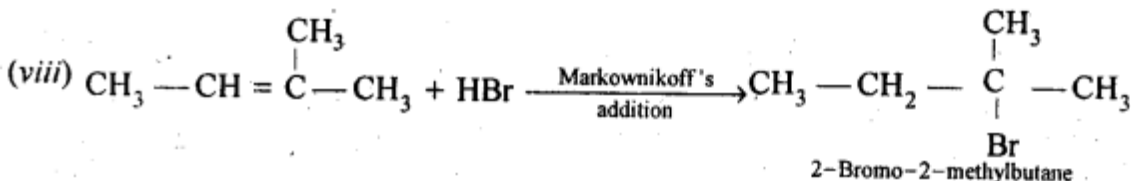
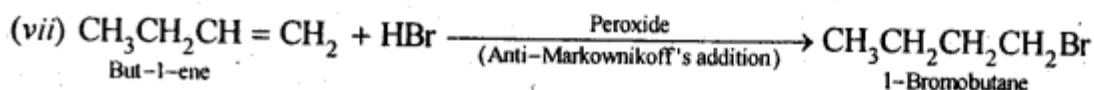
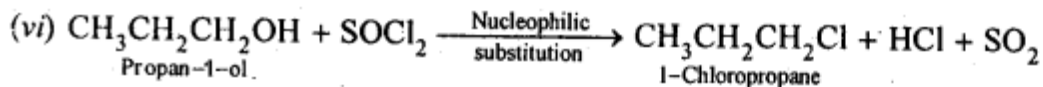
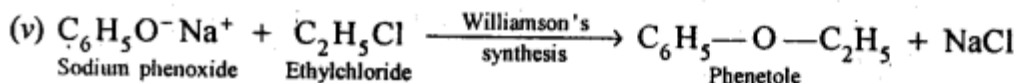
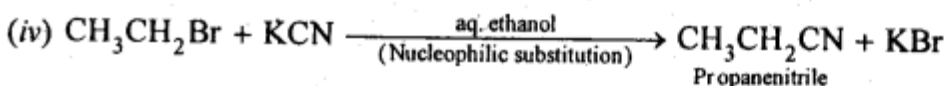
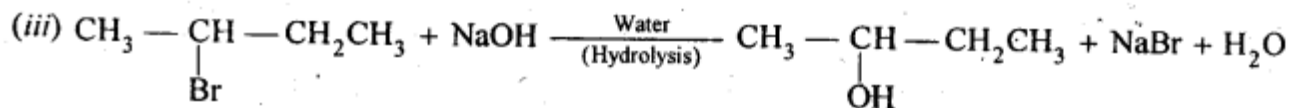
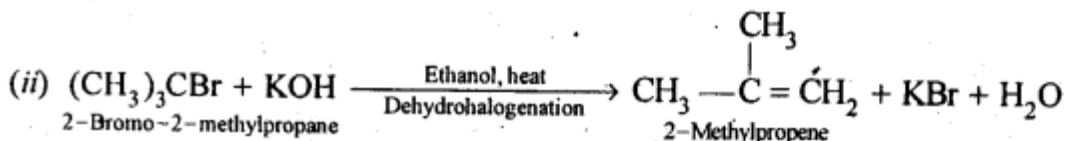
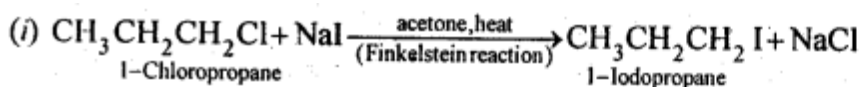
#### **DDT (p -p' – Dichloro diphenyl – trichloro ethane):**

- (i) The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquitoes that spread malaria and other insects which damage crops.
- (ii) However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, it was also discovered to have a high toxicity towards fishes. DDT is not metabolised very rapidly by animals, instead, it is deposited and stored in the fatty tissues. If the ingestion continues at a steady rate, DDT builds up within the animal's overtime.

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



**Ans:**



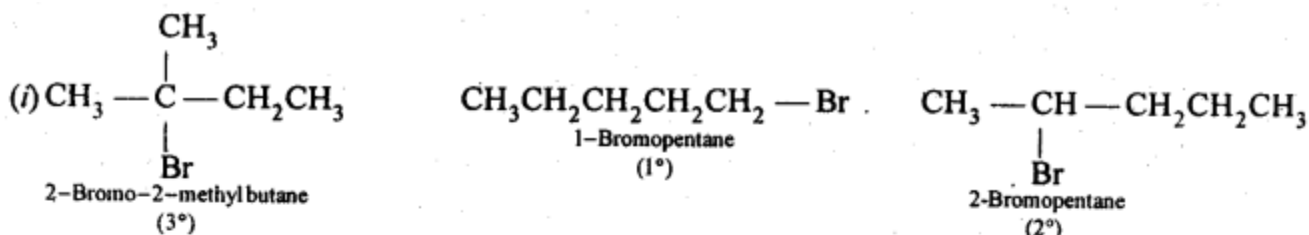
5. Arrange the compounds of each set in order of reactivity towards  $S_N2$  displacement:

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

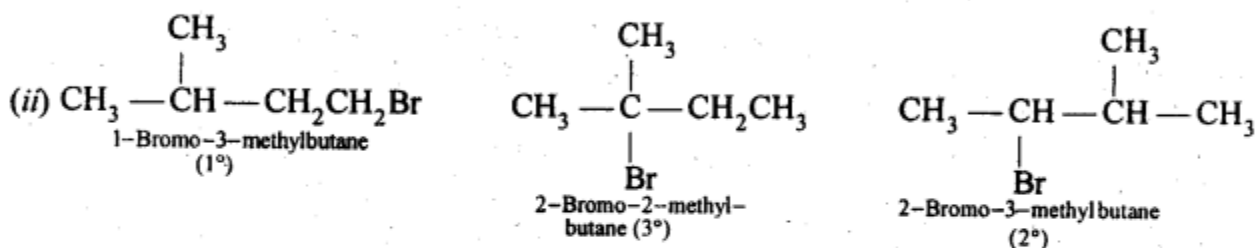
(ii) 1-Bromo-3-methylbutane, 2-Bromo-2-methylbutane, 3-Bromo-2-methylbutane.

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

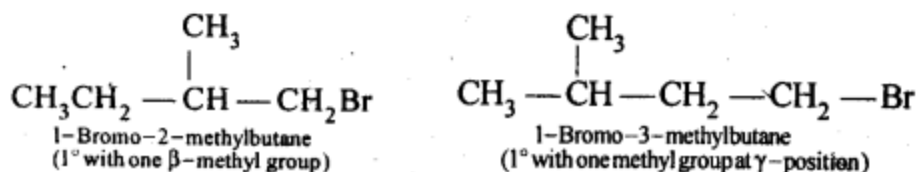
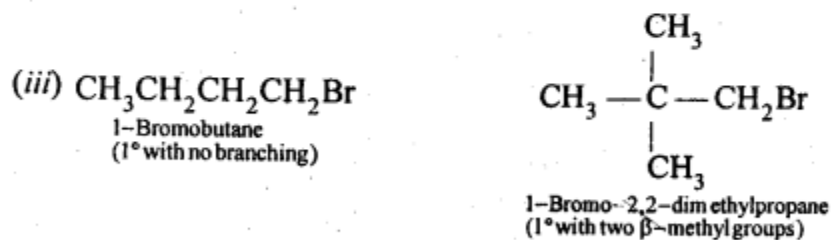
**Ans:** The  $S_N2$  reactions reactivity depends upon steric hindrance. More the steric hindrance slower the reaction. Thus the order of reactivity will be  $1^\circ > 2^\circ > 3^\circ$



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  $\beta$ -position, one substituent at the  $\beta$ -position, two substituents at the  $\beta$ -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-dimethyl propane.

## SUMMARY

1. Haloalkanes are classified as fluoro, chloro, bromo or iodo compounds according to the type of halogen present and as mono-, di- tri-, tetra- haloalkanes, etc., according to the one, two, three, four, etc., halogen atoms respectively present in their molecule.
2. Alkyl halides are further classified as primary ( $1^\circ$ ), secondary ( $2^\circ$ ) and tertiary ( $3^\circ$ ) according to the halogen atom attached to primary, secondary and tertiary carbon atoms, respectively.
3. Due to electronegativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom. As a result, the halogen carries a small negative charge, while the carbon carries a small positive charge. Consequently, C-X bond is a polar covalent bond.
4. **Methods of Preparation of Haloalkanes:** Haloalkanes can be prepared from displacement of alcoholic group in alkyl alcohol by halogen acid,  $\text{PCl}_5$  or  $\text{PCl}_3$ . Haloalkanes can also be prepared by addition of halogen acids or halogens on alkene and alkyne. Alkyl halides can also be prepared by free radical halogenation of alkane.
5. **Methods of preparation of Haloarenes.** Haloarenes can be prepared by side chain halogenation or nuclear halogenation of aromatic hydrocarbons.
6. **From diazonium salts:**
  - (i) By Sandmeyer reaction:
  - (ii) By Gattermann reaction: