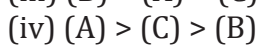
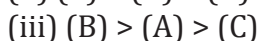
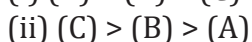
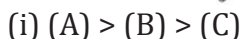
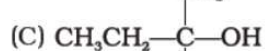
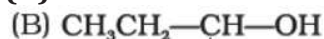
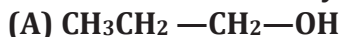


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**Haloalkanes and Haloarenes**  
**Multiple Choice Questions (Type-I)**

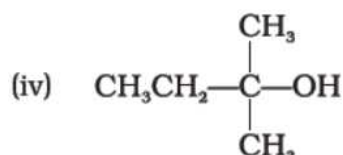
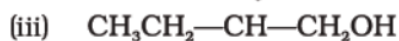
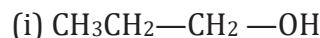
1. The order of reactivity of following alcohols with halogen acids is \_\_\_\_\_.



Ans. (ii)

**Explanation:** Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides,  $3^\circ$  alkyl halides undergo  $\text{S}_{\text{N}}1$  reaction very fast because of the high stability of  $3^\circ$  carbocations.

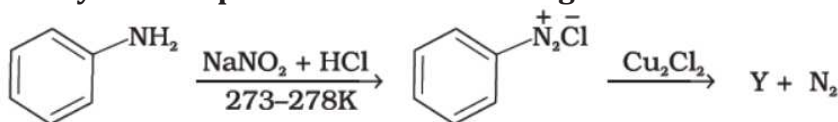
2. Which of the following alcohols will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

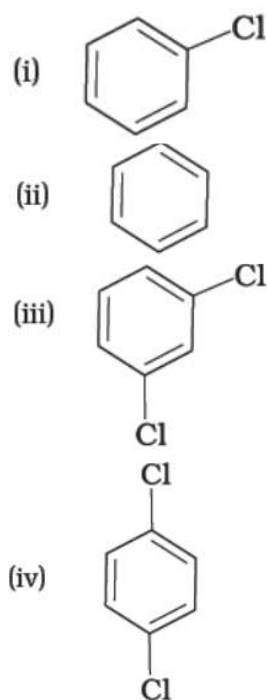


Ans. (iv)

**Explanation:** The reactions of primary and secondary alcohols with HCl require the presence of a catalyst,  $\text{ZnCl}_2$ . With tertiary alcohols, the reaction is conducted by simply shaking with concentrated HCl at room temperature. The order of reactivity of alcohols with a given haloacid is  $3^\circ > 2^\circ > 1^\circ$ .

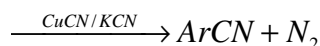
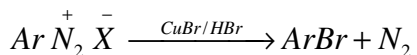
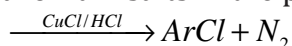
3. Identify the compound Y in the following reaction.





Ans. (i)

**Explanation:** The  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{CN}^-$  nucleophiles can easily be introduced in the benzene ring of diazonium salts in the presence of  $\text{Cu(I)}$  ion.



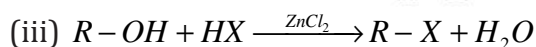
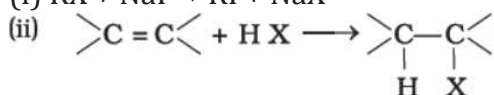
4. Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

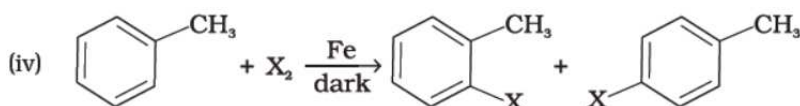
- (i) Electrophilic elimination reaction
- (ii) Electrophilic substitution reaction
- (iii) Free radical addition reaction
- (iv) Nucleophilic substitution reaction

Ans. (ii)

**Explanation:** Aryl Chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron (III) chloride.

5. Which of the following is halogen exchange reaction?





Ans. (i)

**Explanation:** Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with NaI in dry acetone. This reaction is known as Finkelstein reaction.

NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

6. Which reagent will you use for the following reaction?



(i)  $\text{Cl}_2/\text{UV light}$

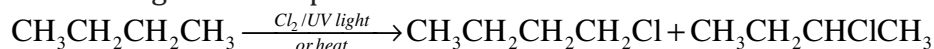
(ii)  $\text{NaCl} + \text{H}_2\text{SO}_4$

(iii)  $\text{Cl}_2$  gas in dark

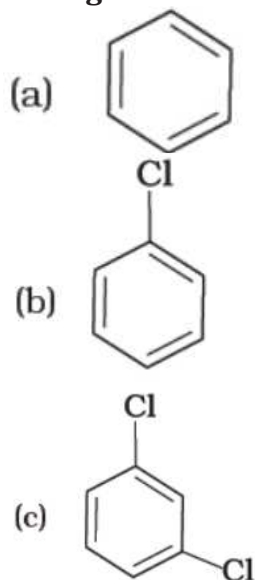
(iv)  $\text{Cl}_2$  gas in the presence of iron in dark

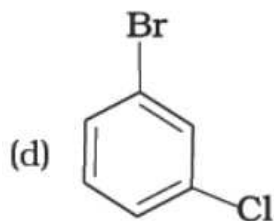
Ans. (i)

**Explanation:** Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to separate as pure compounds. Consequently, the yield of any one free radical chlorination or bromination of alkanes gives a complex



7. Arrange the following compounds in the increasing order of their densities.



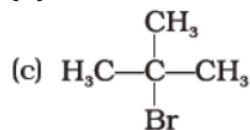
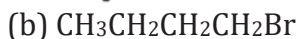
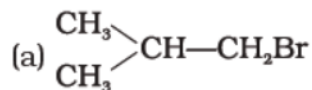


- (i)  $(a) < (b) < (c) < (d)$
- (ii)  $(a) < (c) < (d) < (b)$
- (iii)  $(d) < (c) < (b) < (a)$
- (iv)  $(b) < (d) < (c) < (a)$

Ans. (i)

**Explanation:** Density is related to molecular mass. Higher the mass, higher will be the density of the molecule.

8. Arrange the following compounds in increasing order of their boiling points.

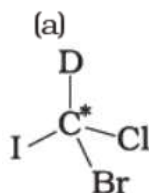
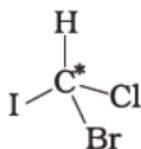


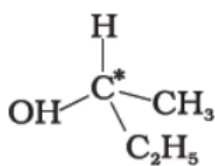
- (i)  $(b) < (a) < (c)$
- (ii)  $(a) < (b) < (c)$
- (iii)  $(c) < (a) < (b)$
- (iv)  $(c) < (b) < (a)$

Ans. (iii)

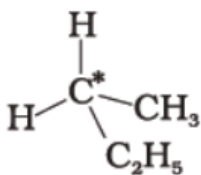
**Explanation:** As the branching increases, surface area of the molecule decreases. Because of these the vander Waals force of attraction between the molecule decreases and consequently boiling point decreases.

9. In which of the following molecules carbon atom marked with asterisk (\*) is asymmetric?





(c)



(d)

(i) (a), (b), (c), (d)

(ii) (a), (b), (c)

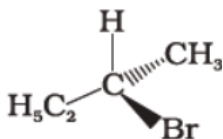
(iii) (b), (c), (d)

(iv) (a), (c), (d)

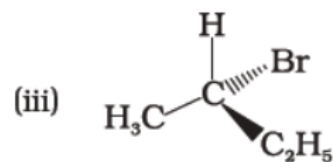
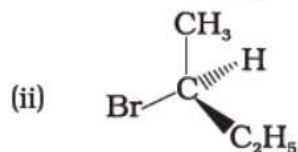
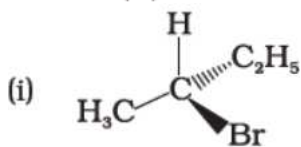
Ans. (ii)

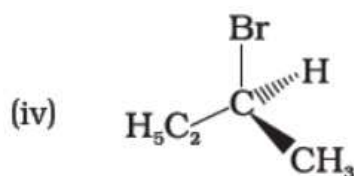
**Explanation:** Carbon atom attached with four different groups is known as asymmetric carbon.

10. Which of the following structures is enantiomeric with the molecule (A) given below :



(A)





Ans. (i)

**Explanation:** The stereoisomers related to each other as non-super imposable mirror images are called enantiomers. Enantiomers possess identical physical properties.

11. Which of the following is an example of *vic*-dihalide?

- (i) Dichloromethane
- (ii) 1,2-dichloroethane
- (iii) Ethylidene chloride
- (iv) Allyl chloride

Ans. (ii)

**Explanation:** In 1,2 dichloroethane, the two chlorine atoms are attached to two adjacent carbon atoms.

12. The position of -Br in the compound in  $\text{CH}_3\text{CH}=\text{CHC}(\text{Br})(\text{CH}_3)_2$  can be classified as \_\_\_\_\_.

- (i) Allyl
- (ii) Aryl
- (iii) Vinyl
- (iv) Secondary

Ans. (i)

**Explanation:** These are the compounds in which the halogen atoms is bonded to an  $\text{sp}^3$ -hybridised carbon atom next to carbon-carbon double bond ( $\text{C}=\text{C}$ ) i.e., to an allylic carbon.

13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of  $\text{AlCl}_3$ . Which of the following species attacks the benzene ring in this reaction?

- (i)  $\text{Cl}^-$
- (ii)  $\text{Cl}^+$
- (iii)  $\text{AlCl}_3$
- (iv)  $[\text{AlCl}_4]^-$

Ans. (ii)

14. Ethylidene chloride is a/an \_\_\_\_\_.

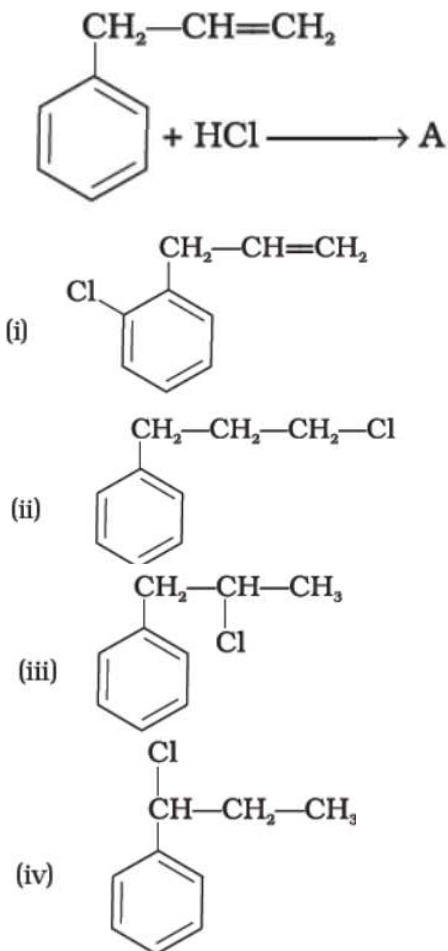
- (i) *vic*-dihalide
- (ii) *gem*-dihalide
- (iii) allylic halide
- (iv) vinylic halide

Ans. (ii)

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**Explanation:** In gem-dihalides, halogen atoms are present on the same carbon atom. They are known as alkylidene halides  $\text{CH}_3\text{—CHCl}_2$ . Both halogen atoms are present on same carbon atom so, it is *gem*-dihalide.

15. What is 'A' in the following reaction?



Ans. (iii)

**Explanation:** In this reaction addition of HCl takes place on doubly bonded carbon atom in accordance with Markovnikov's rule i.e., addition of negative addendum will take place on the carbon which has lesser number of hydrogen.

16. A primary alkyl halide would prefer to undergo \_\_\_\_\_.

- (i)  $\text{S}_{\text{N}}1$  reaction
- (ii)  $\text{S}_{\text{N}}2$  reaction
- (iii)  $\alpha$ -Elimination
- (iv) Racemisation

Ans. (ii)

**Explanation:**  $\text{S}_{\text{N}}2$  type (bimolecular nucleophilic substitution). These reactions proceed in one step and the rate of reaction depends on concentration of alkyl halide as well as nucleophile i.e.  $r = k[\text{RX}][\text{Nu}]$ . It is a second order reaction. During  $\text{S}_{\text{N}}2$  reaction inversion

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in configuration occurs i.e., starting with dextrorotatory halide a laevo product is obtained and vice-versa.

17. Which of the following alkyl halides will undergo  $S_N1$  reaction most readily?

- (i)  $(CH_3)_3C-F$
- (ii)  $(CH_3)_3C-Cl$
- (iii)  $(CH_3)_3C-Br$
- (iv)  $(CH_3)_3C-I$

Ans. (iv)

**Explanation-**  $S_N1$  type (unimolecular nucleophilic substitution). These reactions proceed in two steps. The rate of reaction is dependent on step 1 i.e., only on the concentration of alkyl halide  $r = k[RX]$ . It is a first order reaction.

R-----X bond length in case of iodine is highest and that is why lowest bond dissociation enthalpy. Therefore,  $I^-$  is known as best leaving group.

18. Which is the correct IUPAC name for  $CH_3 - \underset{\substack{| \\ C_2H_5}}{CH} - CH_2Br$ ?

- (i) 1-Bromo-2-ethylpropane
- (ii) 1-Bromo-2-ethyl-2-methylethane
- (iii) 1-Bromo-2-methylbutane
- (iv) 2-Methyl-1-bromobutane

Ans. (iii)

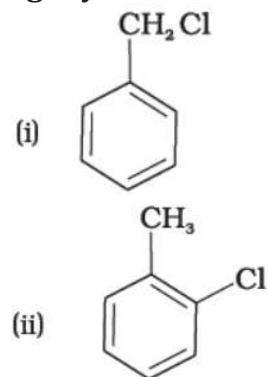
**Explanation:** Numbering will start from the carbon attached with halogen group and the longest chain will be selected.

19. What should be the correct IUPAC name for diethylbromomethane?

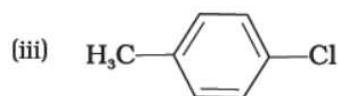
- (i) 1-Bromo-1,1-diethylmethane
- (ii) 3-Bromopentane
- (iii) 1-Bromo-1-ethylpropane
- (iv) 1-Bromopentane

Ans. (i)

20. The reaction of toluene with chlorine in the presence of iron and in the absence of light yields \_\_\_\_\_.



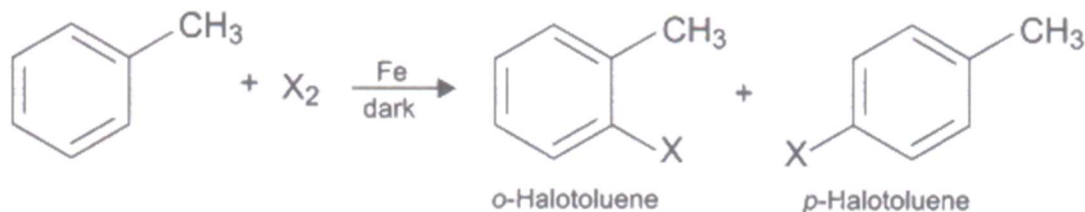




(iv) Mixture of (ii) and (iii)

Ans. (iv)

**Explanation:**



21. Chloromethane on treatment with excess of ammonia yields mainly

(i) N, N-Dimethylmethanamine ( $\text{CH}_3\text{—N} \begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}$ )

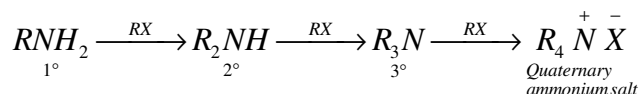
(ii) N-methylmethanamine ( $\text{CH}_3\text{—NH—CH}_3$ )

(iii) Methanamine ( $\text{CH}_3\text{NH}_2$ )

(iv) Mixture containing all these in equal proportion

Ans. (iii)

**Explanation:** Though primary amine is produced as the major product, this process produces a mixture of primary, secondary and tertiary amines, and also a quaternary ammonium salt.



22. Molecules whose mirror image is non-superimposable over them are known as chiral. Which of the following molecules is chiral in nature?

(i) 2-Bromobutane

(ii) 1-Bromobutane

(iii) 2-Bromopropane

(iv) 2-Bromopropan-2-ol

Ans. (i)

**Explanation:** The objects which are nonsuperimposable on their mirror images are called enantiomers. It occurs on that molecule which contains asymmetric carbon or chiral i.e., a carbon atom attached with four different group.

23. Reaction of  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$  with aqueous sodium hydroxide follows \_\_\_\_\_.

(i)  $\text{S}_{\text{N}}1$  mechanism

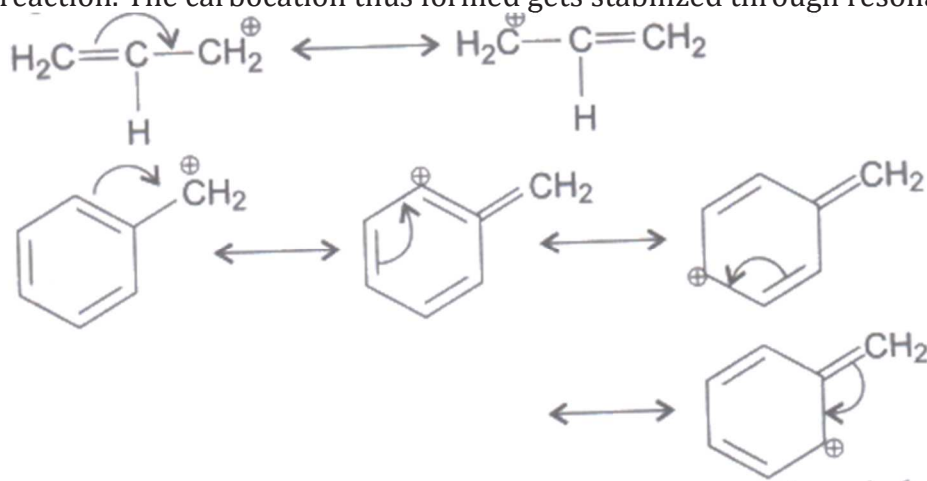
(ii)  $\text{S}_{\text{N}}2$  mechanism

(iii) Any of the above two depending upon the temperature of reaction

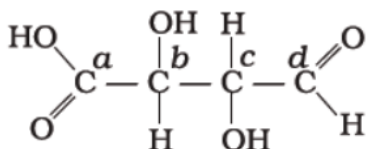
(iv) Saytzeff rule

Ans. (i)

**Explanation:** Greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3° alkyl halides undergo S<sub>N</sub>1 reaction very fast because of the high stability of 3° carbocations. For the same reasons, allylic and benzylic halides show high reactivity towards the S<sub>N</sub>1 reaction. The carbocation thus formed gets stabilized through resonance as shown below:



24. Which of the carbon atoms present in the molecule given below are asymmetric?

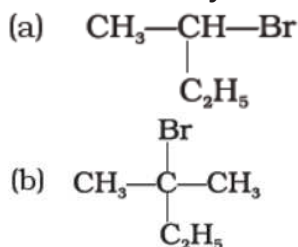


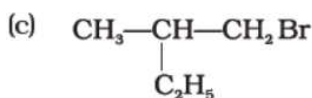
- (i) a, b, c, d
- (ii) b, c
- (iii) a, d
- (iv) a, b, c

Ans. (iii)

**Explanation:** If all the substituents attached to that carbon are different, such a carbon is called asymmetric carbon or stereocentre. The resulting molecule would lack symmetry and is referred to as asymmetric molecule. The asymmetry of the molecule is responsible for the optical activity in such organic compounds.

25. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH<sup>-</sup> ion?





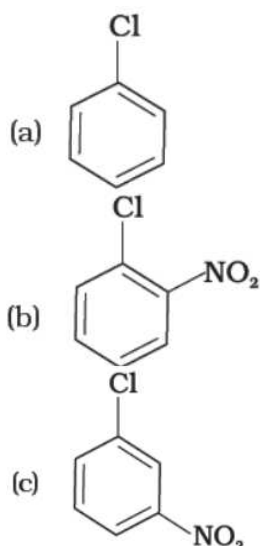
- (i) (a)  
 (ii) (a), (b), (c)  
 (iii) (b), (c)  
 (iv) (a), (c)

Ans. (i)

**Explanation:** A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture or racemic modification. A racemic mixture is represented by prefixing dl or case of optically active alkyl halides,  $\text{S}_{\text{N}}1$  reactions are accompanied by racemisation.

**Note:** In the questions 26 to 29 arrange the compounds in increasing order of rate of reaction towards nucleophilic substitution.

26.



- (i) (a) < (b) < (c)  
 (ii) (c) < (b) < (a)  
 (iii) (a) < (c) < (b)  
 (iv) (c) < (a) < (b)

Ans. (iii)

**Explanation:** Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to the following reasons:

(i) *Resonance effect:* In haloarenes, the electron pairs on halogen atom are in conjugation with electrons of the ring C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

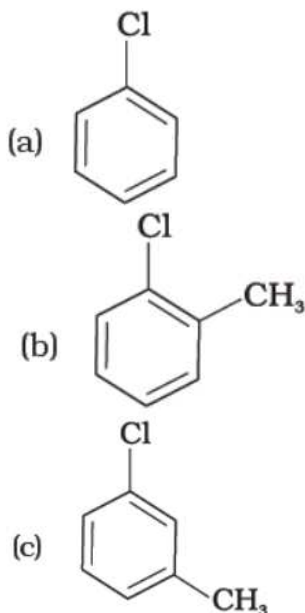
(ii) *Difference in hybridisation of carbon atom in C—X bond:* In haloalkane, the carbon atom attached to halogen is  $\text{sp}^3$  hybridised while in case of haloarene, the carbon atom

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attached to halogen is  $sp^2$ -hybridised. The  $sp^2$  hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than  $sp^3$ -hybridised carbon in haloalkane with less s-character.

(iii) *Instability of phenyl cation*: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilized by resonance and therefore,  $S_N1$  mechanism is ruled out. The presence of an electron withdrawing group ( $-NO_2$ ) at *ortho*- and *para*-positions increases the reactivity of haloarenes.

27.

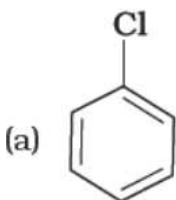


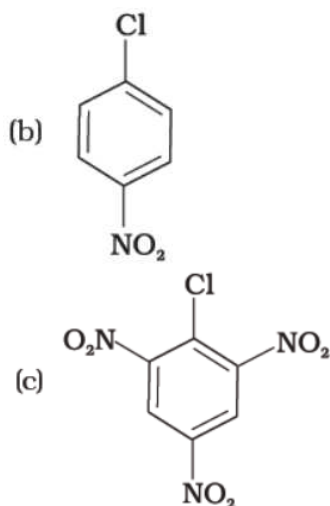
- (i) (a) < (b) < (c)  
(ii) (a) < (c) < (b)  
(iii) (c) < (b) < (a)  
(iv) (b) < (c) < (a)

Ans. (iv)

**Explanation:** The presence of electron releasing group at *ortho*- and *para*-positions decreases the reactivity of haloarenes. Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

28.



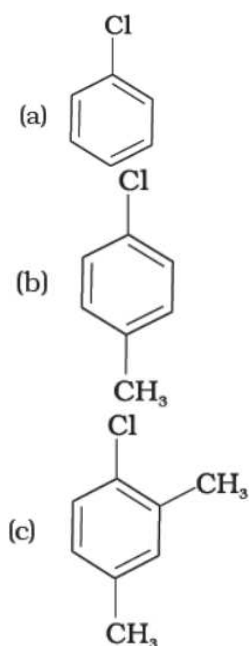


- (i) (c) < (b) < (a)  
 (ii) (b) < (c) < (a)  
 (iii) (a) < (c) < (b)  
 (iv) (a) < (b) < (c)

Ans. (iv)

**Explanation:** The presence of an electron withdrawing group ( $-\text{NO}_2$ ) at ortho- and para-positions increases the reactivity of haloarenes. The presence of nitro group at *ortho*- and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho*- and *para*- positions with respect to the halogen substituent is stabilised by  $-\text{NO}_2$  group.

29.



- (i) (a) < (b) < (c)

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(ii) (b) < (a) < (c)

(iii) (c) < (b) < (a)

(iv) (a) < (c) < (b)

**Ans. (iii)**

**Explanation:** The presence of electron releasing group at ortho-and para- positions decreases the reactivity of haloarenes. Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes. More the electron releasing group is attached lesser, will be the rate of reaction.

**30. Which is the correct increasing order of boiling points of the following compounds?**

1-Iodobutane, 1-Bromobutane, 1-Chlorobutane, Butane

(i) Butane < 1-Chlorobutane < 1-Bromobutane < 1-Iodobutane

(ii) 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane < Butane

(iii) Butane < 1-Iodobutane < 1-Bromobutane < 1-Chlorobutane

(iv) Butane < 1-Chlorobutane < 1-Iodobutane < 1-Bromobutane

**Ans. (i)**

**Explanation:** For the same alkyl group, the boiling points of alkyl halides decrease in the order: RI > RBr > RCl > RF. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

**31. Which is the correct increasing order of boiling points of the following compounds?**

1-Bromoethane, 1-Bromopropane, 1-Bromobutane, Bromobenzene

(i) Bromobenzene < 1-Bromobutane < 1-Bromopropane < 1-Bromoethane

(ii) Bromobenzene < 1-Bromoethane < 1-Bromopropane < 1-Bromobutane

(iii) 1-Bromopropane < 1-Bromobutane < 1-Bromoethane < Bromobenzene

(iv) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

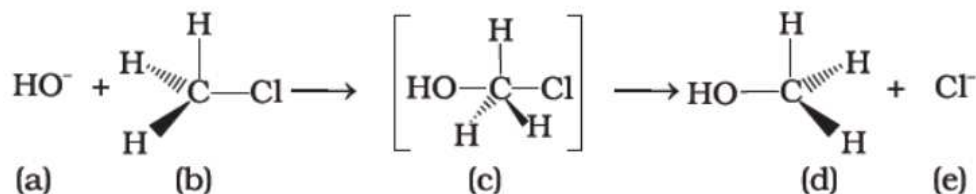
**Ans. (iv)**

**Explanation:** The attractions get stronger as the molecules get bigger in size and have more electrons.

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**Haloalkanes and Haloarenes**  
**Multiple Choice Questions (Type-II)**

**Note:** In the following questions two or more options may be correct. Consider the following reaction and answer the questions no. 32–34.



**32. Which of the statements are correct about above reaction?**

- (i) (a) and (e) both are nucleophiles.
- (ii) In (c) carbon atom is  $sp^3$  hybridised.
- (iii) In (c) carbon atom is  $sp^2$  hybridised.
- (iv) (a) and (e) both are electrophiles.

**Ans. (i) and (iii)**

**Explanation:** It depicts a bimolecular nucleophilic displacement ( $S_N2$ ) reaction; the incoming nucleophile interacts with alkyl halide causing the carbon halide bond to break while forming a new carbon-OH bond. These two processes take place simultaneously in a single step and no intermediate is formed. As the reaction progresses and the bond between the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. In part (c) it is the transition state where carbon atom of the substrate molecule is  $sp^2$  hybridised.

**33. Which of the following statements are correct about this reaction?**

- (i) The given reaction follows  $S_N2$  mechanism.
- (ii) (b) and (d) have opposite configuration.
- (iii) (b) and (d) have same configuration.
- (iv) The given reaction follows  $S_N1$  mechanism.

**Ans. (i) and (ii)**

**Explanation:** As the  $S_N2$  reaction progresses and the bond between the nucleophile and the carbon atom starts forming, the bond between carbon atom and leaving group weakens. As this happens, the configuration of carbon atom under attack inverts in much the same way as an umbrella is turned inside out when caught in a strong wind, while the leaving group is pushed away. This process is called as inversion of configuration.

**34. Which of the following statements are correct about the reaction intermediate?**

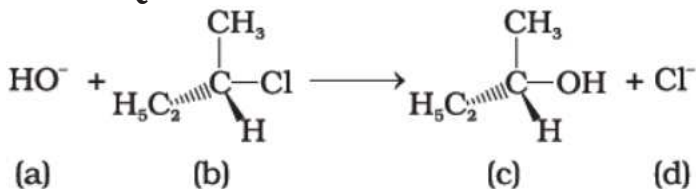
- (i) Intermediate (c) is unstable because in this carbon is attached to 5 atoms.
- (ii) Intermediate (c) is unstable because carbon atom is  $sp^2$  hybridised.
- (iii) Intermediate (c) is stable because carbon atom is  $sp^2$  hybridised.
- (iv) Intermediate (c) is less stable than the reactant (b).

**Ans. (i) and (iv)**

**Explanation:** In the transition state, the carbon atom is simultaneously bonded to incoming nucleophile and the outgoing leaving group and such structure are unstable and

cannot be isolated. This is because the carbon atom in the transition state is simultaneously bonded to five atoms and therefore is unstable.

**Answer Q. No. 35 and 36 on the basis of the following reaction.**



**35. Which of the following statements are correct about the mechanism of this reaction?**

- (i) A carbocation will be formed as an intermediate in the reaction.
- (ii)  $\text{OH}^-$  will attack the substrate (b) from one side and  $\text{Cl}^-$  will leave it simultaneously from other side.
- (iii) An unstable intermediate will be formed in which  $\text{OH}^-$  and  $\text{Cl}^-$  will be attached by weak bonds.
- (iv) Reaction proceeds through  $\text{S}_{\text{N}}1$  mechanism.

**Ans. (i) and (iv)**

**Explanation:** It occurs in two steps. In step I, the polarised C—Cl bond undergoes slow cleavage to produce a carbocation and a chloride ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction. It must be noted that the  $2^\circ$  halides may proceed either through  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  type. The preservation of integrity of the spatial arrangement of bonds to an asymmetric centre during a chemical reaction depict that the reaction is followed by  $\text{S}_{\text{N}}1$  mechanism.

**36. Which of the following statements are correct about the kinetics of this reaction?**

- (i) The rate of reaction depends on the concentration of only (b).
- (ii) The rate of reaction depends on concentration of both (a) and (b).
- (iii) Molecularity of reaction is one.
- (iv) Molecularity of reaction is two.

**Ans. (i) and (iii)**

**Explanation:**  $\text{S}_{\text{N}}1$  occurs in two steps. I, the polarized C—Cl bond undergoes slow cleavage to produce a carbocation and a chloride ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction. Step I is the slowest and reversible. It involves the C—Cl bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.

**37. Haloalkanes contain halogen atom (s) attached to the  $\text{sp}^3$  hybridised carbon atom of an alkyl group. Identify haloalkane from the following compounds.**

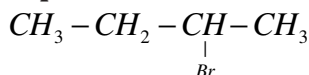
- (i) 2-Bromopentane
- (ii) Vinyl chloride (chloroethene)
- (iii) 2-chloroacetophenone



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(iv) Trichloromethane  
**Ans. (i) and (iv)**

**Explanation:**



Here the -bromo group is attached to a carbon which is  $\text{sp}^3$  hybridised. Similarly, in trichloromethane also the carbon atom is  $\text{sp}^3$  hybridised which is directly attached to the chloro group. In vinyl chloride and 2-chloroacetophenone, halo group is attached to  $\text{sp}^2$  carbon.

**38. Ethylene chloride and ethylidene chloride are isomers. Identify the correct statements.**

- (i) Both the compounds form same product on treatment with alcoholic KOH.
- (ii) Both the compounds form same product on treatment with aq. NaOH.
- (iii) Both the compounds form same product on reduction.
- (iv) Both the compounds are optically active.

**Ans. (i) and (iii)**

**Explanation:** Both will give ethyne on treatment with alc. KOH and both will give ethane on reduction.

**39. Which of the following compounds are *gem*-dihalides?**

- (i) Ethylidene chloride
- (ii) Ethylene dichloride
- (iii) Methylene chloride
- (iv) Benzyl chloride

**Ans. (i) and (iii)**

**Explanation:**  $\text{H}_3\text{C} - \text{CHCl}_2$  and methylene chloride  $\text{CH}_2\text{Cl}_2$ .  
*Ethylidene chloride*  
(*gem*-dihalide)

**40. Which of the following are secondary bromides?**

- (i)  $(\text{CH}_3)_2\text{CHBr}$
- (ii)  $(\text{CH}_3)_3\text{CCH}_2\text{Br}$
- (iii)  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$
- (iv)  $(\text{CH}_3)_2\text{CBrCH}_2\text{CH}_3$

**Ans. (i) and (iii)**

**Explanation:**  $(\text{CH}_3)_2\text{CHBr}$  – Bromide group is attached to sec-carbon or  $2^\circ\text{C}$ .  
 $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$  – here also, the Bromide group is attached to sec-carbon or  $2^\circ\text{C}$ .

**41. Which of the following compounds can be classified as aryl halides?**

- (i)  $p\text{-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$
- (ii)  $p\text{-CH}_3\text{CHCl}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_3$
- (iii)  $o\text{-BrH}_2\text{C}-\text{C}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$
- (iv)  $\text{C}_6\text{H}_5\text{-Cl}$

**Ans. (i) and (iv)**

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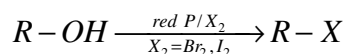
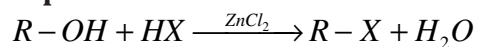
**Explanation:** *Aryl halides:* These are the compounds in which the halogen atom is bonded to the  $sp^2$ - hybridised carbon atom of an aromatic ring.

**42. Alkyl halides are prepared from alcohols by treating with**

- (i)  $HCl + ZnCl_2$
- (ii) Red P +  $Br_2$
- (iii)  $H_2SO_4 + KI$
- (iv) All the above

**Ans. (i) and (ii)**

**Explanation:**

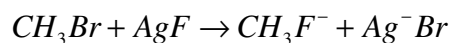


**43. Alkyl fluorides are synthesised by heating an alkyl chloride/bromide in presence of \_\_\_\_\_ or \_\_\_\_\_.**

- (i)  $CaF_2$
- (ii)  $CoF_2$
- (iii)  $Hg_2F_2$
- (iv)  $NaF$

**Ans. (ii) and (iii)**

**Explanation:** The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/ bromide in the presence of a metallic fluoride such as  $AgF$ ,  $Hg_2F_2$ ,  $CoF_2$  or  $SbF_3$ . The reaction is termed as Swarts reaction.



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**Haloalkanes and Haloarenes**  
**Matching Type**

**Note:** Match the items given in Column I and Column II in the following questions.

**79. Match the compounds given in Column I with the effects given in Column II.**

Column I	Column II
(i) Chloramphenicol	(a) Malaria
(ii) Thyroxine	(b) Anaesthetic
(iii) chloroquine	(c) Typhoid fever
(iv) Chloroform	(d) Goiter
	(e) Blood substituent

**Ans.** (i)- (c)  
(ii)- (d)  
(iii)- (a)  
(iv)- (b)

**Explanation:**

Column I	Column II
(i) Chloramphenicol	(c) Typhoid fever (chloramphenicol is a broad-spectrum antibiotic used in the treatment of typhoid fever)
(ii) Thyroxine	(d) Goiter (Thyroxine is a hormone secreted by thyroid gland. Patient with hyperthyroidism have an enlarged thyroid gland i.e., goiter)
(iii) Chloroquine	(a) Malaria (chloroquine prevents the development of malaria in blood)
(iv) Chloroform	(b) Anaesthetic (Chloroform is a colourless volatile liquid. Its vapours decreases the activity of central nervous system and is used as an anaesthetic.

**80. Match the items of Column I and Column II.**


Column I	Column II
(i) $S_N1$ reaction	(a) vic- dibromides
(ii) Chemicals in fire extinguisher	(b) gem- dihalides
(iii) Bromination of alkenes	(c) Racemisation
(iv) Alkylidene halides	(d) Saytzeff rule
(v) Elimination of HX from alkyl halide	(e) Chlorobromocarbons

**Ans.** (i)-(c)  
(ii)-(e)  
(iii)-(a)  
(iv)- (b)  
(v)- (d)

**Explanation:**

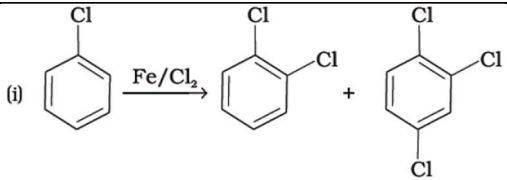
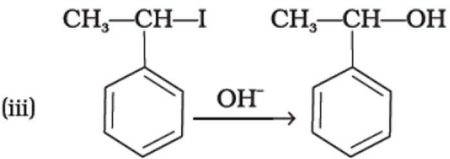
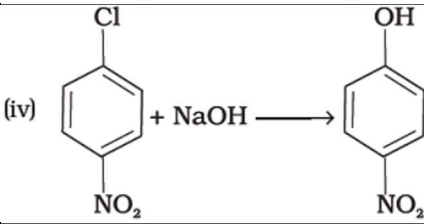
Column I	Column II
(i) $S_N1$ reaction	(c) Racemisation ( $S_N1$ reactions results in the formation of racemic mixture. A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture of racemic modification)
(ii) Chemicals in the fire extinguisher	(e) Chlorobromocarbons (used as fire extinguisher)
(iii) Bromination of alkenes	(a) <i>vic</i> -dibromides (These are the compounds in which the halogen atom is bonded to an $sp^2$ hybridised carbon atom of a carbon-carbon double bond)
(iv) Alkylidene halides	(b) <i>gem</i> -dihalides (halogen atoms are present on the same carbon atom)
(v) Elimination of HX from alkyl halide	(d) Saytzeff rule (in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.)

81. Match the structures of compounds given in Column I with the classes of compounds given in Column II.

Column I	Column II
(i) $\text{CH}_3-\underset{\text{X}}{\text{CH}}-\text{CH}_3$	(a) Aryl halide
(ii) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$	(b) Alkyl halide
(iii) 	(c) Vinyl halide
(iv) $\text{CH}_2=\text{CH}-\text{X}$	(d) Allyl halide

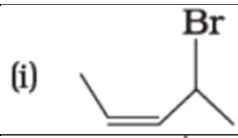
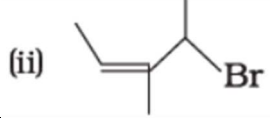
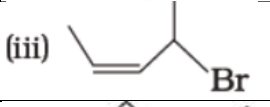
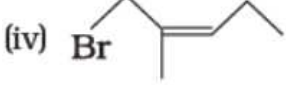
- Ans. (i) (b)  
(ii) (d)  
(iii) (a)  
(iv) (c)

82. Match the reactions given in Column I with the types of reactions given in Column II.

Column I	Column II
(i) 	(a) Nucleophilic aromatic substitution
(ii) $\text{CH}_3\text{—CH=CH}_2 + \text{HBr} \longrightarrow \text{CH}_3\text{—}\underset{\text{Br}}{\text{CH}}\text{—CH}_3$	(b) Electrophilic aromatic substitution
(iii) 	(c) Saytzeff elimination
(iv) 	(d) Electrophilic addition
(v) $\text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}}\text{CH}_3 \xrightarrow{\text{alc.KOH}} \text{CH}_3\text{CH=CHCH}_3$	(e) Nucleophilic substitution ( $\text{S}_{\text{N}}1$ )

Ans. (i)-(b)  
(ii)-(d)  
(iii)-(e)  
(iv)-(a)  
(v)- (c)

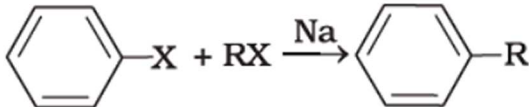
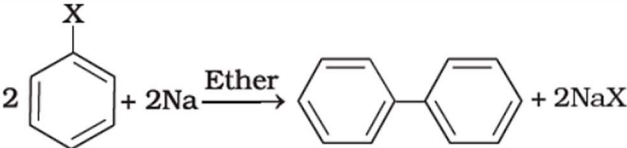
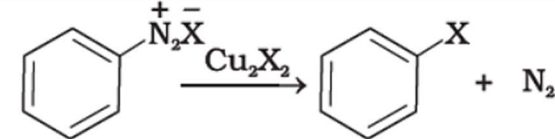
83. Match the structures given in Column I with the names in Column II.

Column I	Column II
(i) 	(a) 4-Bromopent-2-ene
(ii) 	(b) 4-Bromo-3-methylpent-2-ene
(iii) 	(c) 1-Bromo-2-methylbut-2-ene
(iv) 	(d) 1-Bromo-2-methylpent-2-ene

Ans. (i)- (a)

- (ii)-(c)  
 (iii)-(b)  
 (iv)-(d)

84. Match the reactions given in Column I with the names given in Column II.

Column I	Column II
(i) 	(a) Fitting reaction
(ii) 	(b) Wurtz- Fittig reaction
(iii) 	(c) Finkelstein reaction
(iv) $C_2H_5Cl + NaI \xrightarrow{\text{dry acetone}} C_2H_5I + NaCl$	(d) Sandmeyer reaction

- Ans. (i)-(b)  
 (ii)-(a)  
 (iii)-(d)  
 (iv)-(c)

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## Haloalkanes and Haloarenes

### Assertion and Reason Type

**Note:** In the following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

- (i) Assertion and reason both are correct and reason is correct explanation of assertion.
- (ii) Assertion and reason both are wrong statements.
- (iii) Assertion is correct but reason is wrong statement.
- (iv) Assertion is wrong but reason is correct statement.
- (v) Assertion and reason both are correct statements but reason is not correct explanation of assertion.

**85. Assertion:** Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

**Reason:** Phosphorus chlorides give pure alkyl halides.

**Ans.** (ii)

**Explanation:** Thionyl chloride is preferred because the other two products are escapable gases. Hence, the reaction gives pure alkyl halides.

**86. Assertion:** The boiling points of alkyl halides decrease in the order:

$RI > RBr > RCl > RF$

**Reason:** The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.

**Ans.** (v)

**Explanation:** For the same alkyl group, the boiling points of alkyl halides decrease in the order:  $RI > RBr > RCl > RF$ . This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

**87. Assertion:** KCN reacts with methyl chloride to give methyl isocyanide

**Reason:**  $CN^-$  is an ambident nucleophile.

**Ans.** (iv)

**Explanation:** KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond.

**88. Assertion:** *tert*-Butyl bromide undergoes Wurtz reaction to give 2, 2, 3, 3-tetramethylbutane.

**Reason:** In Wurtz reaction, alkyl halides react with sodium in dry ether to give hydrocarbon containing double the number of carbon atoms present in the halide.

**Ans.** (i)

**Explanation: Wurtz reaction:** A reaction in which alkyl halides react with sodium in dry ether to give a hydrocarbon containing double the number of carbon atoms present in the halide.

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**89. Assertion:** Presence of a nitro group at *ortho* or *para* position increases the reactivity of haloarenes towards nucleophilic substitution.

**Reason:** Nitro group, being an electron withdrawing group decreases the electron density over the benzene ring.

**Ans. (i)**

**Explanation:** The presence of nitro group at *ortho*-and *para*-positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho*- and *para*- positions with respect to the halogen substituent is stabilised by -NO<sub>2</sub> group.

**90. Assertion:** In monohaloarenes, further electrophilic substitution occurs at *ortho* and *para* positions.

**Reason:** Halogen atom is a ring deactivator.

**Ans. (v)**

**Explanation:** Halogen atom besides being slightly deactivating is o, p-directing; therefore, further substitution occurs at *ortho*-and *para*-positions with respect to the halogen atom. The o, p-directing influence of halogen atom can be easily understood if we consider the resonating structures.

**91. Assertion:** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidising agent.

**Reason:** Oxidising agent oxidises I<sub>2</sub> into HI.

**Ans. (iii)**

**Explanation:** Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO<sub>3</sub>, HIO<sub>4</sub>) to oxidise the HI formed during iodination.

**92. Assertion:** It is difficult to replace chlorine by -OH in chlorobenzene in comparison to that in chloroethane.

**Reason:** Chlorine-carbon (C—Cl) bond in chlorobenzene has a partial double bond character due to resonance.

**Ans. (i)**

**Explanation:** It is difficult to replace chlorine by—OH in chlorobenzene in comparison to that in chloroethane.

**93. Assertion:** Hydrolysis of (–)-2-bromooctane proceeds with inversion of configuration.

**Reason:** This reaction proceeds through the formation of a carbocation.

**Ans. (iii)**

**Explanation:** Hydrolysis of (—)-2-bromooctane proceeds with inversion of configuration because the reaction proceeds through S<sub>N</sub>2 mechanism.

**94. Assertion:** Nitration of chlorobenzene leads to the formation of *m*-nitrochlorobenzene

**Reason:** —NO<sub>2</sub> group is a *m*-directing group.

**Ans. (iv)**



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**Explanation:** Halogen atom besides being slightly deactivating is *o*, *p*-directing; therefore, further substitution occurs at *ortho*- and *para*-positions with respect to the halogen atom.

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## Haloalkanes and Haloarenes

### Short Answer Type

44. Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides requires presence of an oxidising agent?

Ans. Iodination reactions are reversible in nature. To carry out the reaction in the forward direction, HI formed during iodination is removed by oxidation.  $\text{HIO}_4$  is used as an oxidising agent.

45. Out of *o*- and *p*-dibromobenzene which one has higher melting point and why?

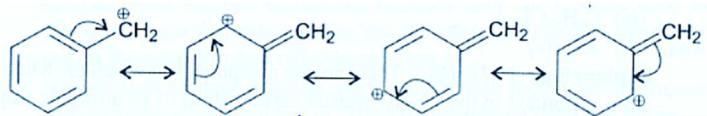
Ans. *p*-Dibromobenzene has higher melting point than its *o*-isomer. It is due to symmetry of *p*-isomer which fits in crystal lattice better than the *o*-isomer.

46. Which of the compounds will react faster in  $\text{S}_{\text{N}}1$  reaction with the  $\text{OH}^-$  ion?

$\text{CH}_3\text{—CH}_2\text{—Cl}$  or  $\text{C}_6\text{H}_5\text{—CH}_2\text{—Cl}$

Ans.  $\text{S}_{\text{N}}1$  reaction depends on the stability of the carbocation since the benzylic cation is more stable than alkyl carbocation.

Benzylic carbocation can be stabilized by resonance. Thus, the rate will be faster in  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ .

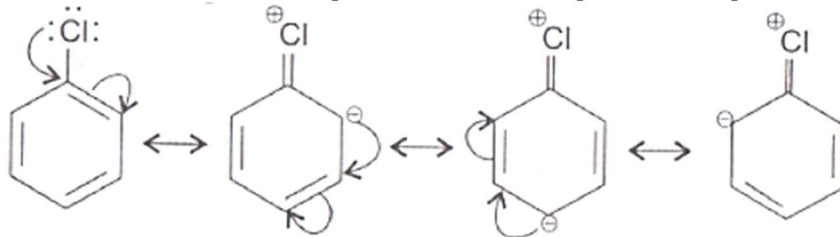


47. Why iodoform has appreciable antiseptic property?

Ans. Due to liberation of free iodine.

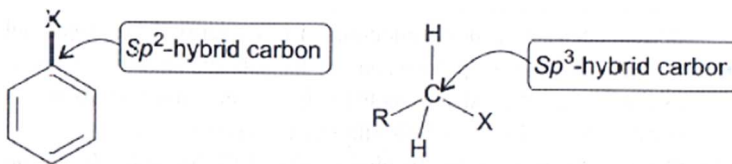
48. Haloarenes are less reactive than haloalkanes and haloalkenes. Explain.

Ans. Haloarenes are less reactive than haloalkanes and haloalkenes due to following reasons:  
(i) *Resonance effect*: In haloarenes, the electron pairs on halogen atom are in conjugation with electrons of the ring and the following resonating structures are possible.



$\text{C—Cl}$  bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) *Different in hybridisation of carbon atom in  $\text{C—X}$  bond*: In haloalkane, the carbon atom attached to halogen is  $\text{sp}^3$  hybridised while in case of haloarene, the carbon atom attached to halogen is  $\text{sp}^2$  hybridised.



The  $sp^2$  hybridised carbon with a greater s-character is more electronegative and can hold the electron pair C-X bond more tightly than  $sp^3$  hybridised carbon in haloalkane with less s character. Thus, C-Cl bond-length in haloalkane is 177 pm while in haloarene is 169 pm. Since, it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reaction than haloalkanes towards nucleophilic substitution reaction.

(iii) *Instability of phenyl cation*: Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich arenes.

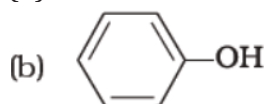
**49. Discuss the role of Lewis acids in the preparation of aryl bromides and chlorides in the dark.**

**Ans.** Role of Lewis acid in this reaction is to generate electrophile. Arenes are characterised by electrophilic substitution reactions proceeded via the following three step:

- Generation of the electrophile
- Formation of carbocation intermediate.
- Removal of proton from the carbocation intermediate.

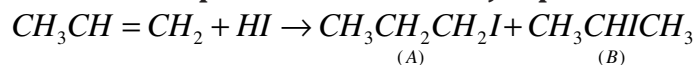
**50. Which of the following compounds (a) and (b) will not react with a mixture of NaBr and  $H_2SO_4$ . Explain why?**

(a)  $CH_3CH_2CH_2OH$



**Ans.** Phenol will not react with  $NaBr + H_2SO_4$   
C—O bond in phenols has partial double bond character due to this it is difficult to cleave.

**51. Which of the products will be major product in the reaction given below? Explain.**



**Ans.** 'B' will be the major product as the reaction is followed by the formation of carbocation; and secondary carbocation is more stable.

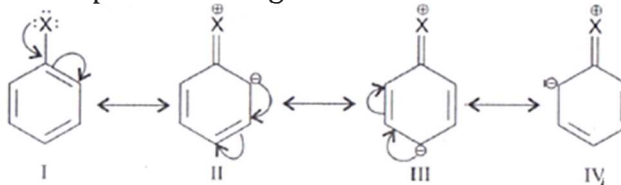
**52. Why is the solubility of haloalkanes in water very low?**

**Ans.** The haloalkanes are only very slightly soluble in water. In order for a haloalkane to dissolve in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low.

53. Draw other resonance structures related to the following structure and find out whether the functional group present in the molecule is ortho, para directing or meta directing.



Ans. Ortho-para directing due to increase in the electron density at ortho and para positions.



54. Classify the following compounds as primary, secondary and tertiary halides.

(i) 1-Bromobut-2-ene

Ans.  $\text{CH}_3\text{—CH=CH—CH}_2\text{—Br}$  (primary halide)

(ii) 4-Bromopent-2-ene

Ans.  $\text{CH}_3\text{—CH=CH—CHBr—CH}_3$  (secondary halide)

(iii) 2-Bromo-2-methylpropane

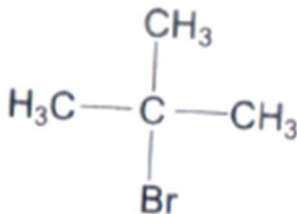
Ans.  $(\text{CH}_3)_3\text{CBr}$  (tertiary halide)

55. Compound 'A' with molecular formula  $\text{C}_4\text{H}_9\text{Br}$  is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.

(i) Write down the structural formula of both compounds 'A' and 'B'.

(ii) Out of these two compounds, which one will be converted to the product with inverted configuration.

Ans. A is tert-butyl Bromide



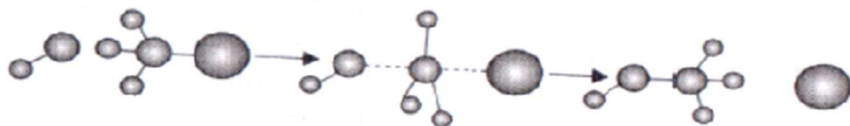
Since the rate of reaction depends on the concentration of A only, it is followed by  $\text{S}_{\text{N}}1$  mechanism.

'B' is sec-butyl bromide-



As the compound, B is optically active, it must be 2-bromobutane.

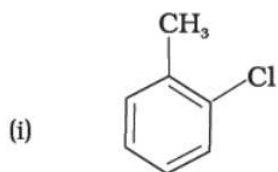
As the rate of reaction depends on the concentration



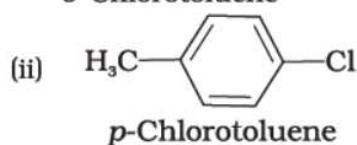
$\text{S}_{\text{N}}2$  results in inversion of configuration.

56. Write the structures and names of the compounds formed when compound 'A' with molecular formula,  $\text{C}_7\text{H}_8$  is treated with  $\text{Cl}_2$  in the presence of  $\text{FeCl}_3$ .

Ans.

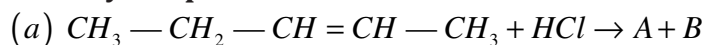


*o*-Chlorotoluene

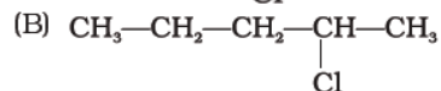
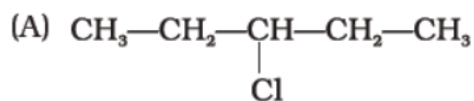


*p*-Chlorotoluene

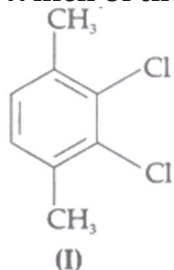
57. Identify the products A and B formed in the following reaction:

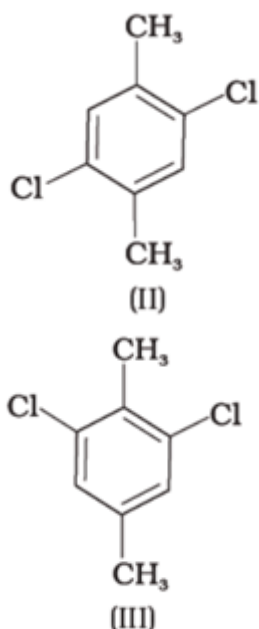


Ans.



58. Which of the following compounds will have the highest melting point and why?



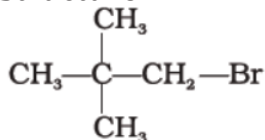


**Ans.** Compound II will have higher melting point since both  $\text{CH}_3$  and  $\text{Cl}$  are at para position. The *para*-isomers are high melting as compared to their *ortho* and *meta*-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to *ortho*- and *meta*-isomers.

**59. Write down the structure and IUPAC name for neo-pentylbromide.**

**Ans. IUPAC Name:** 1-Bromo-2,2 dimethylpropane

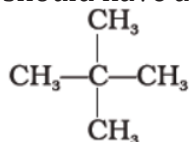
**Structure:**



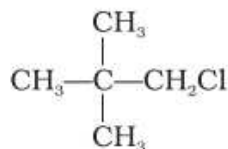
**60. A hydrocarbon of molecular mass  $72 \text{ g mol}^{-1}$  gives a single monochloro derivative and two dichloro derivatives on photo chlorination. Give the structure of the hydrocarbon.**

**Ans.**  $\text{C}_5\text{H}_{12}$ , pentane has molecular mass  $72 \text{ g mol}^{-1}$ , i.e. the isomer of pentane which yields single monochloro derivative should have all the 12 hydrogens equivalent.

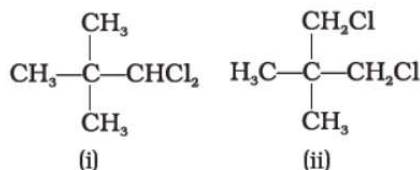
The hydrocarbon is



Monochloro derivative

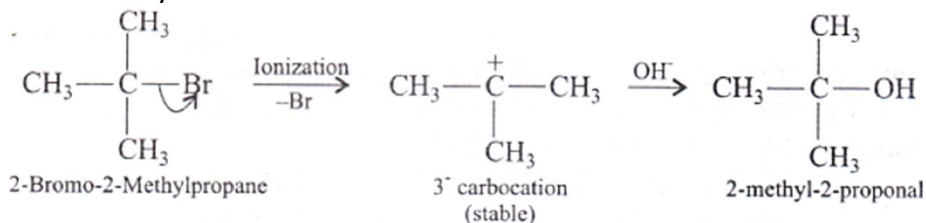


Dichloro derivatives



61. Name the alkene which will yield 1-chloro-1-methylcyclohexane by its reaction with HCl. Write the reactions involved.

Ans. It can be any one in between; 2-bromo-2-methylpropane (Hi) is a  $3^\circ$  alkyl bromide. It readily undergoes ionization for a stable  $3^\circ$  carbocation. Therefore, it reacts with aq. KOH most readily.



62. Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.

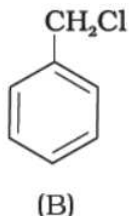
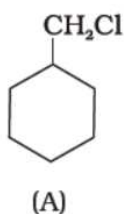
- (i) 1-Bromobutane
- (ii) 2-Bromobutane
- (iii) 2-Bromo-2-methylpropane
- (iv) 2-Chlorobutane

Ans. (iii) Reason: The tertiary carbocation formed in the reaction is stable.

63. Why can aryl halides not be prepared by reaction of phenol with HCl in the presence of  $\text{ZnCl}_2$ ?

Ans. Method is not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has partial double bond character and is difficult to break being stronger than a single bond.

64. Which of the following compounds would undergo  $\text{S}_\text{N}1$  reaction faster and why?



Ans. 'B' compound will undergo  $\text{S}_\text{N}1$  reaction faster because the carbocation formed gets stabilised through resonance.

Resonating structure of Benzyl is shown in ans: no. 46.

**65. Allyl chloride is hydrolysed more readily than *n*-propyl chloride. Why?**

**Ans.** Allyl chloride will be hydrolyzed more readily because the reaction proceeds through  $S_N1$  mechanism and carbocation formed in case of allylic chloride is stabilized by resonance whereas; carbocation formed by propyl chloride is not stabilized by resonance.

**66. Why is it necessary to avoid even traces of moisture during the use of a Grignard reagent?**

**Ans.** Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols and amines are sufficiently acidic to convert them to corresponding hydrocarbons.

It is therefore necessary to avoid even traces of moisture from a Grignard reagent.

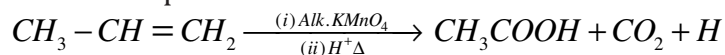
**67. How do polar solvents help in the first step in  $S_N1$  mechanism?**

**Ans.**  $S_N1$  occurs in two steps. In step I, the polarised C—Br bond undergoes slow cleavage to produce a carbocation and a bromide ion. The carbocation thus formed is then attacked by nucleophile in step II to complete the substitution reaction. Step I is the slowest and reversible. It involves the C—Br bond breaking for which the energy is obtained through solvation of halide ion with the proton of protic solvent.

**68. Write a test to detect the presence of double bond in a molecule.**

**Ans.** Presence of multiple bond in a molecule can be tested by following methods:

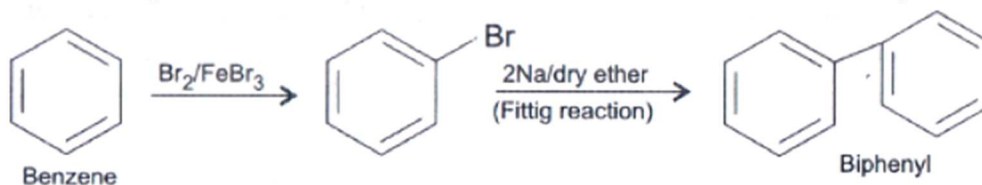
The alkaline potassium permanganate solution is known as Baeyer's reagent. It has bright pink colour. It oxidizes alkenes to glycols which is colourless. This reaction is used as a test for the presence of double bond in a molecule. This is also known as Baeyer's test.



Bromine water test can also be done to detect the presence of double bond.

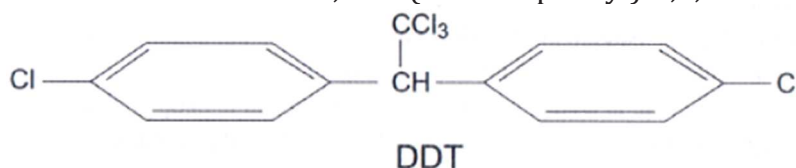
**69. Diphenyls are potential threat to the environment. How are these produced from arylhalides?**

**Ans.** Diphenyl can be prepared by treating two molecules of aryl halide with two molecules of sodium in presence of dry ether. The reaction is called Wurtz-fittig reaction.



**70. What are the IUPAC names of the insecticide DDT and benzenehexachloride? Why is their use banned in India and other countries?**

**Ans.** IUPAC name of DDT is 2,2-bis(4-chlorophenyl)-1,1,1-trichloroethane



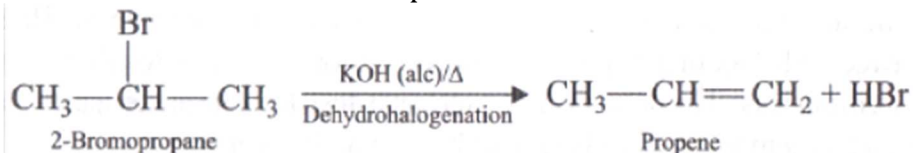


IUPAC name of benzenehexachloride is 1,2,3,4,5,6-hexachlorocyclohexane.

DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. Thus, the use of DDT was banned.

71. **Elimination reactions (especially  $\beta$ -elimination) are as common as the nucleophilic substitution reaction in case of alkyl halides. Specify the reagents used in both cases.**

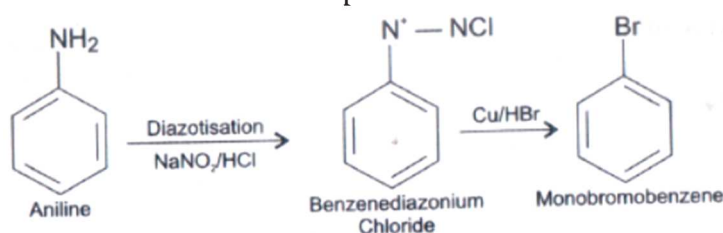
**Ans.** When a haloalkane is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from  $\beta$ -carbon and halogen atom from the  $\alpha$ -carbon atom. As a result, an alkene is formed as a product. Since  $\beta$ -hydrogenation is involved in elimination, it is often called  $\beta$ -elimination. An alkyl halide with  $\alpha$ -hydrogen atoms when reacted with a base or a nucleophile has two competing routes: substitution ( $S_N1$  and  $S_N2$ ) and elimination. Which route will be taken up, depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. For example:



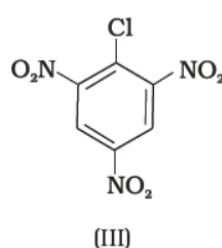
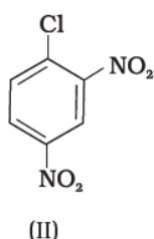
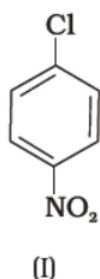
When same alkyl halide treated with aq KOH at low temperature, the product will be 2-propanol.

72. **How will you obtain monobromobenzene from aniline?**

**Ans. Sandmeyer's reaction:** When a primary aromatic amine, dissolved or a suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by  $-\text{Cl}$  or  $-\text{Br}$ .



73. **Aryl halides are extremely less reactive towards nucleophilic substitution. Predict and explain the order of reactivity of the following compounds towards nucleophilic substitution:**



**Ans.** The order of reactivity will be I < II < III

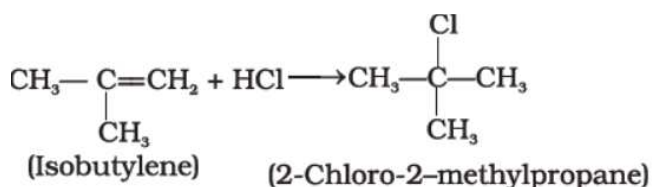
The presence of nitro group at *ortho*- and *para* -positions withdraws the electron density from the benzene ring and thus facilitates the attack of the nucleophile on haloarene. The carbanion thus formed is stabilised through resonance. The negative charge appeared at *ortho*- and *para*-positions with respect to the halogen substituent is stabilised by  $-\text{NO}_2$  group.

**74. *tert*-Butylbromide reacts with aq. NaOH by  $\text{S}_{\text{N}}1$  mechanism while n-butylbromide reacts by  $\text{S}_{\text{N}}2$  mechanism. Why?**

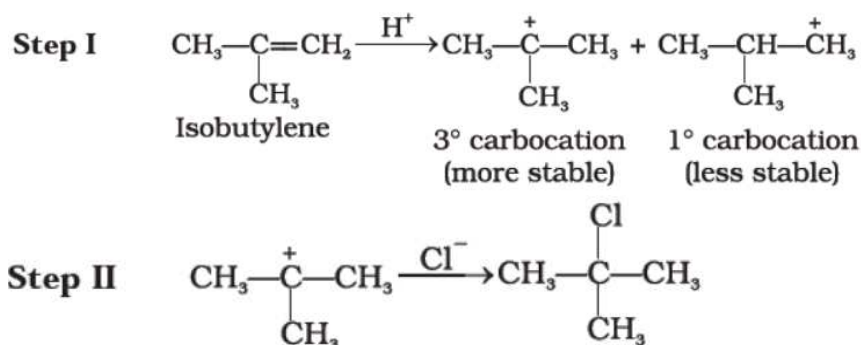
**Ans.** n-butyl bromide reacts by  $\text{S}_{\text{N}}2$  mechanism because there is less steric hinderance. Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus, the order of reactivity followed is: Primary halide > Secondary halide > Tertiary halide. Further, in  $\text{S}_{\text{N}}1$  greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides,  $3^\circ$  alkyl halides undergo  $\text{S}_{\text{N}}1$  reaction very fast because of the high stability of  $3^\circ$  carbocations.

**75. Predict the major product formed when HCl is added to isobutylene. Explain the mechanism involved.**

**Ans.**



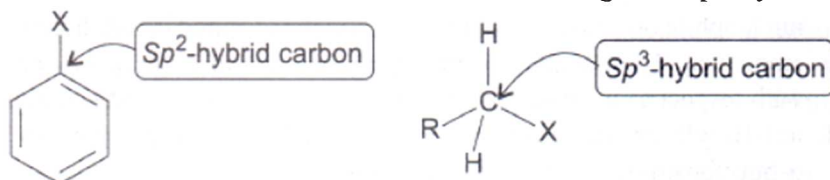
The mechanism involved in this reaction is:



**76. Discuss the nature of C—X bond in the haloarenes.**

**Ans.** In haloarenes, C—X bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

In haloalkane, the carbon atom attached to halogen is  $sp^3$  hybridised while in case of haloarene, the carbon atom attached to halogen is  $sp^2$ -hybridised.



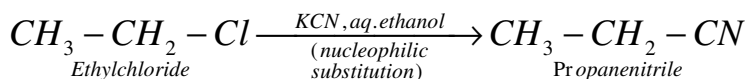
The  $sp^2$  hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than  $sp^3$  hybridised carbon in haloalkane with less s-character. Thus, C—Cl bond-length in haloalkane is 177 pm while in haloarene is 169 pm.

**77. How can you obtain iodoethane from ethanol when no other iodine containing reagent except NaI is available in the laboratory?**

**Ans.**  $C_2H_5OH \xrightarrow{ZnCl_2 / \text{conc } HCl} C_2H_5Cl + NaI \xrightarrow{\text{dry acetone}} C_2H_5I + NaCl$

**78. Cyanide ion acts as an ambident nucleophile. From which end it acts as a stronger nucleophile in aqueous medium? Give reason for your answer.**

**Ans.** Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. Actually, cyanide group is a hybrid of two contributing structures and therefore can act as nucleophile in two different ways: C=H], i.e., linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. It acts as a stronger nucleophile from the carbon end because it will lead to the formation of C—C bond which is more stable than the C—N bond.



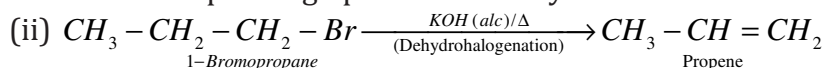
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## Haloalkanes and Haloarenes

### Long Answer Type

95. Some alkyl halides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.

**Ans.** An alkyl halide with hydrogen atoms, when reacted with a base or a nucleophile, has two competing routes: substitution ( $S_N1$  and  $S_N2$ ) and elimination. Which route will be taken up depends upon the nature of alkyl halide, strength and size of base/nucleophile and reaction conditions. Thus, a bulkier nucleophile will prefer to act as a base and abstracts a proton rather than approach a tetravalent carbon atom (steric reasons) and vice-versa. Similarly, a primary alkyl halide will prefer a  $S_N2$  reaction, a secondary halide- $S_N2$  or elimination depending upon the strength of base/nucleophile and a tertiary halide- $S_N1$  or elimination depending upon the stability of carbocation or the more substituted alkene.



If the same reaction is carried out in presence of aq KOH, 1-propanol will be the product.

96. Some halogen containing compounds are useful in daily life. Some compounds of this class are responsible for exposure of flora and fauna to more and more of UV light which causes destruction to a great extent. Name the class of these halo compounds. In your opinion, what should be done to minimise harmful effects of these compounds.

**Ans. Dichloromethane (Methylene Chloride):** Dichloromethane is widely used as a solvent, as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent.

**Trichloromethane (Chloroform):** Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the Freon refrigerant R-22.

**Triiodomethane (Iodoform):** It was used earlier as an antiseptic but the antiseptic properties are due to the liberation of free iodine and not due to iodoform itself.

**Tetrachloromethane (Carbon tetrachloride):** It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals.

**Freons:** The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, non-corrosive and easily liquefiable gases. Freon 12 ( $CCl_2F_2$ ) is one of the most common freons in industrial use.

Green chemistry is a production process that aims at using the existing knowledge and principles of chemistry for developing and implementing chemical products and processes to reduce the use and generation of substances hazardous to the environment. The release of different harmful chemicals (particulates, gases, organic and inorganic wastes) causes environmental pollution. In green chemistry, the reactants to be used in chemical reactions are chosen in such a way that the yield of the end products is up to 100%. This prevents or limits chemical pollutants from being introduced.

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**97. Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?**

**Ans.** Aryl halides are extremely less reactive towards nucleophilic substitution due to following reasons:

(i) **Resonance effect:** In haloarenes, the electron pairs on halogen atom are in conjugation with the ring C—X bond acquires a partial double bond character due to resonance. As result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

(ii) **Difference in hybridisation of carbon atom in C—X bond:** In haloalkane, the carbon atom attached to halogen is  $sp^3$ -hybridised while in case of haloarene, the carbon atom attached to halogen is  $sp^2$ -hybridised

(iii) **Instability of phenyl cation:** In case of haloarenes, the phenyl cation formed as result of self-ionisation will not be stabilised by resonance and therefore,  $S_N1$  mechanism is ruled out. Because of the possible repulsion, it is less likely for the electron-rich nucleophile to approach electron-rich arenes.