



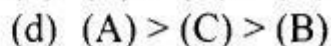
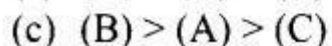
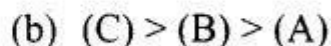
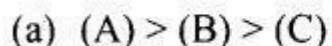
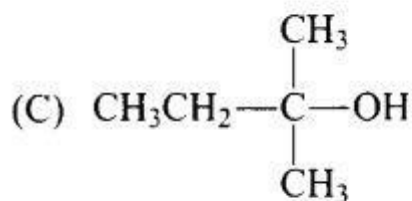
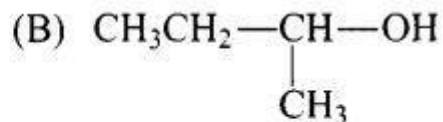
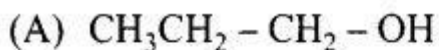
## NCERT Exemplar Problems Class 12 Chemistry

### Chapter 10 Haloalkanes and Haloarenes

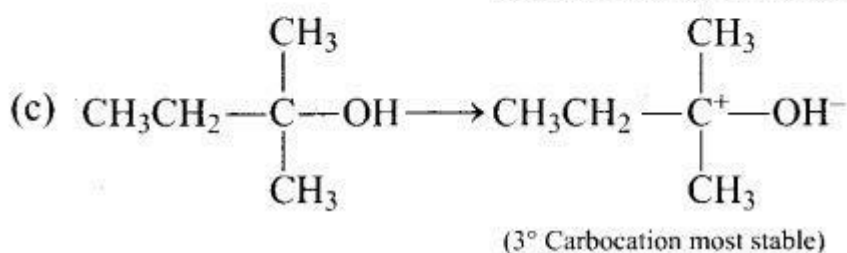
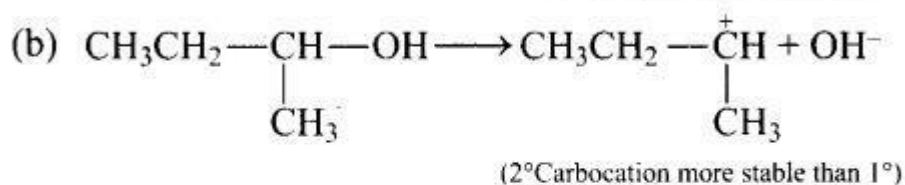
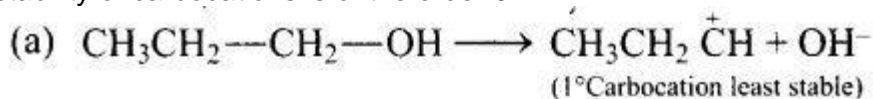
#### Multiple Choice Questions

##### Single Correct Answer Type

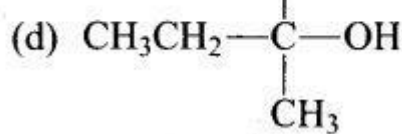
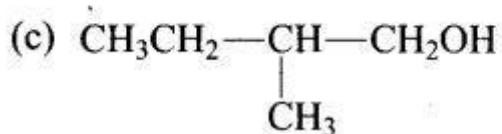
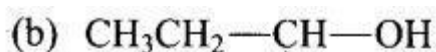
**Question 1.** The order of reactivity of following alcohols with halogen acids is



**Solution:** (b) The reactivity order of alcohols towards halogen acids is  $3^\circ > 2^\circ > 1^\circ$ , since the stability of carbocations is of the order  $3^\circ > 2^\circ > 1^\circ$ .

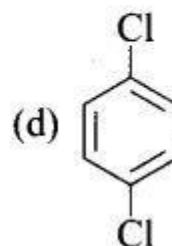
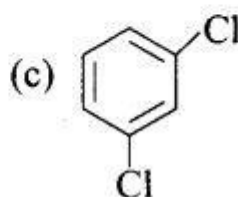
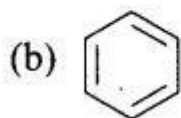
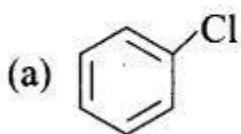
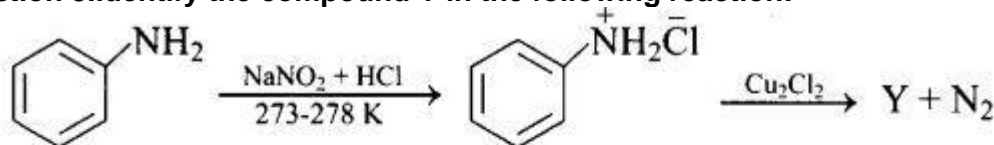


**Question 2.** Which of the following alcohol will yield the corresponding alkyl chloride on reaction with concentrated HCl at room temperature?

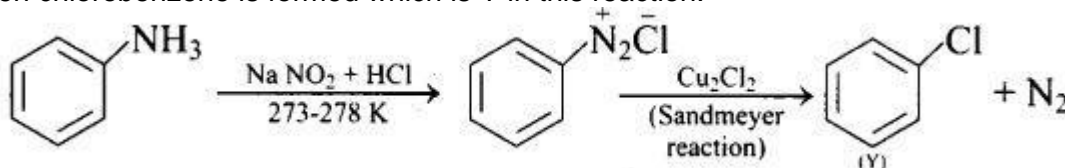


**Solution:** (d) As tertiary carbocation is most stable, so tertiary alcohols are most reactive towards conc. HCl. Hence, the reaction can be conducted at room temperature only, while primary and secondary alcohols require the presence of a catalyst  $\text{ZnCl}_2$ .

**Question 3.** Identify the compound Y in the following reaction:



**Solution:** (a) When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid and treated with sodium nitrite, a diazonium salt is formed. When this freshly prepared diazonium salt is mixed with cuprous chloride, diazonium group is replaced by -Cl. Then chlorobenzene is formed which is Y in this reaction.



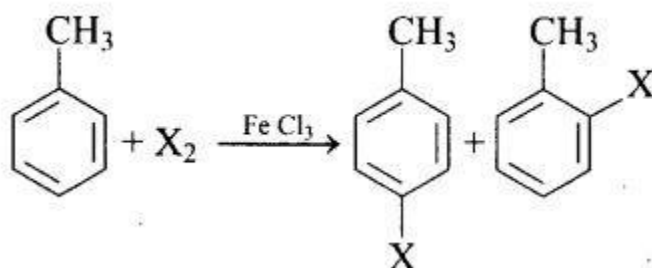
**Question 4.** Toluene reacts with a halogen in the presence of iron (III) chloride giving ortho and para halo compounds. The reaction is

- (a) electrophilic elimination reaction
- (b) electrophilic substitution reaction
- (c) free radical addition reaction
- (d) nucleophilic substitution reaction

**Solution:**

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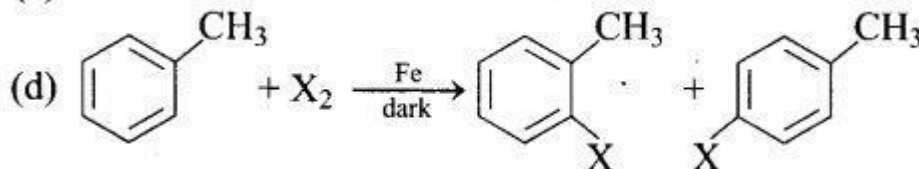
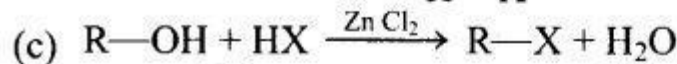
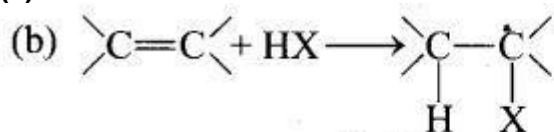
(b)



This is an example of electrophilic substitution reaction.

**Question 5. Which of the following is halogen exchange reaction?**

(a)

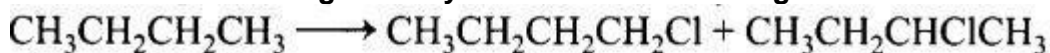


**Solution:** (a) Halogen exchange reaction are those reactions in which one halide replaces another. This reaction is known as Finkelstein reaction.

In

- (a) Halogen (-X) is replaced by iodine
- (b) Addition of hydrogen halide on alkene
- (c) Halogen replaces alcoholic group
- (d) Halogen replaces the hydrogen of benzoic ring

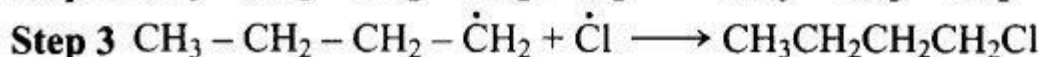
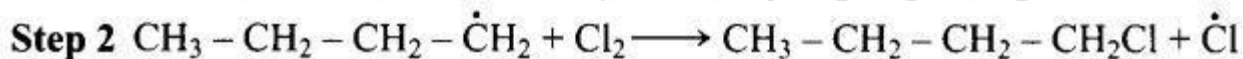
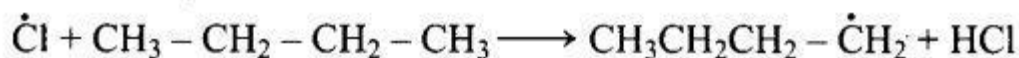
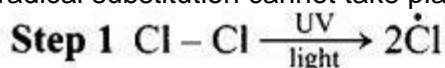
**Question 6. Which reagent will you use for the following reaction?**



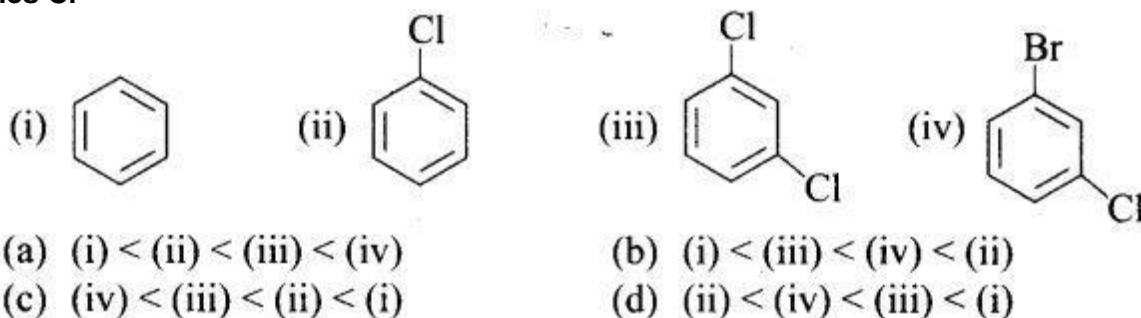
- (a)  $\text{Cl}_2/\text{UV light}$
- (b)  $\text{NaCl} + \text{H}_2\text{SO}_4$
- (c)  $\text{Cl}_2$  gas in dark
- (d)  $\text{Cl}_2$  gas in the presence of iron in dark

**Solution:** (a) The given reaction is a free radical substitution reaction. It occurs in presence of ultraviolet light or at high temperature or peroxides which are free radical generators. Free

radical substitution cannot take place in dark.

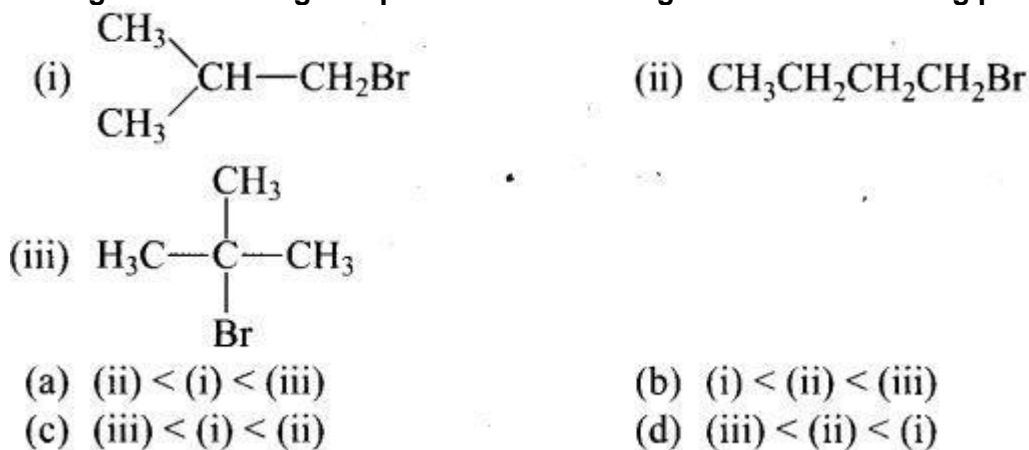


**Question 7.** Arrange the following compounds in the increasing order of their densities Cl



**Solution:** (a) Density increases with increase in molecular mass. The order of molecular masses is

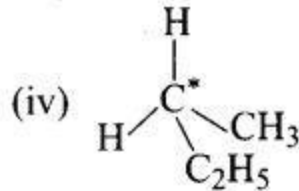
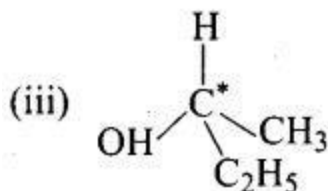
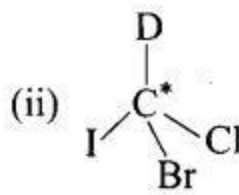
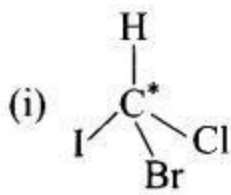
**Question 8.** Benzene < Chlorobenzene < Dichlorobenzene < Bromochlorobenzene  
Arrange the following compounds in increasing order of their boiling points



**Solution:** (c) Boiling points of isomeric haloalkanes decrease with increase in branching as with increase in branching surface area decreases which leads to decrease in intermolecular forces.

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

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(a) (i), (ii), (iii), (iv)

(b) (i), (ii), (iii)

(c) (ii), (iii), (iv)

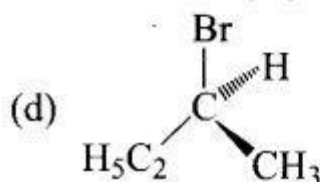
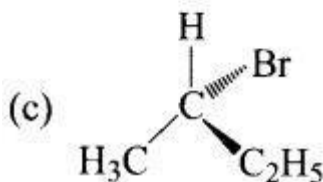
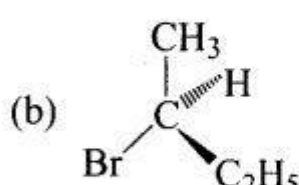
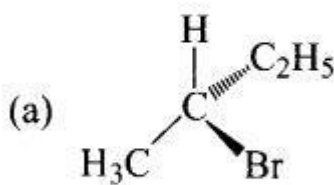
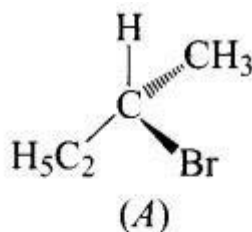
(d) (i), (iii), (iv)

**Solution:** (b) Asymmetric/chiral carbon atom is that in which all of its four valencies with four different groups or atoms.

In molecules (i), (ii) and (iii), all have asymmetric carbon as each carbon has satisfied all four valencies with four different groups or atoms.

In molecule (iv), carbon satisfies two of its valencies with two hydrogen atoms i.e., similar atom. So, it is not an asymmetric carbon atom.

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



**Solution:** (a) Compound (a) is enantiomer of compound (A) because the configuration of two groups, i.e., CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> in them is reversed at the chiral carbon.



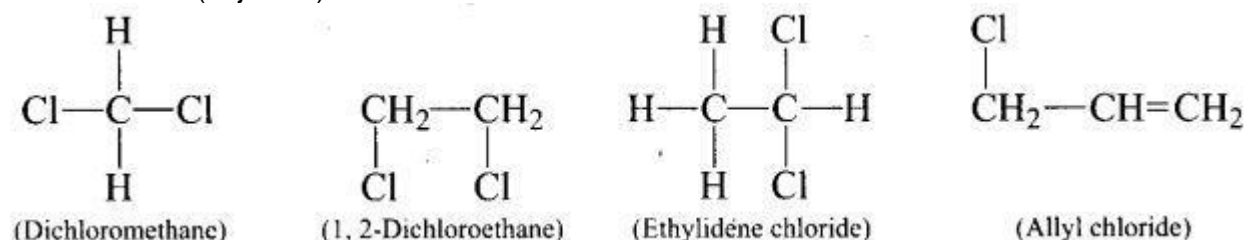


**Question 11. Which of the following is an example of vic-dihalide?**

(a) Dichloromethane (b) 1, 2-dichloroethane

(c) Ethylidene chloride (d) Allyl chloride

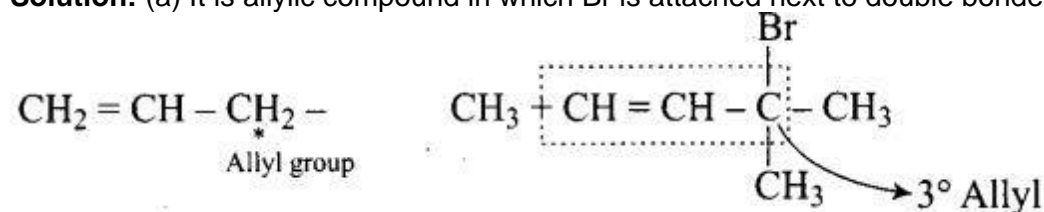
**Solution:** (b) 1, 2-Dichloroethane is a vic-dihalide since two Cl atoms are present on vicinal carbon atoms (adjacent).



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

(a) allyl (b) aryl (c) vinyl (d) secondary

**Solution:** (a) It is allylic compound in which Br is attached next to double bonded carbon.

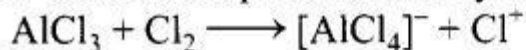


**Question 13. Chlorobenzene is formed by reaction of chlorine with benzene in the presence of  $\text{AlCl}_3$ . Which of the following species attacks the benzene ring in this reaction?**

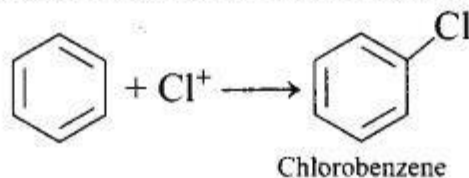
(a)  $\text{CP}$  (b)  $\text{Cl}^+$  (c)  $\text{AlCl}_3$  (d)  $[\text{AlCl}_4]^-$

**Solution:**

(b)  $\text{Cl}^+$  is an electrophile formed by the following reaction.



$\text{Cl}^+$  attacks the benzene ring to give chlorobenzene.



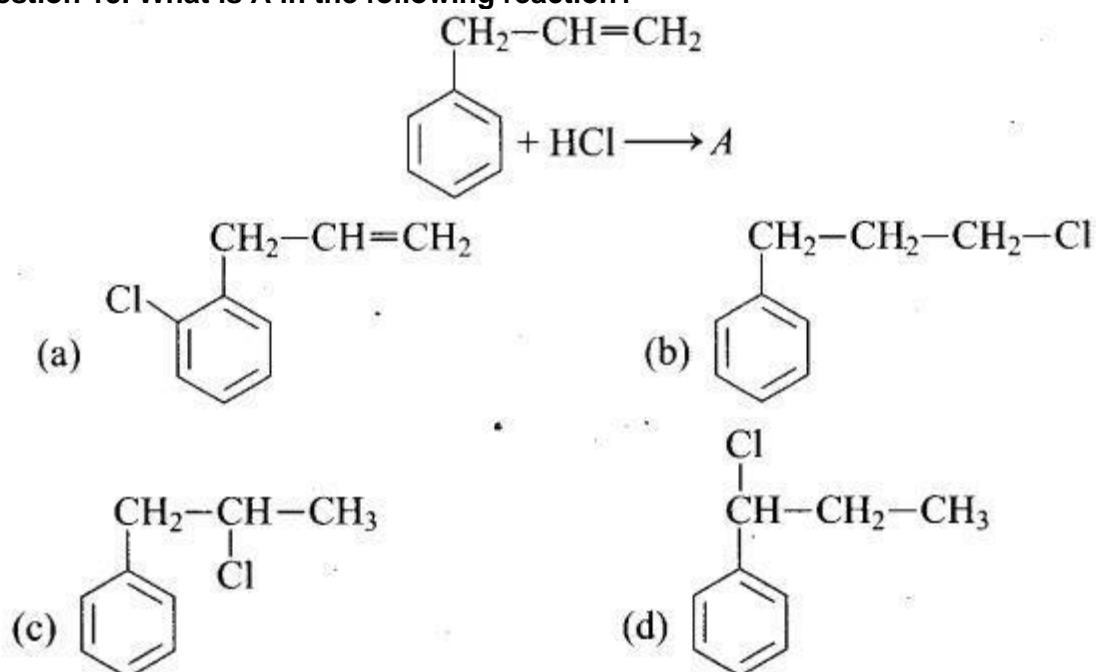
**Question 14. Ethylidene chloride is a/an .**

(a) vic-dihalide (b) gem-dihalide (c) allylic halide (d) vinylic halide

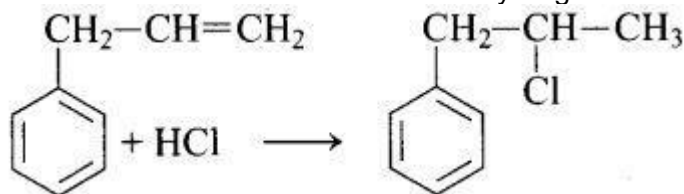


**Solution:** (b) Ethylidene chloride is a gem-dihalide,  $\text{CH}_3 - \text{CHCl}_2$  in which both halogen atoms are attached to the same carbon atom.

**Question 15.** What is A in the following reaction?



**Solution:** (c) In this reaction, addition of HCl takes place on doubly bonded carbons in accordance with Markownikoff's rule i.e., addition of negative addendum will take place on that carbon which has lesser number of hydrogen.



**Question 16.** A primary alkyl halide would prefer to undergo .

- (a)  $\text{S}_\text{N}^1$  reaction (b)  $\text{S}_\text{N}^2$  reaction  
(c)  $\alpha$ -Elimination (d) Racemisation

**Solution:** (b)  $\text{S}_\text{N}^2$  reaction proceeds via formation of transition state which is formed easily in primary alkyl halide due to less steric hindrance.

**Question 17.** Which of the following alkyl halides will undergo  $\text{S}_\text{N}^1$  reaction most rapidly?

- (a)  $(\text{CH}_3)_3\text{C-F}$  (b)  $(\text{CH}_3)_3\text{C-Cl}$   
(c)  $(\text{CH}_3)_3\text{C-Br}$  (d)  $(\text{CH}_3)_3\text{C-I}$

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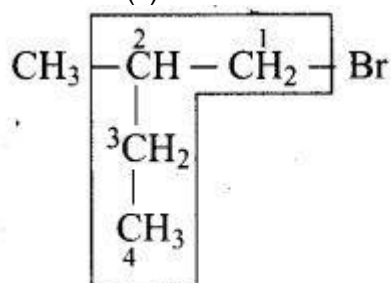
**Solution:** (d)  $(\text{CH}_3)_3\text{C} - \text{I}$  will undergo  $\text{S}_\text{N}1$  reaction most readily as C-I bond is weakest, due to the large difference in the size of carbon and iodine.

**Question 18.**

Which is the correct IUPAC name of  $\text{CH}_3 - \underset{\text{C}_2\text{H}_5}{\text{CH}} - \text{CH}_2 - \text{Br}$  ?

- (a) 1-Bromo-2-ethylpropane
- (b) 1-Bromo-2-ethyl-2-methylethane
- (c) 1-Bromo-2-methylbutane
- (d) 2-Methyl-1-bromobutane

**Solution:** (c) The correct IUPAC name of the given compound is

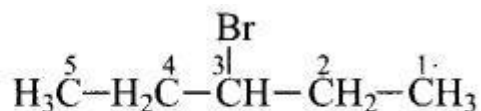


1-bromo-2-methylbutane

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

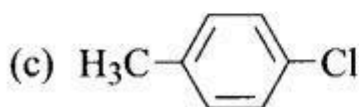
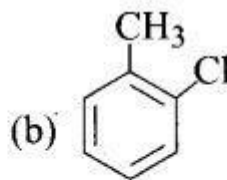
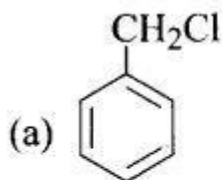
- (a) 1-Bromo-1, 1-diethylmethane
- (b) 3-Bromopentane
- (c) 1-Bromo-1-ethylpropane
- (d) 1-Bromopentane

**Solution:** (b) Diethylbromomethane is



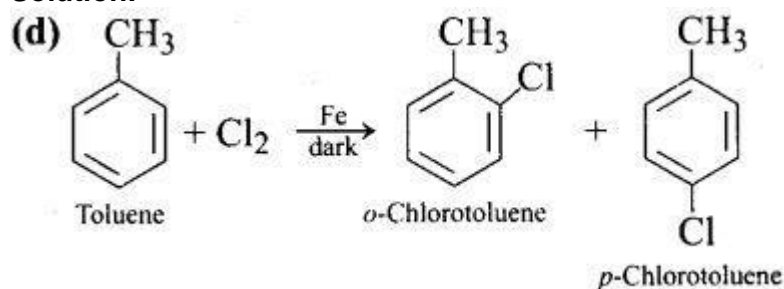
Its IUPAC name is 3-bromopentane.

**Question 20. The reaction of toluene with chloride in the presence of iron and in the absence of light yields**



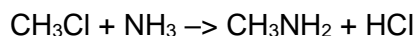
(d) mixture of (b) and (c)



**Solution:****Question 21.** Chloromethane on treatment with excess of ammonia yields mainly

- (a) N, N-Dimethylmethanamine  $\left(\text{CH}_3-\text{N}\begin{matrix} \text{CH}_3 \\ \text{CH}_3 \end{matrix}\right)$
- (b) N-methylmethanamine ( $\text{CH}_3-\text{NH}-\text{CH}_3$ )
- (c) methanamine ( $\text{CH}_3\text{NH}_2$ )
- (d) mixture containing all these in equal proportion.

**Solution:** (c) Chloromethane on treatment with excess of ammonia yields mainly methanamine.

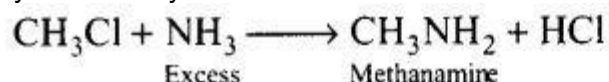


Excess Methanamine

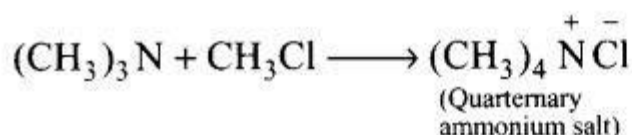
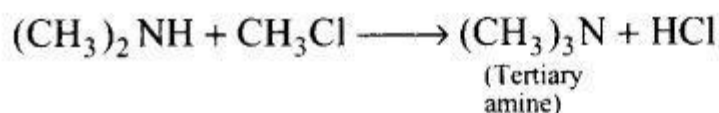
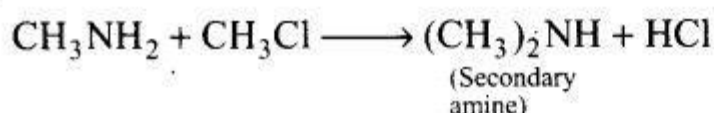
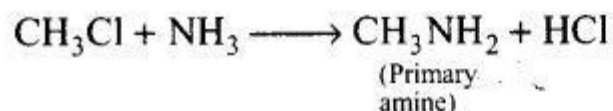
However, if the two reactants are present in the same amount, the mixture of primary,



secondary and tertiary amine is obtained.



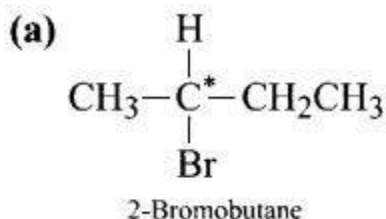
However, if the two reactants are present in the same amount, the mixture of primary, secondary and tertiary amine is obtained.



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

- (a) 2-Bromobutane (b) 1-Bromobutane  
(c) 2-Bromopropane (d) 2-Bromopropan-2-ol

**Solution:**



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

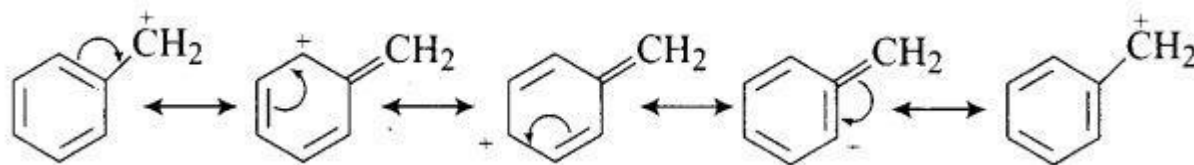
- (a)  $\text{S}_\text{N}1$  mechanism  
(b)  $\text{S}_\text{N}2$  mechanism  
(c) any of the above two depending upon the temperature of reaction  
(d) Saytzeff rule

**Solution:** (a)  $\text{C}_6\text{H}_5\text{CH}_2\text{Br}$  will follow  $\text{S}_\text{N}1$  mechanism on reaction with aqueous sodium hydroxide since the carbocation formed  $\text{C}_6\text{H}_5\text{CH}_2^+$  is a resonance stabilized cation.

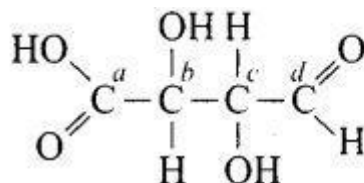
Benzylic halides show high reactivity towards the  $\text{S}_\text{N}1$  reaction.

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The carbocation thus formed gets stabilized through resonance as shown in the structure.



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



(a) a, b, c, d

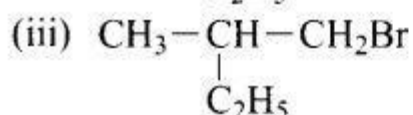
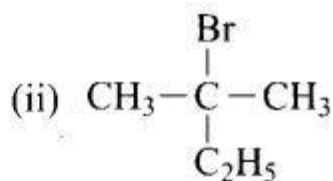
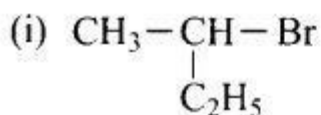
(b) b, c

(c) a, d

(d) a, b, c

**Solution:** (b) Carbon has four valencies. If a carbon atom satisfies all of its four valencies with four different groups then it is termed asymmetric/chiral carbon. In the given compound, b and c carbon are bonded to four different groups, so these are asymmetric.

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



(a) (i)

(b) (i), (ii), (iii)

(c) (ii), (iii)

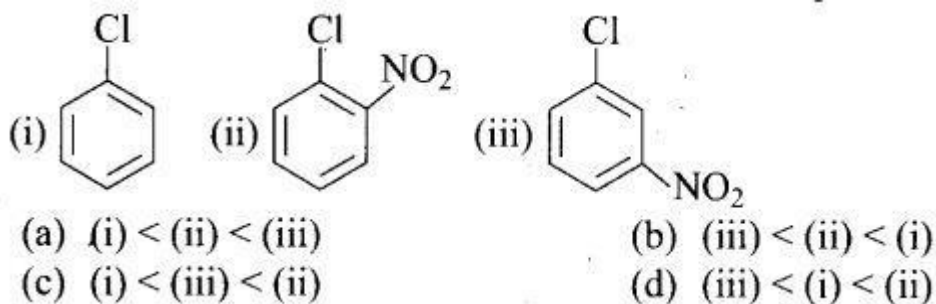
(d) (i), (iii)

**Solution:**

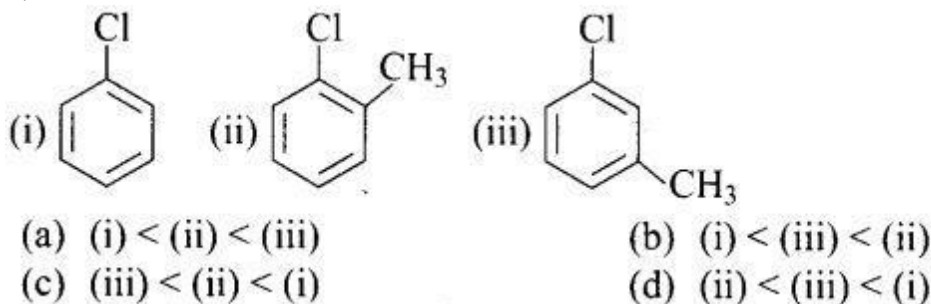
(a)  $\text{CH}_3-\underset{\text{C}_2\text{H}_5}{\text{CH}}-\text{Br}$  will give a racemic mixture on nucleophilic substitution

by OH<sup>-</sup> ion since the alkyl halide has a chiral carbon atom. During the S<sub>N</sub>1 reaction a mixture of enantiomers is formed which are present in equal proportions.

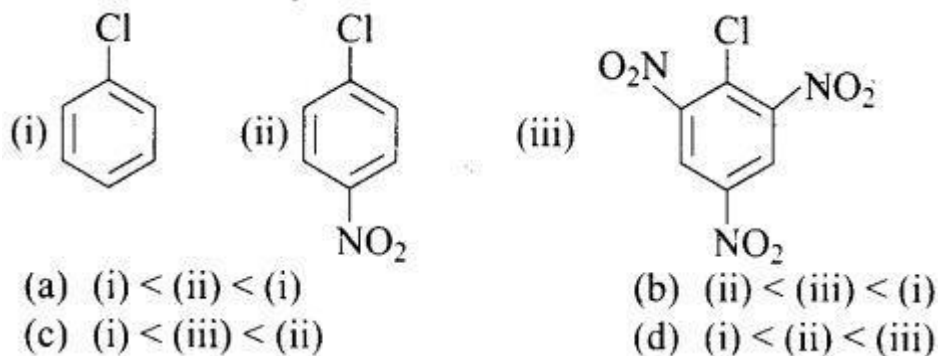
General Instruction: In the question 26 to 29, arrange the compounds in increasing order of rate of reaction towards nucleophilic substitution.

**Question 26.**

**Solution:** (c) Presence of an electron withdrawing group ( $-\text{NO}_2$ ) at ortho and para position facilitates nucleophilic substitution. The effect of presence of electron withdrawing group is very less at meta position.

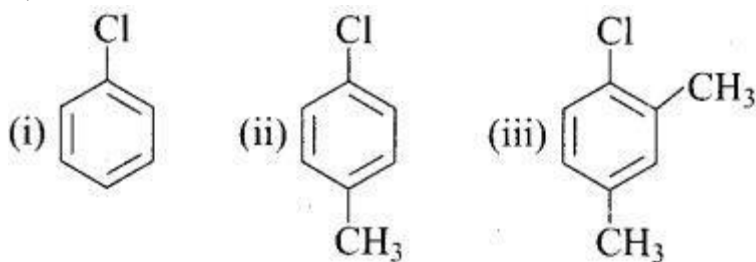
**Question 27.**

**Solution:** (d) Presence of electron releasing group at ortho or para positions decreases the rate of nucleophilic substitution

**Question 28.**

**Solution:** (d) Electron withdrawing group increase the reactivity of aryl halides, more is the number of electron withdrawing group, the more is rate towards nucleophilic substitution.

**Question 29.**



(a) (i) < (ii) < (iii)

(b) (ii) < (i) < (iii)

(c) (iii) < (ii) < (i)

(d) (i) < (iii) < (ii)

**Solution:**(c) Electron releasing group increase the reactivity of aryl halides, less is the number of electron releasing group, the less is rate towards nucleophilic substitution.

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

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

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

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

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

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

**Solution:** (a) The higher the surface area, the higher will be the intermolecular forces of attraction and thus boiling point too. Boiling point increases with increase in molecular mass of halogen atom for the similar type of alkyl halide. Butane has no halogen atom and rest of all three compounds are halo derivatives of butane.

Atomic mass of iodine is highest so the boiling point of 1-iodobutane is maximum among all the given compounds.

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

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

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

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

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

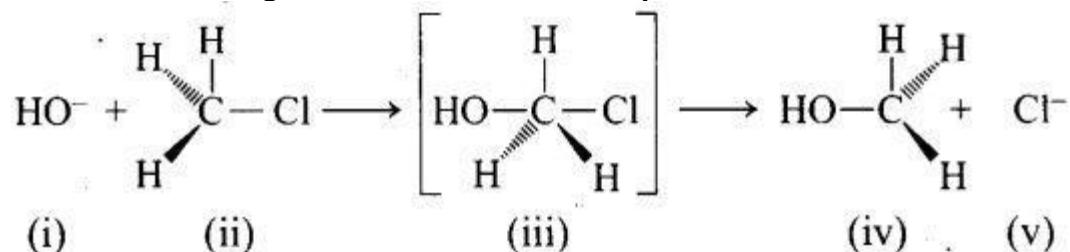
(d) 1-Bromoethane < 1-Bromopropane < 1-Bromobutane < Bromobenzene

**Solution:** (d) Boiling point increases with increase in molecular mass of the alkyl halide.



**More than One Correct Answer Type**

Consider the following reaction and answer the questions no. 32-34



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

- (a) Both (i) and (v) are nucleophiles
- (b) In (iii), carbon atom is  $sp^3$  hybridised
- (c) In (iii), carbon atom is  $sp^2$  hybridised
- (d) Both (i) and (v) are electrophiles

**Solution:** (a, c)  $\text{HO}^-$  and  $\text{Cl}^-$  are nucleophiles. In (iii), C atom is  $sp^2$  hybridised due to formation of C – OH bond and breaking of C – Cl bond simultaneously. So, in transition state, C atom is bonded to only 3 H atoms completely.

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

- (a) The given reaction follows  $S_N^2$  mechanism.
- (b) (ii) and (iv) have opposite configuration.
- (c) (ii) and (iv) have same configuration.
- (d) The given reaction follows  $S_N^1$  mechanism.

**Solution:** (a, b) In the given reaction, alkyl halide is primary in nature. Here, a transitory state is observed in which one bond is broken and one bond is formed synchronously he., in one step. So, it follows  $S_N^2$  mechanism.

In this mechanism, nucleophile attacks the carbon at  $180^\circ$  to the leaving group. So the reactant and product have opposite configuration.

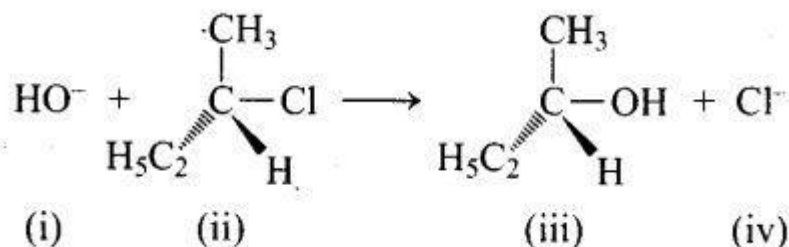
**Question 34. Which of the following statements are correct about the reaction intermediate?**

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



**Solution:** (a, d) In the given reaction intermediate (iii) is unstable because the carbon atom is attached to 5 atoms and is less stable than reactant (ii).

**Answer Questions 35 and 36 on the basis of the following reaction:**



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

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

**Solution:** (a, d) Since it is a tertiary halide, it proceeds through  $\text{S}_\text{N}1$  mechanism and a carbocation is formed as an intermediate.

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

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

**Solution:** (a, c) The above reaction follows  $\text{S}_\text{N}1$  mechanism. In  $\text{S}_\text{N}1$  mechanism, formation of carbocation is a slow step. So, the rate of reaction depends upon the concentration of (ii). So, the rate of reaction depends upon the concentration of only (ii) therefore, molecularity of reaction is one.

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

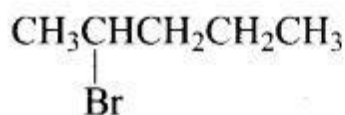
- (a) 2-Bromopentane (b) Vinyl chloride (chloroethene)



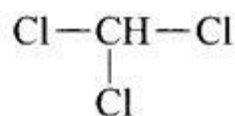
(c) 2-Chloroacetophenone (d) Trichloromethane

**Solution:**

**(a, d)**



2-Bromopentane



Trichloromethane

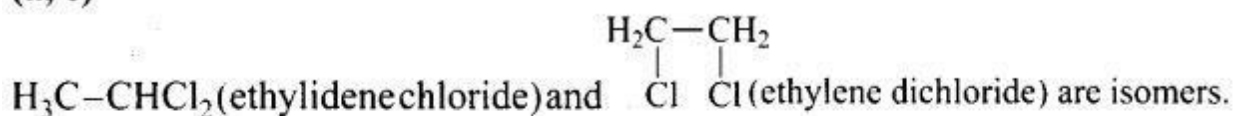
In both of these compounds halogen atoms are attached to  $\text{sp}^3$  hybridised carbon atom of alkyl group.

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

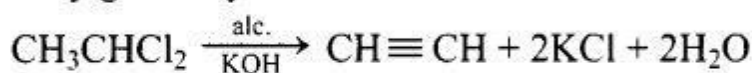
- (a) Both the compounds form same product on treatment with alcoholic KOH
- (b) Both the compounds form same product on treatment with aqueous NaOH
- (c) Both the compounds form same product on reduction
- (d) Both the compounds are optically active

**Solution:**

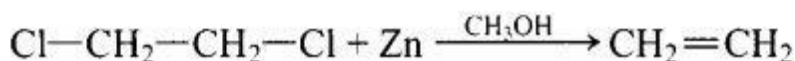
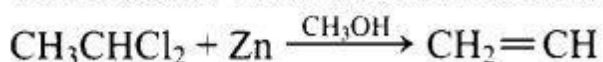
**(a, c)**



(i) They give ethyne on treatment with alcoholic KOH.



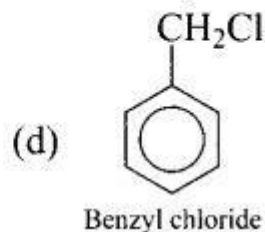
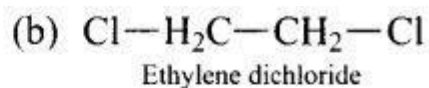
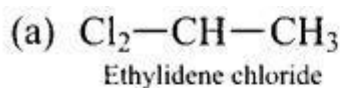
(ii) On reduction with Zn dust in alcohol they give ethylene.



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

- (a) Ethylidene chloride (b) Ethylene dichloride
- (c) Methylene chloride (d) Benzyl chloride

**Solution:** (a, c) Gem-dihalides are those dihalides in which two halogen atoms are bonded to the same carbon atom.



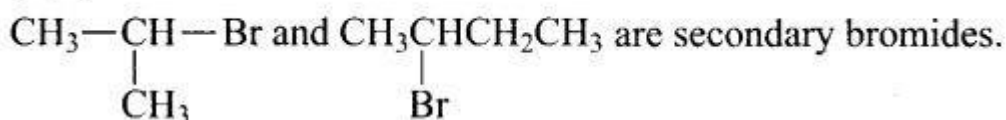
So, in (a) and (c) two halogen atoms are present on the same carbon atom and they are termed gem-dihalides.

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

- (a)  $(\text{CH}_3)_2\text{CHBr}$  (b)  $(\text{CH}_3)_3\text{CCH}_2\text{Br}$   
(c)  $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{CH}_3$  (d)  $(\text{CH}_3)_2\text{CBrCH}_2\text{CH}_3$

**Solution:**

**(a, c)**

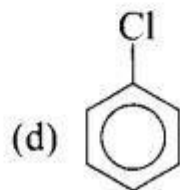
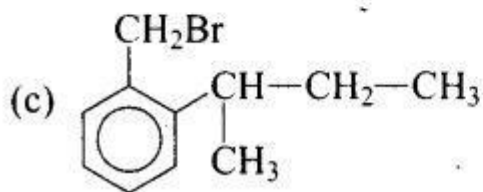
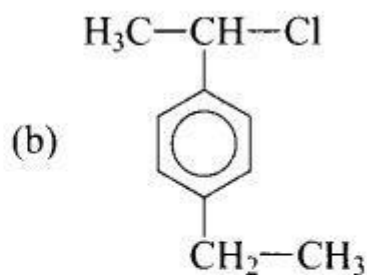
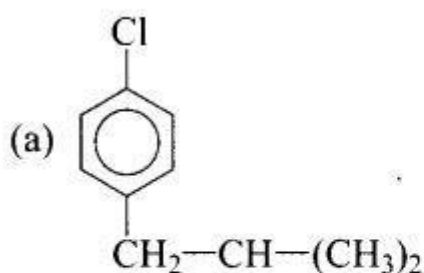


**Question 41. Which of the following compounds can be classified as aryl halides?**

- (a)  $\text{p-ClC}_6\text{H}_4\text{CH}_2\text{CH}(\text{CH}_3)_2$  (b)  $\text{p-CH}_3\text{CHCl}(\text{C}_6\text{H}_4)\text{CH}_2\text{CH}_3$   
(c)  $\text{o-BrH}_2\text{CC}_6\text{H}_4\text{CH}(\text{CH}_3)\text{CH}_2\text{CH}_3$  (d)  $\text{C}_6\text{H}_5\text{Cl}$

**Solution:**

**(a, d)**





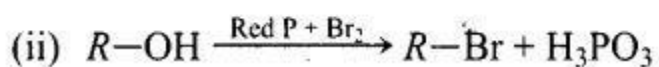
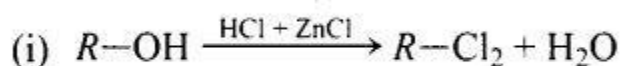
In compound (a) and compound (d), halogen atom is directly bonded to aromatic ring therefore these compounds are classified as aryl halides.

**Question 42.** Alkyl halides are prepared from alcohol by treating with

- (a)  $\text{HCl} + \text{ZnCl}_2$  (b)  $\text{Red P} + \text{Br}_2$   
 (c)  $\text{H}_2\text{SO}_4 + \text{KI}$  (d) all the above

**Solution:**

**(a, b)**



**Question 43.** Alkyl fluorides are synthesized by heating an alkyl chloride/bromide in presence of or

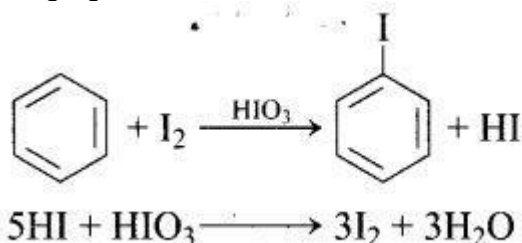
- (a)  $\text{CaF}_2$  (b)  $\text{CoF}_2$  (c)  $\text{Hg}_2\text{F}_2$  (d)  $\text{NaF}$

**Solution:** (b, c) The synthesis of alkyl fluorides is accomplished by heating an alkyl chloride or bromide in presence of metallic fluoride such as  $\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$ ,  $\text{CoF}_2$ , or  $\text{SbF}_3$ . The reaction is known as Swarts reaction.

### Short Answer Type Questions

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

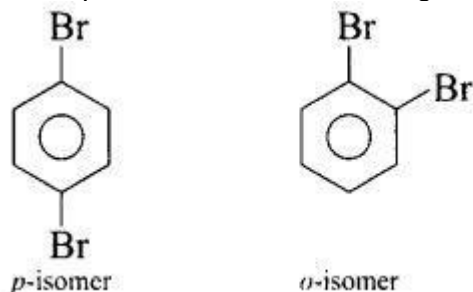
**Solution:** Iodination reactions are reversible in nature. To carry out the reaction in forward direction,  $\text{HI}$  formed during the reaction is removed by oxidation.  $\text{HIO}_3$  is used as an oxidising agent.





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

**Solution:** 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.

**Question 46.** Which of the compounds will react faster in  $S_N1$  reaction with the  $OH^-$  ion?

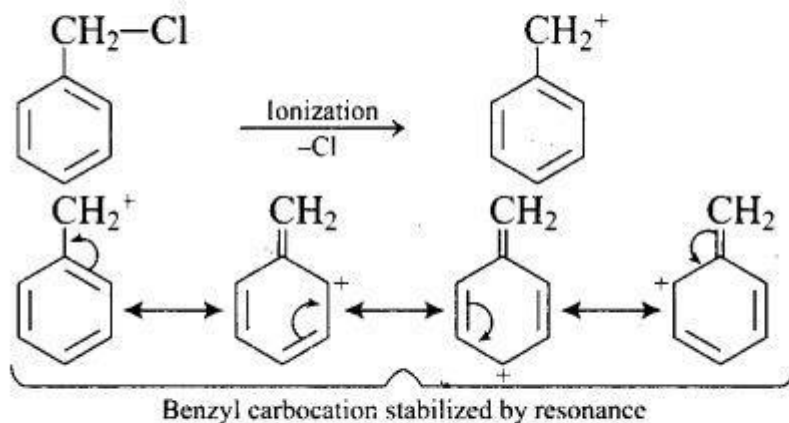
$CH_3 - CH_2 - Cl$  or  $C_6H_5 - CH_2 - Cl$

**Solution:**

$C_6H_5 - CH_2 - Cl$

$S_N1$  reaction proceeds through the formation of carbocation intermediate.

$C_6H_5CH_2Cl$  readily undergoes ionization to give  $C_6H_5CH_2^+$  carbocation, which is stabilized by resonance.



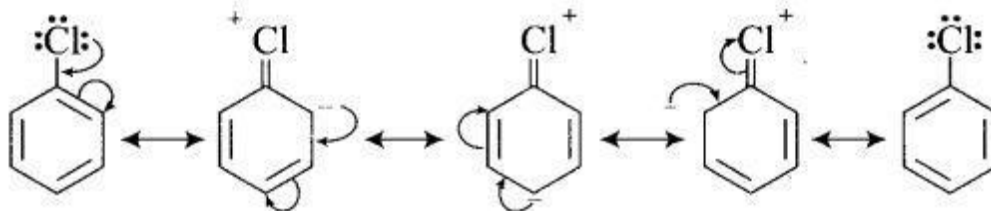
On the other hand,  $CH_3CH_2Cl$  does not undergo ionization to give  $CH_3CH_2^+$  carbocation. Therefore,  $C_6H_5CH_2Cl$  reacts faster than  $CH_3CH_2Cl$  with  $OH^-$  ion.

**Question 47.** Why has iodoform appreciable antiseptic property?

**Solution:** Antiseptic properties of iodoform are due to liberation of free iodine.

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

**Solution:** In haloarenes, the electron pairs on halogen atom are in conjugation with  $\pi$ -electrons of the ring.

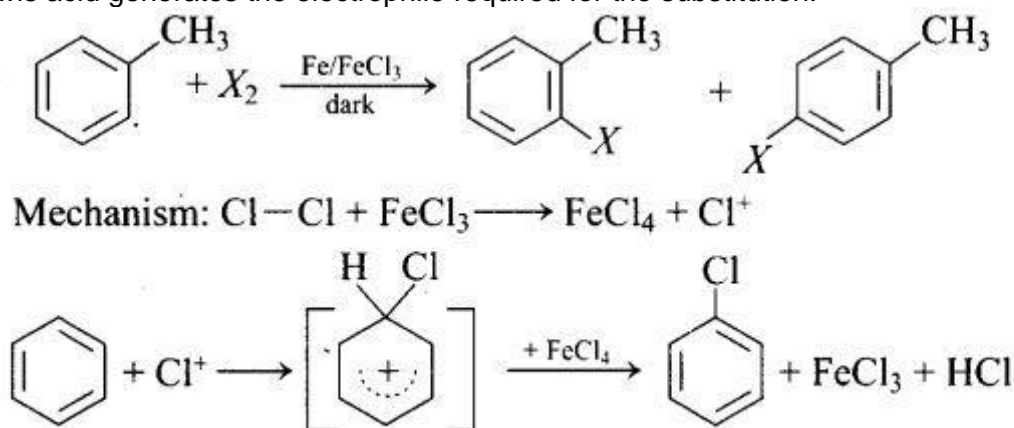


C – Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore they are less reactive towards nucleophilic substitution reaction.

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

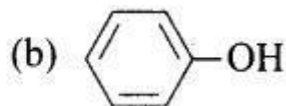
**Solution:** Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively, in the presence of Lewis acid catalysts like iron or iron chloride.

Lewis acid generates the electrophile required for the substitution.



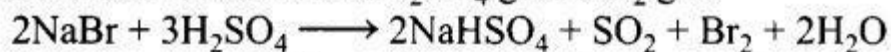
Lewis acid generates the electrophile required for the substitution.

**Question 50. Which of the following compounds (a) and (b) will not react with a mixture of NaBr and  $\text{H}_2\text{SO}_4$ . Explain why?**

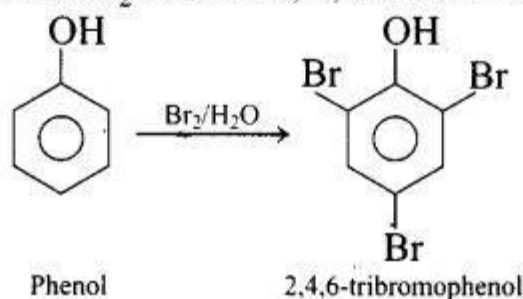


**Solution:**

(b) As mixture of NaBr and  $\text{H}_2\text{SO}_4$  gives  $\text{Br}_2$  gas.

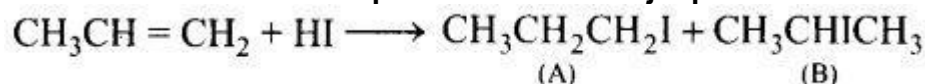


Phenol (b) reacts with  $\text{Br}_2$  to form 2, 4, 6-tribromophenol.



But  $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$  (a) does not react with  $\text{Br}_2$  water.

**Question 51.** Which of the products will be major product in the reaction given



**Solution:** In the given reaction, (B) is the major product of the reactions. According to Markownikoff's rule, H is added to the C atom with higher number of hydrogen atoms.

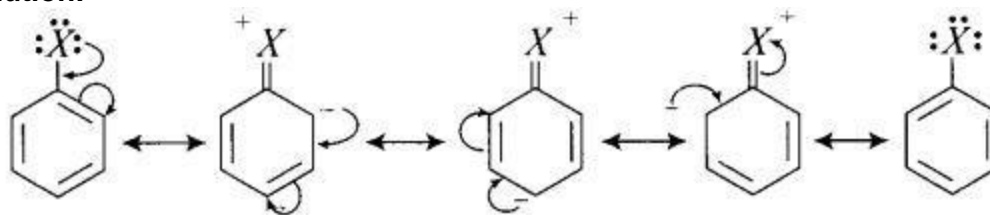
**Question 52.** Why is the solubility of haloalkanes in water very low?

**Solution:** The haloalkanes are only slightly soluble in water. In order to dissolve a haloalkane in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Since less energy is released in the formation of new attractions between haloalkane and water molecules and these are not very strong as the original hydrogen bonds present in water and hence the solubility of haloalkanes is low.

**Question 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.



**Solution:**



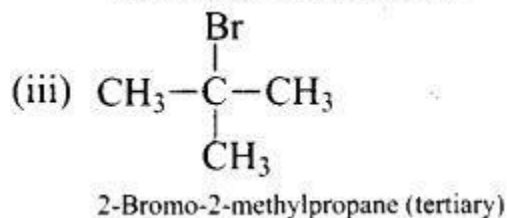
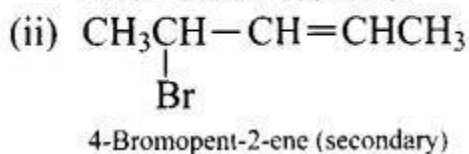
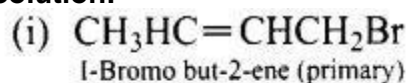
Since the electron density is more at ortho and para positions, the functional group present in the ring is ortho-para directing.

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

(i) 1-Bromobut-2-ene

(iii) 2-Bromo-2-methylpropane

**Solution:**

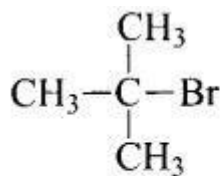


**Question 55. Compound (A) with molecular formula  $\text{C}_4\text{H}_9\text{Br}$  is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound 'A' only. When another optically active isomer 'B' of this compound was treated with aq. KOH solution, the rate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

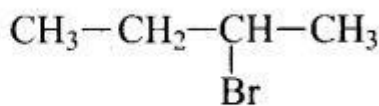
(i) Write down the structural formula of both compounds 'A' and 'B'.

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

**Solution:** (i) The molecular formulae of isomers of  $\text{C}_4\text{H}_9\text{Br}$  are  $\text{CH}_3$

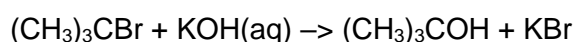


2-Bromo-2-methylpropane (A)



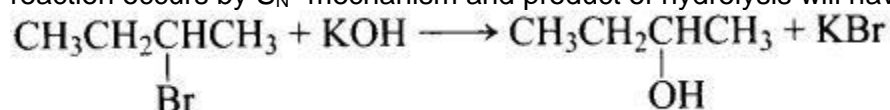
2-Bromobutane (B)

Since the rate of reaction of compound 'A' ( $\text{C}_4\text{H}_9\text{Br}$ ) with aqueous KOH depends upon the concentration of compound 'A' only, therefore, the reaction occurs by  $\text{S}_\text{N}1$  mechanism and compound 'A' is tertiary bromide i.e., 2-Bromo-2-methylpropane.



$$\text{rate} = k[(\text{CH}_3)_3\text{CBr}]$$

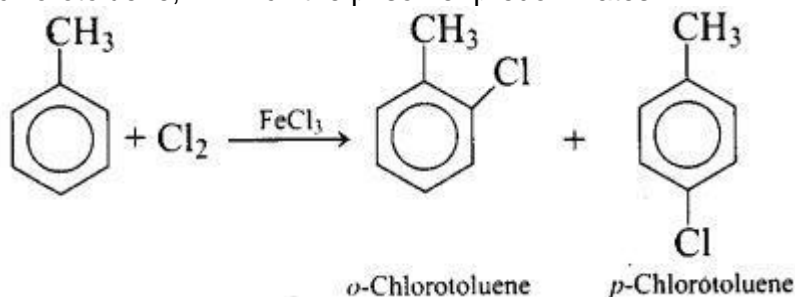
Since compound 'B' is optically active and is an isomer of compound 'A' ( $\text{C}_4\text{H}_9\text{Br}$ ), therefore, compound 'B' must be 2-Bromobutane. Since the rate of reaction of compound 'B' with aqueous KOH depends upon the concentration of compound 'B' and KOH, therefore, the reaction occurs by  $\text{S}_\text{N}2$  mechanism and product of hydrolysis will have inverted configuration.



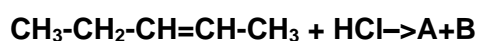
$$\text{rate} = k \left[ \begin{array}{c} \text{CH}_3\text{CH}_2\text{CHCH}_3 \\ | \\ \text{Br} \end{array} \right] [\text{KOH}]$$

**Question 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  $\text{FeCl}_3$ .

**Solution:** The compound with molecular formula  $\text{C}_7\text{H}_8$  is toluene,  $\text{C}_6\text{H}_5\text{CH}_3$ . Since - $\text{CH}_3$  group is o-, p-directing, therefore, chlorination of toluene gives o-chlorotoluene and p-chlorotoluene, in which the p-isomer predominates.



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

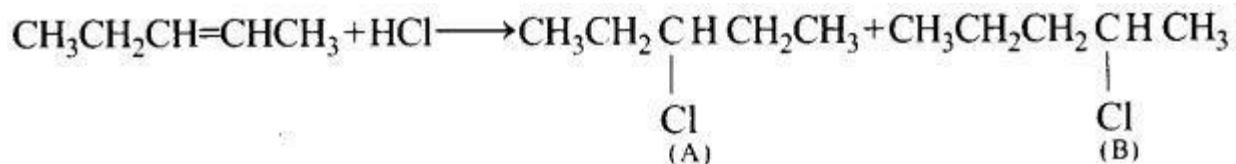


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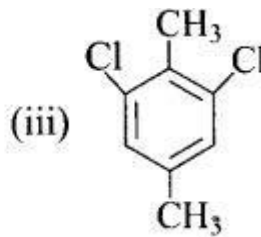
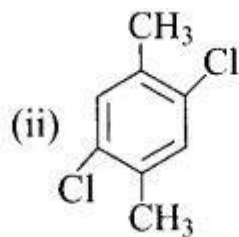
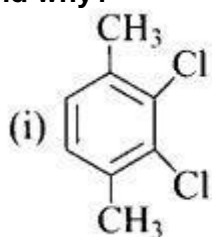




**Solution:**



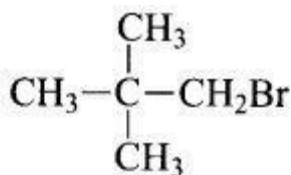
**Question 58.** Which of the following compounds will have the highest melting point and why?



**Solution:** Structure II has a symmetrical structure hence, it will have the highest melting point.

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

**Solution:**



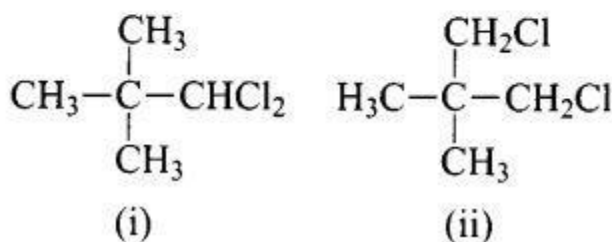
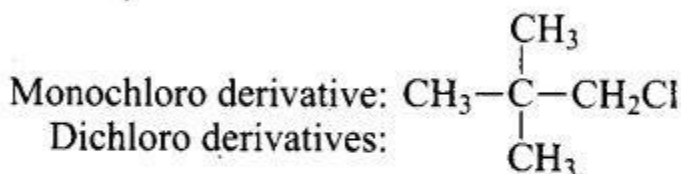
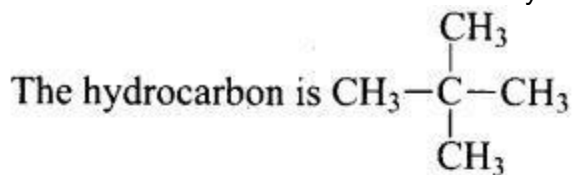
1-Bromo-2, 2-dimethylpropane

**Question 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.

**Solution:**  $\text{C}_5\text{H}_{12}$ , pentane has molecular mass  $72 \text{ g mol}^{-1}$  i.e., isomer of pentane which yields

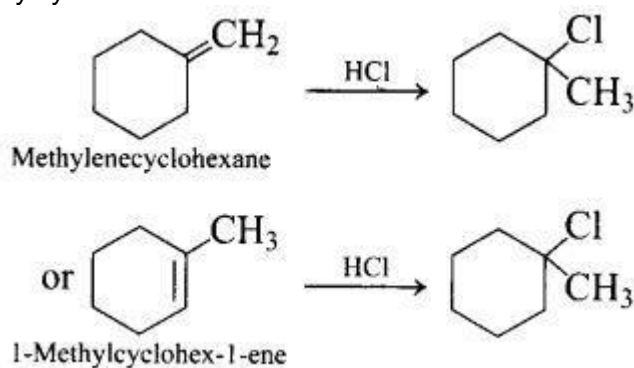


single monochloro derivative should have all the 12 hydrogens equivalents.



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

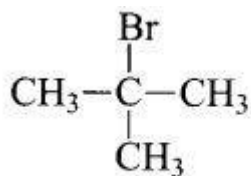
**Solution:** Two alkenes are possible. These are methylene cyclohexane and 1 - Methylcyclohex-1 -ene



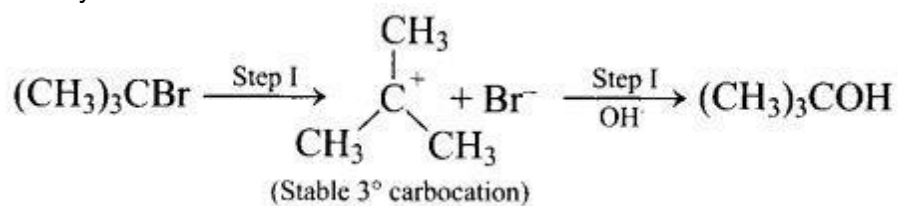
**Question 62.** Which of the following haloalkanes reacts with aqueous KOH most easily? Explain giving reason.

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

**Solution:** (iii) 2-Bromo-2-methylpropane



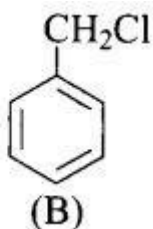
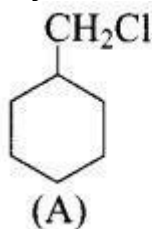
will react the aqueous KOH most easily because the carbocation formed during the reaction is tertiary and most stable.



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

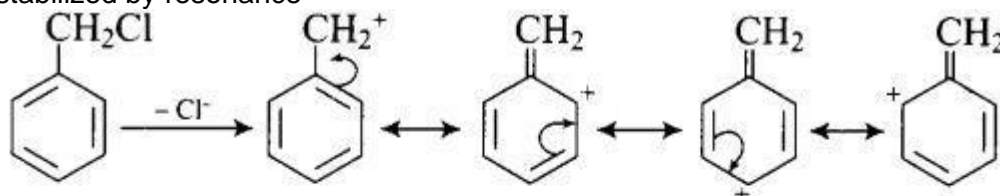
**Solution:** Phenol does not react with HCl and  $\text{ZnCl}_2$  to give aryl halides due to partial double bond character between benzene ring and O which arises by resonance of benzene ring and OH group.

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

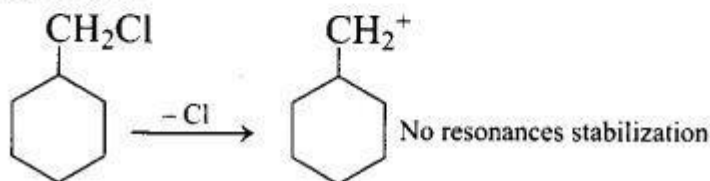


**Solution:** (B) undergoes  $\text{S}_\text{N}1$  reaction faster because the carbocation formed after the loss of

Cl is stabilized by resonance

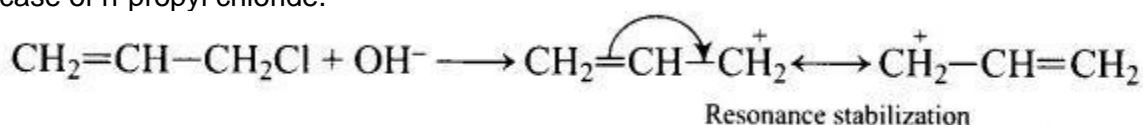


On the other hand, the carbocation formed during the reaction of (A) is not resonance stabilized.



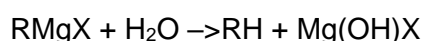
**Question 65. Allyl chloride is hydrolysed more readily than n-propyl chloride. Why?**

**Solution:** Allyl chloride shows high reactivity because the carbocation formed by hydrolysis is stabilised by resonance while no such stabilisation of carbocation exists in the case of n-propyl chloride.



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

**Solution:** Grignard reagents are highly reactive and react with even traces of water to give corresponding hydrocarbons.



**Question 67. How do polar solvents help in the first step in SN1 mechanism?**

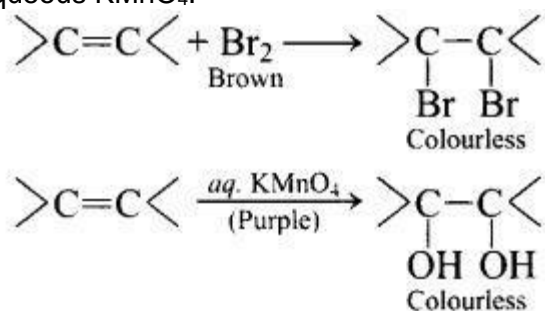
**Solution:** The SN1 mechanism proceeds through the formation of carbocation. It involves breaking of C-halogen bond for which energy is obtained through the solvation of halide ion with the proton of the protic solvent. Thus, polar solvents help in ionisations step by stabilizing the ions by solvation.

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

**Solution:** Presence of a double bond in a molecule can be detected by bromine water test and Baeyer's test. The molecules with a double bond decolourise bromine water and



aqueous  $\text{KMnO}_4$ .

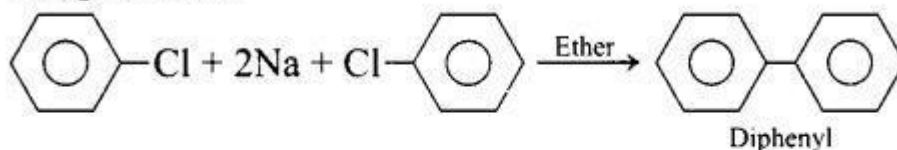


**Question 69.** Diphenyls are potential threat to the environment. How are these produced from arylhalides?

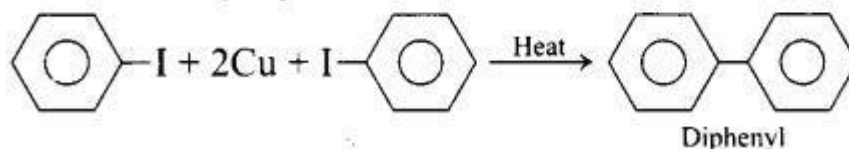
**Solution:** Diphenyls such as p,p'-dichlorodiphenyl trichloroethane (DDT) are posing serious environment problems because of its chemical stability and its fat solubility. Its residue accumulates in environment and its long-term effects could be highly dangerous.

Diphenyls can be prepared from aryl halides by the following two methods:

(i) Fittig reaction



(ii) Ullmann biaryl synthesis

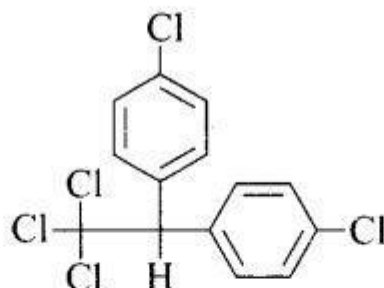


**Question 70.** What are the IUPAC name of the insecticide DDT and benzenehexachloride?

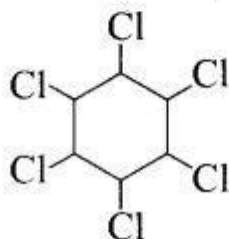
**Why is their use banned in India and other countries?**

**Solution:** 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.

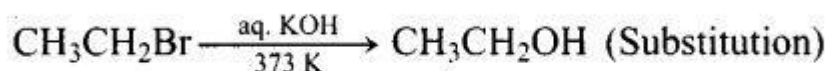
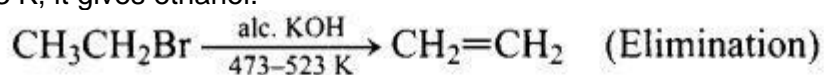


Their use is banned in India and other countries because they are highly toxic and are not biodegradable. Instead they are stored in the fatty tissues and their concentration keeps increasing in the food chain.

**Question 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.**

**Solution:** Alkyl halides undergo nucleophilic substitution as well as elimination (Beta-elimination) reaction.

However, by proper choice of reagents and reaction conditions, a particular product can be obtained. Usually strong and bulky bases and high temperature favour elimination reactions while weaker and smaller bases and lower temperature favour substitution reactions. For example, ethyl bromide on heating with alcoholic KOH (which contains stronger base,  $\text{C}_2\text{H}_5\text{O}^-$  ion) at about 473–523 K undergoes elimination to give ethene. But with aqueous KOH at about 373 K, it gives ethanol.



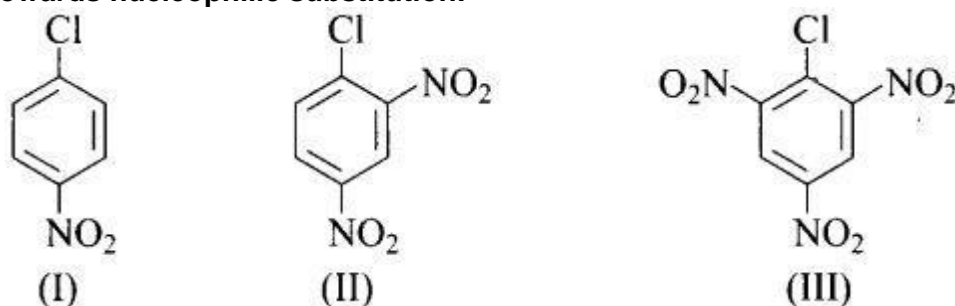
**Nucleophilic substitution:** Reagents used are nucleophiles like  $\text{OH}^-$ ,  $\text{NH}_3$ ,  $\text{C}\equiv\text{N}^-$ ,  $\text{AgCN}$ ,  $\text{O}=\text{N}-\text{O}$ ,  $\text{OR}'$  etc. Also, alc. KOH at lower temperature (373 K) undergoes substitution reaction.

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

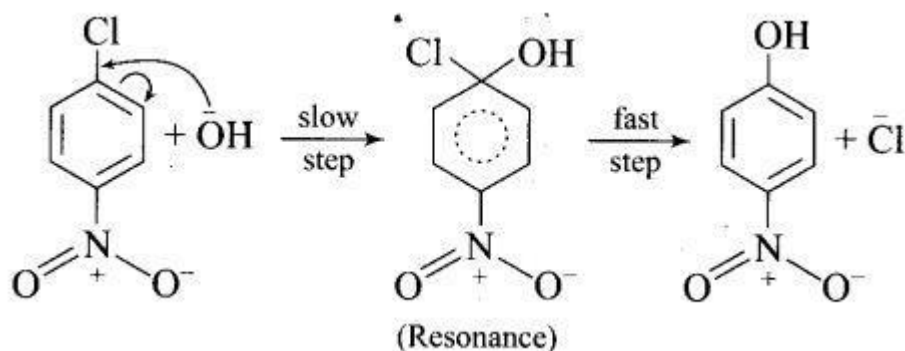
**Solution:**



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

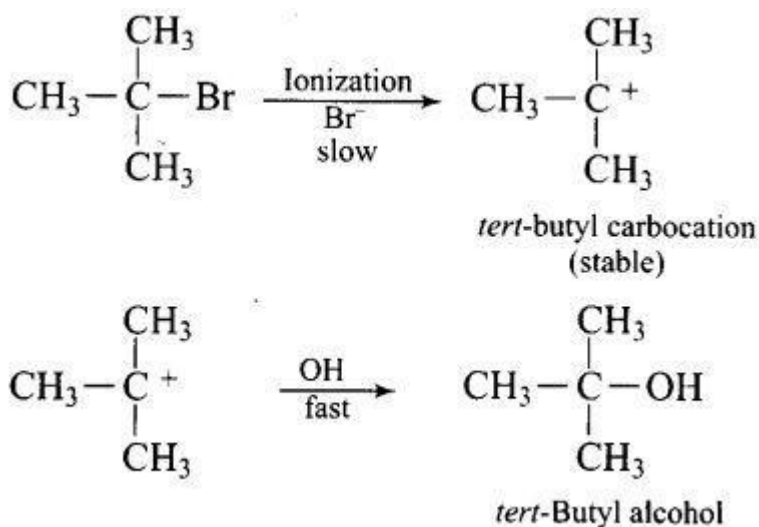


**Solution:** After the attachment of the nucleophile at the carbon carrying -Cl, the intermediate compound is stabilised due to resonance. Due to electron withdrawing nature of -NO<sub>2</sub>, the nucleophile is easily attached to the benzene ring. Greater the number of -NO<sub>2</sub> groups in the molecule, greater will be the ease with which the nucleophile will be attached. Hence, the order of reactivity is III > II > I.

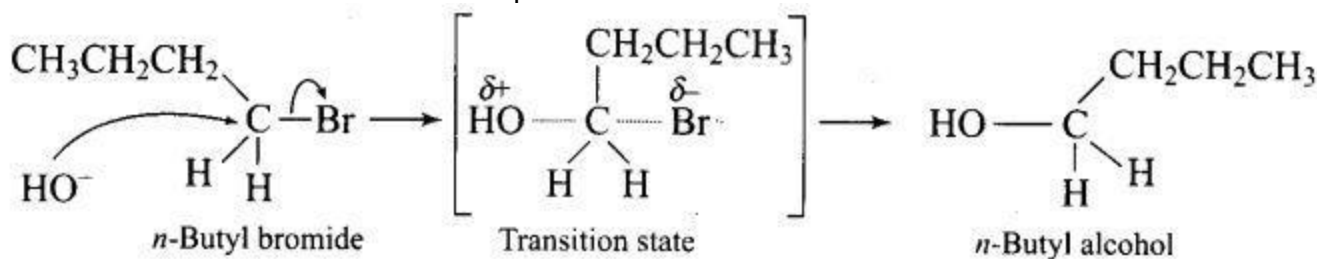


**Question 74.** *tert*-Butylbromide reacts with aq. NaOH by S<sub>N</sub><sup>1</sup> mechanism while *n*-butylbromide reacts by S<sub>N</sub><sup>2</sup> mechanism. Why?

**Solution:** In general, the S<sub>N</sub><sup>1</sup> reaction proceeds through the formation of carbocation. The *tert*-butylbromide readily loses Br<sup>-</sup> ion to form stable 3° carbocation. Therefore, it reacts with aqueous KOH by S<sub>N</sub><sup>1</sup> mechanism as:



On the other hand, *n*-Butyl bromide does not undergo ionization to form *n*-Butyl carbocation ( $1^\circ$ ) because it is not stable. Therefore, it prefers to undergo reaction by  $\text{S}_\text{N}2$  mechanism, which occurs in one step through a transition state involving nucleophilic attack of  $\text{OH}^-$  ion from the back side with simultaneous expulsion of  $\text{Br}^-$  ion from the front side.



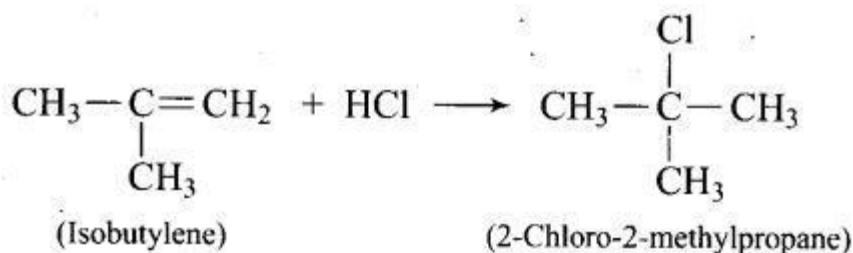
$\text{S}_\text{N}1$  mechanism follows the reactivity order as  $3^\circ > 2^\circ > 1^\circ$  while  $\text{S}_\text{N}2$  mechanism follows the reactivity order as  $1^\circ > 2^\circ > 3^\circ$

Therefore, *tert*-butylbromide ( $3^\circ$ ) reacts by  $\text{S}_\text{N}1$  mechanism while *n*-Butylbromide ( $1^\circ$ ) reacts by  $\text{S}_\text{N}2$  mechanism.

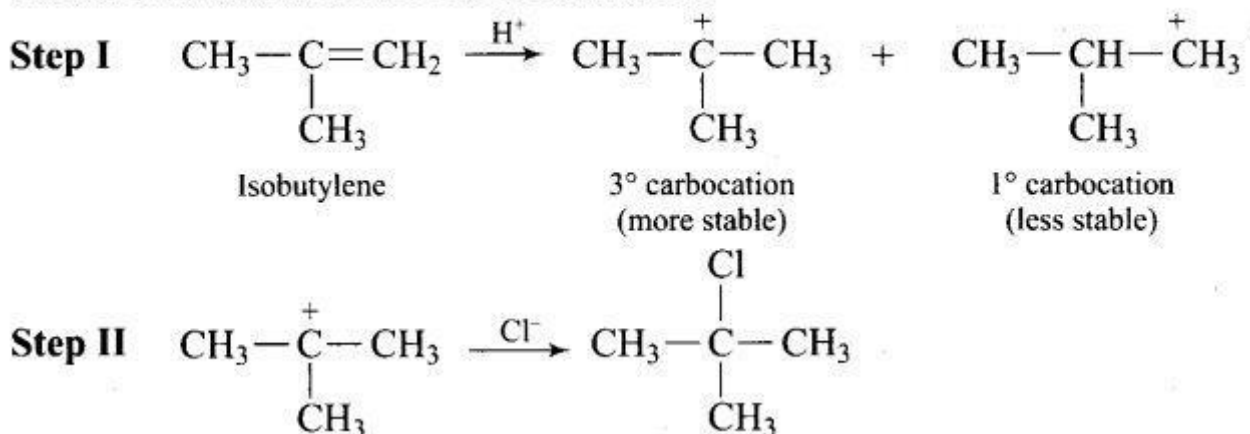
**Question 75.** Predict the major product formed when HCl is added to isobutylene.

**Explain the mechanism involved.**

**Solution:** The major product is 2-chloro-2-methylpropane



The mechanism involved in this reaction is:



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

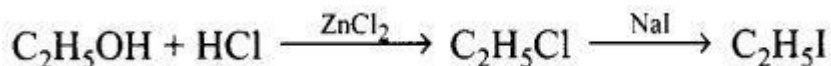
**C – X bond in haloarenes is extremely less reactive towards nucleophilic**

**Solution:** substitution reactions due to:

- (i) Resonance effect: C – X bond acquires a partial double bond character and it becomes difficult to break C – X bond.
- (ii) In C – X bond, C atom attached to halogen is sp<sup>2</sup> hybridised. The sp<sup>2</sup> hybridised carbon with a greater s character is more electronegative and can hold the electron pair of C – X bond more tightly than sp<sup>3</sup> hybridised carbon in haloalkane with less s-character.

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

**Solution:** Ethanol is converted to chloroethane and Cl can be replaced by I.



**Question 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.

**Solution:** 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 (bond between two similar atoms) than C – N bond.

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**Matching Column Type Questions**

**Question 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 |

**Solution:** (i → c), (ii → d), (iii → a), (iv → b)

(i) Chloramphenicol is a broad spectrum antibiotic. It is used in the treatment of typhoid fever.

(ii) Thyroxine is a hormone secreted by thyroid gland. Excessive secretion of thyroxine in the body is known as hyperthyroidism. Most patient with hyperthyroidism have an enlarged thyroid gland i.e., goiter.

(iii) Chloroquine, prevents the development of malaria parasite plasmodium vivax in the blood.

(iv) IUPAC name of chloroform is trichloromethane with formula  $\text{CHCl}_3$ . It is a colourless compound. Volatile, sweet-smelling liquid. Its vapours depresses the central nervous system and used as an anaesthetic.

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

| Column I |                                    | Column II |                    |
|----------|------------------------------------|-----------|--------------------|
| (i)      | $\text{S}_\text{N}1$ 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 alkylhalide | (e)       | Chlorobromocarbons |

**Solution:** (i → c), (ii → e), (iii → a), (iv → b), (v → d)

(i) A mixture containing two enantiomers in equal proportions will have zero optical rotation, such a mixture is known as racemic mixture. The process of conversion of enantiomer into a racemic mixture is known as racemisation. If an alkyl halide follows  $\text{S}_\text{N}1$  mechanism then

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racemisation takes place while if it follows  $S_N^2$  mechanism than inversion takes places.

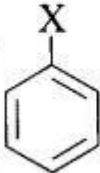
(ii) Chlorobromocarbons are used in fire extinguishers.

(iii) In vicinal dihalides, halogen atoms are present on the adjacent carbon atom. Bromination of alkanes will give vicinal dihalides.

(iv) Alkylidene halides are named gem-dihalides. In gem-dihalides halogen atoms are present on same carbon atom.

(v) Elimination of HX from alkylhalide follows Saytzeff rule. This rule states that "in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms".

**Question 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 |

**Solution:** (i  $\rightarrow$  b), (ii  $\rightarrow$  d), (iii  $\rightarrow$  a), (iv  $\rightarrow$  c)

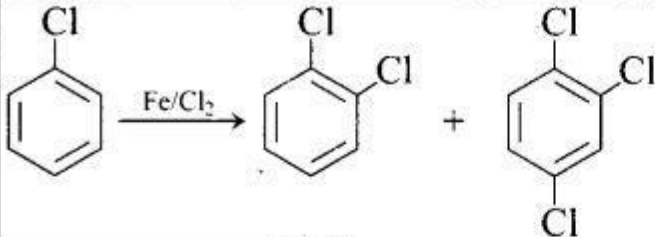
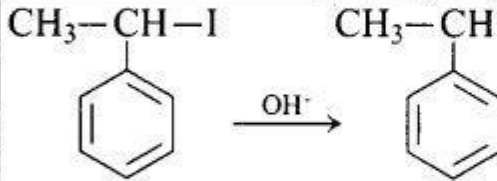
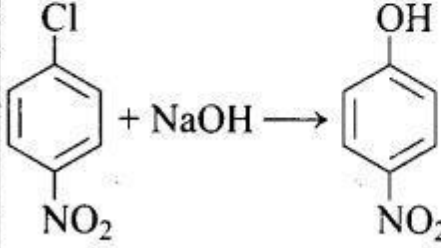
(i) In alkyl halide, halogen atom is bonded to  $sp^3$  hybridised carbon atom, which may be further bonded to one, two or three alkyl group, i.e.,  $\text{CH}_3-\text{CH}(\text{X})-\text{CH}_3$

(ii) Allyl halides are the compounds in which the halogen atom is bonded to  $sp^3$  hybridised carbon atom next to carbon-carbon double bond, i.e.,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{X}$

(iii) Aryl halides are the compounds in which the halogen atom is bonded to  $sp^2$  hybridised carbon atom of an aromatic ring, i.e.,  $\text{C}_6\text{H}_5\text{X}$

(iv) Vinyl halides are the compounds in which the halogen atom is bonded to an  $sp^2$  hybridised carbon atom of a carbon-carbon double bond, i.e.,  $\text{CH}_2=\text{CH}-\text{X}$

**Question 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)     | $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{HBr} \longrightarrow \text{CH}_3-\underset{\text{Br}}{\text{CH}}-\text{CH}_3$                        | (b)       | Electrophilic aromatic substitution                  |
| (iii)    |    | (c)       | Saytzeff elimination                                 |
| (iv)     |   | (d)       | Electrophilic addition                               |
| (v)      | $\text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}}\text{CH}_3 \xrightarrow[\text{KOH}]{\text{alkaline}} \text{CH}_3\text{CH}=\text{CHCH}_3$ | (e)       | Nucleophilic substitution ( $\text{S}_{\text{N}}1$ ) |

**Solution:** (i  $\longrightarrow$  b), (ii  $\longrightarrow$  d), (iii  $\longrightarrow$  e), (iv  $\longrightarrow$  a), (v  $\longrightarrow$  c)

(i) In this reaction, an electrophile  $\text{Cl}^+$  attacks on to the benzene ring and substitution takes place.

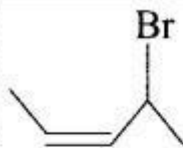
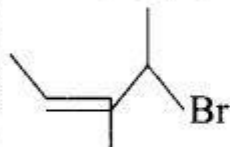
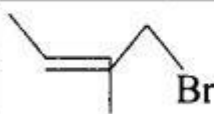
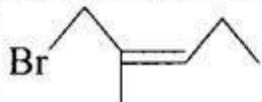
(ii) In this reaction, addition of  $\text{HBr}$  takes place on to the doubly bonded carbons of propene in accordance with Markownikoff's rule and electrophilic addition takes place.

(iii) In this reaction, the reactant is secondary halide. Here, halogen atom is substituted by hydroxyl ion. As it is secondary halide so it follows  $\text{S}_{\text{N}}1$  mechanism.

(iv) In this reaction, halogen atom is directly bonded to aromatic ring. So, it is nucleophilic aromatic substitution as  $\text{OH}^-$  group has substituted halogen of given compound.

(v) It is an elimination reaction. It follows Saytzeff elimination rule.

**Question 83. Match the structures given in Column 1 with the names given 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 |

**Solution:** (i → a), (ii → b), (iii → c), (iv → d)

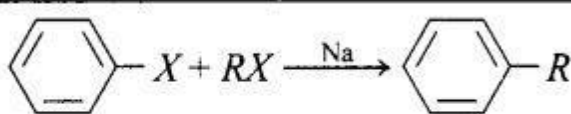
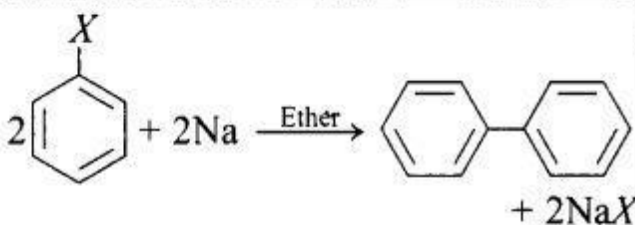
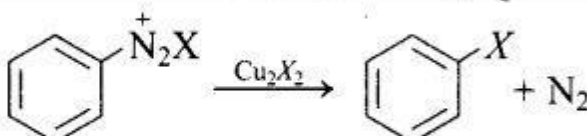
(i) The IUPAC name of compound (A) is 4-bromopent-2-ene.

(ii) The IUPAC name of compound (B) is 4-bromo-3-methylpent-2-ene.

(iii) The IUPAC name of compound (C) is 1-bromo-2-methylbut-2-ene.

(iv) The IUPAC name of compound (D) is 1-bromo-2-methylpent-2-ene.

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

| Column I |  | Column II |                       |
|----------|--|-----------|-----------------------|
| (i)      |                                       | (a)       | Fittig reaction       |
| (ii)     |                                       | (b)       | Wurtz-Fittig reaction |
| (iii)    |                                       | (c)       | Finkelstein reaction  |
| (iv)     | $\text{C}_2\text{H}_5\text{Cl} + \text{NaI} \xrightarrow{\text{dry acetone}} \text{C}_2\text{H}_5\text{I} + \text{NaCl}$ | (d)       | Sandmeyer reaction    |

**Solution:** (i → b), (ii → a), (iii → d), (iv → c)

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- (i) A mixture of an alkyl halide and aryl halides gives an alkylarene when treated with sodium in dry ether and this is called Wurtz-Fittig reaction.
- (ii) Aryl halides give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.
- (iii) Diazonium salt when treated with cuprous chloride or cuprous bromide gives chlorobenzene or bromobenzene. The reaction is known as Sandmeyer's reaction.
- (iv) Alkyl iodides are prepared by the reaction of alkyl chlorides with sodium iodide in dry acetone. The reaction is known as Finkelstein reaction.

### Assertion and Reason Type Questions

In the following questions, a statement of Assertion (A) followed by a statement of Reason (R) is given. Choose the correct option out of the choices given below each question:

- (a) Assertion and Reason both are correct and Reason is the correct explanation of Assertion.
- (b) Assertion and Reason both are wrong.
- (c) Assertion is correct but Reason is wrong.
- (d) Assertion is wrong but Reason is correct.
- (e) Assertion and Reason both are correct statements but Reason is not the correct explanation of Assertion.

**Question 86.**Assertion (A): Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.

Reason (R): Phosphorus chlorides give pure alkyl halides.

**Solution:** (b) Thionyl chloride is best halogen carrier to convert alcohol to alkyl halide because it gives byproducts in gaseous state. Thus, we get pure alkyl halide in this reaction.

**Question 87.**Assertion (A): The boiling points of alkyl halides decrease in the order:  $RI > RBr > RCl > RF$

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

**Solution:** (e) The given sequence of boiling point is correct:

$RI > RBr > RCl > RF$

Halides are polar molecules hence they have greater boiling point than hydrocarbons.



**Question 87. Assertion (A):** KCN reacts with methyl chloride to give methyl isocyanide

**Reason (R):**  $\text{CN}^-$  is an ambident nucleophile.

**Solution:** (d)  $\text{R}-\text{Cl} + \text{KCN} \rightarrow \text{R}-\text{CN} + \text{KCl}$

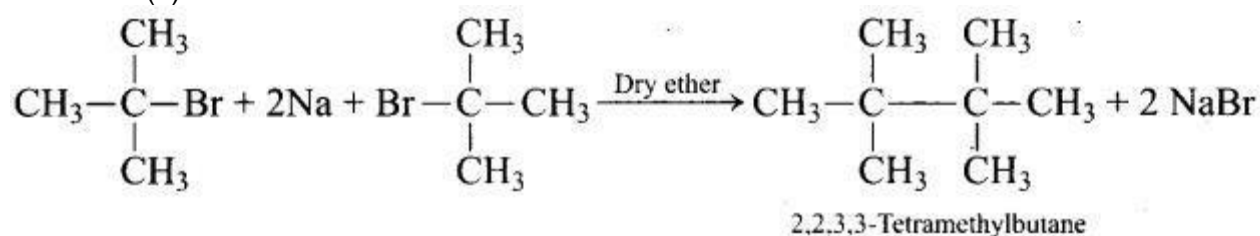
Alkylcyanide

Isocyanide is not obtained in this reaction.  $\text{CN}^-$  is an ambident nucleophile.

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

**Reason (R):** 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.

**Solution:** (a)



**Question 89. Assertion (A):** Presence of a nitro group at ortho or para position

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

**Solution:** (a) Nitro group being electron withdrawing group, decreases the electron density of ring hence increase the reactivity of haloarenes towards nucleophilic substitution.

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

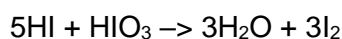
**Reason (R):** Halogen atom is a ring deactivator.

**Solution:** (e) Halogens are ortho-para directing due to (+M) or (+R) effect. Moreover, they are deactivating due to high electronegativity.

**Question 91. Assertion (A):** Aryl iodides can be prepared by reaction of arenes with iodine in the presence of an oxidizing agent.

**Reason (R):** Oxidising agent oxidises  $\text{I}_2$  into  $\text{HI}$ .

**Solution:** (c) Oxidising agent like  $\text{HIO}_3$  converts  $\text{HI}$  to  $\text{I}_2$ , otherwise  $\text{HI}$  may reduce aryl halide to arenes.







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

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

**Solution:** (a) Due to resonance, there is double bond character between benzene ring and halogen hence, nucleophilic substitution of aryl halide is difficult as compared to alkyl halide.

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

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

**Solution:** (c) Hydrolysis of 2-bromooctane follows  $S_N^2$  mechanism hence inversion in configuration takes place. This reaction does not involve the formation of carbocation intermediate.

**Question 94. Assertion (A):** Nitration of chlorobenzene leads to the formation of m-nitrochlorobenzene.

**Reason (R):**  $\text{NO}_2$  group is a w-directing group.

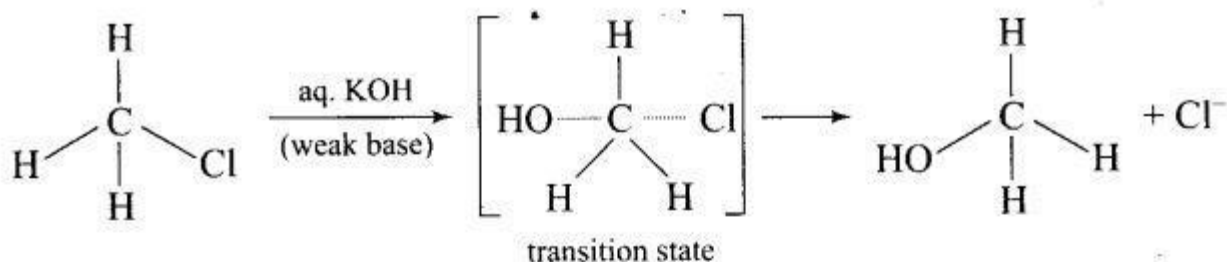
**Solution:** (d) Nitration of chlorobenzene gives ortho and para nitro chlorobenzene. However, nitro group is meta directing in nature.

### Long Answer Type Questions

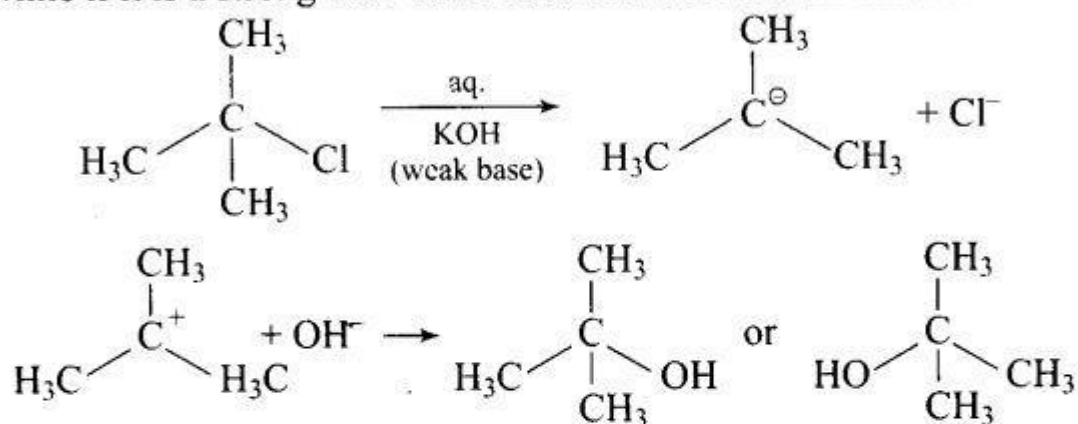
**Question 95. Some alkylhalides undergo substitution whereas some undergo elimination reaction on treatment with bases. Discuss the structural features of alkyl halides with the help of examples which are responsible for this difference.**

**Solution:** Case I: Primary alkyl halides follow  $S_N^2$  mechanism in which a nucleophile attacks from back to the halogen atom. A transition state is formed in which carbon is bonded to nucleophiles and finally halogen atom is pushed out. In  $S_N^2$  mechanism, substitution of

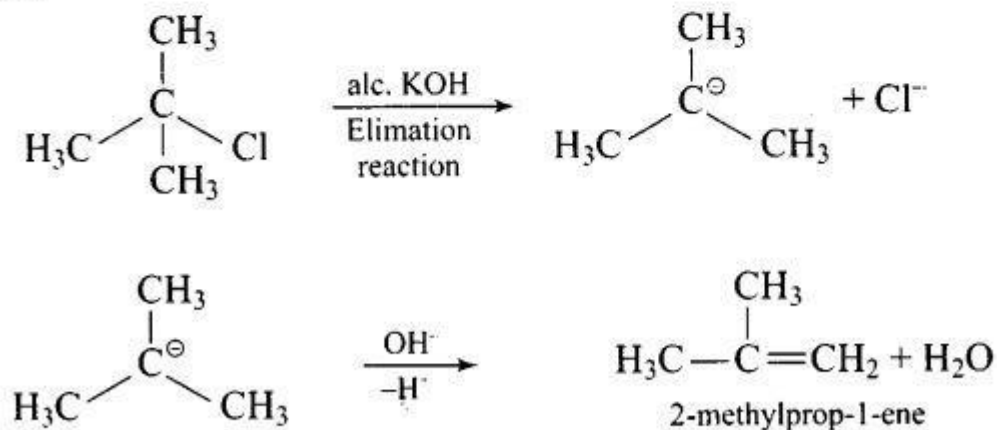
nucleophile takes place as follows:



**Case II:** Tertiary alkyl halides follow  $\text{S}_{\text{N}}1$  mechanism by forming  $3^\circ$  carbocations. Now, if the reagent used is a weak base then substitution occurs while if it is a strong base then instead of substitution elimination occurs.



Here, the reagent used is aq. KOH. It is a weak base so, substitution takes place.



As alc. KOH is a strong base, so elimination competes over substitution and alkene is formed.

**Case III:** Secondary alkyl halides can undergo substitution or elimination depending on type of solvent and temperature conditions.



**Question 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 minimize harmful effects of these compounds.

**Solution:** Uses of halogen containing compounds

Dichloromethane is used as a solvent, paint remover, propellant in aerosols, process solvent in the manufacture of drugs, metal cleaning and finishing solvent.

Trichloromethane is used as a solvent for fats, alkaloids, iodine and other substances.

Triodomethane is used as an antiseptic But some compounds of this class are responding for exposure of flora and fauna to more and more of UV light which causes destruction to great extent. These are as follows

(i) **Tetrachloromethane**

- When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to UV rays leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system. These UV rays cause damage to plants, and reduction of plankton populations in the ocean's photic zone.

(ii) **Freons**

- Freon-113 is likely to remain in the air long enough to reach the upper atmosphere. Here, it provides chlorine atoms which damage the ozone layer. Because of this depletion UV rays enters in our atmosphere and become responsible for damage to great extent.

(iii) **p – p' – Dichlorodiphenyl trichloroethane (DDT)**

- DDT is not completely biodegradable. Instead, it gets deposited in fatty tissues. If ingestion continues for a long time, DDT builds up within the animal and affect the reproductive system.

To minimise the harmful impacts of these compounds i.e., freons, hydrofluoro-carbons, fluorocarbons which are stable in the stratosphere should be used in aerosol propellants and air conditioning equipment.

Government has tightened law's on used of DDT. DDT was banned in the United States.

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

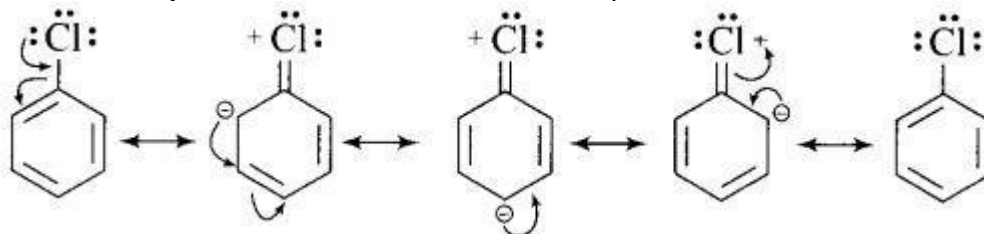
**Solution:** Aryl halides are less reactive towards nucleophilic substitution reaction due to the following reasons.

(i) In haloarenes, the lone pair of electron on halogen are in resonance with benzene ring.

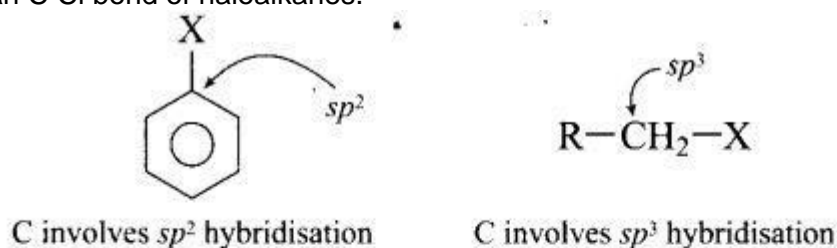
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So, C – Cl bond acquires partial double bond character which strengthen C – Cl bond and difficult to be substituted by nucleophile.

Therefore, they are less reactive towards nucleophilic substitution reaction.

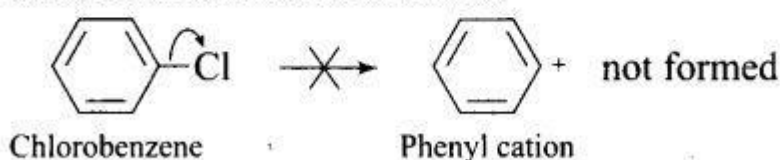


(ii) In haloarenes, the carbon atom attached to halogen is  $sp^2$  hybridised. The  $sp^2$  hybridised carbon is more electronegative than  $sp^3$  hybridised carbon. This  $sp^2$ -hybridised carbon in haloarenes can hold the electron pair of C – X bond more tightly and make this C – Cl bond shorter than C Cl bond of haloalkanes.



Since, it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes.

(iii) In haloarenes, the phenyl cation is not stabilised by resonance therefore  $S_N1$  mechanism cannot be followed.

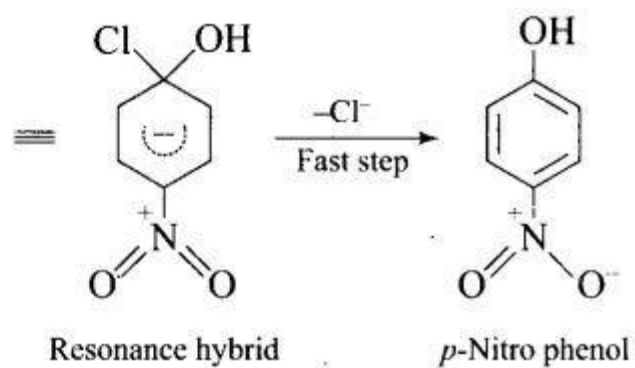
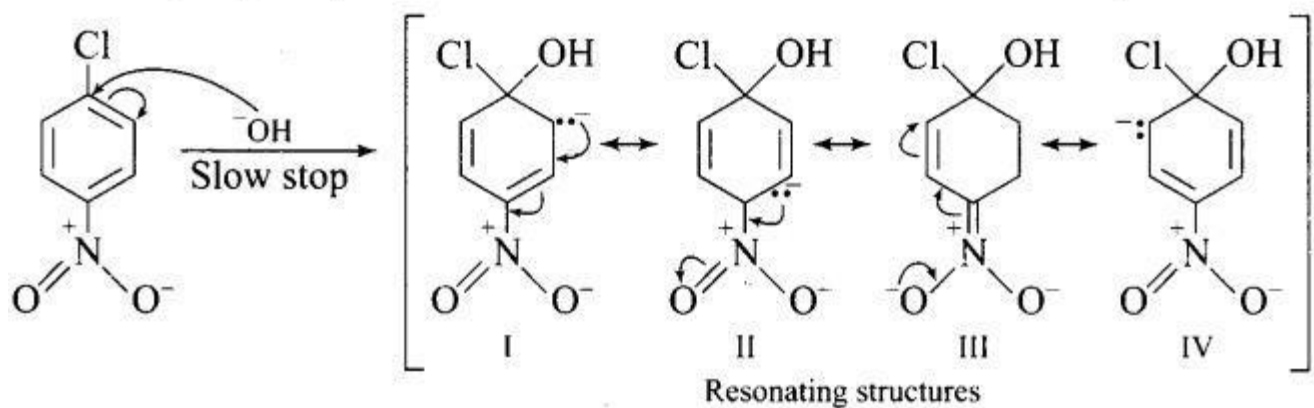


(iv) Because of the repulsion between the nucleophile and electron rich arenes, aryl halides are less reactive than alkyl halides.

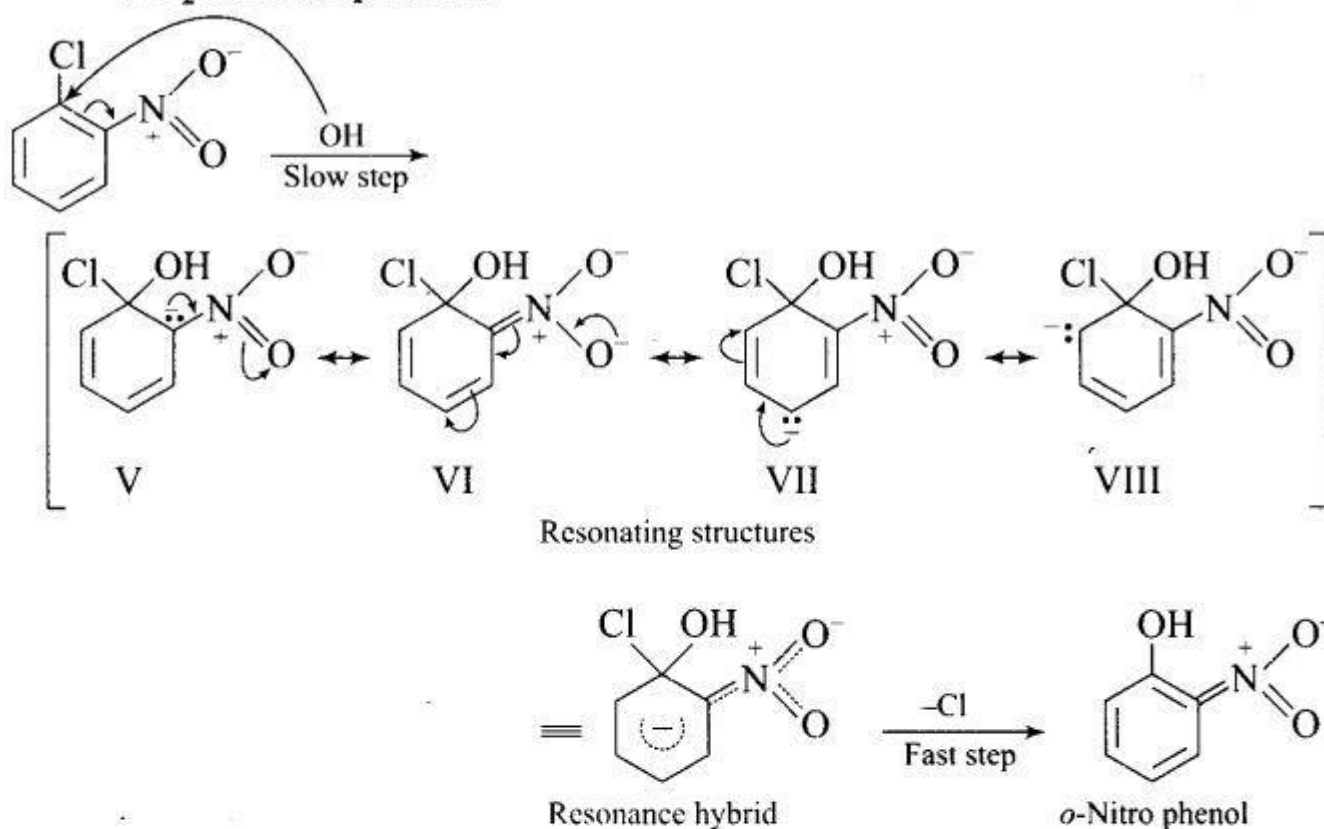
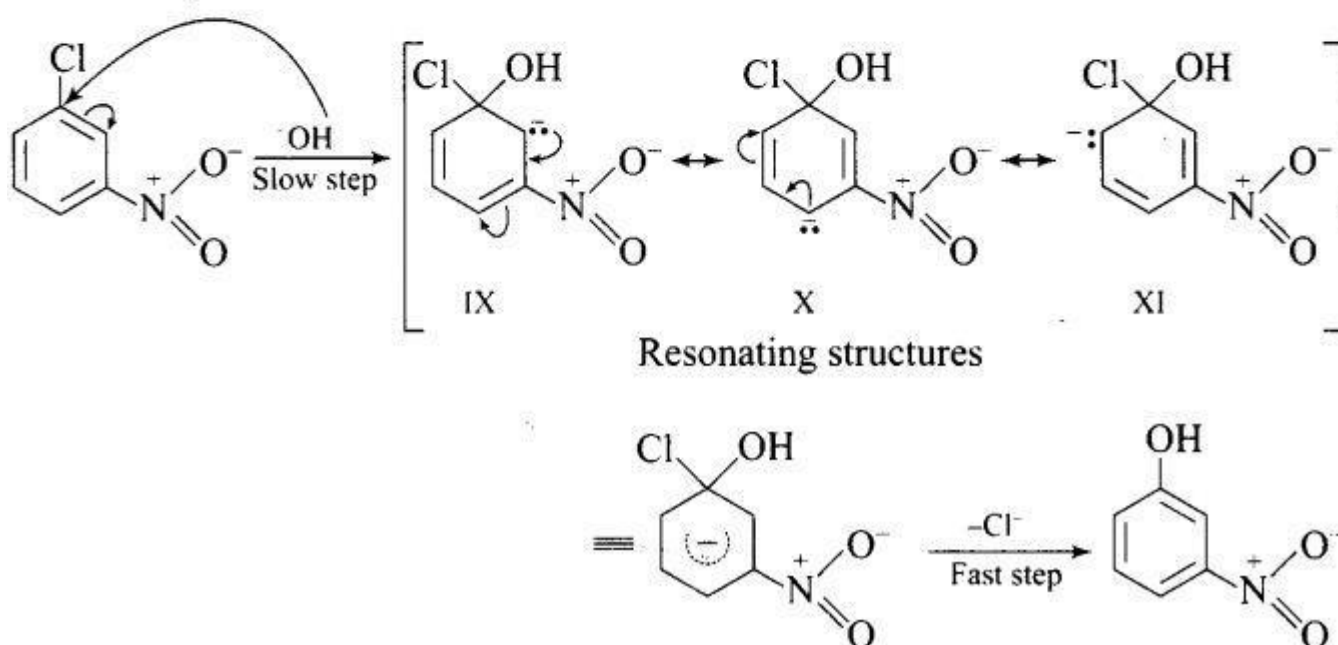
#### How to increase reactivity

The reactivity of aryl halides can be increased by the presence of an electron withdrawing group ( $-NO_2$ ) at ortho and para positions. No effect is observed by the presence of electron withdrawing group at meta-position. Mechanism of the reaction is as depicted with OH<sup>-</sup> ion: The presence of  $NO_2$  groups at ortho and para positions withdraws electron density from the benzene ring and therefore, facilitates the attack of the nucleophile on haloarenes. The carbanion, thus formed is stabilized through resonance as shown below:

**NO<sub>2</sub> at para position**





**NO<sub>2</sub> at ortho position****NO<sub>2</sub> at meta position**

It is clear from above structure that in case of *o*- and *p*-chlorobenzenes, on the resonating structures (II in case of *p*-nitro chlorobenzene and V in case of *o*-chlorobenzene) bear a negative charge on the carbon atom bearing the NO<sub>2</sub> group. Therefore, these



carbanions are stabilized by the  $\text{-NO}_2$  groups as well as  $\pi$ -electrons of the benzene ring. However, in case of m-nitrochlorobenzene, none of the resonating structures bear the negative charge on carbon atom bearing the  $\text{-NO}_2$  group. Therefore, the nitro group at meta position does not stabilize the negative charge but the carbanion is stabilized only by the p-electrons of the benzene ring. In other words, the carbanions formed from o-nitrochlorobenzene and p-nitrochlorobenzene are most stable than that formed from m-nitrochlorobenzene.

Thus, the presence of electron withdrawing groups at o- and p-positions (but not at m-positions) w.r.t. halogen atom activates the aryl halides towards nucleophilic substitution reaction.