

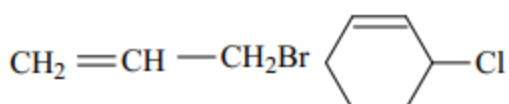
## CHAPTER - 18

# HALOALKANES AND HALOARENES

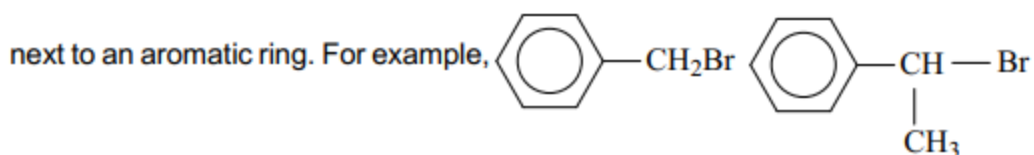
### SYNOPSIS

**Alkyl halides** are the compounds in which one hydrogen atom of alkanes is replaced by a halogen atom. They are classified as primary, secondary and tertiary alkyl halides depending on whether the halogen atom is attached to a primary, secondary or tertiary carbon atom respectively.

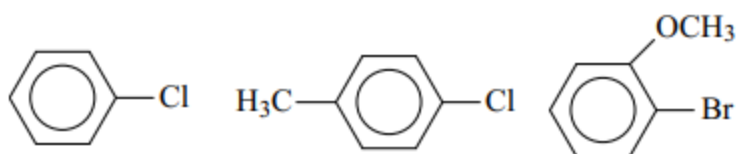
**Allylic halides** are the compounds in which the halogen atom is bonded to an  $sp^3$ -hybridized carbon next to carbon-carbon double bond. For example,



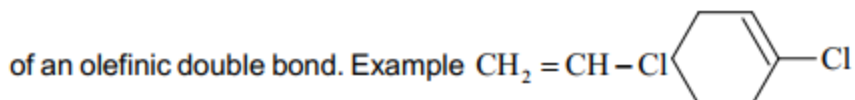
**Benzylic halides** are the compound in which halogen atom is bonded to  $sp^3$ -hybridized carbon atom



**Aryl halides** are the compounds in which halogen atom is attached to an  $sp^2$ -hybridized carbon atom of an aromatic ring.

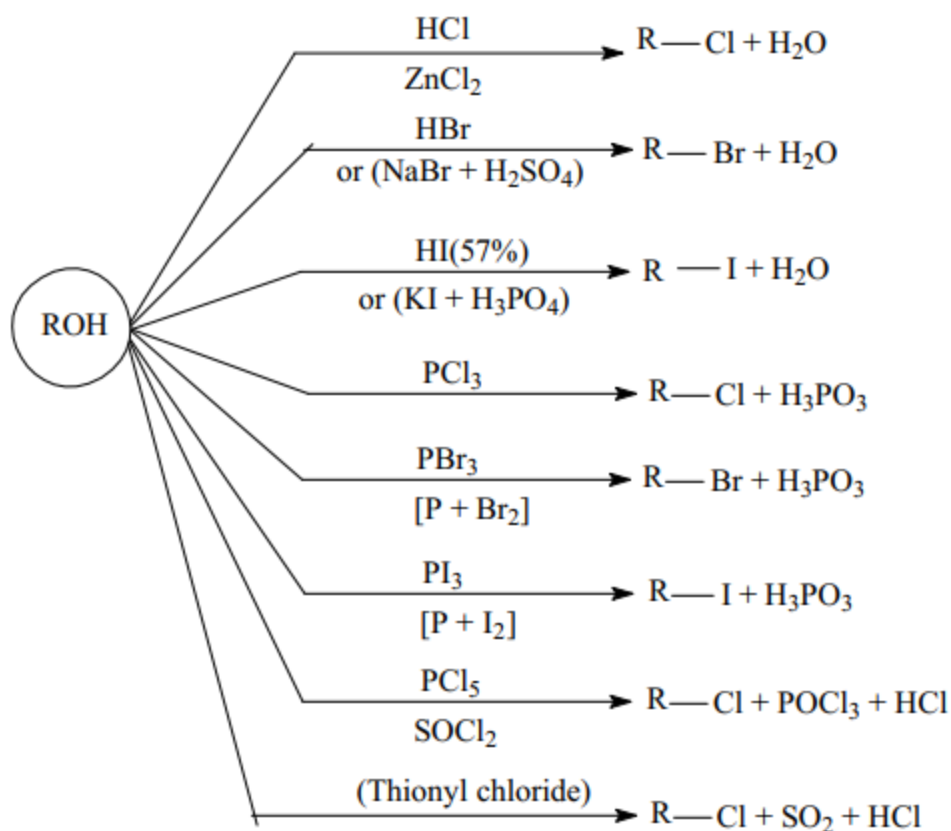


Vinyl halides are the compounds in which halogen atom is attached to an  $sp^2$ -hybridised carbon atom



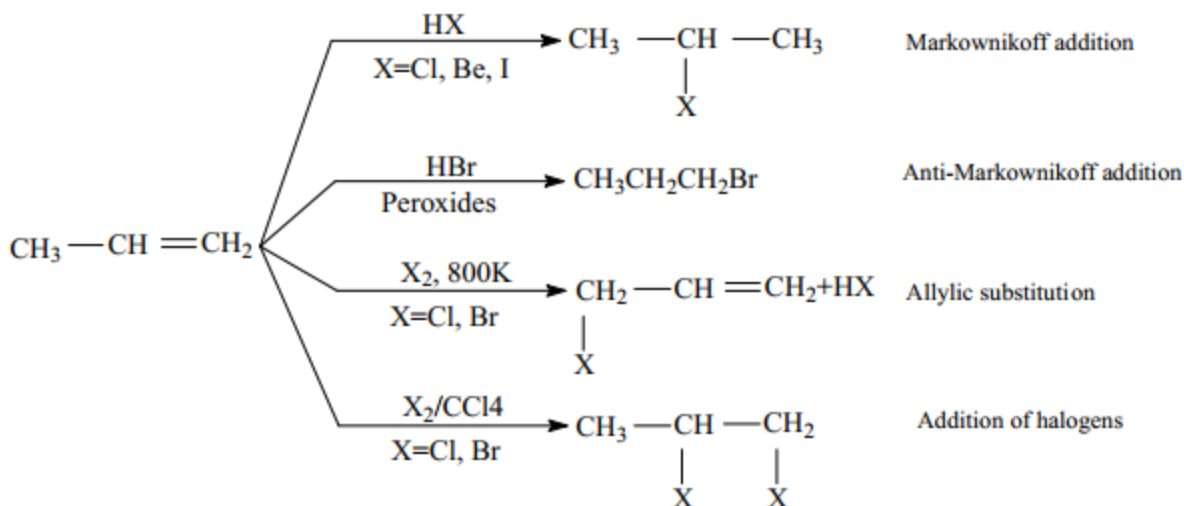
**METHODS OF PREPARATION OF ALKYL HALIDES**

## 1. From Alcohols

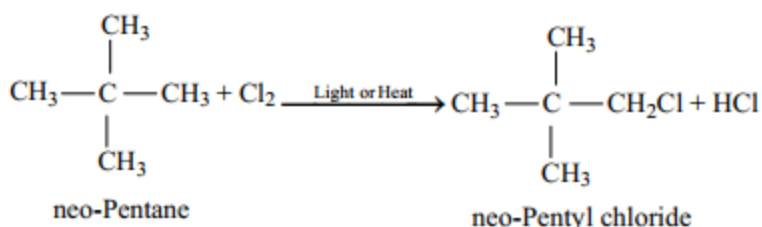
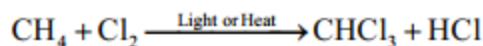


Thionyl chloride is preferred in the preparation of alkyl chlorides because in this case the side products are gaseous and can be easily expelled during distillation

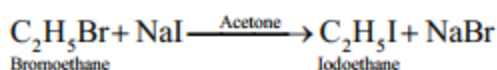
## 2. From Alkenes



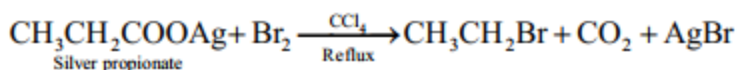
From alkanes



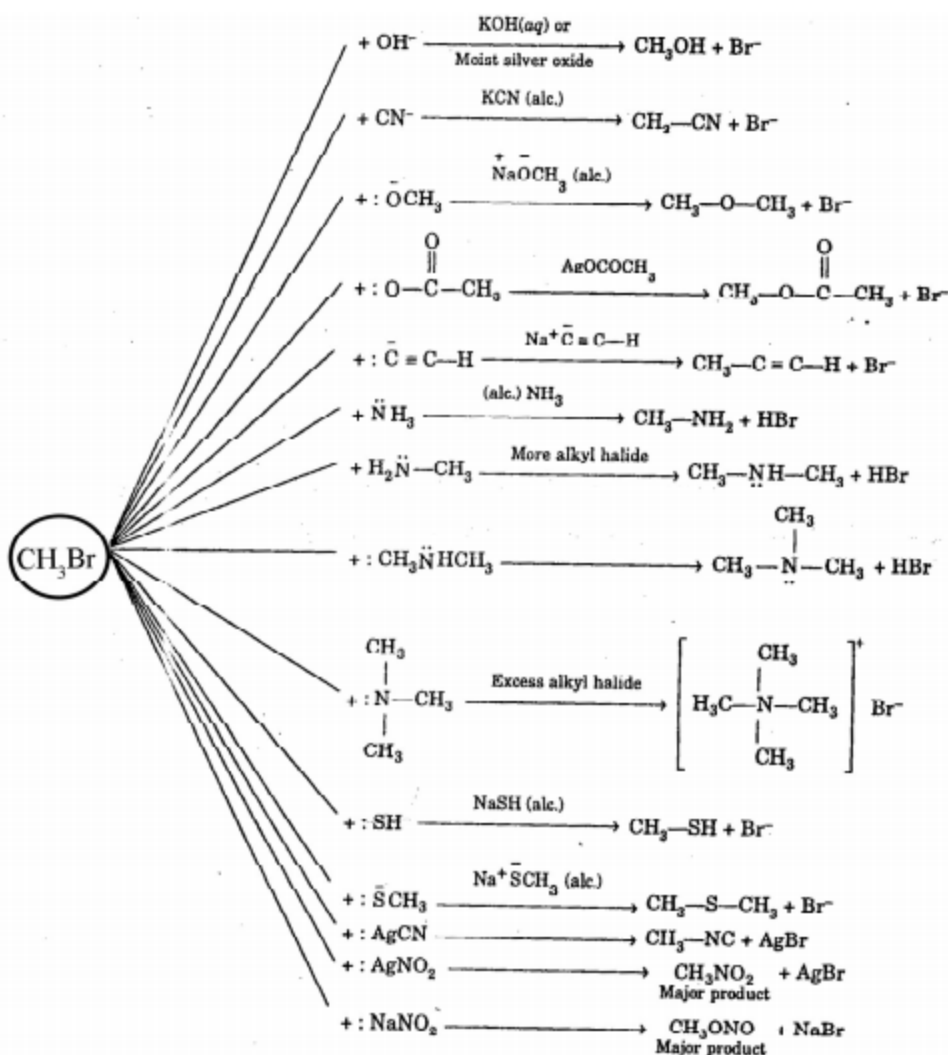
**By halide exchange (Finkelstein Reaction)**



**From silver salt of fatty acids (Hunsdiecker reaction)**

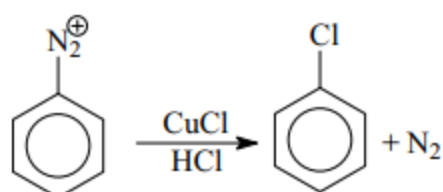


**Chemical properties of alkyl halides**

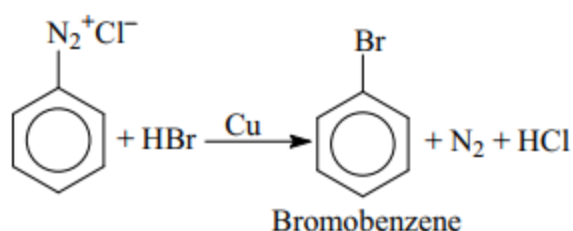
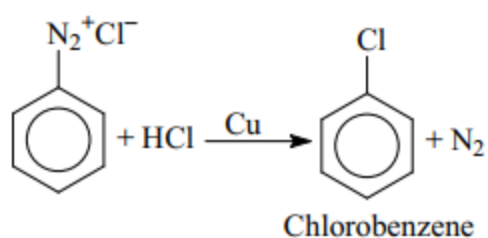




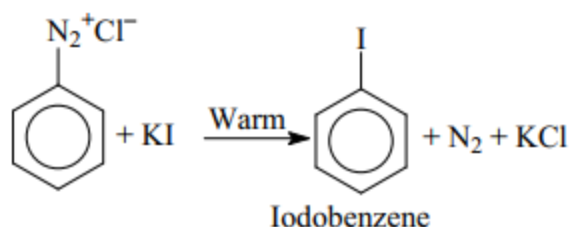
2. **From diazonium compounds.** In this method diazonium salt is treated with CuCl and HCl or CuBr and HBr to give the corresponding haloarene.



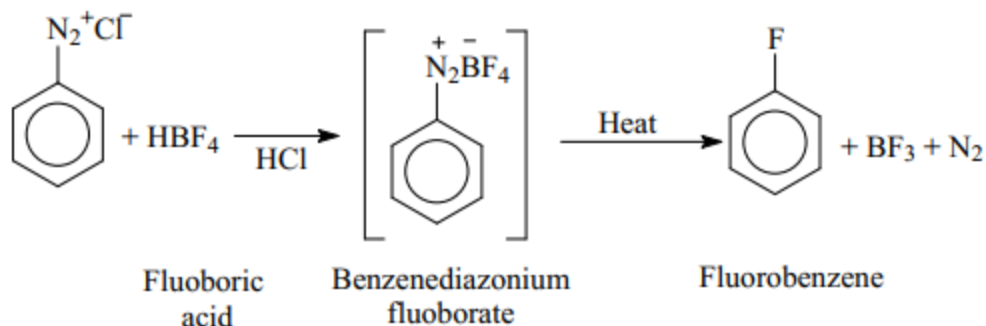
The reaction of diazonium salts with CuCl and CuBr is known as Sandmeyer reaction. If instead of CuCl and CuBr, copper powder and HCl or HBr is used, the reaction is called Gatterman's reaction.



**Iodoarenes** are obtained by the reaction of benzene diazonium salts with KI



**Fluoroarenes** are obtained by the reaction of corresponding diazonium salt with fluoboric acid to produce diazonium fluoborate which on heating produces fluorobenzene.



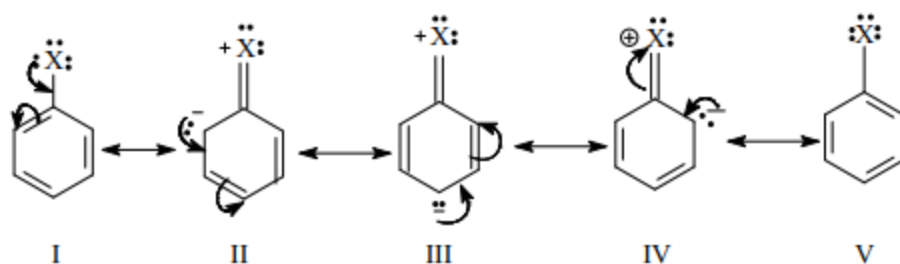
This reaction is called Balz-Schiemann reaction.

**REACTIONS OF ARYL HALIDES****1. Nucleophilic Substitution Reactions**

Aryl halides undergo nucleophilic substitution reactions much less readily than the alkyl halides. This can be explained as follows:

**Stabilization by Resonance**

Aryl halides are resonance hybrid of the following structures:



The contributing structures, II, III and IV indicate that C–X bond has partial double bond character. As a result the C–X bond in halobenzene is shorter and hence, stronger as compared to that in alkyl halides. Thus, cleavage of C–X bond in halobenzene become difficult which makes it less reactive towards nucleophilic substitution.

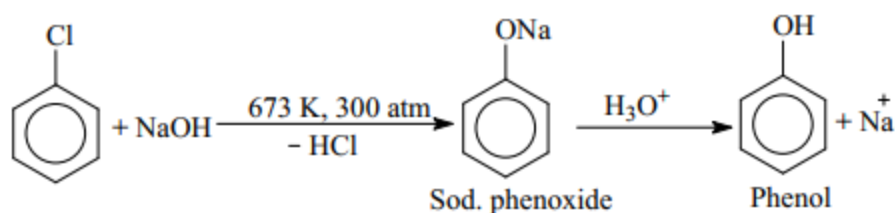
(b)  $sp^2$  hybrid state of the carbon atom carrying halogen : In aryl halides carbon atom, carrying halogen is  $sp^2$  hybridized where as alkyl halides it is  $sp^3$  hybridized.  $sp^2$  hybrid orbital is of smaller size than  $sp^3$  hybrid orbital because of greater s-character and hence the bond formed by its overlap will have smaller bond length and greater strength. Therefore, aryl halides having stronger C–Cl bond are less reactive towards nucleophilic substitution reactions than alkyl halides.

On similar lines we can explain why vinyl halides are less reactive than alkyl halides.

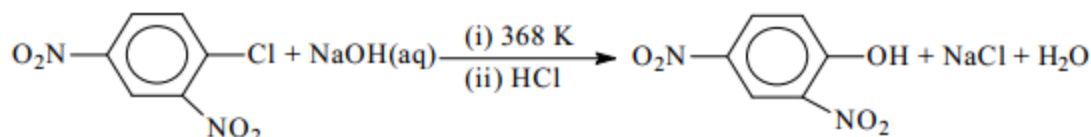


Here also carbon-halogen bond acquires double character due to contribution from structure (II).

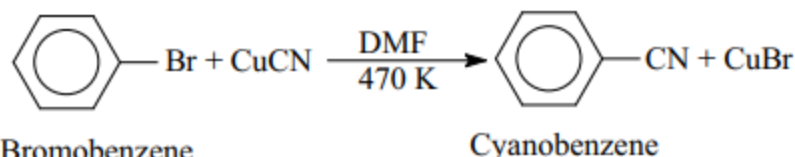
Because of less reactivity aryl halides undergo nucleophilic substitution reactions under drastic conditions.

**I. REPLACEMENT BY HYDROXY GROUP**

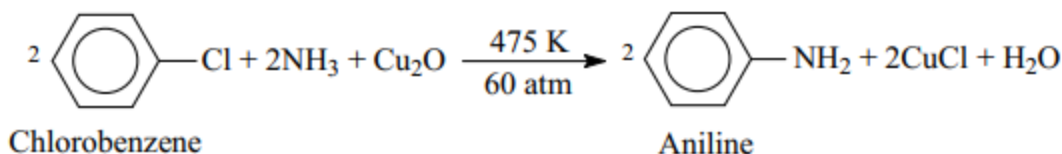
The reactivity of the haloarenes towards nucleophilic substitution reaction increases if some electron withdrawing group such as nitro, cyano, carboxyl group is attached to the ring.



2. **Replacement by cyano group**

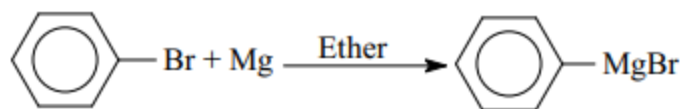


3. **Replacement by amino group**



II. **REACTION WITH METALS**

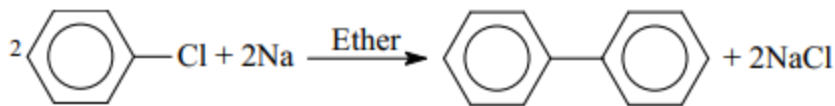
1. **Action with Magnesium (Formation of Grignard Reagents)**



Bromobenzene Phenyl magnesium bromide

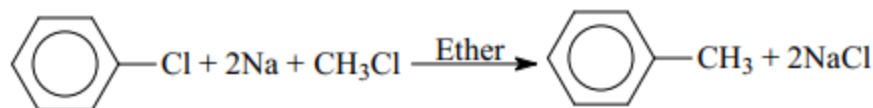
Aryl chlorides, however, form Grignard's reagent in the presence of tetrahydrofuran (THF) as solvent.

2. **Reaction with sodium (Fittig Reaction)**



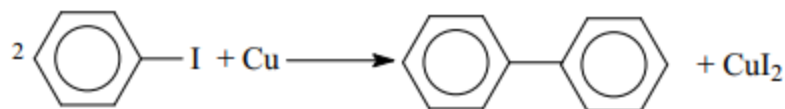
Chlorobenzene Diphenyl

However, aryl halides when treated with haloalkane and sodium in dry ether undergo Wurtz Fittig reaction.



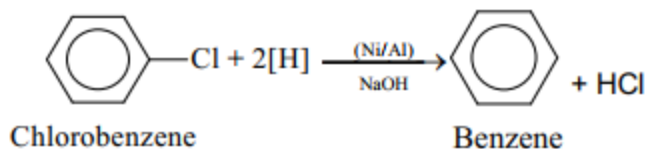
Chlorobenzene Toluene

3. **Reaction with copper powder (Ulmann reaction)**



Iodobenzene Diphenyl

III. **REDUCTION**





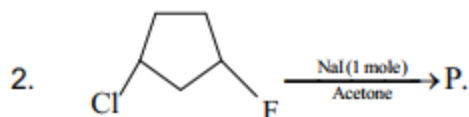
**PART-I (JEE MAIN)****SECTION-I- Straight objective type questions**

1. Assertion : Halogen acids react with alcohols to form haloalkanes.

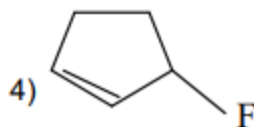
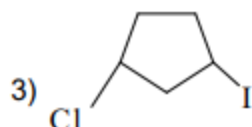
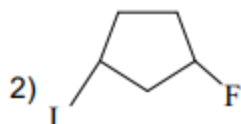
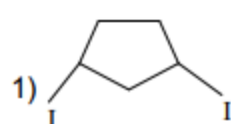
Reason : Order of reactivity of halogen acids is  $\text{HCl} > \text{HBr} > \text{HI}$

Choose the correct option

- 1) Both assertion and reason are true and the reason is the correct explanation of the assertion.
- 2) Both assertion and reason are true but reason is not the correct explanation of the assertion.
- 3) Assertion is true but reason is false.
- 4) Assertion is false but reason is true.



The major product P is



3. The set of reagents that is not suitable for the conversion of aniline to halobenzene is

1)  $\text{HNO}_2$ ;  $\text{CuBr}$       2)  $\text{HNO}_2$ ;  $\text{Cu/HCl}$       3)  $\text{HNO}_2$ ;  $\text{HBF}_4$ ;  $\Delta$       4)  $\text{HNO}_2$ ;  $\text{CuI}_2$

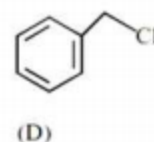
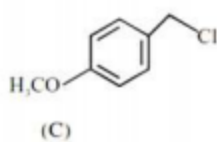
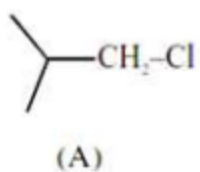
4. **Assertion** : Both aryl halides and vinyl halides do not easily undergo nucleophilic substitution.

**Reason** : The carbon-halogen bond in both aryl halides and vinyl halides acquire a partial double bond character due to resonance

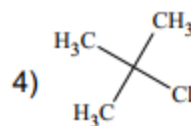
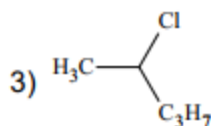
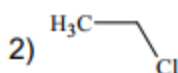
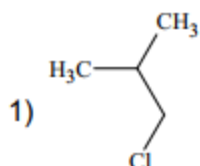
- 1) Both assertion and reason are true and the reason is the correct explanation of the assertion.
- 2) Both assertion and reason are true but reason is not the correct explanation of the assertion.
- 3) Assertion is true but reason is false.
- 4) Assertion is false but reason is true.



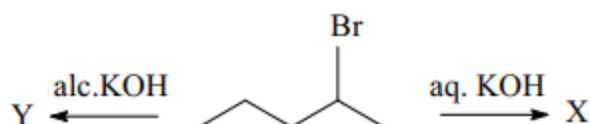
5. Increasing order of reactivity of the following compounds towards  $S_N1$  reaction is:



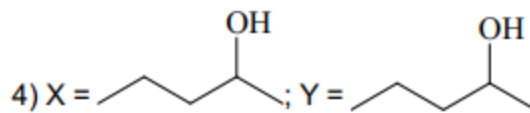
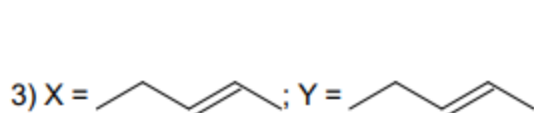
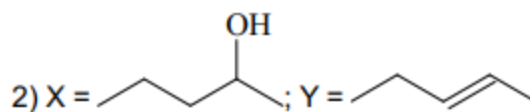
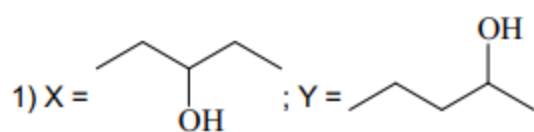
- 1)  $B < C < D < A$       2)  $A < B < D < C$       3)  $B < A < D < C$       4)  $B < C < A < D$
6. Which one of the following compounds does most readily undergo nucleophilic substitution by  $S_N2$  mechanism?

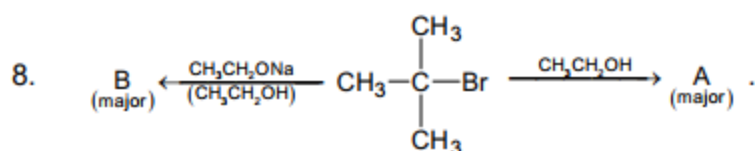


7. X and Y are major products in the following reactions

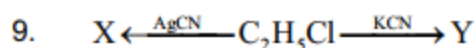
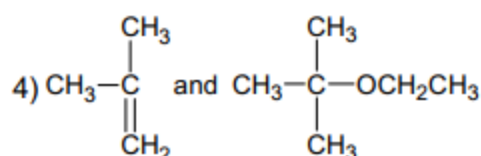
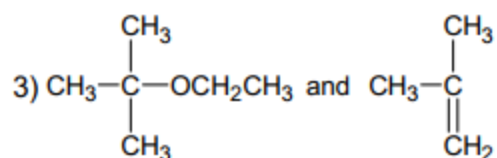
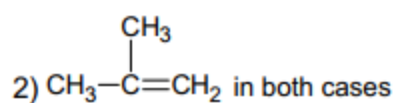
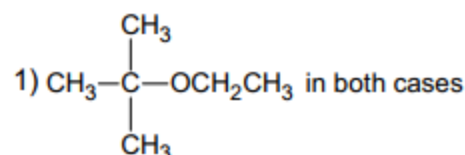


Identify the correct option

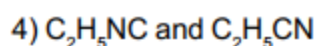
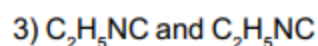
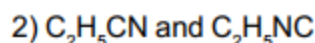
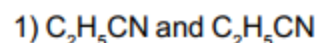




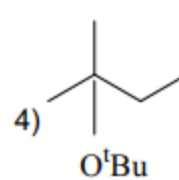
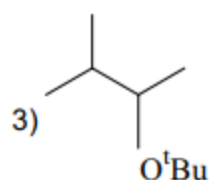
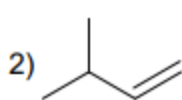
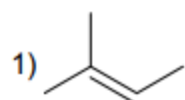
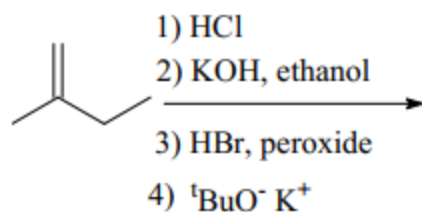
A and B are respectively.



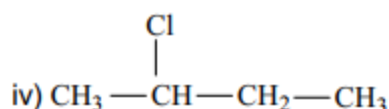
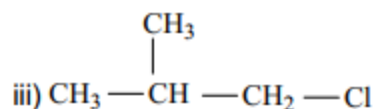
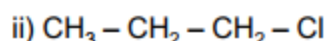
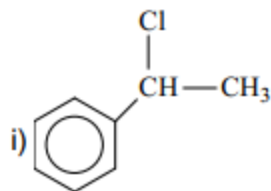
X and Y are respectively



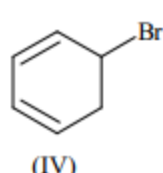
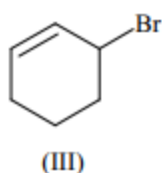
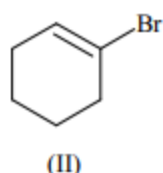
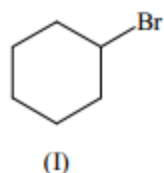
10. Identify the major product in the following reactions scheme



11. Which of the following compounds will undergo racemisation upon hydrolysis with KOH solution?



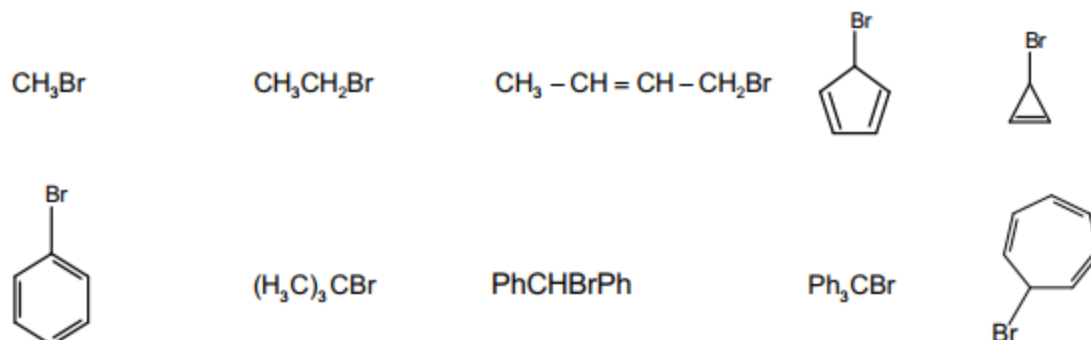
- 1) i and ii      2) ii and iii      3) ii and iv      4) i and iv
12. Which of the following compounds is dehydrobrominated with alcoholic KOH at the fastest rate?



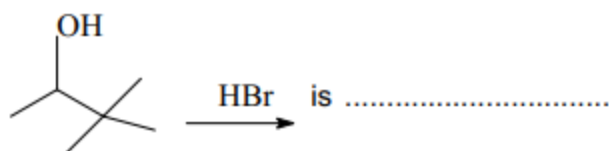
- 1) IV      2) II      3) III      4) I
13. Replacement of  $-\text{Cl}$  group of chlorobenzene with  $-\text{OH}$  group to produce phenol requires drastic conditions but replacement of  $-\text{Cl}$  group of 2,4,6-trinitrochlorobenzene occurs readily. The reason is :
- 1)  $-\text{NO}_2$  makes the ring electron rich at ortho and para positions  
2)  $-\text{NO}_2$  withdraws electron from meta position  
3)  $-\text{NO}_2$  is meta directing in nucleophilic aromatic substitution  
4)  $-\text{NO}_2$  withdraws electron from ortho and para positions
14. Which of following is incorrect arrangement with respect to the property indicated against it?
- 1) p-dichlorobenzene > o-dichlorobenzene > m-dichlorobenzene      - Melting point  
2)  $\text{CH}_3(\text{CH}_2)_2\text{CH}_2\text{Cl} > (\text{CH}_3)_2\text{CHCH}_2\text{Cl} > (\text{CH}_3)_3\text{CCl}$       - Boiling point  
3)  $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$       - Density  
4)  $\text{CH}_3-\text{F} > \text{CH}_3-\text{Cl} > \text{CH}_3-\text{Br} > \text{CH}_3-\text{I}$       - Dipole moment
15. Chloroform is slowly oxidised by air in the presence of light to form an extremely poisonous gas X. X is
- 1) Carbonyl chloride      2) Carbonmonoxide      3) Formyl chloride      4) Chlorine

**SECTION-II - Numerical Type Questions**

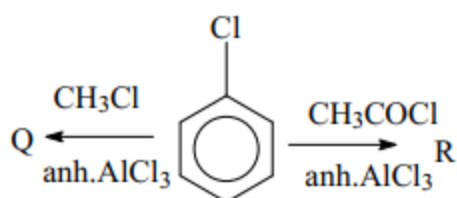
16. The total number of alkenes (including stereoisomers) obtained on treating 2-bromopentane with alcoholic KOH is —
17. How many of the following give(s) a white precipitate when treated with  $\text{AgNO}_3$  solution?



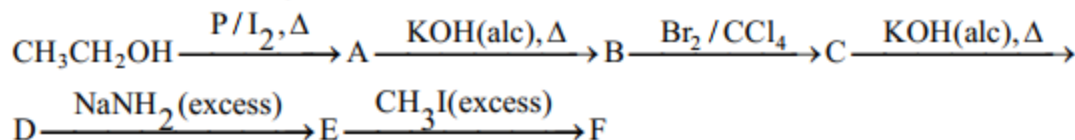
18. Total number of secondary carbon atom(s) present in the major product of the following reaction



19. Total number of  $\text{sp}^2$  hybridised carbon atom(s) present in major products 'Q' and 'R' of the following reaction is —



20. Consider the following sequence of reactions

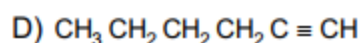
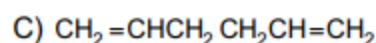
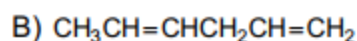
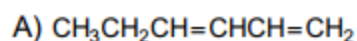
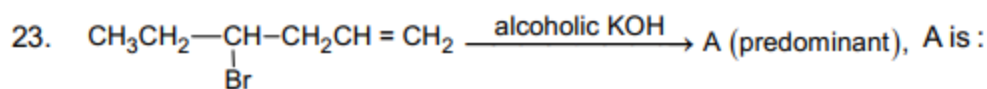
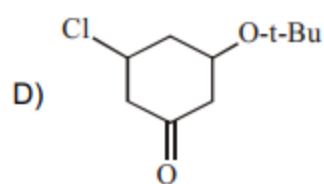
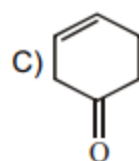
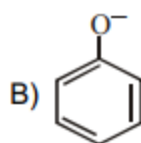
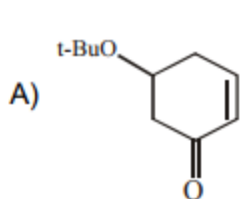
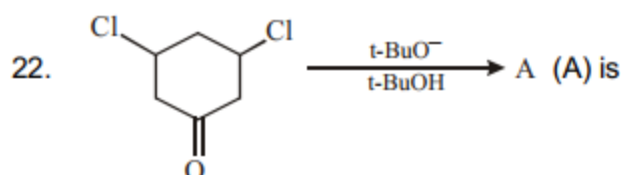
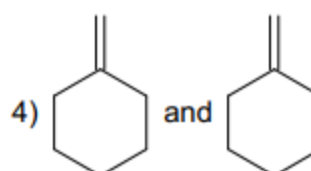
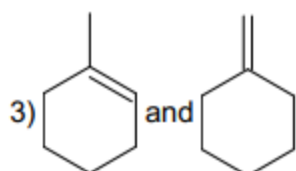
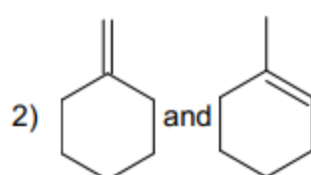
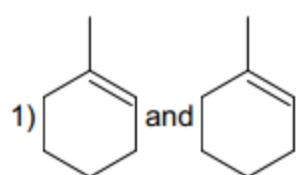
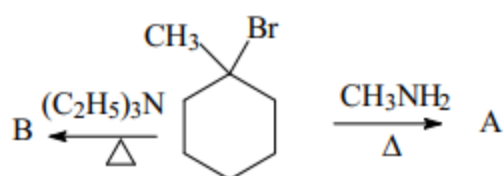


The number of carbon atoms present in compound F is \_\_\_\_\_

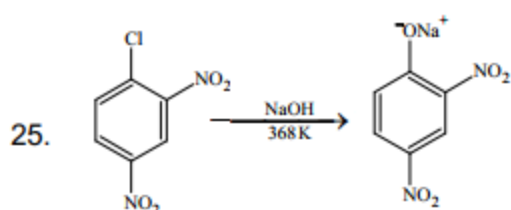
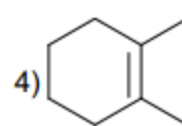
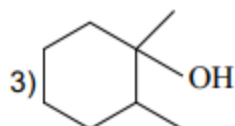
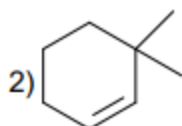
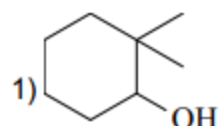
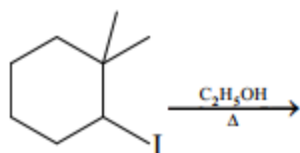
**PART-II (JEE ADVANCED)**

**Section-III - Only one option correct type**

21. The major products A & B in the following reactions are respectively



24. Find the major product of the following reaction



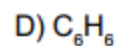
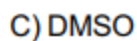
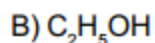
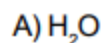
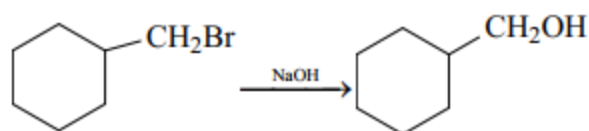
The above transformation proceeds through

- A) Electrophilic addition – elimination mechanism
- B) Electrophilic elimination – addition mechanism
- C) Nucleophilic addition - elimination mechanism
- D) Benzyne mechanism

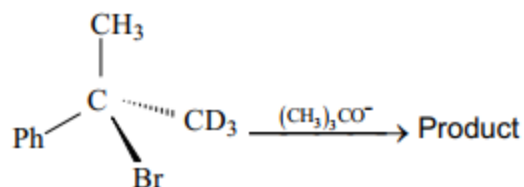
26. Neopentyl alcohol on treatment with HBr gives

- A) neopentyl bromide
- B) 2-bromo-2-methylbutane
- C) 2-methyl-2-butene
- D) 2-methyl-1-butene

27. The most suitable solvent for the reaction given below is



28. Which of the following options correctly describes the reaction shown below?



- A) It involves inversion of configuration      B) It involves retention of configuration  
C) It involves racemisation      D) It involves loss of chirality

**Section IV - One or more option correct type**

29. (–) 2-methylbutan-1-ol on heating with conc. HCl gives (+)1-chloro-2-methylbutane by  $S_N2$  mechanism. Which of the following statements is/are correct?

- A) Reaction proceeds through retention of configuration at stereocentre  
B) Reaction proceeds through inversion of configuration at stereocentre  
C) Reaction proceeds in single step without the formation of an intermediate  
D) Reaction proceeds through a carbocation intermediate

30. Consider an  $S_N1$  reaction



The rate of the above reaction will be —

Choose the correct option(s)

- A) Doubled on doubling the concentration of NaOH  
B) Halved on reducing the concentration of RCl to half  
C) Decreased on increasing the temperature of the reaction  
D) Unaffected by increasing the temperature of the reaction

31. Consider the following statements

Statement-I : Benzene reacts with ICl in presence of  $AlCl_3$  to produce chlorobenzene.

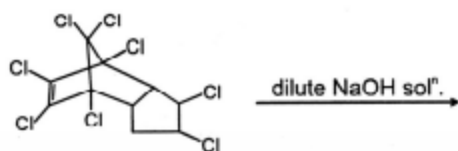
Statement-II : ICl reacts with  $AlCl_3$  to produce  $Cl^+$ .

Choose the correct option(s)

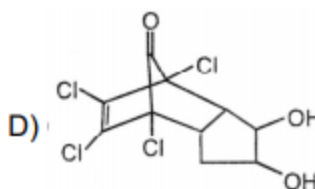
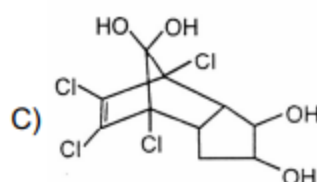
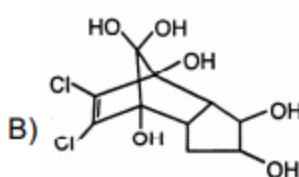
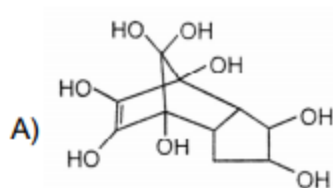
- A) Statement-I is correct  
B) Statement-II is incorrect  
C) Statement-II is correct  
D) Statement-I is incorrect



32. The insecticide chlordane (shown below) is warmed with dilute NaOH solution for some time.

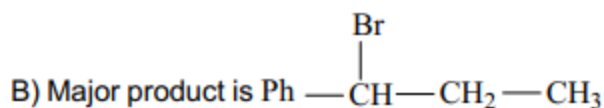
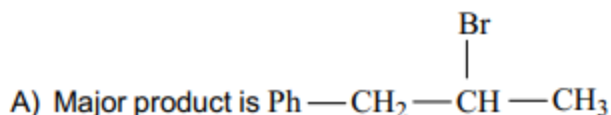


The compound(s) that may not be formed in the above reaction is/are



33. Consider the reaction of 3-phenylpropene with HBr.

Choose the correct option(s)



C) It is an electrophilic addition reaction

D) It is a nucleophilic addition reaction

34. On hydrolysis with aqueous KOH,

A) ethylidene chloride gives acetaldehyde

B) ethylene dichloride gives ethylene glycol

C) ethylene dichloride gives acetaldehyde

D) ethylidene chloride gives ethyne

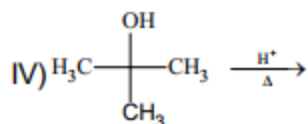
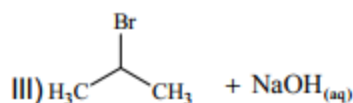
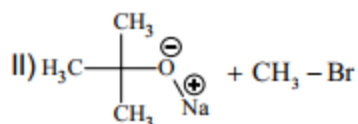
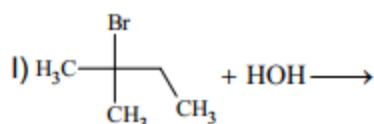
### Section V - Numerical type questions

35. How many of the following aryl halides undergo(es) nucleophilic substitution at a slower rate than chlorobenzene on treatment with NaOH?  
1-chloro-2-nitrobenzene, 1-chloro-4-nitrobenzene, o-chlorotoluene, m-chlorotoluene, p-chlorotoluene, p-chloromethoxybenzene, 4-chloro-N,N-dimethylaniline, 2,4-dinitrochlorobenzene, benzyl chloride.
36. How many moles of gases are liberated when one mole of  $C_2H_5OH$  completely reacts with excess of thionyl chloride?
37. Tert-butyl chloride when treated with sodium in dry ether gives an alkane 'A'.  
Total number of monochloro derivatives (including stereoisomers) possible for 'A' is —
38. How many alkenes (including stereoisomers) are formed in the reaction of 1-bromo-2-methylbutane with sodium ethoxide in ethanol?

### Section-VI - Matrix match type

39. Match the following

#### Column-I (Reaction)



#### Column-II (Product)

P) Ether

Q) Secondary alcohol

R) Tertiary alcohol

S) Alkene

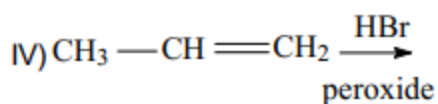
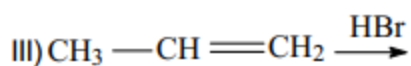
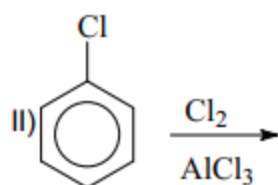
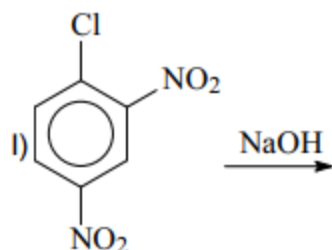
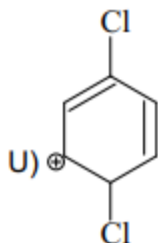
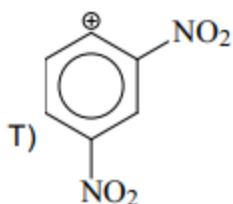
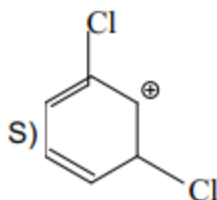
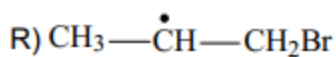
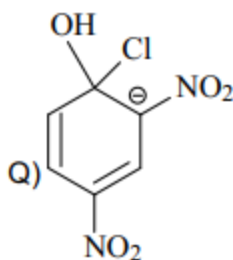
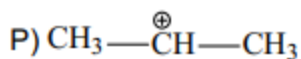
A) I - R, II - P, III - Q, IV - S

B) I - R, II - S, III - Q, IV - S

C) I - P, II - R, III - Q, IV - S

D) I - R, II - P, III - Q, IV - P

40. Match the following

**Column I (Reaction)**

**Column II (Intermediate)**


A) I - Q, II - U, III - P, IV - R

C) I - T, II - S, III - P, IV - R

B) I - Q, II - S, III - P, IV - R

D) I - T, II - S, III - R, IV - P