

NEET | JEE

ESSENTIALS

Class XII

Maximise your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 5

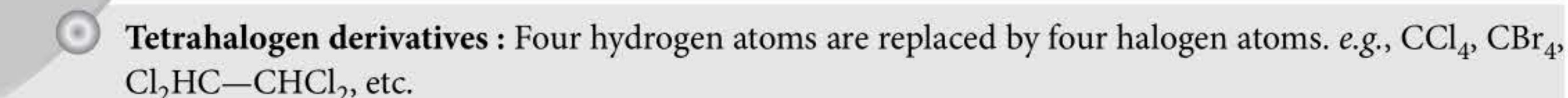
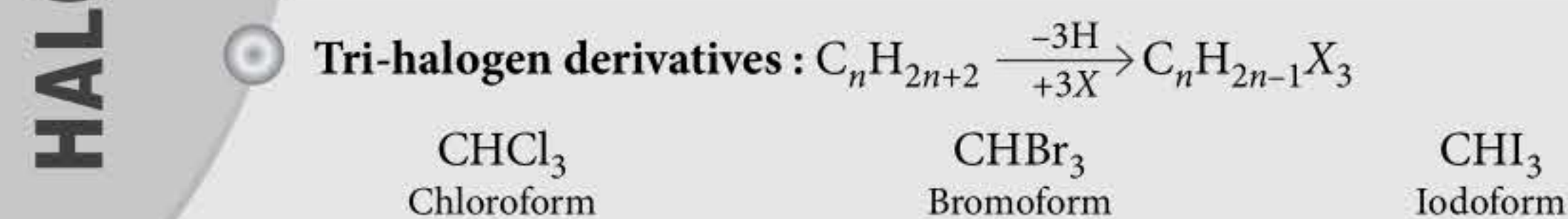
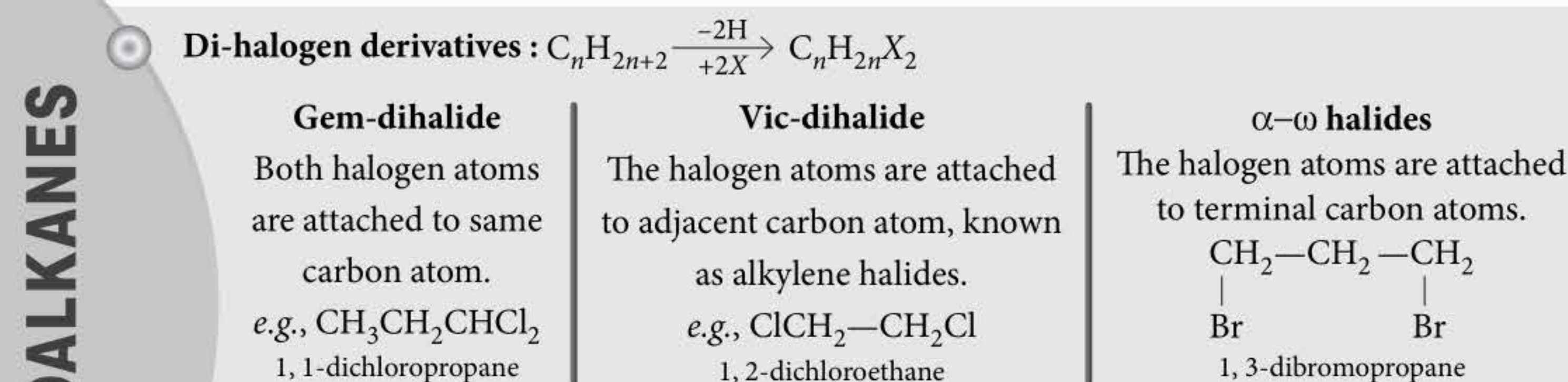
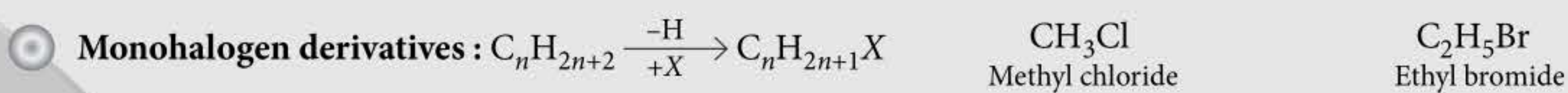
Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers

HALOALKANES AND HALOARENES

HALOALKANES

INTRODUCTION

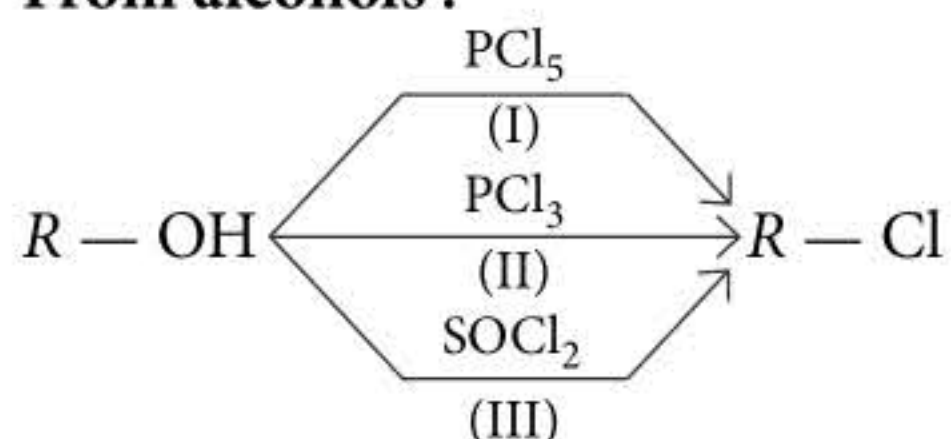
- Compounds derived from alkanes by the replacement of one or more hydrogen atoms by the corresponding number of halogen atoms are termed as halogen derivatives of alkanes or haloalkanes.



HALOALKANES

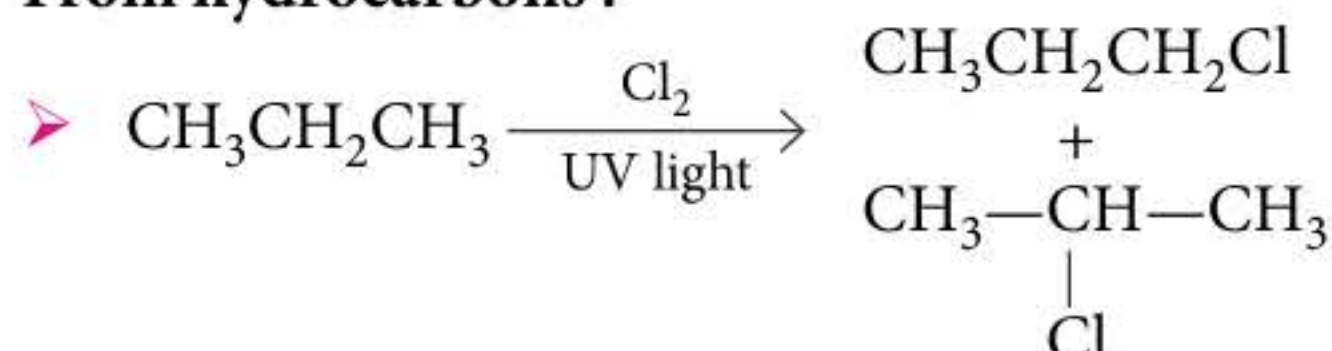
PREPARATION

- From alcohols :



Most preferred method is (III) because other products of this reaction (SO_2 and HCl) are gaseous and can easily escape.

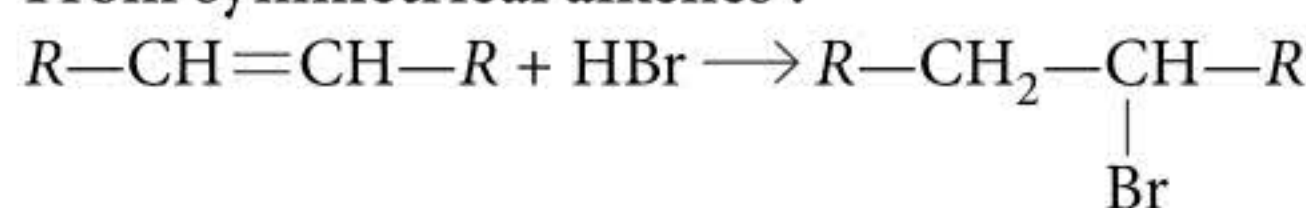
- From hydrocarbons :



- Free radical mechanism is followed.
- Order of ease of substitution : $3^\circ > 2^\circ > 1^\circ$ (alkyl)
Benzylic \approx allylic $>$ alkyl $>$ vinylic \approx aryl

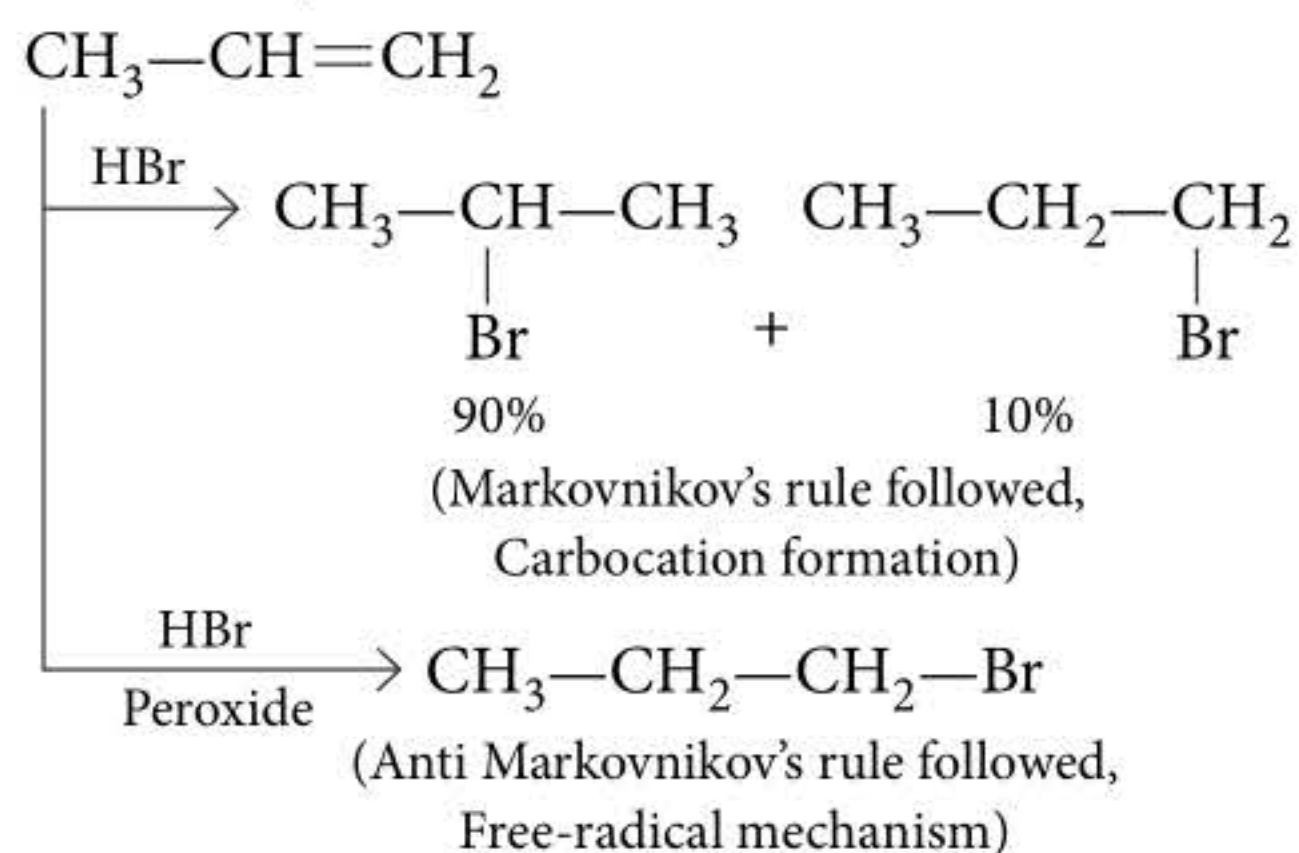
- From alkene (by HX addition) :

- From symmetrical alkenes :



(Single product obtained)

- From unsymmetrical alkenes :

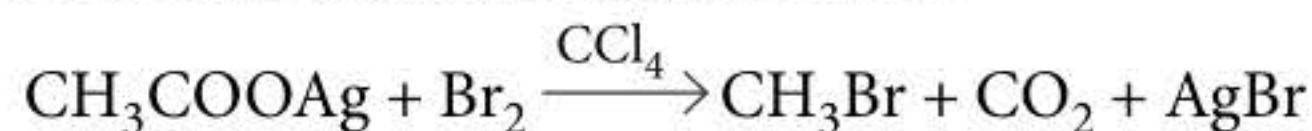


- Markovnikov's rule :** During the addition across unsymmetrical double bond, the negative part of the attacking reagent goes to the carbon atom carrying lesser number of hydrogen atoms while the positive part goes to the carbon atom with more number of hydrogen atoms.
- Anti-Markovnikov's rule :** When HBr is added to unsymmetrical double bond in presence of peroxide, the reaction takes place contrary to the Markovnikov's rule. This is known as anti-Markovnikov's rule, peroxide effect or Kharasch

effect. This law is applicable for the addition of HBr only.

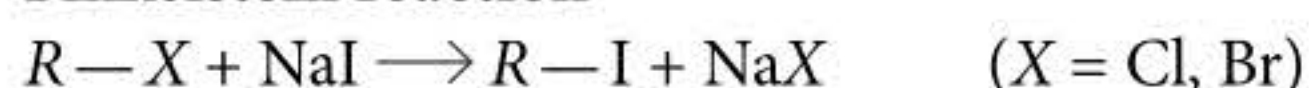
- From silver salts of acids :

- Borodine Hunsdiecker reaction :**



- By halogen exchange method :

- Finkelstein reaction**



- Swartz reaction (For alkyl fluoride)**

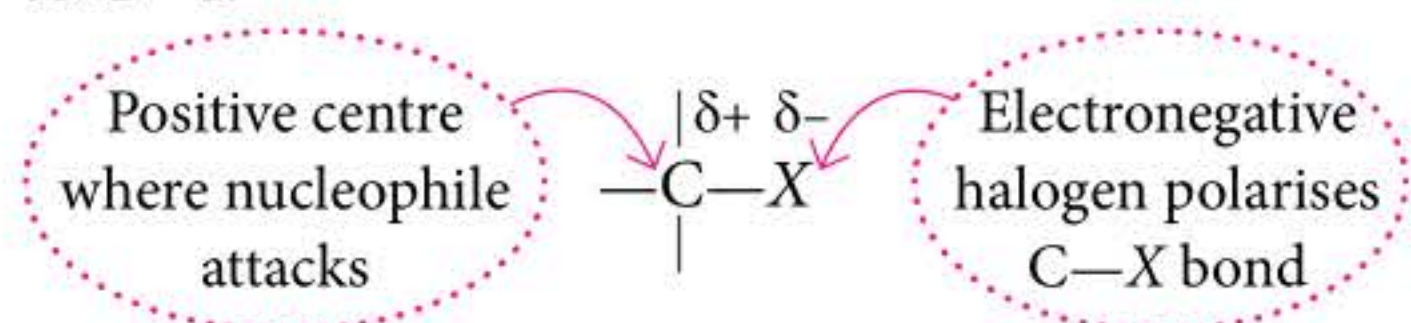


PHYSICAL PROPERTIES

- Alkyl halides are very slightly soluble in water but soluble in organic solvents.
- Alkyl bromides and iodides are heavier than water whereas alkyl chlorides and fluorides are lighter than water.
- The boiling points of alkyl halides are in the order $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$ and the boiling points of alkyl halides increases with increase in size of the alkyl group.
- Alkyl halides are in general toxic compounds and bring unconsciousness when inhaled in large amount.

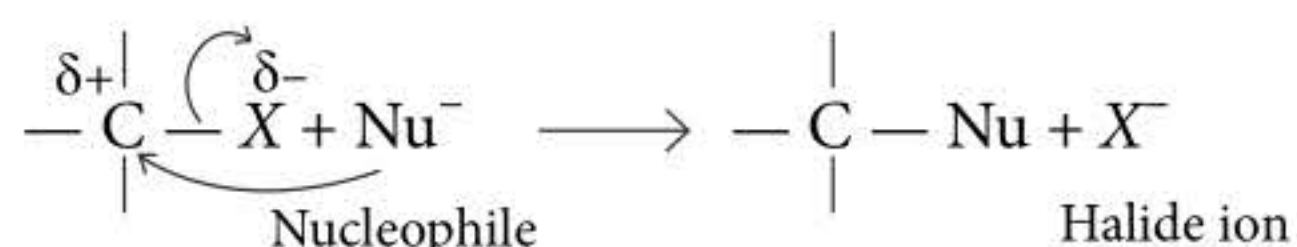
NATURE OF C—X BOND

- In haloalkanes, the carbon is bonded to a halogen atom ($X = \text{F, Cl, Br, I}$) which is more electronegative than carbon. Consequently, the C—X bond is polar in nature and its bond length increases from C—F to C—I.



CHEMICAL PROPERTIES

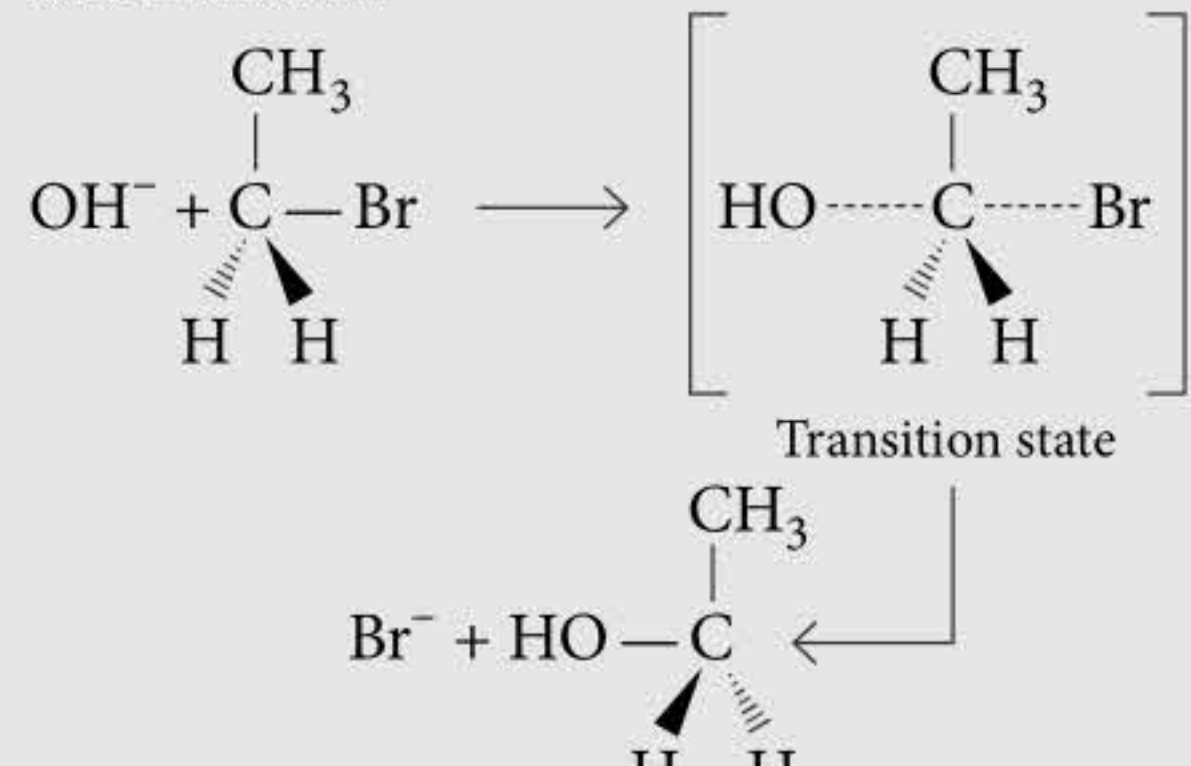
- Nucleophilic substitution reactions :** The reactions in which a stronger nucleophile displaces a weaker nucleophile (leaving group) are called nucleophilic substitution reactions.



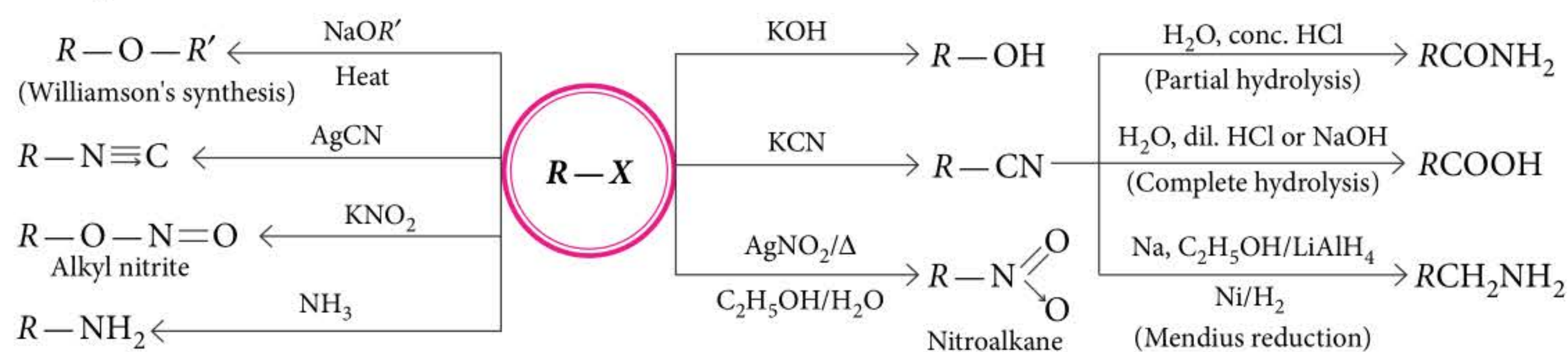
- Leaving group ability :** $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$

- Order of reactivity :** $\text{R}-\text{I} > \text{R}-\text{Br} > \text{R}-\text{Cl} > \text{R}-\text{F}$

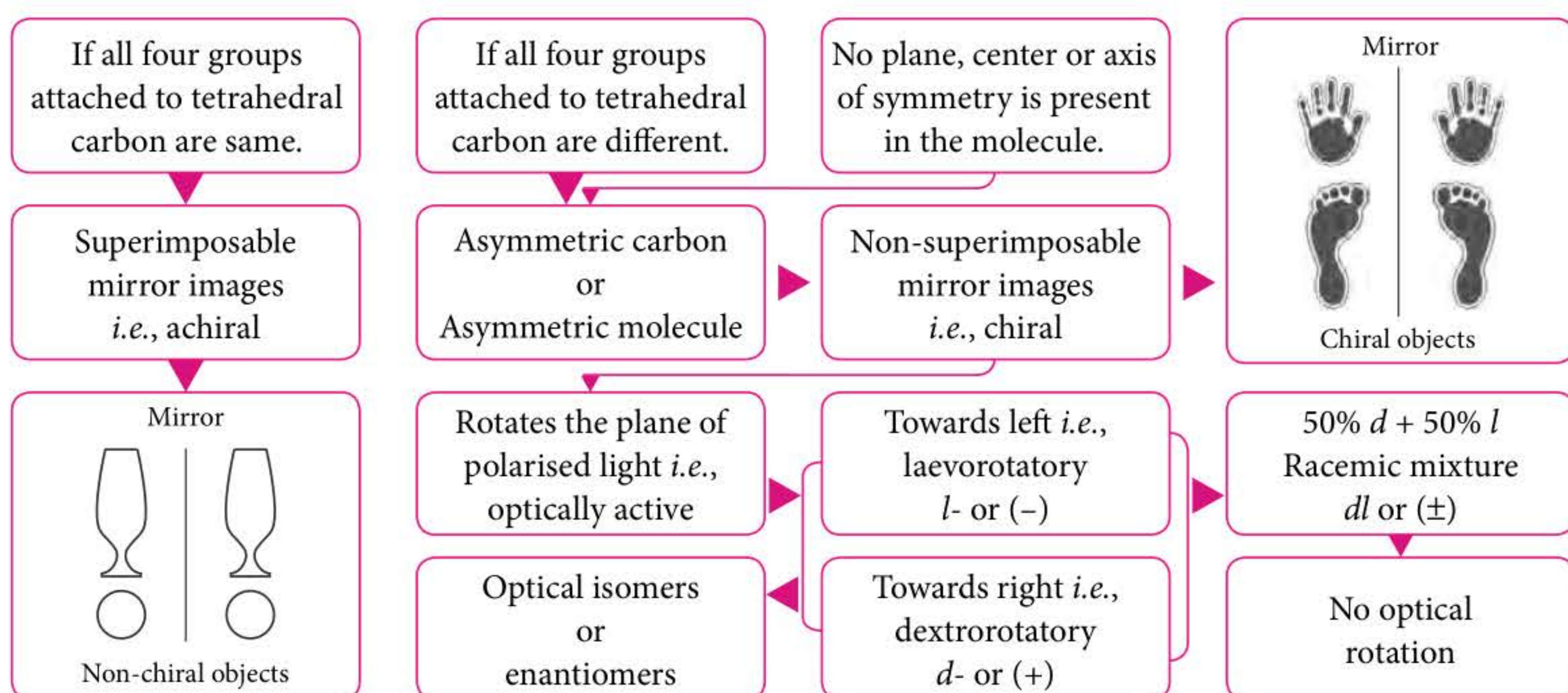
Types of Nucleophilic Substitution Reactions

S _N 2 (Bimolecular)	S _N 1 (Unimolecular)
<p>Mechanism :</p>  <p style="text-align: center;">Transition state</p> <p>Rate = $k[RX][OH^-]$</p> <ul style="list-style-type: none"> ● Single step reaction. ● Inversion of configuration takes place. ● Reactivity order of alkyl halides : $CH_3X > 1^\circ > 2^\circ > 3^\circ$ 	<p>Mechanism :</p> <p>Step I : $CH_3-C(CH_3)_2-Br \rightleftharpoons CH_3-C^+(CH_3)_2 + Br^-$</p> <p>Step II : $CH_3-C^+(CH_3)_2 + OH^- \longrightarrow CH_3-C(CH_3)_2-OH$</p> <p>Rate = $k[RX]$</p> <ul style="list-style-type: none"> ● Two step reaction. ● Carbocation rearrangement may take place. ● Reactivity order of alkyl halides : $3^\circ > 2^\circ > 1^\circ > CH_3X$

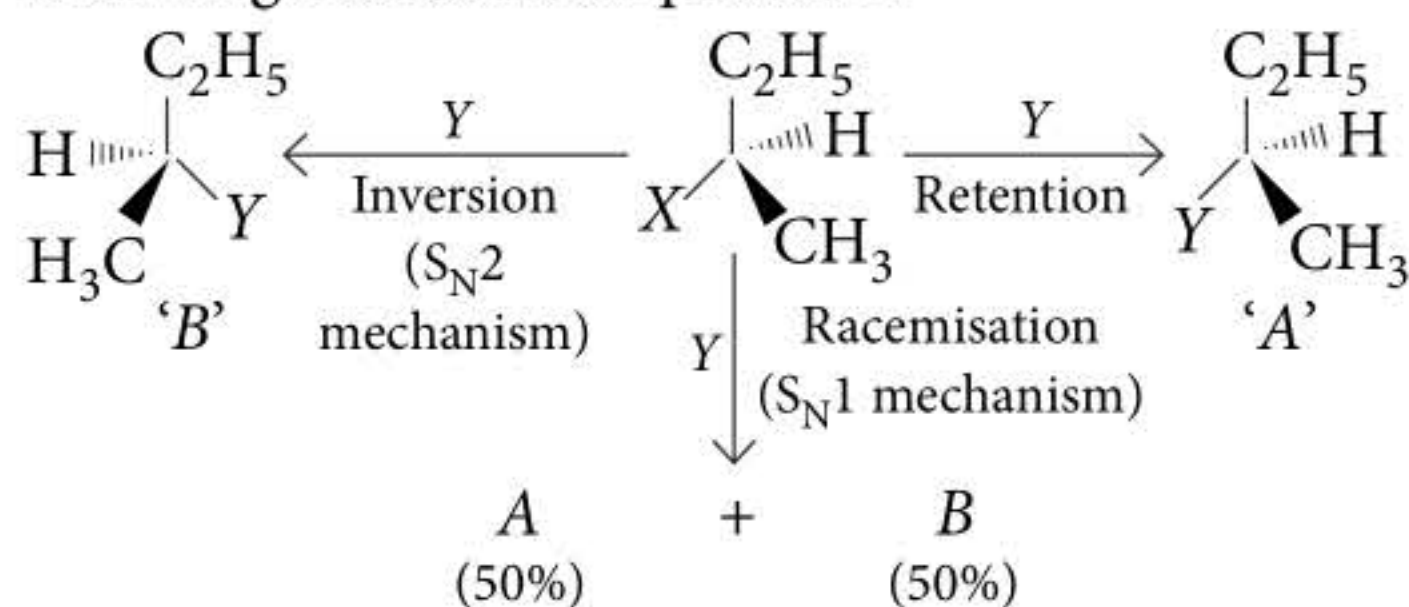
● **Examples of substitution reactions :**



● **Optical Activity :** Compounds which rotate the plane of polarised light when they pass through the prism, are called optically active compounds and the phenomenon is known as optical activity.

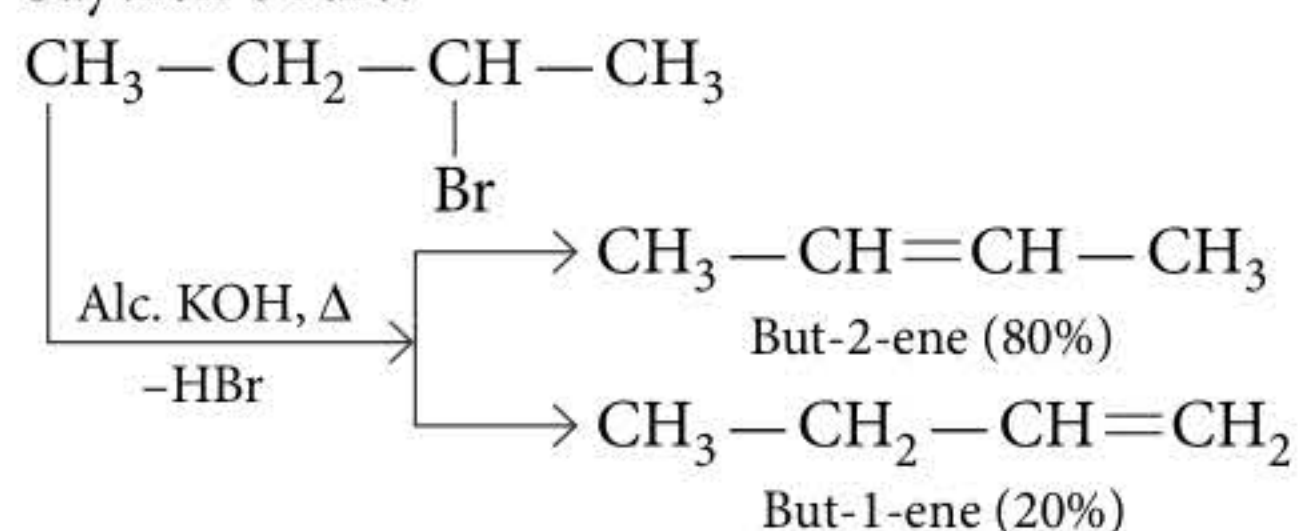


- Inversion, retention and racemisation :** When a reaction takes place at an asymmetric carbon atom following reactions are possible :



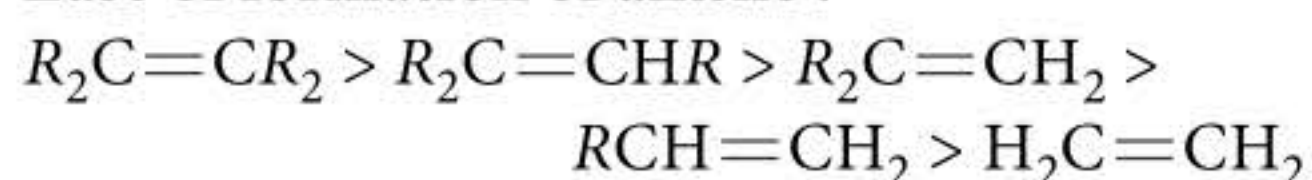
- Elimination reactions :**

- **Dehydrohalogenation :** These reactions are called β -elimination reactions which follow Saytzeff's rule.

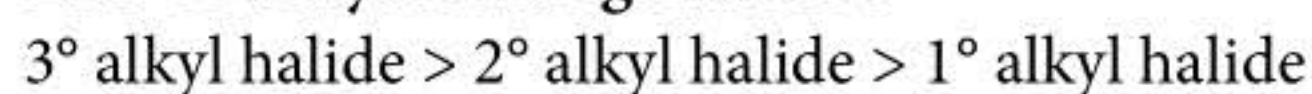


- **Saytzeff rule :** In haloalkane, when elimination of hydrogen halide in two different ways occur, then that alkene will be preferred, in which carbon atoms joined by the double bond are maximum alkylated *i.e.*, contain largest number of alkyl groups.

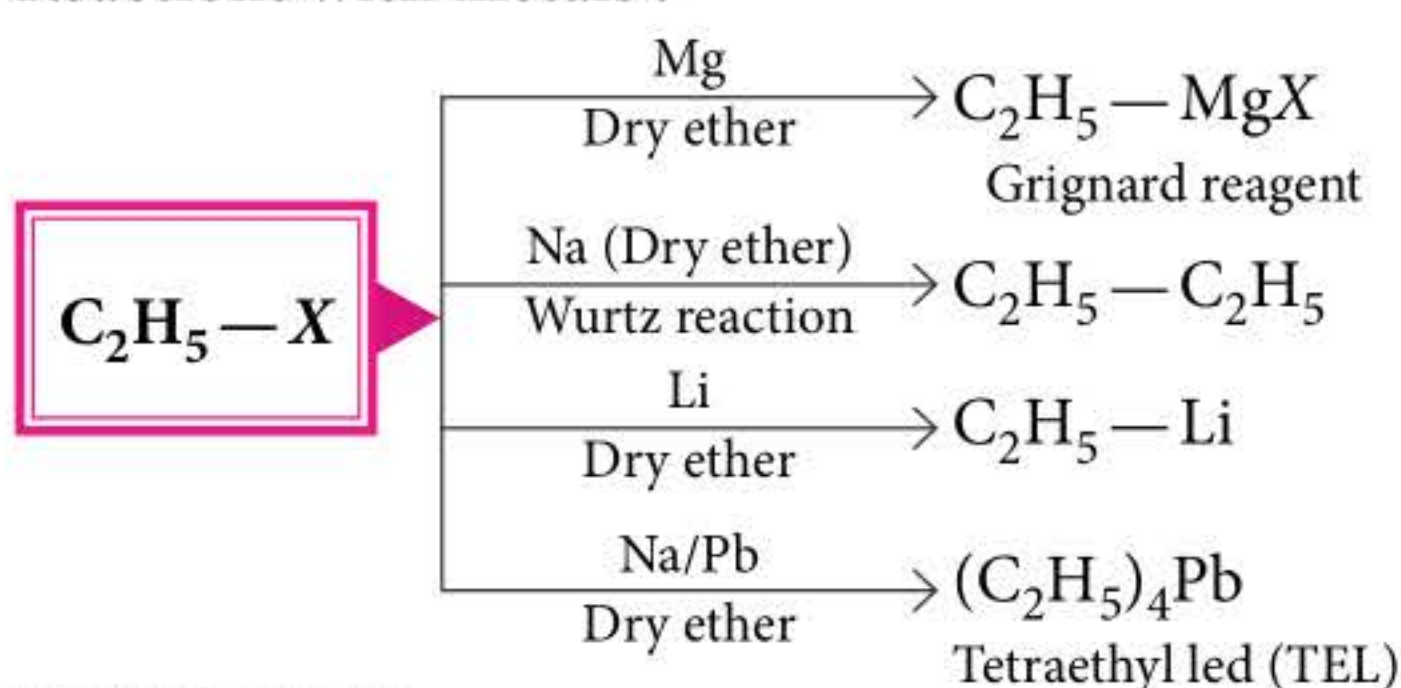
- **Ease of formation of alkene :**



- **Ease of dehydrohalogenation :**

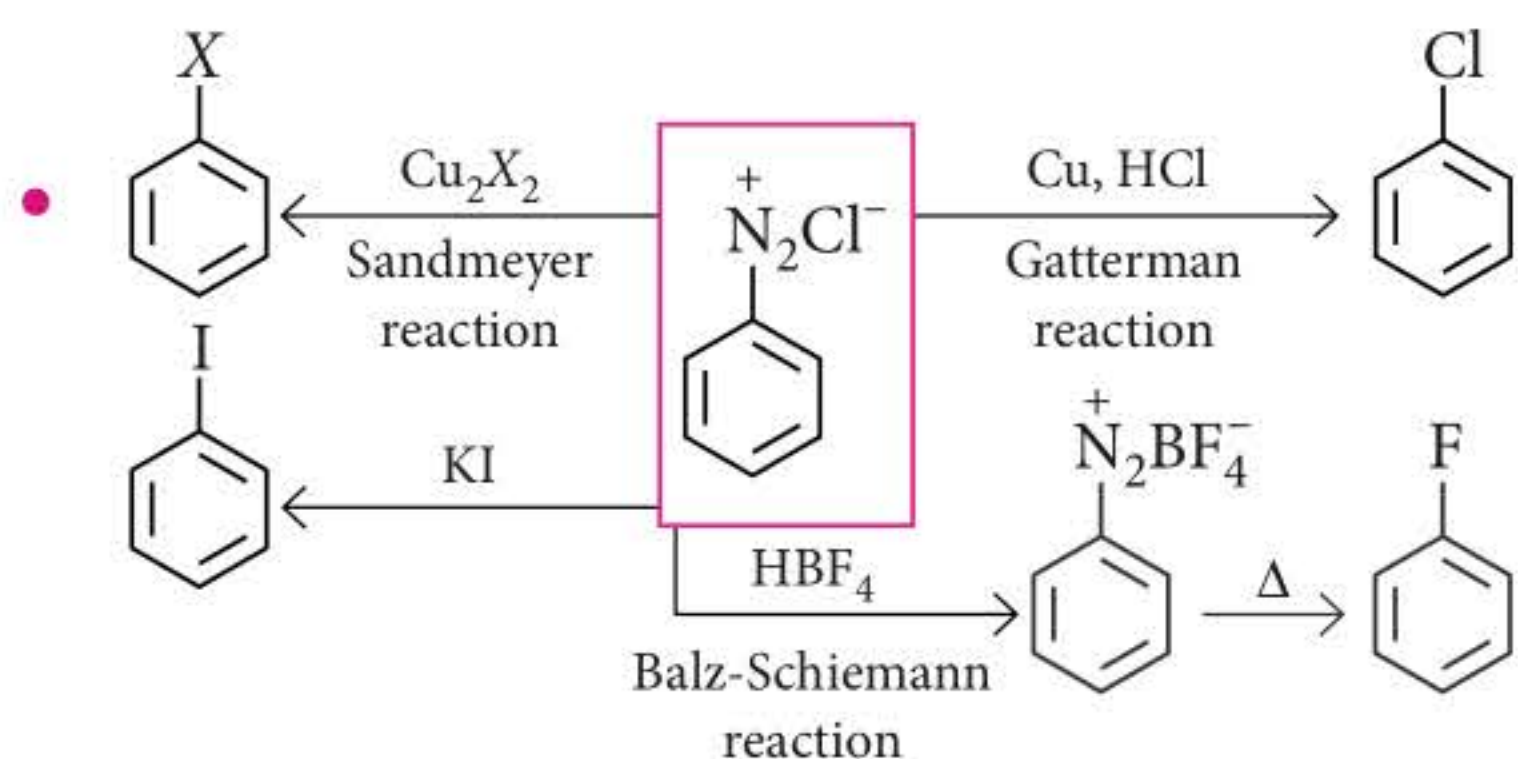
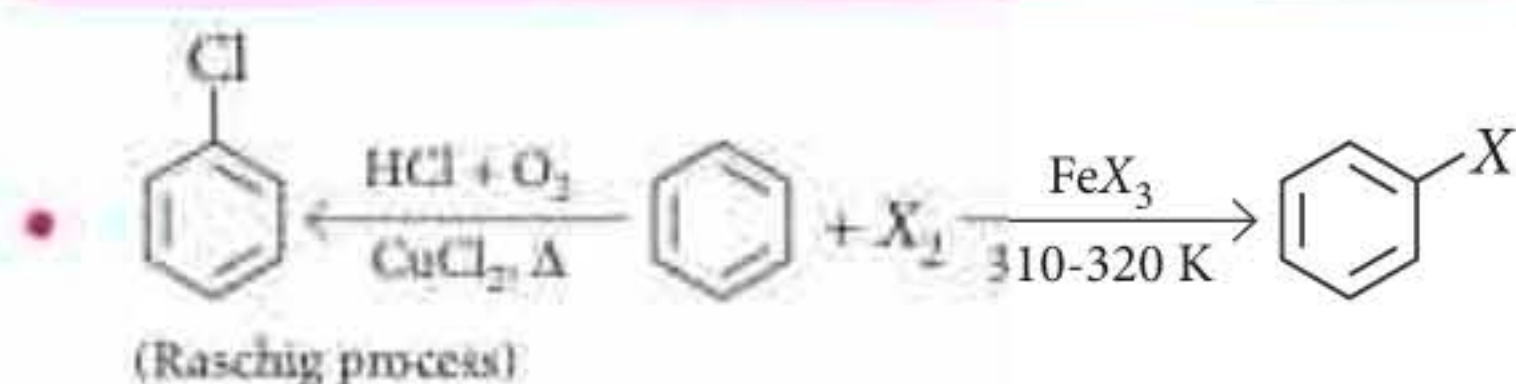


- Reactions with metals :**

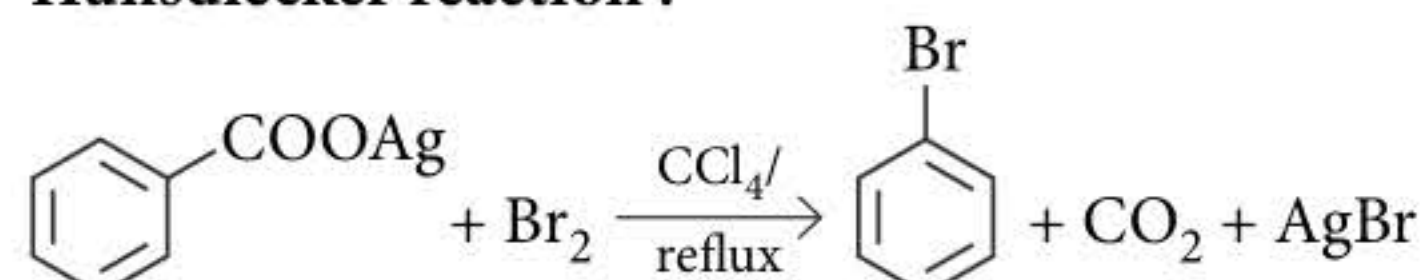


HALOARENES

PREPARATION



- Hunsdiecker reaction :**



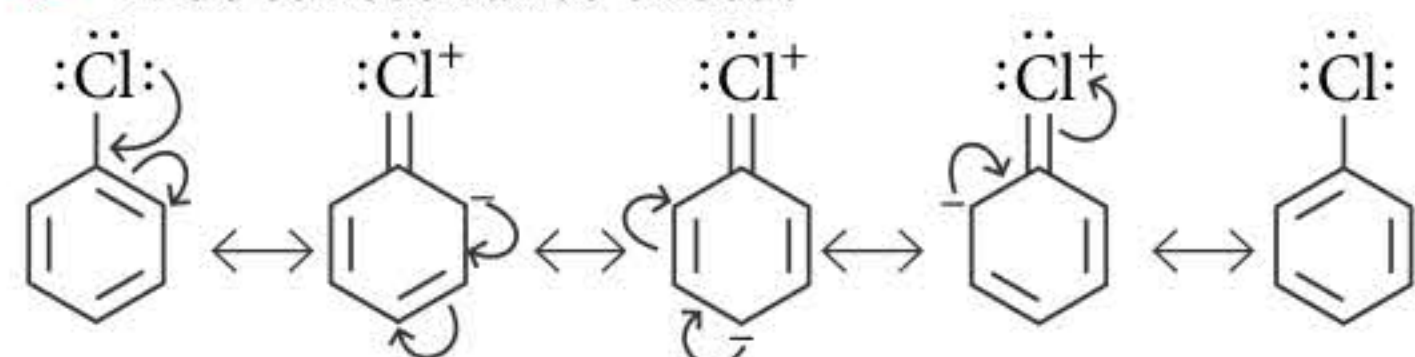
PHYSICAL PROPERTIES

- Aryl halides are colourless stable liquids with pleasant odour, insoluble in water but readily miscible with organic solvents.
- Their boiling points are higher than corresponding alkyl halides. The boiling points rise gradually from fluoro to iodo compounds.

CHEMICAL PROPERTIES

- **Nucleophilic substitution reactions :** Haloarenes are less reactive towards nucleophilic substitution reactions:

- Due to resonance effect :



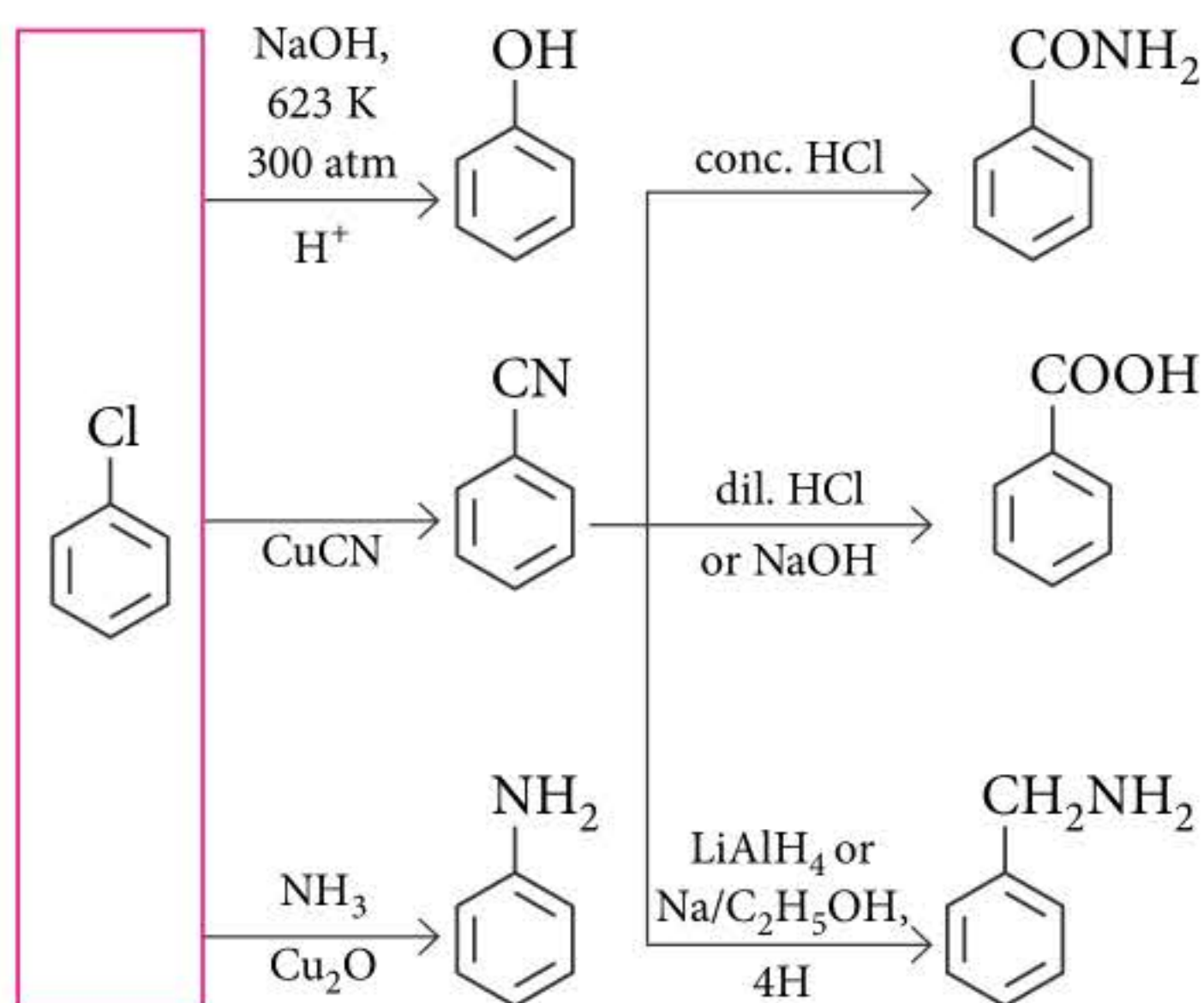
Thus, C—Cl bond acquires double bond character and difficult to break.

- C atom in haloarenes is sp^2 hybridised, thus has greater *s*-character, so difficult to break.
- Instability of phenyl cation : Phenyl cation formed by self-ionisation will not be stabilised hence, S_N1 mechanism ruled out.

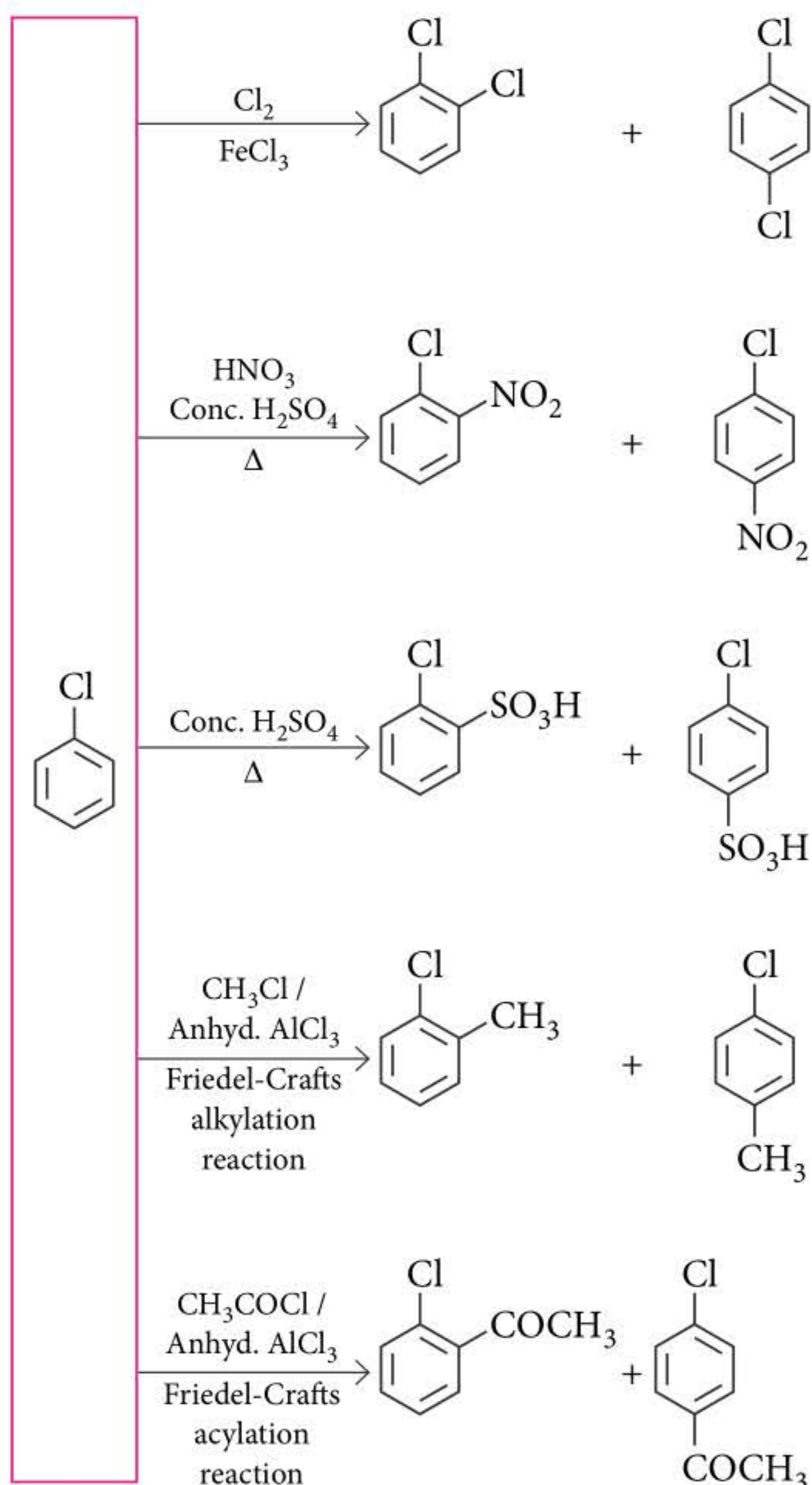
MPP-7 CLASS XI

ANSWER KEY

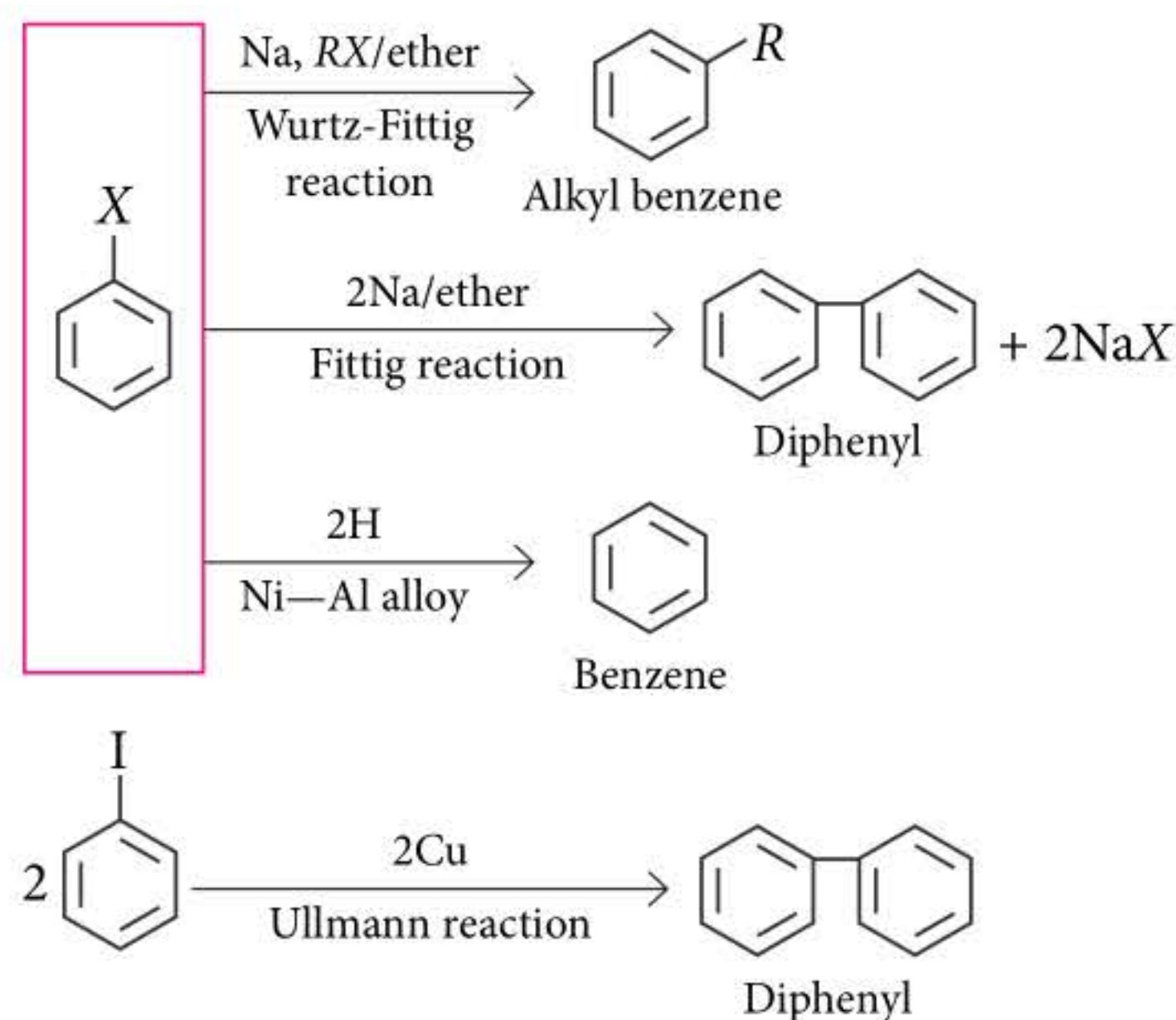
1. (b) 2. (a) 3. (a) 4. (d) 5. (a)
 6. (c) 7. (a) 8. (d) 9. (c) 10. (b)
 11. (a) 12. (a) 13. (c) 14. (a) 15. (b)
 16. (d) 17. (b) 18. (c) 19. (d) 20. (a,b,c)
 21. (a,c) 22. (a,b) 23. (a,b,c,d) 24. (5)
 25. (3) 26. (7) 27. (c) 28. (a) 29. (a)
 30. (b)



- **Electrophilic substitution reactions :** As electron density increases at *o*, *p*-positions, electrophilic substitution reactions occur at *o*, *p*-positions.



- **Other reactions :**



INFOSHOTS

Halogen derivative of 1, 3-disubstituted thiourea!

1, 3-disubstituted thiourea derivatives have attracted an increasing attention due to their potential in medicinal chemistry. Among them, the broad spectrum of biological activities of fluorinated thiourea derivatives has been investigated and various bioactivities, such as antimicrobial, antiviral and anticancer have been reported. In recent years, several chlorophenyl, fluorophenyl and (trifluoromethyl) phenyl thiourea compounds have been described as potent antistaphylococcal and antifungal agents.

Your favourite MTG Books/Magazines available in ORISSA at

- Padmalaya Book Seller - Bhubaneswar
Ph: 0674-2396922, 3039692; Mob: 9437026922
- Pragnya - Bhubaneswar Ph: 0674-2395757, 30396922; Mob: 9861135495
- Sri Ram Books - Bhubaneswar Ph: 0674-2391385; Mob: 9439921093
- Sagar Book Store - Bhubaneswar Ph: 0674-2506040, 2516040; Mob: 8763406040
- Sri Madhab Book Store - Cuttack Ph: 0671-2431158, 2431148; Mob: 9437024244
- A.K. Mishra Agency Pvt. Ltd. - Cuttack
Ph: 0671-2322244, 2322255, 2322266, 2332233; Mob: 9437025991
- Kitab Mahal - Cuttack Ph: 0671-2648333, 2648301; Mob: 9861388145

Visit "MTG IN YOUR CITY" on www.mtg.in to locate nearest book seller OR write to info@mtg.in OR call **0124-6601200** for further assistance.