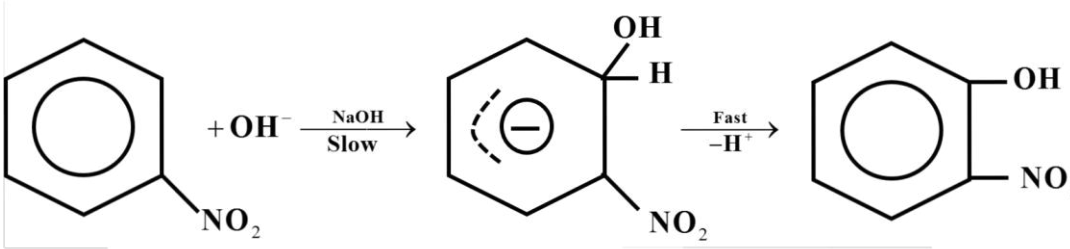
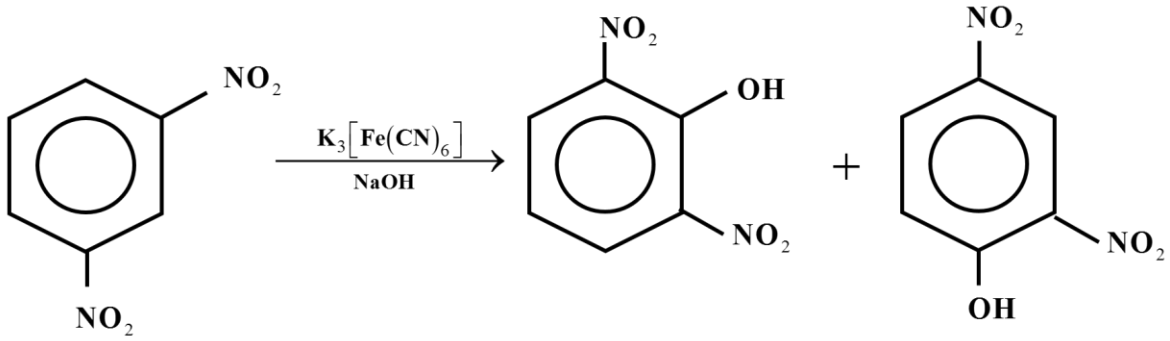
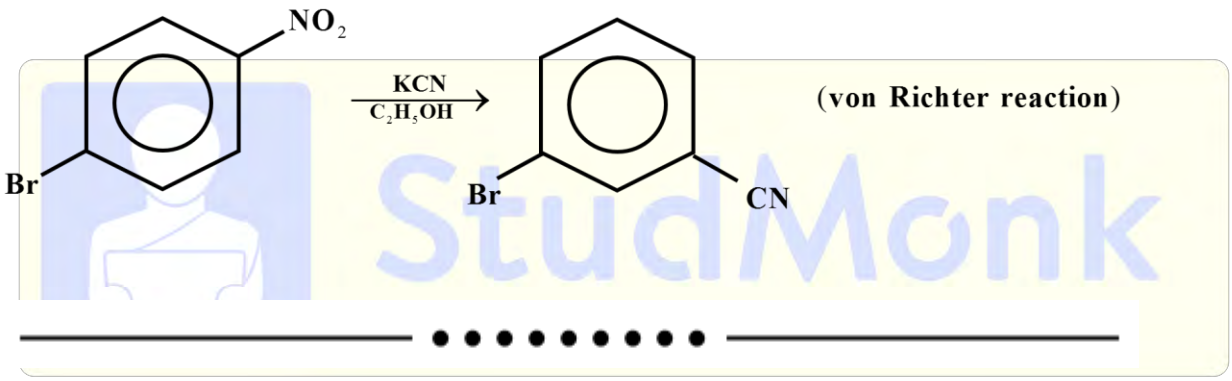


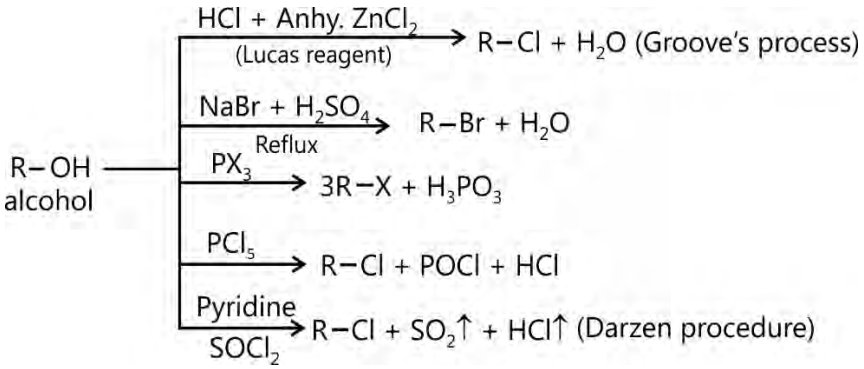




19. HALOALKANES AND HALOARENES

General Methods of Preparation of Haloalkanes

From Alcohols



Free Radical Halogenation of Alkanes

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{UV light or Heat}]{Cl_2} CH_3CH_2CH_2CH_2Cl + CH_3CH_2\underset{\displaystyle Cl}{\underset{|}{C}}HCH_3$$

Addition of hydrogen Halides on Alkenes

$$-\overset{|}{C}-C=C- + HBr \longrightarrow -\overset{|}{C}-\underset{\displaystyle Br}{\underset{|}{C}}-C-$$

2–bromopropane

$$-\overset{|}{C}-C=C- + HBr \xrightarrow{\text{Organic peroxide}} -\overset{|}{C}-C-\underset{\displaystyle Br}{\underset{|}{C}}$$

(i) Halogen Exchange method :

$R-X + NaI \rightarrow R-I + NaX$ **(Finkelstein reaction)**

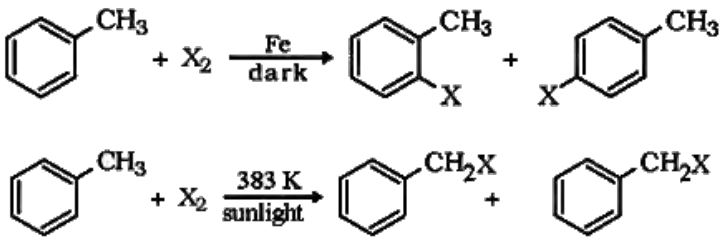
$R-Br + AgF \rightarrow R-F + AgBr$ **(Swarts reaction)**

Hunsdiecker Reaction

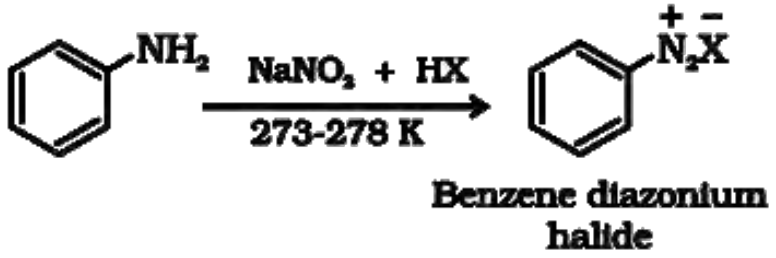
$$CH_3COOAg + Br_2 \xrightarrow[CCl_4]{} CH_3Br + AgBr + CO_2$$

- **Preparation of haloarenes :**

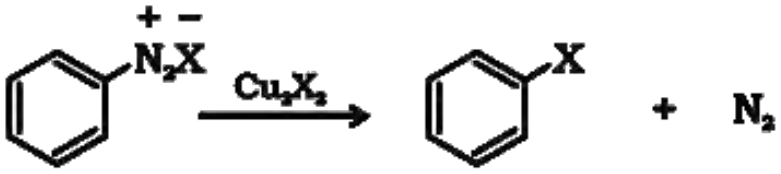
  (a) By electrophilic substitution reaction :



  (b) Sandmeyer's reaction :



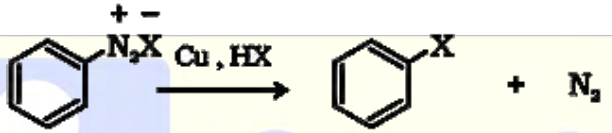
Benzene diazonium halide



Aryl halide

X = Cl, Br

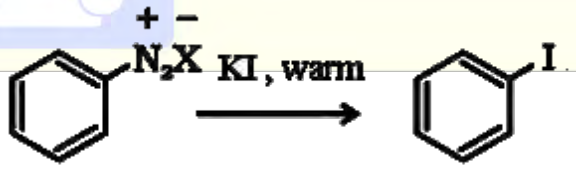
(c) Gattermann reaction :



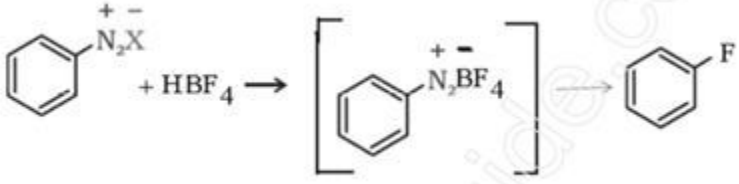
Aryl halide

X = Cl, Br

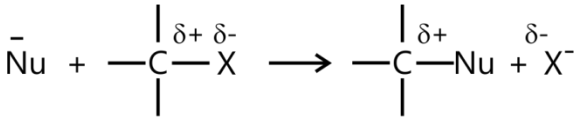
(d) From Diazonium Chloride :

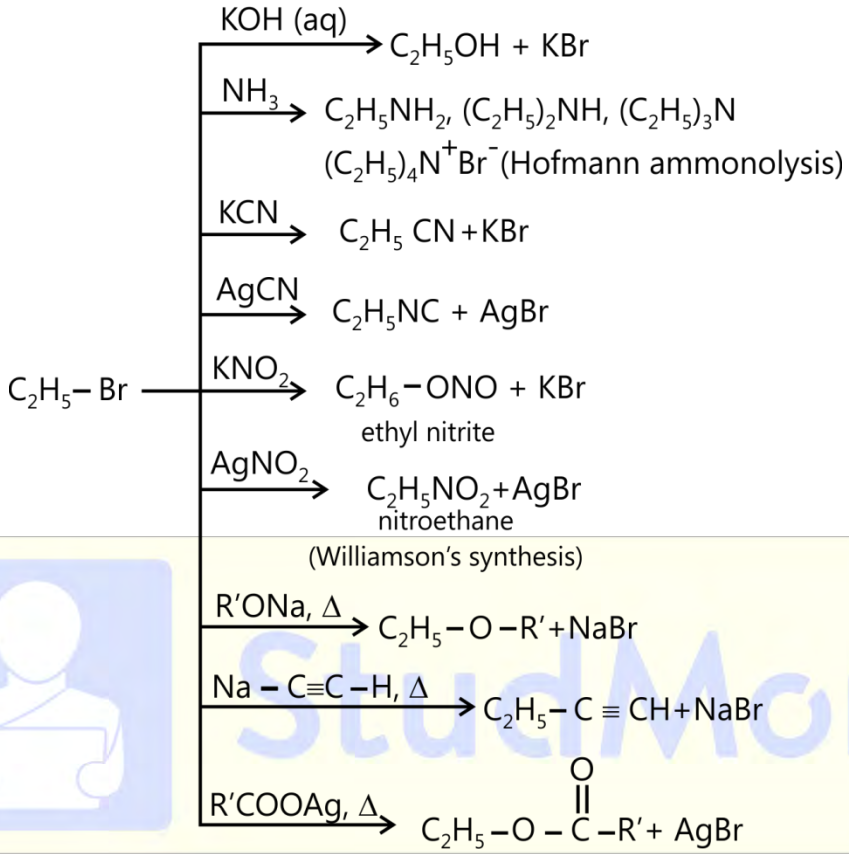


(e) Balz-Schiemann reaction :



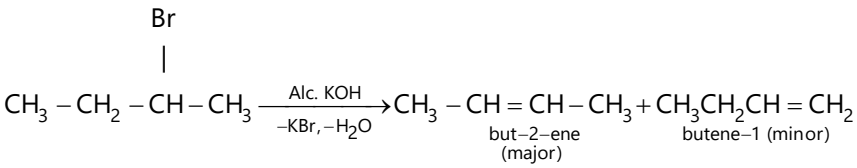
Nucleophilic Substitution Reactions



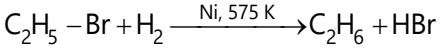


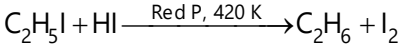
2. Elimination Reactions

Dehydrohalogenation is a β-elimination reaction in which halogen is from α-carbon atom and the hydrogen from the α-carbon according to Saytzeff rule, e.g.



Reduction





Reaction with Metals

(i) Wurtz reaction

$$RX + 2Na + XR \xrightarrow{\text{Dry ether}} R - R(\text{alkane}) + 2NaX$$

(ii) Wurtz-Fitting reaction

$$C_6H_5\text{-}Cl + 2Na + Cl\text{-}CH_3 \xrightarrow{\text{Dry ether}} C_6H_5 - CH_3 + 2NaCl$$

(iii) Reaction with Mg

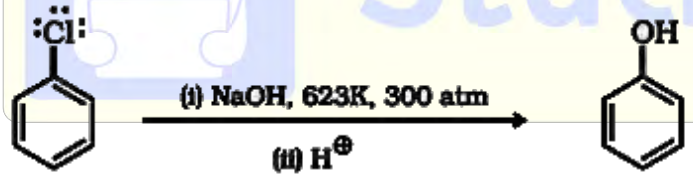
$$C_2H_5Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard's reagent)}}{C_2H_5 - Mg - Br}$$

Isomerisation

$$CH_3CH_2CH_2 - Cl \xrightarrow[\text{or anhy. } AlCl_5]{573\ K} CH_3 - \underset{|}{\overset{Cl}{CH}} - CH_3$$

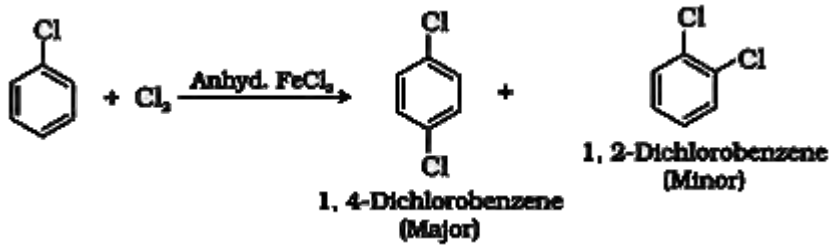
Chemical properties of haloarenes :

(a) Dow's Process

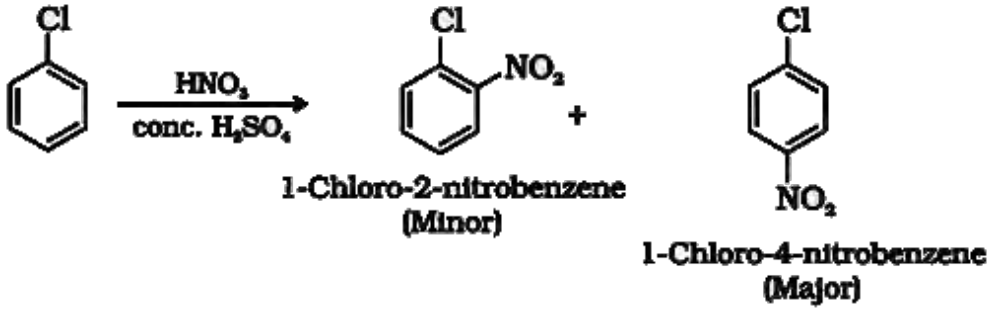


Electrophilic substitution Reactions

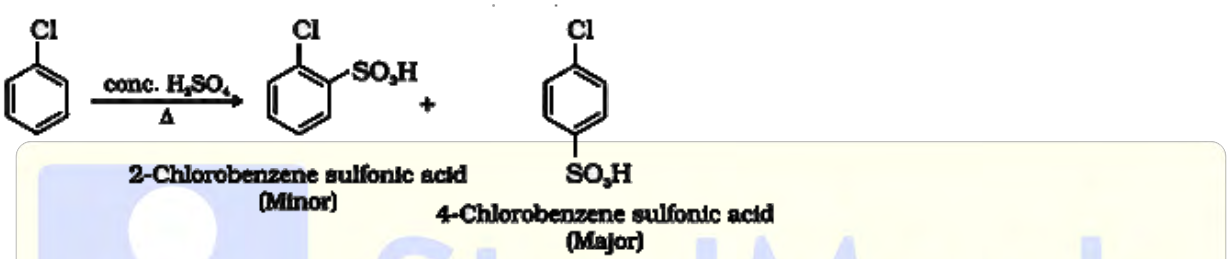
(b) With halogens



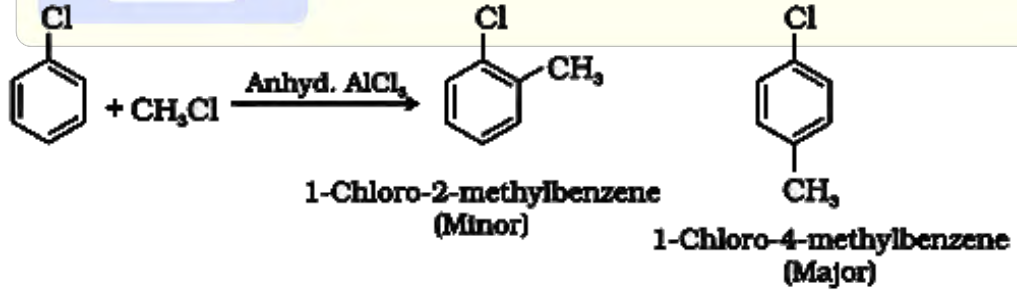
(c) With conc. sulphuric acid and nitric acid



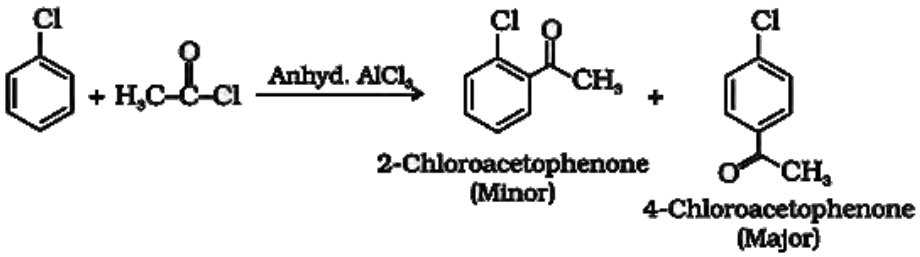
(d) On heating with conc. sulphuric acid



(e) With methyl chloride



(f) With acetyl chloride



(i) Other conversions :

$R-X+KCN \rightarrow R-CN+KX$

$R-CN \xrightarrow{Na, C_2H_5OH \text{ or } LiAH_4 \text{ or } Ni/H_2} R-CH_2NH_2 \xrightarrow{HONO} RCH_2OH$

$R-CN \xrightarrow{H_3O^+} R-COOH \xrightarrow{NH_3} R-CONH_2$

$R-COOH \xrightarrow{LiAlH_4} RCH_2OH$

$R-COOH \xrightarrow{PCl_5 \text{ or } PCl_3 \text{ or } SOCl_2} R-COCl$

$R-X+Mg \xrightarrow{\text{Dry ether}} RMgX$

$RMgX+CO_2 \rightarrow RCOOH$

$RMgX+HCHO \rightarrow \text{Primary alcohol}$

$RMgX+RCHO \rightarrow \text{Secondary alcohol}$

$RMgx+R-CO-R \rightarrow \text{Tertiary alcohol}$

20. HYDROCARBONS

CLASSIFICATION OF HYDROCARBONS: