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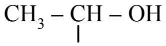
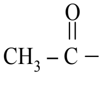
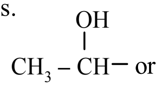
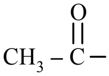
CHAPTER

alkyl and aryl halides

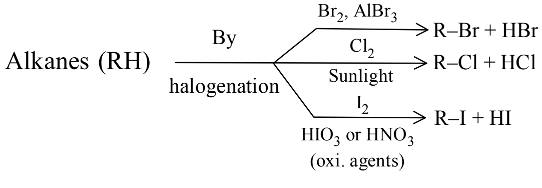
- **Halogen derivatives** are the compounds obtained by the replacement of one or more hydrogen atoms of the hydrocarbon by corresponding number of halogen atoms.
- Because of their greater molecular weight, haloalkanes have considerably higher boiling points than alkanes with the same number of carbons.
- **Haloalkanes** are insoluble in water due to the fact that they can neither form hydrogen bonds with water nor they can break the hydrogen bonds already existing between their molecules.
- Alkyl halides are quite soluble in organic solvents like alcohol, ether, acetone, chloroform, carbon tetrachloride.
- For a given halogen, the boiling point rises with increasing carbon number; as with alkanes, the boiling point rise is 20-30 degrees for each added carbon except for the very small homologs.
- Densities of alkyl halides are in the order
  $R - I > R - Br > R - Cl$.
- Density of alkyl halides goes on decreasing with the increase in the number of carbon atoms in their molecules.
- Relative reactivity of haloalkanes with respect to halogen atom is in the order :
  $RI > RBr > RCl > RF$.
- Haloalkanes undergo hydrolysis on boiling with aqueous alkali to form alcohols.
- Haloalkanes are converted to ethers with alcoholic sodium or potassium alkoxides. This reaction is called **Williamson's synthesis**.
- Haloalkanes reacts with sodium or potassium nitrate to form **alkyl nitrite**.
- Haloalkanes on being heated with an aqueous ethanolic solution of sodium or potassium hydrosulphide form thioalcohols.
- **Nitroalkanes** are formed when an aqueous ethanolic haloalkane is treated with silver nitrite.
- Haloalkanes on treatment with silver salt of a carboxylic acid in ethanol give **esters**.
- Alkyl chlorides or bromides when treated with sodium or potassium iodide in acetone undergo halogen exchange to form alkyl iodides. This is known as **Finkelstein reaction**.
- When a haloalkane is heated with concentrated alcoholic solution of KOH, a molecule of hydrogen halide is eliminated and alkene is formed. This is an example of **β-elimination reaction**.

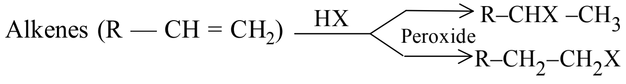
- For a given alkyl halide the ease of dehydrohalogenation is
  R – I > R – Br > R – Cl.
- For a given halogen, the ease of elimination is in the order
  tertiary (3°) > secondary (2°) > primary (1°) alkyl halide.
- **Saytzeff's rule** states that in case a haloalkane can eliminate hydrogen halide in two different ways, then the more substituted alkene is the major product of the dehydrohalogenation.
- Primary alkyl halides follows E2 mechanism (elimination bimolecular).
- For E2 and E1 mechanism, the order of reactivity for a given halogen follows the sequence
  E1 tertiary > secondary > primary alkyl halide
- Tertiary alkyl halides follow E1 mechanism.
- Haloalkanes react with sodium in the presence of dry ether to form alkanes. This reaction is called **Wurtz reaction**.
- E2 mechanism takes place in one step whereas E1 mechanism by two steps.
- Unsymmetrical alkenes can be obtained from alkyl halides by **Corey-House reaction** and the reaction is carried out by treating lithium dialkyl copper with an alkyl halide.
- Haloalkanes react with magnesium in presence of dry ether to form alkyl magnesium halides generally called **Grignard reagents**.
- Alkyl iodides can be easily reduced to alkanes by reducing it with HI in the presence of red phosphorus at 420 K.
- Haloalkanes can be reduced to alkanes by H_2 in presence of finely divided nickel, palladium or platinum (catalytic reduction).
- When a higher alkyl halide is heated to 570 K in the presence of a Lewis acid like anhydrous aluminium chloride which acts as a catalyst, haloalkanes undergo molecular rearrangement to give an isomeric haloalkane. This reaction is also called **isomerization** or **rearrangement reaction**.
- Alkyl halides react with benzene in the presence of a Lewis acid like anhydrous $AlCl_3$ to form homologues of benzene.
- Aryl halides are compounds containing halogen attached directly to an aromatic ring and they have the general formula ArX where Ar is phenyl, substituted phenyl or a group derived from some other aromatic system.
- Bromobenzene can be obtained from benzene diazonium chloride by treating it with CuBr dissolved in HBr.
- In **Balz-Schiemann reaction**, fluoroarenes are obtained by treating corresponding diazonium salt with fluoroboric acid (HBF_4) and it is filtered, dried and heated to get fluoroarenes.
- Aryl halides are generally colourless liquids or crystalline solids at room temperature.
- The melting and boiling points of haloarenes decrease in the following order.
  aryl iodides > bromides > chlorides > fluorides
- The melting point of *p*-isomer is generally 70-100 K higher than the melting points of *ortho* and *meta* isomer.

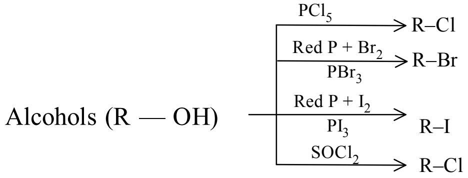
- For the same halogen atom, the melting and boiling points increase as the size of the aryl group increases.
- Densities of aryl halides follow the order :
  aryl iodides > bromides > chlorides > fluorides.
- Haloarenes are soluble in organic solvents like benzene, acetone, chloroform, CCl_4 etc.
- Haloarenes are insoluble in water because they cannot form hydrogen bond with water molecules.
- **Benzonitrile** is formed when aryl bromide is heated with CuCN at 500 K in presence of pyridine or dimethyl formaldehyde (DMF).
- **Phenol** is formed when chlorobenzene is heated with an aqueous solution of NaOH at 625 K and under a pressure of 300 atmosphere.
- Electron-withdrawing groups like $-NO_2$, $-CN$, $\rangle C = O$, $-COOH$ and $-SO_3H$, particularly when present in ortho or para position with respect to halogen activate aryl halide towards nucleophilic substitution.
- Electron-releasing groups like $-NH_2$, $-OH$, $-OR$, $-R$ etc. deactivate aryl halides towards nucleophilic aromatic substitution.
- Low reactivity of aryl halides is due to the fact that the C – X bond is far less polar in aryl halides than in alkyl halides.
- **Diaryls** are produced when aryl halides are treated with sodium in the presence of dry ether. This reaction is called Fittig reaction.
- In **Wurtz-Fittig reaction**, haloarenes are treated with an ethereal solution of an alkyl halide in the presence of sodium to form alkyl derivatives of benzene.
- When an iodoarene is heated with copper powder in a sealed tube, diaryl is formed. This is called **Ullmann reaction**.
- By the action of nickel-aluminium alloy, haloarenes can be reduced to the corresponding arenes.
- Aryl halides undergo electrophilic substitution reactions in the benzene ring such as halogenation, sulphonation, nitration and Friedel-Craft's reaction.
- Pure chloroform can be obtained by distilling chloral hydrate [$CCl_3CH(OH)_2$ or $CCl_3CHO \cdot 2H_2O$] with concentrated aqueous NaOH solution.
- Inhalation of chloroform vapours produces loss of consciousness and is used as a general anaesthetic in surgery.
- **Chloroform** condenses with acetone in the presence of an alkali to give chloretone which is used as a hypnotic.
- Chloroform when treated with chlorine in the presence of sunlight is converted into carbon tetrachloride.
- Chloroform on warming with aniline (or any other 1° amine) and alcoholic potash gives phenyl isocyanide (phenyl carbyl amine) which has an extremely unpleasant odour and this reaction is used as a test for 1° amine. This reaction is known as **Hofmann's carbylamine reaction**.

- Reduction of chloroform with Zn and hydrochloric acid gives dichloromethane (methylene chloride).
- **Chloroform** is a common ingredient of cough syrups.
- **Iodoform test** is used to test the presence of  $CH_3-\underset{|}{C}H-OH$ or  $CH_3-\overset{\overset{O}{||}}{C}-$ groups in alcohols, aldehydes or ketones.
- When a compound containing  $CH_3-\overset{\overset{OH}{|}}{C}H-$ or  $CH_3-\overset{\overset{O}{||}}{C}-$ is refluxed with I_2 and NaOH, a yellow precipitate of iodoform is obtained. The formation of yellow precipitate indicates the presence of either of these two groups.
- CCl_4 is insoluble in water but dissolves readily in organic solvents such as ether, alcohol etc.
- **CCl_4 vapours** are non-inflammable and is used as a fire extinguisher under the name pyrene.
- With antimony trifluoride in the presence of $SbCl_5$ as catalyst, carbon tetrachloride yields **dichlorofluoromethane (freon)**.
- CCl_4 is used as a medicine for the elimination of hook worms.
- Dichlorodifluoro methane, CCl_2F_2 is called **freon**.
- Freons are used as a **refrigerent** in domestic refrigerators and air conditioners.
- **Benzenehexachloride** is used as an insecticide and pesticide in agriculture, under the trade name **gammaxane** or **lindane** or **666**.

Methods of preparation of haloalkanes

- 

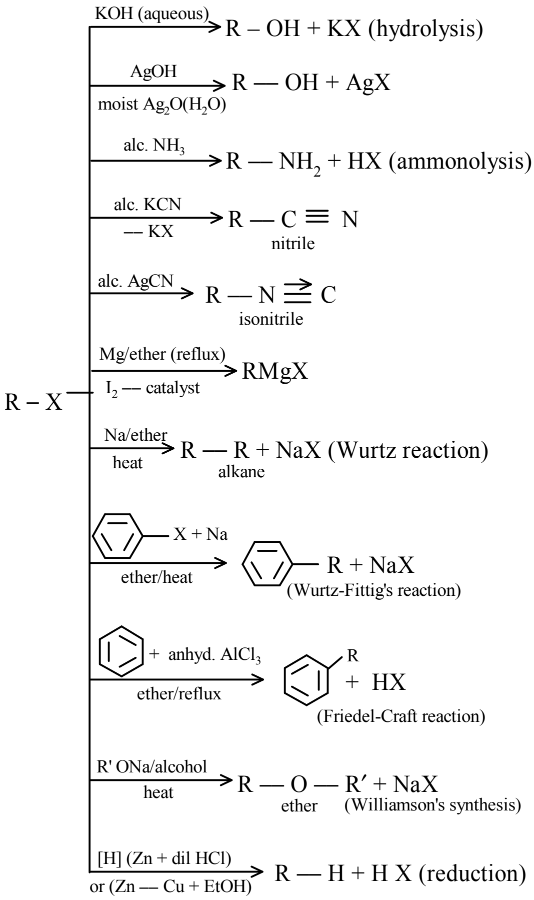
- 

- 

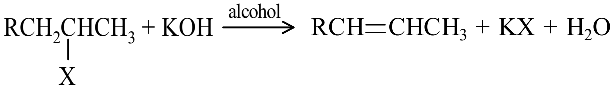
- **Properties**

Chemical Properties :

(i) *Nucleophilic substitution (S_N) reactions* :



(ii) *Dehydrohalogenation* :



$$\underset{\displaystyle X}{RCH_2\overset{}{C}HCH_3} + KOH \xrightarrow{\text{alcohol}} RCH{=}CHCH_3 + KX + H_2O$$

According to Saytzeff's rule, H-atom is eliminated preferentially from the adjacent C-atom which is joined to the least number of H-atoms.

Chloroform ($CHCl_3$) :

- **Preparation :** By the action of moist bleaching powder on ethanol or acetone.

$$CH_3CH_2OH \xrightarrow{\text{Oxi.}} CH_3CHO \text{ (acetaldehyde)}$$

$$CH_3CHO \xrightarrow{\text{chlorination}} CCl_3 \cdot CHO \text{ (chloral)}$$

$$CCl_3CHO \xrightarrow[Ca(OH)_2]{hydrolysis} CHCl_3 \text{ (chloroform)}$$

- **Chemical Properties :**

$$CHCl_3 \xrightarrow[\text{Reduction, In alcohol}]{Zn + HCl} HCl + CH_2Cl_2 \text{ (methylene chloride)}$$

$$CHCl_3 \xrightarrow[\text{Reduction, In water}]{Zn + HCl} CH_4 + HCl$$

$$CHCl_3 \xrightarrow[\text{Air and light}]{\text{Oxidation}} COCl_2 \text{ (phosgene or carbonyl chloride)}$$

$$CHCl_3 \xrightarrow[\text{NaOH or KOH}]{\text{Hydrolysis}} HCOOK \text{ (pot. formate) } \textbf{or } HCOONa \text{ (sod. formate)}$$

$$CHCl_3 \xrightarrow[\text{Pri. Amine + alc. KOH}]{\text{Carbylamine reaction}} RNC \text{ or } C_6H_5NC \text{ (isocyanide)}$$

$$CHCl_3 \xrightarrow[\text{Conc. } HNO_3]{\text{Nitration}} CCl_3.\,NO_2 \text{ (Nitrochloroform or chloropicrin)}$$

Methods of Preparation of haloarenes

- *By direct halogenation of benzene* :

$$C_6H_6 \xrightarrow{Cl_2/FeCl_3} C_6H_5Cl$$

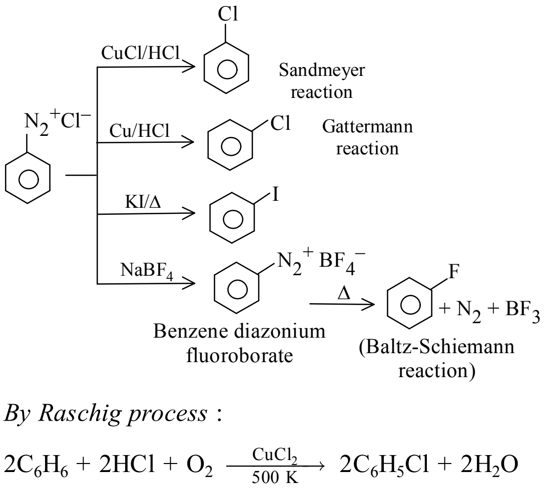
$$C_6H_6 \xrightarrow{Br_2/FeBr_3} C_6H_5Br$$

$$C_6H_6 \xrightarrow{I_2/HIO_3} C_6H_5I$$

- It is an electrophilic substitution reaction.
- Low temperature and the presence of a halogen carrier favour nuclear substitution. The function of the halogen carrier is to generate the electrophile for the attack.

$$\underset{\text{Lewis acid}}{Cl_2 + FeCl_3} \rightarrow \underset{\text{electrophile}}{Cl^+} + FeCl_4^-$$

- *From benzene diazonium salt* :



- *By Raschig process* :

$$2C_6H_6 + 2HCl + O_2 \xrightarrow[500\text{ K}]{CuCl_2} 2C_6H_5Cl + 2H_2O$$

- By Hunsdiecker reaction :

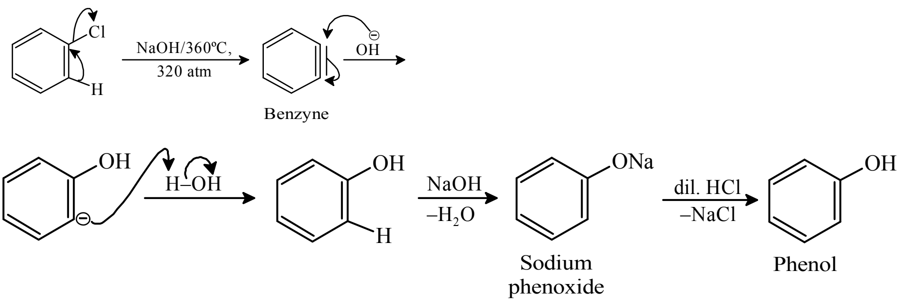
$$C_6H_5COOAg + Br_2 \xrightarrow[CCl_4,\ 350\ K]{\text{Distillation}} C_6H_5Br + AgBr + CO_2$$

Chemical Properties :

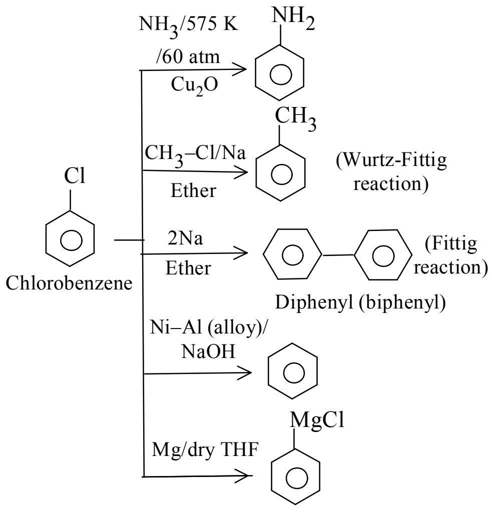
- *Nucleophilic substitution reaction of Chlorobenzene*:
  Reaction with NaOH : Dow's process

$$C_6H_5Cl + 2NaOH \xrightarrow[320\ atm]{360°C} C_6H_5ONa \xrightarrow{\text{dil HCl}} C_6H_5OH$$

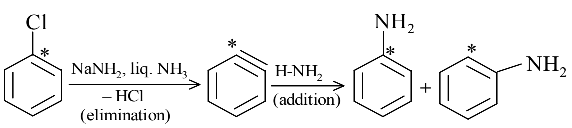
This reaction proceeds through benzyne intermediate.



- If both the *o*-position w.r.t. Cl atom is blocked, then benzyne intermediate is not obtained.



- *Elimination - addition reaction* :

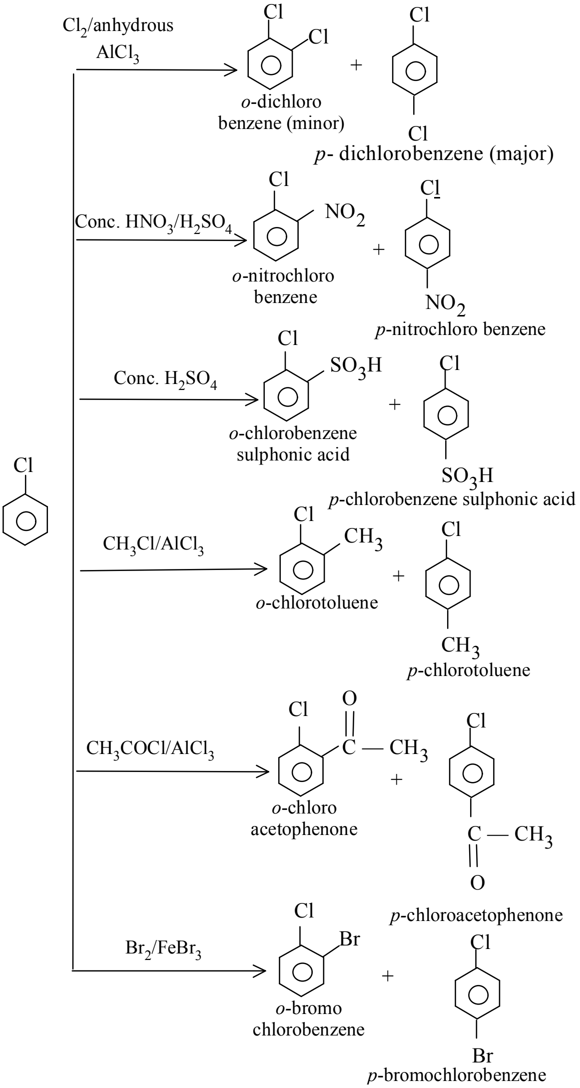


Since in this reaction, first elimination of HCl occurs and then addition of NH_3 takes place, it is called elimination-addition reaction.

Substitution at the C* that is attached to the leaving group is called direct substitution,

substitution at the adjacent carbon is called *cine substitution.*

- *Electrophilic substitution reaction* :



End