

## CHAPTER - 10

(1)

### Haloalkanes and Haloarenes

#### [Topic - 1]

#### • Introduction, Nomenclature and preparation

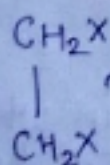
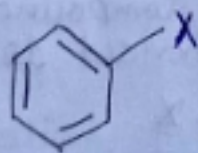
Aliphatic halogen derivatives are called alkyl halides. They have general formula,  $C_n H_{2n+1} X$ . Haloalkanes and Haloarenes are obtained by the replacement of a hydrogen atom of an alkane and arene respectively by a halogen atom (F, Cl, Br, I). Aromatic halogen derivatives are called aryl halides or haloarenes. Haloalkanes contain halogen atoms attached to the  $sp^3$ -hybridised carbon atoms of an alkyl group, whereas haloarenes contain halogen atoms attached  $sp^2$ -hybridised carbon atoms of an aryl atom group.

#### • Classification of haloalkanes and haloarenes

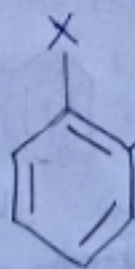
On the Basis of Number of Halogen Atoms -

Haloalkanes and Haloarenes can be classified as mono, di or polyhalogen atoms in the compounds depending on whether they contain one, two or more halogen atoms in the structure.

e.g.  $C_2H_5X$  - Monohaloalkane



Dihaloalkane



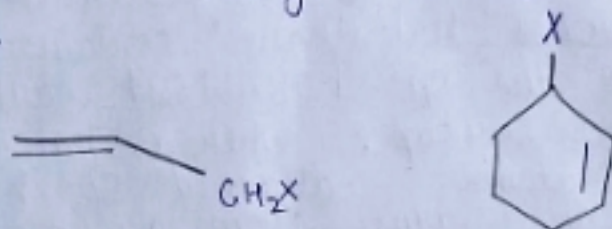
Dihaloarene

Mono halocompounds can be classified according to the hybridisation of the carbon atom to which the halogen is bonded.

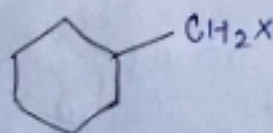
• Compounds containing  $sp^3$  C-bond

(a) Alkyl Halides - In alkyl halides, the halogen atom is bonded to an alkyl group. They can be further classified as primary, secondary or tertiary.

(b) Allylic Halides - These are the compounds in which the halogen atom is bonded to an allylic carbon.

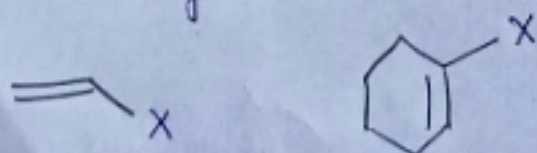


(c) Benzylic Halides - These are the compounds in which the halogen atom is bonded to a  $sp^3$  hybridised carbon atom next to an aromatic compound.



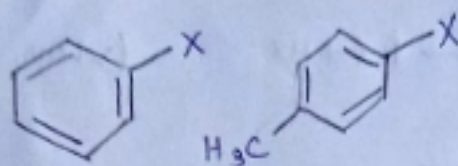
• Compounds containing  $sp^2$  C-bond

a) Vinylic Halides - These are the compounds in which the halogen atom is bonded to vinylic carbon.



b) Aryl Halides - These are the compounds in which the halogen atom is bonded to  $sp^2$  hybridised carbon atom of an aromatic ring.





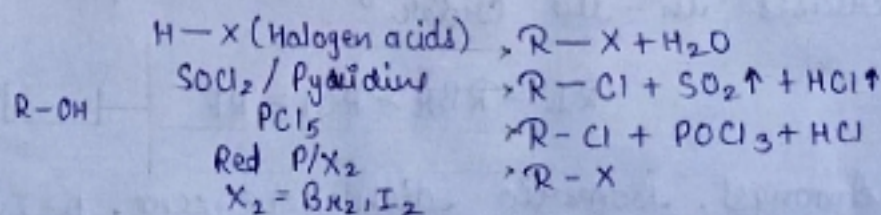
Nomenclature -

The common names of alkyl halides are derived by naming the alkyl group followed by the halide. Alkyl halides are named as halo substituted hydrocarbon in the IUPAC system of nomenclature.

Structure	Common Name	IUPAC Name
$\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CH}_3$ $\text{CH}_2=\text{CHCl}$	sec-butyl chloride Vinyl chloride	2-chlorobutane chloroethene
	o-chlorotoluene	1-chloro-2-methylbenzene
	Benzyl chloride	chloromethylbenzene

### \* Preparation of Haloalkanes

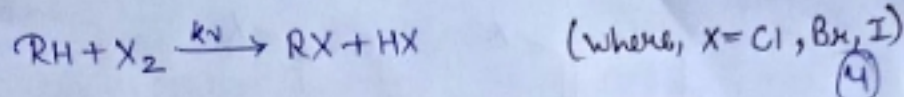
#### • From Alcohols



In the preparation of alkyl halides from alcohols, the best method is the reaction of alcohols with  $\text{SOCl}_2$  as it yields gaseous products leaving behind pure haloalkanes.

#### • From Alkanes

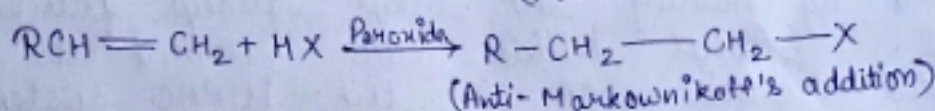
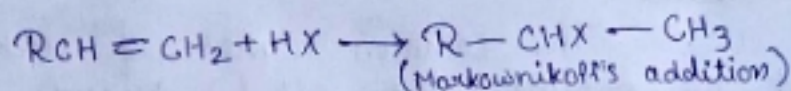
By free radical halogenation



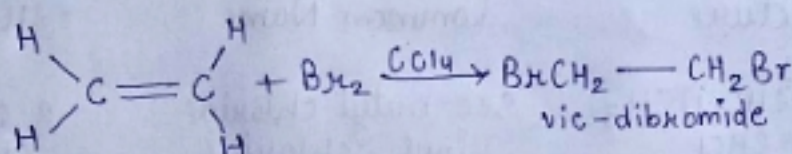
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From Alkenes

Addition of halogen acids —

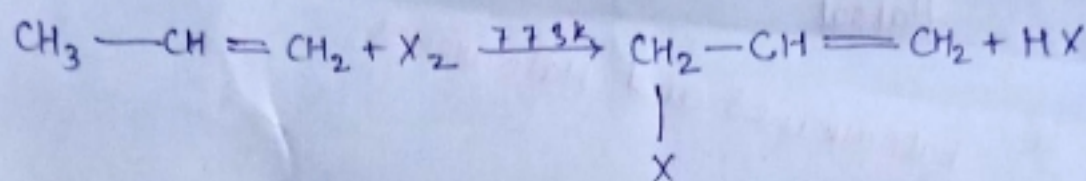


Addition of halogens —



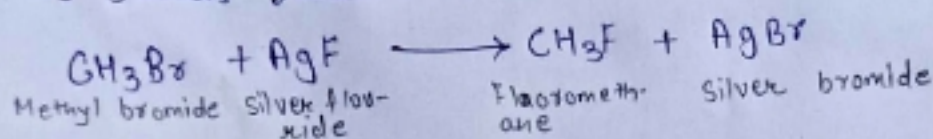
## Allylic halogenation

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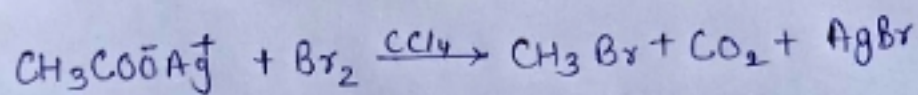
### Swarts Reaction

Fluoroalkanes are prepared by treating alkyl chlorides/bromides in the presence of a metallic fluoride such as  $\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$ ,  $\text{CoF}_2$  or  $\text{SbF}_3$ . This reaction is known as Swarts reaction.



### Barodine - Hunsdiecker reaction

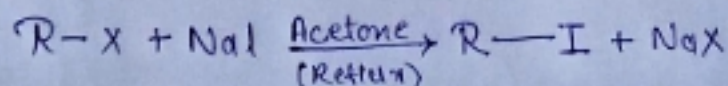
Generally, bromoalkanes are prepared by the reaction known as Barodine - Hunsdiecker reaction.



### Finkelstein reaction

Alkyl iodides are often prepared by the reaction of alkyl chlorides/bromides with  $\text{NaI}$  in dry acetone.

This reaction is known as Finkelstein reaction.



Where,  $\text{X} = \text{Cl}, \text{Br}$ .



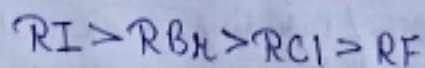
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## Properties of Haloalkanes and Haloarenes including Polyhalogen Compounds

### # Physical Properties

- i) For a given halogen atom, the boiling point of alkyl halides increases with increase in size of alkyl group.
- ii) For the same alkyl group, the boiling point decreases in the order



- iii) Amongst, isomeric dichlorobenzene, p-isomer has highest melting point due to symmetry. For isomeric alkyl halides, boiling point decreases with branching.
- iv) Alkyl halides are slightly soluble in water because they do not form H-bonds with water.
- v) The stability of haloalkanes decreases as the strength of C-X bond decreases, ( $RF > RCl > RI$ ) due to increase in size of halogen atom down the group.

Alternatively, bond dissociation enthalpy for C-X bond decreases down the group. (5)

(vi) C-X bond in aryl halides is shorter (due to partial double bond character acquired by C-X bond due to resonance), stronger and less polar than in alkyl halides.

### # Chemical Properties

#### Nucleophilic Substitution Reactions

Nucleophilic substitution reactions are of two types

**$S_N1$  reactions** — Rate  $\propto [RX]$ , occurs in two steps 1- involving formation of carbocation intermediates, and in step 2, the carbocation thus formed is attacked by the nucleophile. Step 1 is slowest and hence, is a rate determining step favoured by polar solvents. During  $S_N1$  reaction, optically active alkyl halides gives racemic products.  $S_N1$  is shown by  $3^\circ$  alkyl halides.

**$S_N2$  reactions** — Rate  $\propto [RX][OH^-]$  occurs in one step through a transition state, favoured by  $\uparrow$  solvents of low polarity and occurs from back side resulting in  $\uparrow$  inversion of products.  $S_N2$  is shown by  $1^\circ$  alkyl halides.

Order of reactivity in  $S_N1$  and  $S_N2$  mechanism are as follows —

For  $S_N1$   
 $3^\circ, 2^\circ, 1^\circ, CH_3X$   
For  $S_N2$

- For a given alkyl group, reactivity of alkyl halides in  $S_N1$  and  $S_N2$  reaction is  $RI > RBr > RCl > RF$  and order of leaving group tendency is  $I^- > Br^- > Cl^- > F^-$ .
- In case of optically active alkyl halides,  $S_N2$  mechanism results in the inversion of configuration while  $S_N1$



mechanism results in racemisation results in racemisation. (6)

- Ambident nucleophiles have two nucleophilic sites through which they can attack, e.g. nitrite ion.
- Alkyl halides are more reactive than aryl halides towards nucleophilic substitution reaction. It is due to the following reason:-

i) In haloalkanes, there is single bond between R-X which needs less bond dissociation energy, hence, they are more reactive towards nucleophiles. In haloarenes, there is double bond character between C-X bond due to resonance, therefore, has more bond dissociation energy.

ii) Carbon attached to halogen is  $sp^3$ -hybridised in haloalkane and  $sp^2$ -hybridised in haloarenes.  $sp^3$ -hybridised carbon is less electronegative than  $sp^2$ -hybridised carbon due to less s-character. Thus, C-X bond length is shorter in haloarenes than in haloalkanes.

iii) It is difficult for electron rich nucleophiles to approach electron rich benzene ring in haloarenes. There is no such thing in haloalkanes.

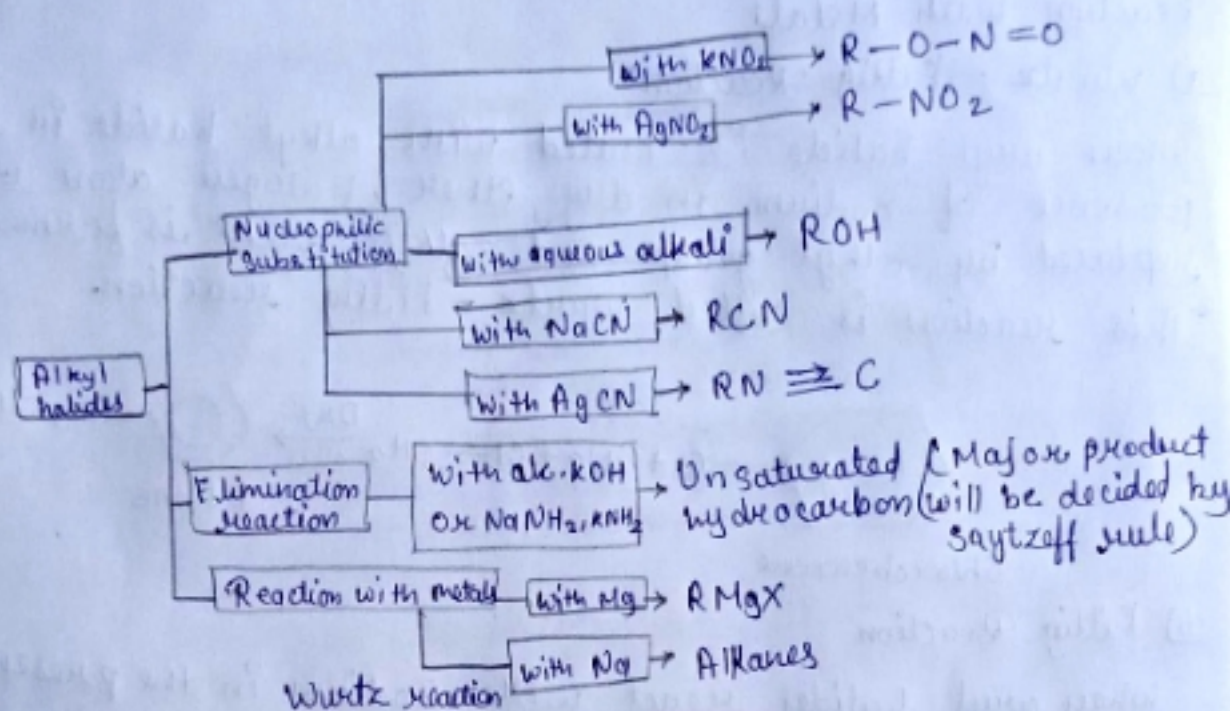
The phenyl cation formed as a result of self ionisation in haloarenes is not stabilised by resonance. Thus, it doesn't undergo  $S_N1$  mechanism.

### # Elimination reactions

Haloalkanes having  $\beta$ -hydrogen atom undergoes  $\beta$ -elimination when heated with alcoholic solution of KOH. Hydrogen atom from  $\beta$ -position and halogen atom from  $\alpha$ -position is eliminated to give unsaturated product.

Flow chart for some chemical properties of Alkyl Halides —





### # Basic Points about optical Isomerism

- The Carbon atom which is attached to four different monovalent atoms is called asymmetric or chiral Carbon atom.
- Enantiomers are the mirror image of each other and are non-superimposable.
- Substances which rotate the plane polarised light towards right are called levorotatory (-).
- If the product formed in a reaction has a same stereochemistry as that of reactant, this process is called retention of Configuration.
- If the product formed in a reaction has a stereochemistry opposite to that of reactant, it leads to inversion of Configuration.

### # Electrophilic Substitution Reactions (In Aryl halides)

Halogen atoms is o-, p-directing in electrophilic substitution reactions since, electron density increases at o and

p-position due to +R-effect.

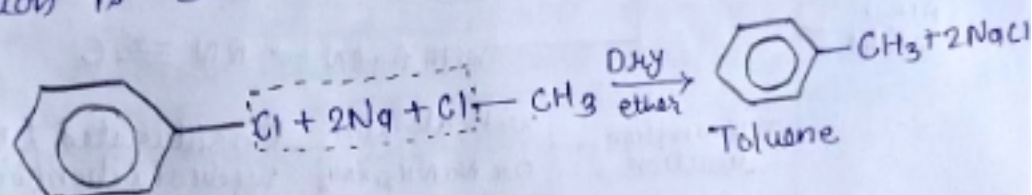
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## Reaction with Metals

### a) Wurtz - Fittig Reaction

When aryl halide is heated with alkyl halide in the presence of sodium in dry ether, halogen atom is replaced by alkyl group and alkyl arene is formed.

This reaction is called Wurtz - Fittig reaction.

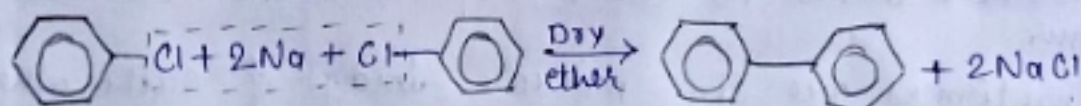


Chlorobenzene

Toluene

### b) Fittig Reaction

When aryl halides react with sodium in the presence of dry ether, two aryl groups are joined together and diphenyl is formed. This reaction is called Fittig reaction.



Diphenyl



# Flow chart for some chemical properties of Aryl halides

