💿 🛛 ALKYL HALIDES & ARYL HALIDES 📀

Compounds derived from hydrocarbons by replacement of one or more H-atoms by corresponding no. of halogen atoms are known as halogen derivatives.

There are three major classes of organohalogen compounds ; alkyl halides, vinyl halides, and aryl halides. An **alkyl halide** simply has a halogen atoms bonded to one of the sp³ hybrid carbon atoms of an alkyl group. A **vinyl halide** or **Aryl halide** has a halogen atom bonded to one of the sp² hybrid carbon atoms or an aromatic ring. They are different from alkyl halides because their bonding and hybridization are different.

Alkyl halides may be further classified as mono, di, tri,..... and primary, secondary or tertiary halides.



The carbon-halogen bond in an alkyl halide is **polar** because halogen atoms are more electronegative than carbon atom. Most reactions of alkyl halides result from breaking this polarized bond. The carbon atom has a partial positive charge, making it some what **electrophilic**.

CLASSIFICATION

On the basis of nature of hydrocarbon from which they are obtained, hydrocarbon derivatives can be classified as:



CH



- (a) Alkyl halides : Halogen derivative of alkanes.
- (b) Alkenyl halides : Halogen derivative of alkenes.
- (c) Alkynyl halides : Halogen derivative of alkynes
- (d) Aryl halides : Halogen derivative of arenes (aromatic)

Alkyl halides : They are further classified on the basis of halogen atoms introduced in the molecule. e.g.

- (i) Mono halides: These involves replacement of one H-atom by halogen atom.
 - General formula $C_n H_{2n+1} X$
- **Ex.** CH_3Cl Methyl chloride (Chloro methane)

CH₂CH₂Br Ethyl bromide (Bromo ethane)

- (ii) **Dihalides :** Replacement of two H-atom by halogen atoms.
- $General formula C_n H_{2n} X_2$ Ex. CH₂X₂ Methylene dihalide

$\begin{array}{c} \mathrm{CH}_2\mathrm{X} \\ \\ \mathrm{CH}_2\mathrm{X} \end{array}$	Ethylene dihalide or	Vicinal dihalide
CH ₃ CHX ₂	Ethylidene dihalide	or geminal dihalide

(iii) Trihalides : Replacement of three H-atoms by halogen atoms. General formula - $C_n H_{2n-1} X_3$.

Ex. CHX₃ Trihalo methane or haloform

CH₃-X

(iv) Tetra halide and Perhalo compounds : Replacement of 4 H-atoms by halogen atoms

 $(in CH_4 \longrightarrow CCl_4) \longrightarrow Tetrahalides.$

When all the H-atoms from an alkane are replaced by halogen atoms, then the compounds are called as perhalo compound - General formula $C_n H_{2n-2} X_4$ (tetra halide).

 $CH_4 \longrightarrow CX_4$ (Per halo methane)

 $C_2H_6 \longrightarrow C_2X_6$ (Per halo ethane)

MONO HALIDES : These are classified on the basis of nature of C-atom carrying the halogen atom .

(A) **Primary halide or 1° alkyl halides :** Halogen atom attached with a **primary or 1° C-atom**.

(B)

Halo methane or methylhalide

Secondary or 2° alkyl halides : Halogen atom linked with 2° C-atom.

Ex.

 $\begin{array}{ccc} CH_{3} - CH - CH_{3} & 2 \text{-halo propane} \\ X & Iso propyl halide \\ CH_{3} - CH - CH_{2} - CH_{3} & 2 \text{-halo butane} \\ X & Sec. butyl halide \\ \end{array}$



(C) Tertiary halide or 3° alkyl halide : halogen atom linked with 3° C-atom. R $\begin{array}{c} R - \stackrel{|}{\underset{R}{\overset{|}{C}}} - X \\ \stackrel{|}{\underset{R}{\overset{|}{R}}} \end{array}$ Ex. (tert.alkyl halide) Isomerism : Alkyl halides shows position and chain isomerism -Ex. $C_{2}H_{7}Cl \longrightarrow CH_{3}CH_{2}CH_{2}Cl$ CH₃CHCH₃ Position isomers Ex. C₄H₉Cl **(a)** 1 - chloro butane CH₃ CH—CH₂Cl 1-chloro-2-methyl propane **(b)** CH₃—CH₂—CH—CH₃ 2 - chloro butane **(c)** CH₂ CH₃-C-Cl (d) 2-chloro-2-methyl propane CH₂ $a, b \longrightarrow$ Chain isomers $a, c \longrightarrow$ Position isomers $a, d \longrightarrow$ Chain and position isomers b,c ----> Chain and position isomers b, $d \longrightarrow$ Position isomers $c, d \longrightarrow$ Chain isomers RI > RBr > RCl > RFReactivity order : The order of reactivity of alkyl halides is -Bond energy values : C-I (57.4), C-Br (65.9), C-Cl (78.5) and C-F (105.4) K.cal/mole C-I bond is most reactive because lower energy is required to break the bond. On the basis of nature of alkyl group the reactivity order of alkyl halide is tert > Sec. > Primary Since alkyl groups, are electron repelling or electron releasing, larger no. of alkyl groups on C-atom of C-X greater is the electron density on C-atom hence ease in release of X atom as X^{-} ion (+ I effect of alkyl group) $\begin{array}{c} CH_{3} \\ CH_{3} \rightarrow C \rightarrow X \\ CH_{.} \end{array} \longrightarrow \begin{array}{c} CH_{3} - CH_{3} - CH_{3} \\ CH_{.} \end{array} \xrightarrow{} CH_{3} - CH_{3} \\ CH_{3} - CH_{3} \end{array}$ Alkyl halides are generally more reactive than the corresponding alkanes due to the presence of polar covalent (-C-X) bond. So alkyl halides (R-X) undergo nucleophilic substitution reaction.

The centre for attacking $\stackrel{1}{\text{Nu}}$ is $-\stackrel{1}{\text{C}}_{\text{atom}}^{+}$



GENERAL METHOD OF PREPARATION OF MONOHALIDES :

1. By direct halogenation of alkanes :

$$R - H + Cl_2$$
 U.V. light $R - Cl + HCl$

(excess)

2. By the addition of H—X on alkenes :

$$\begin{array}{cccc} \text{R--CH} = \text{CHR} + \text{HX} & \longrightarrow & \text{RCH}_2 - \text{CHXR} \\ \text{CH}_2 = \text{CH}_2 + \text{HX} & \longrightarrow & \text{CH}_3 - \text{CH}_2 \text{X} \\ \text{CH}_3 - \text{CH} = \text{CH}_2 + \text{HX} & \longrightarrow & \text{CH}_3 - \text{CH} - \text{CH}_2 \\ & & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & & \\$$

Isopropyl halide

- 3. By Alcohols :
 - (a) By the action of hydrogen halides :

Ex.
$$R$$
— CH_2 — $OH \xrightarrow{H-X} RCH_2$ — X

Mechanism :

$$R - CH_{2} - OH \xrightarrow{H^{+}}_{(H-X)} R - CH_{2} \xrightarrow{O}_{H} - H \xrightarrow{-H,O} R - CH_{2} \xrightarrow{X\Theta} R - CH_{2} - X$$
(unstable) (Product)

In this reaction intermediate **carbocation** is formed so **rearrangement** (H^- shifting or CH_3^- shifting) can take place. ZnCl₂ act as dehydrating agent and absorbs H₂O from the reaction so good yield of halide is obtained. Also it generates H⁺ from HCl.

$$HCl + ZnCl_2 \longrightarrow ZnCl_3^1 + H^{\oplus}$$

Reactivity order for alcohol:

Reactivity ∞ stability of intermediate carbocation, so reactivity order : Tert. alc. > Sec. alc. > Pri. alc.

Reactivity order of H—X is : HI > HBr > HCl

HI is maximum reactive so it reacts readily with 1°, 2° and 3° alcohols.

$$R \longrightarrow OH + HI \longrightarrow R \longrightarrow I + H_2O$$

HCl and also 1° alcohol are less reactive so $ZnCl_2$ or some amount of H_2SO_4 is needed to increase the reactivity.

$$CH_3 - CH_2 - OH + HCl \xrightarrow{ZnCl_2} CH_3 - CH_2 - CH_3$$

Ex. CH_3 -At normal condition :

 $CH_3 \longrightarrow CH_2 \longrightarrow HCl \longrightarrow (no reaction)$

Note : HCl + ZnCl, is called as lucas reagent, alcohol gives turbidity with lucas reagent.

Reactivity towards lucas reagent (difference in 1°, 2° and 3° alcohol).

	1° alcohol	2° alcohol	3° alcohol
Time to	in 30 min.	in 5 min.	in 1 min.
give turbidity	7		



(b) By the action of phosphorus halides $(S_{N^1}$ mechanism) :

 $3R \longrightarrow OH + PCl_3 \longrightarrow 3RCl + H_3PO_3$

 PBr_3 and PI_3 are less stable, thus for bromides and Iodides, $(P + Br_2)$ Or $(P + I_2)$ mixture is used.

(c) By reaction with thionyl chloride - (Darzen's procedure) (S_{N^1} and S_{N^2} mechanism):

 $R - OH + SOCl_2 \xrightarrow{Pyridene} R - Cl + SO_2 + HCl$

One mole One mole

Because of less stability of SOBr₂ and SOI₂, R—Br and RI does not obtained by this method.

4. Borodine – Hunsdicker's reaction :

5. By halide exchange :

R-Cl or R-Br+KI $\xrightarrow{\text{Acctone}}$ R-I + KCl or KBr (Conant finkelstein reaction) 2CH₃Cl + HgF₂ \longrightarrow 2CH₃-F + HgCl₂ (Swartz reaction)

R– I and R—F can be prepared by this method only.

6. By reaction of alkanes with sulphuryl chloride (SO₂Cl₂):

 $R-H + SO_2Cl_2 \xrightarrow{light} R-Cl + HCl + SO_2$

PHYSICAL PROPERTIES

- (a) The lower members CH_3F , CH_3Cl , CH_3Br , C_2H_5Cl and C_2H_5F are gases at room temp. CH₃I and members upto C_{18} are colourless sweet smelling liquids.
- (b) Higher B.P. than parent alkanes.
 Decreasing order of B.P. is : R I > R Br > R Cl > R F among isomeric R - X decreasing order of B.P. is : Primary > Secondary > tertiary
- (c) R—F and R—Cl → lighter than water R—Br and R—I → heavier than water Decreasing order of density is : R—I > R—Br > R—Cl > R—F
 (d) R—X are polar co-valent compounds but insoluble in water because they can not form H-bonds. They dissolve in organic solvents.
 (e) R—X burns with a green flame due to interaction of X with Cu wire. (Beilstein test)
 (f) The stability order is : R—F > R—Cl > R—Br > R—I R—I is least stable and darken in light due to photodecomposition. 2R—I → P·→R—R + I₂



CHEMICAL PROPERTIES :

Α. NUCLEOPHILIC SUBSTITUTION REACTION (SN): Due to electronegativity difference the -X bond is

highly polarised bond. $\begin{pmatrix} |_{\delta^+} & \delta^- \\ - & C \\ | \end{pmatrix}$

Thus the C-atom of the $\overset{\delta_+}{C} - \overset{\delta_-}{X}$ bond becomes centre to attack by a nucleophile (Nu).

 X^{1} ion from R—X molecule is substituted by a $\overset{1}{Nu}$. i.e. S_{N} reaction are the most common reactions in R—X.



Mechanism of S_{N^1} and S_{N^2} :

 \mathbf{C} S_{N^1} Mechanism : S_{N^1} stands for uni molecular nucleophilic substitution. The mechanism involves two steps. Consider the hydrolysis of tert. butyl bromide with aqueous NaOH.

Step 1: The alkyl halide ionises to give a planar carbonium ion. The carbonium ion is planar because the central positively charged carbon is sp² hybridized.



Step-2: The nucleophile can attack the planar carbonium ion from either side to give the product.





- (i) Ionisation is the rate determining step because it is the slow step. In other words, the rate at which alcohol is formed should depend upon the concentration of tertiary alkyl halide alone.
- $\therefore \qquad \text{Rate} = K[R_3C Br]$ It is obvious that the reaction follows first order kinetics, therefore reaction is called S_{N^1} .
- (ii) The reactivity order for S_{N^1} reaction \propto stability of carbocations formed by halides.
- $\therefore \quad \text{reactivity order of halides } (S_N^1) \text{ varies as follows :} \\ \text{Benzyl halide > Alkyl halide > 3°halide > 2° halide > 1° halide > methyl halide.} \\ \end{cases}$
- (iii) Remember that in case alkyl halide is optically active, SN¹ reactions lead to racemisation.

Energetics of the S_N¹



Table - : Dielectric constants (\in) and ionisation rates of t-Butylchloride in common solvents

Solvent	E	Relative rate
H ₂ O	80	8000
CH3OH	33	1000
C ₂ H ₅ OH	24	200
(CH ₃) ₂ CO	21	1
CH ₃ CO ₂ H	6	

 S_{N^2} mechanism : S_{N^2} stands for bimolecular nucleophilic substitution. In this type of nucleophilic substitution reaction, there occurs bond making and bond breaking simultaneously.



(ii) Reactivity order of alkyl halide varies as follows : $CH_3X > 1^\circ$ halide $> 2^\circ$ halide $> 3^\circ$ halide



- (iii) The order of reactivity among 1° alkyl halides is : $CH_3X > C_2H_5X > C_3H_7X$ etc. Remember that in case alkyl halide is optically active, SN² reactions lead to Walden inversion.
- (iv) Thus in short 3° alkyl halides react by S_{N^1} , 1° by S_{N^2} and 2° by either or both of them SN¹ and SN² depend upon the nature of the alkyl halide and the reagent.
- (v) For a given alkyl group the order of reactivity is (for S_{N^1} and S_{N^2} both): RI > RBr > RCI > RF
- (vi) In addition to substitution reaction alkyl halide also undergo elimination reactions to form alkene with the removal of a molecule of hydrogen halide (dehydrohalogenation). In dehydrohalogenation, hydrogen and halogen atoms are eliminated from two adjacent carbon atoms, the reaction also known as β -elimination may proceed by $E_1 \& E_2$ mechanism (analogous to S_{N^1} and S_{N^2} mechanism). The order of elimination reaction is : 3° halides > 2° halides > 1° halides
- (vii) In general 3° halides tend to react by elimination; 1° halides by substitution and 2° halides by either or both of the reactions.

B. ELIMINATION REACTIONS (ER) : Alkyl halides also undergo ER in the presence of base as Nu (Loss of H—X and formation of = bond)

$$\overset{\Theta}{\operatorname{OR}} + \overset{H}{\operatorname{CH}_2} - \overset{\Phi}{\operatorname{CH}_2} - \overset{\Phi}{\operatorname{Cl}} \xrightarrow{\Lambda} \overset{R}{\operatorname{ROH}} + \overset{R}{\operatorname{CH}_3} - \overset{H}{\operatorname{CH}} = \overset{H}{\operatorname{CH}_2} + \overset{\Theta}{\operatorname{CH}_2} + \overset{\Theta}{\operatorname{CH}_2} + \overset{\Phi}{\operatorname{CH}_2} + \overset{\Phi}{\operatorname{CH}_2} \xrightarrow{R} \overset{R}{\operatorname{ROH}_2} + \overset{\Phi}{\operatorname{CH}_3} - \overset{R}{\operatorname{CH}_2} + \overset{\Phi}{\operatorname{CH}_2} + \overset{R}{\operatorname{CH}_2} + \overset{R}{\operatorname{CH}_2} + \overset{R}{\operatorname{CH}_2} + \overset{R}{\operatorname{CH}_2} \xrightarrow{R} \overset{R}{\operatorname{CH}_2} + \overset{R}{\operatorname{C$$

1. NUCLEOPHILIC SUBSTITUTION REACTION (SN):





(h) Reaction with KNO₂ and AgNO₂

$$\stackrel{A+}{R} = \stackrel{A-}{X} + \stackrel{+}{KNO_3} - \stackrel{Ale.}{\Delta} + \stackrel{R-O-N}{R} = O + KX + RNO_2$$

$$\stackrel{A+}{R} = \stackrel{A-}{X} + \stackrel{A}{AgNO_2} - \stackrel{Ale.}{\Delta} + \stackrel{R-N \bigvee_{0}^{O}}{O} + \stackrel{Ag-X + RONO}{O}$$

$$\stackrel{A+}{R} = \stackrel{A-}{X} + \stackrel{A}{AgNO_2} - \stackrel{Ale.}{\Delta} + \stackrel{R-N \bigvee_{0}^{O}}{O} + \stackrel{Ag-X + RONO}{O}$$

$$\stackrel{R-Z + AgNO_2}{covalent boud} - \stackrel{Ale.}{\longrightarrow} - R - N \stackrel{K-DR + NaX}{O}$$
(i) Reaction with NaOR' (Sodium alkoxide): (williamson synthesis reaction)

$$\stackrel{R-X + NaOR'}{R--CH_2 - Cl + NaOCH_3 - \rightarrow CH_3 - CH_2 - O - CH_3 (major)}$$
(i) CH₃ - CH₂ - Cl + NaOCH₃ - \rightarrow CH₃ - Cl₃ - Cl₄ - Cl₄ + CH₃ - CH=CH₂

$$\stackrel{CH_3}{Cl} - \stackrel{CH_3}{Cl} - \stackrel{C-Cl}{Cl} + NaOCH_5 - \rightarrow CH_3 - CH_2 - CH_3 - CH_4 - CH_1 + CH_1 - CH_1 - CH_1 - CH_1 + CH_1 + CH_1 - CH_1 + CH_2 + CH_1 + CH_1 + CH_2 + CH_1 + CH_1 + CH_2 - CH_2 - CH_2 - CH_2 - CH_2 + CH_2 +$$



(vi)
$$CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{1} + NH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{2} + NH_{4}Cl$$

(more reactive) (Elimination is more)
(vii) Reaction with $CH \equiv \overline{C} \stackrel{+}{Na} :$
 $R \xrightarrow{-} X + CH \equiv \overline{C} \stackrel{+}{Na} \xrightarrow{A} R \xrightarrow{C} C \equiv CH + NaX$
 $IF \qquad CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{A} CH_{3} \xrightarrow{C} C = CH_{2} + NaX + CH \equiv CH$
 $CH_{3} \xrightarrow{C} CH_{3} \xrightarrow{$

2. Elimination Reaction : (Dehydrohalogenation) Alkyl halides undergo β - elimination on treatment with KOH (alc.)

Competition between substitution and elemination reactions :

Alkyle halides	S _N 2/E ₂	S _N 1/E ₁
1° Alkyl halides	Mainly give substitution unless	Can not undergo SN^1/E^1
	sterically hindered alkyl halide	-
	or sterically hindered base in	
	which case elimination is favoured	
2° Alkyl halides	Both substitution and elemination,	Both substitution and elemination
A	stronger base/ bulkier base or high	high temp. greater of percentage
	temp. greater percentage of elimination.	ofelimination
3° Alkyl halides	Mainly elimination	Both substitution and elimination,
		high temp greater percentage of
		elimination.









Saytzeff rule : According to this rule "The dehydrohalogenation of an alkyl halide results preferentially in the production of more alkylated alkene i.e. more stable alkene.

3. Wurtz Reaction: When a mixture of different alkyl halides, $(R_1 - X)$ and $(R_2 - X)$ is used a mixture of alkane is formed

$$R_1 - X + 2Na + X - R_2 \xrightarrow{\text{Ether}/\Delta} R_1 - R_2 + R_1 - R_1 + R_2 - R_2 + NaX$$

If 'Zn' is used in place of 'Na' the reaction is called **Frankland's Reaction**.

4. Halogenation of alkyl halides :

$$CH_{3} - Cl + Cl_{2} \xrightarrow{\Delta \text{ or U.V.}} CH_{2}Cl_{2} \xrightarrow{Cl_{2}} CH_{2}Cl_{3} \xrightarrow{Cl_{2}} CH_{4}Cl_{4}$$

Similarly
$$C_2H_5Cl \xrightarrow{Cl_2} C_2H_4Cl_2 \xrightarrow{Cl_2} C_2H_3Cl_3 \xrightarrow{Cl_2} C_2Cl_6$$

5. **Reduction :** R - X are reduced to corresponding alkane.

$$R - X + 2H \xrightarrow{\text{Reducing agent}} R - H + HX$$

(i)
$$CH_3CH_2Br + H_2$$
 Ni $CH_3CH_3 + HBr$

(ii) $CH_3CH_2CH_2Br+2H_Zn/HCI$, $CH_3-CH_2-CH_3+HBr$

(iii)
$$C_2H_5I + HI \underline{\text{Red.P}} C_2H_6 + I_2$$

6. Formation of Organometallic compounds :

(i)
$$R \rightarrow X + Mg \rightarrow RMgX$$
 (Grignard reagent)

(ii)
$$2C_2H_5Br + 2Zn \xrightarrow{dry ether} (C_2H_5)_2Zn + ZnBr_2$$

(iii)
$$2C_2H_5Br + Hg(Na) \longrightarrow (C_2H_5)_2Hg + 2NaBr$$

Sodium Amalgam

$$4C_{2}H_{5}Cl + 4Na/Pb \longrightarrow (C_{2}H_{5})_{4}Pb + 4NaCl + 3Pb$$

Sodium lead Alloy Tetra ethyl lead (used as antiknocking agent)

(iv

7. Friedel - Crafts reaction :



8. Action of heat :

(i)
$$CH_3 - CH_2 - CH_2 - Cl \xrightarrow{At \text{ or below } 300^\circ C}_{(Rearrangement)} CH_3 - CH_3 - CH_3 - CH_3$$

(ii)
$$CH_3 - CH - CH_2 \xrightarrow{Above}{300^{\circ} C} CH_3CH = CH_2 + HI (Elimination)$$

 $H + H + Propylene$

Uses :

(a) As alkylation agent (Wurtz reaction)

(b) As synthetic reagent

(c) Lower members used as anaesthetic agent, refrigerant or solvent.

DIHALIDES

General formula $C_n H_{2n} X_2$. Two H - atom of alkanes, replaced by two halogen atoms to form dihalides.

Dihalides are classified as :

(a) Gem dihalide : The term Gem is derived from geminal means - same position.

Two similar halogen atoms are attached to same C - atom

Ex. CH_3CHX_2 ethylidene dihalide (1, 1 - dihalo ethane)

 $\begin{array}{c} CH_{3} \\ CH_{3} \end{array}$ CHX₂ Isopropylidene dihalide (2, 2 - dihalo propane)

(b) Vic dihalides : Vic term from - Vicinal means adjacent C - atoms Two halogen atoms are attached on adjacent carbon atom.

Ex. $\begin{array}{cccc} H_{2} - CH_{2} & H_{-} \\ I & I \\ X & X \end{array}$ $\begin{array}{cccc} H_{-} - CH_{-} \\ H & X & X \end{array}$ $\begin{array}{cccc} H_{-} \\ H & X & X \end{array}$ Vic and Gem dihalides are position isomers. ethylene dihalide (1,2-dihaloethane) (1,2-dihalopropane)

α, ω dihalides : Halogen atoms are attached with terminal C - atom. They are separated by 3 or more C - atom. They are also known as polymethylene halides.

Ex.
$$\begin{array}{c} CH_2 - CH_2 - CH_2 - CH_2 \\ \downarrow \\ X \\ \end{array}$$
 $\begin{array}{c} CH_2 - CH_2 - CH_2 \\ \downarrow \\ X \\ \end{array}$ $\begin{array}{c} (1,4-dichloro butane) \\ Tetramethylene dichloride \\ \end{array}$



(c)

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PHYSICAL PROPERTIES :

- (i) Lower members are colourless, oily liquids with sweet smell. Higher members are solid.
- (ii) The reactivity of gem dihalides is lesser than vicinal or mono halides. [Reason in presence of one halogen atom (Strong attracting –I effect) the other halogen atom can not be so easily replaced.
- (iii) These are heavier than water.

CHEMICAL PROPERTIES :

Action of KOH(alc.): (Dehydrohalogenation) **(i)** CH₂X CH₂X CH ∭ CH or $(i) \text{ alc. KOH} \rightarrow (i) \text{ NaNH}_2$ Action of KOH(aq.): (Hydrolysis) It is a distinction test for gem and vic dihalides. **(ii)** $CH_2 - Cl$ | $CH_2 - Cl$ $\rightarrow \begin{array}{c} CH_2 - OH \\ | \\ CH_2 - OH \end{array} + 2KCl$ + 2KOH(aq.) -**(a)** Glycol Vic - dihalide. 1, 2 - ethane diol. **(b)** CH₃CHXCH₂Y KOH (aq.) $CH_3 - CH - CH_2$ Vic-dihalide. propane - 1, 2 - diol CH, CH₃ KOH (aq.) $CH_3CX_2CH_3 \xrightarrow{KOH(aq.)} CH_3COCH_3$ and Gem. (Ketone) CHX, CHO Reaction with KCN: Gem and Vic dihalide gives different products (iii) Vic.: + 2KCN $\xrightarrow{-2KCl}$ $\xrightarrow{CH_2 - CN}$ $\xrightarrow{H_2O/H^+}$ $\xrightarrow{CH_2 - COOH}$ $\xrightarrow{\Delta}$ $\xrightarrow{CH_2 - CO}$ $\xrightarrow{CH_2 - CO}$ $\xrightarrow{CH_2 - CO}$ CH₂Cl ĊH,Cl Succinic anhydride Succinic acid



Gem.:

$$CH_{3} - CH < \stackrel{Cl}{\underset{Cl}{\overset{2KCN}{\longrightarrow}}} CH_{3} - CH < \stackrel{CN}{\underset{CN}{\overset{H_{2}O/H^{+}}{\longrightarrow}}} CH_{3} - CH < \stackrel{COOH}{\underset{COOH}{\overset{\Delta}{\xrightarrow{OO_{2}}}} CH_{3} - CH_{2} COOH \xrightarrow{OO_{2}}{\underset{OOO}{\overset{COOH}{\longrightarrow}}} CH_{3} - CH_{2} COOH$$

- **(i)** - CN group on acid hydrolysis gives - COOH
- Two COOH group on one C atom on heating always loose CO2 to form monocarboxylic acid. **(ii)**

CH₃OH

- (iii) Two – COOH group on vic. C – atom on heating loose H₂O to form anhydride.
- **(iv) Dehalogenation**:

Vic.

$$\begin{array}{c} CH_2Br\\ \mid\\ CH_2Br\\ CH_2Br\end{array} + Zn \xrightarrow[\text{Heat}]{} \begin{array}{c} CH_3OH\\ \mid\\ Heat\\ \end{array} \xrightarrow[\text{Heat}]{} \begin{array}{c} CH_2\\ CH_2\\ CH_2\\ \end{array} + ZnBr_2\\ CH_2\\ \end{array}$$

Gem.

$$CH_{3} - CH_{2}CHBr_{2} + Zn \xrightarrow{CH_{3}OH} CH_{3} - CH_{2} - CH = CH - CH_{2} - CH_{3} + ZnBr_{2}$$

(Twice Carbon Product)

$$\boldsymbol{\alpha} - \boldsymbol{\omega}. \quad CH_2 < \begin{pmatrix} CH_2 Br \\ CH_2 Br \end{pmatrix} + Zn \qquad \xrightarrow{CH_3 OH} \qquad H_2 C < \begin{pmatrix} CH_2 \\ H_2 \end{pmatrix} + Zn Br_2$$

 α, ω - dihalide.

cyclopropane

GRIGNARD REAGENT

General Method of Preparation :

Grignard reagents are prepared in the laboratory by the action of alkyl halides on magnesium metal in the presence of dry ether.

$$R - X + Mg \xrightarrow{dry} RMgX$$

(Grignard reagent)

(Alkyl magnesium halide)

The ease of formation of Grignard reagent is in the order RI > RBr > RCI

Ether is used to dissolved the Grignard reagent by coordination.



Chemical Reactions :

	(i) O ₂ (ii) H ₃ O	\rightarrow	R—OH	1° Alcohol
	H ₂ CO/H ₃ O ⁺	\rightarrow	RCH ₂ —OH	1° Alcohol
	CH ₂ —CH ₂ /H ₃ O ⁺	\rightarrow	R—CH ₂ —CH ₂ —OH	1° Alcohol
	RCHO/H ₃ O	\rightarrow	R ₂ CHOH	1° Alcohol
	HCOOEt/H ₃ O ⁺	\rightarrow	R ₂ CHOH	2° Alcohol
	RCOR/H ₂ O	\rightarrow	R ₃ C—OH	3° Alcohol
	RCOOEt/H ₂ O HCOOEt	\rightarrow \rightarrow	R ₃ C—OH RCHO	3° Alcohol aldehyde
RMgX —	RCN/H ₂ O	\rightarrow	RCOR	Ketone
	RCOOEt	\rightarrow	RCOR	Ketone
	$CO_2 + H_2O$	\rightarrow	RCOOH	Acids
	HOH or ROH or NH ₃ or Ph — OH or R—NH ₂ or RNH — R			
	or CH \equiv CH or Ph $-$ NH ₂	\rightarrow	R—H	Alkane
	R—X	\rightarrow	R—R	Alkane
	R ₃ N	\rightarrow	No reaction	
	$CICH_2$ — CH = CH_2	\rightarrow	$\mathbf{R}-\mathbf{CH}_{2}-\mathbf{CH}=\mathbf{CH}_{2}$	Alkene
	CI—NH ₂	→	R—NH ₂	1° Amine
	CI—CN	\rightarrow	R—CN	Cyanides
	X	\rightarrow	R—X	Alkyl halide
	CICOOEt	\rightarrow	RCOOEt	Ester

ARYL HALIDE

If halogen atom is directly attached to the benzene ring, then compound is called as Haloarene.





From Phenol : OH



Cl

$$3C_6H_5OH + POCl_3 \longrightarrow (C_6H_5)_3PO_4 + 3HCl$$
(major)

Sandmeyer's reaction :

$$\begin{array}{c} \overbrace{\bigcirc}^{N_2Cl} + CuCl & \xrightarrow{HCl} & \overbrace{\bigcirc}^{Cl} + N_2 \\ \hline \bigcirc & N_2Cl \\ + CuBr & \xrightarrow{HBr} & \overbrace{\bigcirc}^{Br} + N_2 \end{array}$$

Reaction with KI :

 $\rightarrow \qquad \bigcirc \qquad I + N_2 + KCl$

Balz-schiemann's reaction :

$$\bigcirc N_2 Cl + HBF_4 \longrightarrow \bigcirc N_2 BF_4 \longrightarrow \bigcirc HBF_3 + N_2$$

Hunsdicker reaction :

$$\bigcirc \overset{\text{COOAg}}{\longrightarrow} + \text{Cl}_2 \longrightarrow \bigcirc \overset{\text{Cl}}{\longrightarrow} + \text{CO}_2 + \text{AgCl}$$

Raschig Process :

$$2 \bigcirc + 2\text{HCl} + O_2 \xrightarrow{\text{CuCl}} 2 \bigcirc + 2\text{H}_2\text{O}$$

CHEMICAL PROPERTIES

- (i) Chlorobenzene is essentially inert to aqueous sodium hydroxide at room temperature.
- (ii) Aryl halide are very less reactive than alkyl halides in nucleophilic substitution reactions.
- (iii) The carbon-halogen bonds of aryl halides are too strong & aryl cations are too high in energy to permit aryl halides to ionize readily $S_{N^{1}}$ -type process.
- (iv) The optimal transition state geometry required for S_{N^2} process cannot be achieved.
- (v) Nucleophilic attack from the side opposite the carbon-halogen bond is blocked by the aromatic ring.



The Elimination-Addition Mechanism of Nucleophilic Aromatic Substitution (Benzyne)

(i) Very stong base such as sodium or potassium amide react with aryl halide, even those without electron withdrawing substituents to give products corresponding to nucleophilic substitution of halide by the base.



Mechanism

Step-1: Elimination stage ; Amide ion is a very strong base and brings about the dehydrohalogenation of chlorobenzene by abstracting a proton from the carbon adjacent to the one that bears the leaving group. The product of this step is an unstable intermediate called benzyne.



Step-2: Beginning of addition phase ; Amide ion acts as a nucleophile and adds to one of the carbons of the triple bond. The product of this step is a carbanion.



Step-3: Completion of addition phase ; The aryl anion abstracts a proton from the ammonia used as the solvent in the reaction.





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NOTE: The sp² orbital in the plane of the ring in benzyne are not properly aligned for good overlap thus π bonding is weaker than alkyne.





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- (ii) An ortho nitro group exert a comparable rate-enhancing effect, m-chloronitrobenzyne while much more reactive than chlorobenzyne itself, is thousand of times less reactive than either o-or p-chloronitrobenzene.
- (iii) The effect of o- & p-nitro substituents is cummulative, as the rate data for substitution with methoxide ion in a series of nitro-substituted chlorobenzene derivative demostrate increasing rate of reaction as :



(iv) In contrast to nucleophilic substitution in alkyl halides, where alkyl fluorides are exceedingly unreactive, aryl fluorides undergo nucleophilic substitution readily when the ring bears an o-or a p-nitro group.



- (v) Indeed, the order of leaving group reactivity in nucleophilic aromatic substitution is the opposite of that seen in alphatic substitution.
- (vi) Fluoride is the best reactive leaving group in nucleophilic aromatic substitution, iodide the least reactive.

Relative reactivity towards sodium methoxide in methanol (50°C) X = F Cl Br I 312 1.0 0.8 0.4 NO₂

(vii)

Kinetic studies of many of the reactions described in teh section have demostrated that they follow a second-order rate law.

Rate = k[aryl halide] [nucleophile]

(viii) Second order kinetics is usually interpreted in terms of a bimolecular rate determining step.



CHEMISTRY FOR JEE MAIN & ADVANCED



Mechanism :

Step -1 - Addition stage. The nucleophile, in this case methoxide ion, adds to the carbon atom that bears the leaving group to give a cyclohexadienyl anion intermediate.



Step -2 - Elimination stage. Loss of halide form the cyclohexadienyl intermediate restores the aromaticity of the ring and gives the product of nucleophilic aromatic substitution.



Presence of deactivating group in ortho and para position makes the nucleophilic substitution easier. **Reactivity Order :** (Towards nucleophilic substitution)





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1. Miscellaneous Reactions :

Freons (Polychlorofluoro Alkane)

(i)
$$\operatorname{CCl}_4 + \operatorname{HF} \xrightarrow{\operatorname{SbCl}_4} \operatorname{CCl}_3 F + \operatorname{HCl}$$

(Freen-11)

(ii)
$$CCl_3F$$
 + HF \longrightarrow CCl_2F_2 + HCl
(Freon-12)

(iii) $C_2Cl_6 + 2HF \longrightarrow C_2Cl_4F_2 + 2HCl$ (Freon-112)

Nomenclature of Freons :

Freon is expressed as Freon - cba

Where: a – [Number of F-atoms]

b - [1 + Number of H-atoms]

c - [Number of C-atoms -1]

```
Ex. C_2 Cl_4 F_2 is expressed as Freon-112
```

a = 2; b = 1 + 0; c = 2 - 1 cab = 112

• Freon is odourless, non-corrosive, non-toxic gas. It can easily be liquefied hence widely used as refrigerant.

2. Carbon tetrachloride (pyrene) :

Preparations & reactions :





- CCl₄ is stable to heat and its vapours do not catch fire thus it is used as fire extinguisher.
- CCl₄ used as medicine for elimination of hook worms.

3.

- **Reactions of chloroform :** air \rightarrow COCl₂ (Phosgene) Ag/∆ **>** H–C≡C–H 0 AICI. > (C₆H₅)₃CH OH $(CH_3)_2C = O/OH (CH_3)_2CCCl_3 \quad Chloritone (hypnotics)$ 0 KOH Carbylamine reaction RNH₂/KOH R-NC OH CHCl₃-OH OH 0 KOH .CHO (Reimer-Tiemann reaction) 0 ĊHO Conc. HNO₃ \rightarrow Cl₂C-NO₂ Cl_2/hv >CCl₄ KOH ➤ HCOOK Zn/HCl CH,Cl, Zn/H₂O CH. Zn/HCl(alc) \rightarrow CH₃Cl
- Purity of chloroform (presence of phosgene) can be tested before use as anaesthetic by treating with aqueous solution of AgNO₃ because the presence of COCl₂ may cause cardiac failure.
- Chloroform is stored in dark colour bottle containing small amount of ethyl alcohol. (It converts phosgene into diethylcarbonate).
- 4. Summary of Nucleophilic substitution Reactions (SN₁ and SN₂)

 $\mathbf{R} - \mathbf{X} =$

Nuc/ Base Strength	methyl	1°	2°	3°
Strong/strong	SN_2	SN ₂	E ₂	E ₂
strong/weak	SN_2	SN ₂	SN_2	no reaction
weak / strong	no reaction	E2	E ₂	E ₂
weak/ weak	no reaction	n	no reaction	SN_1/E_1

