

02

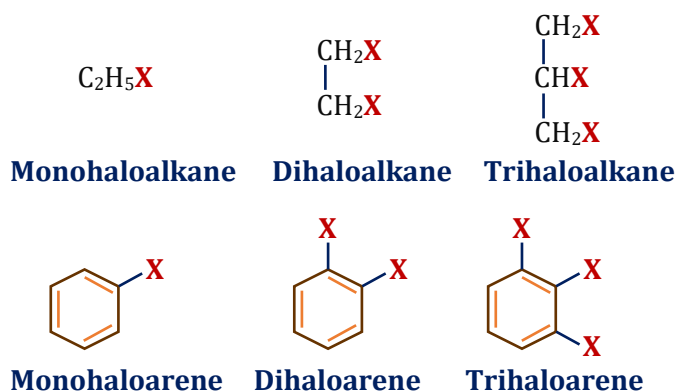
Haloalkanes and Haloarenes

The replacement of hydrogen atom(s) in an aliphatic or aromatic hydrocarbon by halogen atom(s) results in the formation of alkyl halide(haloalkane) and aryl halide (haloarenes) respectively.

Classification of Haloalkanes and Haloarenes :

On the basis of number of halogen(X) atoms:

Haloalkanes and haloarenes may be classified as follows:

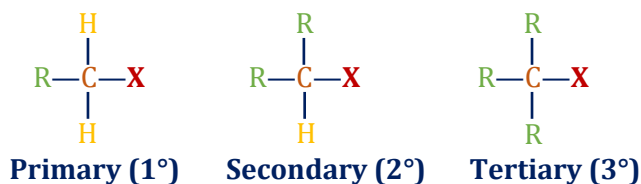


Monohalocompounds may further be classified according to the hybridisation of the carbon atom to which the halogen is bonded, as discussed below.

(1) Compounds containing $\text{sp}^3 \text{C}-\text{X}$ bond:

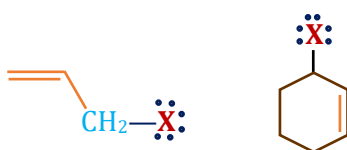
(a) Alkyl halides or haloalkanes

In alkyl halides halogen atom is bonded to an alkyl group.



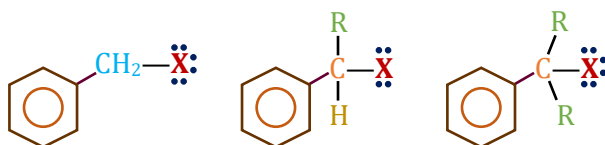
(b) Allylic halides

These are the compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom next to carbon-carbon double bond.



(c) Benzylic halides

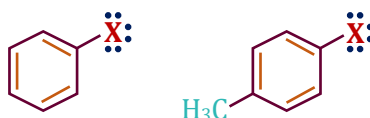
These are the compounds in which the halogen atom is bonded to an sp^3 hybridised carbon atom next to an aromatic ring.



(2) Compounds containing sp^2 C—X bond:

(a) Aryl halides or haloarenes

These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom of an aromatic ring.



(b) Vinylic halides

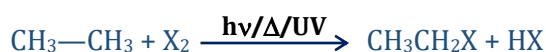
These are the compounds in which the halogen atom is bonded to an sp^2 hybridised carbon atom of a carbon-carbon double bond.



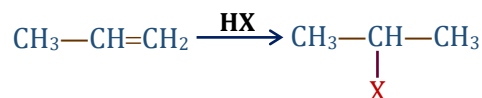
Methods of Preparation of Haloalkanes :

(A) From hydrocarbons:

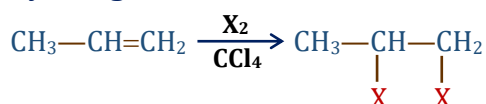
(a) By halogenation of alkane



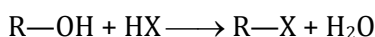
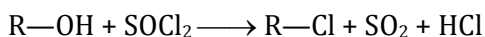
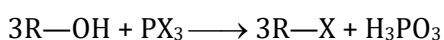
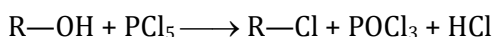
(b) By hydrohalogenation of alkene



(c) By halogenation of alkene



(B) From alcohol:



(C) Halogen Exchange Reaction:

(a) Finkelstein reaction (Preparation of alkyl iodide)



(b) Swarts reaction (Preparation of alkyl fluoride)

The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF , Hg_2F_2 , CoF_2 or SbF_3

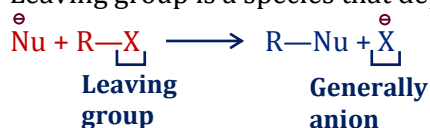


Physical Properties :**Boiling point of Haloalkanes:**Boiling Point $\propto$ Intermolecular force of attraction $\propto$ Molecular weight $\propto \frac{1}{\text{Branching}}$ (If molecular weight same)

Due to stronger intermolecular forces of attraction, boiling point of halogen derivatives is more compared to its parent hydrocarbon.

R—H < R—X**Leaving Group :**

Leaving group is a species that departs with the bonded pair of electrons.

Leaving group ability $\propto$ Stability of anion**Note:**

Weaker bases are good leaving group

**BEGINNER'S BOX-1**

- | | | | |
|----|--|--|--------|
| 1. | Alkyl fluorides are synthesized by
(1) Finkelstein reaction
(3) Kolbe reaction | (2) Swarts reaction
(4) Wurtz reaction | CHH143 |
| 2. | Which is Finkelstein reaction ?
(1) $\text{R-X} + \text{NaI} \xrightarrow{\text{Acetone}}$
(3) $\text{R-X} + \text{NaF} \longrightarrow$ | (2) $\text{R-X} + \text{AgF} \longrightarrow$
(4) $\text{R-F} + \text{AgCl} \longrightarrow$ | CHH144 |
| 3. | Which of the following has the highest boiling point ?
(1) $\text{CH}_3\text{CH}_2\text{I}$ (2) CH_3Cl (3) CH_3I (4) CH_3Br | | CHH145 |
| 4. | Correct order of leaving group tendency is :-
(1) $\text{I}^\ominus > \text{Br}^\ominus > \text{Cl}^\ominus > \text{F}^\ominus$
(3) $\text{Cl}^\ominus > \text{F}^\ominus > \text{Br}^\ominus > \text{I}^\ominus$ | (2) $\text{F}^\ominus > \text{Cl}^\ominus > \text{Br}^\ominus > \text{I}^\ominus$
(4) $\text{I}^\ominus > \text{Cl}^\ominus > \text{Br}^\ominus > \text{F}^\ominus$ | CHH146 |
| 5. | Leaving group tendency is maximum in :-
(1) $\text{CH}_3-\text{O}^\ominus$ (2) $\text{CH}_3-\text{C} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O}^\ominus \end{smallmatrix}$ (3) $\text{Ph}-\text{O}^\ominus$ (4) $\text{CH}_3^\ominus$ | | CHH147 |
| 6. | Which is best leaving group ?
(1) $\text{H}_3\text{C}-\text{O}^\ominus$ (2) $\text{H}_3\text{C}-\text{S} \begin{smallmatrix} \text{O} \\ \parallel \\ \text{O}^\ominus \end{smallmatrix}$ (3) $\text{H}_3\text{C}-\text{CH}_2^\ominus$ (4) $\text{H}_3\text{C}-\text{NH}^\ominus$ | | CHH148 |

Solvent :

Substrate + Reagent $\xrightarrow{\text{Solvent}}$ Product

There are two types of solvents: (1) Polar solvent ($\mu \neq 0$) and (2) Non-polar solvent ($\mu = 0$).

Polar Solvent

Polar Protic Solvent

1. H atom is directly bonded to a more electronegative atom.

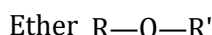
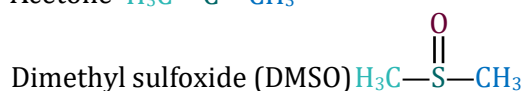
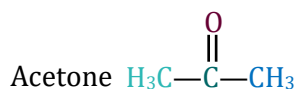
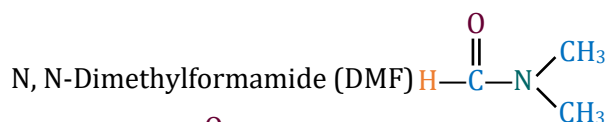
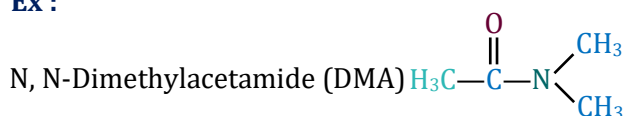
Ex :

H_2O , ROH , CH_3COOH , NH_3 etc.

Polar Aprotic Solvent

1. H atom is not directly bonded to a more electronegative atom.

Ex :



Non-polar solvent : Ex. CCl_4 , CS_2 etc.

Nucleophilicity and Basicity :

Nucleophilicity is a measure of how fast a nucleophile is able to attack an electrophilic centre. It is a kinetic property.

Basicity is a thermodynamic property.

Note: Stable anion $\Rightarrow$ Weak base or $\text{Basicity} \propto \frac{1}{\text{stability of Anion}}$

Factors affecting nucleophilicity:

1. A negatively charged nucleophile is a better nucleophile than its conjugate acid.
2. Across the period nucleophilicity and basicity order is same
 $\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$
3. When the attacking nucleophile is different in size (in a group) then role of solvent (down the group nucleophilicity and basicity order may or may not be same)

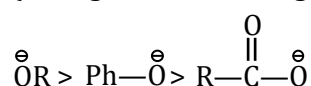
Polar protic solvent : $\text{F}^- < \text{Cl}^- < \text{Br}^- < \text{I}^-$

Polar aprotic solvent : $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ (No solvation of anion)

Basicity order : $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$

Note: If nothing is mentioned consider polar protic solvent.

4. In case of same donor atom, generally nucleophilicity and basicity order is same. (stronger base is stronger nucleophile)



Chemical Reactions of Haloalkanes :

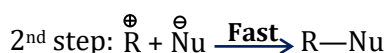
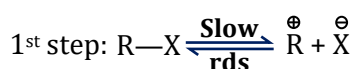
The reactions of haloalkanes may be divided into the following categories:

- (i) Nucleophilic Substitution Reaction
- (ii) Elimination Reaction
- (iii) Reaction with metals

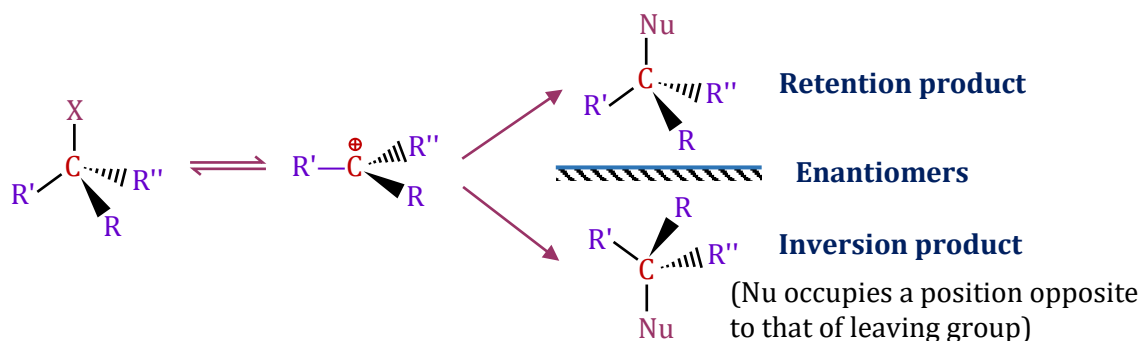
(i) Nucleophilic Substitution Reaction (S_N):**Mechanism:**

This reaction has been found to proceed by two different mechanisms.

1. S_N1 (Unimolecular Nucleophilic Substitution)
2. S_N2 (Bimolecular Nucleophilic Substitution)

Unimolecular Nucleophilic Substitution (S_N1) :**Mechanism:****Characteristics:**

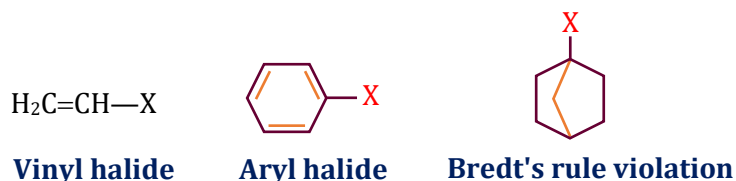
1. It is a two step reaction.
2. Kinetics of reaction
 $\text{Rate} = k[\text{alkyl halide}] \quad \text{ROR} \propto [\text{Alkyl halide}]$
 order = 1
 Molecularity = 1
3. Rate is independent of concentration of nucleophile.
4. Carbocation intermediate is formed. Rearrangement may be possible.
5. S_N1 reaction is favoured by polar protic solvent (Ex. H₂O, ROH)
6. Stereochemistry of S_N1 reaction



Note: Theoretically, racemic mixture must be formed but inversion product dominates over retention product. Partial racemisation takes place.

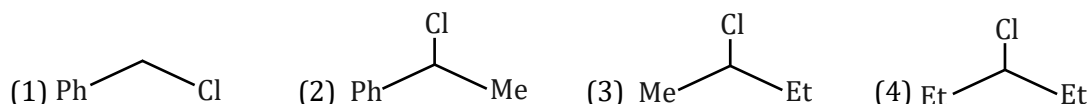
7. Reactivity towards S_N1 reaction $\propto$ Stability of carbocation intermediate

8. S_N1 reaction does not take place in :



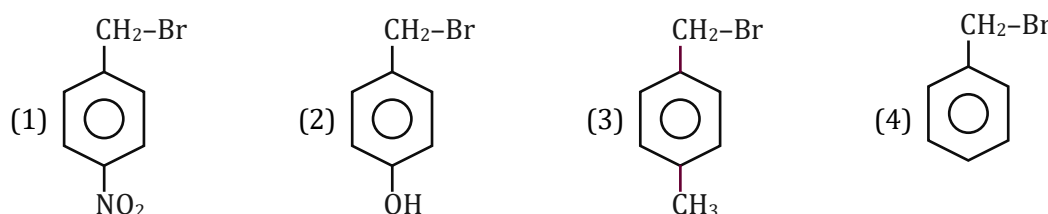
BEGINNER'S BOX-2

1. Which is most reactive for S_N1 reaction :-



CHH149

2. Which is most reactive for S_N1 ?



CHH150

3. In S_N1 the first step involves the formation of

- (1) Free radical (2) Carbanion (3) Carbocation (4) None of these

CHH151

4. Most stable carbocation formed from $(CH_3)_3C-Br$, $(C_6H_5)_3CBr$, $(C_6H_5)_2CHBr$ and $C_6H_5CH_2Br$ would be

- (1) $C_6H_5\overset{+}{C}H_2$ (2) $(CH_3)_3\overset{+}{C}$ (3) $(C_6H_5)_3\overset{+}{C}$ (4) $(C_6H_5)_2\overset{+}{C}H$

CHH152

5. S_N1 reaction on optically active substrates mainly gives

- (1) Retention in configuration (2) Inversion in configuration
 (3) Racemised product (4) No product

CHH153

Bimolecular Nucleophilic Substitution Reaction (S_N2) :



Mechanism:

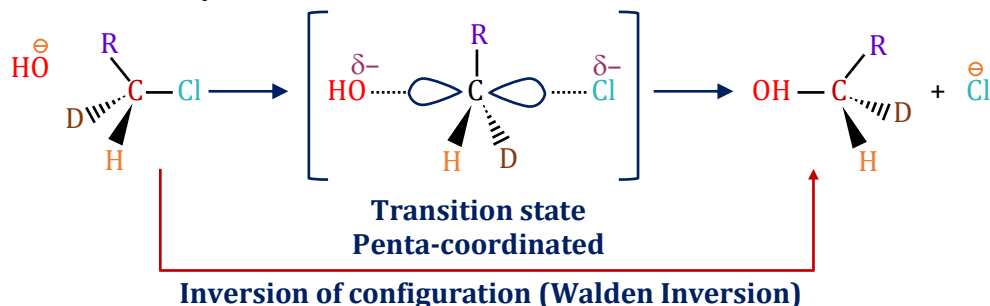


Characteristics:

- It is a single step reaction.
- Kinetics of reaction
 $Rate = k[\text{Alkyl halide}][\text{Nucleophile}]$ $ROR \propto [\text{Alkyl halide}][\text{Nucleophile}]$
 Order = 2
 Molecularity = 2
- Rate is dependent on concentration of nucleophile also.
- No carbocation intermediate is formed. Hence no rearrangement.

Haloalkanes and Haloarenes

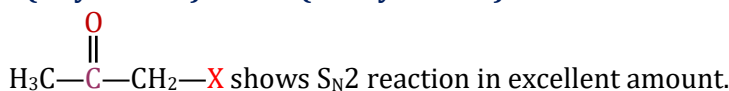
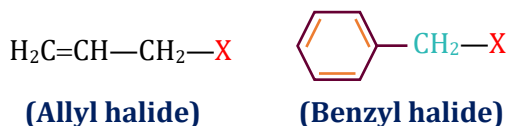
- S_N2 reaction is favoured by polar aprotic solvent.
(Ex: DMSO, DMF, acetone etc.)
- Stereochemistry of S_N2 reaction



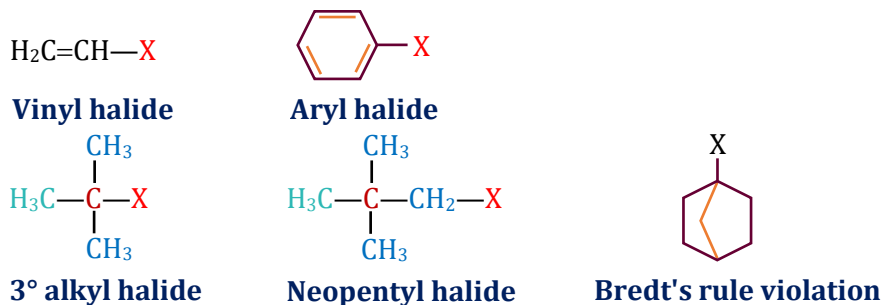
Note: S_N2 reaction completes with 100% inversion of configuration.

- Reactivity towards S_N2 reaction $\propto \frac{1}{\text{Steric hindrance}}$
 $\propto$ Electrophilicity of carbon attached to halogen.

Note: Allyl and benzyl halide shows S_N2 reaction in good amount.



- S_N2 reaction does not take place in :-

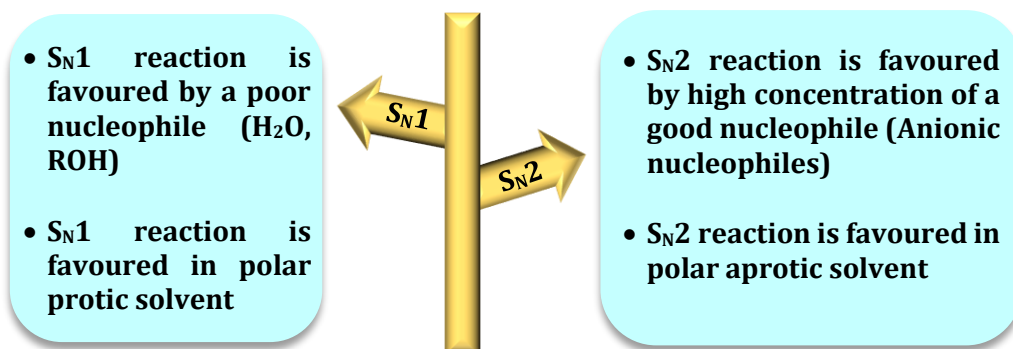


Note: S_N1 and S_N2 reaction does not take place at sp^2 hybridised carbon atom.

Nucleophilic Substitution Reaction :

Generally,

2° alkyl halides





BEGINNER'S BOX-3

1. Which of the following is least reactive towards S_N2 ?

- (1) $(CH_3)_3C-Br$ (2) $Ph-CH_2-Br$ (3) CH_3-Br (4) $CH_3-\overset{\overset{O}{\parallel}}{C}-CH_2-Br$

CHH154

2. Arrange the following compound in their order of reactivity toward S_N2 reaction :-

- CH_3-F CH_3-Cl CH_3-Br CH_3-I
I II III IV

- (1) $I > II > III > IV$ (2) $IV > III > II > I$ (3) $III > IV > I > II$ (4) $II > III > IV > I$

CHH155

3. Select the correct statement about S_N2 reaction

- (1) Molecularity of reaction is 2
(2) Order of reaction is 2
(3) On increasing concentration of nucleophile rate of reaction increases
(4) All of these

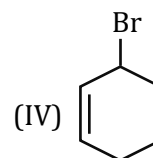
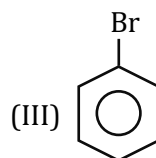
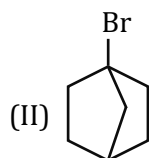
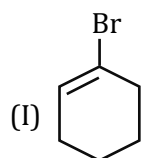
CHH156

4. Which of the following is the correct decreasing order of S_N2 reactivity?

- (1) $R-CH_2-X > R_3CX > R_2CHX$ (2) $R-CH_2X > R_2CHX > R_3CX$
(3) $R_3CX > R_2CHX > R-CH_2X$ (4) $R_2CHX > R_3CX > R-CH_2X$

CHH157

5. S_N2 reaction will not occurs in-



(1) Only IV

(2) I, II, III

(3) I, III

(4) Only II

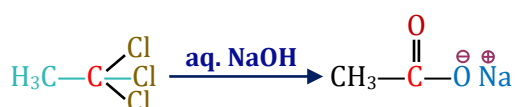
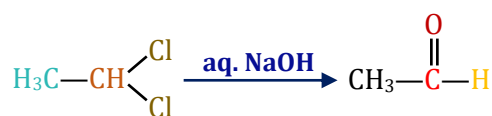
CHH158

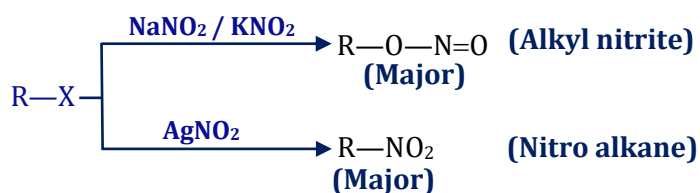
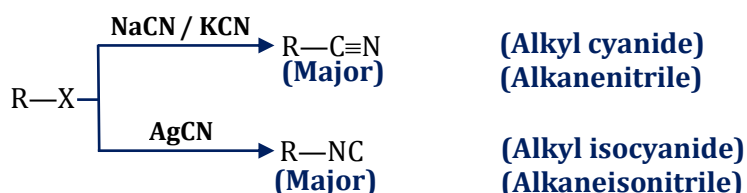
6. For S_N2 reaction, which is most reactive ?

- (1) $CH_3-CH_2-CH_2-Br$ (2) $CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br$ (3) $CH_3-\overset{\overset{CH_3}{|}}{CH}-CH_2-Br$ (4) CH_3-CH_2-Br

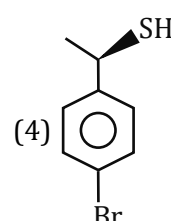
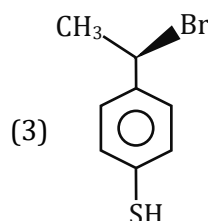
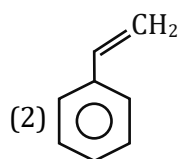
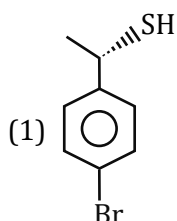
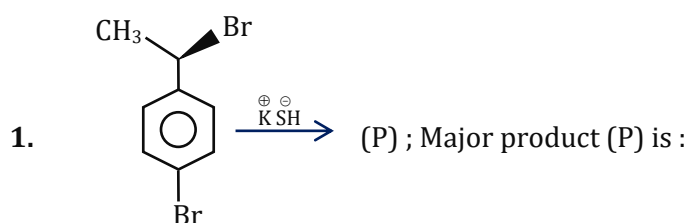
CHH159

1. Reaction with aq. NaOH / aq. KOH

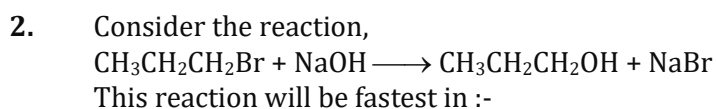


2. Reaction of alkyl halide with $\text{NaNO}_2 / \text{KNO}_2$ and AgNO_2 3. Reaction of alkyl halide with NaCN / KCN and AgCN 

BEGINNER'S BOX-4



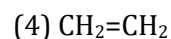
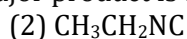
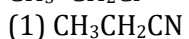
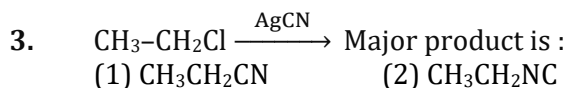
CHH160



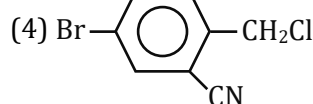
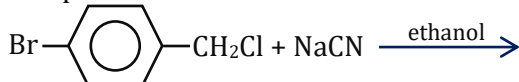
- (1) Water
 (3) Methanol

- (2) Ethanol
 (4) N, N'-dimethylformamide (DMF)

CHH161

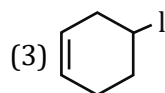
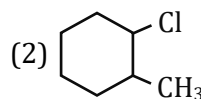
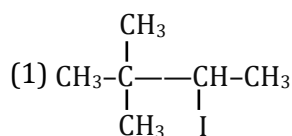


CHH162



CHH163

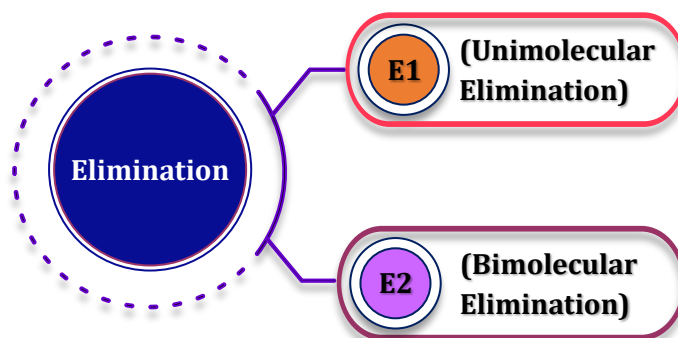
5. Which of the following alkyl halide undergoes rearrangement in S_N1 reaction ?



(4) All of these

CHH164

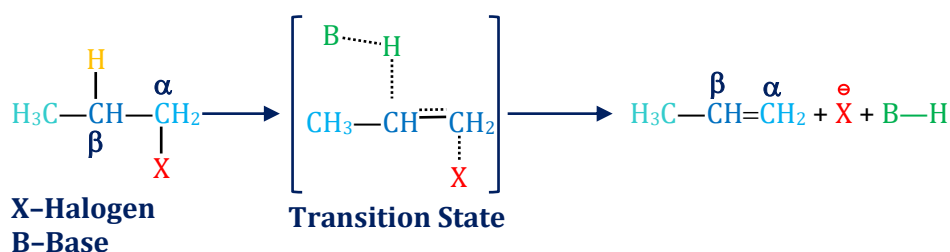
(ii) Elimination Reactions :



(A) Dehydrohalogenation of Halide :

E2 (Bimolecular Elimination)

1. It is also known as α , β - elimination / 1,2 - elimination.
2. It is a single step reaction. No intermediate is formed.



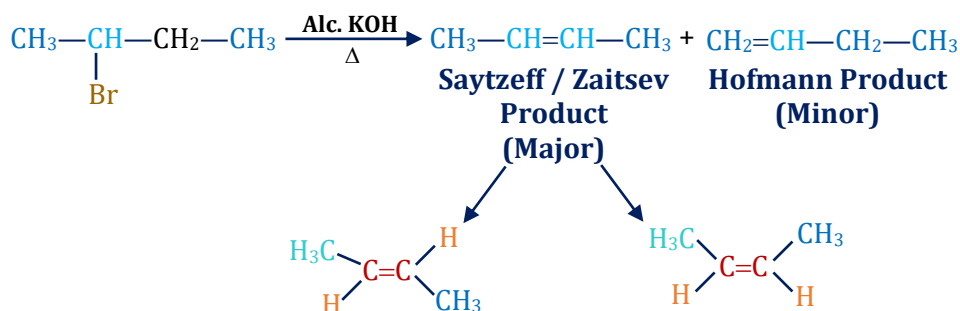
3. Rate = $k[\text{Alkyl halide}][\text{Base}]$
Order = 2
Molecularity = 2
4. Rate of E2 $\propto$ Stability of alkene
5. In rate determining step (rds), C-H and C-X bond breaking takes place.
Hence, rate of reaction will depend on the bond strength of these bonds.
6. Reagents:
Alcoholic KOH/ Δ
NaNH₂/ Δ (Sodamide)
R—O⁻ Na⁺ (Sodium alkoxide)

Haloalkanes and Haloarenes

7. Stereochemistry of E2 reaction.

E2 reaction – Anti Elimination

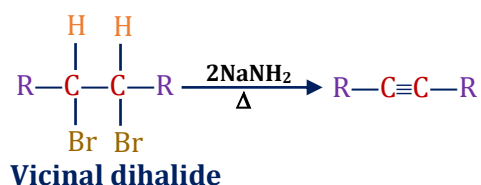
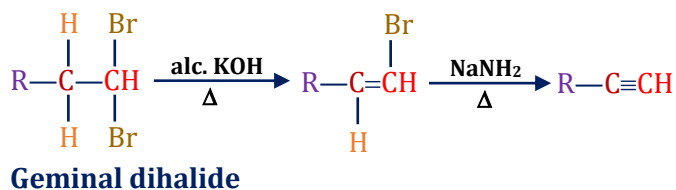
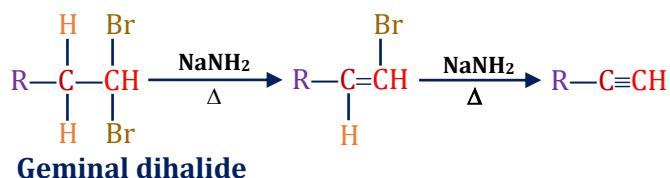
Leaving group and β hydrogen must be anti to each other.



8. Saytzeff /Zaitsev alkene : More stable alkene

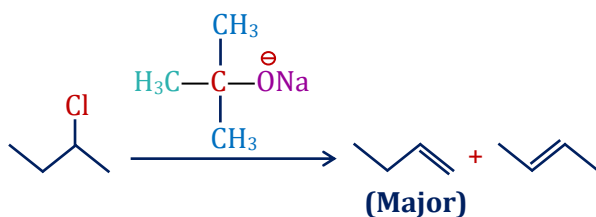
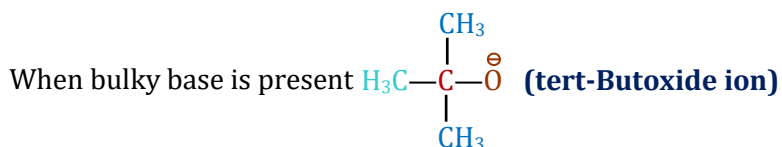
Hoffmann alkene : Less stable alkene

Note: When an alkyl halide has more than one type of β hydrogen mixture of products formed.
Geminal and vicinal dihalide react with NaNH_2 to give alkyne as major product.



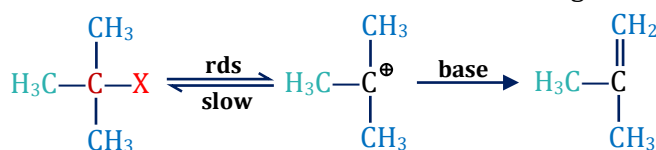
Elimination Reactions :

Generally Saytzeff alkene is formed as major product but in following cases Hoffmann alkene may form as major product.



E1 (Unimolecular Elimination) :

1. It is a two step reaction.
2. Carbocation intermediate is formed. Rearrangement is possible.

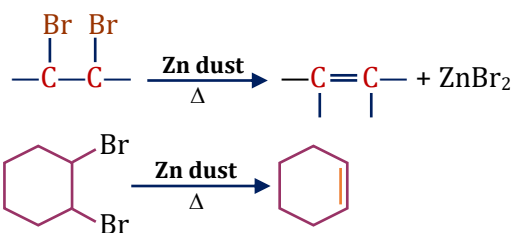


X-Halogen

3. Kinetics of reaction.
Rate = $k[\text{Alkyl halide}]$
Order = 1
Molecularity = 1
4. Rate of E1 $\propto$ Stability of carbocation formed
5. In rate determining step (rds), C-X bond breaking takes place.
Hence, rate of reaction will depend on the bond strength of this bond.
6. Reagents:
 $\text{H}_2\text{O}/\Delta$
 ROH/Δ

(B) Dehalogenation of Vicinal Dihalide :

Dehalogenation is also an example of elimination(E2) reaction.
Reagent used: Zn dust/ Δ

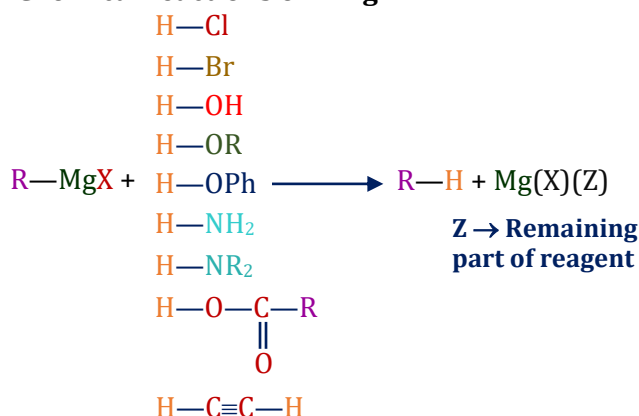


(iii) Reaction with Metals :

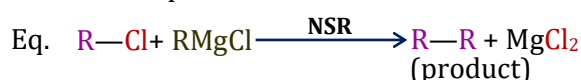
Grignard reagent



Chemical reactions of R MgX



Note: Grignard reagent behaves like a base (reacts with compounds containing acidic H) as well as like a nucleophile.





BEGINNER'S BOX-5

1. The reactivity of alkyl halides in E2 elimination reactions follows the order

- (1) $R-I < R-Br < R-Cl < R-F$ (2) $R-F < R-Cl < R-Br < R-I$
 (3) $R-I > R-Cl > R-Br < R-F$ (4) $R-I < R-Br < R-F < R-Cl$

CHH165

2. Which of the following alkyl halides gives a mixture of alkenes on dehydrohalogenation?

- (1) n-Propyl halide (2) Isopropyl halide (3) s-Butyl bromide (4) t-Butyl bromide

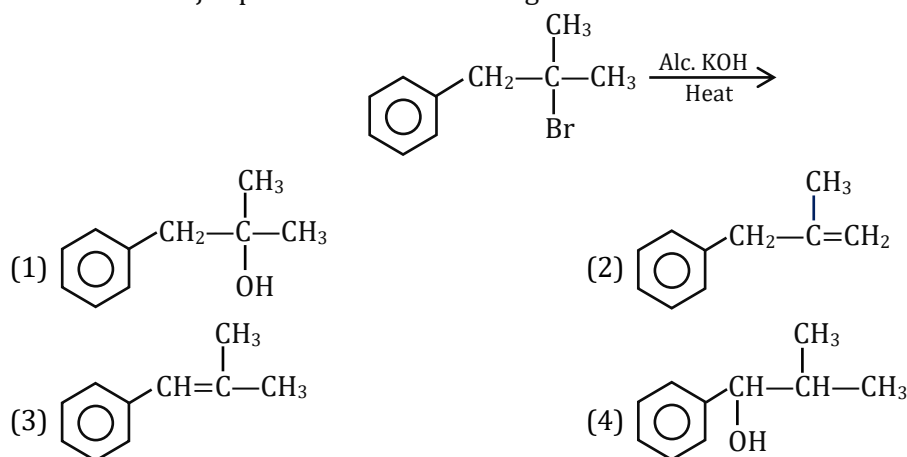
CHH166

3. Which of the following cannot undergo E2 reaction?



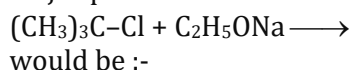
CHH167

4. What is the major product of the following reaction?



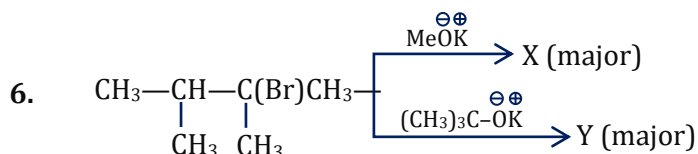
CHH168

5. Major product of the reaction :

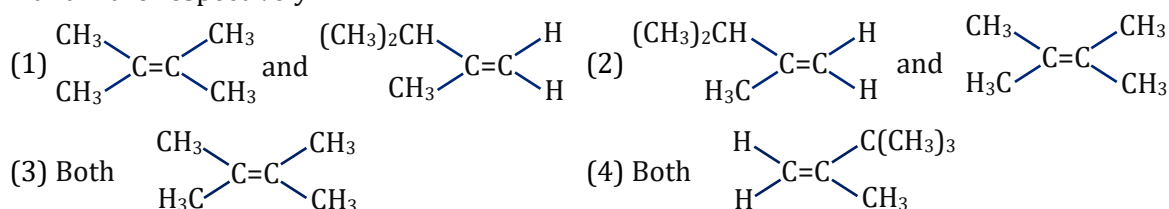


- (1) $(CH_3)_3C-OC_2H_5$ (2) $(CH_3)_3C-C_2H_5$ (3) $(CH_3)_2C=CH_2$ (4) $CH_3-CH=CH-CH_3$

CHH169



X and Y are respectively :-

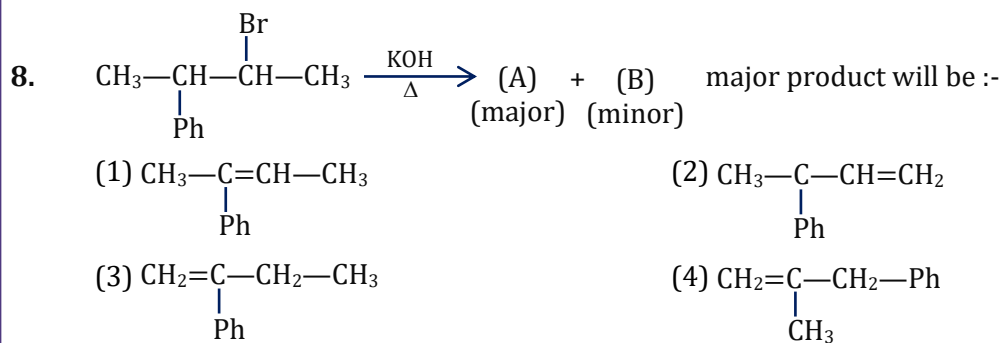


CHH170

7. 1-phenyl-2-chloro propane when treated with alc. KOH mainly gives :-

- (1) 1-phenyl propene (2) 3-phenyl propene
 (3) 1-phenyl-2-propanol (4) 3-phenyl-1-propene

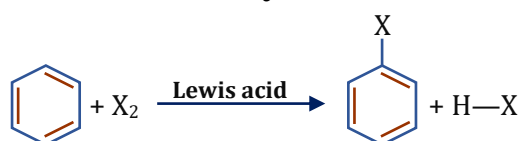
CHH171



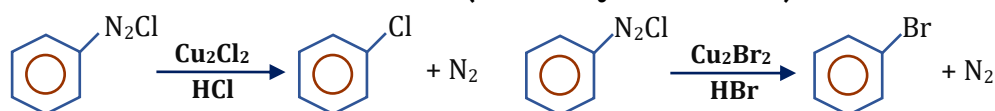
CHH172

Methods of Preparation of Haloarenes :

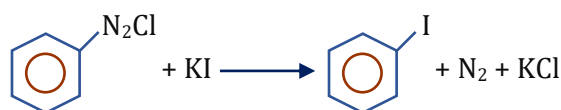
1. From aromatic hydrocarbons :



2. From benzene diazonium salt (Sandmeyer reaction) :



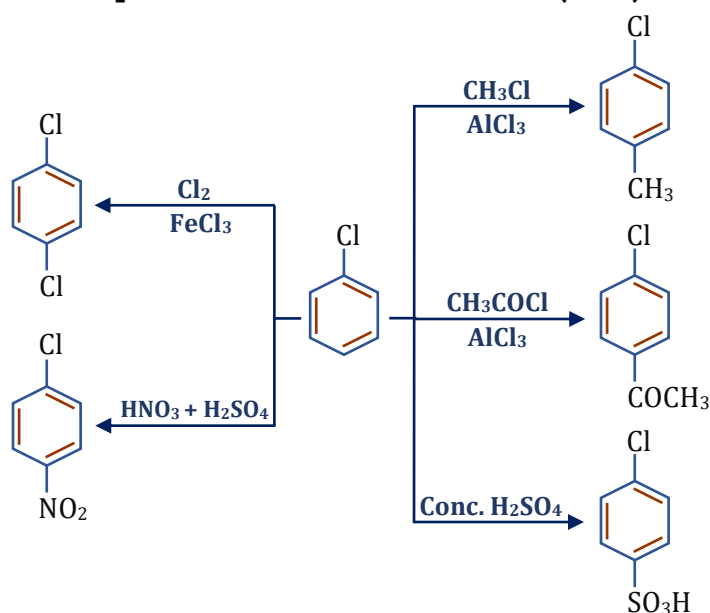
Note:



Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.

Chemical Reactions of Haloarenes :

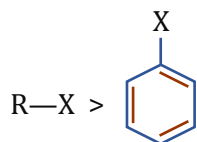
1. Electrophilic Substitution Reaction (ESR) :



2. Nucleophilic Substitution Reaction (S_NAr) :

Aryl halides are extremely less reactive towards nucleophilic substitution reaction.

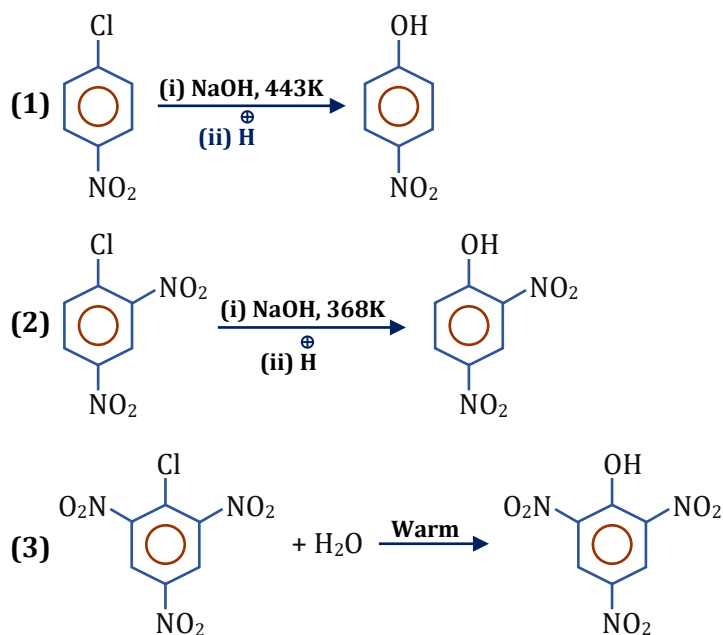
Reactivity order :

**Reasons :**

- (i) C-X bond acquires partial double bond character due to resonance. As a result bond cleavage in haloarene is difficult than haloalkane.
- (ii) Difference in hybridisation of carbon atom in C-X bond. (As % 's' character increases, bond length decreases, bond strength increases.)

Nucleophilic Aromatic Substitution (S_NAr) by Addition Elimination

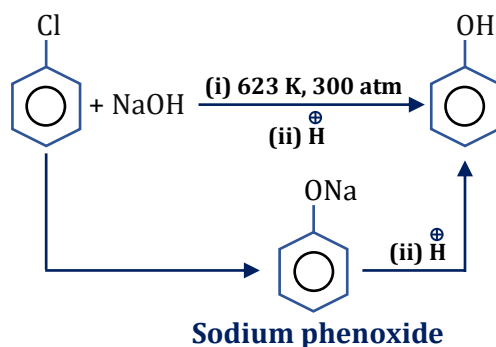
Nucleophilic aromatic substitution can occur when strong electron withdrawing groups are present at ortho or para position with respect to the halogen atom.



Note: Electron withdrawing groups present at ortho-para position with respect to the leaving group increases rate of reaction.

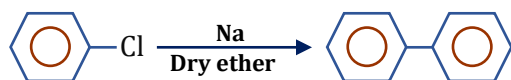
Aryl halide without electron withdrawing substituents don't react with most nucleophiles under ordinary conditions.





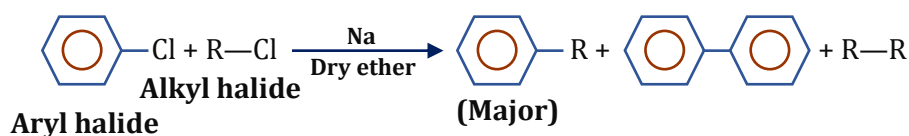
3. Reaction with metals :

Fittig Reaction



Aryl halide

Wurtz Fittig Reaction

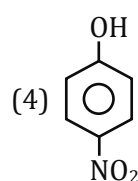
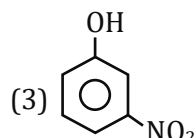
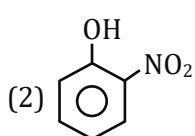
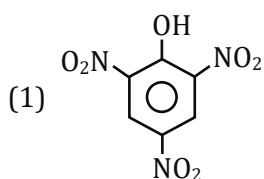
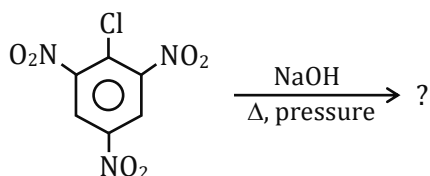


Aryl halide



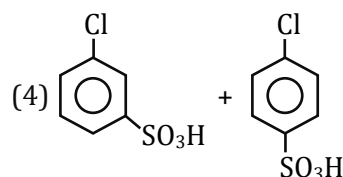
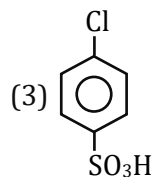
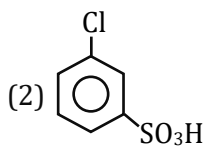
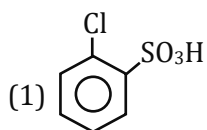
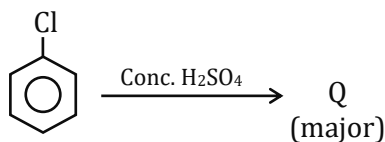
BEGINNER'S BOX-6

1.

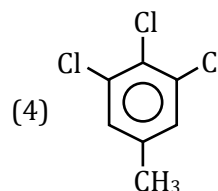
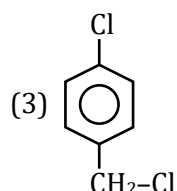
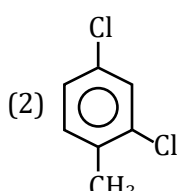
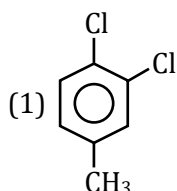
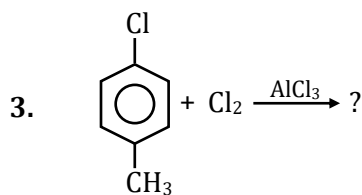


CHH173

2.

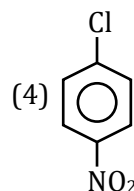
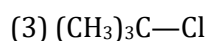
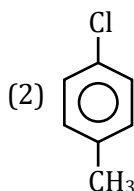
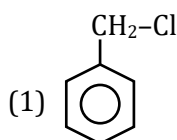


CHH174



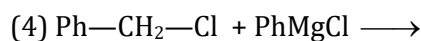
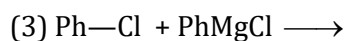
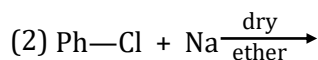
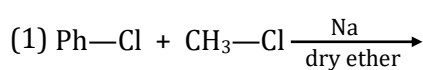
CHH175

4. Which is minimum reactive towards hydrolysis ?



CHH176

5. Which is best method to obtained Biphenyl ?



CHH177

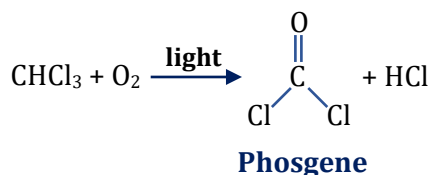
Polyhalogen Compounds :

CHCl_3 and CHI_3 (chloroform and iodoform) :

CHCl_3 (Chloroform)

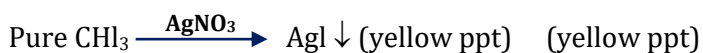
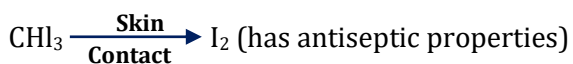
It was used as an anaesthetic.

Chloroform is slowly oxidized by air in the presence of sunlight to an extremely poisonous gas 'phosgene'



CHI_3 (Iodoform)

It was used as an antiseptic.



Freons

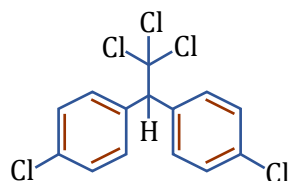
The chlorofluoro carbon compounds of methane and ethane are called freons.

Examples: CCl_2F_2 , $\text{C}_2\text{F}_4\text{Cl}_2$ etc.

They are produced for aerosol propellants, refrigeration and air conditioning purposes. Excess use results in ozone layer depletion.

DDT(p, p'-Dichlorodiphenyltrichloroethane)

It was used as insecticide.



BEGINNER'S BOX

ANSWER KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6		
	Ans.	2	1	1	1	2	2		

BEGINNER'S BOX-2	Que.	1	2	3	4	5			
	Ans.	2	2	3	3	3			

BEGINNER'S BOX-3	Que.	1	2	3	4	5	6		
	Ans.	1	2	4	2	2	4		

BEGINNER'S BOX-4	Que.	1	2	3	4	5			
	Ans.	1	4	2	1	4			

BEGINNER'S BOX-5	Que.	1	2	3	4	5	6	7	8	
	Ans.	2	3	3	3	3	1	1	1	

BEGINNER'S BOX-6	Que.	1	2	3	4	5				
	Ans.	1	3	2	2	2				