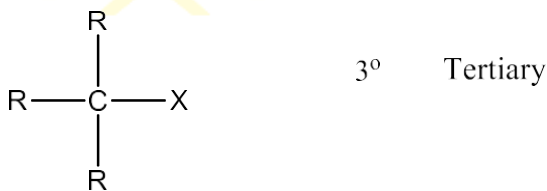
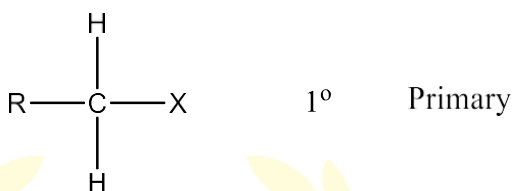


Class XII UNIT 10 Halo Alkanes and Haloarenes

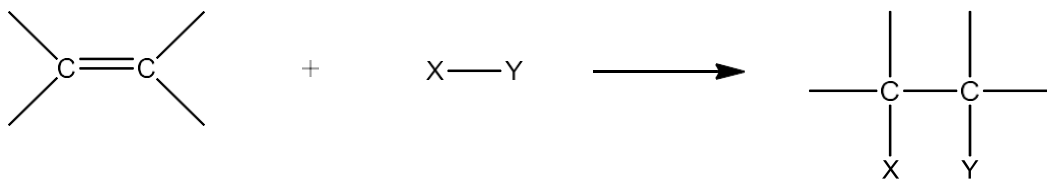
1. Haloalkanes (Alkyl halides) are halogen derivatives of alkanes with general formula $[C_nH_{2n+1}X]$. (X = F, Cl, Br or I). they are further classified as primary, secondary or tertiary depending on the nature of carbon to which halogen is attached.



Addition Reaction

A new compound is formed by the reaction of two or more compounds. It is generally the attack of a reagent on a π bond.

Example-1



Substitution Reaction

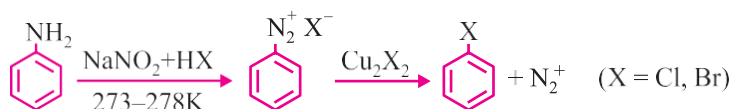
When a functional group attacks and replaces other functional group in a compound, the type of reaction is known as substitution reaction. The group which is replaced is called as the leaving group.

Example-2



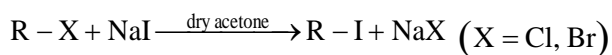
Name Reactions:

- (a) **Sandmeyer Reaction:** The Sandmeyer Reaction was named after Traugott Sandmeyer in 1884. Sandmeyer Reaction is a chemical reaction in which aryl diazonium salts is used to synthesize aryl halides. Sandmeyer Reaction provides the capability of performing some unique transformations to benzene such as hydroxylation, trifluoromethylation, cyanation, and halogenation.

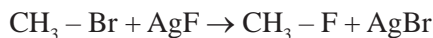


- (b) **Finkelstein Reaction :**

The Finkelstein Reaction is named after Hans Finkelstein, a German chemist. The Finkelstein Reaction deals with the exchange of a halogen atom by a Substitution Nucleophilic Bimolecular reaction.

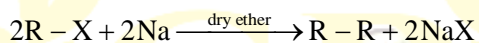


(c) **Swartz Reaction:** Swartz reaction and Finkelstein reactions are halogen exchange reactions that are associated with alkyl halides.

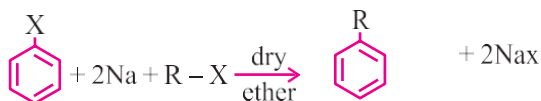


Instead of Ag - F, other metallic fluoride like Hg_2F_2 , CoF_2 or SbF_3 can also be used.

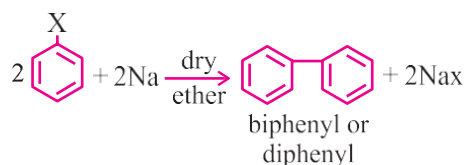
(d) **Wurtz Reaction:** The Wurtz reaction, named after Charles-Adolphe Wurtz, is a coupling reaction in organic chemistry, organometallic chemistry and recently inorganic main group polymers, whereby two alkyl halides are reacted with sodium metal in dry ether solution to form a higher alkane.



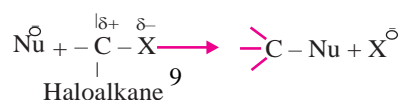
(e) **Wurtz-Fittig Reaction :** The Wurtz-Fittig reaction is the chemical reaction of aryl halides with alkyl halides and sodium metal in the presence of dry ether to give substituted aromatic compounds.



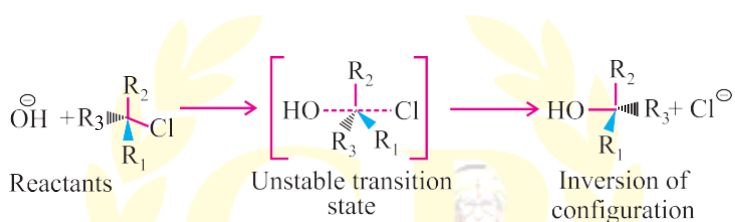
(f) **Fittig Reaction:**



Nucleophilic Substitution Reactions: In this reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to a halogen. Substitution takes place and halogen atom called the leaving group departs as halide ion.



(a) Substitution nucleophilic bimolecular (S_N2): in this reaction rate depends on the



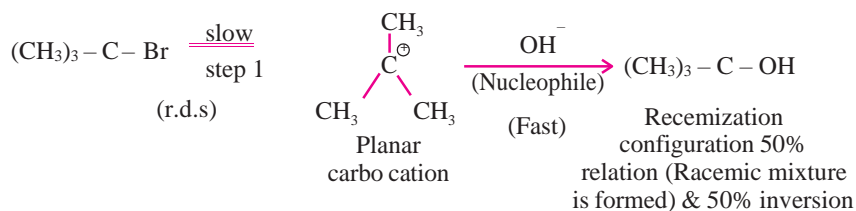
concentration of both the reactants. The incoming nucleophile interacts with alkyl halide causing the carbon-halide bond to break and a new bond is formed between carbon and attacking nucleophile. Both these processes take place simultaneously in single step and no intermediate is formed.

1. 1° haloalkane
2. Bimolecular, 2nd order
3. One step

Order of reactivity: $1^\circ > 2^\circ > 3^\circ$

Deciding factor: Steric hindrance

(b) Substitution nucleophilic unimolecular (S_N¹): These reactions are generally carried out in polar solvents (like water, alcohol, acetic acid, etc.). the reaction between ter-butyl bromide and hydroxide ion yield ter-butyl alcohol and follows the first order kinetics which means that the rate of reaction depends upon the concentration of only one reactant.



1. 3° haloalkane
2. Unimolecular, 1st order
3. Two steps

Order of reactivity: 3° > 2° > 1°

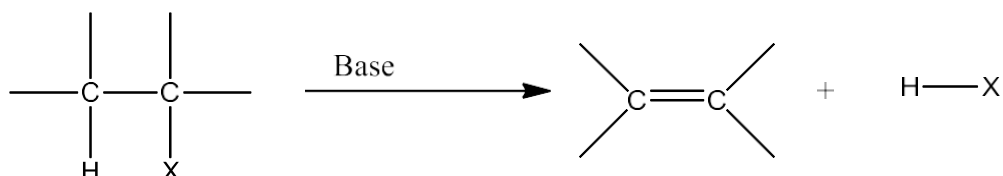
Deciding factor: Stability of carbo cation



* Allylic $\left[\begin{array}{c} \text{CH}_2 \\ | \\ \text{---C---} \end{array} \right]_2$ and benzylic $\left[\text{C}_6\text{H}_5\text{CH}_2 \right]$ halides undergo reaction via SN^1 mechanism as the corresponding carbo cations are resonance stabilized.

Elimination Reactions

Example-3



The removal of adjacent hydrogen, a hydrogen and adjacent halide as well as vicinal halides to form unsaturated compound is generally called as elimination reaction. It proceeds via three kinds of mechanism.

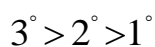
Elimination Bimolecular- E2

Example-4



Main Features of E2 Mechanism:

1. Single step reaction.
2. $\text{Rate} = k[\text{RX}]$
3. Single transition state with no intermediate.
4. No rearrangement
5. Strong bases are generally used as reagents.
6. Order or reactivity of alkyl halides:



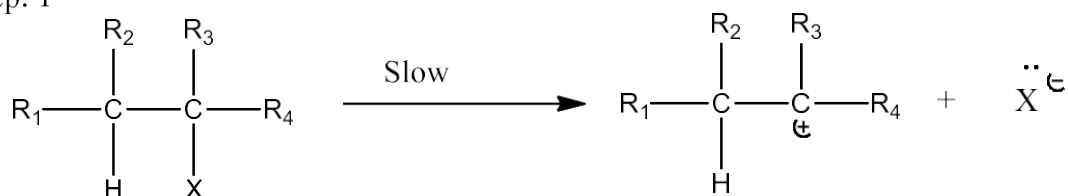
The number of alpha hydrogens will increase as we go from higher to lower alkene leading to alkene stability.

7. Favored by aprotic solvents.

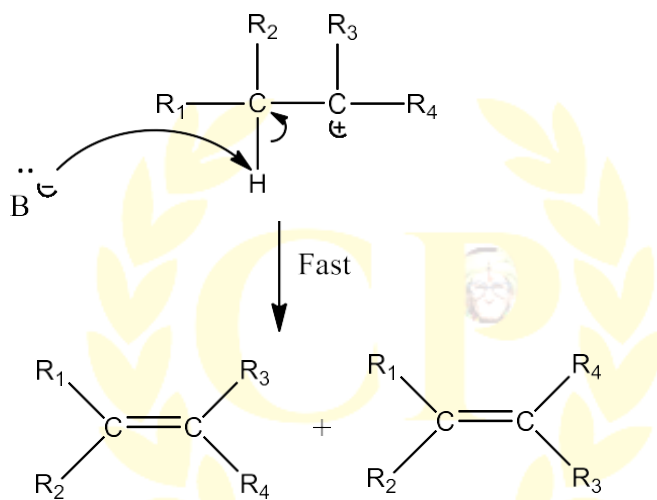
Elimination Unimolecular-E1

Example-9

Step: 1



Step 2:



Main Features of E₁ Mechanism

1. It is a two-step reaction. First step involves formation of carbocation by loss of the leaving group and the second step is the deprotonation by using a nucleophilic base (generally weak).

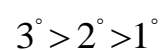
2. Rate = $k[\text{RX}]$

3. Carbocation is formed as intermediate.

4. Rearrangement generally occurs until the carbocation is at its most stable position.

5. Observed in presence of weak bases.

6. Order or reactivity of alkyl halides:



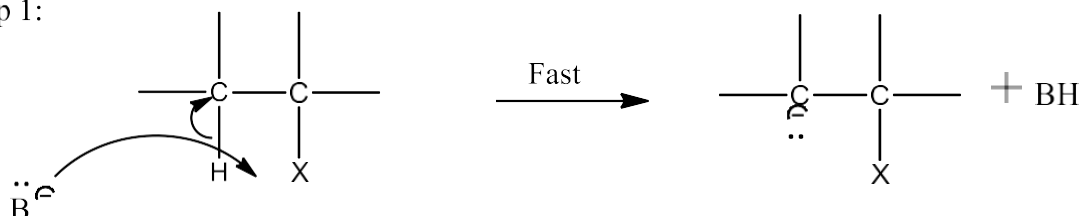
This can be attributed to the stability of carbocation formed as well as the stability of alkene formed.

7. Favored by protic solvents.

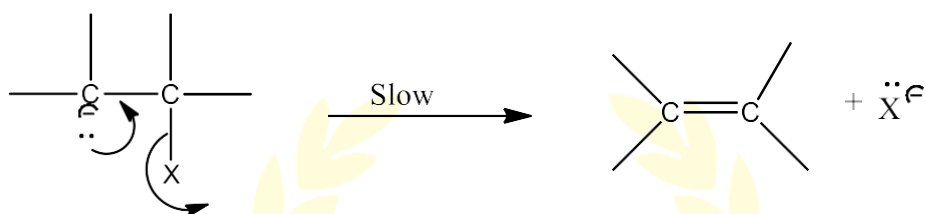
Elimination Unimolecular via Conjugate base E1cB

Example-10

Step 1:



Step 2:



Key Features of E1 Mechanism

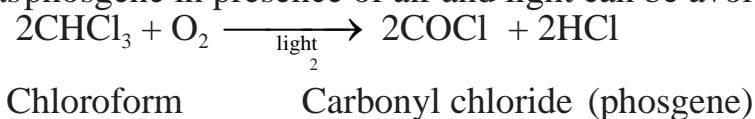
1. It is a two-step reaction. First step is the formation of carbanion as intermediate and the second step is the loss of the leaving group.
2. $\text{Rate} = k[\text{RX}][\text{Base}]$
3. Carbanion is formed as intermediate.
4. Occurs when a poor leaving group is present.

Haloarenes / Aryl Halides

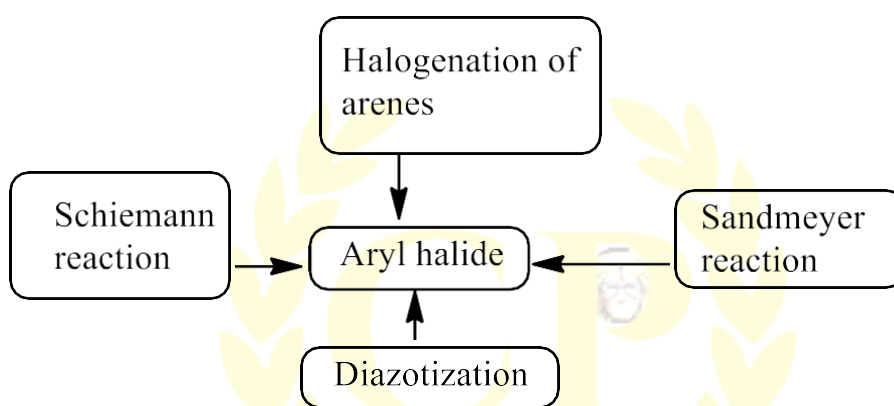
1. Haloarenes (Aryl halides) are halogen derivatives of arenes with general formula Ar-X .
2. Since halogen is more electronegative than C, hence C-X bond is polar.



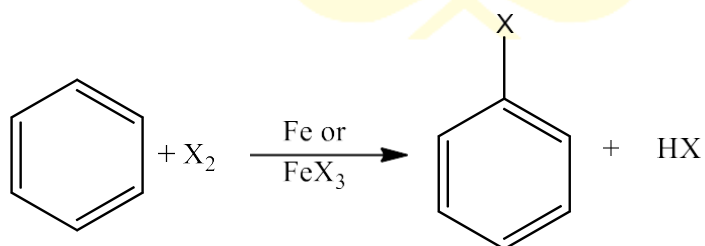
3. Aryl halides are much less reactive towards nucleophilic substitution reactions than haloalkanes.
4. Halogen is deactivating but *o*, *p*-directing in electrophilic substitution reaction of haloarenes.
5. CHCl_3 is stored in dark bottles upto brim so that formation of poisonous gas phosgene in presence of air and light can be avoided.



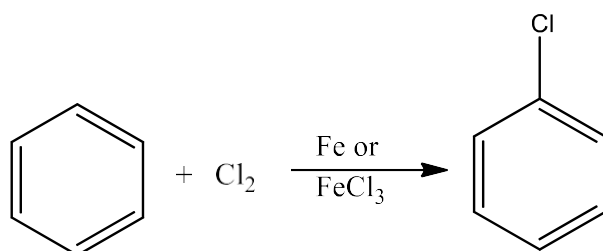
Preparation of Aryl Halide/Haloarenes



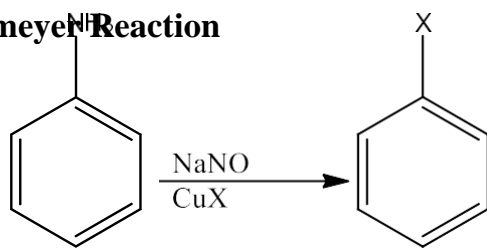
(a) Halogenation of Arenes



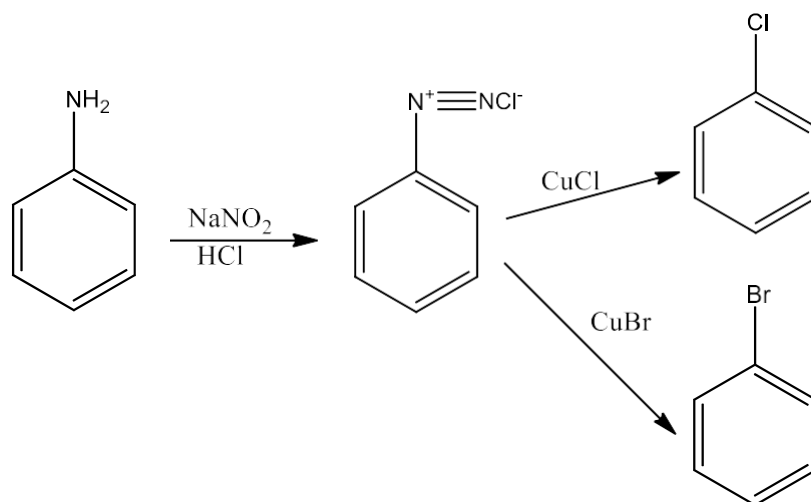
Example-14



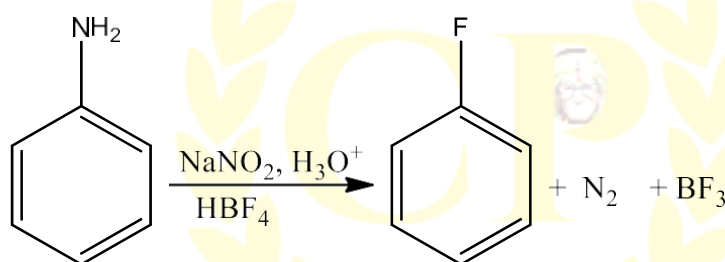
(b) Sandmeyer Reaction



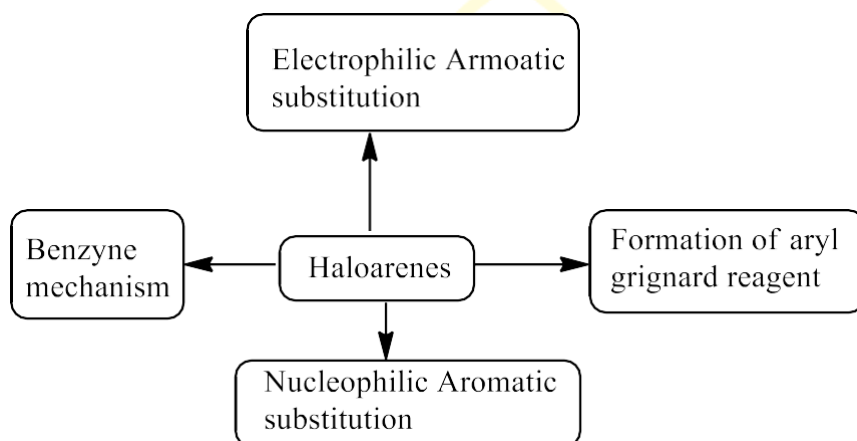
(c) Diazotiation



(d) Schiemann Reaction

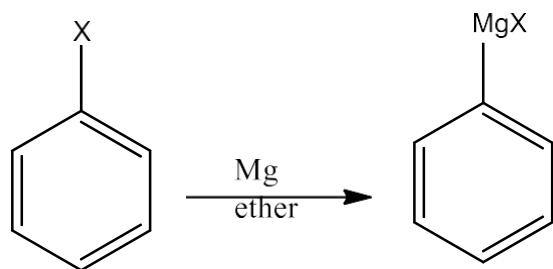


Reactions of Aryl Halide/Haloarenes

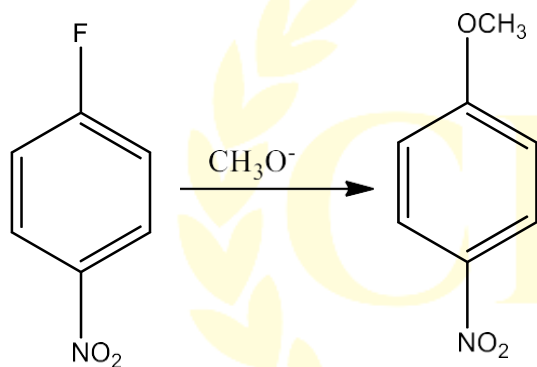


Electrophilic Aromatic Substitution Reaction: Halogens are weakly deactivating as they have strong induction effect and weak mesomeric effect. They are ortho/para directing.

(a) Formation of Aryl Grignard Reagent:

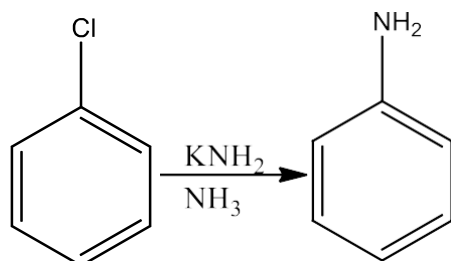


(b) S_NAr - Aromatic Nucleophilic Substitution Reaction



(c) Benzyne Mechanism (Elimination Addition Mechanism)

Strong bases such as Na, K and amide react readily with aryl halides.

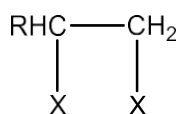


Reactions of Special Alkyl Halides

Di-Halides



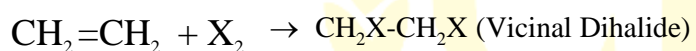
Alkydene Dihalides or
Geminal Dihalides



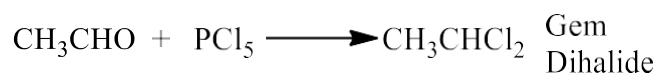
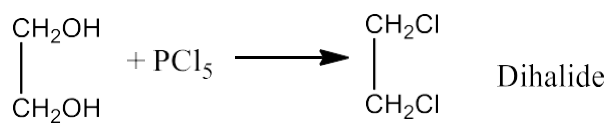
Alkylene Dihalides or
Vicinal(1,2) Dihalides

Preparation of:

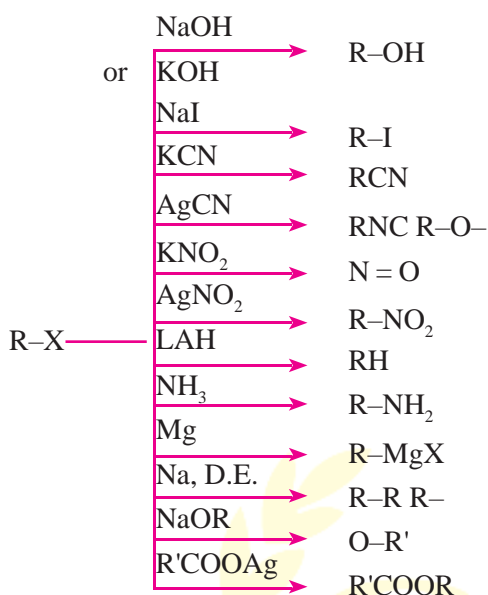
(a) Halogenation of Alkenes and Alkynes



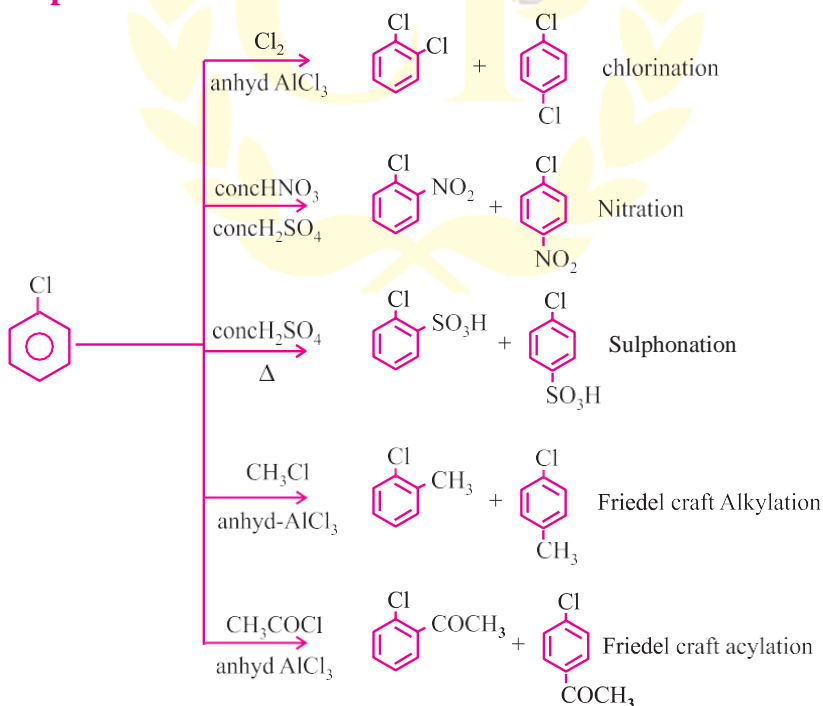
(b) PCl_5 with Diols and Carbonyl Compounds



Reaction of Haloalkanes:

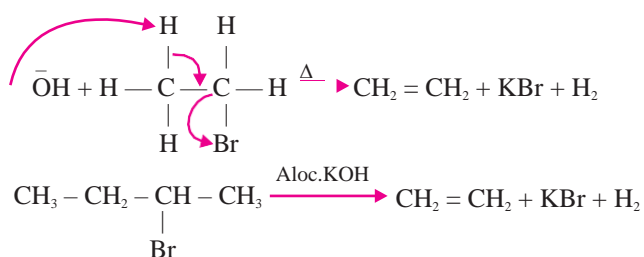


Electrophilic Substitution Reaction of Haloarenes:



Elimination reaction: Two groups or atoms attached to two adjacent carbon atom and simultaneous formation of multiple bonds between these carbon atoms. [Reverse of addition]

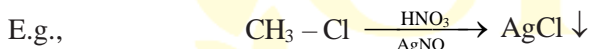
Saytzaﬀ's Rule



81% More highly substituted
Alkenes, More stable

Distinguishing test for alkyl chlorides, bromides and iodide:

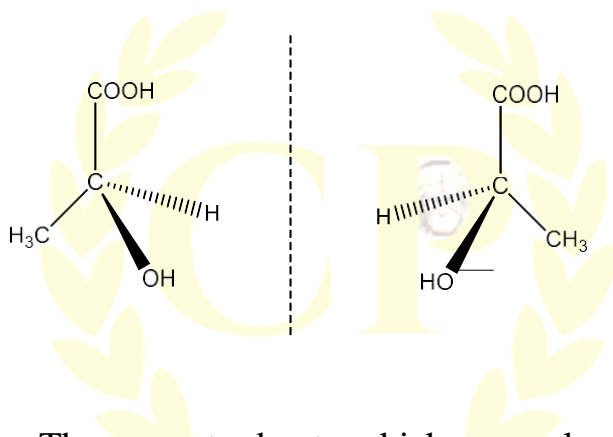
Alkyl chlorides react with AgNO_3 to give white precipitate which is soluble in alcoholic ammonium hydroxide. Alkyl bromides react with AgNO_3 to give a yellow precipitate which is sparingly soluble in alcoholic ammonium hydroxide. Alkyl iodides react with AgNO_3 to give dirty yellow precipitate, which is insoluble in alcoholic ammonium hydroxide.



Some Important Concepts in Organic Chemistry:

- **Optical Activity:** The property due to which some compounds are able to rotate the plane of plane-polarized light when it is passed through their solution.
- **chirality and enantiomers:** The compounds when they are optically active are known as chiral molecule and they exist in pair such that they are mirror images of each other also known as enantiomers. If a mixture have enantiomers in equal quantity, then the mixture will have zero optical rotation and such mixtures are known as **racemic mixtures** and process of making such mixtures is known as **racemisation**.

Eg:



- **Retention:** The property due to which some elements are able to maintain both their absolute and relative configuration and position in space. In simple word the configuration of the stereocenter remains unchanged.
- **Inversion:** Here the absolute and relative configurations become reverse of each other which means their symmetry becomes different than what was it before.