

ORGANIC CHEMISTRY

Topic-1

Halogen compounds

VERY SHORT ANSWER QUESTIONS

1. How halogen compounds are classified?

Ans: Compounds derived from hydrocarbons by the replacement of one or more hydrogen atom(s) by the corresponding number of halogen atom(s) are known as halogen derivatives. The halogen derivatives are classified on the basis of nature of hydrocarbon from which they are obtained as

- (i) **Alkyl halides:** Halogen derivative of alkanes
- (ii) **Alkenyl halides:** Halogen derivative of alkenes (Not included in syllabus)
- (iii) **Alkynyl halides:** Halogen derivative of alkynes (Not included in syllabus)
- (iv) **Aryl halides:** Halogen derivative of arenes. (See aromatic part)

2. How Alkyl halides are classified?

Alkyl halides are further classified as

- (i) **Mono halides:** These involve replacement of one H atom by halogen atoms i.e., $C_nH_{2n+1}X$ e.g.

CH_3Cl : methyl chloride or chloromethane

C_2H_5Cl : ethyl chloride or chloroethane

- (ii) **Di halides:** These involve replacement of two H atoms by halogen atoms i.e., $C_nH_{2n}X_2$

CH_2X : methylene halide
 CH_2X
| : ethylene dihalide or vicinal dihalides
 CH_2X

CH_3
| : ethylidene dihalide or geminal dihalides
 CHX_2

(iii) **Tri halides:** These involve replacement of three H atoms by halogen atoms i.e. $C_nH_{2n-1}X_3$ e.g.,

CHX_3 : trihalo methane or haloform

(iv) **Tetra halide:** These involve replacement of four H atoms by halogen atoms i.e. $C_nH_{2n-2}X_4$ e.g., CCl_4 .

3. How mono halides are classified?

Monohalides or Alkyl halides

(1) General formula $C_nH_{2n+1}X$ e.g., CH_3X , C_2H_5X ,

(2) Mono halides are further classified as

(A) **Primary halides:** Halogen atom attached on 1° carbon or methyl carbon

e.g. CH_3X : halomethane or methyl halide

CH_3CH_2X : haloethane or ethyl halide

$CH_3CH_2CH_2X$: 1-halopropane or n-propyl halide

(B) **Secondary halides:** Halogen atoms are attached on 2° carbon atom

CH_3CHXCH_3 : 2-halopropane or sec. propyl halide or isopropyl halide

$CH_3CHXCH_2CH_3$: 2-halobutane or sec. butyl halide

(C) **Tertiary halides :** Halogen atoms are attached on 3° carbon atom

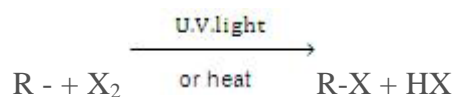
$\begin{array}{l} H_3C \\ H_3C \\ H_3C \end{array} \begin{array}{l} \diagdown \\ \diagup \\ \diagup \end{array} CX$: 2-methyl, 2-halopropane or t.butyl halide

SHORT ANSWER QUESTIONS

1. Give the methods of preparation of monohalides

Preparation of Monohalides:

(1) **By direct halogenations of alkanes:** (See halogenations of alkanes)

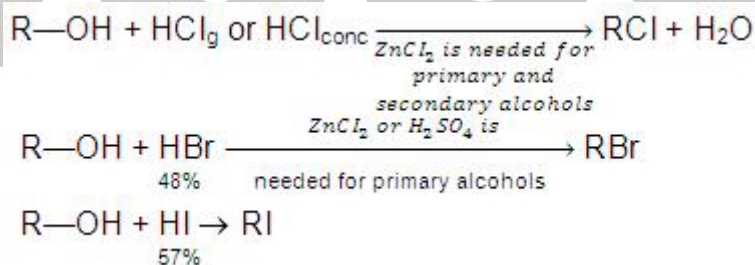


(2) **By the addition of HX on alkenes:**



(3) **By alcohols:**

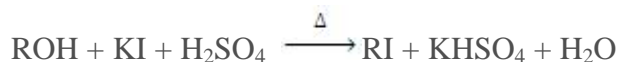
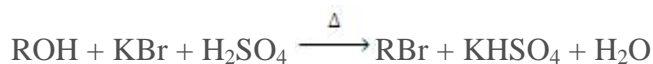
(a) Action of halogen acids:



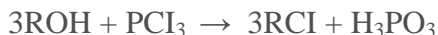
The reactivity order for alcohols is: tertiary > secondary > primary alcohol

The reactivity order for halogen acid is: HI > HBr > HCl

Note: Bromides and iodides are also obtained as:

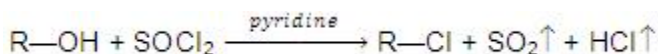


(b) Action of phosphorus halides:



Note: PBr_3 & PI_3 being less stable & thus for bromides & iodides, $\text{P} + \text{Br}_2$ or $\text{P} + \text{I}_2$ mixture is used.

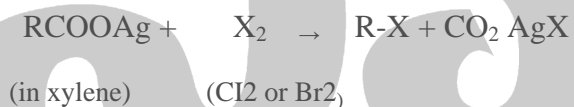
(c) Action of thionyl chloride: or Darzen's method



Note: SOBr_2 is less stable & SOI_2 does not exist and thus bromides & iodides are prepared by this method.

Explain Borodine-Hunsdicker reaction.

Ans: Borodine-Hunsdicker reaction: Alkyl chlorides and alkyl bromides are obtained by the action of Cl_2 or Br_2 in CCl_4 on silver salt of the fatty acids. The reaction proceeds through free radical mechanism.



Note:

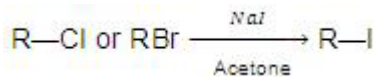
1. The yield of alkyl halide is primary > secondary > tertiary
2. Hunsdiecker reaction is used to reduce the length of carbon chain (descent of series).
3. Only bromides are obtained in good yield in this reaction. The chlorides can also be obtained by this reaction but the yield is poor. Iodides however cannot be obtained because these form esters with silver salts.



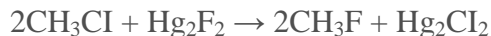
This reaction is called Birnbaurn-Simonini reaction.

2. Explain how halide exchange takes place.

Halide exchange: Iodides are usually prepared by this method. The halogen exchange reaction is called Finkelstein reaction.



This method is also used to prepare fluorides.



3. Explain the physical properties of Alkyl halides.

Physical Properties of Alkyl Halides:

1. Physical state:

(a) CH_3Cl , $\text{C}_2\text{H}_5\text{Cl}$, CH_3Br only are gases at room temperature. The alkyl halides up to C_{18} are colourless liquids, while higher are colourless solids.

(b) The b.pt of halides shows following order:

Alkyl iodide > alkyl bromide > alkyl chloride (for a given alkyl group)

Methyl halide < ethyl halide < propyl halide (for a given halide)

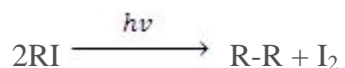
1° halide > 2° halide > 3° halide (for a given halide and alkyl group)

2. Alkyl fluorides & alkyl chlorides are lighter than water, alkyl bromides and alkyl iodides are heavier than water. The density of halides thus follow the order : iodide > bromide > chloride > fluoride.

3. Alkyl halides are soluble in organic solvents but insoluble in water.

4. Alkyl halides burn on Cu wire with green edge flame. This is Beilstein test for halogens. The green or blue colour to flame is due to interaction of halogens with Cu wire.

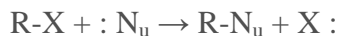
5. Alkyl iodides are less stable and darken their colour on exposure to light on standing due to adsorption of liberated iodine.



4. Explain the chemical properties of Alkyl halides.

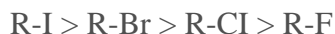
Chemical nature of Alkyl halides:

(a) The alkyl halides are highly reactive due to the high electronegativity difference between carbon & halogen atom which provides polarity in $C^{+d} - X^{-d}$ bond & thus carbon atom of C-X bond is easily attacked by a nucleophile to show nucleophilic substitution.



The nucleophilic substitution may follow S_N1 or S_N2 mechanism. In addition to nucleophilic substitution alkyl halides also show elimination reactions.

(b) Furthermore the reactivity order of alkyl halide is :



The reactivity does not follow the polarity order of bond. On the contrary it has been explained in terms of increasing bond length of C-X bond (maximum in C-I) which gives rise to lower bond energy and thus less stability to C-X bond.

(c) The reactivity order for given alkyl halide also shows the order :



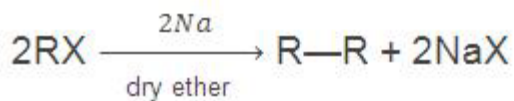
This has been explained in terms of +ve inductive effect of alkyl groups which increases the polarity of C-X bond & thereby making it more reactive.

(d) Primary alkyl halides undergo reactions by S_N2 mechanism. The presence of bulky groups in primary halides (in spite of more +ve I.E.) cause steric hindrance & bring them less reactive towards.

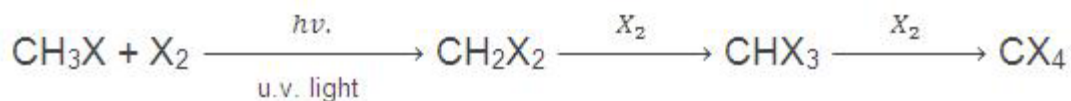


5. Explain the chemical properties of Alkyl halides.

Ans: 1. Wurtz reaction:

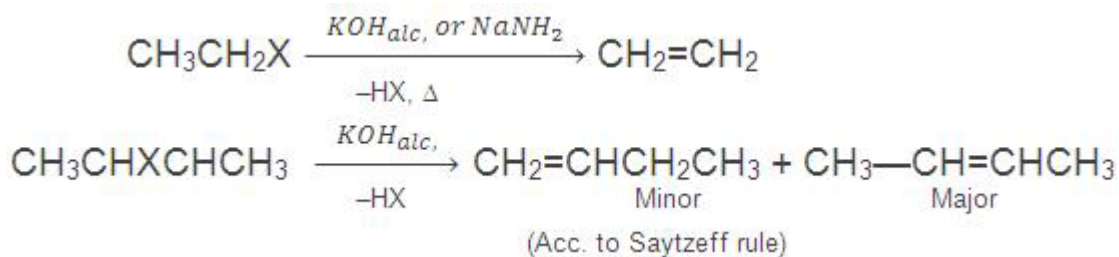


2. Action of halogen:

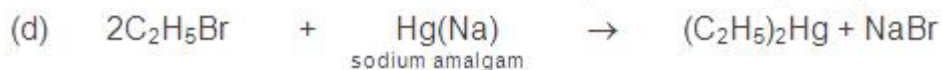
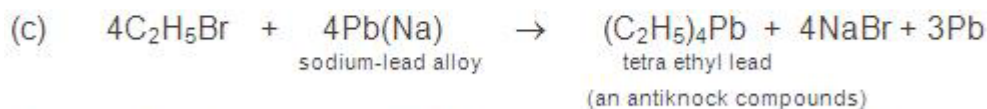
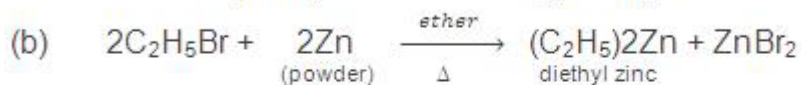
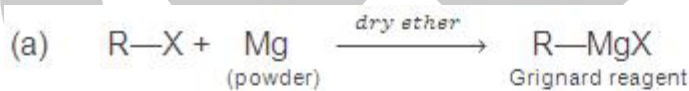


Note: C₂Cl₆ (hexachloroethane) is a solid and is known as artificial camphor.

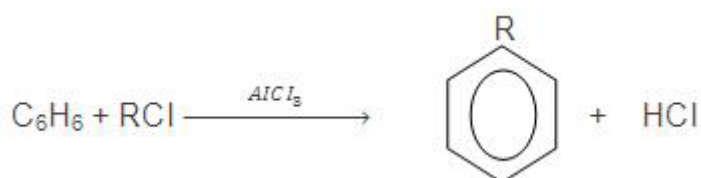
3. Dehydrohalogenation: An α, β-elimination of HX by KOH_{alc.}



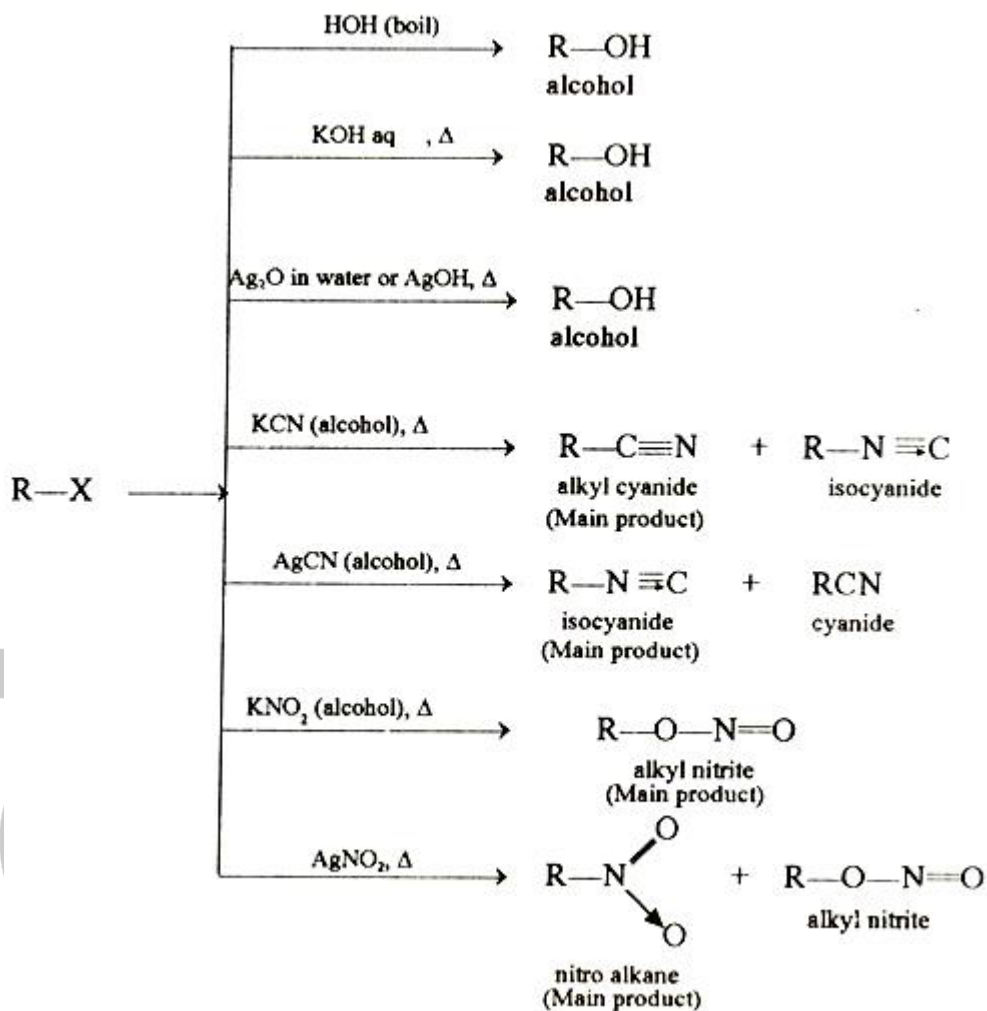
6. Reactions with metals:

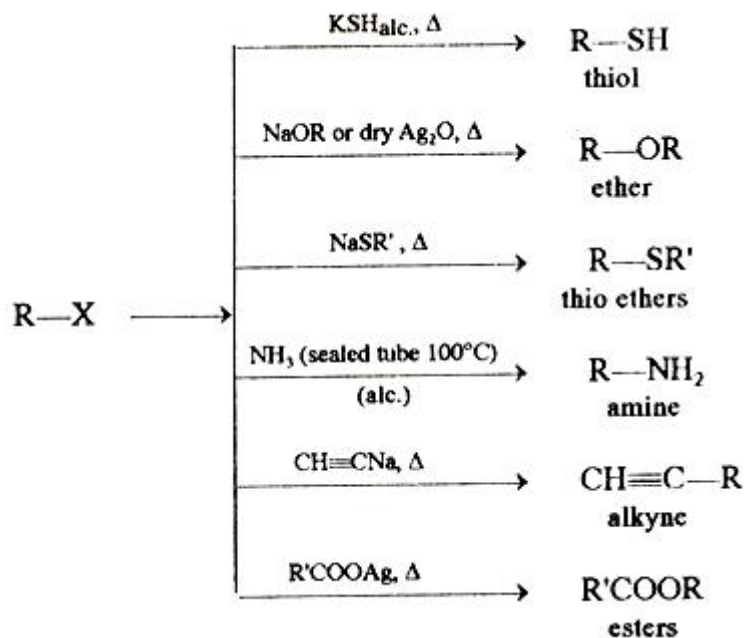


7. Friedel-Crafts reaction: Alkyl halides react with benzene in presence of anhydrous AlCl₃ to form homologues of C₆H₆.

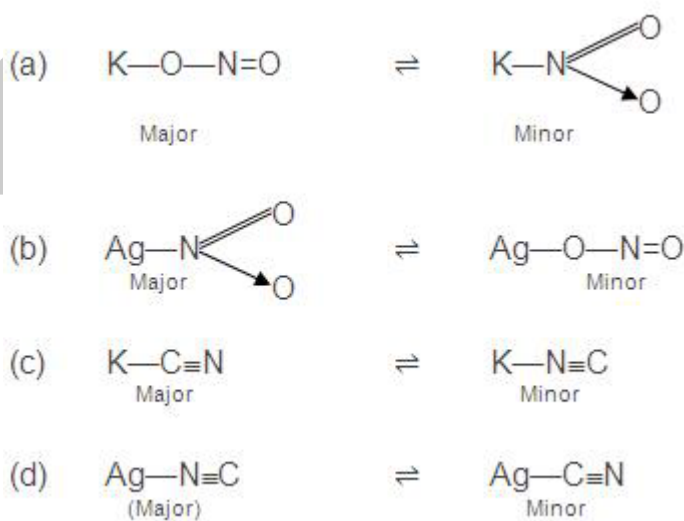


8. Nucleophilic substitution on alkyl halides: Halogen atom of alkyl halides is easily replaced by other nucleophiles to give a large variety of S_N reactions.





Note: The two products formed on reaction of $R-X$ with KNO_2 and $AgNO_2$ as well as with KCN and $AgCN$ are due to tautomerism in these molecules.



Uses:

- (i) As alkylating agent i.e. to introduce alkyl gp in a molecule.
- (ii) Lower members are used as anaesthetic agent, refrigerant and solvents.
- (iii) As synthetic reagent.

6. Write a Short note on dihalides

(i) Two H atoms of alkanes are replaced by two halogen atoms to form dihalides.

(ii) General formula $C_nH_{2n}X_2$.

(iii) Dihalides are classified as :

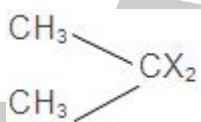
(a) Gem dihalides :

(i) The term gem has derived from geminal meaning for same position.

(ii) The two similar halogen atoms are attached to same carbon atom e.g.

CH_3CHX_2 ethylidene dihalide or 1, 1-dihaloethane

$CH_3CH_2CHX_2$ propylidene dihalide or 1, 1-dihalopropane



isopropylidene dihalide or 2, 2-dihalopropane

(b) vic dihalides:

(i) The term vic has been derived from vicinal meaning for adjacent carbon atoms.

(ii) The two halogens are attached one each on adjacent carbon atoms e.g.

CH_2XCH_2X ethylene dihalide or 1, 2-dihaloethane

CH_3CHXCH_2X propylene dihalide or 1, 2-dihalopropane

(c) α - ω dihalides:

In these compounds halogen atoms are attached to terminal carbon atoms and are separated by three or more carbon atoms. They are also known as polymethylene halides e.g.

$CH_2X-CH_2-CH_2-CH_2X$ tetra methylene dichloride or 1, 4-dihalobutane

(iv) vic and gem dihalides are position isomers to each other.

7. Write a note on trihalides?

The trihalogen derivative of alkanes is prepared by replacement of three hydrogen atoms by three halogen atoms.

(ii) Their general formula is $C_nH_{2n-1}X_3$:

(iii) The trihalogen derivative of methane are also known as haloform

chloroform,
 $CHCl_3$
colourless liquid

bromoform
 $CHBr_3$
colourless liquid

and

iodoform
 CHI_3
yellow solid

8. How chloroform is prepared?

Chloroform ($CHCl_3$) Preparation:

(i) Lab method and Industrial method: By the distillation of ethyl alcohol or acetone with bleaching Powder:

(a) Bleaching powder on hydrolysis gives slaked lime and Cl_2 which acts as oxidizing agent as well as chlorinating agent.



By ethanol:



chloroform Ca formate

By acetone:



(b) Chloroform is collected with water in lower layer. It is washed with dilute alkali and dried over $CaCl_2$ and then redistilled at 60-65°C.

(c) The yield is better if acetone is used.

9. Explain what is haloform reaction?

Haloform reaction :

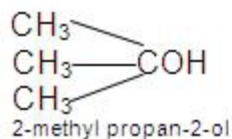
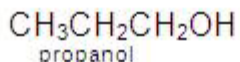
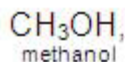
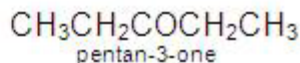
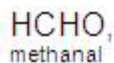
(a) Acetaldehyde and all methyl ketones (2-ones) or carbonyl compounds having $\text{CH}_3\text{-C}(=\text{O})\text{-}$ units as well as alcohols [primary (only ethanol) and secondary (only 2-ol)] which produce this unit on oxidation by halogen undergo haloform reaction on heating with halogen and NaOH to give haloform.

(b) If $\text{I}_2 + \text{NaOH}$ is used, the haloform reaction yields yellow solid as precipitate confirming the presence of $\text{CH}_3\text{-C}(=\text{O})\text{-}$ unit or $\text{CH}_3\text{-CH(OH)-}$ in the molecule attached to C or H.

This is known as iodoform test for confirming the presence of acetaldehyde, methyl ketones and alcohols (which produce $\text{CH}_3\text{-C}(=\text{O})\text{-}$ unit on oxidation)

e.g.

Reactants which give iodoform test because of during oxidation :



(Since it is not oxidised by I_2)

10. Write the physical properties of trihalides.

Properties of Trihalides:

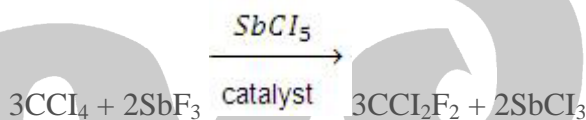
(i) Pure chloroform and bromoform are colourless liquids, and iodoform is yellow solids.

- (ii) All are heavier than water and soluble in organic solvents, but insoluble in water.
- (iii) CHCl_3 brings temporary unconsciousness when vapours are inhaled for sufficient time and thus used as anaesthetic agent.
- (iv) CHCl_3 is non inflammable but like other halides its vapours when ignited on Cu wire burn with green edge flame. (Beilstein test).

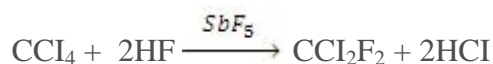
11. Explain what is Freon?

Freons: The chloro fluoro derivatives of methane and ethane are called freons. Some of the derivatives are: CHF_2Cl (monochlorodifluoromethane), CF_2Cl_2 (dichloro difluoro methane), $\text{HCF}_2\text{CHCl}_2$ (1, 1-dichloro 2, 2-difluoroethane). These are non-inflammable, colourless, non-toxic and low boiling liquids. These are stable upto 550°C . The most important and useful derivative is CF_2Cl_2 which is commonly known as **Freon** or **Freon-12**.

Freon or freon-12 (CF_2Cl_2) is prepared by treating carbon tetrachloride with antimony trifluoride in the presence of antimony penta chloride (a catalyst).



or by reacting carbon tetrachloride with hydrofluoric acid in presence of antimony penta fluoride.

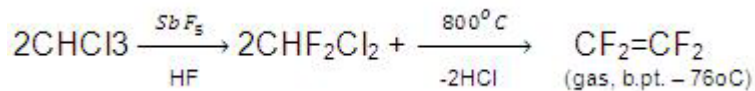


Under normal conditions Freon is a gas. (b.pt. -29.8°C). It can easily be liquefied. It is chemically inert and is used in air-conditioning and in domestic refrigerators.

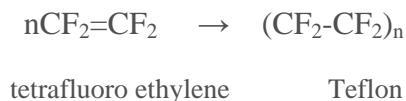
Note: Freon-14 is CF_4 , Freon-13 is CF_3Cl , Freon-11 is CFCl_3 . All these are used as refrigerant.

10. Explain what is Teflon?

Teflon: A plastic like substance produced by the polymerization of tetrafluoroethylene ($\text{CF}_2=\text{CF}_2$). Tetrafluoroethylene is formed when chloroform is treated with antimony trifluoride and hydrofluoric acid.



On polymerization, tetrafluoro ethylene forms a plastic-like material which is called teflon.

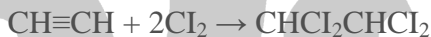


Teflon is chemically inert substances. It is not affected by strong acids and even by boiling aquaregia. It is stable at high temperature and thus, used for electrical insulation and preparation of gasket materials.

12. Explain what is Westron?

Ans: Acetylene tetrachloride (Westron), $\text{CHCl}_2\text{CHCl}_2$:

Acetylene tetrachloride is also known as sym. tetrachloroethane. It is prepared by the action of chlorine on acetylene in presence of a catalyst such as ferric chloride, aluminium chloride, iron, quartz or kieselguhr.



In absence of catalyst, the reaction between chlorine and acetylene is highly explosive producing carbon and HCl. The reaction is less violent in presence of catalyst.

It is a heavy, non-inflammable toxic liquid with smell like CHCl_3 . It is insoluble in water but soluble in organic solvents.

On further chlorination, it forms penta and hexachloroethane. On heating with lime (calcium hydroxide), it is converted to a useful product **westrosol** ($\text{CCl}_2=\text{CHCl}$)



Both westron and westrosol are used as solvent for oils, fats and varnishes

LONG ANSWER QUESTIONS

1. Explain the mechanisms of nucleophilic substitution reactions S_N1 and S_N2

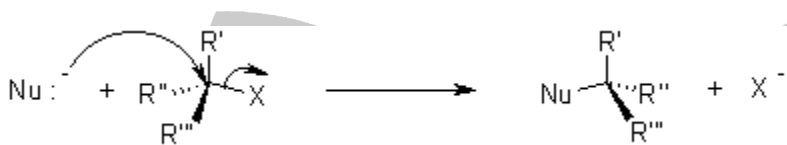
Nucleophilic Substitution (S_N1 and S_N2)



Nucleophilic substitution is the reaction of an electron pair donor (the nucleophile, Nu) with an electron pair acceptor (the electrophile). An sp^3 -hybridized electrophile must have a leaving group (X) in order for the reaction to take place.

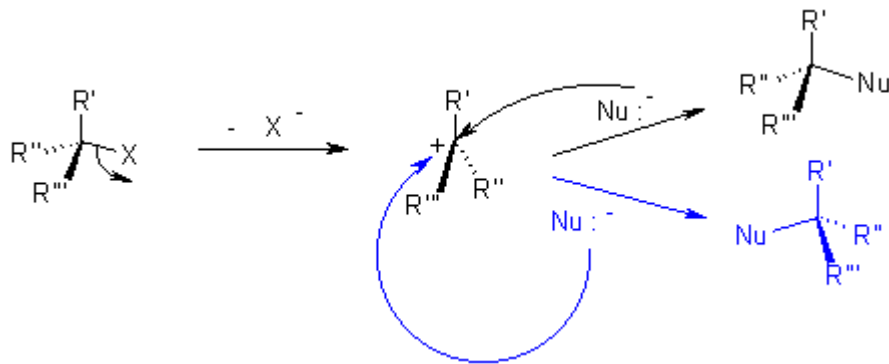
Mechanism of Nucleophilic Substitution

The term S_N2 means that two molecules are involved in the actual transition state:



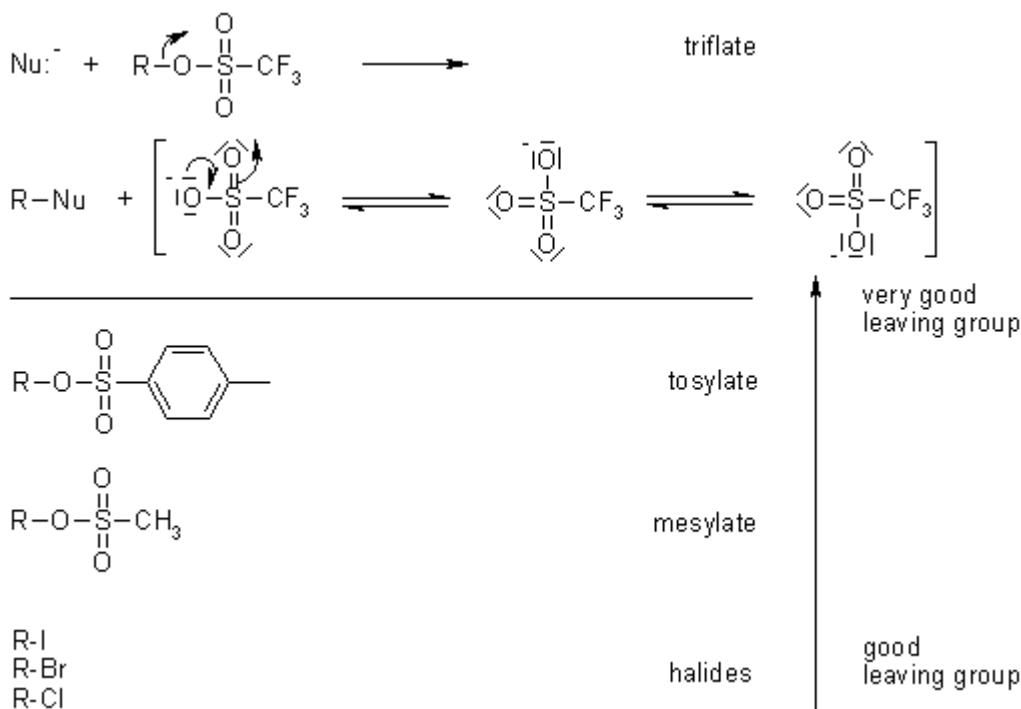
The departure of the leaving group occurs simultaneously with the backside attack by the nucleophile. The S_N2 reaction thus leads to a predictable configuration of the stereocenter - it proceeds with inversion (reversal of the configuration).

In the S_N1 reaction, a planar carbenium ion is formed first, which then reacts further with the nucleophile. Since the nucleophile is free to attack from either side, this reaction is associated with racemization.

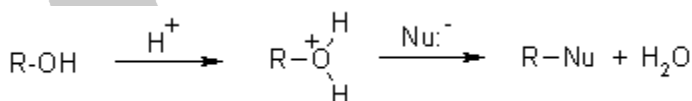


In both reactions, the nucleophile competes with the leaving group. Because of this, one must realize what properties a leaving group should have, and what constitutes a good nucleophile. For this reason, it is worthwhile to know which factors will determine whether a reaction follows an S_N1 or S_N2 pathway.

Very good leaving groups, such as triflate, tosylate and mesylate, stabilize an incipient negative charge. The delocalization of this charge is reflected in the fact that these ions are not considered to be nucleophilic.



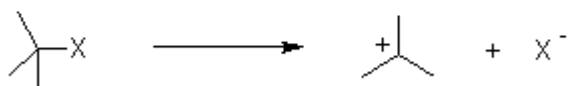
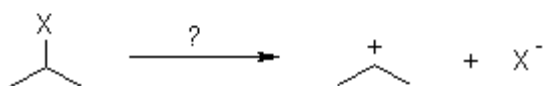
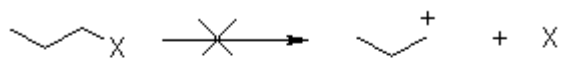
Hydroxide and alkoxide ions are not good leaving groups; however, they can be activated by means of Lewis or Brønsted acids.



The solvent also plays an important role in determining which pathway the reaction will take, $\text{S}_{\text{N}}1$ versus $\text{S}_{\text{N}}2$. It may safely be assumed that a primary-substituted leaving group will follow an $\text{S}_{\text{N}}2$ pathway in any case, since the formation of the corresponding unstable primary carbenium ion is disfavored. Reaction by the $\text{S}_{\text{N}}1$ pathway is highly probable for compounds with tertiary substitution, since the corresponding tertiary carbenium ion is stabilized through hyperconjugation:

The better the solvent stabilizes the ions, the more probable that the reaction will follow an $\text{S}_{\text{N}}1$ pathway (e.g., in polar protic solvents such as water/acetone). The more highly substituted is the incipient carbenium ion, the more probable that the reaction will follow an $\text{S}_{\text{N}}1$ pathway. The more unreactive the nucleophile, the more probable it becomes that a reaction with secondary and tertiary electrophiles will follow an $\text{S}_{\text{N}}1$ pathway. A weaker nucleophile is not as effective in the backside attack, since this location is sterically shielded, especially in the case of tertiary substrates. Carbenium ions are planar

and therefore less sterically hindered, and are naturally more reactive as electrophiles than the uncharged parent compound.



The hydrolysis of tert-butyl chloride is a typical $\text{S}_{\text{N}}1$ reaction:

