

SECTION I

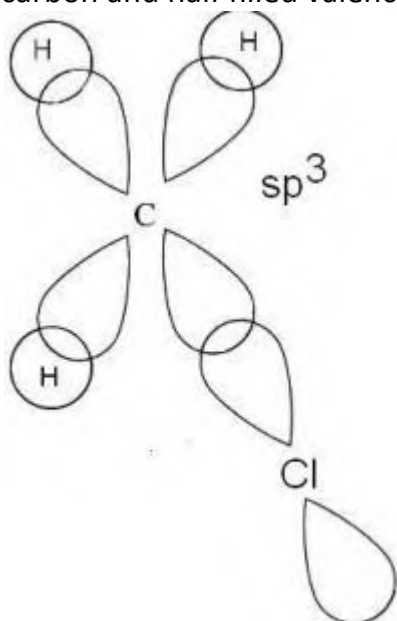
HALOALKANES

Compounds derived from alkanes by the replacement of one or more Hydrogen atoms by corresponding number of halogen atoms (fluorine, chlorine, bromine or iodine) are termed as haloalkanes.

Alkyl halides are represented by general formula $C_nH_{2n+1}X$, here X is halogen atom

ORBITAL STRUCTURE

In alkyl halides, carbon-halogen σ bond is formed by overlap of sp^3 hybrid orbital of carbon and half filled valence p-orbital of halogen atom:



Haloalkanes may be classified on the basis of number of halogen atoms

(1) Monohalogen derivatives

One halogen atom is attached to carbon atom. Its general formula is $C_nH_{2n+1}X$

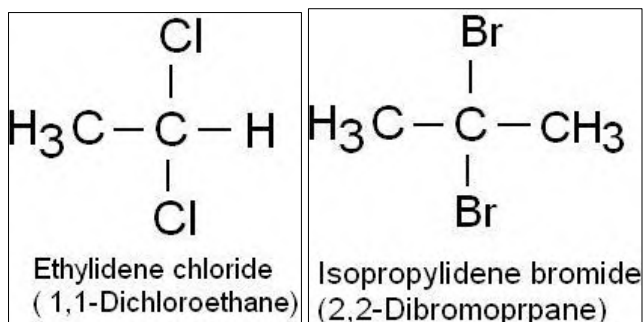
Example CH_3Cl (methyl chloride).

(2) Dihalogen derivatives

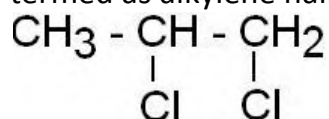
These are derived by replacement of two hydrogen atoms by two halogen atoms
Dihalides derivatives are of three types

(a) Gem-dihalides

Halogen atoms are attached to same carbon atom. These are called alkylidene halides.

**(b) Vic-dihalides**

Halogen atoms are attached to adjacent (vicinal) carbon atoms. These are termed as alkylene halides.



Propylene chloride
(1,2 - Dichloropropane)

(c) $\alpha - \omega$ halides (terminal halides)

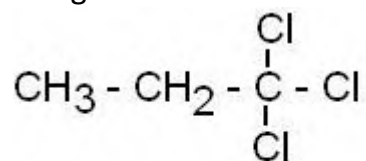
Halogen atoms are attached to terminal carbon atoms. These are also called polymethyl halides



Trimethyl di bromide (1,3 - dibromopropane)

(3)Trihalogen derivatives

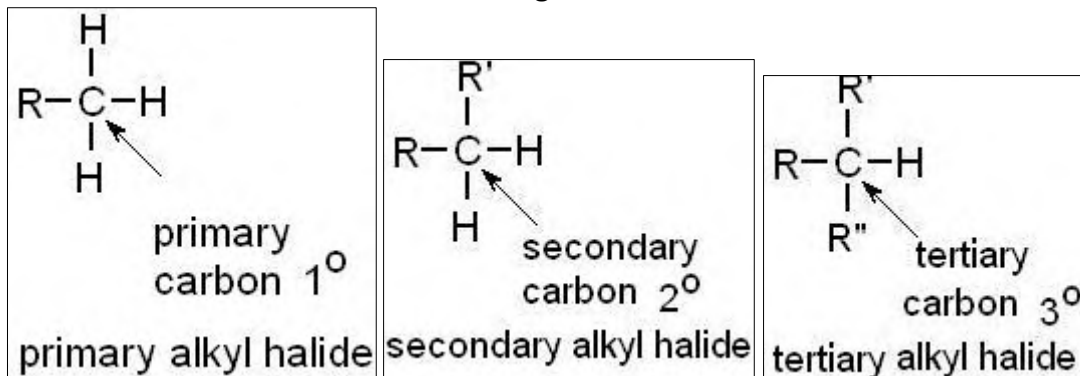
Trihalogen derivatives are derived by replacing three hydrogen atoms by three halogen atoms. General formula is $\text{C}_n\text{H}_{2n-1}\text{X}$



1,1,1-trichloropropane

CLASSIFICATION OF MONOHALOGEN COMPOUND

(1) Alkyl halides are classified as primary 1° , secondary 2° , tertiary 3° depending upon nature of carbon to which halogen is attached



(2) Compounds containing sp^3 , C – X bond

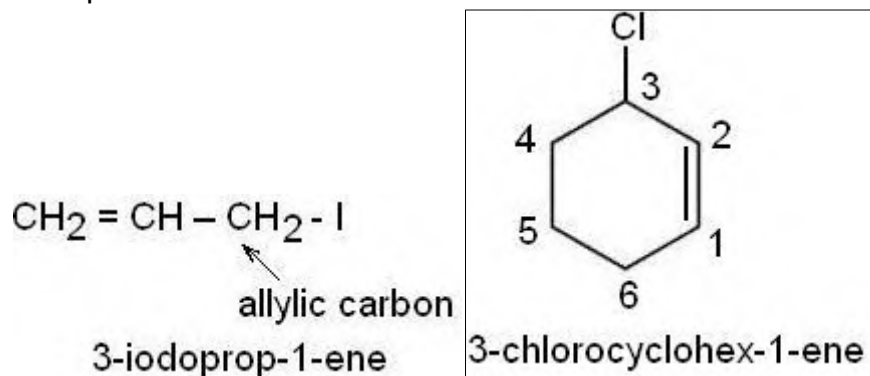
(a) Alkyl halides



(b) Allylic carbon

Halogen atom attached to allylic carbon. i.e. carbon atom next to C = C.

Example

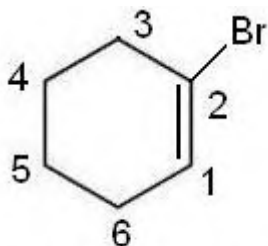


(3) Compound containing sp^2 , C – X bond

Vinylic halides

In these halides, halogen atom is attached to vinylic carbon i.e. one of the carbon atoms of C = C





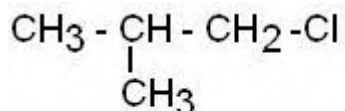
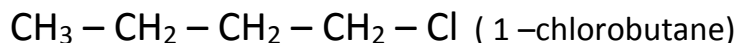
1-bromocyclohex-1-ene

(4) Compounds containing sp , C – X bond Haloalkynes

In these halides, the halogen atom is attached to one of the carbon atoms of $C \equiv C - Br$ (Bromoethyne)

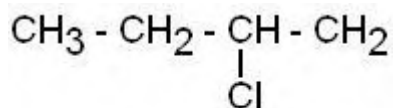
ISOMERISM OF MONOHALOGEN COMPOUNDS

(1) Chain isomerism: This is due to different arrangement of carbon in alkyl group



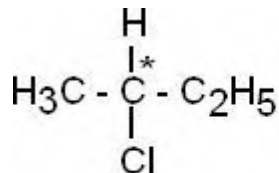
1-chloro-2-methylpropane

(2) Position isomerism: This is due to different position of halogen atom in the molecules



2- chlorobutane

(3) Optical isomerism: This is due to presence of an asymmetric carbon atom (asymmetric carbon atom : all four substituent atoms or molecules attached to carbon are different)



* asymmetric carbon atom

(4) Conformations: Haloalkanes can also form conformers due to free rotation of C-C bond.

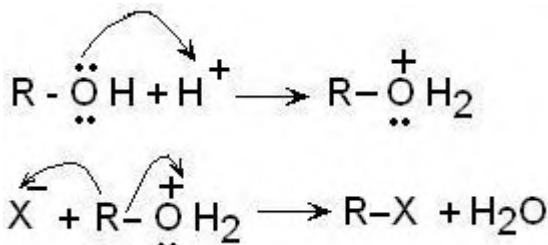
GENERAL METHODS OF PREPARATION

(1) From alcohol

(a) Action of hydrogen halides

1° alcohols follows S_N2 whereas 2° and 3° alcohol follows S_N1 mechanism.

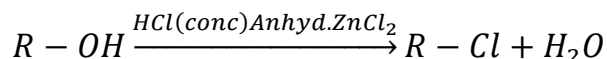
In these S_N mechanisms, the nucleophile (X^-) attacks the protonated alcohol molecule with elimination of water.



Since nucleophilicity (i.e. tendency to donate electron pair to the carbon) of halide ion decreases in the order $\text{I}^- > \text{Br}^- > \text{Cl}^-$, the order of reactivity of halogen acid decreases in the same order $\text{HI} > \text{HBr} > \text{HCl}$

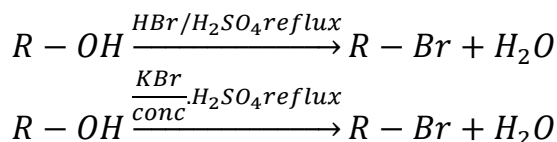
Order of reactivity of different alcohol is

Allyl > 3° alcohol > 2° alcohol > 1° alcohol



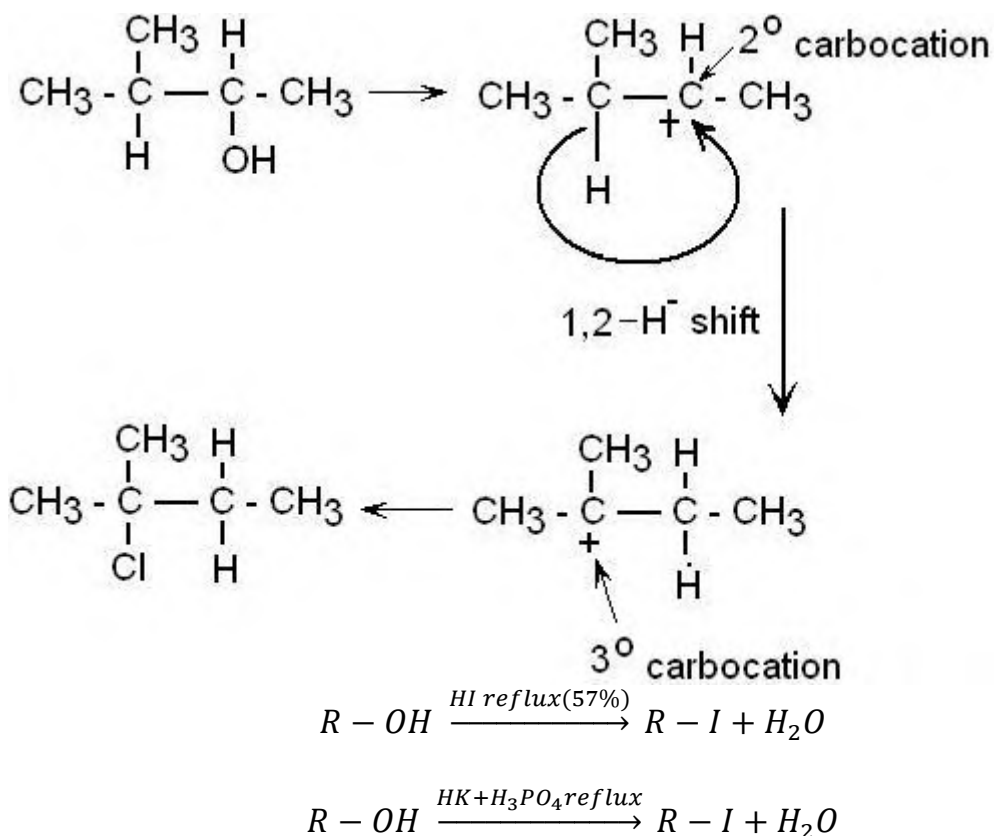
HCl do not require anhyd. ZnCl_2 for 3° alcohol because 3° are very reactive.

The mixture (1:1) of con. HCl and anhyd ZnCl_2 is called LUCAS reagent. It is used to distinguish 3° , 2° , 1° alcohols because their reactivity towards this reagent is 3° alcohol > 2° alcohol > 1° alcohol

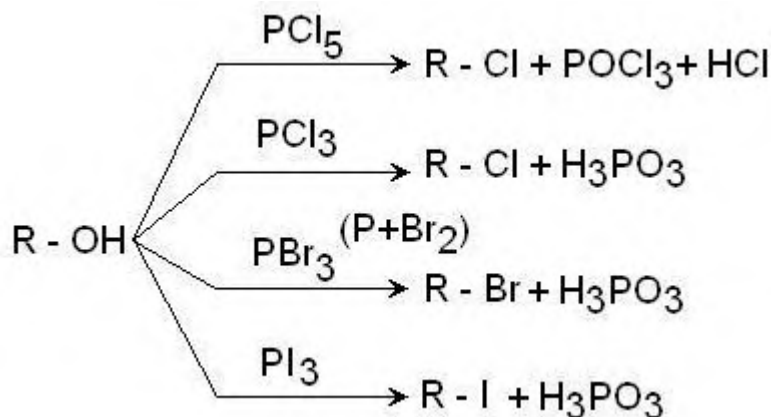


The mixture of KBr and H_2SO_4 is not used in case of secondary and tertiary alcohol as they can cause dehydration.

Rearranged product may also be obtained due to hydride or methyl shift in carbocation intermediate



(b) Action of phosphorous halide

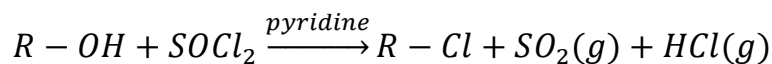


4th method gives good yield of 1° haloalkanes but poor yields 2° and 3° haloalkanes because secondary and tertiary alcohol on heating forms alkene.

PBr₃ and PI₃ are obtained in situ by action of red phosphorus and bromine or iodine respectively

(c) Action of thionyl chloride

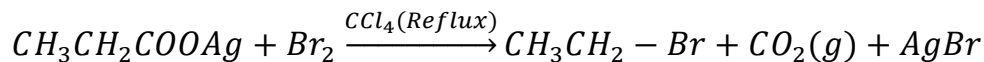
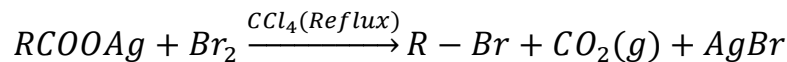
Darzen's method



This method is preferred because other two byproducts are escapable gases.

SOBr_2 is less stable and SOI_2 does not exist. Thus R-Br and RI can't be prepared by Darzen's method.

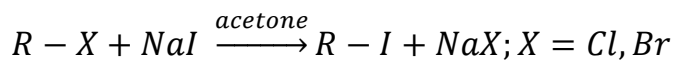
(d) Hunsdiecker reaction



The reaction gives product with one carbon atom less than fatty acid and yield of halide is $1^\circ > 2^\circ > 3^\circ$

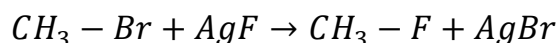
(2) Halide exchange method

(a) Finkelstein reaction



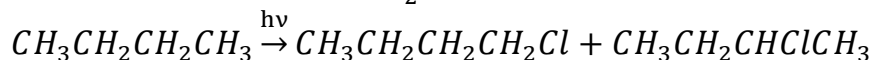
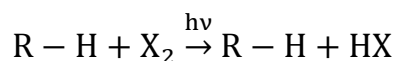
NaCl or NaBr is precipitated in dry acetone. It facilitates forward reaction

(b) Swarts reaction



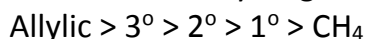
Other than AgF , Hg_2F_2 , CoF_2 or SbF_3 can also be used.

(3) Halogenation of alkanes

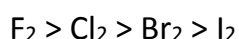


Iodination being reversible process requires the presence of oxidizing agent such as HIO_3 , conc. HNO_3

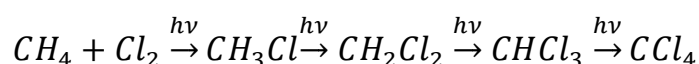
a) Abstraction of hydrogen for a particular halogen follows order



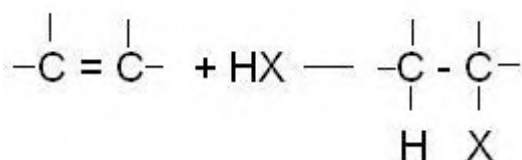
b) Abstraction of halogen go the above reaction follows order



c) Direct halogenation proceed through free radical mechanism



(4) Addition of hydrogen halide to alkene



Reaction follows electrophilic addition mechanism

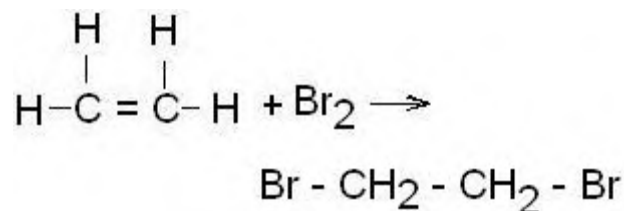
$\text{CH}_3\text{-CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CHBrCH}_3$ [absence of peroxide, Markonikoff's addition]

$\text{CH}_3\text{-CH} = \text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{Br}$ [presence of peroxide, Antimarkonikoff]

HCl and HI do not show peroxide effect.

Product may be obtained due to 1,2-hydride or 1,2-methyl shift.

Addition of bromine in CCl_4 to an alkene results in discharge of reddish brown colour of bromine constitutes an important method for detection of double bond in a molecule.



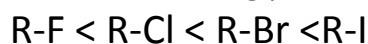
PHYSICAL PROPERTIES OF ALKYL HALIDES

(1) Physical state and smell:

Haloalkanes, the lower members are colourless gas at room temperature. The other alkyl halides up to C_{18} are colourless sweet smelling liquids while higher members are colourless solids.

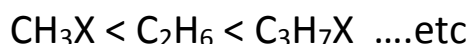
(2) Boiling point:

(i) The boiling point increases from $\text{R}-\text{F}$ to $\text{R}-\text{I}$



Iodine has a larger surface area and outer electrons are loosely bounded. This makes iodine a highly polarizable atom. A polarizable atom increases London forces of attraction which causes an increase in boiling point.

(ii) Boiling point increases with increase in size of alkyl group



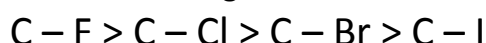
For isomeric alkyl halides, boiling point decreases with branching.

(3) Solubility

Halo-alkanes are polar in nature. Yet they are insoluble in water but soluble in organic solvents. It is not soluble in water because they are not able to form hydrogen bond with water molecule.

(4) Bond strength

In haloalkanes, bond strength of carbon-halogen bond decreases with increase in the bond length as one move from fluorine to iodine



(5) Density

The densities of haloalkanes increases with atomic mass of halogen and decreases with increase in size of alkyl group.

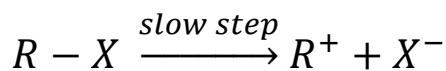
- (i) For same alkyl group, density follows the order
 $R-I > R-Br > R-Cl > R-F$
- (ii) Same halogen density follows
 $CH_3X > C_2H_5X > C_3H_7Cl$
- (iii) Fluoro and chloroalkanes are lighter than water whereas bromides and iodides are heavier than water.

(6) Dipole moment

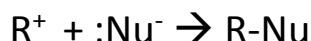
- (i) Haloalkanes are polar compounds and their polarity depends on electro negativity of halogen. Dipole moment of halomethanes are
 $CH_3Cl > CH_3F > CH_3Br > CH_3I$
 1.86 D 1.84D 1.83D 1.63D
- (ii) Dipole moment of fluoromethane is less than chloromethane is due to very small size of fluorine.

CHEMICAL PROPERTIES, REACTIVITY OF HALOALKANES**1) Nucleophilic substitution reaction****(a) S_N1 mechanism (Unimolecular nucleophilic substitution)**

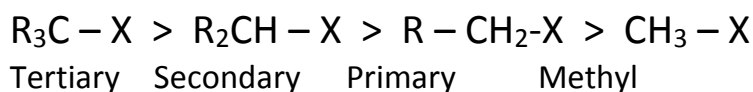
- (i) In this type, the rate of reaction depends only on the concentration of the substrate i.e. haloalkane and the reaction is of the first order change i.e.
 $Rate \propto [substrate]$ or $Rate = [R-X]$
- (ii) This type of reaction proceeds in TWO steps as
 STEP I: The haloalkanes undergoes heterolytic fission forming an intermediate, carbocation. This step is slow and hence is the rate determining step of the reaction.



STEP II: The carbocation ion being a reactive species, immediately reacts with the nucleophile [:Nu⁻] to give the substitution product



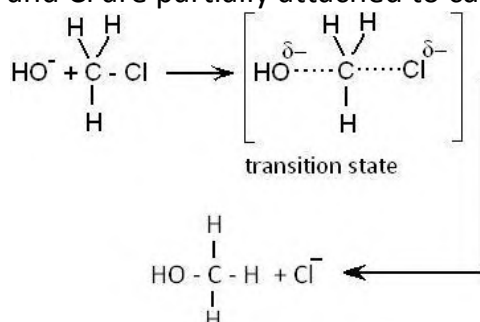
- (iii) If the haloalkane is optically active then the product is racemic mixture.
- (iv) The order of reactivity depends upon the stability of carbocation in the first step:



- (v) S_N1 order
 $Benzyl > allyl > 3^\circ > 2^\circ > 1^\circ > methyl \text{ halide}$

(b) S_N2 mechanism (Bimolecular nucleophilic substitution)

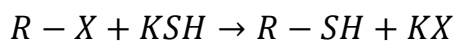
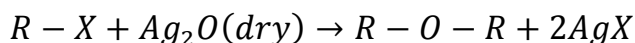
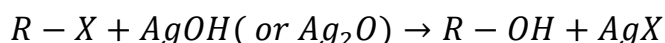
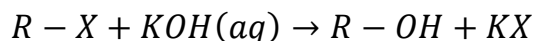
- (i) In this type, the rate of reaction depends on the concentration of both substrate and nucleophile and the reaction second order change.
Rate \propto [Substrate] [nucleophile]
Rate = k [R - X] [:Nu⁻]
- (ii) Hydrolysis of methyl chloride is an example of S_N2 reaction and high concentration of nucleophile (OH⁻) favours S_N2 reaction. The chlorine atom present in methyl chloride is most electronegative than carbon atom. Therefore C-Cl bond is partially polarised H₃C^{δ+}- Cl^{δ-}.
- (iii) When the methyl chloride is attacked by OH⁻ strong nucleophile from the opposite side of chlorine atom, a transition state results in which both OH and Cl are partially attached to carbon atom

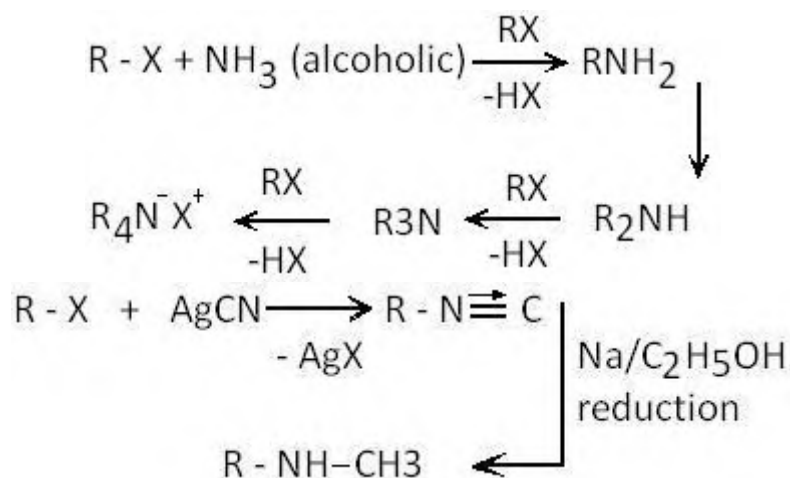
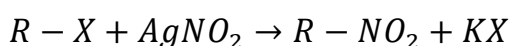
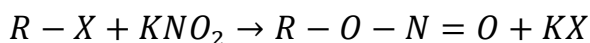
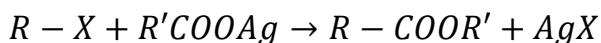
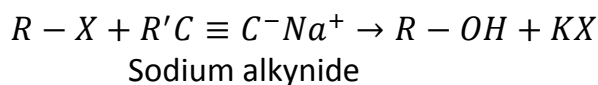
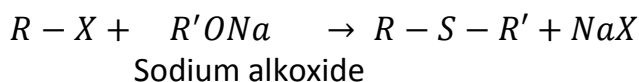


- (iv) In transition state chlorine starts taking hold of electron pair through which it is bonded to carbon and OH⁻ ion offers a pair of electrons for the formation of bond with carbon. Finally chlorine leaves the molecule as a chloride ion (Cl⁻). S_N2 reaction of optically active halides are concentrated reactions and configuration of carbon is changed. This process is called inversion of configuration also known as Walden inversion
- (v) S_N2 reaction is favoured by small groups on the carbon, atom attached to halogens, so
CH₃ - X > RCH₂ - X > R₂-CH-X > R₃C - X
- (vi) S_N2 order
Methyl > 1° > 2° > 3° > allyl > benzyl

NUCLEOPHILIC SUBSTITUTION REACTION OF ALKYL HALIDES

SUMMARY

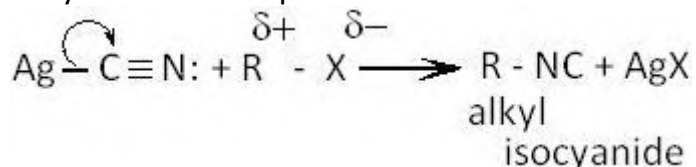




Some important points

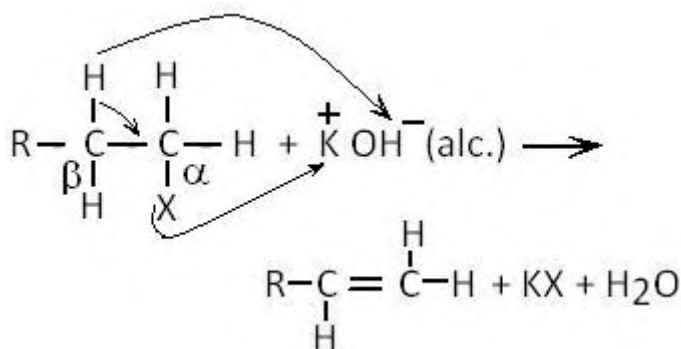
- (i) Groups which possess two nucleophilic centre are called ambident nucleophiles. Example cyanides and nitrites.
- (ii) KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in position to donate electron pairs, the attack takes place mainly through carbon atom and not nitrogen atom since C - C bond is more stable than C - N bond. Therefore when haloalkanes reacts with $KC \equiv N$ alkyl cyanides is obtained.

$$K^+ C^- \equiv N + R^{\delta+} - X^{\delta-} \rightarrow R - C \equiv N + K - X$$
- (iii) AgCN is mainly covalent and nitrogen is free to donate electron pair forming isocyanide as main product.

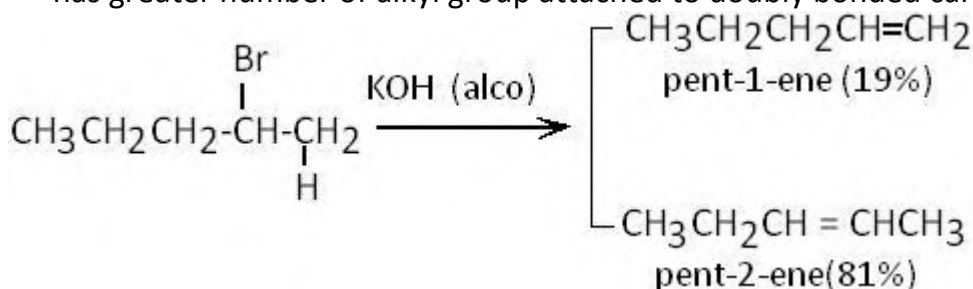


2) Elimination reaction-dehydro-halogenation

- (a) Alkyl halides undergoes β – elimination reaction in presence of potassium hydroxide in ethanol to yield alkene

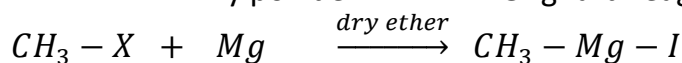
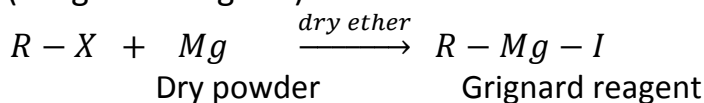


- (b) Reactivity of haloalkanes towards elimination reaction is
Tertiary > Secondary > primary
This is due to +I effect of the alkyl group which increases polarity of C-X bond
- (c) In dehydrohalogenation of secondary and tertiary haloalkanes there is a possibility of formation of two isomers, then it is governed by Saytzeff's rule which can be summarized as
"In dehydrohalogenation reactions, the preferred product is that alkene which has greater number of alkyl group attached to doubly bonded carbon atoms."



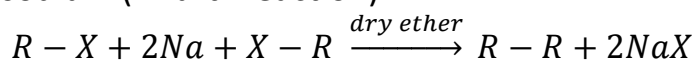
3) Reaction with metals

- (a) With magnesium (Grignard reagent)

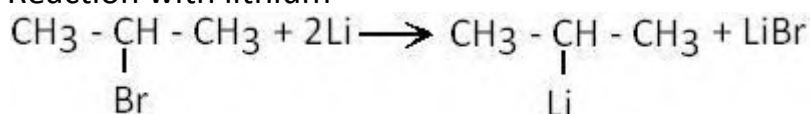


Carbon –magnesium is highly polar covalent whereas magnesium halogen bond is ionic

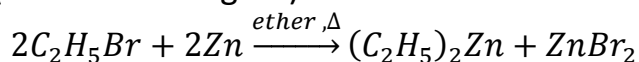
- (b) Reaction with sodium (Wurtz reaction)



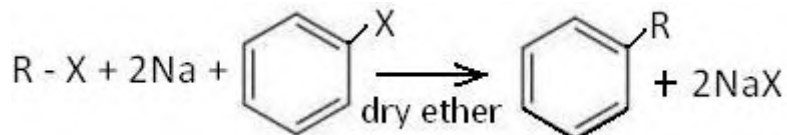
- (c) Reaction with lithium



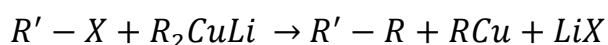
(d) Reaction with zinc (Frankland reagent)



(e) Wurtz – Fiting reaction



(f) Corey-house reaction



SECTION II

HALOARENES

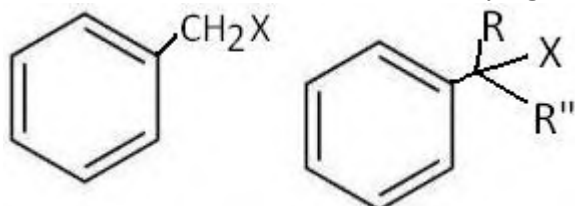
Compound in which the halogen atom is linked directly to the carbon atom of benzene are called arylhalides or haloarenes.

CLASSIFICATION OF HALOARENES

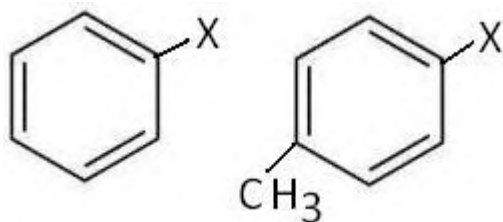
(1) Compounds containing sp^3 C – X bond

Benzylic halides

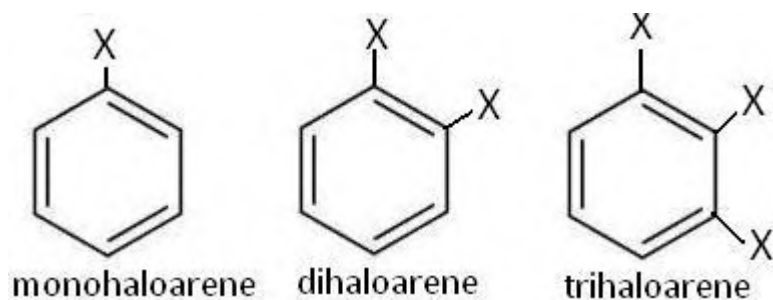
In these halides, the halogen atom is attached to a benzylic carbon i.e. the carbon atom of the side chain carrying the aryl group.

(2) Compound containing sp^2 C – X bond

Aryl halides: These are the compounds in which the halogen atom is bonded to sp^2 – hybridized carbon atom of an aromatic ring.

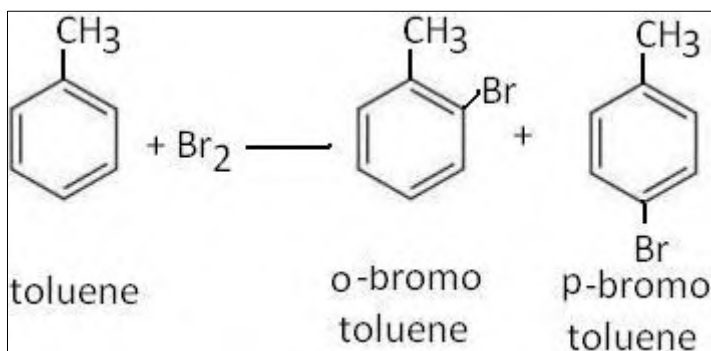
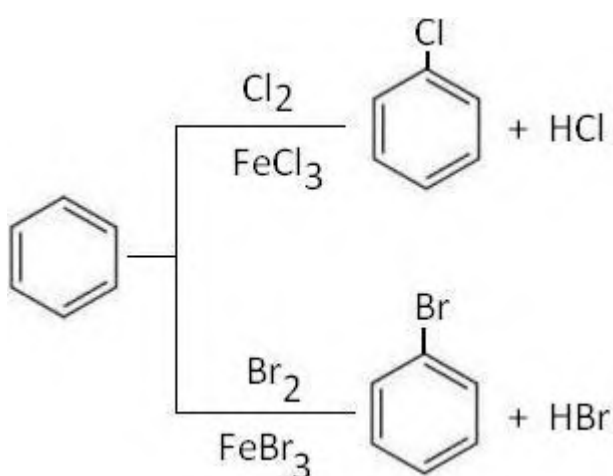


(3) On the basis of number of halogen atoms

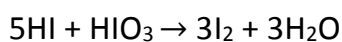
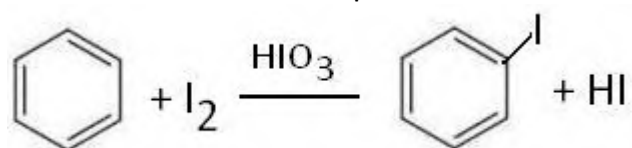


GENERAL METHODS OF PREPARATION OF HALOARENES

1) Direct halogenations of aromatic hydrocarbon



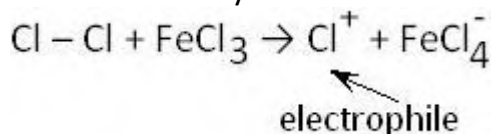
Direct iodination is not possible since, the reaction is reversible with iodine. Thus the reaction is carried in the presence of oxidizing agent. Such as HIO_3 , HNO_3 .



MECHANISM OF HALOGENATION

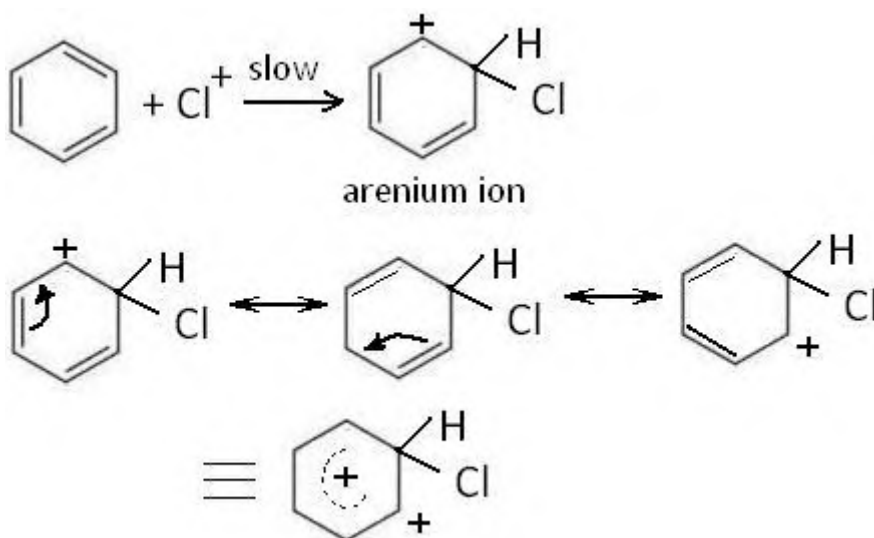
STEP I

Generation of electrophile i.e. halonium ion by action of Lewis acid on the halogen



STEP II

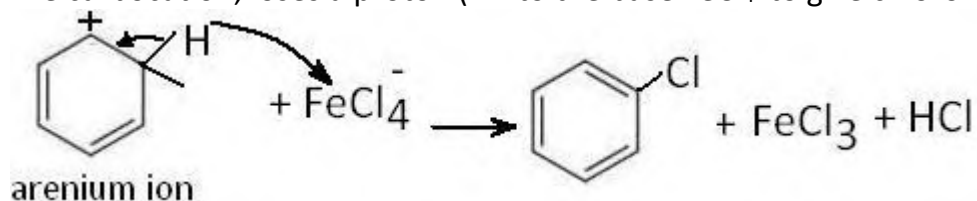
The electrophile attacks the benzene ring to form an intermediate known as σ - complex or a carbocation (arenium ion) which is stabilized by resonance.



The formation of intermediate arenium ion is slow and hence is the rate determining step of the reaction.

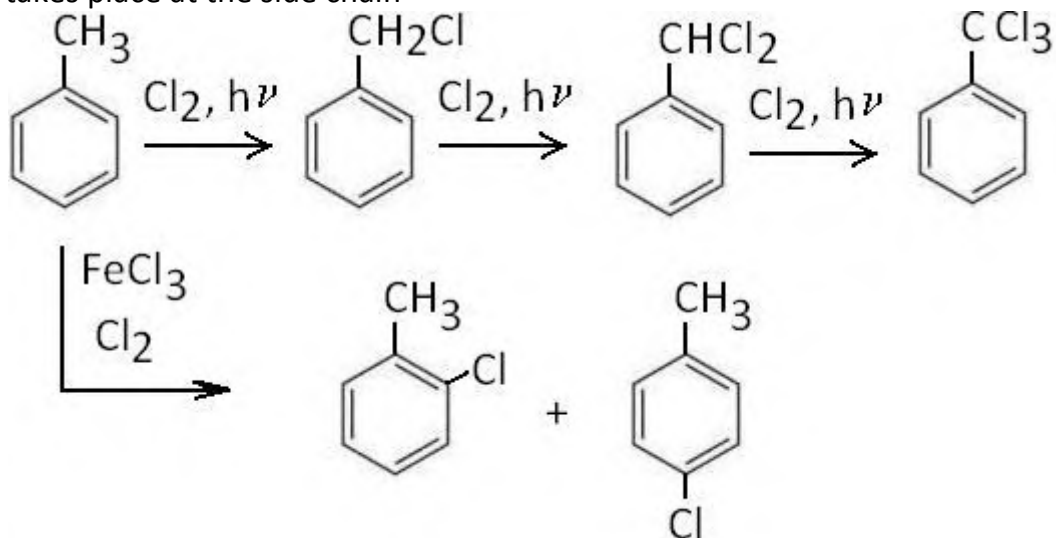
STEP III

The carbocation, loses a proton (H^+ to the base FeCl_4^- to give chloro-benzene)



2) Side chain halogenations

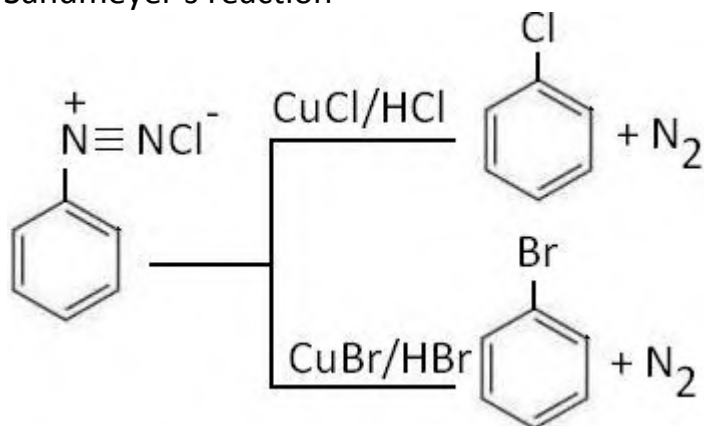
Halogenation in the presence of heat or sunlight and in absence of halogen carrier takes place at the side chain



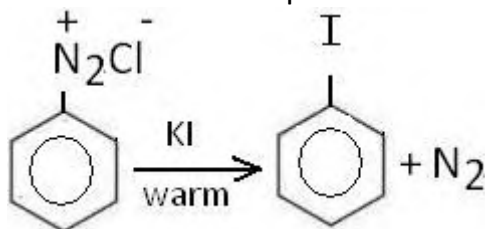
Side chain halogenations takes place by free radical mechanism.

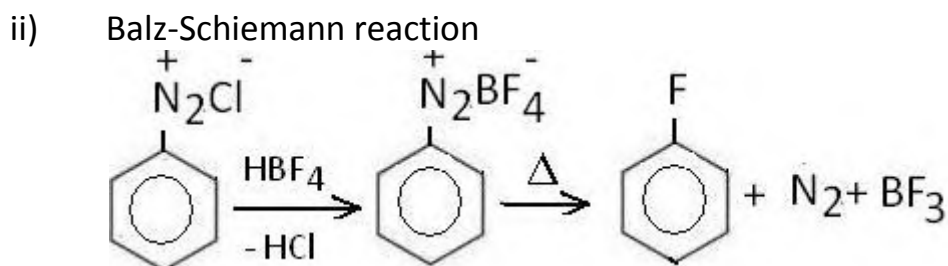
3) From diazonium salt

i) Sandmeyer's reaction

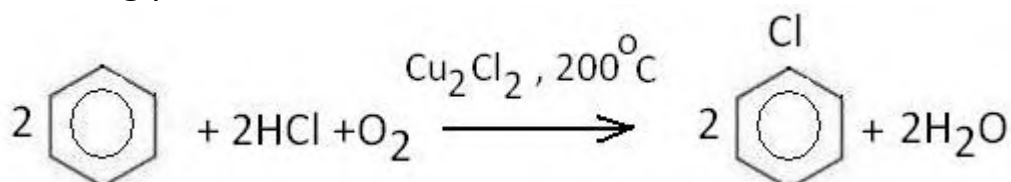


Replacement of the diazonium group by iodine is done simply by shaking the diazonium salt with potassium iodide.

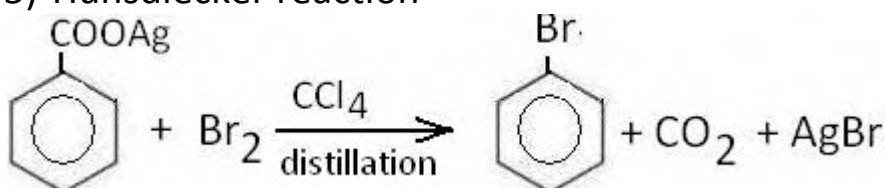




4) Rasching process



5) Hunsdiecker reaction



PHYSICAL PROPERTIES OF HALOARENES

1) Physical state and smell

Haloarenes are generally colourless liquids with pleasant odour or are crystalline solids with characteristic smell

2) Boiling point

i) The boiling point of monohalogen derivatives of benzene are in order Iodo > Bromo > Chloro > Fluoro

ii) Boiling and melting points increases as the size of the aryl group increases

iii) Melting point of the para isomers are always higher than that of ortho or meta isomers. This is due to the reason that para isomer is more symmetrical and hence its molecules pack closely in the crystal lattice. As a result intermolecular and therefore, greater energy lattice and it melts at higher temperature.

3) Solubility

Aryl halides are insoluble in water but readily miscible with organic solvents.

4) Density

Aryl halides are heavier than water. Their density follows the order Aryl iodide > aryl bromide > aryl chloride

5) Dipole moment

The dipole moment of haloarenes lies as follows

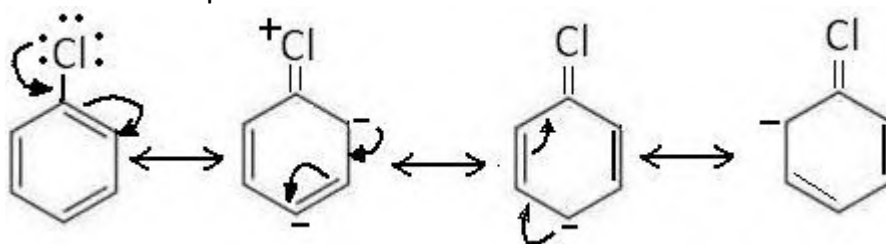
Fluorobenzene < Chlorobenzene < Bromobenzene \approx Iodobenzene

CHEMICAL PROPERTIES OF HALOARENES

1) Nucleophilic substitution

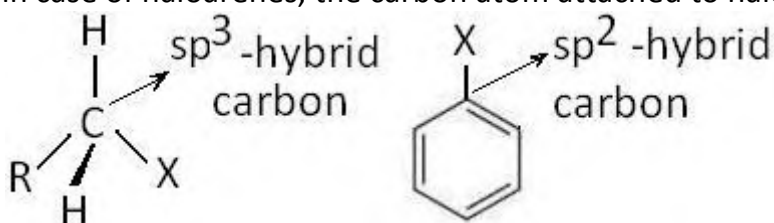
Aryl halides are extremely less reactive towards nucleophilic substitution reactions due to following reasons

- (i) Resonance effect : In haloarenes, the electron pairs of halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible



C-Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.

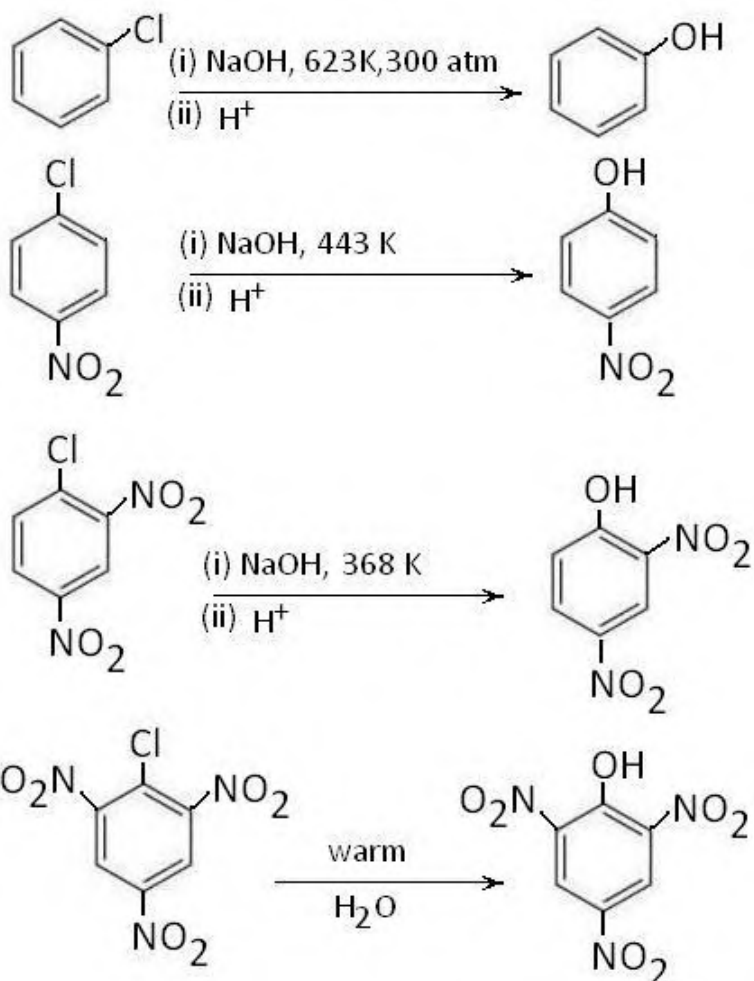
- (ii) Difference in hybridisation of carbon atom in C-X bond
In haloalkane, the carbon atom attached to halogen is sp^3 hybridized, where in case of haloarenes, the carbon atom attached to halogen is sp^2 hybridized



The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C-X bond more tightly than sp^3 -hybridised carbon in haloalkanes with less s-character. Thus C-Cl bond length in haloalkane is 177pm. While in haloarenes is 169pm. Since it is difficult to break a shorter bond than a longer bond, Therefore haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction

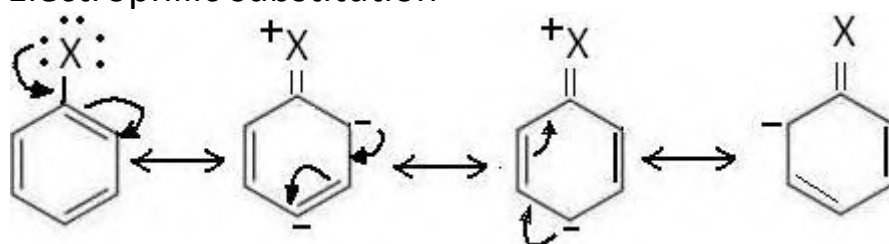
- (iii) Instability of phenyl cation
In case of haloarenes, the phenyl cation formed as a result of self ionization, will not be stabilized by resonance and therefore S_N1 mechanism is ruled out
- (iv) Because of the possible repulsion it is less likely for the electron rich nucleophile to approach electron rich arenes

2) Replacement by hydroxyl group



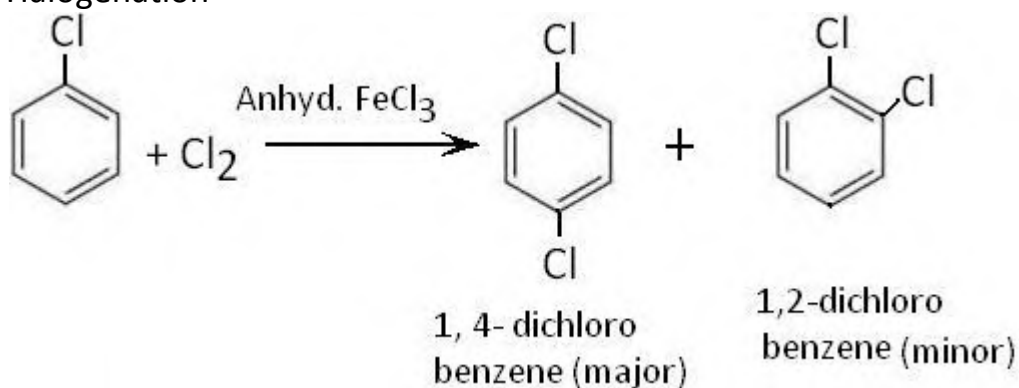
The presence of electron withdrawing group ($-\text{NO}_2$) at ortho and para positions increases the reactivity of haloarenes

3) Electrophilic substitution

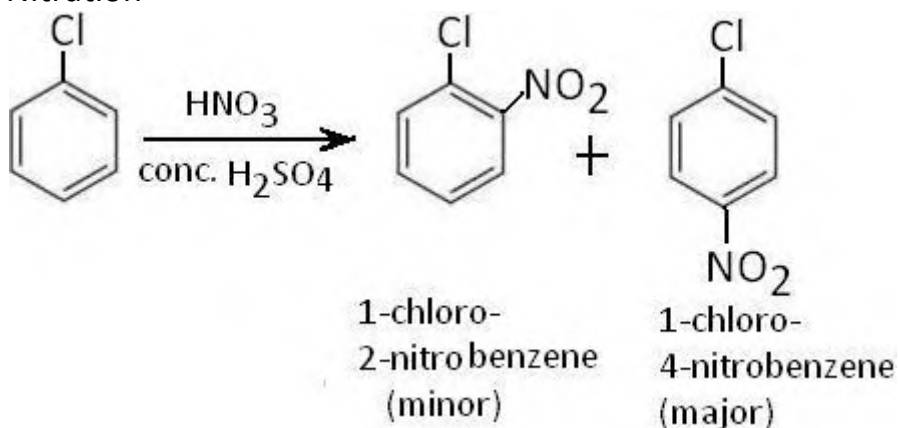


- Due to resonance, the electron density increases more at ortho and para-positions than at meta-positions and hence the electrophile is more likely to attack on these positions resulting in formation of o- and p- substituted products
- Halogen atoms because of their $-I$ effect have some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated and hence the electrophilic substitution reactions in haloarenes occur slowly

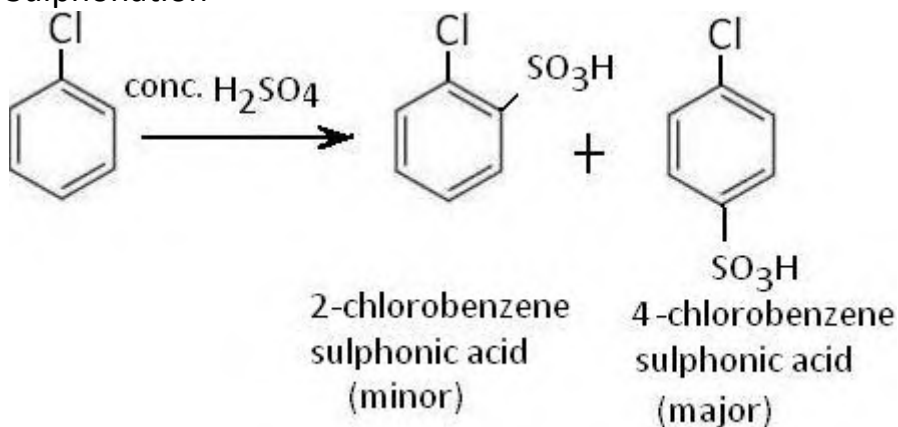
(i) Halogenation



(ii) Nitration

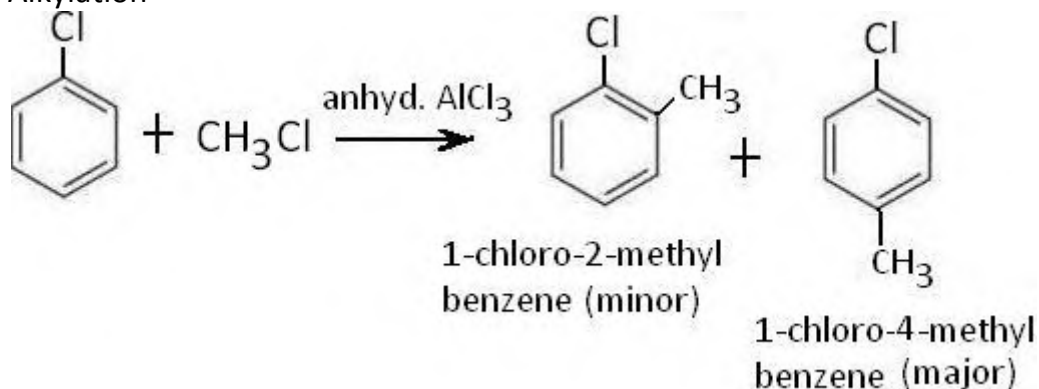


(iii) Sulphonation

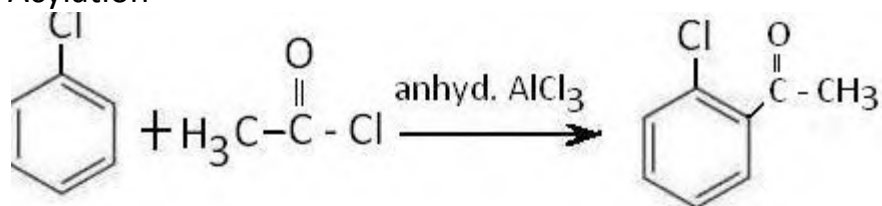


(iv) Friedel-Craft reaction

(a) Alkylation

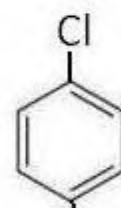


(b) Acylation



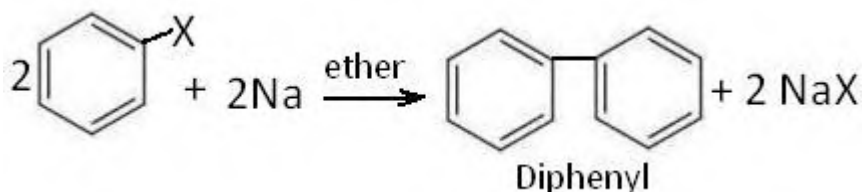
2-chloro
acetophenone
(minor)

+

O = C - CH₃

4-chloro
acetophenone
(major)

4) Fitting reaction



Diphenyl

POLYHALOGEN COMPOUNDS

1. Dichloromethane (CH₂Cl₂)

(A) Uses: It is used as

- (i) A solvent in drug industry
- (ii) Paint remover and propellant in aerosols
- (iii) A cleaning agent for metals

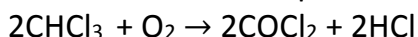
(B) Environmental impact

- (i) Its direct contact to our skin develops redness and burning sensation
- (ii) It is harmful to our central nervous system
- (iii) Its high level in air causes nausea, numbness in finger and toes

2. Trichloromethane CHCl₃ (Chloroform)

- Chloroform is a sweet smelling liquid boiling point 334K, non-inflammable but its vapour causes unconsciousness.

- When exposed to sunlight and air it slowly decomposes into phosgene (COCl_2), a poisonous gas. It is therefore stored in closed dark coloured bottle completely filled so that air is kept out



(A) Uses : It is used

- (i) As a solvent for fats, oils, varnishes, waxes, resins and rubber etc.
- (ii) For the preparation of chloretone (a drug) and chloropicrin (insecticide)
- (iii) As an anesthetic after being mixed with ether
- (iv) In the manufacture of Freon (refrigerant)

(B) Environmental impact

- (i) On inhalation, it depresses the central nervous system and causes headache and dizziness.
- (ii) Chronic exposure damages liver and kidneys.
- (iii) On exposure to sunlight and air it slowly decomposes into phosgene.
- (iv) Ethanol (1%) is added to retard the oxidation of phosgene into harmless ethyl carbonate.

(C) Tests of chloroform: It gives isocyanide test (Pungent smell). Pure CHCl_3 does not give white precipitate with AgNO_3 , but with Tollen's reagent, it gives grey precipitate of silver. On heating with Fehling's solution, it gives brown precipitate

3. Tri-iodomethane CHI_3 (Iodoform)

- It is a yellow crystalline solid pungent characteristic odour. Melting point is 392K and is steam volatile. It is used as a antiseptic for dressing wound

(A) Uses : It is used as

- (i) As an antiseptic for dressing of wound.
- (ii) In the manufacture of certain pharmaceuticals.

(B) Environmental impact

- (i) When it comes in contact with skin, iodine is liberated which is responsible for antiseptic properties.
- (ii) It has an objectionable smell.

4. Tetra chloromethane CCl_4 (carbon tetra chloride)

- It is a liquid, boiling point 350K, non-flammable, hence used as a solvent for fats, oils, waxes and resins etc. It is used as a fire extinguishers under the same name pyrene.

(A) Uses : It is used

- (i) As a fire extinguishers
- (ii) As a solvent and also dry-cleaning
- (iii) In medicine as helmenthicide for elimination of hook worm

(B) Environmental impact

- (i) Its vapours when breathed causes nausea, dizziness, vomiting and may cause damage nerve cells permanently
- (ii) On exposure it causes cancer, irregular heart beat and a person may go to coma.

- (iii) Its vapour depletes ozone layer. Ozone hole permits the ultraviolet radiation to reach on earth and may cause skin cancer, eye disease and disorder, it may adversely affect our immune system

5. Freons (CFC's)

* Freons are small organic molecules containing C, Cl and F. The most common freons are CF_2Cl (Freon -12) and CF_3Cl (Freon -11)

(A) Uses

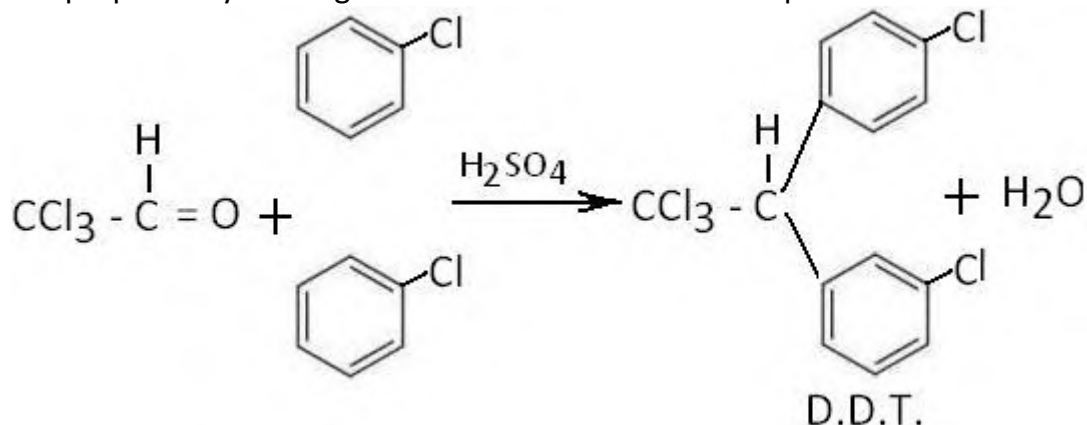
- (i) In air conditioning and domestic refrigerators for cooling purpose
- (ii) As propellents in aerosol and foams to spray out deodorants, cleaners and Insecticides. Halothane (CF_3CHBrCl) is used as inhalation anaesthetic.

(B) Environmental impact

Most Freon eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, Freon is able to initiate radical chain reaction that can upset the natural ozone layer surrounding earth.

6. p,p' – Dichlorodiphenyl trichloro ethane (DDT)

- It is prepared by heating chlorobenzene with chloral in presence of conc H_2SO_4



(A) Uses :

- (i) As an effective insecticide for mosquitoes, flies and crop pests.
- (ii) As an antimalarial.

(B) Environmental impact

It is non-biodegradable and its residue accumulates in environment, a cause of danger. It is not metabolized by the system and get deposited on the tissue, thus raises alarming danger. It is highly toxic to fish.