Haloalkanes and Haloarenes

10

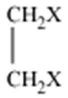
Classification and Nomenclature

Classification based on number of halogen atoms

* Monohalogen
* Dihalogen
* Polyhalogen (tri-, tetra-, penta- etc.)
* Examples of haloalkanes:

CH_3X

Monohaloalkane



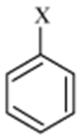
CH_2X-CH_2X

Dihaloalkane

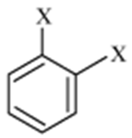
$CH_2X-CHX-CH_2X$

Trihaloalkane

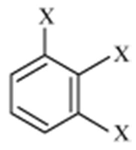
* Examples of haloarenes:



Monohaloarene



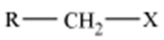
Dihaloarene



Trihaloarene

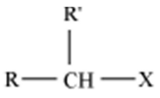
* Based on the hybridisation of C− atom of C− X bond of **monohalocompounds**
* Compounds containing sp^3 C− X bond (X = F, Cl, Br, I)

(i) Alkyl halides or haloalkanes (R− X) →They form homologous series of general formula $C_nH_{2n+1}X$. They are further classified into primary, secondary, and tertiary.



$R-CH_2-X$

Primary (1°)



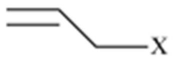
$R-CH(R')-X$

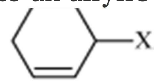
Secondary (2°)

$R-C(R')(R'')-X$

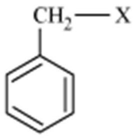
Tertiary (3°)

(ii) Allylic halides →Compounds containing halogen atom bonded to an allylic carbon

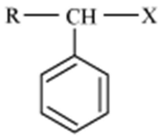




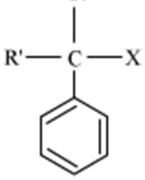
(iii) Benzylic halides →Compounds containing halogen atom bonded to an sp^3 hybridised carbon atom next to an aromatic ring



Primary (1°)



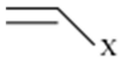
Secondary (2°)

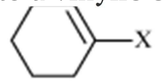


Tertiary (3°)

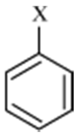
* Compounds containing sp^2 C− X bond (X = F, Cl, Br, I)

(i) Vinylic halides →Compounds containing halogen atom bonded to a vinylic carbon





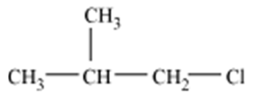
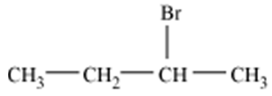
(ii) Aryl halides →Compounds containing halogen atom bonded to an sp^2 hybridised carbon atom of an aromatic ring



Nomenclature

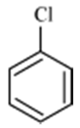
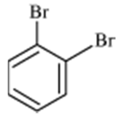
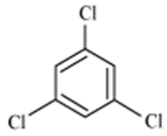
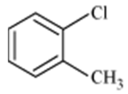
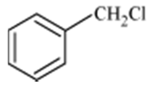
- For haloalkanes
- Common name →Name of alkyl group followed by name of the halide
- IUPAC name →Named as halo-substituted hydrocarbon in IUPAC

Examples:

Structure	Common Name	IUPAC Name
$CH_3CH_2CH_2CH_2Br$	*n*− Butyl bromide	1-Bromo butane
 $CH_3-CH(CH_3)-CH_2-Cl$	Isobutyl chloride	1-Chloro-2-methyl-propane
 $CH_3-CH_2-CH(Br)-CH_3$	*sec*-butyl bromide	2-Bromo butane
$CH_3CH_2CH(Cl)CH_3$	*sec*-Butyl chloride	2-Chloro butane
$(CH_3)_3CCH_2Br$	*neo*-entyl bromide	1-Bromo-2,2-dimethylpropane
$(CH_3)_3CBr$	*tert*-Butyl bromide	2-Bromo-2-methylpropane
CH_2Cl_2	Methylene chloride	Dichloromethane

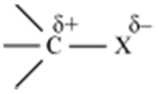
- For haloarenes
- Named as halo-substituted hydrocarbon (for both common and IUPAC name)
- For dihalogen derivatives:
  In common names →prefixes *o*-, *m*-, *p*- are used
  In IUPAC names →numerals 1, 2; 1, 3; 1, 4 are used

Examples:

Structure	Common name	IUPAC name
	Chlorobenzene	Chlorobenzene
	*o*-Dibromobenzene	1,2-Dibromobenzene
	*sym*-Trichloro benzene	1,3,5-Trichlorobenzene
	*o*-Chlorotoluene	1-Chloro-2-methylbenzene or 2-Chlorotoluene
	Benzyl chloride	Chlorophenylmethane

Nature of C− X bond

- C-atom bears partial positive charge and X-atom bears partial negative charge.



- C− X bond length increases down the group.
- Reason − Size of halogen atom increases down the group.

Methods of Preparation

From Alcohols

- $3R-OH + PX_3 \longrightarrow 3R-X + H_3PO_3$ (X = Cl, Br)
- $R-OH + PCl_5 \longrightarrow R-Cl + POCl_3 + HCl$
- $R-OH \xrightarrow[X_2=Br_2,I_2]{\text{red P/X}_2} R-X$
- $R-OH + SOCl_2 \longrightarrow R-Cl + SO_2 + HCl$

- $R - OH + NaCl + H_2SO_4 \longrightarrow R - Cl + NaHSO_4 + H_2O$
- $R - OH + HX \xrightarrow{ZnCl_2} R - X + H_2O$
- For this reaction, the increasing order of reactivity of alcohols is 1° < 2° < 3°
- This reaction cannot be applied to produce aryl halides.
- Reason – It is difficult to break carbon-oxygen bond in phenols as it possesses a partial double bond character.

From Hydrocarbons

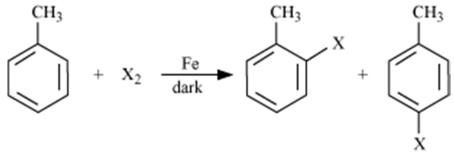
Free radical halogenation

- Gives a complex mixture of isomeric mono- and poly- haloalkanes This method is not of much practical use as it is difficult to separate the complex mixture.
- When only mono-substitution is carried out

$$CH_3CH_2CH_2CH_3 \xrightarrow[\text{or heat}]{X_2/\text{UV light}} CH_3CH_2CH_2CH_2X + CH_3CH_2CHXCH_3$$

$(X = Cl, Br)$

Electrophilic Substitution

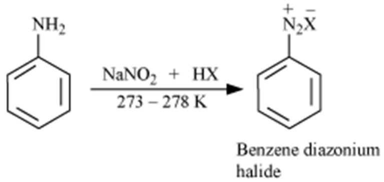


$(X = Cl, Br)$

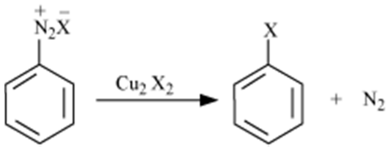
- However, iodination is a reversible reaction. Oxidising agent such as HNO_3 or HIO_4 is required to oxidise HI formed during the reaction.

Sandmeyer's Reaction

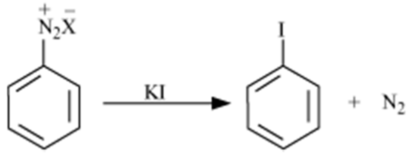
- Applicable to primary aromatic amine



For Cl and Br:

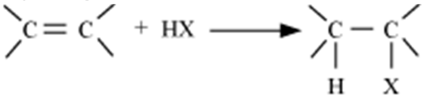


For I:



From Alkenes

- By adding hydrogen halides



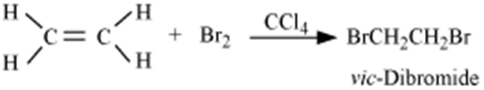
$(X = Cl, Br, I)$

$$CH_3CH = CH_2 + HI \longrightarrow CH_3CH_2CH_2I + CH_3CHICH_3$$

(Minor) (Major)

(According to Markovnikov's rule)

- By adding halogens



This method is used to detect double bond in a molecule as reddish brown colour of bromine is discharged during the reaction.

Halogen Exchange

Finkelstein Reaction

$$R - X + NaI \longrightarrow R - I + NaX$$

$(X = Cl, Br)$

- This reaction in forward direction can be favoured by precipitating NaX formed in dry acetone (according to Le Chatelier's principle).

Swarts Reaction

- Preparation of alkyl fluoride
- Requires metallic fluoride such as AgF, Hg_2F_2, CoF_2, or SbF_3

$$H_3C-X + AgF \longrightarrow H_3C - F + AgX$$

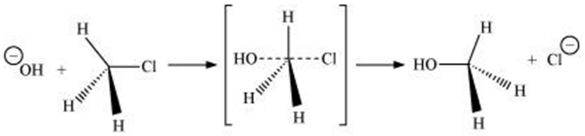
$(X = Cl, Br)$

Solved Examples

Ex.1 Which compound in each of the following pairs will react faster in S_N2 reaction with ^-OH? Why?

(i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

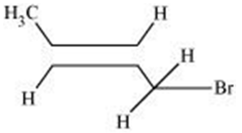
Sol. The S_N2 mechanism proceeds in the given manner.



(i) Due to the larger size of the iodide group, it is a better leaving-group than the chloride group. Hence, among CH_3Br and CH_3I, CH_3I will react faster.

(ii) Among $(CH_3)_3CCl$ and CH_3Cl, CH_3Cl will react faster. The rate of S_N2 decreases by stearic hindrance. The presence of bulky groups in $(CH_3)_3CCl$ has an inhibiting effect on the reaction.

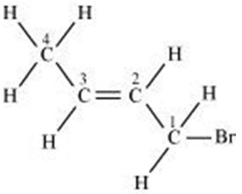
Ex.2 (a) State the IUPAC name of the following compound:



(b) Complete the following chemical equation:

$CH_3CH_2CH=CH_2 + HBr \xrightarrow{\text{peroxide}}$ ......

Sol. (a)

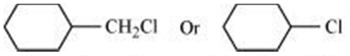


1-Bromo-but-2-ene

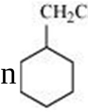
(b)

$$\underset{\text{1-Butene}}{CH_3CH_2CH=CH_2} + HBr \xrightarrow[\text{Anti-Markovnikov addition}]{\text{Peroxide}} \underset{\text{1-Bromobutane}}{CH_3CH_2CH_2CH_2Br}$$

Ex.3 Which ones in the following pairs of substances undergoes S_N2 substitution reaction faster and why?

(i) 

(ii)  or 

Sol. (i)  undergoes S_N2 substitution reaction faster than . This is because the alkyl group present in benzyl chloride increases its basicity due to +I effect. Stronger the base, lesser is its leaving ability. So,  reacts faster.

(ii) Iodide is a weaker base than chloride. Weaker the base, greater is its leaving ability. So,  undergoes S_N2 substitution reaction faster.

Physical Properties

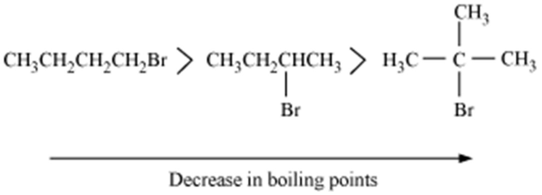
- * Pure alkylhalides are colourless. However, in the presence of light, bromides and iodides become coloured.
- * Some halides are sweet in smell.

Melting and Boiling Points

- * Chlorides, bromides, and iodides have higher boiling points than hydrocarbons of comparable molecular mass.
- * Reason − Chlorides, bromides, and iodides are polar in nature whereas hydrocarbons are non-polar. Therefore, these halides have greater intermolecular forces of attraction (dipole − dipole) than their parent hydrocarbons and hence, have higher boiling points.

$$\xrightarrow[\text{Increase in boiling points}]{RF < RCl < RBr < RI}$$

- * Reason − Vander Waals forces increase with increase in size and mass of halogen atoms and hence, boiling point also increases.
- * Boiling points of isomeric haloalkanes decrease with increase in branching.
- * For example,



$$CH_3CH_2CH_2CH_2Br > \underset{\displaystyle Br}{CH_3CH_2CHCH_3} > H_3C-\overset{\displaystyle CH_3}{\underset{\displaystyle Br}{C}}-CH_3$$

Decrease in boiling points

- * The boiling points of isomeric dihalobenzenes are nearly the same.

- However, the melting point of para-isomer is higher than those of ortho- and meta-isomers.
- Reason – Better fit of para-isomer in crystal lattice due to its symmetry
- Lower members (such as CH_3Cl, CH_3Br, C_2H_5Cl) are gases whereas higher members are liquids or solids at room temperature.

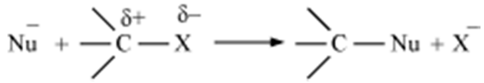
Density

- increases with the number of carbon atoms
- increase in number of halogen atoms
- atomic mass of the halogen atoms
- Very slightly soluble in water, but soluble in organic solvents

  Reason – The energy required to overcome the intermolecular attraction between the haloalkane molecules is greater than the energy released during dissolution in water.

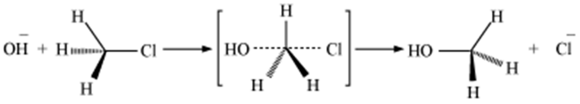
Reactions of Haloalkanes

Nucleophilic Substitution Reactions



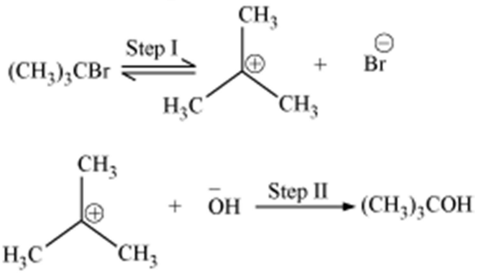
Mechanism

- **Substitution nucleophilic bimolecular (S_N2)**

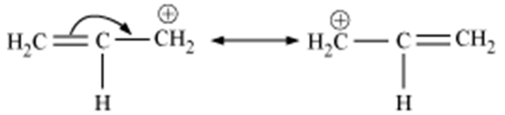


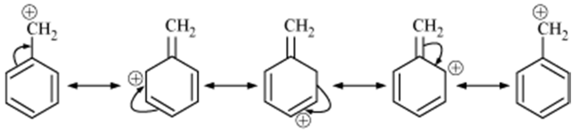
- Inversion of configuration takes place.
- The increasing order of reactivity is 3° halide < 2° halide < 1° halide
- Reason – Due to the presence of bulky substituents in 3° and 2° halides, nucleophile cannot approach.

Substitution nucleophilic unimolecular (S_N1)



- Carried out in polar protic solvents such as water, alcohol, acetic acid, etc.
- The increasing order of reactivity is 1° halide < 2° halide < 3° halide
- Reason – Greater the stability of carbocation, more easily the alkyl halide is formed and hence, faster is the reaction rate. The increasing order of stability of carbocation is 1° < 2° < 3°. Since 1° halide forms 1° carbocation, 2° halide forms 2° carbocation, and 3° halide forms 3° carbocation. Therefore, the increasing order of reactivity is 1° halide < 2° halide < 3° halide.
- Allylic and benzylic halides are very reactive towards S_N1 reaction because of stabilisation of their carbocations through resonance.





- For both S_N1 and S_N2 reaction, the order of reactivity of halides is R–F << R–Cl < R–Br < R–I

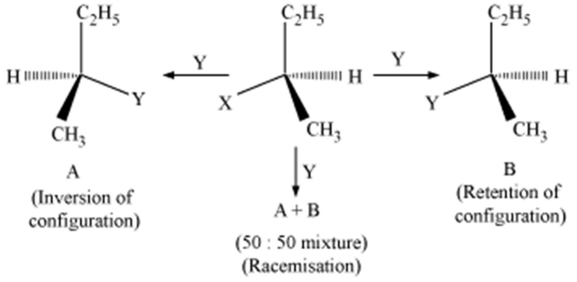
Stereochemical Aspects of Nucleophilic Substitution

- In S_N2 reaction, complete stereochemical inversion takes place.
- In S_N1 reaction, racemisation takes place.

Some Stereochemical Terms:

- Compounds that rotate the plane polarised light are called optically active compounds.
- Angle of rotation of plane polarised light is measured by an instrument called polarimeter.
- Dextrorotatory or *d*-form – Compounds that rotate plane polarised light to right
- Laevorotatory or *l*-form – Compounds that rotate plane polarised light to left

- *d*- and *l*- forms of a compound are called optical isomers and the phenomenon is called optical isomerism.
- Asymmetric carbon or stereocentre – Carbon atom with all the four substituents attached to it are different.
- The objects which are non-superimposable on their mirror images are known as chiral and the property is known as chirality.
- The objects which are superimposable on their mirror images are known as achiral.
- Enantiomers are stereoisomers which are non-superimposable mirror images.
- There are three outcomes for a reaction at an asymmetric carbon atom.
- Inversion
- Retention
- Racemisation



Solved Examples

Ex. 4 What are enantiomers and diastereomers? Differentiate between chiral and achiral molecules.

Sol. Enantiomers are mirror images that cannot be superimposed on one another. Diastereomers are stereoisomers that are not mirror images of each other.

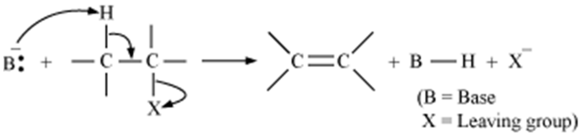
Chiral molecules are the molecules which cannot be superimposed upon their mirror images. On the other hand, achiral molecules are the molecules which can be superimposed upon their mirror images.

Ex.5 A solution of KOH hydrolyses $CH_3CHClCH_2CH_3$ and $CH_3CH_2CH_2Cl$. Which one of these is more easily hydrolysed?

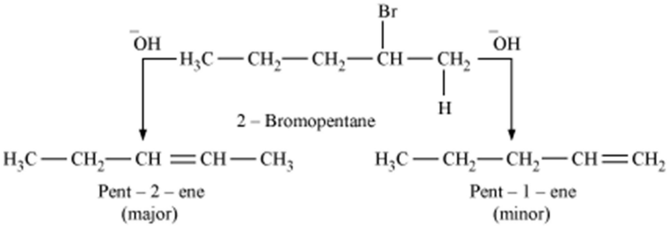
Sol. $CH_3CHClCH_2CH_3$ will undergo hydrolysis reaction with KOH more easily.

Elimination Reactions

- On heating a haloalkane containing □-hydrogen atom with alcoholic KOH solution, elimination of H from □ carbon and a halogen from □ takes place.



- Also called □-elimination as □-hydrogen is eliminated
- In case of more than one product:
- Saytzeff's rule – In dehydrohalogenation reactions, the alkene with the greater number of alkyl groups attached to the doubly bonded carbon atoms is preferably formed.



Reaction with Metals

- Chlorides, bromides, and iodides react with certain metals to form organo-metallic compounds such as Grignard reagents.

$$CH_3CH_2Br + Mg \xrightarrow{\text{dry ether}} CH_3CH_2MgBr$$

- Grignard reagent
- Wurtz Reaction

$$2RX + 2Na \xrightarrow{\text{dry ether}} R-R + 2NaX$$

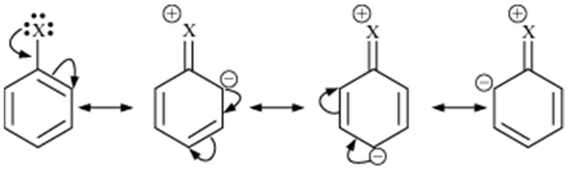
- Hydrocarbon containing double the number of carbon atoms present in the halide is formed.

Reactions of Haloarenes

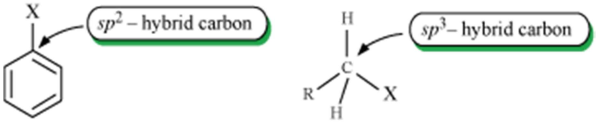
The aryl and vinyl halides are much less reactive than the alkyl halides.

Nucleophilic Substitution Reactions

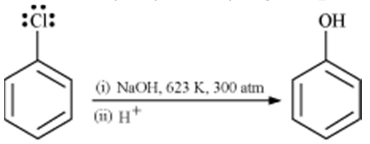
- Haloarenes are much less reactive towards nucleophilic substitution reactions due to the following reasons:
- In haloarenes, the benzene ring undergoes resonance and as a result, the C− X bond acquires a partial double bond character. Therefore, it becomes difficult to break the C− X bond.



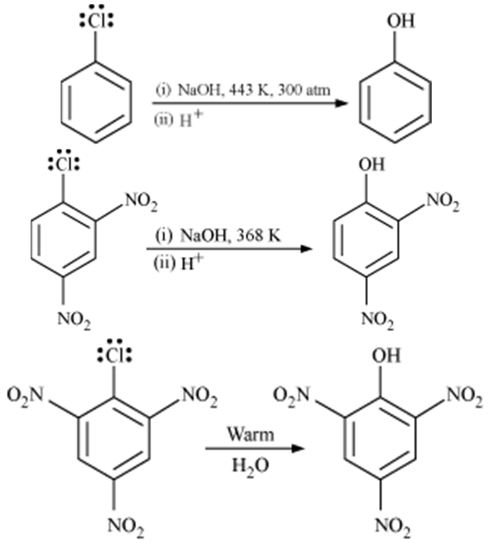
- In haloalkanes, the halogen atom is attached to an sp^3 hybridised carbon atom while in haloarenes, it is attached to an sp^2 hybridised carbon atom. Since an sp^2 hybridised carbon has more *s*-character than sp^3 hybridised carbon, the former is more electronegative than the latter. As a result, the electron pair of C− X bond is held by carbon atom more tightly in haloarenes than haloalkanes. Therefore, the C− X bond becomes shorter in haloarenes and hence, becomes stronger.



- The phenyl cation formed by the self ionisation is unstable and hence, S_N1 mechanism is avoided.
- Electron-rich nucleophile cannot approach electron-rich arenes due to repulsion.
- Replacement by hydroxyl group

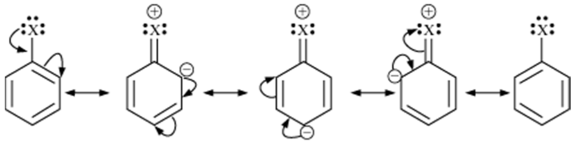


- Reactivity increases if an electron withdrawing group (−NO_2) is present at ortho- and para- positions. This can be observed as the temperature required carrying out the reaction decreases in the presence of −NO_2 group at *o*-and *p*-positions.

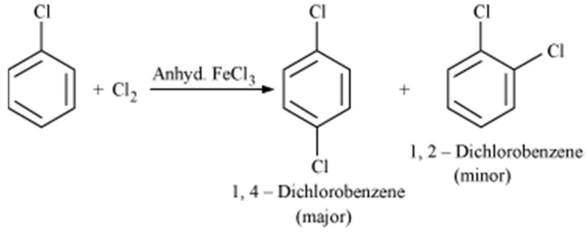


Electrophilic Substitution Reactions

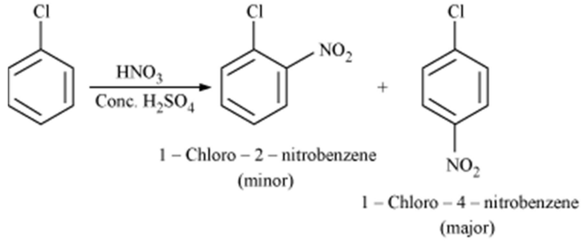
- Substitution occurs at *o*- and *p*-direction due to availability of electrons at these positions because of resonance.



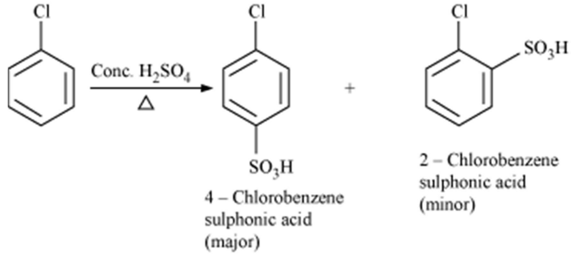
- Halogenation



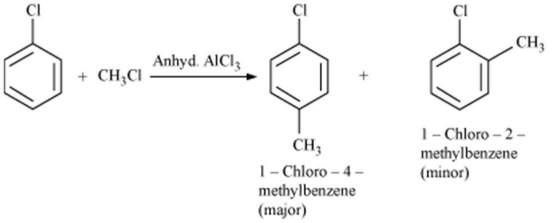
- Nitration



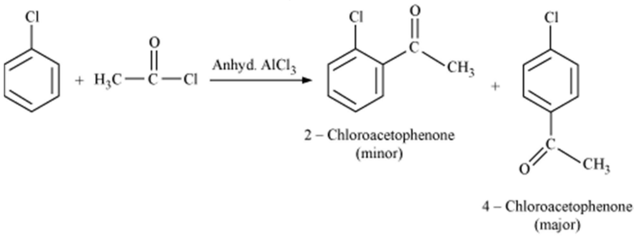
- Sulphonation



* Friedel− Crafts Alkylation

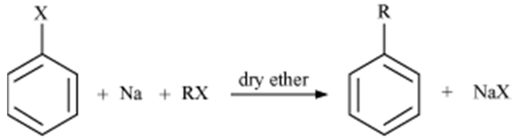


* Friedel-Crafts Acylation

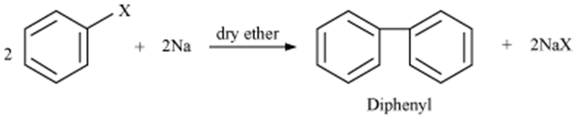


Reaction with Metals

* Wurtz− Fittig Reaction



* Fittig reaction

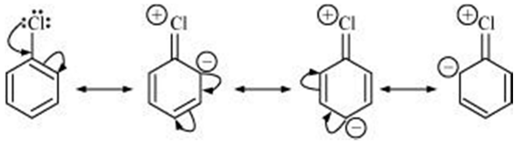


Solved Examples

Ex.6 Explain as to why haloarenes are much less reactive than haloalkanes towards nucleophilic substitution reactions.

Sol. Haloarenes are less reactive towards nucleophilic substitution reactions than haloalkanes because of the following reasons.

(i) Haloarenes are stabilised by resonance as shown.



Thus, C− Cl bond gains a partial double-bond character and the compound becomes more stable. As a result of the partial double-bond character, the breaking of the bond becomes difficult and the reactivity of haloarenes towards nucleophilic substitution reactions decreases.

(ii) The carbon atom in haloarenes is sp^2 hybridised, while in haloalkanes, it is sp^3 hybridised. The sp^2 hybridised carbon has a greater *s*-character and is more electronegative than the sp^3 hybridised carbon. Therefore, in haloarenes, C− X bond is shorter and stronger (C− Cl bond length in haloalkanes is 177 pm, while that in haloarenes is 169 pm). Therefore, haloarenes are less reactive towards nucleophilic substitution reactions than haloalkanes.

(iii) The phenyl cation formed by the loss of the halogen atom is not resonance stabilised. Therefore, it is not very stable. Thus, substitution cannot proceed via the S_N1 mechanism.

(iv) A nucleophile is an electron-rich species and so is the benzene ring. Therefore, there is little repulsion between the nucleophile and the arene, making the reaction between the two difficult.

Polyhalogen Compounds

* Polyhalogen compounds are carbon compounds containing more than one halogen atom.

Dichloromethane or Methylene Chloride (CH_2Cl_2)

Uses

* As propellant in aerosols

* As metal finishing and cleaning solvent

* As a process solvent in the manufacture of drugs

Toxicity

* Harms the human central nervous system

* Lower levels of CH_2Cl_2 in air can lead to slightly impaired hearing and vision.

- Higher levels of CH_2Cl_2 in air can cause dizziness, nausea, tingling and numbness in the fingers and toes.
- Direct skin contact causes intense burning and mild redness of the skin.

Trichloromethane or Chloroform ($CHCl_3$)

Uses

- As a solvent for fats, alkaloids, iodine, and other substances
- In the production of the freon refrigerant R-22
- Earlier used as anaesthetic, but has been replaced due its toxicity

Toxicity

- Inhaling of $CHCl_3$ vapours can cause depression of the central nervous system, dizziness, fatigue, and headache.
- Chronic chloroform exposure may lead to damage of the liver and kidneys.
- Immersion of skin in $CHCl_3$ leads to development of sores.
- $CHCl_3$ is oxidised to an extremely poisonous gas phosgene ($COCl_2$) in the presence of light.

$$2CHCl_3 + O_2 \xrightarrow{\text{Light}} 2COCl_2 + 2HCl$$

- That is why chloroform is stored in closed dark-coloured bottles completely filled so that no air is left inside the bottles.

Triiodomethane or Iodoform (CHI_3)

Uses

- Earlier used as an antiseptic, but has been replaced due to its objectionable smell
- Its antiseptic properties are not due to iodoform itself, but due to the liberation of free iodine.

Trichloromethane or Carbon Tetrachloride (CCl_4)

Uses

- In the manufacture of refrigerants and aerosol propellants
- As feedstock in the synthesis of chlorofluorocarbons
- In pharmaceutical manufacturing
- As industrial solvent
- As cleaning fluid
- As fire extinguisher

Toxicity

- Causes lives cancer, dizziness, light headedness, nausea, vomiting these effects may lead to stupor, coma, unconsciousness, or death.
- Leads to irregularity in heart beat or even stop
- Causes irritation of eyes on contact
- Causes depletion of ozone layer, leading to increase in skin cancer, eye diseases

Freons

- Chlorofluorocarbon compounds of methane and ethane are collectively called freons.
- Physical properties:
- Stable and unreactive
- Non-toxic and non-corrosive
- Easily liquefiable gas

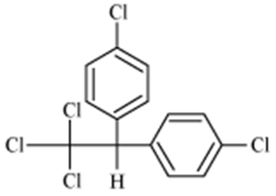
Uses

- In aerosol propellants, refrigeration, and air conditioning purposes

Toxicity

- Upsets the natural ozone balance
- Freon 12 (CCl_2F_2) is one of the most common freons that have industrial use.

p,p′ -Dichlorodiphenyltrichloroethane (DDT)



DDT

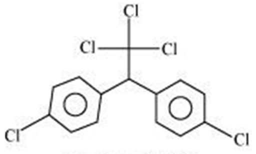
First Chlorinated Organic Insecticide

- Effective against mosquitoes that spread malaria and lice that carry typhus
- **Toxicity**
- DDT is highly stable and is not metabolised very rapidly by animals. Rather it is deposited and stored in the fatty tissues. It is proved to be toxic to living beings. It is banned in many countries due to its toxicity.

Solved Examples

Ex.7 Expand DDT. Write its structure.

Sol. DDT is dichlorodiphenyltrichloroethane.



Structure of DDT

Ex.8(i) State one use each of DDT and iodoform.

(ii) Which compound in the following couples will react faster in S_N2 displacement and why?

(a) 1-Bromopentane or 2-bromopentane

(b) 1-bromo-2-methylbutane or 2-bromo-2-methylbutane.

Sol. (i) Use of DDT:

DDT is widely used as an insecticide.

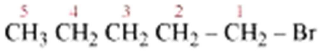
Use of iodoform:

Iodoform is used as an antiseptic.

(ii)

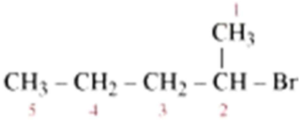
(a) 1-bromopentane will undergo S_N2 displacement reaction faster than 2-bromopentane.

Generally 1° alkyl halides react by S_N2 mechanisms, 2° alkyl halides by both S_N1 and S_N2 reactions and 3° alkyl halides by S_N2 reactions.



$$\overset{5}{CH_3}\ \overset{4}{CH_2}\ \overset{3}{CH_2}\ \overset{2}{CH_2} - \overset{1}{CH_2} - Br$$

1-bromopentane



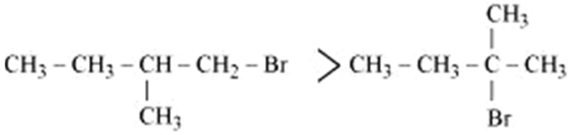
$$\underset{5}{CH_3} - \underset{4}{CH_2} - \underset{3}{CH_2} - \underset{2}{\overset{\overset{1}{CH_3}}{CH}} - Br$$

2-bromopentane

This is due to the fact that the electron density on α-carbon atom goes on increasing by inductive effect of the alkyl groups. This increased electron density on the α-carbon atom repels the direct attack of the nucleophile and thus retards S_N2 reaction. Moreover, the transition state of S_N2 reactions become over crowded as the size of the alkyl group increases. This also slows down the S_N2 reaction.

(b) 1-bromo-2-methylbutane will undergo S_N2 reaction faster than 2-bromo-2-methylbutane

Thus, the order of S_N2 reaction is



$$CH_3 - CH_3 - \underset{CH_3}{CH} - CH_2 - Br > CH_3 - CH_3 - \underset{Br}{\overset{CH_3}{C}} - CH_3$$

1- bromo-2-methyl butane proceeds by forming 1° carbocation while 2-bromo-2 methylbutane proceeds by forming 3° carbocation. The electron density on the α-carbon atom of the latter compound is more due to presence of more alkyl groups. This increased electron density on the α-carbon atom repels the direct attack of the nucleophile and thus retards S_N2 reaction. It rather proceeds by S_N1 reaction.