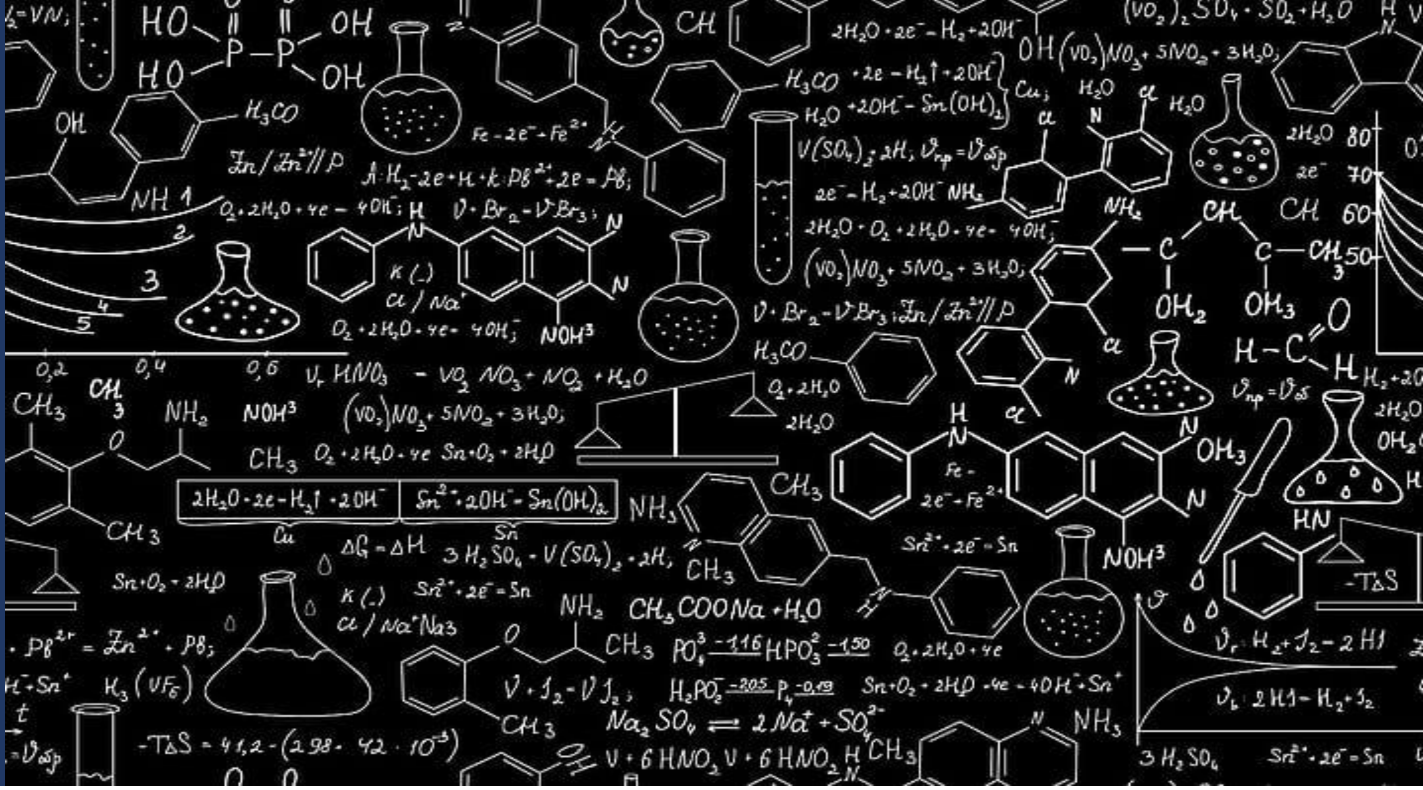
HALOALKANES AND HALOARENES



CHAPTER – 10

HALOALKANES AND HALOARENES

Aliphatic hydrocarbons $\xleftrightarrow{H\text{-}X}$ **Alkyl halides**
[haloalkanes]

Aromatic hydrocarbons $\xrightarrow{\text{Replacement of hydrogen by halogen}}$ **aryl**
halide [haloarene]

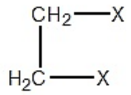
Example

$CH_4 \xrightarrow{H-Cl} CH_3Cl$ methyl chloride

Haloalkanes: Haloalkanes are compounds that contain a halogen atom attached to the sp^3 hybridized carbon atom of the alkyl group.

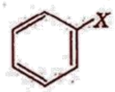
C_2H_5X

Monohaloalkane

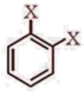


Dihaloalkane

Haloarenes: Haloarenes are compounds that contain a halogen atom attached to the sp^2 hybridized carbon atom of the aryl group.



monohaloarene



Dihaloarene

Trihaloarene

Classification of the basis of number of atoms

If one halogen atom is present in structure of alkanes/arenes: Monohaloalkanes

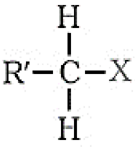
If two halogen atoms are present: dihaloalkanes

Similalrly if three halogen atoms are present: trihalalkanes/Trihaloarenes

Classification of halo alkanes and halo arenes on the basis of compounds containing sp^{3}C—X Bond

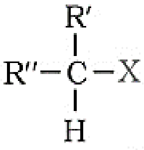
(a) **Alkyl halides or halo alkanes (R—X)**

They create a homologous series represented by $C_nH_{2n+1}X$ and can be further classified as primary, secondary or tertiary.



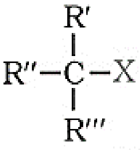
$R'-\overset{H}{\underset{H}{C}}-X$

Primary (1°)



$R''-\overset{R'}{\underset{H}{C}}-X$

Secondary (2°)

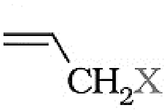


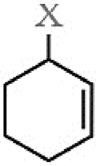
$R''-\overset{R'}{\underset{R'''}{C}}-X$

Tertiary (3°)

(b) **Allylic halides**

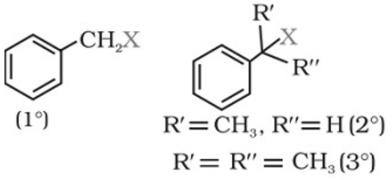
The compounds with halogen atoms bonded to sp^3-hybridised carbon to carbon-carbon double bond (C=C) i.e. to an allylic carbon.





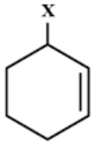
(c) Benzylic halides

The halogen atom of these compounds is bonded to sp^3-hybridised carbon atom placed next to an aromatic ring.

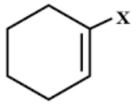


Compounds containing sp2 C-X bond

Vinylic halide: X is bonded to carbon-carbon double bond

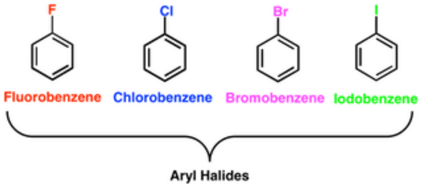


allylic halide



Vinylic halide
Halide attached to sp^2 carbon is the vinylic halide

Aryl halide: halogen atom is bonded to the carbon of aromatic ring.



Nomenclature

There are two names associated with every compound:

Common name – It is different from a trivial name in the sense that it also follows a rule for its nomenclature.

IUPAC name – The IUPAC (International Union of Pure and Applied Chemistry) naming system is the standard naming system that is generally used by chemists.

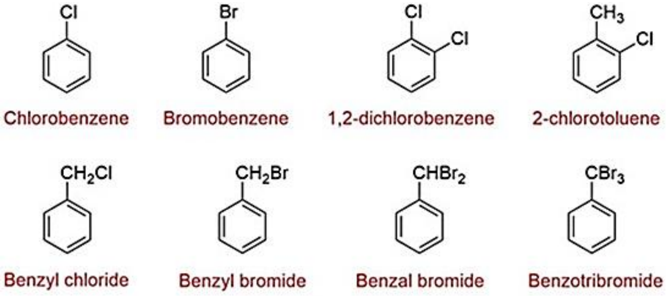
Nomenclature of Haloalkanes

- Select the longest chain of carbon atoms containing the halogen atom.
- Number the chain to give the minimum number to the carbon-carrying halogen atom.
- If multiple bonds (double or triple bonds) are present, then it is given the preference in numbering the carbon chain.
- The IUPAC name of any halogen derivative is always written as one word.

Compound	Common Name	IUPAC Name
CH_3-Cl	Methyl Chloride	Chloromethane
CH_3-CH_2-Br	Ethyl bromide	Bromoethane
CH_3-$C(CH_3)_2$-Br	tert-Butyl bromide	2-Bromo-2-methylpropane
$CHCl_3$	Chloroform	Trichloromethane
CH_3-$CH(Br)_2$	Ethylidene bromide	1,1-Dibromoethane
CH_2=CH-CH_2-I	Allyl iodide	3-Iodoprop-1-ene

Nomenclature of Haloarenes

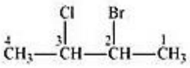
- Aryl halides are named by prefixing "halo" to the name of the parent aromatic hydrocarbon.
- If there is more than one substituent on the ring then the relative positions of the substituents are indicated by mathematical numerals.
- In the common system, the relative position of two groups is shown by prefixes ortho, meta or para.
- The common and IUPAC names of some representative haloarenes are given below.



Q. **Give the IUPAC names of the following compounds:**

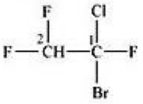
Sol.
(i) $CH_3CH(Cl)CH(Br)CH_3$
(ii) $CHF_2CBrClF$
(iii) $ClCH_2C\equiv CCH_2Br$
(iv) $(CCl_3)_3CCl$
(v) $CH_3C(p\text{-}ClC_6H_4)_2CH(Br)CH_3$
(vi) $(CH_3)_3CCH=CClC_6H_4I\text{-}p$

(i)



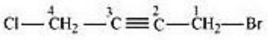
2-Bromo-3-chlorobutane

(ii)



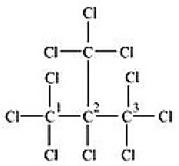
1-Bromo-1-chloro-1, 2, 2-trifluoroethane

(iii)



1-Bromo-4-chlorobut-2-yne

(iv)



2-(Trichloromethyl)-1,1,1,2,3,3,3-heptachloropropane

Nature of C-X bond in alkyl halides –

Haloarenes are the chemical compounds containing arenes, where one or more hydrogen atoms bonded to an aromatic ring are replaced with halogens. The nature of the C-X bond depends on both the nature of carbon in the aromatic ring and the halogen attached. Halogens are generally denoted by “X”.

As we know halogens are group 17 elements having high electronegativity namely, fluorine (F), chlorine (Cl), bromine (Br), iodine (I) and astatine (At). Out of them, fluorine has the highest electronegativity. The elements in this group are just one electron short of completing their nearest noble gas configuration.

Carbon in haloarenes is a 14th group element with comparatively lesser electronegativity in comparison to halogen molecules. This is due to the fact that electronegativity increases across a period from left to right.

Salient Points on the Nature of C-X Bond in Haloarenes

The C-X bond in haloarenes is polarized, as halogens are more electronegative than carbon. Due to the high electronegativity of halogen, it attracts the electron cloud more towards itself and thus gains a slight negative charge, on the other hand, carbon obtains a slight positive charge.

As halogens need only one electron to achieve their nearest noble gas configuration, only one sigma bond is formed between one carbon and one halogen atom.

Due to the increase in atomic size from fluorine to astatine, the C-X bond length in haloarenes increases from fluorine to astatine and bond strength decreases resulting in a decrease in bond dissociation enthalpy.

The dipole moment depends on the difference in electronegativity of carbon and halogens (group 17 trends properties) and as we know that the electronegativity of halogens decreases down the group, the dipole moment also decreases. There is an exception to C-Cl and C-F dipole moments. Though the electronegativity of Cl is less than F, the dipole moment of a C-Cl bond is more than C-F.

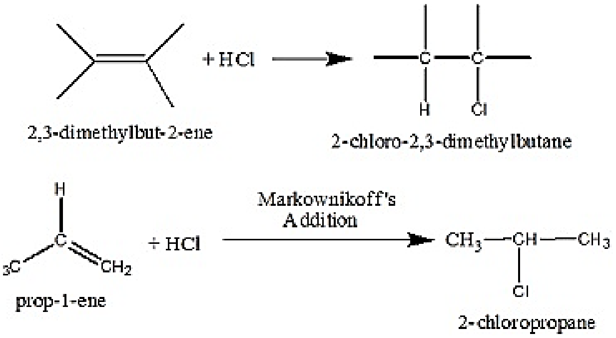
Bond	Bond length/pm	C-X Bond enthalpies/ kJ/mol
CH_3-F	139	452
CH_3-Cl	178	351
CH_3-Br	193	293
CH_3-I	214	234

Methods of preparation haloalkanes

By halogenation of alkanes before light, catalyst or heat:

$$\underset{\text{Ethane}}{C_2H_6} + Cl_2/hv \longrightarrow \underset{\text{Chloroethane}}{C_2H_5Cl} + HCl$$

By halogenation of alkenes with HX:



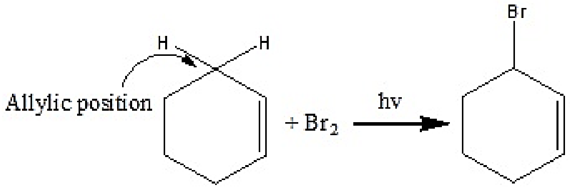
Hunsdiecker reactions:

The Hunsdiecker reaction is an instance of a halogenation reaction which involves an organic between silver salts of carboxylic acids and halogens resulting in the formation of organic halides.

$CH_3CH_2COOAg + Br_2CCl_4 \rightarrow CH_3CH_2Br + CO_2 + AgBr$.

Allylic halogenation:

When there is a presence of halogen around the unsaturated carbon such as alkenes, the expected reaction that occurs is the addition reaction to the double bond carbons which results in the formation of the vicinal dihalide (halogens on adjacent carbons). So as to avoid the reaction of the halogen to the carbons that are in the double bond, that is, alkene carbons, the concentration of the halogen is kept low so that the substitution reaction takes place at the allylic position rather than addition at the double bond. So, the reaction ends up in the formation of the halogen with the carbon that is placed next to the double-bonded carbons which is known as allylic halides. It is obtained by a radical chain mechanism.



Electrophilic substitution reaction: By this method, the preparation of aryl bromides and aryl chlorides becomes very easy. In the presence of the lewis acid, the electrophilic substitution reaction results in the formation of the aryl chlorides or aryl bromides by using halogens such as bromines and chlorines. In order to generate the proper electrophiles, certain specific conditions need to be maintained for the reaction to occur. The conditions for the reaction to occur is that the reaction should be carried out in the dark and there should be the presence of Lewis acid. Thus, the reactions to obtain the electrophiles are:

$Cl_2 + Fe \rightarrow FeCl_3$

$FeCl_3 + Cl_2 \rightarrow FeCl_4 + Cl^+$ (to obtain Cl^+ as an electrophile)

$Br_2 + Fe \rightarrow FeBr_3$

$FeBr_3 + Br_2 \rightarrow FeBr_4 + Br^+$ (to obtain Br^+ as an electrophile)

Preparation of alkyl halides from alcohols:

HCl alcohol treatment in the presence of anhydrous pentachloride of phosphorus $ZnCl_2$, PX_3 ($P_4 + X_2$) or $SOCl_2$ leads to alkyl halide formation.

$CH_3CH_2OH + SOCl_2 \rightarrow CH_3CH_2Cl + SO_2 + HCl$
$CH_3CH_2OH + PCl_2 \rightarrow CH_3CH_2Cl + P(OH)_3 + HCl$
$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + P(OH)_3 + HCl$
$CH_3CH_2OH + PBr_3 \rightarrow CH_3CH_2Br + P(OH)_3 + HBr$

By the action of halogen acid:

$$\underset{\text{Ethanol}}{CH_3CH_2OH + HCl} \xrightarrow{ZnCl_2} \underset{\text{Chloroethane}}{CH_3CH_2Cl + H_2O}$$

Primary and Secondary degree alcohols require anhydrous ZnCl2 while alcohols do not require $ZnCl_2$. Mixture of conc. HCl and anhydrous $ZnCl_2$ is called Lucas reagent.

Primary and secondary alkyl chlorides are prepared from their respective alcohols by using HCl gas and anhydrous $ZnCl_2$.

By the action of phosphorus halides:

$3ROH + PX_3$ à $3RX + H_3PO_3$.

Alkyl chloride can be synthesized by the action of PCl_3 or PCl_5.

Darzen method:

Darzens halogenation is a chemical processs involving the preparation of alkyl halides from alcohols by treating with reflux of thionyl chloride or bromide (SOX_2) in the presence of small quantity of a nitrogen base like tertiary amine or pyridine, or the equivalent hydrochloride.

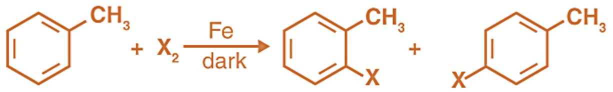
Alkyl bromides and iodides cannot be prepared by this method. The reason behind this is that thionyl bromide is unstable and thionyl iodide does not exist. This method is preferred for preparing alkyl chlorides because here by-products are gaseous SO_2 and HCl which escape easily. But this does not happen in the method involving phosphorous chloride; hence it is not used for preparing alkyl chlorides.

$$ROH + SOCl_2 \xrightarrow[\text{Reflux}]{\text{Pyridine}} RCl + SO_2 + HCl$$

Methods of preparation aryl halides:

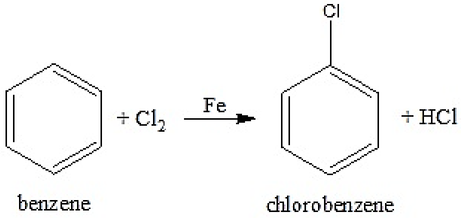
Preparation of Aryl Halides via Electrophilic Substitution Reactions

Aryl halides can be prepared by electrophilic aromatic substitution of arenes with halogens in the presence of a Lewis acid



Nuclear halogenation:

This method can be used to prepare aryl chlorides and bromides. This is done by the arene's treatment with chlorine or bromine where there is no sunlight and there is a halogen carrier such as $AlCl_3$, $FeCl_3$ etc. at low temperatures. It is an electrophilic substitution.



From phenols:

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[\text{or } SOCl_2]{HX,\ PX_3} \text{No Reaction}$$

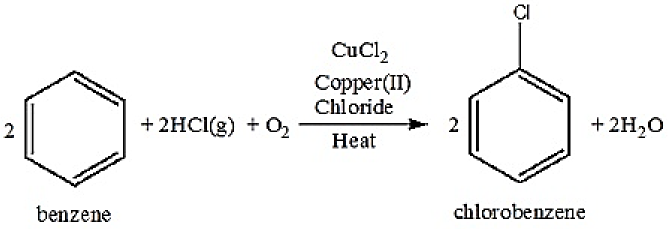
$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{chlorobenzene}}{C_6H_5Cl} + HCl + \underset{\text{Phosphoryl Chloride}}{POCl_3}$$

However the yield of chlorobenzene is very poor as the main product is triphenyl phosphate.

By Hunsdiecker reaction:

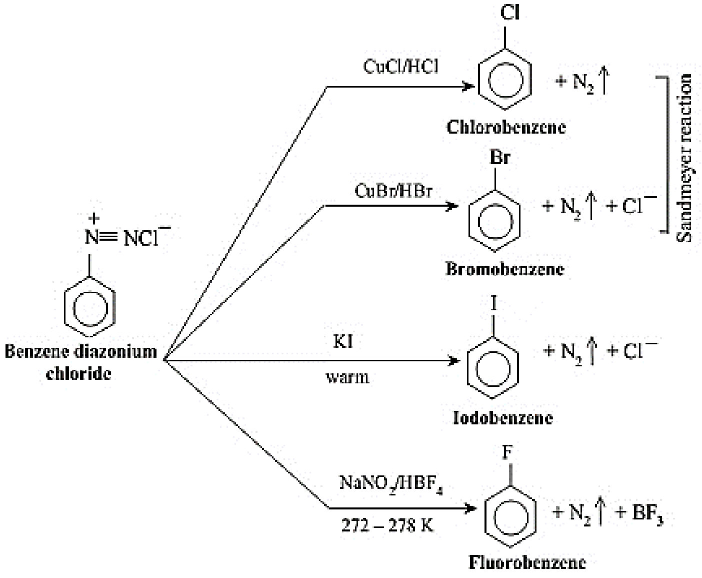
$$\underset{\text{Silver propionate}}{C_2H_5COOAg} + Br_2 \xrightarrow[CCl_4 \text{ as solvent}]{\text{Acetone or}} \underset{\text{Bromoethane}}{C_2H_5Br} + CO_2 + \underset{\text{Silver bromide}}{AgBr}$$

Rasching process:



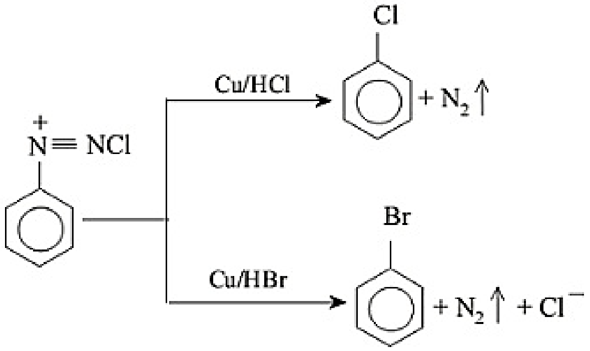
Sandmeyer reaction:

Diazonium salts are highly reactive compounds used to prepare arene derivatives. Treating diazonium salt with copper (I) chloride (Cu_2Cl_2) or copper (I) bromide (Cu_2Br_2) leads to the formation of corresponding haloarene. This reaction is known as Sandmeyer reaction.



Gattermann reaction:

Gattermann's reaction, a chemical reaction in which aromatic compounds were made into a mixture of hydrogen cyanide and hydrogen chloride in the presence of Lewis acid catalyst such as $AlCl_3$. It is named after German chemist Ludwig Gattermann and is similar to the Friedel – Crafts reaction.



Physical properties of haloalkanes:

Physical State

Alkyl halides are colourless in nature in its pure state. However, bromides and iodides develop colour on exposure to light. The reason for the development of colour is the decomposition of halogens in presence of light. The reaction representing the phenomenon is

$2R{-}I \rightarrow R{-}R + I_2$

Many of the halogen compounds having volatile nature have a sweet smell. Haloarenes are also colourless liquids or crystalline solids that have a characteristic smell.

Melting Point and Boiling Point of Haloalkanes

There is a large electronegativity difference between halogens and carbon resulting in highly polarised molecules. The higher molecular mass and greater polarity as compared to the parent hydrocarbon results in stronger intermolecular forces of attraction (dipole-dipole and van der Waals) in the halogen derivatives. The boiling Point depends upon the intermolecular forces of attraction and hence the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

As we go down in homologous series of haloalkanes, the forces of attraction become stronger due to the increase in molecular size and mass, hence the boiling point increases down the homologous series. But the boiling point decreases with branching.

The melting point of a compound depends upon the strength of the lattice structure of a compound. The melting point also follows the same trend as the boiling point. An exception to this is para-isomers. The para-isomers have higher melting as compared to their ortho and meta-isomers. It is due to the symmetry of para-isomers that fits in the crystal lattice better as compared to ortho– and meta-isomers.

Density of Haloalkanes

Density is directly proportional to the mass of the compound, hence down the homologous series, density increase due to increase in the mass, also fluoro derivatives are less dense than chloro derivatives; chloro derivatives are less dense than bromo derivatives and so on.

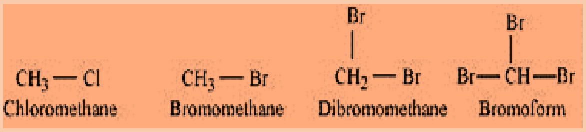
RI > RBr > RCl

Solubility of Haloalkanes

Haloalkanes are slightly soluble in water. This is because of the relatively larger amount of energy required to break the bond between halogen and carbon and the smaller amount of energy released when the bond is formed after the dissolution of ion and water.

Q. **Arrange each set of compounds in order of increasing boiling points.**

Sol. (i) Bromomethane, Bromoform, Chloromethane, Dibromomethane.



$CH_3{-}Cl$ Chloromethane, $CH_3{-}Br$ Bromomethane, $\overset{Br}{\overset{|}{CH_2}}{-}Br$ Dibromomethane, $Br{-}\overset{Br}{\overset{|}{CH}}{-}Br$ Bromoform

Note

The physical properties of any compound depend largely on

Its mass.

The type of intermolecular and intramolecular forces of attraction.

Physical characteristics of haloalkanes:

- Alkyl halides are colourless in pure form. Bromides and iodides develop colour when exposed to light
- Flexible halogen mixtures have a pleasant smell.
- The intermolecular force of attraction of halogen derivatives is stronger due to the greater polarity and mass of the cells and compared to the parent hydrocarbon thus resulting in higher boiling points of chloride, bromides and iodides compared to the hydrocarbons of the weight molecule equal.
- The boiling points of the alkyl halide of the same alkyl group follow the order: RI> RBr> RCl> RF due to the increase in size and weight of the halogen atom thereby increasing the van der Waal energy level.

Chemical properties of haloalkanes:

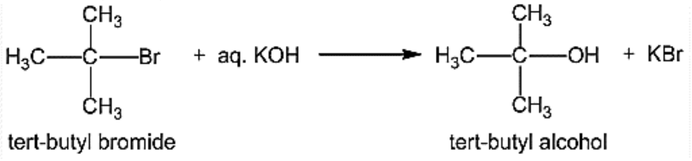
Nucleophilic substitution reaction:

In this reaction substitution reaction is initiated by a nucleophile so it is called nucleophilic substitution reaction.

These are of two types:

Sn_1 Reaction (Substitution, nucleophilic, unimolecular) -

SN_1 reaction is also known as unimolecular nucleophilic substitution reaction. Such reaction are generally shown by secondary and tertiary haloalkanes. For example, hydrolysis of tertiary butyl bromide with aq. KOH.



Kinetics of SN_1 reaction:

Rate of SN_1 reaction depends upon the concentration of alkyl halide and is independent of the concentration of nucleophile. Thus the reaction follows first order kinetics.

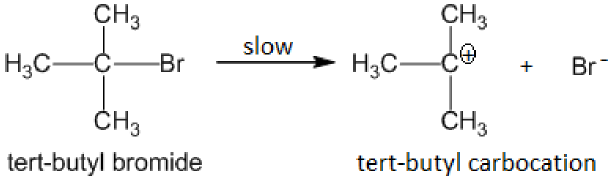
$$\text{Rate} \propto [\text{alkyl halide}]$$

$$\text{Rate} = k[(CH_3)_3C - Br]$$

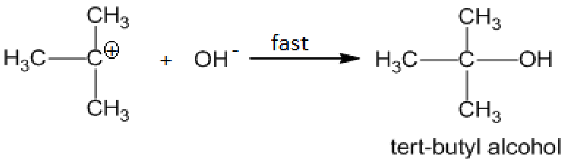
Mechanism of SN_1 reaction:

SN_1 reaction occurs in two steps.

Step I : In first step, the carbon-halogen bond of tertiary butyl bromide slowly breaks heterolytically to form an intermediate carbocation i.e. tert-butyl carbocation.



Step II : The carbocation formed combines rapidly with nucleophile i.e. OH^- to give tertiary butyl alcohol.



Slow step is the rate determining step, thus, step (I) is the rate determining step.

Stereochemistry of SN_1 reaction:

In SN_1 reaction, carbocations are formed as the intermediate which are trigonal and planar. Carbocation has a flat structure so that nucleophile can attack it from either side (i.e. front or back) resulting in the formation of two products, one with retention of configuration and other with inversion of configuration. Thus, if the alkyl halide is optically active (i.e. when halogen carrying carbon is chiral), the product would be racemic mixture and optically inactive. However, in actual practice, the product as a whole is not racemic. Usually there is a larger proportion of molecules with inverted configuration than of same configuration.

For example, when (-)-2-bromooctane is hydrolyzed by SN_1 reaction, partially racemized product is formed.

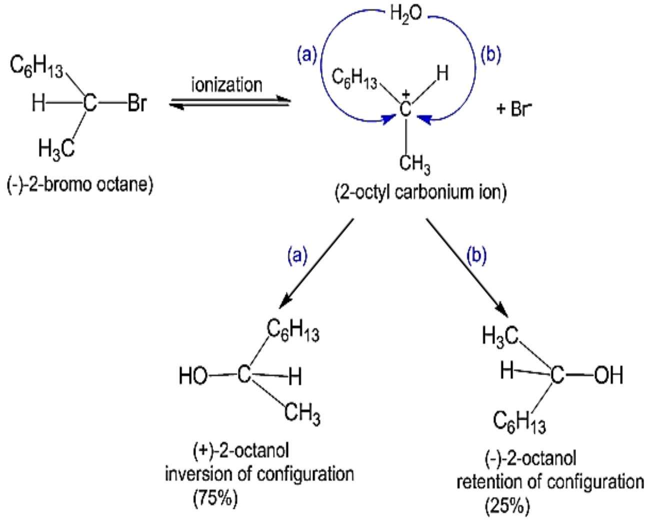


Fig. SN^1 reaction : Racemization plus inversion i.e. partial racemization

Reactivity of alkyl halides towards SN_1 reaction:

The rate of SN_1 reaction depends on the stability of carbocation formed. Therefore, the order of reactivities of alkyl halides towards the SN_1 reaction is:

$$3^0 \text{ halide} > 2^0 \text{halide} > 1^0 \text{ halide} > \text{Methyl halide}$$

A tertiary carbocation is more stable than a secondary carbocation which is more stable than a primary carbocation. Greater the stability of the carbocation, greater will be the ease of formation of carbocation, and hence faster will be the rate of the reaction.

Sn_2 Reaction (Substitution, nucleophilic, bimolecular) -

SN_2 reaction

SN_2 reaction is also known as bimolecular nucleophilic substitution reaction. Such reactions are generally shown by primary haloalkanes. For example, hydrolysis of ethyl bromide with aq. KOH

$$\underset{\text{(bromomethane)}}{CH_3\text{–}Br} + \text{aq.KOH} \longrightarrow \underset{\text{(methanol)}}{CH_3OH} + KBr$$

Kinetics of SN_2 reaction:

Rate of SN_2 reaction depends upon the concentration of both substrate (i.e. alkyl halide) and nucleophile. Thus the reaction follows second order kinetics since both the reactants are present in rate determining step.

$$\text{Rate} \propto [\text{Alkyl halide}]\,[\text{Nucleophile}]$$

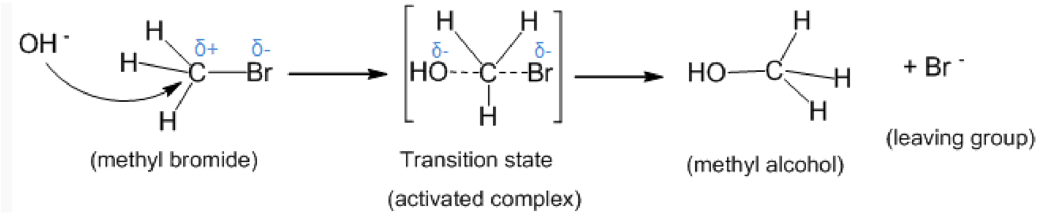
$$\text{Rate} = k\,[R - X]\,[OH^-]$$

Mechanism and Stereochemistry of SN_2 reaction:

The mechanism of SN_2 reaction involves a single step. Therefore, the breaking of carbon – halogen (C – X) bond and making of carbon – nucleophile (C – OH) bond occurs simultaneously.

It is assumed that the nucleophile attacks the carbon atom attached to the halogen atom from the side opposite to the halogen (i.e. backside attack). As a result a transition state (activated complex) is formed in which carbon atom is partially bonded to both nucleophile and leaving group (halogen atom).

Activated complex is unstable and it is a species having high energy content. Finally, bromine leaves the molecule as a bromide ion and hydroxide ion forms a covalent bond with carbon giving alcohol having inverted configuration is formed as the product.

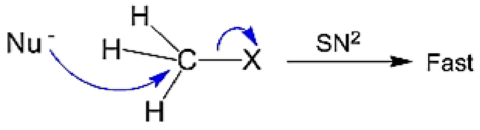


Reactivity of alkyl halides towards SN_2 reaction:

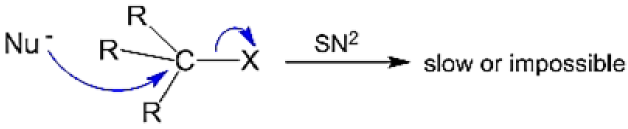
The order of reactivities of alkyl halides towards the SN2 reaction is:

Methyl halide > 1^0 halide > 2^0halide > 3^0 halide

The reaction is faster when the alkyl group of the substance is methyl. When the hydrogen atoms of methyl group are replaced by bulkier alkyl groups, the increased crowding around central atom hinders the attack of nucleophile. This is called steric hindrance. Greater the steric hindrance, slower is the reaction



(Primary alkyl halide)



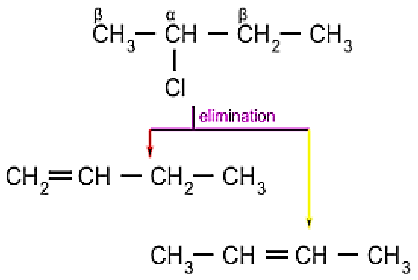
(tertiary alkyl halide)

.Comparison between S_N1 and S_N2

Related Concepts	S_N1 Reaction	S_N2 Reaction
Rate law	Unimolecular	Bimolecular
Haloalkane reactivity (electrophile)	$3^o>2^o>1^o$	$3^o<2^o<1^o$
Solvent	Polar solvent (protic solvent)	Polar aprotic solvent
Nucleophile	Weak nucleophile	Strong nucleophile
Stereochemistry	A mix of retention and inversion	Inversion

Elimination reaction:

This reaction involves the loss of two atoms or groups from the substrate as by product with formation of pi-bond. A halogen along with a hydrogen atom is removed from adjacent carbon atoms to form a double bond. This elimination introduces multiple bonds. It can be classified into E_1 and E_2 reaction.



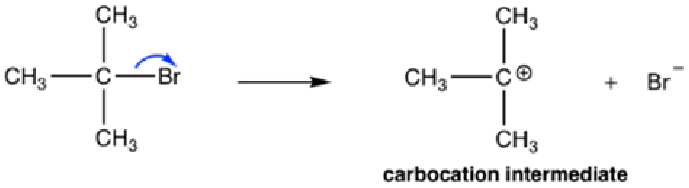
E_1 reaction

It is a unimolecular reaction. Rate determining step consist of formation of carbocation intermediate. Stability of carbocation intermediate determines the reactivity of E_1 reaction.

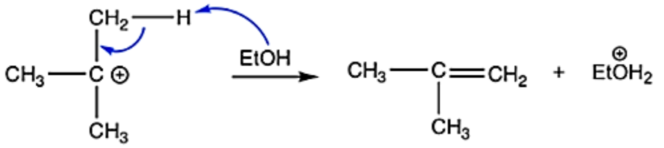
Order of reactivity for E_1 reaction is $3^0 > 2^0 > 1^0$. Both elimination and substitution reaction involves the use of (same reactive intermediate) carbocation. Therefore both the products are formed in comparable amount. This reaction is favoured by entropy of reaction therefore increase in temperature favours the E_1 reaction.

Mechanism

Step 1: Cleavage of C-Br bond slowly to form the carbocation intermediate.



Step 2: Base (EtOH) removes H from Beta-carbon, and double bond produced.



Conditions of E_1 reaction:

The factors that favors SN_1 reaction also favors E_1 reaction which are as follows:

Alkyl halide:

E_1 reaction occurs faster if the carbocation intermediate is more stable and has a lower activation barrier.

3^0 carbocation > 2^0 carbocation > 1^0 carbocation.

Leaving group:

The leaving group with a full negative charge is always expelled out. As a result the best leaving groups are those that can best stabilize an anion. In this reaction, it will not be odd to consider water as a leaving group.

Solvent:

When a carbocation undergoes solvation it allows the carbocation to get surrounded by more electron density thereby making the +ve charge more stable. The solvent can be protic or Aprotic but it must be polar.

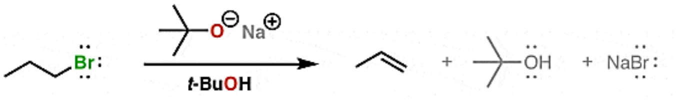
Nucleophiles:

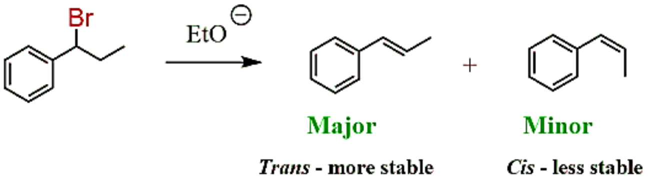
Those nucleophiles that undergo E_1 mechanism are weak neutral molecules. Any nucleophiles stronger than this is also a strong base that results in elimination reactions.

Like the E_2 reaction, the E_1 favors the Zaitsev product (always).

E_2 reaction

It's a biomolecular reaction. It is a single step reaction whose rate depends on the concentration of base and substrate. Reactivity depends on both strength of base and nature of alkyl halide. Order of reactivity for E_1 reaction is $3^0 > 2^0 > 1^0$. This reaction proceeds at room temperature.

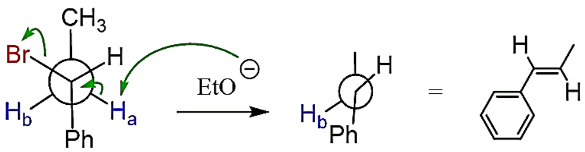




Stereochemistry of E_2 reaction:

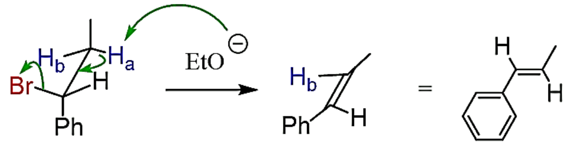
E_2 eliminations may or may not lead to the more stable stereochemistry. Initial material for this reaction has two sp^3 hybridized carbons which on rehybridization forms two sp^2 hybridized carbons. The C-X bond and the C-H bond lines up in the same plane and faces in anti-directions to each other.

Conformation 2



***E*- alkene**

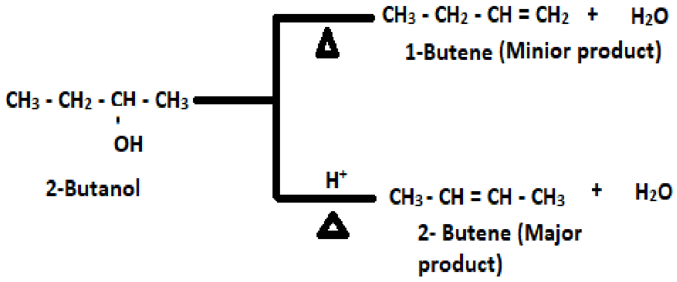
Same mechanism can be shown using a sawhorse representation:



***E*- alkene**

Saytzeff's rule of elimination:

According to this rule although alkene synthesis leads to the formation of more than one product, the more substituted alkene is the major product.



Conditions of E_2 reaction:

The conditions favouring SN_2 reaction favours E_2 reactions which are as follows:

Alkyl halide: SN_2 reaction will be slowed down if there exists steric congestion around the carbon atom undergoing the inversion process.

i.e. we conclude that if there is less congestion then the reaction will be faster.
$CH_3X > RCH_2X >> R_2CHX >>> R_3CX$

Leaving group: the leaving group with a full negative charge is always expelled out. As a result the best leaving groups are those that can best stabilize an anion.

Solvent: Surroundings which the solvent surrounds can cause a reaction to go faster or slower. Solvent are of two types:

Protic solvent: Nucleophile suffers salvation in which protic solvent hydrogen bonds with anion that tries to attack the alkyl halide thus creating a shield around the nucleophiles. As a result reaction is slowed down. E.g. Alcohol, water

Aprotic (polar) solvent: Aprotic solvents are those not capable of donating H's. Due to which it's favourable in SN_2 reaction because it's a 1step reaction and it doesn't require forming or having H's to stabilize the Carbocation step. E.g. Acetone, DMSO.

Strong nucleophile & Weak Nucleophile

Strong nucleophile

Usually anions with a full negative charge and no steric hindrance. Nucleophilicity increase with increase in charge density. For example, NaOR, RLi, NaOH or KOH, NaCN or KCN, NaCCR, $NaNH_2$, NaNHR, NaI, LiBr, KI, NaN_3
NaI Na + I- ➔ Strong Nucleophile Weak Base
NaOH Na + OH- ➔ Strong Nucleophile Strong Base

Basicity and Nucleophilicity essentially describe same phenomenon, except basicity concerns donation of lone pair of hydrogen and Nucleophilicity concerns donations of lone pair to all other atoms.

Organometallic Compounds

Most organic chlorides and iodides react with certain metals to give compounds containing carbon-metal bonds called organo-metallic compounds.

For example, RMgX is referred to as Grignard Reagent in 1900 by Victor Grignard.

Carbon-magnesium bond is covalent but highly polar.

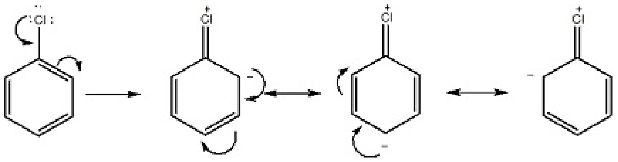
Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons.

Chemical properties:

It involves
Nucleophile Substitution
Elimination Reaction
Reaction with metals

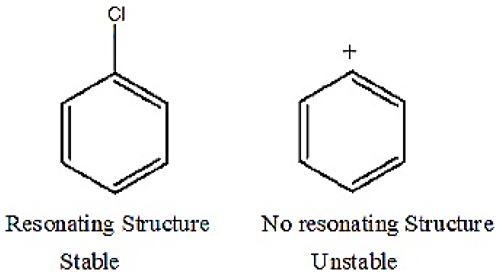
Nucleophilic Substitution: Resonance effect

Aryl halides are extremely less reactive towards Nucleophilic substitution reactions. Let us now discuss resonance effect.



Nucleophilic Substitution:sp² hybridised

C-X bond in halo alkane is 177 Pico meter. Whereas C-X bond in haloarenes is 169 Pico meter. Therefore the C-x bond in haloarenes is strong and stable and hence difficult to break. Hence the Nucleophilic substitution in haloarenes is difficult.
Nucleophilic Substitution: unstable cation



In figure II resonance structure is not possible. Cation formation is not possible as the cation is unstable.

This shows that SN^1 is totally ruled out.
SN^2 is possible.

Reaction with metals:

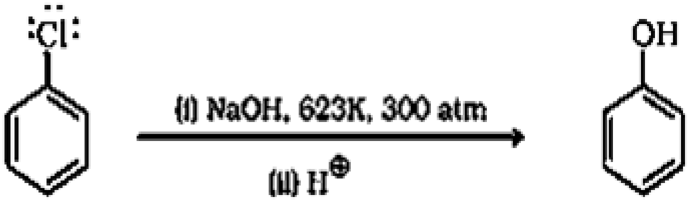
$$(i)\quad \underset{\text{Alkyl halides}}{R-X} + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Grignard reagent}}{R-Mg-X}$$

(ii) Wurtz reaction:

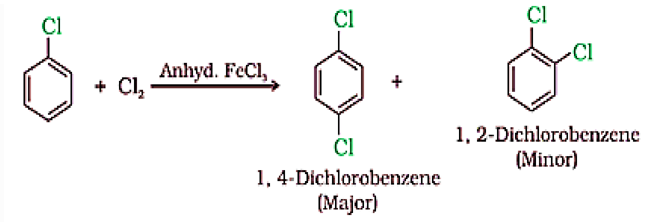
$$R-\boxed{X+2\,Na+X}-R \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2Na^+X^-$$

Chemical properties of haloarenes:

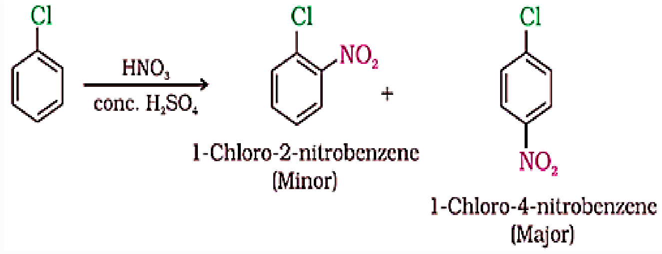
1 Dow's process:



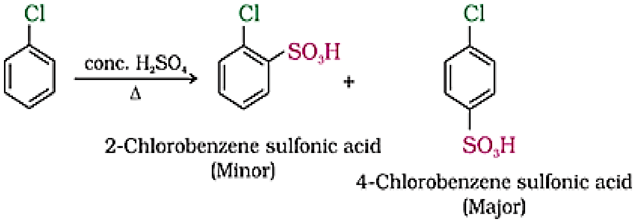
2 Reaction with halogens:



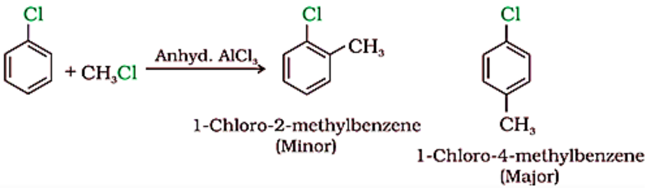
3. Reaction with conc. Nitric and sulphuric acid:



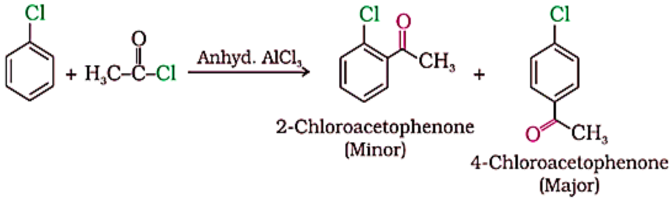
4. On heating with conc. Sulphuric acid:



5. With methyl chloride:

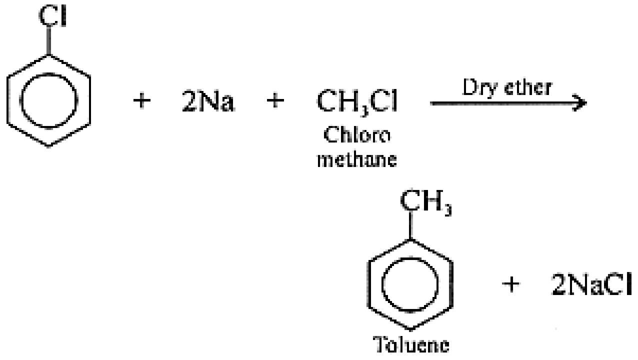


6. Reaction with acetyl chloride:



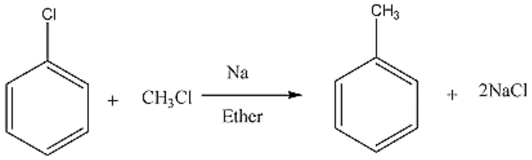
7. Fittig reaction:

In this reaction, a mixture of haloarenes reacts with sodium in the presence of dry ether. The product effect is diaryl.



8. Wurtz-Fittig reaction

In this reaction, a mixture of alkyl halide reacts with aryl halide in the presence of dry ether and sodium. The product effect is alkyl arene.



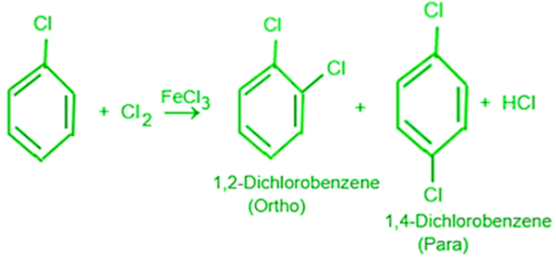
Electrophilic substitution reaction:

Haloarene undergoes normal electrophilic substitution reactions of benzene ring such as halogenation, nitration, sulphonation, Friedel Crafts reactions. The halogen atom ceases to function slowly and o, p-directing.

Halogenation

Haloarenes reactions occur when haloarene reacts with chlorine in the presence of a solvent (say ferric chloride). The chlorine molecule tends to be naturally polar and develops a slightly better charge. Thus, chlorine acts as an electrophile and will attack the electron-rich Ortho and Para position compound.

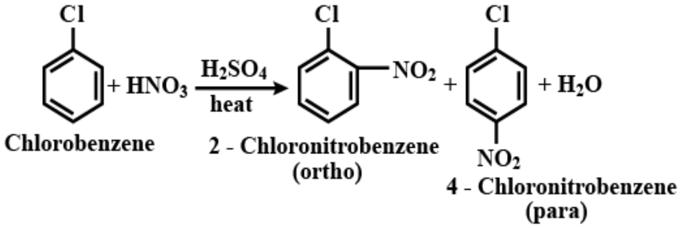
The reaction will lead to the formation of both Ortho and Para compounds. However, the Para isomer will be a major product and the Ortho isomer will be minor product. In the example below chlorobenzene reacts with Lewis acid and forms ortho and para instead of dihalobenzenes.



Nitration

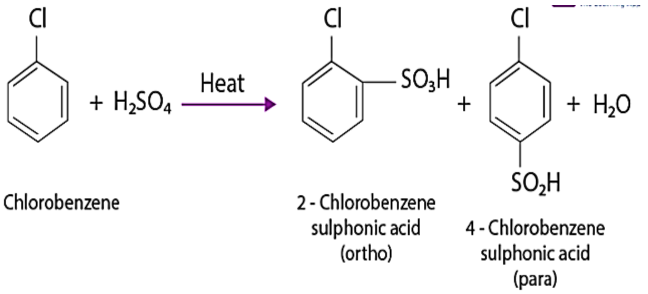
The reaction begins with the formation of NO_2^+ from nitric acid in initiation by sulphuric acid. NO_2 contains an electrophilic center due to the electronegative oxygen atoms present in the molecule itself. Also, the electrophile will attack the electron-rich ortho and para positions. The reaction will lead to the formation of Para isomer and Ortho isomer as the main product and the smallest product respectively.

In the example below, halobenzene nitration will lead to the formation of ortho and para products instead of nitric and sulphuric acid. The electrophile, in this case, is NO_2^+.



Sulphonation

In sulphonation SO_3 acts as an electrophile. It strikes an electron-rich haloarene at Ortho and Para positions. The reaction results in the formation of Para and Ortho Chlorobenzenesulphonic acid, where the Para isomer forms a larger product and the Ortho isomer forms a smaller product.



Friedel-Crafts reaction

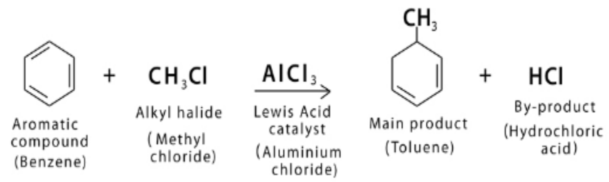
There are usually two types of Friedel-Crafts reactions

Friedel-Crafts Alkylation Reactions

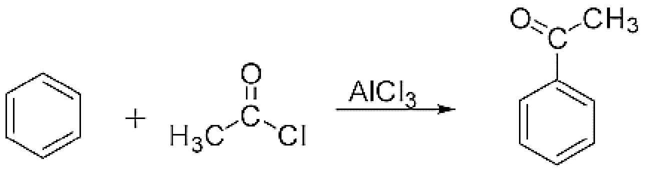
Friedel-Crafts Acylation Reaction

In this case, the electrophile is an alkyl and acetonic group due to the positive charge present in the carbon atom.

Friedel-Crafts Alkylation Reaction



Friedel-Crafts Acylation Reactions



Trichloromethane (Chloroform):

The main use of chloroform today is in the production of feron R-22 refrigerator. Chloroform is stored in sealed, dark-filled bottles to prevent air from entering because it is slowly released into the atmosphere by light to a highly toxic gas, carbonyl chloride.

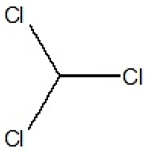
$$2CHCl_3 + O_2 \xrightarrow{light} \underset{\text{Phosgene}}{2COCl_2} + 2HCl$$

Polyhalogen Compounds

Dichloromethane (Methylene chloride)

Methylene chloride

- It is used as solvent, paint remover, propellant in aerosols, process solvent in the manufacture of drugs.
- It is used as metal cleaning and finishing solvent.
- But human beings can be adversely affected when exposed to Methylene
- It causes harm to human mental health.
- Human exposure to even lower levels of mythlene chloride in air can lead to dizziness, nausea, tingling, numbness in fingers and toes, etc.
- Direct exposure to Methylene chloride can cause intense burning and mild redness in the skin.
- Cornea of eyes can be adversely burnt on direct exposure to Methylene

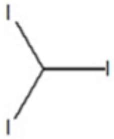


Chloroform

- Chloroform is a sweet smelling, heavy and colorless liquid. It has low B.P. of 61o
- It is insoluble in water but soluble in organic solvents.
- If it is inhaled it causes unconsciousness.
- It is used as anesthetic because when pure chloroform is inhaled it affects the heart due to which after mixing with ether and other suitable anesthetics chloroform can be used as anesthetic.
- Chloroform on oxidation in air leads to the formation of phosgene which is a poisonous gas due to which it should be stored in a dark colored bottle.

$$CHCl_3 + 1/2\ O_2 \xrightarrow{light} COCl_2 + HCl$$

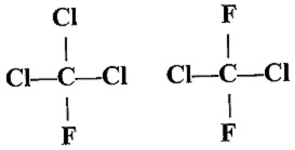
Before using chloroform as an anesthetic it is tested with AgNO3. Poisonous chloroform gives white precipitate with AgNO3.



Iodoform

- They are used in manufacturing refrigerants and propellants for aerosol cans.
- They are also used for the synthesis of chlorofluorocarbons, pharmaceutical etc.
- It was extensively used as cleaning agent in industry and as a degreasing agent at home as well.
- It is also used as a spot remover and fire extinguisher.
- Exposure to CCl_4 can adversely affect the heart beat and make it beat irregularly or make it permanently stop.
- Exposure to eyes can cause irritation.
- Exposure to atmosphere can lead ozone depletion that may lead to rise in the level of exposure to ultraviolet rays. This in turn leads to increased risk of skin cancer, eye diseases and other disorders as well as weakened immune system.

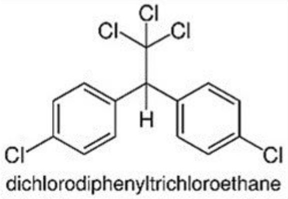
Freons



Freon-11 Freon-12

- The chlorofluorocarbon compounds of methane and ethane are jointly called freons.
- They are very stable, non-corrosive, non-toxic, and unreactive liquefiable gases.
- Freon 12 (CCl_2F_2) is most commonly used Freons in industrial sector.
- Freons are manufactured from tetra chloromethane using Swarts reaction.
- Freons are extensively used in aerosol propellants, refrigerants and air conditioners.

p,p'-Dichlorodiphenyltrichloroethane(DDT)



- DDT stands to be the first chlorinated organic insecticides originally discovered in 1873 which was then further studied and it was 1939 when Paul Muller discovered the effectiveness of DDT as an insecticide.
- It is highly poisonous to all living organisms as it does not get metabolized rapidly by animals and gets deposited and stored in the fatty tissues.

SUMMARY

Alkyl/aryl halides may be classified as mono, di or polyhalogen compounds depending on whether they contain one, two or more halogen atoms in their structures. Since halogen atoms are more electronegative than carbon, the carbon-halogen bond of alkyl halide is polarised; the carbon atom prop up a partial positive charge, and the halogen atom hold up a partial negative charge.

Alkyl halides are prepared by the free radical halogenation of alkanes, addition of halogen acids to alkenes, replacement of -OH group of alcohols with halogens using phosphorus halides, thionyl chloride or halogen acids. Aryl halides are prepared by electrophilic substitution to arenes. Fluorides and iodides are best prepared by halogen exchange method.

The boiling points of organohalogen compounds are comparatively higher than the corresponding hydrocarbons because of strong dipole-dipole and Vander Waals forces of attraction. These are slightly soluble in water but completely soluble in organic solvents.

The polarity of carbon-halogen bond of alkyl halides is responsible for their nucleophilic substitution, elimination and their reactions with metal atoms to form organometallic compounds. Nucleophilic substitution reactions are categorised into SN1 and SN2 on the basis of their kinetic properties. Chirality has a profound role in understanding the reaction mechanism of SN1 and SN2 reactions. SN2 reactions are characterized by racemisation.

A number of polyhalogen compounds e.g., dichloromethane, chloroform, iodoform, carbon tetrachloride, freon and DDT have many industrial applications. However, some of these compounds cannot be easily decomposed and even cause depletion of ozone layer and are proving environmental hazards.

MIND MAP

Haloalkanes and Haloarenes

Classification

1. Based on number of halogen atoms: Mono, -di, poly-
2. Compounds containing sp^3 C-X bond: Alkyl halides, Allylic halides, Benzylic halides
3. Compounds containing sp^2 C-X bond: Vinylic halides, Aryl halides

Physical properties

1. Boiling point of alkyl halides: RI > RBr > RCl > RF
2. Density increases with increase in: Carbon atom, halogen atom, atomic mass of halogen atoms
3. Solubility:
   Water → Slightly soluble
   Organic solvents → Soluble

Chemical Reactions of haloalkanes

1. Nucleophilic substitutions
2. Elimination reaction
3. Reaction with metals
   Wurtz reactions (sodium in dry ether)

Nomenclature

IUPAC name: Halosubstituted hydrocarbons

Chemical reactions of Haloarenes

1. Nuclephilic substitution
2. Electrophilic substitution
   Halogenation
   Nitration
   Sulphonation
   Friedel-Craft reaction
3. Reaction with metals
   Wurtz-Fittig reaction
   Fittig Reactions

Nature of C-X Bond

1. Polarised
2. Bond length: C-F < C-Cl < C-Br < C-I

Preparation method of Haloalkanes

1. From alcohols
2. From Hydrocarbons
   - ❖ From alkanes by free radical halogenation
   - ❖ From alkenes by:
     Addition of hydrogen halides
     Addition of halogens
3. Halogen exchange

Polyhalogen compounds

1. Dichloromethane (Methylene chloride)
2. Trichloromethane (Chloroform)
3. Triiodomethane (Iodoform)
4. Tetrachloromethane (Carbon Tetrachloride)
5. Freons
6. p, p'-dichlorodiphenyltrichloroethane (DDT)

Preparation method of Haloarenes

- ➢ From hydrocarbon by electrophilic substitution
- ➢ From amines by Sandmeyer's reaction

QUESTIONS FOR PRACTICE

Q1. When chlorine is passed through propene at 400^0 C, which of the following is formed?

(a) PVC (b) Allyl chloride

(c) Propyl chloride (d) 1,2-Di-chloroethane

Q2. Two possible streo-structures of $CH_3CHOHCOOH$, which are optically active are called

(a) Atropisomers (b) Enantiomers

(c) Mesomers (d) Diastereomers

Q3. In an SN_1 reaction on chiral centres, there is

(a) Inversion more than retention leading to partial racemisation

(b) 100% inversion

(c) 100% retention

(d) 100% racemisation

Q4. Which of the following acids does not exhibit optical isomerism?

(a) Maleic acid (b) A-amino acid

(c) Lactic acid (d) Tartaric acid

Q5. How many stereoisomers does this molecule have? $CH_3CHCHCH_2CHBrCH_3$

(a) 8 (b) 2

(c) 4 (d) 6

Q6. Which of the following is not chiral?

(a) 2-Hydroxypropanoic acid (b) 2-Butanol

(c) 2,3-Dipromopentane (d) 3-Bromopentane

Q7. Obtained by chlorination of n-butane will be

(a) Meso form (b) Racemic mixture

(c) D-form (d) I-form

Q8. The alkyl halide is converted into an alcohol by

(a) Elimination

(b) Dehydrohalogenation

(c) Addition

(d) Substitution

Q9. Which of the following is an optically active compound

(a) 1-Butanol (b) 1-Propanol

(c) 2-Chlorobutane (d) 4-Hydroxypentane

Q10. Phosgene is a common name for

(a) Phosphoryl chloride

(b) Thionyl chloride

(c) Carbon dioxide and phosphine

(d) Carbonyl chloride

Q11. Good conductor of electricity and heat is

(a) Anthracite coke (b) Diamond

(c) Graphite (d) Charcoal

Q12. The hybridisation of carbon in diamond is

(a) sp^3 (b) sp^2

(c) sp (d) dsp^2

Q13. Alkene gives which of the following reactions?

(a) Addition reaction (b) Substitution reaction

(c) Both (a) and (b) (d) None of these

Q14. The compound having general formula C_nH_{2n+2} is

(a) Alkene (b) Alkyne

(c) Alkane (d) None of these

Q15. Which of the following is not correctly matched with its IUPAC name?

(a) $CHF_2CBrClF$: 1-Bromo-1-chIoro-1, 2, 2-trifluoroethane

(b) (CCl3)3CCl : 2-(Trichloromethyl)-1, 1, 2, 3, 3-heptachloropropane

(c) CH3C (p-ClC6H4)2CH(Br)CH3 : 2-Bromo-3, 3-bis (4- chlorophenyl) butane

(d) o-BrC6H4CH (CH3) CH2CH3 : 2-Bromo-1-methylpropylbenzene

Q16. Which of the following compounds can yield only one monochlorinafed product upon free radical chlorination?

(a) 2, 2-Dimethylpropane

(b) 2-Methylpropane

(c) 2-Methylbutane

(d) n-Butane

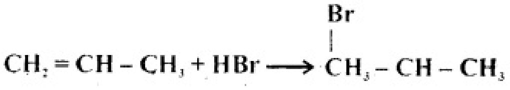
Q17. The reaction is an example of

(a) Nucleophilic addition

(b) Free radical addition

(c) Electrophilic addition

(d) Electrophilic substitution



$$CH_2=CH-CH_3+HBr \longrightarrow CH_3-\overset{\overset{\displaystyle Br}{|}}{CH}-CH_3$$

Q18. Bromination of methane in presence of sunlight is a

(a) Nucleophilic substitution

(b) Free radical substitution

(c) Electrophilic substitution

(d) Nucleophilic addition

Q19. Which of the following compounds has the highest boiling point?

(a)CH_3CH_2CH2Cl (b) $CH_3CH_2CH_2CH_2Cl$

(c) $CH_3CH(CH_3)CH_2Cl$ (d) $(CH_3)_3CCl$

Q20. Arrange the following compounds in-decreasing order of their boiling points

(i) CH_3Br (ii) CH_3CH_2Br

(iii) $CH_3CH_2CH_2Br$ (iv) $CH_2CH_2CH_2CH_2Br$

(a) (i) > (ii) > (iii) > (iv)

(b) (iv) > (iii) > (ii) > (i)

(c) (i) > (iii) > (ii) > (iv)

(d) (iii) > (iv) > (i) > (ii)

Q21. Alkyl halides are immiscible in water though they are polar because

(a) They react with water to give alcohols

(b) They cannot form hydrogen bonds with water

(c) C -X bond cannot be broken easily

(d) They are stable compounds and are not reactive

Q22. Which of the following compounds will have highest melting point?

(a) Chlorobenzene (b) o-Dichlorobenzene

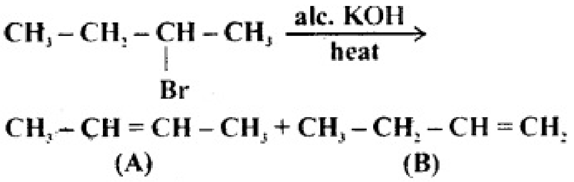
(c) m-Dichlorobenzene (d) p-Dichlorobenzene

Q23. Ethyl alcohol is obtained when ethyl chloride is boiled with

(a) Alcoholic KOH (b) Aqueous KOH

(c) Water (d) Aqueous $KMnO_4$

Q24. Which of the following reactions will give the major and minor products?



$$CH_3-CH_2-\underset{\large Br}{\underset{|}{CH}}-CH_3 \xrightarrow[\text{heat}]{\text{alc. KOH}} \underset{(A)}{CH_3-CH=CH-CH_3} + \underset{(B)}{CH_3-CH_2-CH=CH_2}$$

(a) (a) is major product and (b) is minor product

(b) (a) is minor product and (b) is major product

(c) Both (a) and (b) are major products

(d) Only (b) is formed and (a) is not formed

Q25. Methyl bromide reacts with AgF to give methyl fluoride and silver bromide. This reaction is called

(a) Fittig reaction (b) Swartz reaction

(c) Wurtz reaction (d) Finkelstein reaction

Q26. A mixture of 1-chloropropane and 2-chloropropane when treated with alcoholic KOH gives

(a) Prop-1-ene

(b) Prop-2-ene

(c) A mixture of prop-1 -ene and prop-2-ene

(d) Propanol

Q27. An alkyl halide, RX reacts with KCN to given propane nitrile, RX is

(a) C_3H_7Br (b) C_4H_9Br

(c) C_2H_5Br (d) $C_5H_{11}Br$

Q28. Grignard reagents are formed by the reaction of alkyl halides by warming

(a) With alcoholic solution

(b) With $MgCl_2$

(c) Mg in presence of dry ether

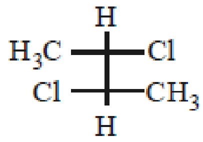
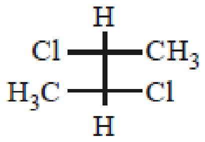
(d) With $MgCO_3$

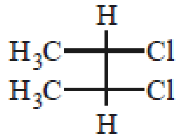
Q29. Which of the following is the most reactive towards nucleophilic substitution reaction?

(a) $ClCH_2-CH=CH_2$ (b) $CH_2=CH-Cl$

(c) $CH_3CH=CH-Cl$ (d) C_6H_6Cl

Q30. Which of the following is optically inactive?

(a)  (b) 

(c)  (d) none of these.

Q31. The pesticide DDT slowly changes to

(a) CCl_3, CHO and chlorobenzene

(b) p-p′Dichlorodiphenylethene

(c) p-p′Dichlorodiphenyldichloroethane

(d) p-p′ Dichlorodiphenyldichloroethene

Q32. The increasing order of nucleophilicity would be?

(a) $Cl^- < Br^- < I^-$ (b) $I^- < Cl^- < Br^-$

(c) $Br^- < Cl^- < I^-$ (d) $I^- < Br^- < Cl^-$

Q33. $CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$, will be fastest in

(a) Ethanol

(b) Methanol

(c) N, N-dimethylformamide

(d) Water

Q34. C-Cl bond of chlorobenzene in comparison to C-Cl bond in methyl chloride is

(a) Longer and weaker

(b) Shorter and weaker

(c) Shorter and stronger

(d) Longer and stronger

Q35. The decreasing order of boiling points of alkyl halides is

(a) RF > RCl > RBr > RI

(b) RBr > RCl > RCl > RF

(c) RI > RBr > RCl > RF

(d) RCl > RF > RI > RBr

Q36. The reaction of tert butyl bromide with sodium methoxide produces mainly
(a) Isobutane
(b) Isobutylene
(c) Tert-butyl methyl ether
(d) Sodium tert butoxide

Q37. Gem-dibromide is
(a) $CH_3CH(Br)CH_2(Br)$ (b) $CH_3CBr_2CH_3$
(c) $CH_2(Br)CH_2CH_2$ (d) CH_2BrCH_2Br

Q38. Which of the following is a primary halide?
(a) Isopropyl iodide
(b) Secondary butyl iodide
(c) Tertiary butyl bromide
(d) Neohexyl chloride

Q39. When two halogen atoms are attached to same carbon atom then it is :
(a) Vic-dihalide (b) Gem-dihalide
(c) α, ω -halide (d) α, β –halide

Q40. How many structural isomers are possible for a compound with molecular formula C_3H_7Cl ?
(a) 2 (b) 5
(c) 7 (d) 9

Q41. The compound which contains all the four 1°, 2°, 3° and 4° carbon atoms is
(a) 2, 3-dimethyl pentane
(b) 3-chloro-2, 3-dimethylpentane
(c) 2, 3, 4-trimethylpentane
(d) 3, 3-dimethylpentane

Q42. Conant Finkelstein reaction for the preparation of alkyl iodide is based upon the fact that
(a) Sodium iodide is soluble in methanol, while sodium chloride is insoluble in methanol
(b) Sodium iodide is soluble in methanol, while NaCl and NaBr are insoluble in methanol
(c) Sodium iodide is insoluble in methanol, while NaCl and NaBr are soluble
(d) The three halogens differ considerably in their electronegativity

Q43. Chlorobenzene is prepared commercially by
(a) Raschig process
(b) Wurtz Fittig reaction
(c) Friedel-Craft's reaction
(d) Grignard reaction

Q44. The catalyst used in the preparation of an alkyl chloride by the action of dry HCl on an alcohol is
(a) Anhydrous $AlCl_3$ (b) $FeCl_3$
(c) Anhydrous $ZnCl_2$ (d) Cu

Q45. Which of the following is liquid at room temperature (b.p. is shown against it)?
(a) CH_3I (b) CH_3Br
(c) C_2H_5Cl (d) CH_3F

Q46. In which of the following conversions, phosphorus pentachloride is used as the reagent?
(a) $H_2C = CH_2 \rightarrow CH_3CH_2Cl$
(b) $CH_3CH_2OH \rightarrow CH_3CH_2Cl$
(c) $H_3C\text{-}O\text{-}CH_3 \rightarrow CH_3Cl$
(d) $CH \equiv CH \rightarrow CH_2 = CHCl$

Q47. In the preparation of chlorobenzene from aniline, the most suitable reagent is
(a) Chlorine in the presence of ultraviolet light
(b) Chlorine in the presence of $AlCl_3$
(c) Nitrous acid followed by heating with Cu_2Cl_2
(d) HCl and Cu_2Cl_2

Q48. The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with
(a) PCl_5
(b) dry HCl in the presence of anhydrous $ZnCl_2$
(c) $SOCl_2$ in presence of pyridine
(d) None of these

Q49. Which of the following halide is 2° ?
(a) Isopropyl chloride (b) Isobutyl chloride
(c) n-propyl chloride (d) n-butyl chloride

Q50. The IUPAC name of $CH_2 = CH—CH_2Cl$ is
(a) Allyl chloride (b) 1-chloro-3-propene
(c) Vinyl chloride (d) 3-chloro-1-propene

ASSERTION AND REASONING

Q1. **Assertion:** CCl4 is not a fire extinguisher.
Reason: CCl4 is insoluble in water.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.

Q2. **Assertion:** SN2 reaction of an optically active aryl halide with an aqueous solution of KOH always gives an alcohol with opposite sign of rotation.
Reason: SN2 reactions always proceed with inversion of configuration.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) if Assertion is incorrect and Reason is correct

Q3. **Assertion:** Alkylbenzene is not prepared by Friedel-Crafts alkylation of benzene.

Reason: Alkyl halides are less reactive than acyl halides.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) if Assertion is incorrect and Reason is correct

Q4. **Assertion:** Exposure of ultraviolet rays to human causes the skin cancer, disorder and disrupt the immune system.

Reason: Carbon tetrachloride is released into air it rises to atmosphere and depletes the ozone layer.

(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) if Assertion is incorrect and Reason is correct

TRUE/FALSE

Q1. The dipole moment of CH_3F is greater than CH_3Cl.

(a) True (b) False

Q2. Haloarenes are soluble in water.

(a) True (b) False

Q3. O-dichlorobenzene has a higher melting point than that of p -dichlorobenzene.

(a) True (b) False

HOMEWORK

Q1. Which of the followings reagents forms an isonitrile when reacted with an alkyl halide?

(a) $AgNO_2$ (b) KCN
(c) AgCN (d) KNO_2

Q2. Which of the following is not an ambident nucleophile?

(a) Nitrite (b) Hydroxide
(c) Thiocyanate (d) Cyanide

Q3. Identify the nucleophile that gives a primary amine and hydrogen bromide on reaction with bromoethane.

(a) H (b) NH_2
(c) NH_3 (d) H_2O

Q4. Which of the following statements in incorrect regarding SN_2 mechanisms?

(a) There is inversion of configuration
(b) The rate of the reaction depends on the concentration of both reactants
(c) The complete mechanism takes place in a single step
(d) The transition state is stable

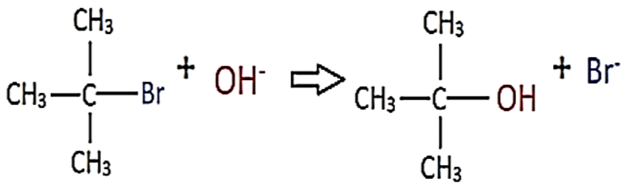
Q5. A haloalkane is known to have an SN_2 reaction rate 30 times faster than that of ethyl bromide. Identify the haloalkane.

(a) neo-Pentyl bromide (b) Methyl bromide
(c) Isopropyl bromide (d) tert-Butyl bromide

Q6. Which of the following statements is correct regarding unimolecular nucleophilic substitution reactions?

(a) None of the steps are reversible.
(b) It takes place in three steps.
(c) The rate of the reaction depends on the concentration of all the reactants.
(d) The first step is the slowest and determines the rate of reaction.

Q7. The rate of the following reaction depends on the concentration of which reactant(s)/?



$(CH_3)_3C{-}Br + OH^- \Rightarrow (CH_3)_3C{-}OH + Br^-$

(a) None of the reactants
(b) tert-Butyl bromide
(c) Hydroxide ion
(d) Both tert-Butyl bromide and hydroxide ion

Q8. As the stability of carbocation formed in the first step of SN_1 reaction increases, the rate of the reaction ____

(a) may increase or decrease
(b) increases
(c) decreases
(d) remains same

Q9. The SN_1 reaction cannot be carried out in which of the following media?

(a) Water (b) Acetic acid
(c) Acetone (d) Ethanol

Q10. Which of the following compounds does not have a stereocenter?
(a) 2-Bromopentane
(b) Propan-2-ol
(c) Butan-2-ol
(d) 2-Bromo-1-chlorobutane

Q11. Which of the following has a chiral carbon atom?
(a) 2-Bromopentane
(b) 2-Chloro-2-methylpentane
(c) 1,1-Dibromoethane
(d) Pentan-3-ol

Q12. What is the chirality of 2-Chlorobutane?
(a) Symmetric
(b) Chiral
(c) Achiral
(d) Superimposable mirror images

Q13. A chiral compound with an 'X' group attached to the stereocenter has been replaced by a 'Y' group. The product obtained rotates the plane of polarised light in the direction opposite to that of the original compound. Name the process that has taken place.
(a) Inversion or retention
(b) Inversion
(c) Retention
(d) Racemisation

Q14. When (-)-2-bromooctane reacts with potassium hydroxide over an SN2 mechanism, what will be the product formed?
(a) (-)-octan-1-ol (b) (+)-octan-1-ol
(c) (-)-octan-2-ol (d) (+)-octan-2-ol

Q15. The heating of 1-Chlorobutane along with alcoholic KOH results in ________
(a) no reaction
(b) elimination of hydrogen from α-carbon atom
(c) elimination of hydrogen from β-carbon atom
(d) elimination of hydrogen from γ-carbon atom

Q16. How many β-carbon atoms does 2-Bromobutane have?
(a) 3 (b) 0
(c) 1 (d) 2

Q17. Which of the following is the suitable medium for preparing Grignard reagents?
(a) Alcoholic KOH
(b) Dry acetone
(c) Dry ether
(d) Concentrated HCl

Q18. What is formed when ethyl magnesium bromide reacts with water?
(a) Magnesium hydroxide
(b) Grignard reagent
(c) Ethane
(d) Ethanol

Q19. What will be the product of the following reaction?
$2CH_3CH_2Br + 2Na$ + dry ether = ________
(a) Ethane
(b) 1-Bromoethane
(c) Butane
(d) 1-Bromobutane

Q20. Compared to haloalkanes, the reactivity of haloarenes towards nucleophilic substitution reactions is
(a) equal (b) low
(c) high (d) very high

Q21. Which of the following compounds is most easily converted to a phenol when heated with aqueous NaOH solution?
(a) 2,4,6-Trinitrochlorobenzene
(b) Chlorobenzene
(c) 4-Chloronitrobenzene
(d) 2,4-Dinitrochlorobenzene

Q22. What is the major product formed when chlorobenzene reacts with nitric acid in concentrated sulphuric acid?
(a) 1-Chloro-4-nitrobenzene
(b) Nitrobenzene
(c) 1-Chloro-2-nitrobenzene
(d) 1-Chloro-3-nitrobenzene

Q23. Which is the metal involved in Wurtz-Fittig reaction?
(a) Sodium (b) Iron
(c) Magnesium (d) Aluminium

Q24. Predict the minor product formed when chlorobenzene reacts with chloromethane in the presence of anhydrous $AlCl_3$?
(a) p-Chlorotoluene (b) Toluene
(c) m-Chlorotoluene (d) o-Chlorotoluene

Q25. Which of the following haloalkanes exist as liquids at room temperature?
(a) Propyl bromide (b) Methyl chloride
(c) Methyl bromide (d) Ethyl chloride

Q26. For a particular alkyl group R, what is the correct order of boiling points of the following compounds?
(a) RBr > RCl > RF (b) RF > RCl > RBr
(c) RCl > RBr > RF (d) RF > RBr > RCl

Q27. If chloromethane has a boiling point of 250K, what will be the probable boiling point of methane?
(a) 315K (b) 110K
(c) 250K (d) 275K

Q28. Which of the following has the highest boiling point?
(a) Tetrachloromethane
(b) Chloromethane
(c) Dichloromethane
(d) Trichloromethane

Q29. What is the correct order of boiling of isomeric dichlorobenzenes?
(a) meta>ortho>para (b) ortho>meta>para
(c) para>meta>ortho (d) para>ortho>meta

Q30. Which of the following has the lowest boiling point?
(a) Dibromomethane (b) Bromomethane
(c) Bromoform (d) Chloromethane

ASSERTION AND REASONING

Q1. **Assertion:** CHCl3 is stored in dark bottles.
Reason: CHCl3 is oxidised in dark.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) if Assertion is incorrect and Reason is correct

Q2. **Assertion:** The boiling points of alkyl halides decrease in the order :
RI > RBr > RCl > RF
Reason: The boiling points of alkyl chlorides, bromides and iodides are considerably higher than that of the hydrocarbon of comparable molecular mass.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) if Assertion is incorrect and Reason is correct

Q3. **Assertion:** Phosphorus chlorides (tri and penta) are preferred over thionyl chloride for the preparation of alkyl chlorides from alcohols.
Reason: Phosphorus chlorides give pure alkyl halides.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) if Assertion is incorrect and Reason is correct

Q4. **Assertion:** Presence of a nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution.
Reason: Nitro group, being an electron-withdrawing group decreases the electron density over the benzene ring.
(a) If both Assertion and Reason are correct and the Reason is a correct explanation of the Assertion.
(b) If both Assertion and Reason are correct but Reason is not a correct explanation of the Assertion.
(c) If the Assertion is correct but Reason is incorrect.
(d) If both the Assertion and Reason are incorrect.
(e) if Assertion is incorrect and Reason is correct.

TRUE/FALSE

Q1. The C–X bond in haloarenes is less polar than in haloalkanes.
(a) True (b) False

Q2. An increase in the number of $-NO_2$ groups at o - and p - positions decreases the reactivity of chlorobenzene towards nucleophilic substitution reactions.
(a) True (b) False

Q3. Iodoform test is given by all methyl ketones.
(a) True (b) False

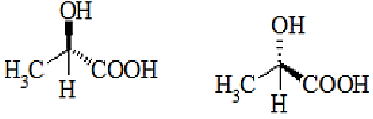
SOLUTIONS

S1. **(b)** When chlorine gas is reacted with propene at high temperature (400∘ C), then substitution takes place in place of addition reaction. Hence, allyl chloride is formed.

$$CH_3CH = CH_2Cl \xrightarrow{400°C} ClCH_2CH = CH_2 + HCl.$$

S2. **(b)** Two possible stereo-structures of $CH_3CHOHCOOH$, which are optically active, are called enantiomers.

They are non-superimposable mirror images of each other and are shown in the image.

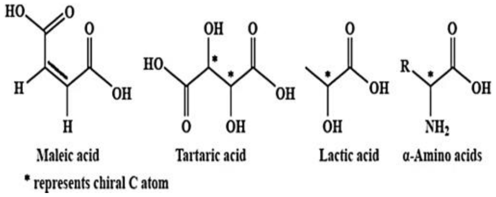


S3. **(a)** In an SN^1 reaction on chiral centres, there is inversion more than retention leading to initial racemization.

Thus if we start with a pure enantiomer and carry out SN^1 substitution on chiral carbon, the product will be racemic. This is because a planar carbocation intermediate is obtained. The nucleophile can attack from either side of this intermediate.

S4. **(a)** Maleic acid does not exhibit optical isomerism as it lacks chiral C atom.

Tartaric acid, lactic acid and α− amino acids exhibit optical isomerism as they contain chiral C atoms.

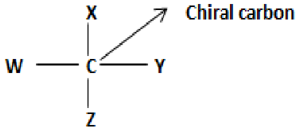


S5. **(c)** the number of stereogenic centres which comprises of optically active carbon and the carbon showing geometrical isomerism. In the above picture, there is only one geometric isomer and chiral carbon. So there is 2 stereogenic centre.

Stereoisomers = $2^n = 2^2 = 4$

S6. **(d)** 3-bromopentane.

If a carbon atom in molecule is attached with four different groups then the carbon is known as chiral carbon.



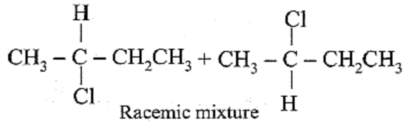
X, y, z different group

S7. **(b)** Chlorination of n-butane takes place by free radical mechanism are as follows:

$$CH_3CH_2CH_2CH_3 \xrightarrow{\dot{C}l} CH_3\dot{C}HCH_2CH_3 + HCl$$

sp^2 - hybrid planar shape intermediate and $\dot{}Cl$ may attack from either side to give

$$CH_3\dot{C}HCH_2CH_3 + \dot{C}l \longrightarrow$$



$$CH_3-\underset{Cl}{\overset{H}{C}}-CH_2CH_3 + CH_3-\underset{H}{\overset{Cl}{C}}-CH_2CH_3$$

Racemic mixture

(Mixture of 50% *d*-form and 50% *l*-form)

S8. **(d)** Alkyl halides on alkaline hydrolysis get converted into alcohols. This takes place by a nucleophilic substitution reaction where the −X atom is substituted by a nucleophile i.e −OH group.

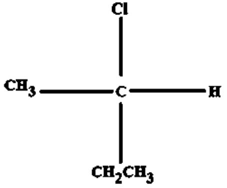
The primary alkyl halides undergo nucleophilic substitution reaction by SN_2 mechanism, while tertiary alkyl halides follow SN_1 mechanism.

R−X + KOH → R−OH + KX

The above is the example of a substitution reaction.

S9. **(c)** For an optical activity, the compound should have a chiral carbon. Chiral carbon is a carbon whose all four valencies are satisfied by 4 different group.

2-chlorobutane contains one chiral carbon. So, it is optically active.



S10. **(d)** Chloroform is slowly oxidised into a poisonous compound called phosgene in the presence of air or light. This compound is also called carbonyl chloride ($COCl_2$)

$$CHCl_3 + \tfrac{1}{2}O_2 \xrightarrow[\text{light}]{\text{Air}} \underset{\substack{\text{Carbonyl chloride}\\ \text{(phosgene)}}}{COCl_2} + HCl$$

S11. **(c)** Graphite is a good conductor of heat of electricity.

S12. **(a)** In diamond each carbon atom undergoes sp^3 hybridisation and linked to four other carbon atoms by using hybridised orbitals in tetrahedral fashion.

S13. (a) Alkenes are unsaturated hydrocarbon having double bond so generally gives addition reaction.

Example: $CH_2 = CH_2 + HBr \rightarrow CH_3 - CH_2Br$

S14. (b) Hydrocarbons having at least one triple bond between two carbon atoms are known as alkyne. General formula of alkyne is C_nH_{2n-2}. As in case of alkene, minimum two carbon atoms are required to form alkyne.

S15. (d) IUPAC system is one of the systematic method of naming organic compound. The numerals 1,2; 1,3 and 1,4 are used in IUPAC system. The option D is not correctly matched with its IUPAC name because the correct IUPAC name for the structure o–$BrC_6H_4CH(CH_3)CH_2CH_3$ is 1 Bromo-2-1-methlypropylbenzene.

S16. (a) All the hydrogen atoms in 2, 2-dimethyl - propane are equivalent, hence it can form only one monochlorinated product.

S17. (a) The reaction is nucleophilic addition reaction as the Br^- ions is attached to the given compound by breaking of double bond.

$$CH_2 = CH - CH_3 + HBr \longrightarrow CH_3 - \overset{\oplus}{C}H - CH_3 \xrightarrow{Br^-} CH_3 - CHBr - CH_3$$

S18. (b)

S19. (b) Straight chain alkyl halides have greater boiling point than their isomers. So, $CH_3CH_2CH_2CH_2$ Cl has highest boiling point.

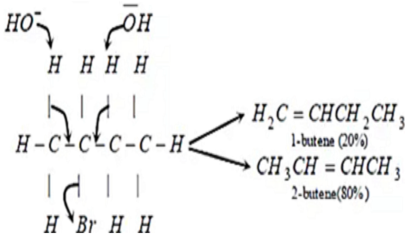
S20. (b) The boiling point of haloalkanes decreases with increase in branching. For the alkyl/aryl group, the boiling points of alkyl halides decrease in order RI>RBr>RCl>RF. This is because with the increase in size and mass of halogen atom, the magnitude increases.

S21. (b) The molecules of water are held together by hydrogen bonds. As the new force of attraction between water and alkyl halides molecules are weaker than the forces of attraction already existing between alkyl halide- alkyl halide molecules and water - water molecules, they cannot form hydrogen bonds with water.

S22. (d) p - Dichlorobenzene is more symmetrical than the o- and m- isomers. So, it fits more closely in the crystal lattice. Therefore more energy is required to break the crystal lattice of p - dichlorobenzene. Therefore p - dichlorobenzene has highest melting point than the 0- and m- isomers. It has melting point of 53.5 degree Celsius.

S23. (b) $C_2H_5Cl + KOH_{(aq)} \longrightarrow C_2H_5OH + KCl$

S24. (a) If the dehydrohalogenation of an alkyl halide can yield more than one alkene, then according to the saytzeff rule, the main product is the most highly substituted alkene.



S25. (b) The best reaction to produce alkyl fluorides is Swarts reaction. This is done by heating an alkyl bromide in the presence of a metallic fluoride such as AgF, CoF_2, Hg_2F_2, SbF_3. This is Swarts reaction.

$$H_3C - Br + AgF \rightarrow H_3C - F + AgBr$$

S26. (a) The product we get after the reaction of chloropropane when treated with alcoholic KOH is prop-1-ene.

S27. (c) $C_2H_5Br + KCN \longrightarrow \underset{\text{Propane nitrile}}{C_2H_5CN} + KBr$

S28. (c) Grignard reagents form via the reaction of an alkyl or aryl halide with magnesium metal. The reaction is conducted by adding the organic halide to a suspension of magnesium in an ethereal solvent, which provides ligands required to stabilize the organomagnesium compound.

The reaction is as follows:

$$R - X + Mg \xrightarrow{\text{dry ether}} \underset{\text{Grignard reagent}}{R - Mg - X}$$

S29. **Cl–CH₂–CH=CH₂**

It is more reactive towards SN Reaction because carbocation formed at allylic position is highly stabilized through resonance.

$$\overset{+}{\text{CH2}}\text{-CH=CH2} \rightarrow \text{CH2-CH-}\overset{+}{\text{CH2}}$$

S30. (c)

S31. (d)

S32. (a) As we come down the group atomic size increases, thus bond length decreases, bond strength increases and acidic strength increases and basic strength increases and nucleophiles having different donor atoms in the same group then nucleophilicity is anti-parallel to basic strength.

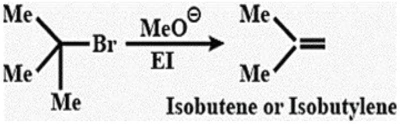
Hence order is $Cl^- < Br^- < I^-$

S33. (c) The reaction is SN2, most suitable solvent should be polar aprotic i.e., DMF.

S34. (c) The C−Cl bond in C_6H_5Cl is shorter than in CH_3Cl and therefore, stronger.
The lone pair on chlorine are dispersed throughout the benzene ring by resonance. This gives the C−Cl bond a double bond character.

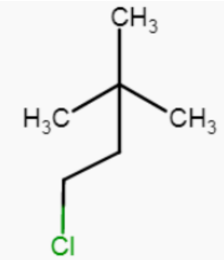
S35. (c) The boiling points of alkyl halides decrease in the order RI> RBr> RCl> RF. This is because as the size of halogen increases, the magnitude of van der Waals forces increase, and hence the boiling point increase.

S36. (b)

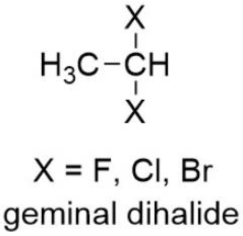


S37. (b) Gem-dihalides are those in which two halogen atoms are attached on the same carbon atom.

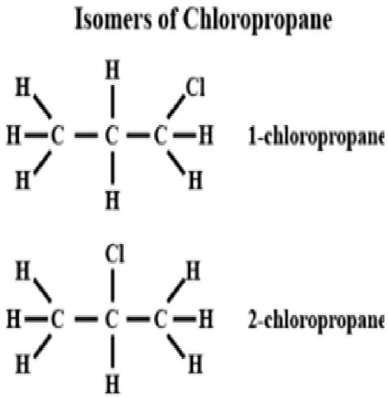
S38. (d) Neo-hexyl chloride is the primary halide. Because in it Cl atom is attached to a primary carbon atom. It is can be seen in its structure.
While others are not primary halides. They are secondary or tertiary halides.



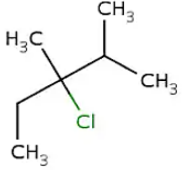
S39. (b) When two halogen atoms are attached to same carbon atom then it is known as gem - dihalide.



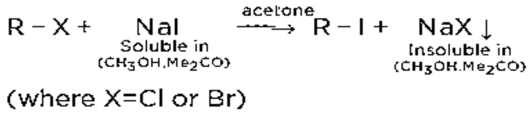
S40. (a) The compound having the molecular formula C_3H_7Cl will have two different structural isomers which are 1-chloropropane and 2-chloropropane.



S41. (b) 3 chloro2,3 dimethylpentene have all carbon are



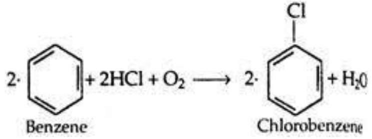
S42. (b) Sodium iodide is soluble in methanol, while NaCl and NaBr are insoluble in methanol



$$R-X+\underset{\substack{\text{Soluble in}\\(CH_3OH, Me_2CO)}}{NaI}\xrightarrow{\text{acetone}}R-I+\underset{\substack{\text{Insoluble in}\\(CH_3OH, Me_2CO)}}{NaX\downarrow}$$

(where X=Cl or Br)

S43. (a) Chlorobenzene is prepared commercially by Raschigs process in which benzene is treated with HCl in presence of oxygen



S44. (c) Given: R-OH → R-Cl
To find catalyst.
Anhyd. AlCl3 is a lewis acid which favours electrophilic substitution rather than nucleophilic substitution. Same happens with FeCl3. But anhyd. ZnCl2 is a polar medium which favour nucleophilic substitution by dissociating H+ and Cl-. So that Cl- can attack on alcohol. Whereas copper act as oxidising agent which oxidised alcohol to aldehyde.

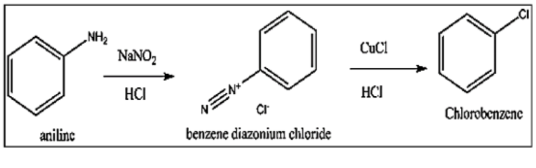
S45. (a) CH3I is a liquid at room temperature and solidifies at −66.5∘C others CH_3F, CH_3CI, CI, CH_3Br and C_2H_5CI are gases at room temperature .

$$CH_3-O-CH_3+PCl_5\rightarrow 2CH_3Cl+POCl_3$$

S46. (b), (c)

$$CH_3CH_2OH+PCl_5\rightarrow CH_3CH_2Cl+HCl+POCl_3$$

S47. (c) Chlorobenzene can be prepared by reacting aniline with nitrous acid followed by heating with cuprous chloride.
The first step is the formation of diazonium salt.
The second step is Sandmeyer reaction in which a diazonium group is replaced by chloro group.



S48. (c) The best method for the conversion of an alcohol into an alkyl chloride is by treating the alcohol with $SOCl_2$ in the presence of pyridine.

$$ROH+SOCl_2\longrightarrow RCl+HCl+SO_2$$

The other products being gases escape leaving behind pure alkyl halide.

S49. **(a)** 2^0 halide means the chlorine should be bonded to the secondary carbon.
So, the compound in which the chlorine is bonded with secondary carbon is 2^0 degree halide.

S50. **(d)** Following steps are followed in naming the compound; $CH_2=CH-CH_2-Cl$
i) The parent chain consists of 3 carbon atoms, thus the root word; -prop is used.
ii) It is an unsaturated hydrocarbon with a double bond, thus the suffix; -ene is used.
iii) Chloro is used as a prefix for the halogen (chlorine) present as a substituent.
iii) Numbering is done from left to right as a double bond is assigned the lowest number.

ASSERTION AND REASONING

S1. **(d)** CCl_4 is used as a fire extinguisher. The dense, non-combustible vapours cover the burning substance and prevents of availability of oxygen round burning material.

S2. **(e)** Aryl halides do not undergo nucleophilic substitution under ordinary conditions. This is due to resonance, because of which the C-Cl bond acquires partial double bond character, hence it becomes shorter and stronger and thus cannot be replaced by nucleophiles. So assertion is false however reason is true.

S3. **(b)** Alkyl benzene is not prepared by Friedel-Craft's alkylation of benzene.

Di, tri alkylated benzenes are also formed in addition to monoalkylated benzene and the separation of these products is difficult.

Alkyl benzene is prepared by Friedel-Craft's alkylation of benzene followed by reduction of acyl benzene to alkyl benzene. This gives mno alkylated product.

Alkyl halides are less reactive than acyl halides.

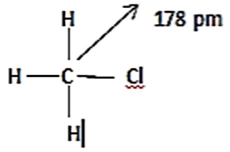
The carbonyl C atom is more electrophilic than C atom of alkyl haliodes.

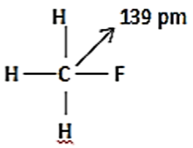
Both Assertion and Reason are correct but Reason is not the correct explanation for Assertion.

S4. **(a)** Carbon tetrachloride rises to atmosphere and deplete the ozone layer. This depletion of ozone layer increases exposure of UV rays to human being which lead to increases of skin cancer, eye disease and disorder with discruption of the immune system.

TRUE/FALSE

S1. **(b)**





C-Cl bond distance in CH_3Cl is 178 pm and C-F bond. CH_3F is 139 pm as dipole moment is a product of distance and charge, dipole moment of CH_3Cl would be greater even if it is lesser electronegative than that of fluorine.
$CH_3Cl > CH_3F$

S2. **(b)** Haloarenes are insoluble in water but soluble in all polar organic solvents like ethyl alcohol, diethyl ether, etc. Their insolubility in water is because of their low polarity which prevents them from forming hydrogen bonds with water molecules and also prevents them from breaking the already existing hydrogen bonds in water.
Therefore, the given statement, Haloarenes are soluble in water, is a FALSE statement.
The correct statement will be: Haloarenes are insoluble in water.

S3. **(b)** p - dichlorobenzene has a symmetrical structure due to which they can pack more closely in the crystal lattice as compared to the ortho and meta isomers. So, the intermolecular forces in the para isomer is stronger and a greater energy is required to break the lattice. So, the p - isomer has a higher melting point than the o - isomer.

Therefore, the given statement, O-dichlorobenzene has a higher melting point than that of p -dichlorobenzene, is a FALSE statement.

The correct statement will be O-dichlorobenzene has a lower melting point than that of p - dichlorobenzene.

HOMEWORK

S1. **(c)** AgCN has a lone pair of electrons on the N atom and attacks from the N side to forms a compound of the type RNC, where R is the alkyl group.

S2. **(b)** Ambident nucleophiles are those that have two nucleophilic centres and can link through any of their two atoms to result in the formation of different compounds.

S3. **(c)** Ammonia reacts with alkyl halides to undergo nucleophilic substitution and form amine and a mineral acid.

S4. **(d)** In the transition state of SN_2 mechanisms, the carbon atoms is simultaneously bonded to the incoming nucleophile and the outgoing group and is hence bonded to five atoms at the same time. Such a geometry is unstable and cannot be isolated.

S5. **(b)** The presence of bulky groups around the C atom has an inhibiting effect on the rate of SN_2 reaction. Since methyl bromide has only three H atoms around the C, it will have a higher rate than ethyl bromide.

S6. **(d)** SN1 reactions follow first order kinetics and take place in two steps, of which the first one is the slowest, rate determining and reversible step.

S7. **(b)** This is an example of a SN_1 reaction, where the rate depends on the concentration of only the alkyl halide, because that will determine the concentration of carbocation formed in the first step.

S8. **(b)** Greater the stability of the carbocation, greater will be the ease of formation from alkyl halide and faster will be the reaction rate.

S9. **(c)** SN1 reactions are carried out in polar protic solvents like water, alcohol and acetic acid. These solvents promote the ionisation step by stabilising the ions by solvation.

S10. **(b)** A stereocenter is an asymmetric carbon that has four different groups attached to it. Propan-2-ol has two methyl groups attached to the carbon.

S11. **(a)** A chiral carbon atom is that which has four different substituent groups attached to it. 2-Bromopentane has one of each H, CH_3, C_3H_7 and Br groups attached to its C atom.

S12. **(b)** 2-Chlorobutane has four different groups attached to the tetrahedral carbon and is chiral as it forms non-superimposable mirror images.

S13. **(a)** Since the product rotates the plane of polarised light in some direction, it cannot be racemic. The product formed is a completely new compound from the original one and may have different or same optical behaviour as compared to the original compound.

S14. **(d)** The OH nucleophile attaches itself opposite to where the halide was present but one the same carbon. This results in an inversion of configuration and hence changes in the direction in which the plane of polarised light rotates.

S15. **(c)** When a haloalkane with a β-hydrogen atom is heated with alc. KOH, it results in a β-elimination reaction to form alkenes.

S16. **(c)** A beta carbon is the carbon atom that is adjacent to the carbon atom that is attached to the halogen. In 2-Bromobutane, the halogen is at position C-2, so the alpha carbon has one carbon on either side, making it two beta carbons

S17. **(c)** When haloalkanes react with magnesium metal in dry ether, special organo-metallic compounds called Grignard reagents are formed.

S18. **(c)** Ethyl magnesium bromide is a Grignard reagent and is highly reactive to any proton giving source because of the polar nature of bonding present in it. It forms hydrocarbons when reacted with water.

S19. **(c)** Alkyl halides react with sodium metal in dry ether to form hydrocarbons that have double the number of carbon atoms as that in the alkyl halide. This is called the Wurtz reaction.

S20. **(b)** Haloarenes form resonating structures in which the carbon-halogen bond acquires a partial double bond character and its cleavage is difficult. Hence, they are less reactive towards nucleophilic substitution reactions.

S21. **(a)** The presence of electron withdrawing groups like NO_2 at ortho and para positions with respect to the halogen, increases the reactivity of the haloarene. Chlorobenzene has no such group and converts to phenol at the highest temperature and pressure.

S22. **(a)** This is the nitration of chlorobenzene which is an electrophilic substitution reaction. The major product is that where the nitro group is present at a para position to Cl.

S23. **(a)** When an aryl halide and alkyl halide and together treated with sodium metal in dry ether, an alkylarene is formed. This is called Wurtz-Fittig reaction.

S24. **(d)** This is the Friedel-Crafts alkylation reaction, where o-Chlorotoluene is the minor product and p-Chlorotoluene is the major product. This is because halogen group is ortho and para directing.

S25. **(a)** The lower members like methyl chloride, methyl bromide and ethyl chloride exist as gases at room temperature. The higher members exist as liquids or solids.

S26. **(a)** As the size of halogen atom increases, the magnitude of van der Waal forces increases, that is why RF has the lowest boiling point as it is the smallest halogen atom with weakest van der Waal attraction.

S27. **(b)** Haloalkanes are polar in nature and have higher intermolecular forces of attraction in terms of dipole-dipole and van der Waal forces. Hence, the boiling points of haloalkanes are higher than their respective hydrocarbons.

S28. **(a)** The boiling points increase with the number of halogen atoms as the molecular masses increase and so do the intermolecular forces of attraction.

S29. **(d)** Para isomers have the highest melting points due to their symmetry and ease with which they can fit into a crystal lattice compared to meta and ortho isomers.

S30. **(d)** Since boiling point increases with increases in molecular mass, chloromethane has the lowest molecular mass and hence the lowest boiling point.

ASSERTION AND REASONING

S1. **(b)** Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas 'phosgene'. Therefore, it is stored in dark bottles, completely filled so that air is kept out.

S2. **(b)** Assertion and reason both are correct statements but reason is not the correct explanation of assertion.

For the same hydrocarbon part, the boiling point depends upon the atomic mass of the halogen atom. Higher the mass of the halogen atom, the higher will be the boiling point.

So, we can say that the boiling point decreases with a decrease in the atomic mass of the halogen atom.

S3. **(d)** Thionyl chloride is best halogen carrier to convert alcohol to alkyl halide because it gives by-products in gaseous state. Thus, we get pure alkyl halide in this reaction.

$$R-OH+SOCl_2 \rightarrow R-Cl+SO_2\uparrow +HCl\uparrow$$

S4. **(a)** The presence of nitro group at ortho or para position increases the reactivity of haloarenes towards nucleophilic substitution because $-NO_2$ group, being an electron-withdrawing group decreases the electron density over the benzene ring.

TRUE/FALSE

S1. **(a)** Haloarenes have sp2 hybridized carbon atoms. So, they are more electronegative and has less tendency to release electrons to the halogen atom compared to haloalkanes which have sp^3 hybridized carbon atom present in haloalkanes. So, the C - X bond in haloarenes is less polar than in haloalkanes.

Therefore, the given statement, The C - X bond in haloarenes is less polar than in haloalkanes, is a TRUE statement.

S2. **(b)** The presence of electron withdrawing groups like $-NO_2$ at ortho and para positions to the halogen atom greatly activates the halogen towards nucleophilic substitution reaction. Greater the number of $-NO_2$ groups at such positions, greater will be the reactivity of the haloarenes towards nucleophilic substitution reaction.

Therefore, the given statement, An increase in the number of $-NO_2$ groups at o - and p - positions decreases the reactivity of chlorobenzene towards nucleophilic substitution reactions, is a FALSE statement.

The correct statement will be: An increase in the number of $-NO_2$ groups at o - and p - positions increases the reactivity of chlorobenzene towards nucleophilic substitution reactions.

S3. **(a)** Iodoform test is given by all methyl ketones and is an important test to detect the presence of CH_3 CO^- group in a compound. When a compound containing methyl ketone is heating with iodine and an aqueous solution of sodium carbonate or sodium hydroxide, a yellow coloured precipitate of iodoform is obtained. The reaction involves oxidation, iodination and hydrolysis.