

Haloalkanes and Haloarenes

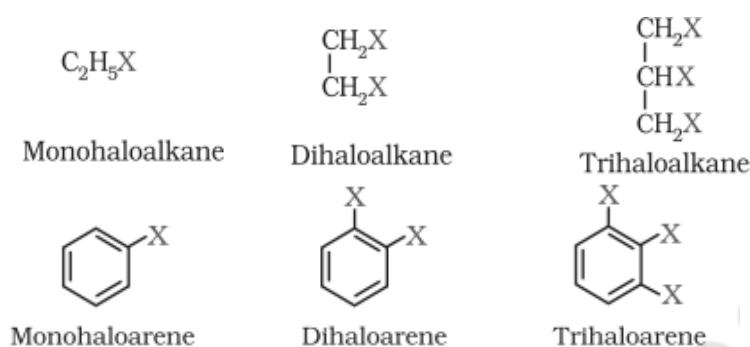
The replacement of hydrogen atom(s) in an aliphatic or aromatic hydrocarbon by halogen atom(s) results in the formation of alkyl halide (haloalkane) and aryl halide (haloarene), respectively.

Haloalkanes contain halogen atom(s) attached to the sp^3 hybridised carbon atom of an alkyl group whereas haloarenes contain halogen atom(s) attached to sp^2 hybridised carbon atom(s) of an aryl group.

Classification:

- **On the Basis of Number of Halogen Atoms:**

These may be classified as mono, di, or polyhalogen (tri-, tetra-, etc.) compounds depending on whether they contain one, two or more halogen atom(s) in their structures. For example,

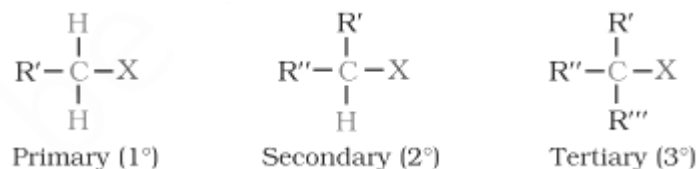


- **On the basis of hybridization of carbon to which halogen is attached:**

I. Compounds Containing sp^3 C—X Bond (X = F, Cl, Br, I):

(a) **Alkyl halides or haloalkanes (R—X):**

They form a homologous series represented by $C_nH_{2n+1}X$. They are further classified as primary, secondary or tertiary according to the nature of carbon to which halogen is attached.



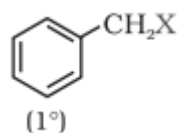
(b) **Allylic halides :**

These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom adjacent to carbon-carbon double bond (C=C) i.e. to an allylic carbon

$CH_2=CH-CH_2-X$ (Allyl Halide)

(c) **Benzylic halides:**

These are the compounds in which the halogen atom is bonded to an sp^3 -hybridised carbon atom attached to an aromatic ring.



(Benzyl Halide)

II. Compounds Containing sp^2 C—X Bond:

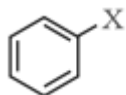
(a) Vinylic halides :

These are the compounds in which the halogen atom is bonded to a sp^2 -hybridised carbon atom of a carbon-carbon double bond ($C = C$).



(b) Aryl halides:

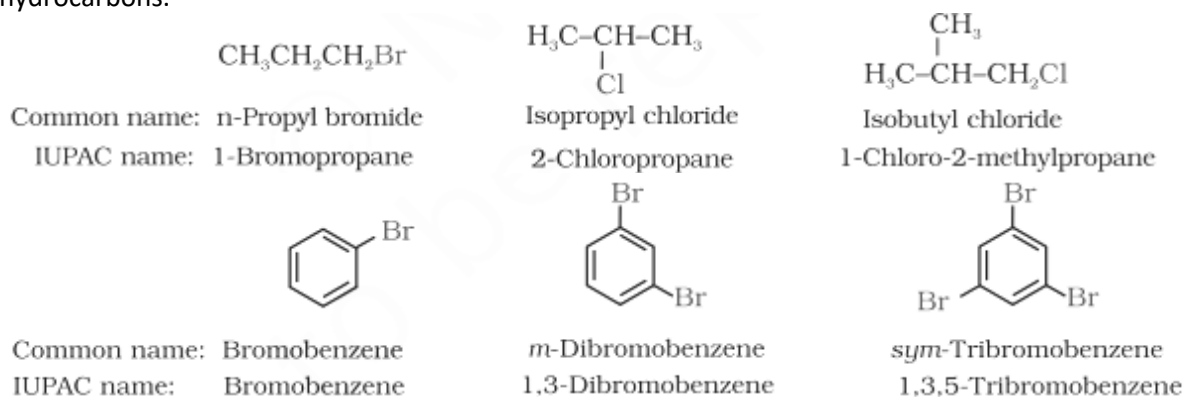
These are the compounds in which the halogen atom is directly bonded to the sp^2 -hybridised carbon atom of an aromatic ring.



(Halobenzene)

Nomenclature:

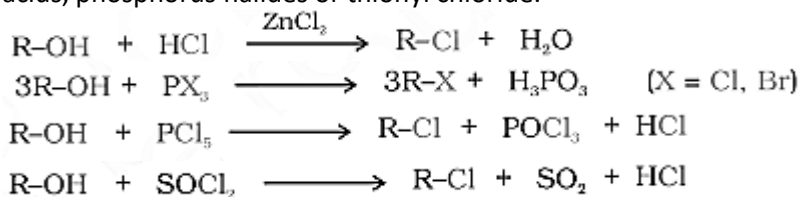
The common names of alkyl halides are derived by naming the alkyl group followed by the name of halide. In the IUPAC system of nomenclature, alkyl halides are named as halosubstituted hydrocarbons.



Methods of Preparation of Haloalkanes:

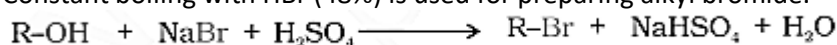
I. From Alcohols:

The hydroxyl group of an alcohol is replaced by halogen on reaction with concentrated halogen acids, phosphorus halides or thionyl chloride.



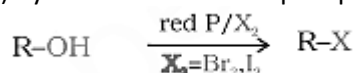
Thionyl chloride is preferred because in this reaction alkyl halide is formed along with gases SO_2 and HCl . The two gaseous products are escapable, hence, the reaction gives pure alkyl halides. The reactions of primary and secondary alcohols with HCl require the presence of a catalyst, $ZnCl_2$. With tertiary alcohols, the reaction is conducted by simply shaking the alcohol with concentrated HCl at room temperature.

Constant boiling with HBr (48%) is used for preparing alkyl bromide.



Good yields of $R-I$ may be obtained by heating alcohols with sodium or potassium iodide in 95% orthophosphoric acid.

Phosphorus tribromide and triiodide are usually generated in situ (produced in the reaction mixture) by the reaction of red phosphorus with bromine and iodine respectively.

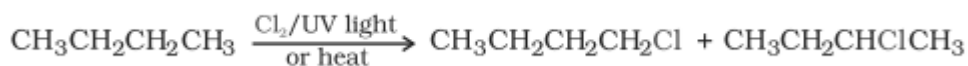


The order of reactivity of alcohols with a given haloacid is $3^\circ > 2^\circ > 1^\circ$.

The above methods are not applicable for the preparation of aryl halides because the carbon-oxygen bond in phenols has a partial double bond character and is difficult to break being stronger than a single bond.

2. From Hydrocarbons:

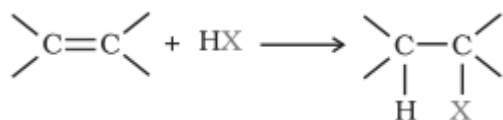
(I) From alkanes by free radical halogenation:



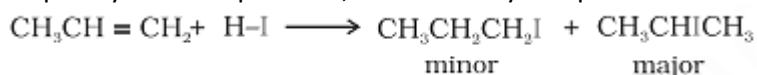
From alkanes by free radical halogenation Free radical chlorination or bromination of alkanes gives a complex mixture of isomeric mono- and polyhaloalkanes, which is difficult to separate as pure compounds. Consequently, the yield of any single compound is low.

(II) From alkenes:

(i) Addition of hydrogen halides: An alkene is converted to corresponding alkyl halide by reaction with hydrogen chloride, hydrogen bromide or hydrogen iodide.

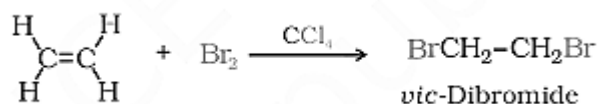


Propene yields two products, however only one predominates as per Markovnikov's rule.



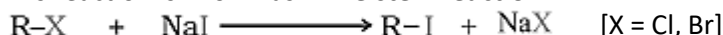
(ii) Addition of halogens:

The addition results in the synthesis of vic-dibromides, which are colourless.



3. By Halogen Exchange reaction:

Alkyl iodides are often prepared by the reaction of alkyl chlorides/ bromides with NaI in dry acetone. This reaction is known as **Finkelstein reaction**.



NaCl or NaBr thus formed is precipitated in dry acetone. It facilitates the forward reaction according to Le Chatelier's Principle.

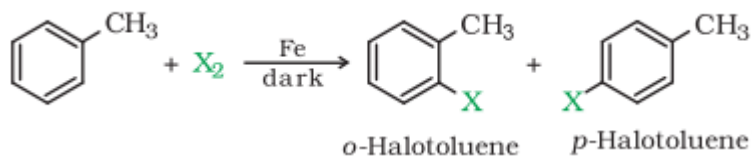
The synthesis of alkyl fluorides is best accomplished by heating an alkyl chloride/bromide in the presence of a metallic fluoride such as AgF, Hg₂F₂, CoF₂ or SbF₃. The reaction is termed as **Swarts reaction**.



Preparation of Haloarenes:

(i) From hydrocarbons by electrophilic substitution :

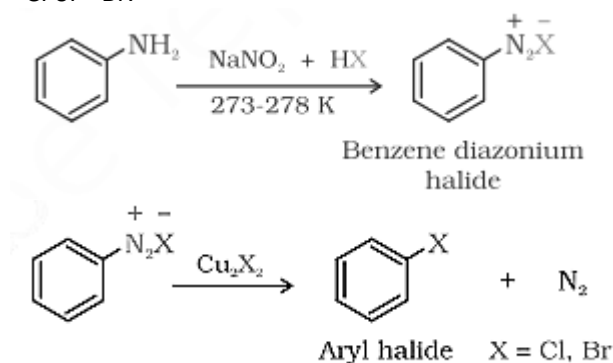
Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts like iron or iron(III) chloride which act as halogen carrier.



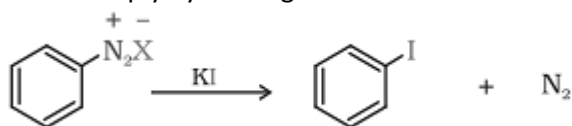
The ortho and para isomers can be easily separated due to large difference in their melting points. Reactions with iodine are reversible in nature and require the presence of an oxidising agent (HNO_3 , HIO_4) to oxidise the HI formed during iodination. Fluoro compounds are not prepared by this method due to high reactivity of fluorine.

(ii) From amines by Sandmeyer's reaction :

When a primary aromatic amine, dissolved or suspended in cold aqueous mineral acid, is treated with sodium nitrite, a diazonium salt is formed. Mixing the solution of freshly prepared diazonium salt with cuprous chloride or cuprous bromide results in the replacement of the diazonium group by $-\text{Cl}$ or $-\text{Br}$.



Replacement of the diazonium group by iodine does not require the presence of cuprous halide and is done simply by shaking the diazonium salt with potassium iodide.

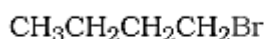


Melting and boiling points:

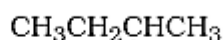
Molecules of organic halogen compounds are generally polar. Due to greater polarity as well as higher molecular mass as compared to the parent hydrocarbon, the intermolecular forces of attraction (dipole-dipole and van der Waals) are stronger in the halogen derivatives. That is why the boiling points of chlorides, bromides and iodides are considerably higher than those of the hydrocarbons of comparable molecular mass.

The attractions get stronger as the molecules get bigger in size and have more electrons. For the same alkyl group, the boiling points of alkyl halides decrease in the order: $\text{RI} > \text{RBr} > \text{RCl} > \text{RF}$. This is because with the increase in size and mass of halogen atom, the magnitude of van der Waal forces increases.

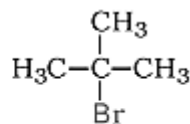
The boiling points of isomeric haloalkanes decrease with increase in branching. For example, 2-bromo-2-methylpropane has the lowest boiling point among the three isomers.



b.p./K 375

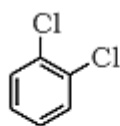


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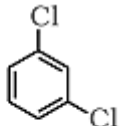
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Boiling points of isomeric dihalobenzenes are very nearly the same. However, the para-isomers are high melting as compared to their ortho and meta-isomers. It is due to symmetry of para-isomers that fits in crystal lattice better as compared to ortho- and meta-isomers.



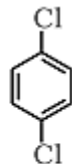
b.p./K 453

m.p./K 256



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Density :

Bromo, iodo and polychloro derivatives of hydrocarbons are heavier than water. The density increases with increase in number of carbon atoms, halogen atoms and atomic mass of the halogen atoms.

Solubility:

The haloalkanes are very slightly soluble in water. In order to dissolve haloalkane in water, energy is required to overcome the attractions between the haloalkane molecules and break the hydrogen bonds between water molecules. Less energy is released when new attractions are set up between the haloalkane and the water molecules as these are not as strong as the original hydrogen bonds in water. As a result, the solubility of haloalkanes in water is low. However, haloalkanes tend to dissolve in organic solvents because the new intermolecular attractions between haloalkanes and solvent molecules have much the same strength as the ones being broken in the separate haloalkane and solvent molecules.

Chemical Reactions:

The reactions of haloalkanes may be divided into the following categories:

1. Nucleophilic substitution
2. Elimination reactions
3. Reaction with metals.

1. Nucleophilic substitution :

Nucleophiles are electron rich species. Therefore, they attack at that part of the substrate molecule which is electron deficient. The reaction in which a nucleophile replaces already existing nucleophile in a molecule is called nucleophilic substitution reaction. Haloalkanes are substrate in these reactions. In this type of reaction, a nucleophile reacts with haloalkane (the substrate) having a partial positive charge on the carbon atom bonded to halogen. A substitution reaction takes place and halogen atom, called leaving group departs as halide ion. Since the substitution reaction is initiated by a nucleophile, it is called nucleophilic substitution reaction.



Some important examples are as follows:

Reagent	Nucleophile (Nu ⁻)	Substitution product R-Nu	Class of main product
NaOH (KOH)	HO ⁻	ROH	Alcohol
H ₂ O	H ₂ O	ROH	Alcohol
NaOR'	R'O ⁻	ROR'	Ether
NaI	I ⁻	R—I	Alkyl iodide
NH ₃	NH ₃	RNH ₂	Primary amine
R'NH ₂	R'NH ₂	RNHR'	Sec. amine
R'R''NH	R'R''NH	RNR'R''	Tert. amine
KCN	$\text{C}\equiv\text{N:}$	RCN	Nitrile (cyanide)
AgCN	Ag-CN:	RNC (isocyanide)	Isonitrile
KNO ₂	O=N—O	R—O—N=O	Alkyl nitrite
AgNO ₂	Ag—O—N=O	R—NO ₂	Nitroalkane
R'COOAg	R'COO ⁻	R'COOR	Ester
LiAlH ₄	H	RH	Hydrocarbon
R'-M ⁺	R ⁻	RR'	Alkane

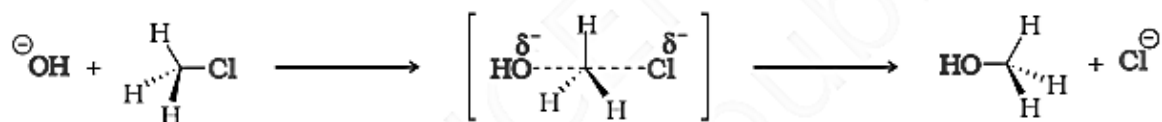
Groups like cyanides and nitrites possess two nucleophilic centres and are called ambident nucleophiles. Actually cyanide group is a hybrid of two contributing structures and therefore can act as a nucleophile in two different ways [$\text{C}\equiv\text{N:} \leftrightarrow \text{:C}=\text{N:}$], i.e., linking through carbon atom resulting in alkyl cyanides and through nitrogen atom leading to isocyanides. Similarly nitrite ion also represents an ambident nucleophile with two different points of linkage [$\text{O}=\text{N}-\ddot{\text{O}} \leftrightarrow \ddot{\text{O}}-\text{N}=\text{O}$]. The linkage through oxygen results in alkyl nitrites while through nitrogen atom, it leads to nitroalkanes.

- KCN is predominantly ionic and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through carbon atom and not through nitrogen atom since C—C bond is more stable than C—N bond. However, AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

Mechanism:

(a) Substitution nucleophilic bimolecular (S_N2):

The reaction between CH₃Cl and hydroxide ion to yield methanol and chloride ion follows a second order kinetics, i.e., the rate depends upon the concentration of both the reactants.



Here, two processes take place simultaneously in a single step and no intermediate is formed, only a transition state is formed.

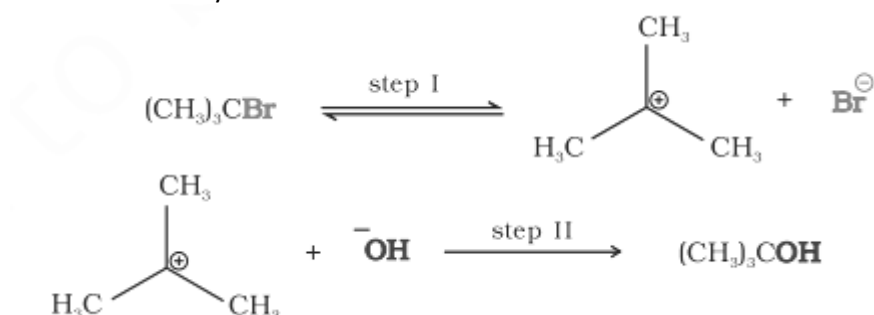
In transition state all the three C-H bonds are in the same plane and the attacking and leaving nucleophiles are partially attached to the carbon(sp² hybridised). Clearly, the reaction leads to the inversion of configuration (**Walden inversion**).

Since this reaction requires the approach of the nucleophile to the carbon bearing the leaving group, the presence of bulky substituents on or near the carbon atom have a dramatic inhibiting effect. Of the simple alkyl halides, methyl halides react most rapidly in S_N2 reactions because there are only three small hydrogen atoms. Tertiary halides are the least reactive because bulky groups hinder the approaching nucleophiles. Thus the order of reactivity followed is:

Primary halide > Secondary halide > Tertiary halide.

(b) Substitution nucleophilic unimolecular (S_N1) :

S_N1 reactions are generally carried out in polar protic solvents (like water, alcohol, acetic acid, etc.). The reaction between tertbutyl bromide and hydroxide ion yields tert-butyl alcohol and follows the first order kinetics, i.e., the rate of reaction depends upon the concentration of only one reactant, which is tert- butyl bromide.

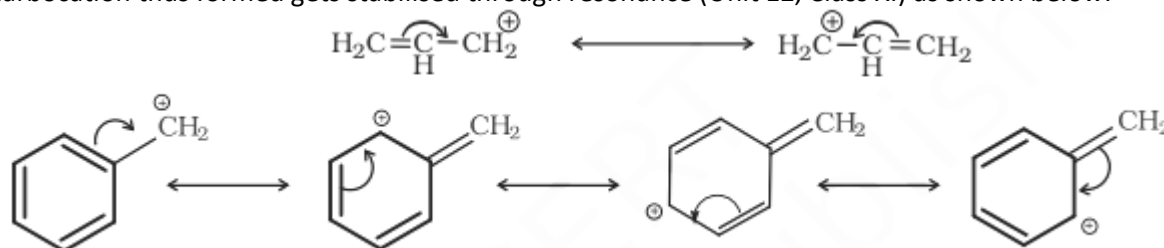


Step I is the slowest and reversible. Since the rate of reaction depends upon the slowest step, the rate of reaction depends only on the concentration of alkyl halide and not on the concentration of hydroxide ion.

Further, greater the stability of carbocation, greater will be its ease of formation from alkyl halide and faster will be the rate of reaction. In case of alkyl halides, 3° alkyl halides undergo S_N1 reaction very fast because of the high stability of 3° carbocations. Thus the order of reactivity followed is:

Primary halide < Secondary halide < Tertiary halide.

For the same reasons, **allylic** and **benzylic** halides show high reactivity towards the S_N1 reaction. The carbocation thus formed gets stabilised through resonance (Unit 12, Class XI) as shown below:



For a given alkyl group, the reactivity of the halide, R-X, follows the same order in both the mechanisms $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$.

(c) Stereochemical aspects of nucleophilic substitution reactions:

In order to understand the stereochemical aspects of substitution reactions, we need to learn some basic stereochemical principles and notations (optical activity, chirality, retention, inversion, racemisation, etc.).

(i) Optical activity: Plane of plane polarised light produced by passing ordinary light through Nicol prism is rotated when it is passed through the solutions of certain compounds. Such compounds are called **optically active compounds**. The angle by which the plane polarised light is rotated is measured by an instrument called polarimeter. If the compound rotates the plane of plane polarised light to the right, i.e., clockwise direction, it is called **dextrorotatory** (Greek for right rotating) or the d-form and is indicated by placing a positive (+) sign before the degree of rotation. If the light is rotated towards left (anticlockwise direction), the compound is said to be **laevo-rotatory** or the l-

form and a negative (–) sign is placed before the degree of rotation. Such (+) and (–) isomers of a compound are called optical isomers and the phenomenon is termed as optical isomerism.

(ii) Molecular asymmetry, chirality and enantiomers: The observation of Louis Pasteur (1848) that crystals of certain compounds exist in the form of mirror images laid the foundation of modern stereochemistry. He demonstrated that aqueous solutions of both types of crystals showed optical rotation, equal in magnitude (for solution of equal concentration) but opposite in direction. He believed that this difference in optical activity was associated with the three dimensional arrangements of atoms in the molecules (configurations) of two types of crystals.

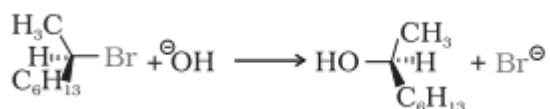
Dutch scientist, J. Van't Hoff and French scientist, C. Le Bel in the same year (1874), independently argued that the spatial arrangement of four groups (valencies) around a central carbon is tetrahedral and if all the substituents attached to that carbon are different, the mirror image of the molecule is not superimposed (overlapped) on the molecule; such a carbon is called asymmetric carbon or stereocentre. The resulting molecule would lack symmetry and is referred to as asymmetric molecule. The asymmetry of the molecule along with non superimposability of mirror images is responsible for the optical activity in such organic compounds.

The objects which are nonsuperimposable on their mirror image (like a pair of hands) are said to be **chiral** and this property is known as chirality. Chiral molecules are optically active, while the objects, which are, superimposable on their mirror images are called **achiral**. These molecules are optically inactive.

A mixture containing two enantiomers in equal proportions will have zero optical rotation, as the rotation due to one isomer will be cancelled by the rotation due to the other isomer. Such a mixture is known as racemic mixture or racemic modification.

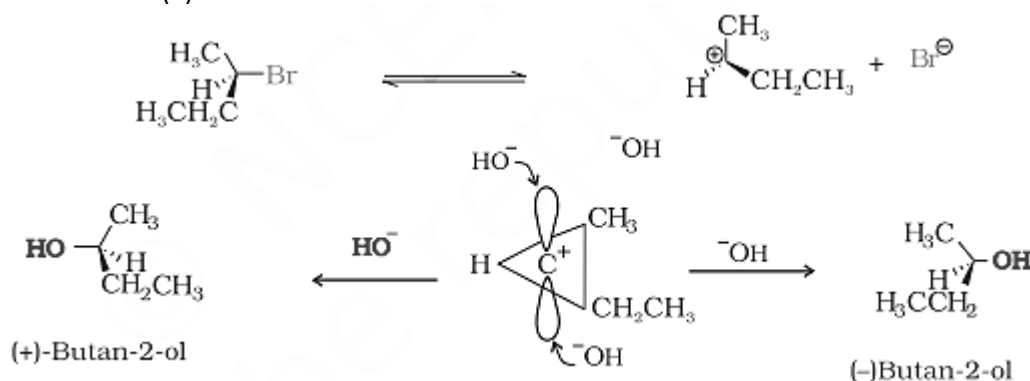
Now let us have a fresh look at S_N1 and S_N2 mechanisms by taking examples of optically active alkyl halides.

S_N2 reactions of optically active halides are accompanied by inversion of configuration because the nucleophile attaches itself on the side opposite to the one where the halogen atom is present. For example, When (–)-2-bromooctane is allowed to react with sodium hydroxide, (+)-octan-2-ol is formed with the –OH group occupying the position opposite to what bromide had occupied.



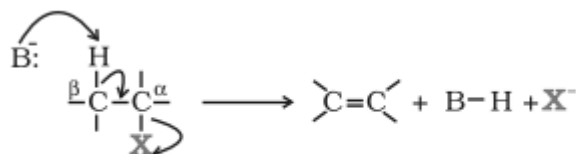
In case of optically active alkyl halides, S_N1 reactions are accompanied by racemisation.

Here the carbocation formed in the slow step being sp^2 hybridised is planar (achiral). The attack of the nucleophile may be accomplished from either side of the plane of carbocation resulting in a mixture of products, one having the same configuration (the –OH attaching on the same position as halide ion) and the other having opposite configuration (the –OH attaching on the side opposite to halide ion). This may be illustrated by hydrolysis of optically active 2-bromobutane, which results in the formation of (±)-butan-2-ol.



2. Elimination reactions:

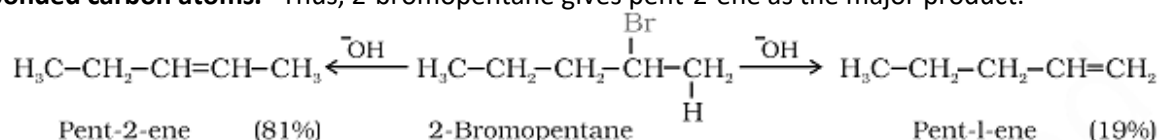
When a haloalkane with β -hydrogen atom is heated with alcoholic solution of potassium hydroxide, there is elimination of hydrogen atom from β -carbon and a halogen atom from the α -carbon atom.



B=Base ; X=Leaving group

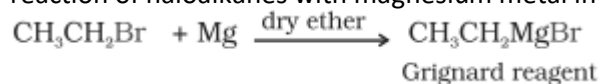
As a result, an alkene is formed as a product. Since β -hydrogen atom is involved in elimination, it is often called β -elimination.

If there is possibility of formation of more than one alkene due to the availability of more than one β -hydrogen atoms, usually one alkene is formed as the major product. These form part of a pattern first observed by Russian chemist, Alexander Zaitsev (also pronounced as Saytzeff) who in 1875 formulated a rule which can be summarised as “**in dehydrohalogenation reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.**” Thus, 2-bromopentane gives pent-2-ene as the major product.

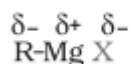


3. Reaction with metals :

Most organic chlorides, bromides and iodides react with certain metals to give compounds containing carbon-metal bonds. Such compounds are known as organo-metallic compounds. An important class of organo-metallic compounds discovered by Victor Grignard in 1900 is alkyl magnesium halide, RMgX , referred as Grignard Reagents. These reagents are obtained by the reaction of haloalkanes with magnesium metal in dry ether.



In the Grignard reagent, the carbon-magnesium bond is covalent but highly polar, with carbon pulling electrons from electropositive magnesium; the magnesium halogen bond is essentially ionic.



Grignard reagents are highly reactive and react with any source of proton to give hydrocarbons. Even water, alcohols, amines are sufficiently acidic to convert them to corresponding hydrocarbons



It is therefore necessary to avoid even traces of moisture from a Grignard reagent. That is why reaction is carried out in dry ether. On the other hand, this could be considered as one of the methods for converting halides to hydrocarbons.

Wurtz reaction:

Alkyl halides react with sodium in dry ether to give hydrocarbons containing double the number of carbon atoms present in the halide. This reaction is known as Wurtz reaction.

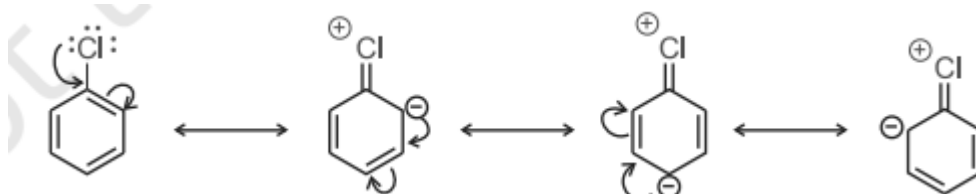


Reactions of Haloarenes:

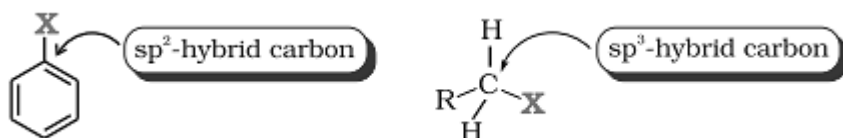
1. Nucleophilic substitution:

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

(i) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π -electrons of the ring and the following resonating structures are possible. C—Cl bond acquires a partial double bond character due to resonance. As a result, the bond cleavage in haloarene is difficult than haloalkane and therefore, they are less reactive towards nucleophilic substitution reaction.



(ii) Difference in hybridisation of carbon atom in C—X bond: In haloalkane, the carbon atom attached to halogen is sp^3 hybridised while in case of haloarene, the carbon atom attached to halogen is sp^2 -hybridised. The sp^2 hybridised carbon with a greater s-character is more electronegative and can hold the electron pair of C—X bond more tightly than sp^3 -hybridised carbon in haloalkane with less s-character. Thus, C—Cl bond length in haloalkane is 177pm while in haloarene is 169 pm. Since it is difficult to break a shorter bond than a longer bond, therefore, haloarenes are less reactive than haloalkanes towards nucleophilic substitution reaction.

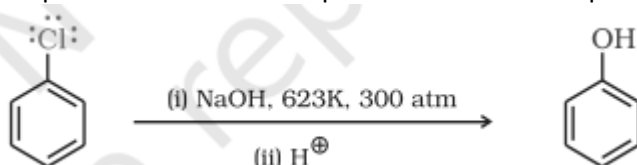


(iii) Instability of phenyl cation: In case of haloarenes, the phenyl cation formed as a result of self-ionisation will not be stabilised by resonance and therefore, SN_1 mechanism is ruled out.

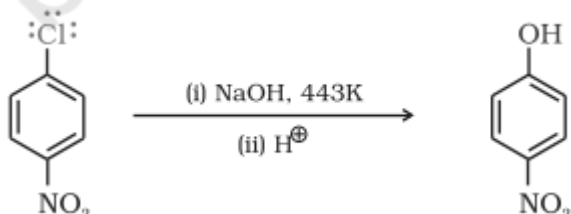
(iv) Because of the possible repulsion, it is less likely for the electron rich nucleophile to approach electron rich arenes.

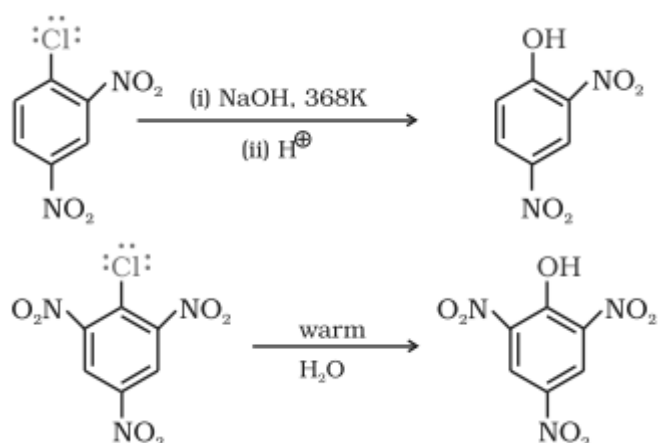
Replacement by hydroxyl group:

Chlorobenzene can be converted into phenol by heating in aqueous sodium hydroxide solution at a temperature of 623K and a pressure of 300 atmospheres.



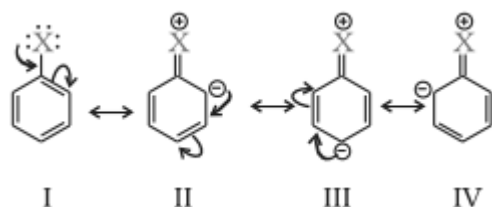
The presence of an electron withdrawing group ($-NO_2$) at ortho- and para-positions increases the reactivity of haloarenes.





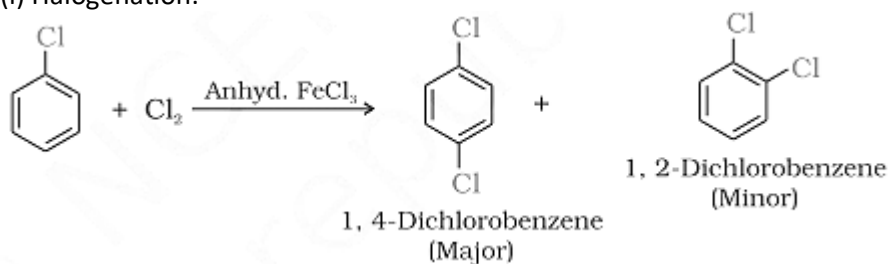
2. Electrophilic substitution reactions:

Haloarenes undergo the usual electrophilic reactions of the benzene ring such as halogenation, nitration, sulphonation and Friedel-Crafts reactions. Halogen atom besides being slightly deactivating is o, p-directing; therefore, further substitution occurs at ortho- and para positions with respect to the halogen atom. The o, p-directing influence of halogen atom can be easily understood from the the resonating structures of halobenzene as shown:

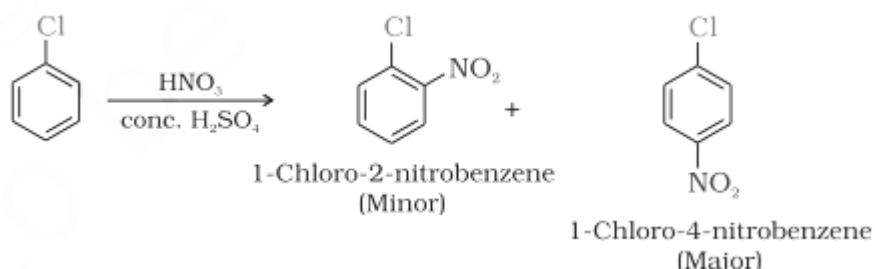


Due to resonance, the electron density increases more at ortho- and para-positions than at meta-positions. Further, the halogen atom because of its $-I$ effect has some tendency to withdraw electrons from the benzene ring. As a result, the ring gets somewhat deactivated as compared to benzene and hence the electrophilic substitution reactions in haloarenes occur slowly and require more drastic conditions as compared to those in benzene.

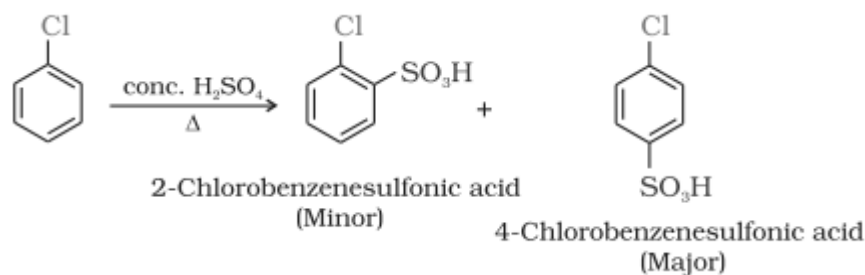
(i) Halogenation:



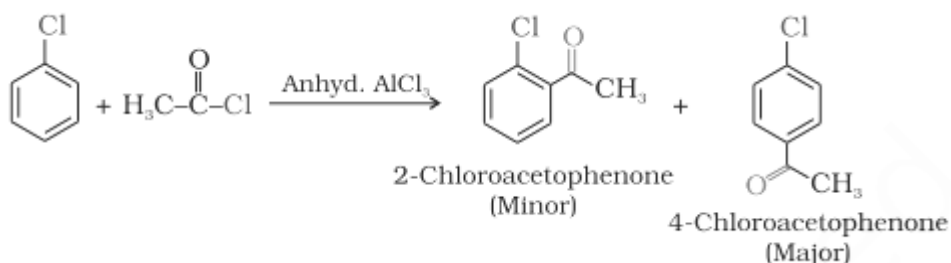
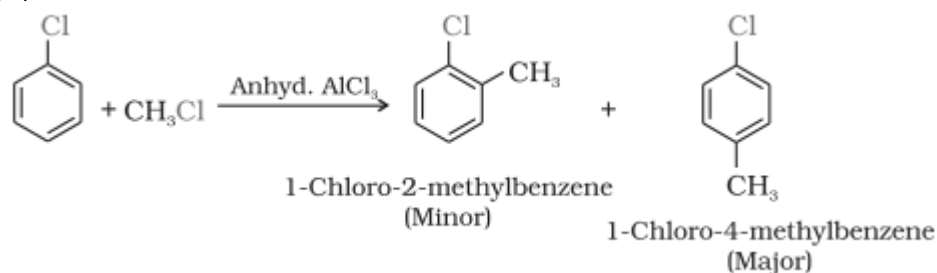
(ii) Nitration:



(iii) Sulphonation:

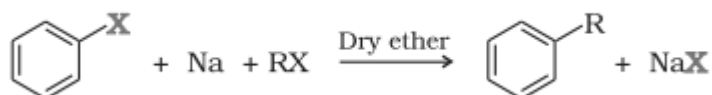


(iv) Friedel-Crafts reaction:



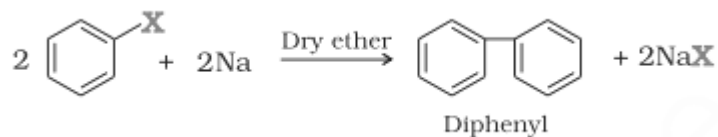
3. Reaction with metals:

Wurtz-Fittig reaction: A mixture of an alkyl halide and aryl halide gives an alkylarene when treated with sodium in dry ether and is called Wurtz-Fittig reaction.



Fittig reaction:

Aryl halides also give analogous compounds when treated with sodium in dry ether, in which two aryl groups are joined together. It is called Fittig reaction.

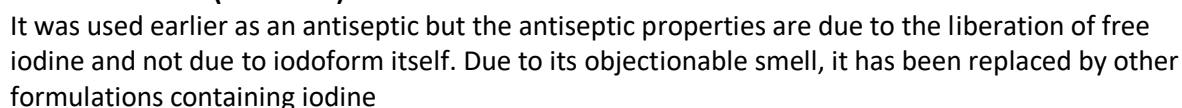
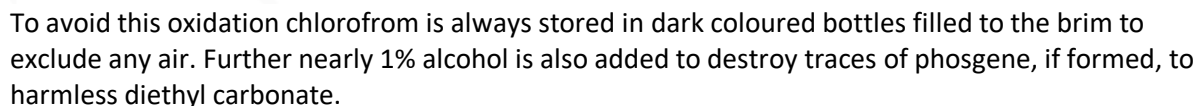


Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Many of these compounds are useful in industry and agriculture. Some polyhalogen compounds are described in this section.

Dichloromethane is widely used as a solvent as a paint remover, as a propellant in aerosols, and as a process solvent in the manufacture of drugs. It is also used as a metal cleaning and finishing solvent. Methylene chloride harms the human central nervous system. Exposure to lower levels of methylene chloride in air can lead to slightly impaired hearing and vision. Higher levels of methylene chloride in air cause dizziness, nausea, tingling and numbness in the fingers and toes. In humans, direct skin contact with methylene chloride causes intense burning and mild redness of the skin. Direct contact with the eyes can burn the cornea.

Chemically, chloroform is employed as a solvent for fats, alkaloids, iodine and other substances. The major use of chloroform today is in the production of the freon refrigerant R-22. It was once used as a general anaesthetic in surgery but has been replaced by less toxic, safer anaesthetics, such as ether. As might be expected from its use as an anaesthetic, inhaling chloroform vapours depresses the central nervous system. Breathing about 900 parts of chloroform per million parts of air (900 parts per million) for a short time can cause dizziness, fatigue, and headache. Chronic chloroform exposure may cause damage to the liver (where chloroform is metabolised to phosgene) and to the kidneys, and some people develop sores when the skin is immersed in chloroform.

Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas, carbonyl chloride, also known as phosgene. It is therefore stored in closed dark coloured bottles completely filled so that air is kept out.



Tetrachloromethane (Carbon tetrachloride):

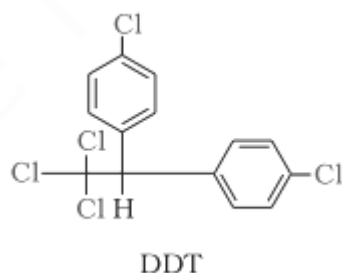
It is produced in large quantities for use in the manufacture of refrigerants and propellants for aerosol cans. It is also used as feedstock in the synthesis of chlorofluorocarbons and other chemicals, pharmaceutical manufacturing, and general solvent use. Until the mid 1960s, it was also widely used as a cleaning fluid, both in industry, as a degreasing agent, and in the home, as a spot remover and as fire extinguisher. There is some evidence that exposure to carbon tetrachloride causes liver cancer in humans. The most common effects are dizziness, light headedness, nausea and vomiting, which can cause permanent damage to nerve cells. In severe cases, these effects can lead rapidly to stupor, coma, unconsciousness or death. Exposure to CCl₄ can make the heart beat irregularly or stop. The chemical may irritate the eyes on contact. When carbon tetrachloride is released into the air, it rises to the atmosphere and depletes the ozone layer. Depletion of the ozone layer is believed to increase human exposure to ultraviolet rays, leading to increased skin cancer, eye diseases and disorders, and possible disruption of the immune system.

Freons:

The chlorofluorocarbon compounds of methane and ethane are collectively known as freons. They are extremely stable, unreactive, non-toxic, noncorrosive and easily liquefiable gases. Freon 12 (CCl₂F₂) is one of the most common freons in industrial use. It is manufactured from tetrachloromethane by Swarts reaction. These are usually produced for aerosol propellants, refrigeration and air conditioning purposes. By 1974, total freon production in the world was about 2 billion pounds annually. Most freon, even that used in refrigeration, eventually makes its way into the atmosphere where it diffuses unchanged into the stratosphere. In stratosphere, freon is able to initiate radical chain reactions that can upset the natural ozone balance.

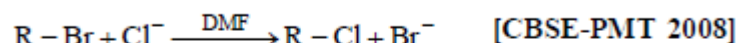
p,p'-Dichlorodiphenyltrichloroethane(DDT):

DDT, the first chlorinated organic insecticides, was originally prepared in 1873, but it was not until 1939 that Paul Muller of Geigy Pharmaceuticals in Switzerland discovered the effectiveness of DDT as an insecticide. Paul Muller was awarded the Nobel Prize in Medicine and Physiology in 1948 for this discovery. The use of DDT increased enormously on a worldwide basis after World War II, primarily because of its effectiveness against the mosquito that spreads malaria and lice that carry typhus. However, problems related to extensive use of DDT began to appear in the late 1940s. Many species of insects developed resistance to DDT, and it was also discovered to have a high toxicity towards fish. The chemical stability of DDT and its fat solubility compounded the problem. DDT is not metabolised very rapidly by animals; instead, it is deposited and stored in the fatty tissues. If ingestion continues at a steady rate, DDT builds up within the animal over time. The use of DDT was banned in the United States in 1973, although it is still in use in some other parts of the world.



Important questions(MCQ):

1. In a S_N2 substitution reaction of the type



which one of the following has the highest relative rate ?

- (a) $CH_3-CH_2-CH_2Br$ (b) $CH_3-\underset{\substack{| \\ CH_3}}{CH}-CH_2Br$
- (c) $CH_3-\underset{\substack{| \\ CH_3}}{\overset{\substack{CH_3 \\ |}}{C}}-CH_2Br$ (d) CH_3CH_2Br

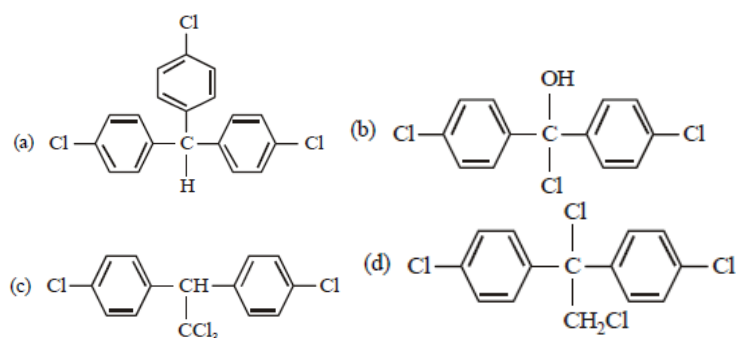
2. Which of the following reactions is an example of nucleophilic substitution reaction? [CBSE-PMT 2009]

- (a) $2RX + 2Na \rightarrow R-R + 2NaX$
 (b) $RX + H_2 \rightarrow RH + HX$
 (c) $RX + Mg \rightarrow RMgX$
 (d) $RX + KOH \rightarrow ROH + KX$

3. Benzene reacts with CH_3Cl in the presence of anhydrous $AlCl_3$ to form: [CBSE-PMT 2009]

- (a) chlorobenzene (b) benzylchloride
 (c) xylene (d) toluene

4. Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces : [CBSE-PMT 2009]



5. The reaction of toluene with Cl_2 in presence of $FeCl_3$ gives 'X' and reaction in presence of light gives 'Y'. Thus, 'X' and 'Y' are : [CBSE-PMT 2010]

- (a) X = Benzal chloride, Y = o-Chlorotoluene
 (b) X = m-Chlorotoluene, Y = p-Chlorotoluene
 (c) X = o-and p-Chlorotoluene,
 Y = Trichloromethylbenzene
 (d) X = Benzyl chloride, Y = m-Chlorotoluene

6. Which one is most reactive towards S_N1 reaction ? [CBSE-PMT 2010]

- (a) $C_6H_5CH(C_6H_5)Br$ (c) $C_6H_5C(CH_3)(C_6H_5)Br$
(b) $C_6H_5CH(CH_3)Br$ (d) $C_6H_5CH_2Br$

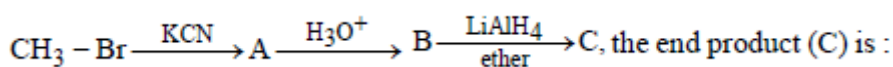
7. Consider the reactions : [CBSE-PMT 2011 M]

- (i) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5OH} (CH_3)_2CH-CH_2OC_2H_5 + HBr$
(ii) $(CH_3)_2CH-CH_2Br \xrightarrow{C_2H_5O^-} (CH_3)_2CH-CH_2OC_2H_5 + Br^-$

The mechanisms of reactions (i) and (ii) are respectively :

- (a) S_N1 and S_N2 (b) S_N1 and S_N1
(c) S_N2 and S_N2 (d) S_N2 and S_N1

8. In the following sequence of reactions [CBSE-PMT 2012]



- (a) acetone (b) methane
(c) acetaldehyde (d) ethyl alcohol
9. Bottles containing C_6H_5I and $C_6H_5CH_2I$ lost their original labels. They were labelled A and B for testing. A and B were separately taken in test tubes and boiled with NaOH solution. The end solution in each tube was made acidic with dilute HNO_3 and then some $AgNO_3$ solution was added. Substance B gave a yellow precipitate. Which one of the following statements is true for this experiment ? [AIEEE 2003]
- (a) A was $C_6H_5CH_2I$ (c) Addition of HNO_3 was unnecessary
(b) B was C_6H_5I (d) A was C_6H_5I

10. The compound formed on heating chlorobenzene with chloral in the presence of concentrated sulphuric acid, is [AIEEE 2004]

- (a) freon (b) DDT
(c) gammexene (d) hexachloroethane
11. Tertiary alkyl halides are practically inert to substitution by S_N2 mechanism because of [AIEEE 2005]
- (a) steric hindrance (b) inductive effect
(c) instability (d) insolubility

12. Alkyl halides react with dialkyl copper reagents to give [AIEEE 2005]

- (a) alkenyl halides (b) alkanes
(c) alkyl copper halides (d) alkenes
13. Which types of isomerism is shown by 2, 3-dichlorobutane? [AIEEE 2005]
- (a) Structural (b) Geometric
(c) Optical (d) Diastereo

14. Elimination of bromine from 2-bromobutane results in the formation of – [AIEEE 2005]

(a) predominantly 2-butyne
 (b) predominantly 1-butene
 (c) predominantly 2-butene
 (d) equimolar mixture of 1 and 2-butene

15. Fluorobenzene (C_6H_5F) can be synthesized in the laboratory [AIEEE 2006]

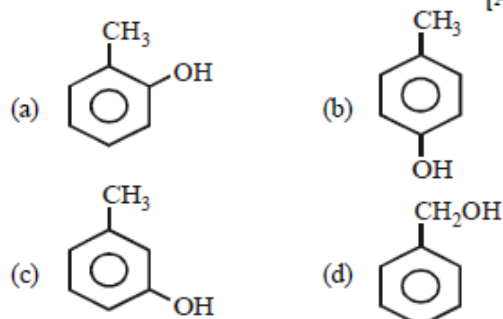
(a) by direct fluorination of benzene with F_2 gas
 (b) by reacting bromobenzene with NaF solution
 (c) by heating phenol with HF and KF
 (d) from aniline by diazotisation followed by heating the diazonium salt with HBF_4

16. $CH_3Br + Nu^- \longrightarrow CH_3 - Nu + Br^-$ The decreasing order of the rate of the above reaction with nucleophiles (Nu^-) A to D is [AIEEE 2006]

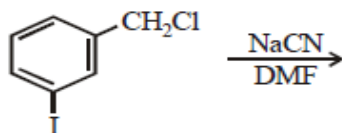
[$Nu^- = (A) PhO^-, (B) AcO^-, (C) HO^-, (D) CH_3O^-$]

(a) $A > B > C > D$ (b) $B > D > C > A$
 (c) $D > C > A > B$ (d) $D > C > B > A$

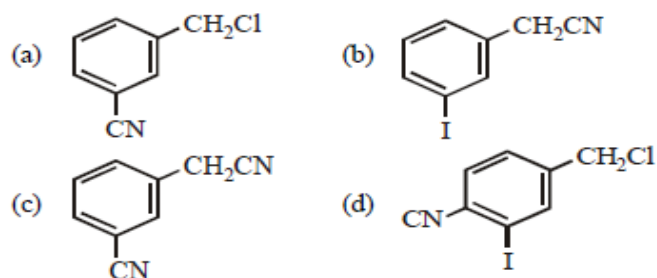
17. The structure of the compound that gives a tribromo derivative on treatment with bromine water is [AIEEE 2006]



18. The structure of the major product formed in the following reaction [AIEEE 2006]



is



19. Which of the following is the correct order of decreasing S_N2 reactivity? [AIEEE 2007]

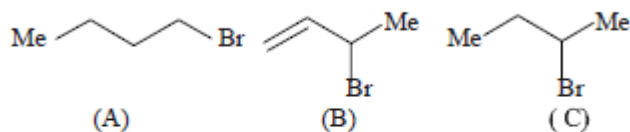
- (a) $R_2CHX > R_3CX > RCH_2X$ (c) $RCH_2X > R_2CHX > R_3CX$
 (b) $RCHX > R_3CX > R_2CHX$ (d) $R_3CX > R_2CHX > RCH_2X$

20. The organic chloro compound, which shows complete stereochemical inversion during a S_N2 reaction, is

[AIEEE 2008]

- (a) $(C_2H_5)_2CHCl$ (b) $(CH_3)_3CCl$
 (c) $(CH_3)_2CHCl$ (d) CH_3Cl

21. Consider the following bromides :



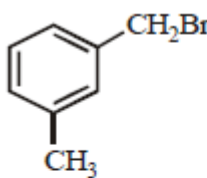
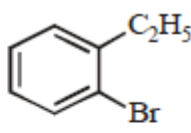
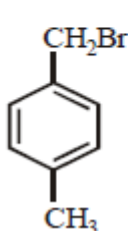
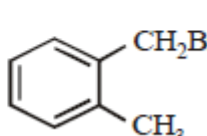
The correct order of S_N1 reactivity is [AIEEE 2010]

- (a) $B > C > A$ (b) $B > A > C$
 (c) $C > B > A$ (d) $A > B > C$

22. Iodoform can be prepared from all except : [AIEEE 2012]

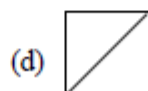
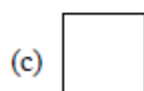
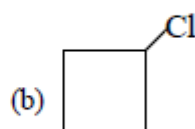
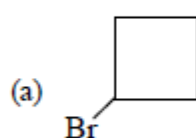
- (a) Ethyl methyl ketone (c) 3-Methyl 2-butanone
 (b) Isopropyl alcohol (d) Isobutyl alcohol

23. Compound (A), C_8H_9Br , gives a white precipitate when warmed with alcoholic $AgNO_3$. Oxidation of (A) gives an acid (B), $C_8H_6O_4$. (B) easily forms anhydride on heating. Identify the compound (A). [JEE M 2013]

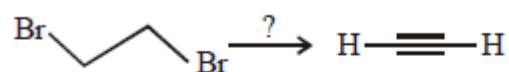
- (a) 
 (b) 
- (c) 
 (d) 

24. What would be the product formed when

1-bromo-3-chlorocyclobutane reacts with two equivalents of metallic sodium in ether? [IIT-JEE 2005 S]



25. The reagent(s) for the following conversion,



is/are

[IIT-JEE 2007]

- (a) alcoholic KOH
- (b) alcoholic KOH followed by NaNH_2
- (c) aqueous KOH followed by NaNH_2
- (d) $\text{Zn}/\text{CH}_3\text{OH}$