

Definition of haloalkanes

The haloalkanes are a group of chemical compounds comprised of an alkane with one or more hydrogens replaced by a halogen atom (fluorine, chlorine, bromine, or iodine).

Example: Chloroethane ($\text{CH}_3\text{CH}_2\text{Cl}$).

Preparation of haloalkanes from hydrocarbons

Haloalkanes can be prepared from alkanes and alkenes when the halogen atom replaces the hydrogen atom. In the presence of ultra-violet light halogens ($\text{Cl}_2, \text{Br}_2, \text{I}_2$) react with alkanes to form haloalkanes. In this method, polysubstituted halides are obtained that are difficult to separate. When pure components are needed, they can be obtained by fractional distillation.

Markovnikov's rule

The rule states that with the addition of a protic acid HX to an unsymmetrical alkene, the acid hydrogen (H) becomes attached to the carbon with fewer alkyl substituents, and the halide (X) group becomes attached to the carbon with more alkyl substituents. Alternatively, the rule can be stated that the hydrogen atom is added to the carbon with the greater number of hydrogen atoms while the X component is added to the carbon with the fewer number of hydrogen atoms.

Kharasch effect

In the presence of peroxide and light, addition of HBr to unsymmetrical alkenes occur contrary to Markovnikov's rule. But HCl and HI do not show peroxide effect. Radical chain reactions are successful when propagation steps are exothermic.

Exceptional behavior of HBr

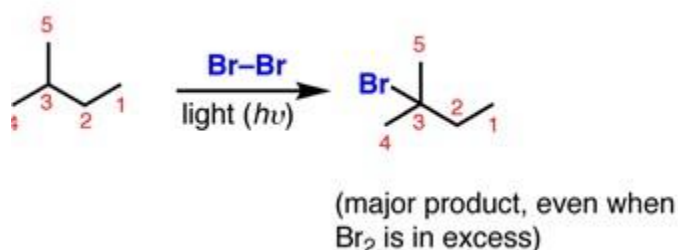
Mechanisms that avoid the carbocation intermediate may react through other mechanisms that are regioselective, not predicted by Markovnikov's rule, such as free radical addition. Such reactions are said to be anti-Markovnikov, since the halogen adds to the less substituted carbon, exactly the opposite of Markovnikov reaction. Physically, like the positive charge, the radical is most stable when it is in the more substituted position. The anti-Markovnikov rule can be explained best by taking an example of hydrogen bromide addition to propene in the presence of benzoyl peroxide. The reaction of HBr with substituted alkenes was prototypical in the study of free-radical additions. Early chemists discovered that the reason for the variability in the ratio of Markovnikov to anti-Markovnikov reaction products was due to the unexpected presence of free radical ionizing substances such as peroxides. The explanation is that HBr produces a Br radical,

which then reacts with the double bond. Since the bromine atom is relatively sizable, it is more likely to encounter and react with the least substituted carbon. In this case the terminal carbon is a reactant which produces a primary addition product instead of a secondary addition product, in the case of propene.

Addition of halogens to alkenes

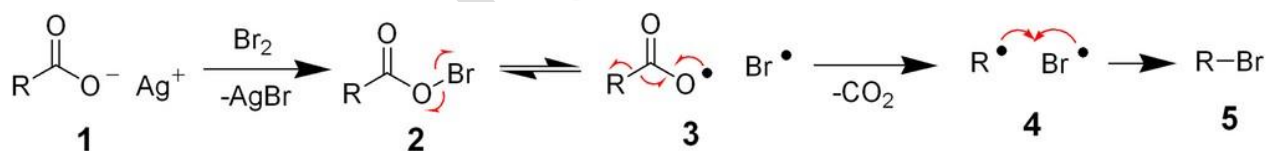
Addition of halogens in alkenes gives dihalogen derivatives by ionic reactions.

Haloalkanes from alkanes by free radical halogenation



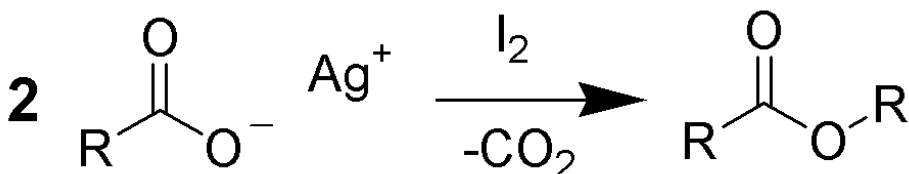
Alkanes react with halogens by free radical halogenation. In this reaction a hydrogen atom is removed from the alkane, then replaced by a halogen atom by reaction with a diatomic halogen molecule. The reactive intermediate in this reaction is a free radical and the reaction is called a radical chain reaction.

Borodin Hunsdiecker reaction



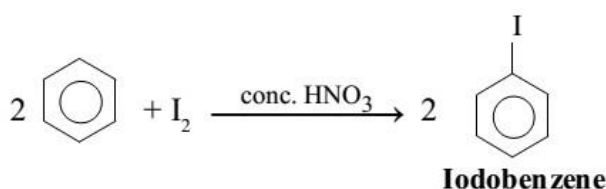
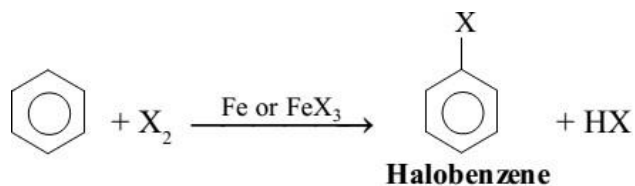
The Hunsdiecker reaction is the organic reaction of silver salts of carboxylic acids with halogens to give organic halides. It is an example of a halogenation reaction.

Birnbaum-Simonini reaction

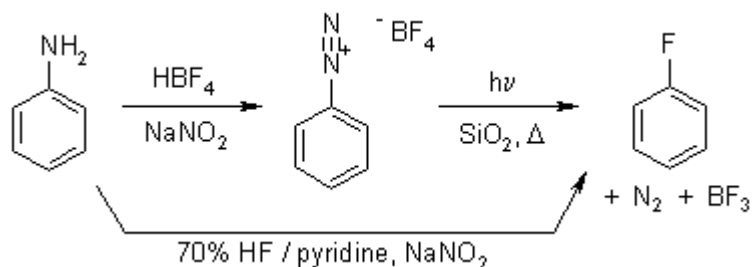


The reaction of silver salts of carboxylic acids with iodine is called the Simonini reaction.

Direct halogenation of aromatic hydrocarbons

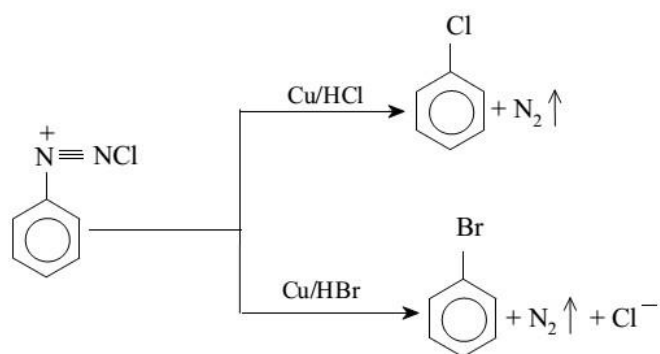


Balz-Schiemann reaction



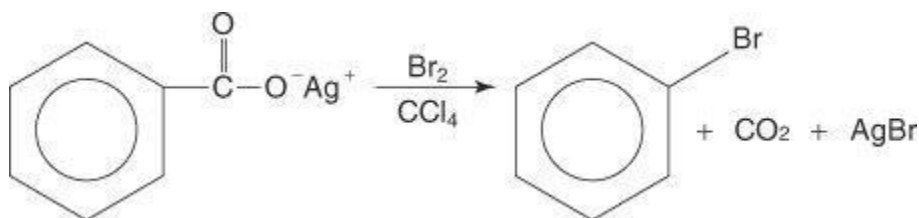
The conversion of aryl amines to aryl fluorides via diazotisation and subsequent thermal decomposition of the derived tetrafluoroborates or hexafluorophosphates. The decomposition may also be induced photochemically.

Gattermann reaction



Haloarenes can also be prepared by reacting benzene diazonium chloride with copper powder in presence of corresponding halogen acid. This reaction is called Gattermann reaction.

Hunsdiecker reaction



The silver(I) salts of carboxylic acids react with halogens to give unstable intermediates which readily decarboxylate thermally to yield alkyl halides. The reaction is believed to involve homolysis of the C-C bond and a radical chain mechanism.

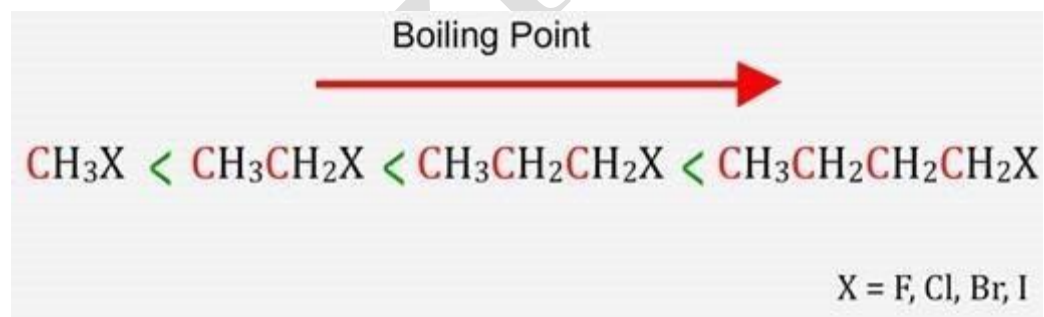
Physical state

Halo alkanes are commonly colourless, odourless, and hydrophobic. There are relatively heavier than the alkanes. Haloarenes are normally colourless or crystalline solid. Haloarenes are heavier than the water.

Trends in melting point of haloalkanes

The *para*-isomers have higher 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.

Boiling point of haloalkanes



There is large electronegativity difference between halogens and carbon resulting in highly polarized 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. 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 homologues series of haloalkanes, the forces of attraction becomes stronger due to increase in molecular size

and its mass, hence the boiling point increases down the homologues series. But the boiling point decreases with branching.

Melting point

Melting point of a compound depends upon the strength of lattice structure of a compound. Melting point also follows the same trend as 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 symmetry of *para*-isomers that fits in crystal lattice better as compared to *ortho* and *meta*-isomers.

Melting point and boiling point of haloarenes

Boiling point and melting point of haloarenes are near about same as of alkyl halides, which containing same number of carbon atoms.

Monohalogen derivative of benzene have boiling point in a proper order i.e. iodo>bromo>chloro>fluoro.

The melting point and boiling point of halogens atoms increases with an increase in the size of the aryl group.

Trends in boiling point of haloarenes

Due to doubly character of C-X bond in aryl halides, the C-X bond is shorter in length and stronger than in the alkyl halides, hence, boiling points are higher than alkyl halides. Boiling points increases as number of halogen atoms increases to ring.

Density of haloalkanes

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

Dipole moment of haloarenes

In haloarenes halogen groups are attached to carbon atoms hence dipole moment develops between them. The dipole moment increases as number of halogen atoms increases.

Solubility of haloalkanes and haloarenes

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

The haloalkanes are only very slightly soluble in water, but dissolve in organic solvents. This is because for dissolving haloalkanes in water, the strong hydrogen bonds present in the latter have to be broken. When dissolved in organic (non polar) solvents, the intermolecular attractions are almost the same as that being broken.

Nature of C-X bond

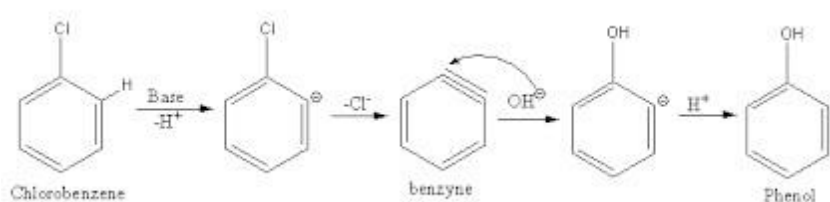
The C-X bond in haloarenes is polarized, as halogens are more electronegative than carbon. Due to the high electronegativity of halogen it attracts the electron cloud more towards itself and thus gains a slight negative charge, on the other hand carbon obtains a slight positive charge.

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 dissociation strength decreases.

Dipole moment depends on the difference in electronegativity of carbon and halogens and as we know that the electronegativity of halogens decreases down the group, the dipole moment also decreases. There is an exception of C-Cl and C-F dipole moments. Though the electronegativity of Cl is less than F, but the dipole moment of C-Cl bond is more than C-F.

Preparation of alcohol from alkyl halides by the substitution method



Ammonolysis reaction

Haloalkanes react with alcoholic NH_3 to form amine. But when haloalkane is in excess, the reaction does not stop rather continues till tertiary amine is formed. This continuous ammonolysis is called Hoffmann's ammonolysis.

other. the groups arranged in the clockwise direction rotate plane polarised light to right and the groups arranged in the anticlockwise direction rotate it to left.

Polarimeter

Polarimeter is an instrument for measuring the polarization of light, and especially for determining the effect of a substance in rotating the plane of polarization of light.

Define , identify and give example of laevorotatory substance

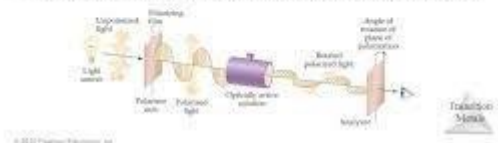
The organic compound which can rotate plane polarized light to left is called as laevorotatory substance.

l-glucose is an example.

Optical isomerism

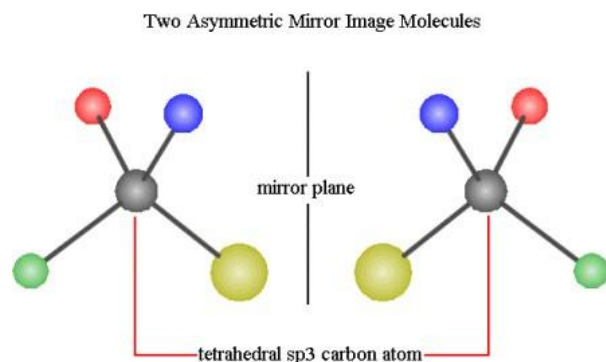
Optical Isomers

- Enantiomers are distinguished from each other by the way they rotate plane-polarized light.
 - Substances that rotate plane-polarized light to the right are **dextrorotatory**.
 - Substances that rotate plane-polarized light to the left are **levorotatory**.
 - A mixture of the two is called a **racemic mixture**.



Stereoisomerism in which the isomers are identical in most of physical and chemical properties but differ in their effect on rotation of polarise light , are called optical isomers. e.g. In medicines a particular property which one isomer hide, other ravel due to which one can use as life saving drug whereas other becomes toxic or of no use.

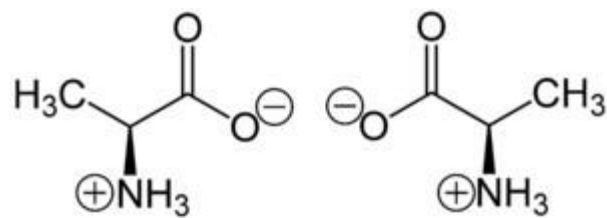
Asymmetric carbon and asymmetric molecules



An asymmetric carbon atom (chiral carbon) is a carbon atom that is attached to four different types of atoms or groups of atoms.

As an example, malic acid has 4 carbon atoms but just one of them is asymmetric

Chirality

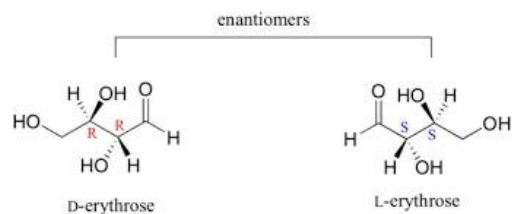


Chirality is a geometric property of some molecules and ions. A chiral molecule/ion is non-superposable on its mirror image. The presence of an asymmetric carbon atom is one of several structural features that induce chirality in organic and inorganic molecules.

Achiral compounds

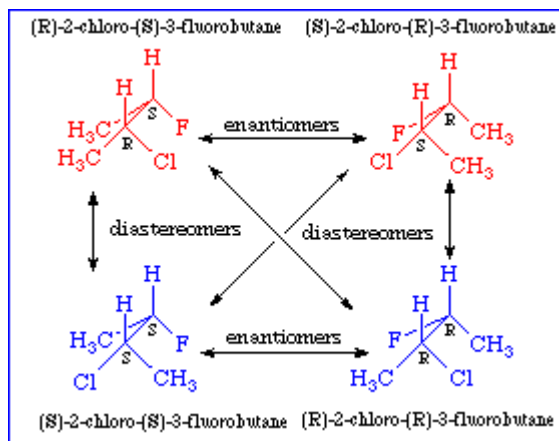
A molecule is achiral if it is superimposable on its mirror image. Most achiral molecules do have a plane of symmetry or a center of symmetry. Achiral molecules that contain a stereocenter are called meso.

Enantiomers and enantiomerism



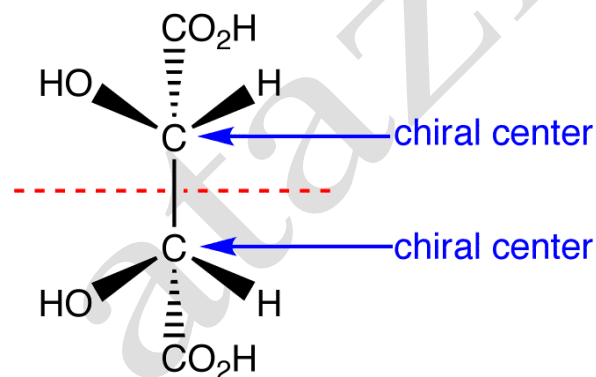
Enantiomers are chiral molecules that are mirror images of one another. Furthermore, the molecules are non-superimposable on one another. This means that the molecules cannot be placed on top of one another and give the same molecule. Chiral molecules with one or more stereocenters can be enantiomers.

Diastereomers



Diastereomers are stereoisomers that are not mirror images of one another and are non-superimposable on one another. Stereoisomers with two or more stereocenters can be diastereomers. It is sometimes difficult to determine whether or not two molecules are diastereomers.

Meso compounds



A meso compound is a molecule with multiple stereocenters that is superimposable on its mirror image. These particular traits lead to specific qualities that meso compounds do not share with most other stereoisomers. One such quality is the internal mirror plane.

Racemic mixture

A racemic mixture is one that has equal amounts of left- and right-handed enantiomers of a chiral molecule. The first known racemic mixture was racemic acid, which found to be a mixture of the two enantiomeric isomers of tartaric acid.

A racemic mixture is denoted by the prefix *dl-* (for sugars the prefix *dl-* may be used), indicating an equal (1:1) mixture of dextro and levo isomers. Also the prefix *rac-* (or *racem-*) or the symbols *RS* and *SR* are used.

Racemization

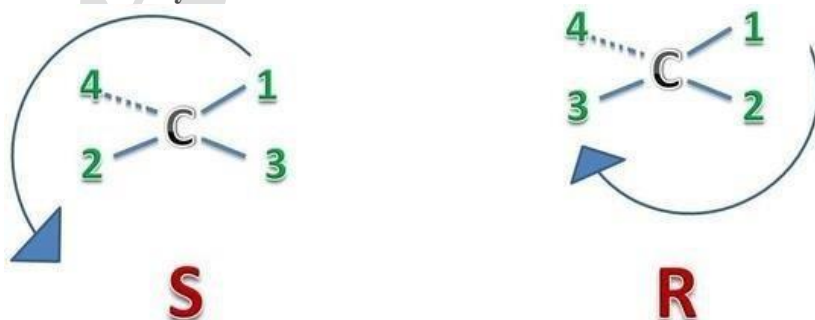
Racemization is the conversion of an enantiomerically pure mixture (where only one enantiomer is present) into a mixture where more than one of the enantiomers are present. An enantiomer, also known as an optical isomer, refers to a pair of molecules that are non-superimposable mirror images of each other. If the racemization results in a mixture where the D and L enantiomers are present in equimolar quantities, the resulting sample is a racemic mixture, a racemate.

Retention of configuration and inversion of configuration

If the net change in a reaction is the replacement of a ligand on a chiral center in a reactant molecule, and, if in the product the replacement ligand occupies the same site on the chiral center as the replaced ligand did in the reactant, the reaction is said to occur with retention of configuration.

If the net change of a reaction is the replacement of a ligand on a chiral center in a reactant and if, in the product, the replacement ligand occupies the site opposite to that occupied by the replaced ligand in the reactant, the reaction is said to occur with inversion of configuration.

D-L and R-S system of nomenclature



The enantiomer that rotates plane polarized light clockwise (+) was arbitrarily labeled D and other enantiomer (-) became L.

According to the RS rule, the four substituents of a tetrahedral chirality center are ranked in order of decreasing atomic number of the atoms directly bonded to the chirality center. Isotopes of the same chemical element are listed in order of decreasing atomic mass.

Configuration of a compound

The precise arrangement of substituents at a stereogenic center is known as the absolute configuration of the molecule.

This is usually accomplished by solving the x-ray crystal structure of a molecule, by inference based on chemical reactions of specific stereochemistry involving a compound whose absolute configuration is known.

The arrangement of atoms in an optically active molecule, based on chemical interconversion from or to a known compound, is a relative configuration. Relative, because there is no way of knowing just by looking at a structure whether the assignment of (+) or (-) is correlated to a particular isomer, R or S.

Define , identify and give example of the D-series

The substance which are capable of rotating plane polarized light to right is belong to d-series. Example: d-glucose, d-fructose, d-sucrose etc.

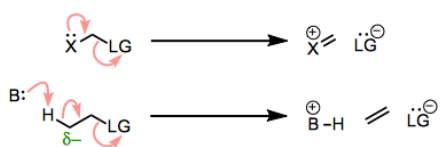
L-series

The organic compound which can rotate plane polarized light to left is called as laevorotatory substance. The substance which are laevorotatory belongs l-series.

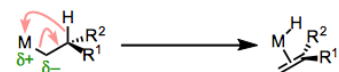
l-glucose is the example.

beta-elimination reactions

organic β -eliminations



organometallic β -eliminations



- There is no change in oxidation state at M.
- Total electron count increases by 2.
- A new π -bond ligand appears on M.

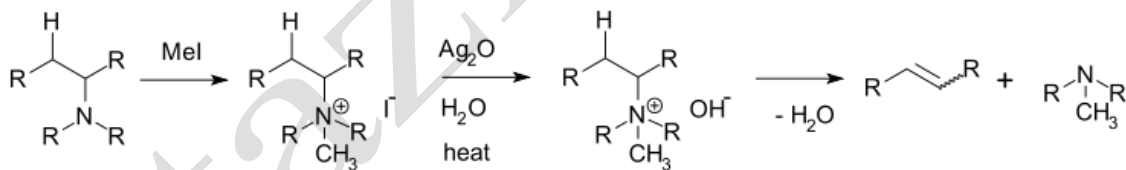
Saytzeff rule

In elimination reactions according to the Saytzeff's rule (Zaitsev's rule) during elimination more substituted alkene is formed as a major product. Since greater the substitution on double bond more will be the stability of alkene.

factors favoring dehydrohalogenation

ease of dehydrogenation of different alkyl halides increases as the number of beta-hydrogens increases : tertiary > secondary > primary .

Hofmann elimination rule

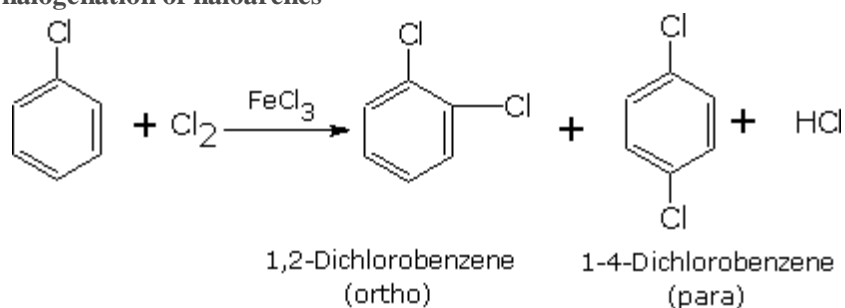


According to the Hofmann elimination rule less substituted alkene is the major product. This is a process where a quaternary ammonium salt is treated with silver oxide, water, and heat to produce an alkene and a tertiary amine.

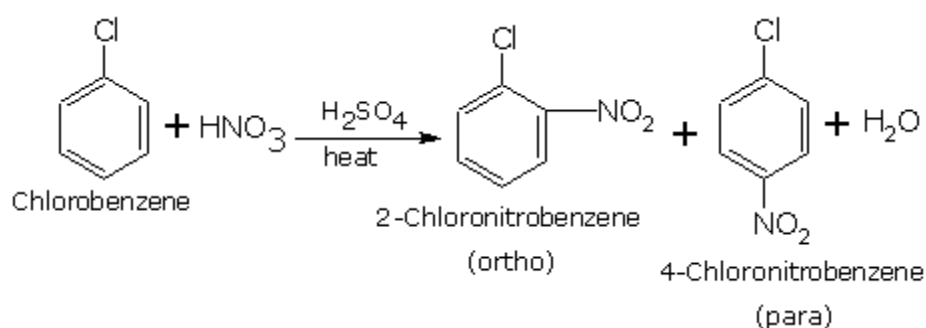
reasons for low reactivity of haloarenes and vinyl halides

- 1) Resonance effect
- 2) difference in hybridization of Carbon atom in C-X
- 3) Polarity of the carbon-halogen bond
- 4) Instability of phenyl cation
- 5) Electronic repulsion

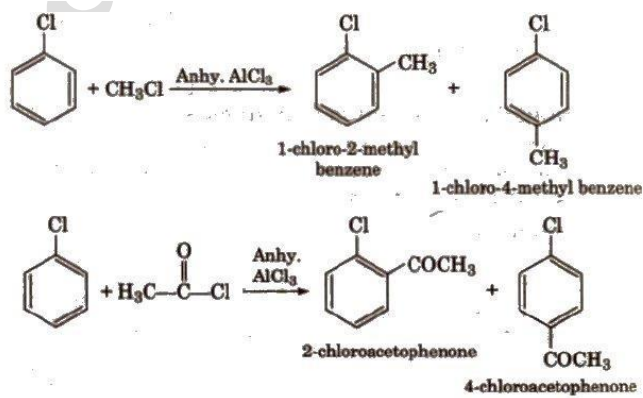
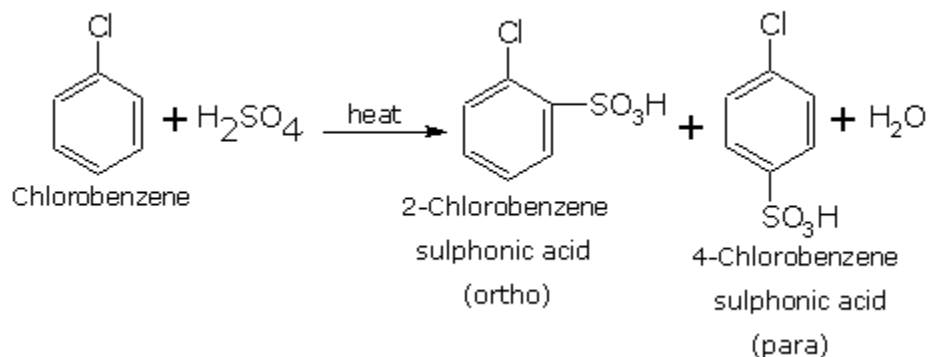
halogenation of haloarenes



nitration of haloarenes



sulphonation of haloarenes



Friedel craft's react

ion of haloarenes

Wurtz-fittig reaction of haloarenes

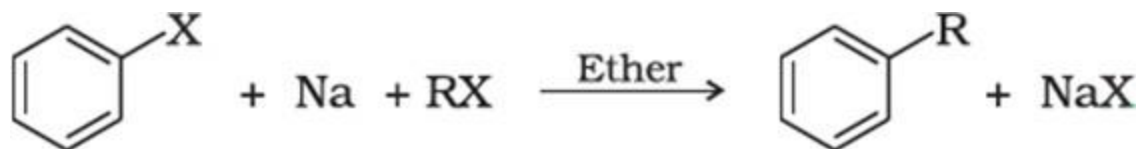
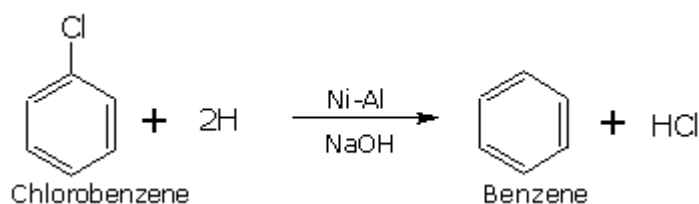


Fig: Wurtz-Fittig reaction

reduction of haloarenes



Chloroform

Trichloroethane or chloroform is an organic compound in which carbon atom is bonded to three halogen atoms. The central carbon atom shows sp^3 hybridization. The formula for the compound is CHCl_3 . Compound is sweet-smelling colorless liquid. It is used for preparing many chemical compounds. Chloroform is commonly used for anesthesia in medicinal field.

Iodoform

Iodoform is the organoiodine compound with the formula CHI_3 . A pale yellow, crystalline, volatile substance, it has a penetrating and distinctive odor and analogous to chloroform, sweetish taste.

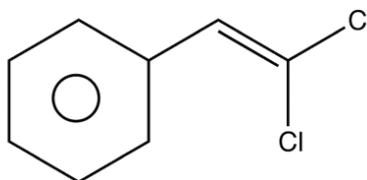
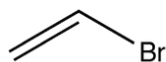
Freons

They are gases which can make large numbers of free radicals which can turn irreversibly the ozone of ozonosphere into Oxygen. So, It is harmful to Ozone layer & banned in many contries. It is mainly used in reffridgerant & Propalant.

p-p' dichloro diphenyl trichloro ethane

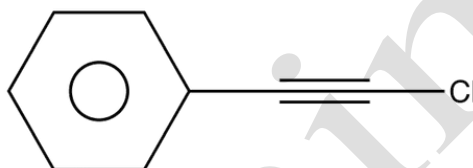
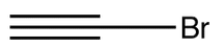
Non-water soluble chlorinated hydrocarbon in use since Second World War (1939-1945) as an insecticide for the control of lice (that spread typhus) and mosquitoes (that spread malaria and yellow fever).

Definition of haloalkenes or alkenyl halides



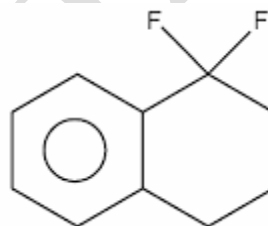
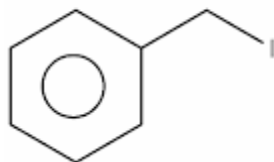
An alkenyl halide or haloalkene is a compound whose molecule has one or more halogen atoms bonded to an alkenyl group.

definition of haloalkynes or alkynyl halides



An alkynyl halide or haloalkyne is a compound whose molecule has one or more halogen atoms bonded to an alkynyl group.

Benzylic halides



Halogen atom is attached to carbon present on aromatic ring.

IUPAC system of naming alkyl halides

Common name: Alkyl halide

IUPAC name: Halo alkane

- 1) Select the longest chain containing halogen atom.
- 2) Follow least sum rule while giving number to the carbon containing X-atom.
- 3) Indicating the position of other substitutes (if any) name the alkyl halide as haloalkane.