

## Halo alkenes & halo arenes

### **Haloalkanes & Haloarenes**

When a hydrogen atom in an aliphatic or aromatic hydrocarbon is replaced by halogen atoms then the compounds are termed as haloalkanes and haloarenes. If a hydrogen atom is replaced from an aliphatic hydrocarbon by a halogen atom the resulting compound formed is called as haloalkane. It is also known as alkyl halide and halogenoalkane.

However, if a hydrogen atom is replaced from an aromatic hydrocarbon by a halogen atom the resulting compound formed is known as haloarene. It is also known as aryl halide or halogen arene. In a haloalkene ( $R - X$ ), X represents halogen group. It is attached to a  $sp^3$  hybridized atom of an alkyl group whereas in haloarene ( $Ar - X$ ) the halogen is attached to a  $sp^2$  hybridized atom of an aryl group.

Examples of Haloalkanes

Ethyl bromide –  $CH_3CH_2 - Br$  ( $sp^3C$ )

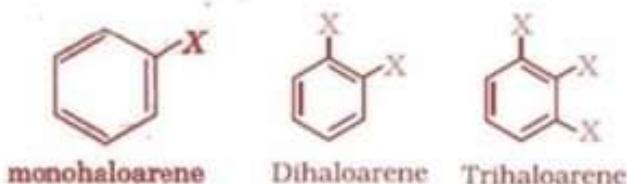


Monohaloalkane      Dihaloalkane

Examples of haloalkanes

Example of Haloarenes

Bromobenzene –  $C_6H_5Br$  ( $sp^2C$ )



Examples of haloarene

The key difference between haloalkanes and haloarenes is that haloalkanes are obtained from open-chain hydrocarbons (alkanes) whereas haloarenes are obtained from aromatic hydrocarbons (it is a type of hydrocarbon that forms a circular structure or ring-like structure due to sigma bonds and delocalized pi electrons between carbon atoms)

### **Definition of Haloalkanes**

Haloalkanes are organic chemical compounds formed by replacement of one or more hydrogen atom from an alkane group by a halogen group (elements of group 17 such as chlorine, bromine, Fluorine, iodine, etc.).

Haloalkanes are saturated organic compounds that have all the chemical bonds attached to the carbon atom in single bonds and the halogen atom is attached to a single carbon atom.

## Definition of Haloarenes

Aryl Halides/Haloarenes/Halogenoarene are aromatic compounds in which one or more hydrogen atoms attached to an aromatic ring is replaced by a halogen group. Haloarenes mainly differ from haloalkanes in the method of preparation and in its properties. This class compound and its derivatives are very broad and used for several purposes. One of the most important members of haloarene class is aryl chlorides.

## Classification of Haloalkanes & Haloarenes

They can be classified on the basis of-

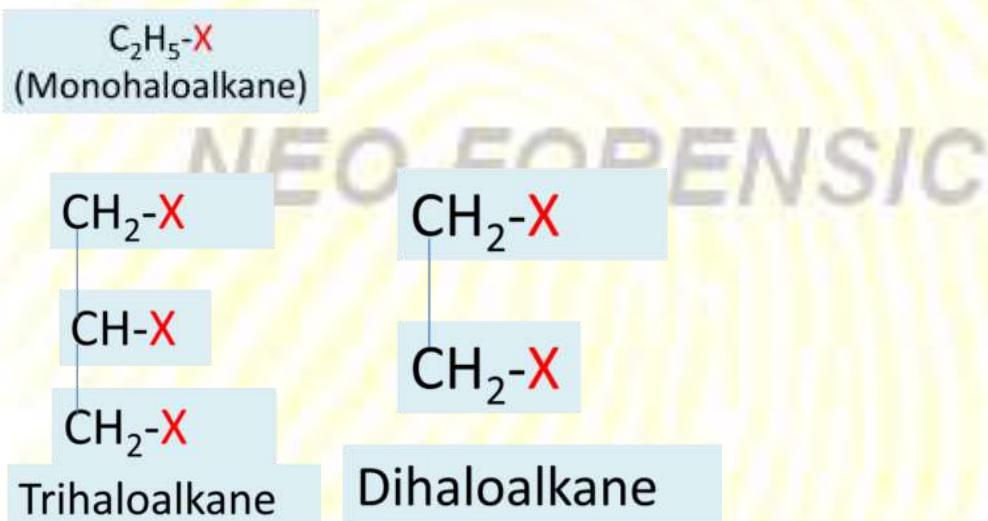
Number of hydrogen atoms

Compounds with  $sp^3$  C—X Bond

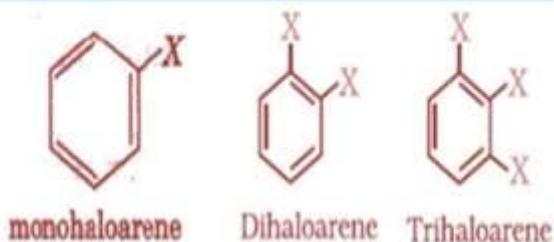
Compounds having the  $sp^2$  C-X Bond

### 1) Number of Hydrogen Atoms

On the basis of the number of hydrogen, they can be divided into mono, di or poly (tri, tetra, and so on) compounds of haloalkanes and haloarenes. It is named depending on the number of halogen atom these compounds contain in their structures. For example,



## Haloarenes



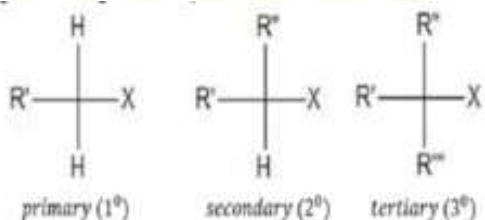
Monohalocompounds can again be classified into classes and subclasses on the basis of hybridization of the carbon atom to which the halogen atom is attached.

2) Compounds with  $sp^3$  C—X Bond [Here X (Halogen Group) = F, Cl, Br, I]

These compounds can be further divided into three types. They are:

i) Alkyl Halides/ Haloalkanes ( $R - X$ )

In this class, the halogen atom is attached to an alkyl group. The general homologous formula followed by this class is  $C_nH_{2n+1}X$ . They are further classified into mainly three types on the basis of the carbon atom to which the carbon bearing halogen (X) atom is bonded- primary, secondary, and tertiary. This classification is based on the nature of carbon atom to which the halogen is attached.

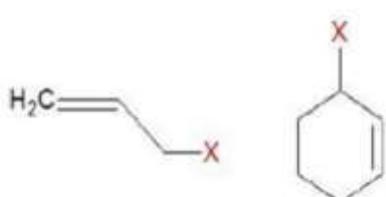


Classification of alkyl halides on the basis of nature of carbon atom to which the halogen is attached

### Classification of Alkyl-Halide

ii) Allylic Halides

This classification of compounds is formed by bonding of halogen group having  $sp^3$  hybridized carbon atom present next to a carbon-carbon double bond structure ( $C=C$ ). The carbon-carbon double bond structure is also known as allylic carbon. Thus, the name allylic halides.

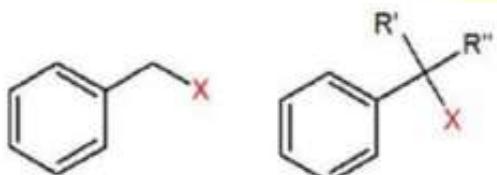


Examples of Allylic Halides- formed when halogen is bonded to  $sp^3$  hybridised allylic carbon

### Example of Allylic Halides

#### iii) Benzylic Halides

This type of compounds is formed when halogen atom is attached to an  $sp^3$  hybridized carbon atom. The  $sp^3$  hybridized carbon atom should be present next to an aromatic ring in order to form benzyl halides.



- When  $R' = CH_3, R'' = H (2^0)$
- When  $R' = R'' = CH_3 (3^0)$

**Benzylic Halides** halogen atom is attached to a  $sp^3$  hybridised carbon atom present next to an aromatic ring

#### Examples of Benzylic Halides

#### 3) Compounds Having the $sp^2C-X$ Bond

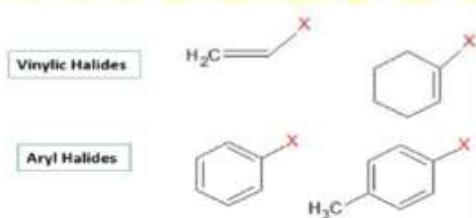
This class of compounds includes vinyl halides and aryl halides.

##### i) Vinyl Halides

These compounds are formed when halogen atom is attached to an  $sp^2$  hybridized carbon atom present next to a carbon-carbon double bond ( $C=C$ ).

##### ii) Aryl Halides

This class of compounds is formed when the halogen group is bonded to an  $sp^2$  -hybridized atom of carbon in an aromatic ring.



**Classification of compounds having  $sp^2C-X$  bond**

#### Compounds Having $sp^2C-X$ Bond

#### Applications of Haloalkanes and Haloarenes

Haloalkanes and haloarenes are used for many industrial and day to day purposes. They are used as flame retardants, propellants, solvents, pharmaceuticals, refrigerants, fire extinguishants, and many more.

They are used as solvents for non-polar compounds.

The derivatives of these compounds are used for medicinal purposes such as chloramphenicol is used for the treatment of typhoid fever.

Synthetic halogen compounds such as chloroquine are used for the treatment of people suffering from malaria.

DDT is utilized as insecticides

### **Environmental Effects**

There is a widespread use of these compounds for commercial purposes. However, halocarbons are linked with serious pollutants and toxins that adversely affect the environment. For example, a popular compound CFC (chlorofluorocarbon) is one of the significant reasons for ozone depletion in the atmosphere. Another very controversial fumigant linked to many harmful environmental effects is methyl bromide. These compounds have been time and again proved to be the major problem to the environment because of its harmful effect.

However, there are compounds such as Methyl iodide that does not cause any ozone-depleting effects to the environment. Furthermore, USEPA (the United States Environmental Protection Agency) has termed the compound as a non-ozone layer deplete.

### **Methods of Preparation**

Different methods of preparation include conversion of alcohols to alkyl halides, the addition of halogens to alkenes, and hydrohalogenation of alkenes. The preparation techniques were so reliable and efficient that it became an inevitable part of industrial chemistry.

There are primarily 4 different types of preparation techniques of Haloalkanes and Haloarenes. They include Preparation of Haloalkanes and Haloarenes from:

#### **Alcohols**

#### Hydrocarbons

Alkenes by addition of hydrogen halides and halogens

Halogen exchange reaction.

#### 1) Preparation from Alcohols (Haloalkanes)

The most convenient method of preparation of haloalkane is from alcohols. R-OH when reacts with suitable reagents, the reaction results in the formation of R – X. The suitable reagents that help in the reaction are

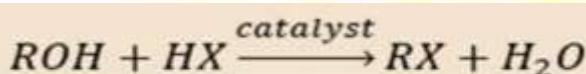
Concentrated halogen acids (HX)

Phosphorus halides (PX5 or PX3)

Thionyl chloride (SOCl2)

#### i) The Reaction of Alcohols with Halogen Acid

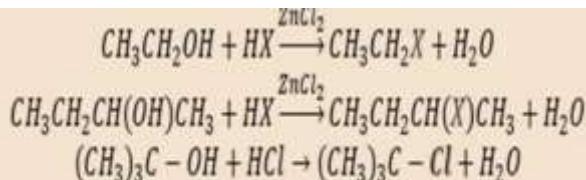
An organic compound derivative of alcohol reacts with halogen acid (H-X) to form haloalkanes as the major product.



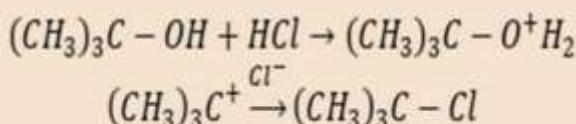
Reaction when Alcohol Reacts with Conc. Halogen Acids

Example-Preparation of Chloroalkanes

Preparation of chloroalkane is an example of the reaction of an alcohol with halogen acid to form haloalkane. In this case, primary alcohol and secondary alcohol react with HCl acid gas to form haloalkane in the presence of anhydrous ZnCl<sub>2</sub>, which act as a catalyst in this reaction.



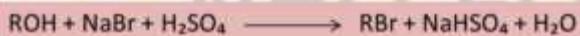
#### Preparation of Chloroalkanes



#### Mechanism of the Reaction

### Preparation of Bromoalkanes

Hydrogen bromide (HBr) reacts with alcohols to form bromoalkanes. Hydrogen bromide synthesis of the reaction takes place by the reaction of sodium bromide or potassium bromide and H<sub>2</sub>SO<sub>4</sub> (sulphuric acid). In the reaction below, NaBr and H<sub>2</sub>SO<sub>4</sub> react to form HBr which further reacts with alcohol.



#### Preparation of Bromoalkanes

### Example of Preparation of Bromoethane from Ethanol



#### Bromoethane from Ethanol

The tertiary carbonation which occurs due to tertiary alcohols is more stable than secondary and primary alcohols. Therefore tertiary carbocations offer more stability in comparison to the primary and secondary form of the compound. Hence, tertiary is more reactive than primary and secondary. The order of reactivity is 30 > 20 > 10.

Additionally, the reactivity of haloacids follows the order HI > HBr > HCl > HF. HI is easily and highly reacting haloacid among all of them because the HI bond is weaker than the other three. Therefore, it can be broken easily in comparison to the other halogen bonds to form H<sup>+</sup> and I<sup>-</sup> ions.

However, this preparation method will not be able to synthesize aryl halides/haloarenes. C-OH bond in the phenol structure contains partial double bond character because of the delocalization of lone pair of electrons present on the oxygen atom of the benzene ring. Therefore, the bond formed in the structure cannot be easily broken down by any sort of reaction with haloacids.

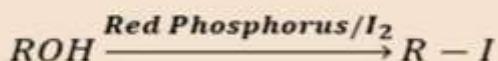
Ar – OH + HX → No reaction

ii) The Reaction of Alcohols with Phosphorus halides (PX<sub>5</sub> or PX<sub>3</sub>)

This reaction helps in the formation of Chloroalkanes, bromoalkanes, and iodoalkanes. In this reaction phosphorus halides interchange the functional group of alcohols ( $-\text{OH}$ ) with the corresponding halides. The reaction is as follows:

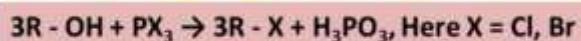


The above reaction is for the formation of alkyl chloride. Similarly, alkyl bromide or alkyl iodide formation is possible by the reaction of an alcohol with phosphorus tribromide and triiodide. To achieve the reaction, red phosphorus reacts with bromine or iodine by in-situ preparation (during the reaction) of phosphorus tribromide and triiodide.



In-situ Preparation of Phosphorus Tribromide and Triiodide

Note: Fresh preparation of the phosphorus tribromide and phosphorus triiodide is made with red phosphorus and bromine or iodine due to the instability of the compounds. Thus, alcohol reacts with phosphorus trihalides ( $\text{PX}_3$ ) to obtain three molecules of alkyl halide. The general overall reaction is



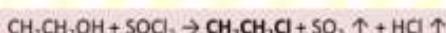
Example: Reaction of ethanol with  $\text{PCl}_3$  for the formation of chloroethane



Reaction of Ethanol with  $\text{PCl}_3$

iii) The Reaction of Alcohols with Thionyl chloride as Suitable Reagent

This reagent is the most preferred and suitable in between the three reactions of alcohols. Alcohol reacts with Thionyl chloride ( $\text{SOCl}_2$ ) to form alkyl chlorides. However, the by-products formed in this reaction are gaseous in nature. Therefore, the by-products can easily escape into the atmosphere, leaving the pure alkyl halide. This method helps in the generation of pure alkyl halide.



Reaction of Ethanol with  $\text{SOCl}_2$

## 2) Preparation of Haloalkanes & Haloarenes from Hydrocarbons

Preparation of Haloalkanes and haloarenes from hydrocarbons is possible by 3 different methods. They are

Free radical halogenation of haloalkanes

Electrophilic Substitution Reactions

**Sandmeyer reaction**

i) Free Radical Halogenation

Alkyl bromides and alkyl chloride formation are possible by the free radical halogenation reaction. However, radicals are very non-selective in nature. Moreover, radicals are non-specific and highly reactive intermediates that result in the formation of the mixture of products.

For instance bromination or chlorination of free radical results in the formation of a number of haloalkanes. This causes difficulty in the isolation of a single product. Therefore it is not the preferred method for the preparation of haloalkanes. Example- When butane reacts with chlorine in the presence of light as energy, a mixture of product formation takes place.

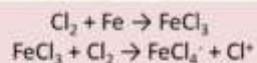


#### Free Radical Halogenation

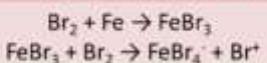
#### ii) Electrophilic Substitution Reaction

This method helps in the preparation of haloarenes such as aryl bromides and aryl chlorides. Electrophilic substitution forms the aryl bromides and aryl chlorides by using halogens such as chlorine and bromine in the presence of Lewis acid. However, the reaction requires the following of certain specific condition for the generation of proper electrophile.

For example, the reaction should be conducted in presence of Lewis acid. Additionally, the reaction must be carried out in the dark. The reactions to obtain the electrophiles are

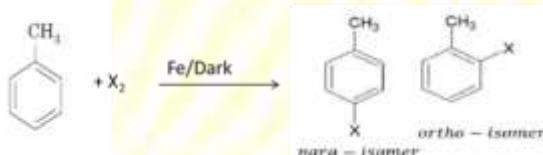


To Obtain  $Cl^+$  as electrophile



To Obtain  $Br^+$  as electrophile

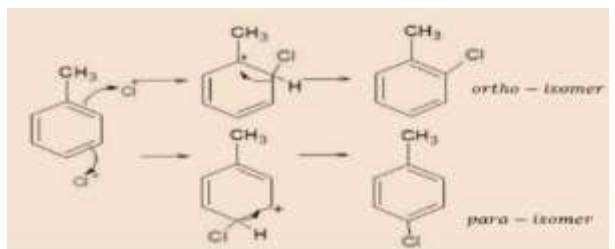
The electrophiles in the above reactions are  $Cl^+$  and  $Br^+$  and  $HCl$  and  $HBr$  are the by-products of the reaction. Therefore, the electrophilic substitution reaction for the preparation of aryl bromide and aryl chloride is



#### Mechanism of Electrophilic Substitution Reaction

In the above reaction, two different isomers of the aryl chlorides are formed. They are Ortho and Para isomer. The  $\pi$ -electron in the benzene ring attacks the  $Cl^+$  electrophile to produce an intermediate complex. However, the  $H^+$  bond from the intermediate complex moves in order to compensate for the positive charge of the carbon atom.

Thus the reaction forms two different isomers of the product-ortho and para. The melting points of both the isomer differ significantly. And para-isomer has the higher boiling point than ortho-isomer. Therefore, they can be easily separated from each other.



Mechanism of Electrophilic Substitution Reaction

Preparation of aryl chloride and bromide is possible from this reaction. Aryl fluoride formation is not possible due to the high reactivity of the halogen fluorine. Additionally, iodine reaction is also not possible as iodine is reversible in nature. Thus, it requires a strong oxidizing agent such as Conc.  $\text{HNO}_3$  or  $\text{HIO}_4$  for the oxidation of  $\text{HI}$  and converting it to  $\text{I}_2$ . Therefore, driving the reaction in forwarding direction is difficult and requires a strong oxidizing agent

### iii) Sandmeyer's Reaction

Sandmeyer's Reaction is a two-step method which includes:

Diazonium salt formation

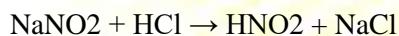
Diazonium salt reaction with a cuprous halide ( $\text{Cu}_2\text{X}_2$ )

Primary aromatic amine reacts with sodium nitrite in the presence of cold mineral acid to form the diazonium salt. In this case,  $\text{HNO}_2$  is prepared within the reaction by reacting sodium nitrite and  $\text{HX}$  in the temperature of 273-278K.



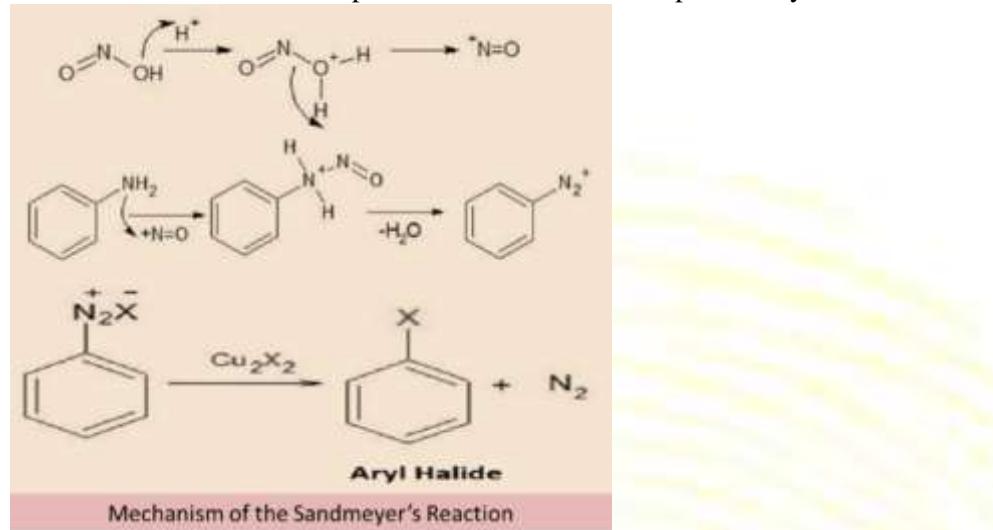
### Mechanism of the Sandmeyer's Reaction

#### In the first step-



The  $\text{HNO}_2$  formed in the presence of  $\text{H}^+$  undergo protonation to form  $\text{NO}_2^+$  as the electrophile. The lone pair of the atom from the primary amine will react with the electrophile to form an intermediate compound which further gives diazonium salt after elimination of  $\text{H}_2\text{O}$ . In the second step, the

diazonium salt reacts with cuprous halide to form the respective aryl halide



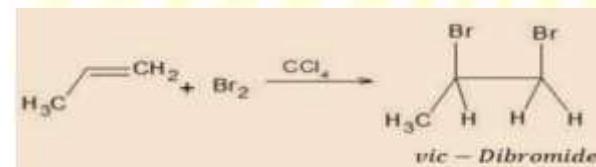
Mechanism of the Sandmeyer's Reaction

### 3) Haloalkanes & Haloarenes from Alkenes

Haloalkanes and haloarenes preparation is possible by the addition of halogens ( $\text{X}_2$ ) across the double bond of the alkene. It is also possible by the addition of hydrogen halides ( $\text{HX}$ ). In this halogen can be chlorine, bromine or even iodine.

#### i) Addition of $\text{HX}$

Alkene can be converted to haloalkane by an electrophilic addition reaction. Alkene reacts with  $\text{HX}$  to form  $\text{R}-\text{X}$ . The order of reactivity of halides with respect to alkenes follows the order  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ . The general reaction will be



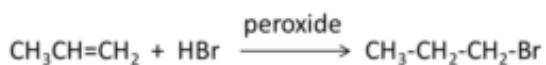
Formation of Haloalkane by Addition of Halogen to an Alkene

The reaction, in this case, is an example of a regioselective reaction. In this type of reaction, we get products in major and minor quantity. Additionally, the reaction follows Markovnikov's rule of addition for the determination of the major product by the addition of across the double bond of the alkene.

According to Markovnikov's rule, in an addition reaction of unsymmetrical alkenes, the negative part of the reagent or halogen will attach itself to the carbon that contains less number of hydrogen atoms. For example, prop-1-ene reacts with hydrogen bromide to form 2-bromopropane as a major product.

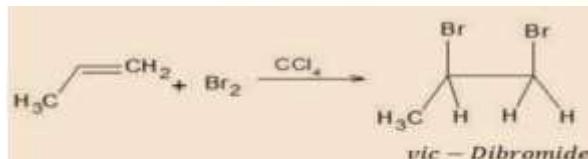
#### Peroxide effect (Kharash effect)

There is another possibility where the reaction contradicts Markovnikov's rule. This effect is known as Peroxide effect/ Kharash effect/ anti-markovnikov's rule. In this reaction, alkene reacts with  $\text{HBr}$  in the presence of peroxide. The  $\text{Br}-$  or the negative part of the reagent will attach itself to the carbon having more number of hydrogen atoms. For example, Prop-1-ene reacts with hydrogen bromide to form 1-bromopropane as a major product in the presence of peroxide.



## ii) Addition of Halogens

Similarly, alkenes can also react with halogens (X<sub>2</sub>). For example, Bromine reacts with an alkene in the presence of carbon tetrachloride (CCl<sub>4</sub>) to form vic-dibromide. It is a common test to determine a double bond or an alkene compound. The reaction will release reddish brown colour during the reaction.

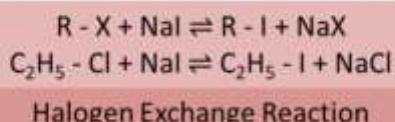


Formation of Haloalkane by Addition of Halogen to an Alkene

## 4) Haloalkanes and Haloarenes from Halogen exchange reaction

### i) Finkelstein Reaction

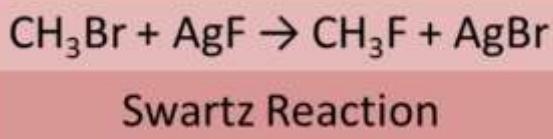
The last method of preparation of haloalkane and haloarene is halogen exchange reaction. In this reaction, an alkyl chloride or alkyl bromide reacts with sodium iodide in acetone to form alkyl iodides.



The reaction is an equilibrium reaction so there is a possibility of forming other products. The solubility difference of alkyl halides in acetone is used for driving the reaction in the forward direction. We know that sodium iodide is soluble in acetone but NaCl or NaBr are insoluble. Therefore, they precipitate out in the reaction which is easy to remove from the reaction mixture.

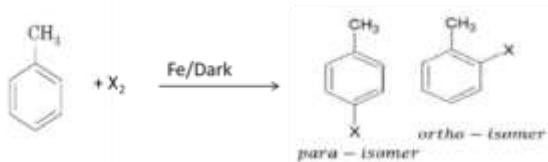
### ii) Swartz Reaction

In this reaction, alkyl fluorides formation is possible by heating of Alkyl fluorides RBr/RCI. The reaction is carried out in the presence of metallic fluoride such as SbF<sub>3</sub>, Hg<sub>2</sub>F<sub>2</sub>, AgF, CoF<sub>2</sub>.

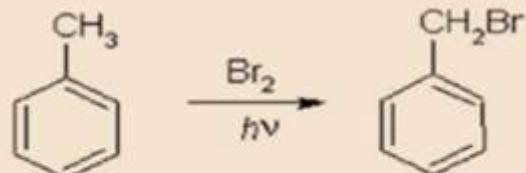


### A Solved Question for You

Q: Why the reaction given below takes place in the dark?



Solution: Halogens are capable of undergoing free radical reaction in the presence of light. Therefore, the reaction will form benzyl bromide as the product. As we have seen previously, this result of the reaction is different from the product of electrophilic substitution reaction. The reaction must be carried out in dark in order to get the product of electrophilic substitution reaction.



Free Radical Reaction in the Presence of Light

**NEO-FORENSIC**