Introduction and Classification of Haloalkanes and Haloarenes

Do you know haloalkanes and haloarenes persist in the environment? Haloarenes were used as herbicides during Vietnam War for defoliating the jungles and making it easier to fight in the war. These haloarenes cannot be decomposed and broken down by microorganisms like bacteria. As a result of which it is still intact in the soils of the jungles to this day.

Do you know haloalkanes containing halogens like chlorine, bromine, and iodine are a threat to the atmospheric ozone layer? One of the very common examples of the haloalkane compound that lead to ozone depletion is chlorofluorocarbon. We might have come across haloalkanes and haloarenes several times in our day to day life as well as industries for various applications. Let us know more about these organic compounds.

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- Physical properties
- Methods of Preparation

- Chemical Reactions – Nucleophilic Substitution Reactions
- Chemical Reactions and Stereochemistry
- Polyhalogen compounds
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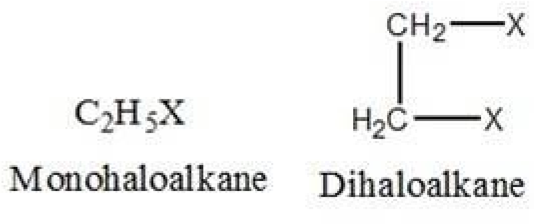
Haloalkanes & Haloarenes

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 halogenalkane.

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 halogenoarene. In a haloalkene (R – X), X represents halogen group. It is attached to an sp_3 hybridized atom of an alkyl group whereas in haloarene (Ar – X) the halogen is attached to an sp_2 hybridized atom of an aryl group.

Examples of Haloalkanes

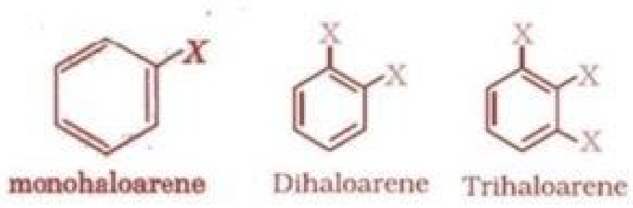
Ethyl bromide − $CH_3CH_2 - Br$ (sp^3C)



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)

Learn the methods of preparation of Haloalkanes and Haloarenes here.

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.

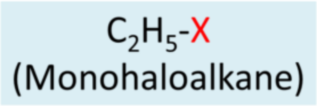
Classification of Haloalkanes & Haloarenes

They can be classified on the basis of-

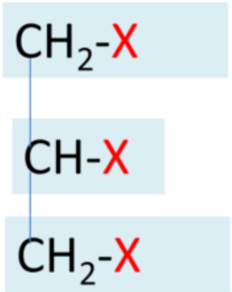
- Number of hydrogen atoms
- Compounds with sp^3 C—X Bond
- Compounds having the sp^2 C-X Bond

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,

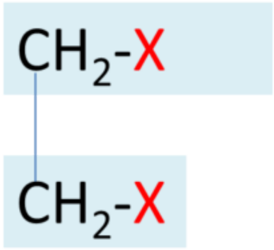


C_2H_5-X
(Monohaloalkane)



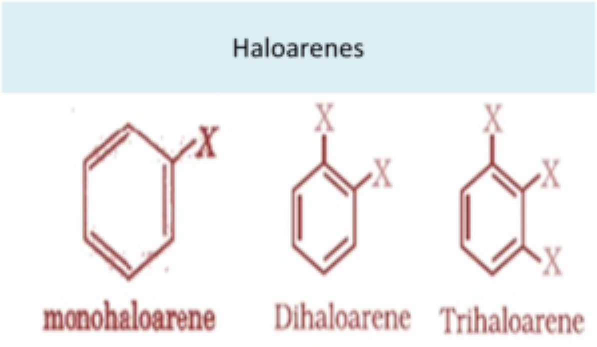
$$\begin{array}{l} CH_2\text{-}X \\ | \\ CH\text{-}X \\ | \\ CH_2\text{-}X \end{array}$$

Trihaloalkane



$$\begin{array}{l} CH_2\text{-}X \\ | \\ CH_2\text{-}X \end{array}$$

Dihaloalkane



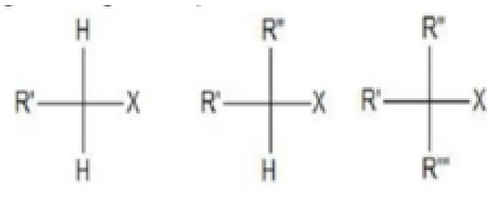
Monohalocompounds can again be classified into classes and subclasses on the basis of hybridization of the carbon atom to which the halogen atom is attached.

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.



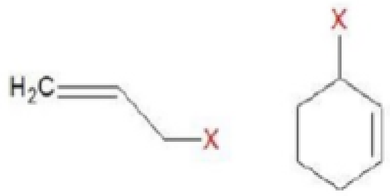
primary (1°) secondary (2°) tertiary (3°)

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.

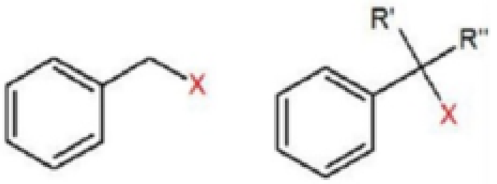


Examples of Allylic Halides- formed when halogen is bonded to sp^3 hybridised allylic carbon

Example of Allylic Halides

iii) Benzylic Halides

This type of compounds is formed when halogen atom is attached to an sp3 hybridized carbon atom. The sp3 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

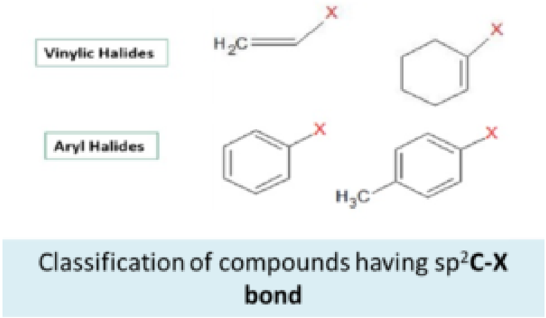
This class of compounds includes vinyl halides and aryl halides.

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.



Compounds Having sp2C-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.

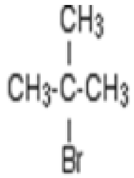
However, there are compounds such as Methyl iodide that does not cause any ozone-depleting effects to the environment. Furthermore, USEPA (the United States Environmental Protection Agency) has termed the compound as a non-ozone layer deplete.

A Solved Question for You

Q: Identify 1°, 2° and 3° haloalkanes from the structures given below.

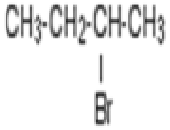
1) $CH_3\text{-}Cl$

2)



$CH_3\text{-}\overset{CH_3}{\underset{Br}{C}}\text{-}CH_3$

3)



$CH_3\text{-}CH_2\text{-}\underset{Br}{CH}\text{-}CH_3$

Solution: 1)- Primary (1° haloalkane), 2)- Tertiary (3° haloalkane), 3)- Secondary (2° haloalkane)

Nomenclature and Nature of C-X Bond

Do you know initially there was no proper system of naming a compound even though nomenclature and nature of C-X bond is an essential part of organic chemistry? There were just trivial names given on the basis of country and region. Sometimes the naming of a compound was done on the basis of the discoverer, nature of compound or even the place of the discovery.

However, soon scientists realized that the naming system was not standard and it can lead to confusion. Therefore, there was the need for a standard naming system of compounds including organic compounds. This led IUPAC to develop a certain set of rules that can be used universally for the naming of organic compounds.

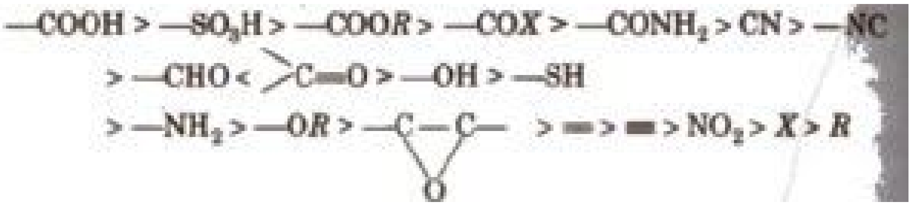
Two Names for Every Compound

- Common name- This is separate from the trivial name because nomenclature of the common name also requires a set of rules.
- IUPAC name

Nomenclature

- Naming of compounds by following a certain set of rules is called nomenclature. We have to find three primary things for naming a compound in IUPAC format.
- Find the parent chain of the compounds (longest hydrocarbon).
- Find the functional group. It will form the suffix.
- Find the substituents and its position. It will form the prefix.

The functional group will form suffix or prefix depending upon the priority series.



$$-COOH > -SO_3H > -COOR > -COX > -CONH_2 > CN > -NC > -CHO < >C{=}O > -OH > -SH > -NH_2 > -OR > \underset{O}{-C-C-} > {=} > \equiv > NO_2 > X > R$$

Priority Series

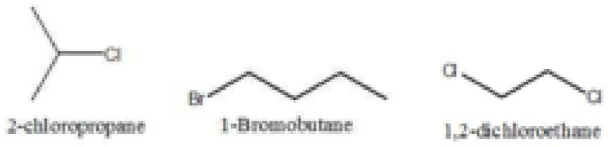
Step by Step Rules of Nomenclature

- Initially, we have to find the longest carbon chain of the compound.
- The carbon chain should be numbered in such a way that the carbon atom(s) containing the halogen(s) or the X group is/are having the least possible number. Furthermore, the carbon-containing double or triple bond is given the lowest number.
- If multiple halogen atoms are present in the compound, they are named with Greek numerical prefixes like di, tri, tetra, etc to represent the total number of same halogen atoms forms attached to the carbon atom. If more than one halogen atom is joined with the carbon atom, the numeral is repeated that many times.
- If different halogen groups are present in the same compound they are named according to the alphabets in ascending order.

- The position of the halogen atom in the compound is labelled by writing their respective positions and names of the halogen group members just before the name of the original (parent) hydrocarbon.

Nomenclature of Haloalkanes

The common name of haloalkane is alkyl halide. IUPAC name of haloalkane is written in the format-“numerical position-alphabetically placed halo- root-word-ane”



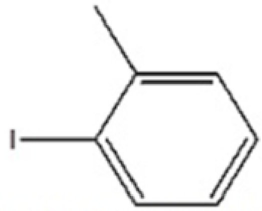
2-chloropropane 1-Bromobutane 1,2-dichloroethane

Examples- Nomenclature of Haloalkanes

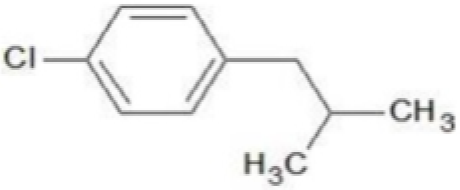
Nomenclature of Haloarenes

The common name of haloarene- Aryl Halide. IUPAC Name- In this nomenclature system, the naming of numerical prefixes depends on the basis of the position of the halogen atom in the aromatic ring.

If more than one halogen atoms are present, the aromatic ring is numbered and the halogen group is named on the basis of the numerical position of the aromatic ring. Numerical prefixes are written as (1, 2) ; (1,3) ; (1,4). The halogen atom is always given the lowest number.

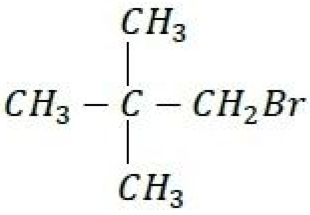

1-IODO-2-METHYL BENZENE

Example- Nomenclature of Haloarenes


1 - Chloro - 4- (2 - methylpropyl)benzene

Example- Nomenclature of Haloarenes

Nomenclature of Some Compounds



$$CH_3-\underset{CH_3}{\overset{CH_3}{\underset{|}{\overset{|}{C}}}}-CH_2Br$$

- Common name of the compound: neo − Pentylbromide. IUPAC Name of the compound: 1 − Bromo − 2,2 − dimethylpropane

$$CH_2 = CH – CH_2Br$$

- Common Name of the compound: Allyl Bromide. IUPAC Name of the compound: − 3 – Bromoprop – 1 – ene

Alkylidene/ Alkylene Dihalides

The dihaloalkanes having identical halogen atoms are termed as alkylidene or alkylene dihalides. They can be divided into two types:

- Geminal dihalides- When the halogen atoms are placed on the same carbon atom.

- Vicinal dihalides- When the halogen atoms are placed on the adjacent carbon atoms.

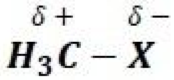
Examples of Geminal Hihalides and Vicinal Dihalides

CH_3 – $CHCl_2$	Ethylidene chloride	gem-dihalide	1,1 − Dichloroethane
CH_2Cl – CH_2Cl	Ethylene dichloride	vic-dihalide	1,2 – Dichloroethane

Nature of C-X Bond

It is essential to understand the nature of C-X bond because it determines the reactivity of compound having this kind of bond. The C-X bond is highly polar in nature because halogen atoms are electronegative and the carbon atom is electropositive. The difference in electronegativity results in withdrawal of electron density from sigma bond pair towards the halogen atom.

This result in polarization of C-X bond is polarized in a manner that the carbon atom develops partial positive charge whereas halogen atom in the bond develops a partial negative charge. Therefore, the carbon-halogen bond of any alkyl halide is polarized. This is represented as



$$\overset{\delta +}{H_3C} - \overset{\delta -}{X}$$

The electronegativity of the halogen group varies from one another. The size increases as we go down the group so fluorine atom is the smallest one in the group and iodine atom is largest. Thus, fluorine has the highest electronegativity followed by chlorine then bromine and finally iodine.

Electronegativity of X: F(3.98) > Cl(3.16) > Br(2.96) > I(2.66). However, the electronegativity of carbon atom is 2.55. The electronegativity difference between C-F is maximum. Therefore, C-F is the most polar among all of them.

Parameters Related to Nature of C-X Bond

1) Bond Length (A_0)

Nature of C-X bond depends upon the bond length between the carbon atom and halogen group. We have previously mentioned that size of the halogen group increases as we move down the group ($F < Cl < Br$

< *I*). Consequently, the difference in the C-F bond will be the smallest and C-I bond will be the largest. It can be represented as

$$C-F < C-Cl < C-Br < C-I$$
$$1.39 < 1.78 < 1.93 < 2.14$$

2) Bond Enthalpy Order

Nature of C-X bond depends upon bond enthalpy order. The size of the carbon and fluorine atom is very similar so the orbitals overlap (2p-2p overlap) into one another. This leads to the formation of a very strong bond. In C-I the atomic size of iodine is very large in comparison to carbon atom so the orbital interaction is very weak.

This results in the formation of weak bond strength. We can conclude that less the bond length stronger will be the bond. Hence, the bond length of C-F is 1.39 A_0. The stronger the bond, the amount of energy required increases to break that bond. Therefore, C-F has highest bond enthalpy. The bond enthalpy order is

$$C-F > C-Cl > C-Br > C-I$$

3) Dipole Moment

Dipole moment helps to calculate the polarity of a chemical bond within a molecule. It occurs due to the separation of positive and negative charges. It is the product of both charge and the distance between them. Bond dipole (μ) is given by the formula

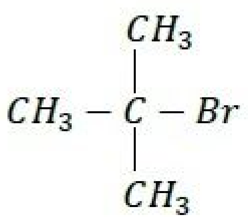
$$\mu = q \times d$$

The order of dipole moment in C-X is $CH_3Cl > CH_3F > CH_3Br > CH_3I$. Dipole moments of haloalkanes are − CH_3F − 1.847D, CH_3Cl − 1.860 D, CH_3Br − 1.830 D, CH_3I − 1.636 D

Can you notice the abnormal order of the dipole moment in the case where $CH_3Cl > CH_3F$? Even though fluorine is more electronegative than Chlorine but the C-F bond (139 pm) is shorter than C-Cl bond C − Cl (178 pm). Thus, the dipole moment will be lower in case of CH_3F in comparison to CH_3Cl.

Solved Example for You

Q1: Give the IUPAC name of the compound given below.



$$\begin{array}{ccccc} & & CH_3 & & \\ & & | & & \\ CH_3 & - & C & - & Br \\ & & | & & \\ & & CH_3 & & \end{array}$$

Solution: IUPAC Name − 2 − Bromo − 2 – methylpropane

Physical Properties

Is there a difference between the hardness of a small rock and a larger rock? Shockingly there isn't. A small rock will be comparable in its hardness to the larger rock of the same type. This quality is because of the physical property of the rock. Similarly, everything in nature including compounds like haloalkane and haloarene has some physical properties as well as chemical properties. In this topic, we will understand more about the physical properties of haloalkanes and haloarenes.

What are the Physical Properties?

Physical properties of a compound are those properties that are related to the physical aspects of the compound. For eg. shape, size, color, mass, boiling point, etc. The physical properties of any compound primarily depend upon,

- The mass of the compound
- Different forces of attraction including intermolecular and intramolecular forces of attraction.

When a hydrogen atom in an aliphatic or aromatic hydrocarbon is replaced by halogen atoms then the compounds are known as haloalkanes and haloarenes. Halogens are the less reactive functional group in comparison to carboxyl or aldehyde group. Therefore, halogen group when attached as a functional group do not bring a drastic difference in the overall physical properties of a compound. However, some differences can be seen as we move down the group in the homologous series of haloalkanes and haloarenes due to the difference in the atomic masses.

Physical Properties of Haloalkanes & Haloarenes

1) Physical State

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

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

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

2) Boiling Point

We know there is a large difference in electronegativity between the carbon and halogen atom of any given compound resulting in the development of highly polarized molecules. The polarity of the C-X bond and higher molecular mass in comparison to the actual hydrocarbon results in the development of very strong intermolecular forces of attraction in the derivatives of halogen.

The stronger intermolecular forces of attraction are due to dipole-dipole and van der Waals interaction. The boiling point of haloalkanes and haloarenes depends upon the intermolecular forces of attraction. Hence, the boiling points of derivatives of chlorides, bromides, and iodides are comparatively higher the hydrocarbons of the similar molecular mass.

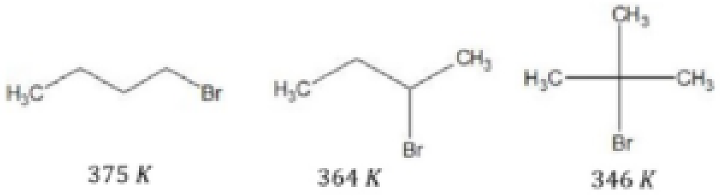
The size and molecular mass of halogen members increase when we move down the group in the homologous series thereby forming stronger forces of attraction. Hence the boiling point increases as we move down the group in the homologous series.

The order of the boiling point of alkyl halides are RI > RBr > RCl > RF

Additionally, the boiling point also increases for isomeric haloalkanes. However, the boiling point decreases with the branching of the compound. This is because branching of haloalkanes results in the lesser surface area, thus decreasing the van der Waal's forces interaction.

Moreover, as the branching increases the molecule forms sort of a spherical shape resulting in the decrease in the area of contact and forming weaker intermolecular forces. Derivatives such as methyl chloride, ethyl chloride, methyl bromide and few chlorofluoromethanes are gases at room temperature. However, the higher members of the group are usually solids or liquids.

Boiling points of haloarenes follow the order: Iodoarene > Bromoarene > Chloroarene. Moreover, the boiling point of isomeric dihaloarenes is almost similar.



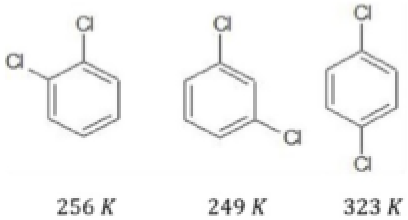
Difference in the Boiling Point of Haloalkanes

3) Melting Point

The melting point is based on the strength of the lattice structure of a compound. Isomeric dihalobenzenes have almost similar boiling points but the difference can be seen in the melting points. Para-isomer have a higher melting point in comparison to ortho-isomer and meta-isomer of the same compound.

It is because para-isomers have highly compact crystal lattice in comparison to ortho-isomer and meta-isomer. Therefore, higher numbers of molecules are packed compactly in the crystal lattice.

Hence, higher energy is required to break the lattice structure thereby increasing the melting point temperature of the compound.



Difference in the Melting Point of Haloarenes

4) Density

Density is directly proportional to the mass of any compound. Therefore, as the mass increases down the homologous series, the density increases. Thus, the derivatives of fluorine are less dense than derivatives of chlorine and derivatives of chlorine are less dense than derivatives of bromine.

Additionally, density increases with the increase in the number of carbon and halogen atoms. Furthermore, it depends upon the atomic mass of the halogen atom. For example, refer to the below diagram

$$n - C_3H_7Cl < n - C_3H_7Br < n - C_3H_7I$$

$$0.89\ g/mL \qquad 1.33\ g/mL \qquad 1.75\ g/mL$$

In the above example, the number of carbon atoms remains same but the mass of halogen atoms is different from one another. This, in turn, increases the density of the derivatives. Therefore, the arrangement of relative densities are

$$RI > RBr > RCl$$

5) Solubility

Alkyl halides are slightly soluble in water. Even though haloalkanes and haloarenes are polar compounds, they are immiscible with water. Relatively larger amount of energy is required for dissolution of a compound and to break the attractive forces between halogen and the carbon atom.

However, less energy is released when a bond is formed after dissolution ion and water. Moreover, the stability of R-X bond is very low in comparison to the bond formed in water molecules polarity difference.

Thus, haloalkanes and haloarenes neither develop new H-bond nor it breaks the old H-bonds. Hence, the solubility of R-X is low. However, these compounds are soluble in organic solvents because of the low polarity of organic solvents such as ether, benzene etc.

Therefore, the strength of the intermolecular forces between organic solvents and carbon-halogen compounds is similar to carbon-halogen molecules and solvent molecules. In the case of haloarenes, para-isomer is less soluble than ortho-isomer.

Here's a Solved Question for You

Q: Why does p-Dichlorobenzene have a higher melting point than the corresponding ortho-isomer and meta-isomers?

Solution: The para-isomer of Dichlorobenzene is symmetrically more compact and forms a more compact crystal lattice structure. This helps in the development of stronger intermolecular forces of attraction in comparison to of ortho-isomer and meta-isomers. Hence para-isomer of Dichlorobenzene requires a higher amount of energy to melt than its corresponding ortho-isomer and meta-isomers.

Methods of Preparation

What is the most common haloalkane? It is bromoalkane. There are over 1600 halogenated organic compounds existing today. There are different methods of preparation of haloalkanes and haloarenes. We can trace back the presence of haloalkane to the 15th century. The first haloalkane produced was chloroethane. Later on, in the 19th-century preparation and synthesis of such compounds were done in order to understand organic chemistry and structure of alkanes.

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. So let's learn about the methods of preparation of Haloalkanes and Haloarenes.

Methods of Preparation

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.

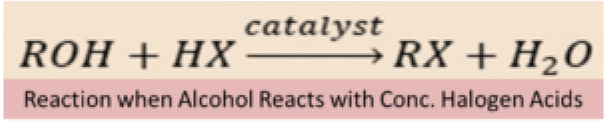
1) Preparation from Alcohols (Haloalkanes)

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.

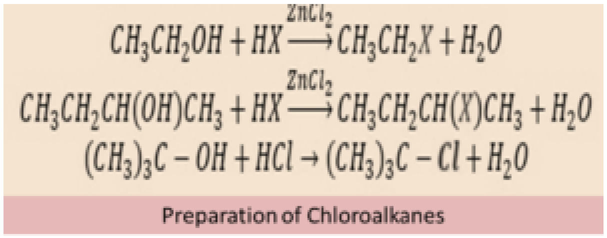


$$ROH + HX \xrightarrow{catalyst} RX + H_2O$$

Reaction when Alcohol Reacts with Conc. Halogen Acids

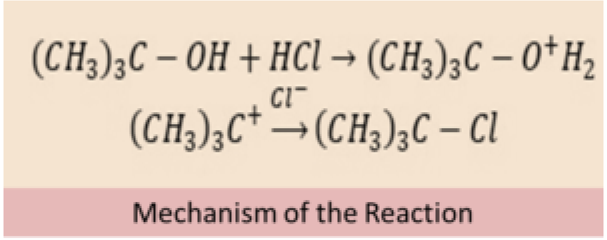
Example-Preparation of Chloroalkanes

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 ZnCl2, which act as a catalyst in this reaction.



$$CH_3CH_2OH + HX \xrightarrow{ZnCl_2} CH_3CH_2X + H_2O$$
$$CH_3CH_2CH(OH)CH_3 + HX \xrightarrow{ZnCl_2} CH_3CH_2CH(X)CH_3 + H_2O$$
$$(CH_3)_3C - OH + HCl \rightarrow (CH_3)_3C - Cl + H_2O$$

Preparation of Chloroalkanes

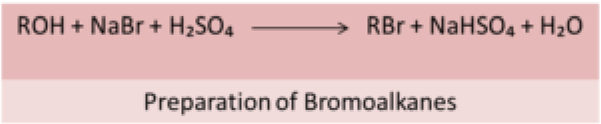


$$(CH_3)_3C - OH + HCl \rightarrow (CH_3)_3C - O^+H_2$$
$$(CH_3)_3C^+ \xrightarrow{Cl^-} (CH_3)_3C - Cl$$

Mechanism of the Reaction

Preparation of Bromoalkanes

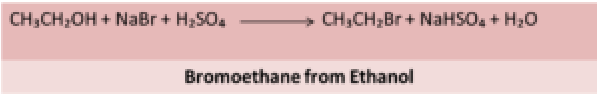
Hydrogen bromide (HBr) reacts with alcohols to form bromoalkanes. Hydrogen bromide synthesis of the reaction takes place by the reaction of sodium bromide or potassium bromide and H2SO4 (sulphuric acid). In the reaction below, NaBr and H2SO4 react to form HBr which further reacts with alcohol.



$ROH + NaBr + H_2SO_4 \longrightarrow RBr + NaHSO_4 + H_2O$

Preparation of Bromoalkanes

Example of Preparation of Bromoethane from Ethanol



$CH_3CH_2OH + NaBr + H_2SO_4 \longrightarrow CH_3CH_2Br + NaHSO_4 + H_2O$

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+ and I− 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.

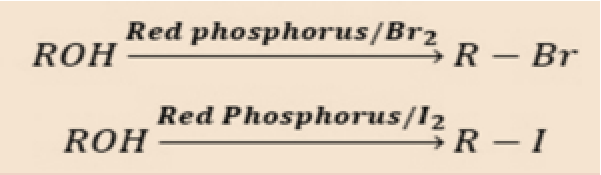
$$Ar – OH + HX \rightarrow \text{No reaction}$$

ii) The Reaction of Alcohols with Phosphorus halides (PX_5 or PX_3)

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

$$ROH + PCl_5 \rightarrow RCl + POCL_3 + HCl$$

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.

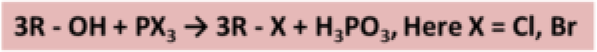


$$ROH \xrightarrow{Red\ phosphorus/Br_2} R-Br$$

$$ROH \xrightarrow{Red\ Phosphorus/I_2} R-I$$

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 (PX_3) to obtain three molecules of alkyl halide. The general overall reaction is



$3R-OH + PX_3 \rightarrow 3R-X + H_3PO_3$, Here X = Cl, Br

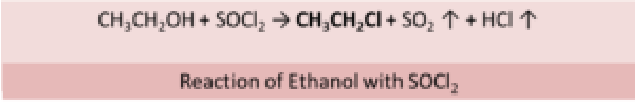
Example: Reaction of ethanol with PCl_3 for the formation of chloroethane.

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

Reaction of Ethanol with 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 (SOCl2) 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.



$$CH_3CH_2OH + SOCl_2 \rightarrow \mathbf{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

Reaction of Ethanol with $SOCl_2$

2) Preparation of Haloalkanes & Haloarenes from Hydrocarbons

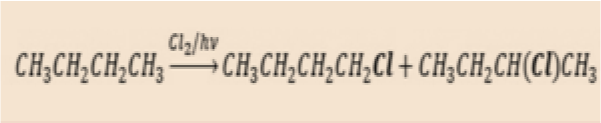
Preparation of Haloalkanes and haloarenes from hydrocarbons is possible by 3 different methods. They are

- 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.



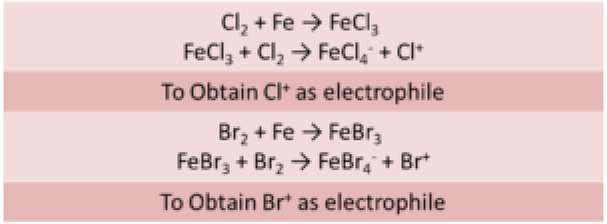
$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2/h\nu} CH_3CH_2CH_2CH_2Cl + CH_3CH_2CH(Cl)CH_3$$

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



$Cl_2 + Fe \rightarrow FeCl_3$

$FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$

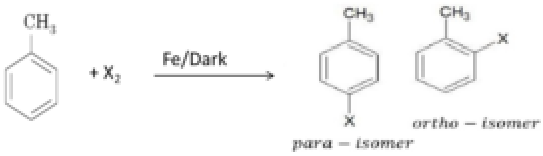
To Obtain Cl^+ as electrophile

$Br_2 + Fe \rightarrow FeBr_3$

$FeBr_3 + Br_2 \rightarrow FeBr_4^- + Br^+$

To Obtain Br^+ as electrophile

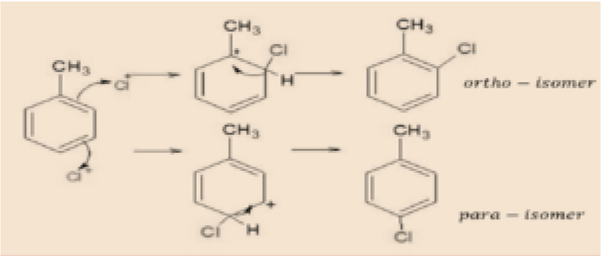
The electrophiles in the above reactions are $Cl+$ and $Br+$ and HCl and HBr are the by-products of the reaction. Therefore, the electrophilic substitution reaction for the preparation of aryl bromide and aryl chloride is



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 π-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

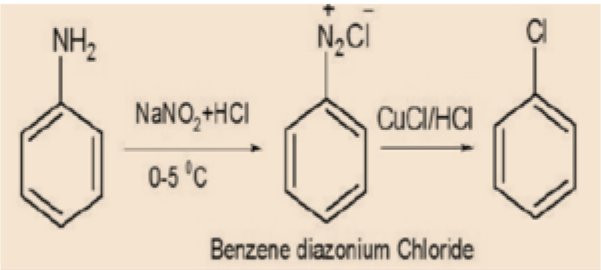
Preparation of aryl chloride and bromide is possible from this reaction. Aryl fluoride formation is not possible due to the high reactivity of the halogen fluorine. Additionally, iodine reaction is also not possible as iodine is reversible in nature. Thus, it requires a strong oxidizing agent such as Conc. HNO_3 or HIO_4 for the oxidation of HI and converting it to 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 (Cu_2X_2)

Primary aromatic amine reacts with sodium nitrite in the presence of cold mineral acid to form the diazonium salt. In this case, HNO_2 is prepared within the reaction by reacting sodium nitrite and HX in the temperature of 273-278K.



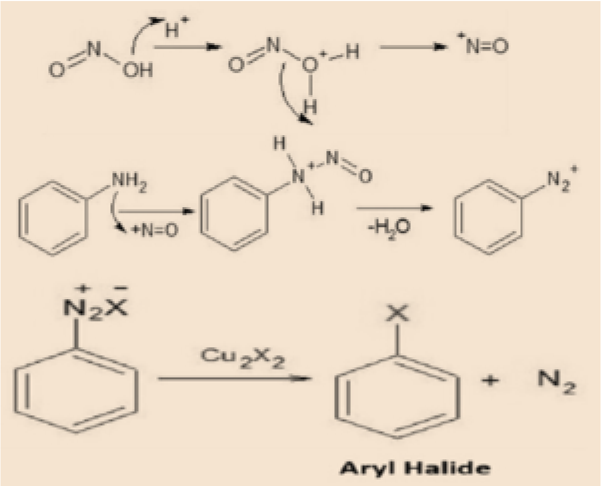
Sandmeyer's Reaction

Mechanism of the Sandmeyer's Reaction

In the first step-

$$NaNO_2 + HCl \rightarrow HNO_2 + NaCl$$

The HNO_2 formed in the presence of H^+ undergo protonation to form NO^+ 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 H_2O. In the second step, the diazonium salt reacts with cuprous halide to form the respective aryl halide



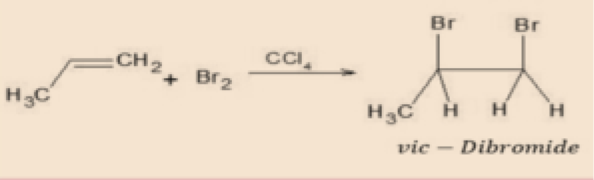
Mechanism of the Sandmeyer's Reaction

3) Haloalkanes & Haloarenes from Alkenes

Haloalkanes and haloarenes preparation is possible by the addition of halogens (X2) across the double bond of the alkene. It is also possible by the addition of hydrogen halides (*HX*). In this halogen can be chlorine, bromine or even iodine.

i) Addition of HX

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

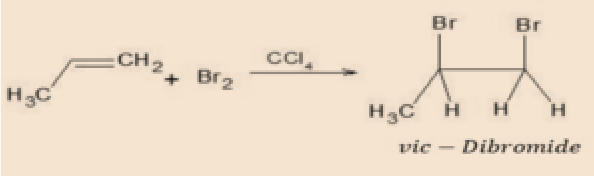
Peroxide effect (Kharash effect)

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 HBr in the presence of peroxide. The 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.

$$CH_3CH{=}CH_2 + HBr \xrightarrow{\text{peroxide}} CH_3\text{-}CH_2\text{-}CH_2\text{-}Br$$

ii) Addition of Halogens

Similarly, alkenes can also react with halogens (X2). For example, Bromine reacts with an alkene in the presence of carbon tetrachloride (CCl4) 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.

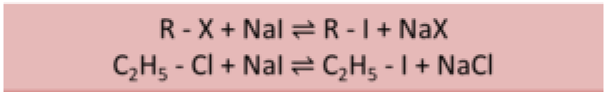


Formation of Haloalkane by Addition of Halogen to an Alkene

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.



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

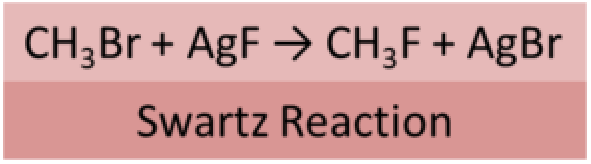
$$C_2H_5 - Cl + NaI \rightleftharpoons C_2H_5 - I + NaCl$$

Halogen Exchange Reaction

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/RCl. The reaction is carried out in the presence of metallic fluoride such as SbF_3, Hg_2F_2, AgF, CoF_2.

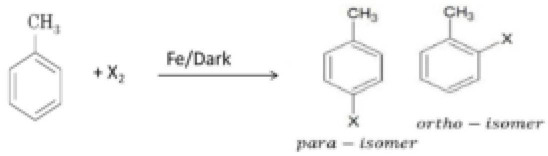


$$CH_3Br + AgF \rightarrow CH_3F + AgBr$$

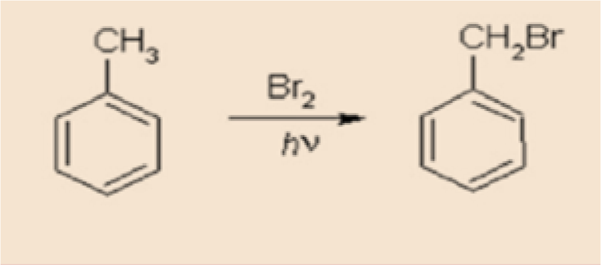
Swartz Reaction

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

Chemical Reactions- Nucleophilic Substitution Reactions

Do you know there are more than 1600 different types of haloalkanes existing today? Out of all the halogenated organics, bromoalkanes are the most common ones. Haloalkanes are responsible for an important and wide range of chemical reactions. We will study these chemical reactions in two parts. Let us go through these nucleophilic substitution reactions one by one.

Substitution Reactions of Haloalkanes

Chemical reactions in haloalkanes primarily fall into 3 different categories. They are:

- Nucleophilic Substitution Reaction (SN_1 and SN_2 reactions)
- Elimination Reactions
- Reaction with Metals

Nucleophilic Substitution Reactions

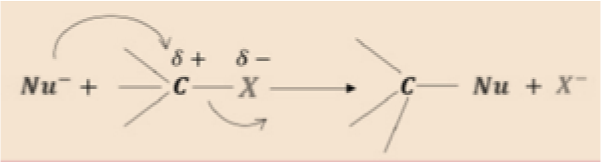
In this type of chemical reactions of haloalkanes, the nucleophile will attack a site having electron deficiency and will substitute the halogen or X there.

In case of alkyl halides, the electronegative halogen member will cause electrons withdrawal from the σ bond and attract the electrons toward it thereby polarizing the bond. As a result of which a partial positive charge will develop on the carbon atom making the carbon an electron deficient site.

Browse more Topics Under Haloalkanes And Haloarenes

- Introduction and Classification
- Nomenclature and Nature of C-X bond
- Physical properties
- Methods of Preparation
- Chemical Reactions – Nucleophilic Substitution Reactions
- Chemical Reactions and Stereochemistry
- Polyhalogen compounds
- Reactions of haloarenes

Now if a nucleophile will attack the electron deficient carbon atom. It will cause the departure of the halogen member from the compound as a halide ion. The order of the leaving of halogen group will be I– > Br– > Cl– > F–. The type of product formed will depend upon the nucleophile attacking the electron deficient carbon.



Mechanism of Nucleophilic Substitution Reaction

Formation of Product on the Basis of a Nucleophile

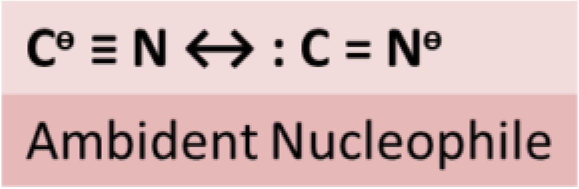
Type of Nucleophile (Nu^-)	Formation of Class of Compounds	Resultant compound ($R - Nu$)
H_2O	Alcohol	$R - OH$
NaI	Haloalkane	$R - I$
$R'M^+$	Alkane	$R - R'$
KCN	Nitrile	$R - CN$
AgCN	Isonitrile	$R - NC$
$NaOR'$	Ether	$R - O - R'$

$R_2' NH$	Tertiary amine	$R - N - R_2'$
$K - O - N = O$	Alkyl nitrite	$R - O - N = O$
$LiAlH_4(H)$	Hydrocarbon	$R - H$
$AgNO_2$	Nitroalkane	$R - NO_2$

There are certain groups that consist of two nucleophilic centres. We call this type of nucleophiles as ambident nucleophiles.

Ambident Nucleophiles

Groups such as nitrites and cyanides consist of two nucleophilic centres, hence they are ambident nucleophiles.



$C^{\ominus} \equiv N \leftrightarrow :C = N^{\ominus}$

Ambident Nucleophile

Substitution Reactions of Haloalkanes with Nucleophiles

KCN

When KCN reacts with a haloalkane (R-X), C acts as the nucleophile. The reaction results in the formation of alkyl cyanides as the product. We know that KCN is ionic in nature. Thus, KCN in the solution will dissociate into K^+ and $CN^-$and the negative charge will be present on the carbon atom.

The reaction results in the formation of Alkyl cyanide. Therefore, it will have a C-C bond which is highly stable. The reaction can be represented as

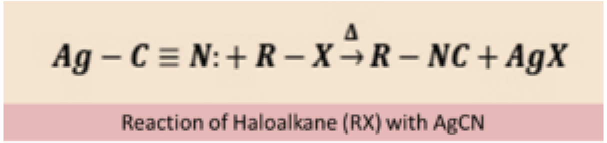
$$R-X+C^{\ominus}\equiv N:\xrightarrow{\Delta}R-C\equiv N+X^{-}$$

Reaction of R-X with KCN

AgCN

The reaction of haloalkane (R-X with AgCN) results in the formation of the product alkyl isocyanides. In this case, N act as the nucleophile. The bond present between Ag and C is covalent in nature because of the less difference in electronegativity between C and Ag.

The bond in AgCN is “Ag-C≡ N.” Therefore, carbon cannot act as the nucleophile but the nitrogen has a lone pair of electrons which makes it a better nucleophile. Thus, in AgCN nitrogen acts as a nucleophile.



$$Ag - C \equiv N: + R - X \xrightarrow{\Delta} R - NC + AgX$$

Reaction of Haloalkane (RX) with AgCN

Reactions of Haloalkanes – Nucleophilic Substitution Reactions

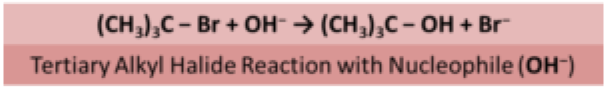
There are generally two types of nucleophilic substitution reaction.

- SN1
- SN2

Substitution Nucleophilic Unimolecular (SN1)

In this section, we will study about SN1 chemical reaction and what conditions haloalkanes require for undergoing this reaction. The meaning of SN1 reaction lies in the name itself “substitution, nucleophilic, and unimolecular.” Therefore, this reaction will follow the first order kinetics. In another term, we can say that the rate determining step in this reaction is unimolecular.

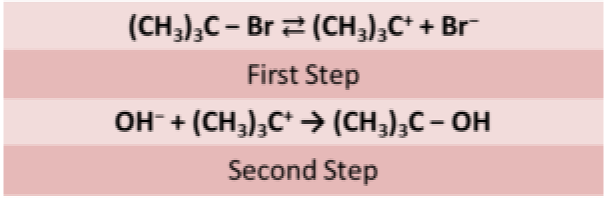
Moreover, the rate of reaction will depend upon the concentration of the one species which in this case is haloalkane or alkyl halide. For instance, if a tertiary alkyl halide and reacts with a nucleophile result in the formation of tertiary alcohol and halide ion.



$(CH_3)_3C-Br + OH^- \rightarrow (CH_3)_3C-OH + Br^-$

Tertiary Alkyl Halide Reaction with Nucleophile (OH^-)

From the reaction, we can decipher that S_N1 reaction is a two-step process and it leads to the formation of carbocation intermediates.

- The First Step: Polarization and cleaving of C-X bond occur to form carbocation intermediates. The first step is the reversible process. It is also the rate determining step of the reaction.
- The Second Step: Nucleophile attacks the carbocation to form the respective product.
- 

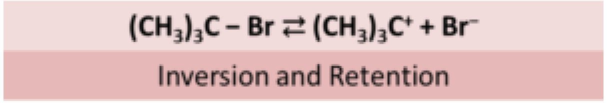
$(CH_3)_3C-Br \rightleftarrows (CH_3)_3C^+ + Br^-$

First Step

$OH^- + (CH_3)_3C^+ \rightarrow (CH_3)_3C-OH$

Second Step

- The planar nature of carbocation results in both inversion and retention configuration.



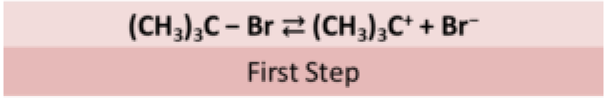
$(CH_3)_3C - Br \rightleftharpoons (CH_3)_3C^+ + Br^-$

Inversion and Retention

Conditions of SN1 Reaction

The rate of the reaction will depend on the concentration of the alkyl halide and it will not depend upon the nucleophile. This is because the rate always depends on the slowest step which in this case is the breakdown of the C-Br bond in order to form a carbocation. Therefore, the reaction will be a first-order reaction. The breakdown energy for breaking the bond is obtained from solvation of the leaving group.

Water and alcohol are types of polar protic solvent. These solvents have the capacity to attract the halogen group thereby facilitating the breakdown of C-X bond in the reaction. This will result in the formation of carbocation intermediate. Additionally, the stabilization of leaving the group is possible with the help of the protic solvents through hydrogen bonding. Hence, the first step is



$(CH_3)_3C - Br \rightleftarrows (CH_3)_3C^+ + Br^-$

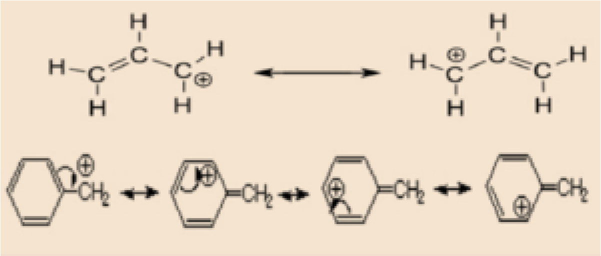
First Step

The stability of carbocation will determine the speed of the rate of reaction (more the stability faster the reaction). Therefore the more easily the leaving group (X–) can leave the compound the more easily the nucleophile can attack the compound and leads to substitution process.

Order of Reactivity

Therefore, the reactivity of halides towards SN1 reaction is R − I > R − Br > R − Cl > R – F. We know that C-I bond of the alkyl iodides can be easily broken and it is easy to release I– or the leaving group. Therefore, it becomes easy for the nucleophile to attack the alkyl halides and result in the substitution. On the other hand, it is tough to break C-F bond because it is very strong and in turn, it is difficult for the nucleophile to attack.

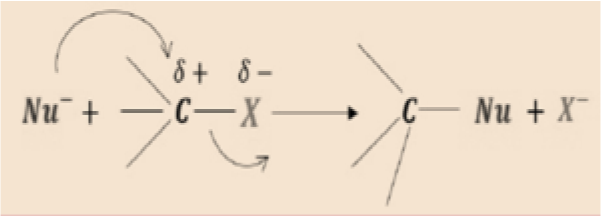
The reactivity order of alkyl halides in the case of SN1 reaction is- 30 > 20 > 10 > methyl. The same reason is responsible for more reactivity of compounds such as benzylic halide and allylic halides towards SN1 reaction because it leads to the formation of highly stable resonance structures of carbocation intermediates.



Resonance Structures in S_N1 reaction

Substitution Nucleophilic Bimolecular (SN2)

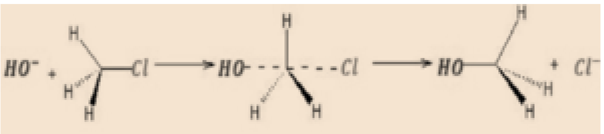
SN2 chemical reactions follow second order kinetics. The rate determining step depends on both the concentration of alkyl halides (R-X) and the nucleophile present in the reaction. The SN2 reaction is a one-step process and there is no formation of intermediates. The basic mechanism of the reaction is



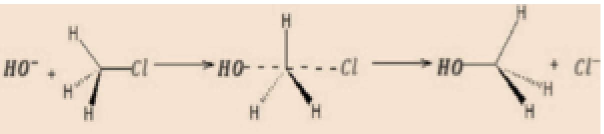
S_N2 Reaction

Mechanism of SN2 Reaction

We will study the mechanism of SN2 chemical reactions with the help of an example. Let’s take an example of CH_3Cl haloalkane reacting with the nucleophile OH^-.



Example of S_N2 Reaction



Example of S_N2 Reaction

This reaction is a one-step process, unlike SN1 reaction. In this reaction, there is no formation of intermediates. The reaction undergoes a transition state where the nucleophiles are attached to the alkyl halides. Hence it is very clear the rate determining step is dependent on the concentration as well as the nucleophile.

However, the transition state is highly unstable because in the transition state carbon is bonded to 5 atoms. This is because there is the simultaneous breaking of C-Cl bond and the formation of C-OH bond. Moreover, the nucleophile attacks the alkyl halide substrate in a backside method thereby inverting the configuration of the product.

Order of Reactivity

Since the attack of the substrate occurs from back-side method, it is not favourable to use a bulky nucleophile or a bulky substrate. This is because the SN2 mechanism is very prone to steric inhibition. Hence the order of reactivity of alkyl halide towards this type of reaction is $1^0 > 2^0 > 3^0$.

The order of reactivity follows this particular order because as the crowding around the actual C-X bond increases the steric inhibition increases. Thus, it decreases the reactivity in the SN2 reaction. Thus it is very easy to react if the alkyl halide substrate is methyl halide. It is also quite convenient to undergo SN2 reaction in ethyl halide but it is difficult to undergo SN2 reaction in case of a secondary and tertiary halide such as isopropyl halide and t-butyl halide.

The order of reactivity of the halides are $R - I > R - Br > R - Cl > R - F$

Conditions of the SN2 Chemical Reactions

There is a requirement of the strong nucleophile to undergo SN2 reaction. The reaction takes place in the presence of solvents that are polar aprotic such as DMSO, DMF. The SN2 reaction does not occur in presence of polar protic solvent because these types of solvent deactivate the charged nucleophile during the bond formation of polar protic solvent with the strong nucleophile.

Thus, it decreases the reactivity of the nucleophile and ceasing the possibility of an SN2 reaction.

Solved Example for You

Q. List the important difference between SN1 Reaction and SN2 Reaction

Solution:

Difference between SN1 Reaction and SN2 Reaction

SN1 Reaction	SN2Reaction
Two-step process	One step process

Formation of carbocation intermediates	Lack of carbocation intermediates formation.
The strength of Nucleophile is not important	Requirement of a Strong nucleophile.
The requirement of Polar protic solvent.	The requirement of Polar Aprotic solvent.
Configuration- Retention and inversion.	Configuration-Inversion

Chemical Reactions and Stereochemistry of Haloalkanes

Do you think the arrangement of atoms in space affects how they react with other atoms to form compounds? Yes! Stereochemistry plays a very important role in determining the formation of the product in chemical reactions of haloalkanes. But what exactly is stereochemistry? Let us study how stereochemistry affects the formation of the product. In this article, we will learn about the other two types of chemical reactions of haloalkanes- elimination reactions and reaction with metals and how stereochemistry affects these reactions. Let’s begin.

Stereochemistry and Reaction of Haloalkanes

Stereochemistry refers to the study of the arrangement of atoms in space. Stereoisomers are compounds having the same molecular formula but they differ in the spatial arrangement(i.e. arrangement in space). Stereoisomers fall into two main categories:

- Geometric Isomers
- Optical Isomers

It is important to understand optical isomers and their involvement in these chemical reactions.

Browse more Topics under Haloalkanes And Haloarenes

- Introduction and Classification
- Nomenclature and Nature of C-X bond
- Physical properties
- Methods of Preparation
- Chemical Reactions – Nucleophilic Substitution Reactions

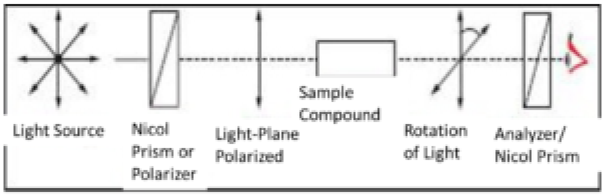
- Polyhalogen compounds
- Reactions of haloarenes

Optical Isomers

Optical isomers are compounds having the same molecular formula but they differ in the manner they rotate a plane polarized light. Plane polarized light formation takes place when an ordinary light passes through a Nicol prism thereby causing diffraction and resulting in the formation of a single wavelength light. This light of the single wavelength is plane polarized light.

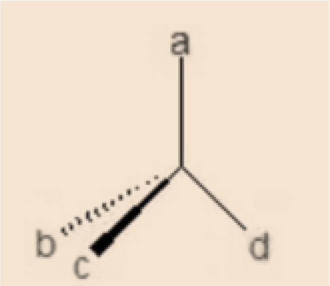
Set-Up of Polarimeter

The instrument that helps in the generation of plane polarized light from an ordinary light is a polarimeter.



Asymmetry of a Molecule

Asymmetry of a molecule also determines whether the molecule will be chiral or achiral. There are objects or compounds that are non-superimposable. These types of objects are known as chiral objects or chiral compound. However, there are many compounds/objects, such as a sphere, that is identical with its mirror image and it is superimposable as well. This type of compounds/objects is called achiral object. Therefore, asymmetry of a carbon atom in a particular molecule will determine the chirality of that molecule.



Determination of Asymmetry of an Organic Molecule

Why are we studying the chirality? This is because it will help us to study about enantiomers. Enantiomers are nothing but the stereoisomers that cannot form superimposable mirror images of each other. Enantiomers have same physical properties such as boiling point, index of refraction etc. The compounds vary in the manner of rotation of a plane polarized light (dextro or laevo).

However, if the particular composition of a mixture contains an equal amount of both the types of enantiomers, the net optical rotation becomes zero because dextro and laevo cancel out each other. This type of mixture is a racemic mixture and the process is racemization.

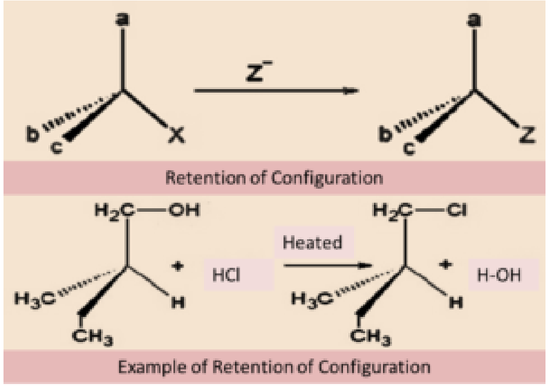
Stereochemistry – Configuration

In an organic compound, there are different types of spatial arrangement. In this section, we will study about the spatial arrangements of an organic compound with respect to stereochemistry.

Retention of Configuration

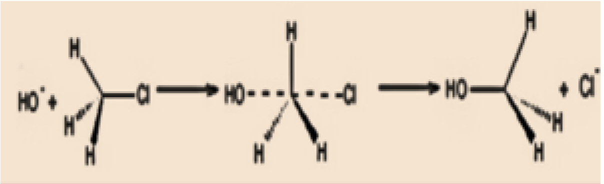
Retention of configuration is the ability of an asymmetric carbon to retain the spatial arrangement of the substituents/groups during a chemical reaction. This can only happen when the bond of carbon stereocenter remain intact. Therefore, a substituent will be replaced by other without disturbing the structure. Thus, the relative arrangement of the reactant and the product can be correlated.

For example, the reaction of 2 − methylbutan − 1 – ol upon heating with conc. HCl.



Inversion of Configuration

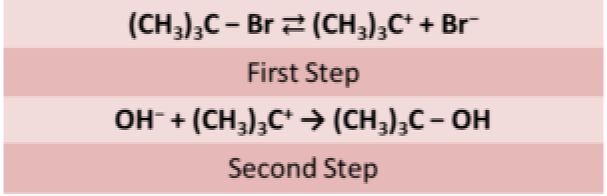
If an asymmetric carbon atom is not able to retain its spatial arrangement during a chemical reaction is known as inversion. An inversion occurs during SN_2 reactions. This is because the nucleophile attacks the C-X bond of an alkyl halide by the backside method. As a result of which, the configuration of the molecule gets inverted. Therefore, optically active alkyl halides in an SN_2 reaction leads to the inversion of configuration.



Inversion of Configuration

Racemization

Considering the two-step process of SN1 reactions, we will note that in the first step planar carbocation generation and in the second step attack of a nucleophile occur. The carbocation is planar which allow the nucleophile in the second step to attack the carbon atom either from below or above. This, in turn, results in both configurations- retention, and inversion.



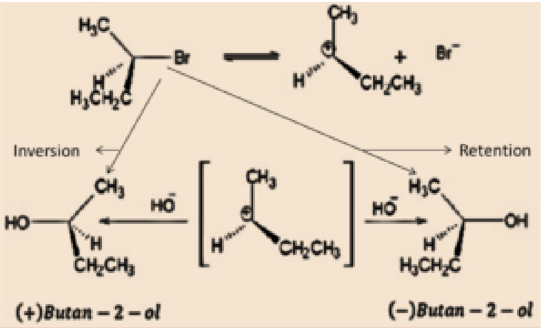
$(CH_3)_3C - Br \rightleftarrows (CH_3)_3C^+ + Br^-$

First Step

$OH^- + (CH_3)_3C^+ \rightarrow (CH_3)_3C - OH$

Second Step

There is also a possibility that 50 percent of the mixture will have the inversion of configuration and 50 percent will have retention of configuration. In the below example, both inversion and retention of configuration have taken place with respect to the actual reactant. Retention ((−)Butan − 2 − ol) Inversion ((+)Butan − 2 − ol).



Inversion, Retention and Racemization

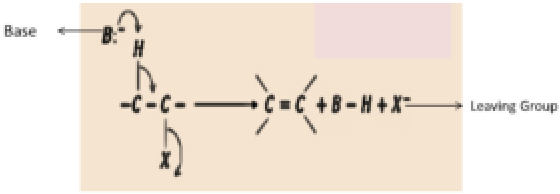
Thus a reaction of an asymmetric carbon can lead to the formation of three different configurations- Retention of Configuration, Inversion of Configuration, and Racemization.

Chemical Reactions of Haloalkanes- Elimination Reactions

The primary condition for a haloalkane to undergo elimination reaction is the presence of β −hydrogen atom.

Dehydrohalogenation or β – elimination

Elimination reaction occurs when an alkyl halide reacts with alcoholic KOH solution under heating conditions. The elimination takes place of hydrogen from β –carbon and the elimination of halogen member occur from α –carbon. The reaction will result in the formation of alkene as the final product.



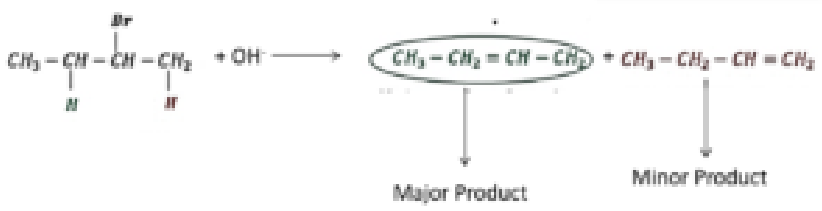
Mechanism of Dehydrohalogenation or β – elimination

The above reaction mechanism demonstrates a haloalkane. The α –carbon contains a halogen group whereas the β –carbon contains the hydrogen. When the base reacts with the hydrogen of the β –carbon, bond shifting occurs. Ond shifting results in the elimination of halogen group present in the reactant thereby forming an alkene as the major product and a corresponding by-product.

However, if there is more than 1β −hydrogen atom then multiple eliminations will occur thereby forming multiple alkenes. In such cases, the major product will be the most stable alkenes out of all the alkenes. Generally, the alkene which undergoes most substitution is generally the most stable. The major product is also known as Zaitsev′s product.

Zaitsev′s Product

The most substituted alkene refers to the alkene which has the greater number of alkyl group joined with the double bond. Hence, the more the number of alkyl group present with the double bond, more is the stability of the alkene. This happens due to the process of hyperconjugation. Example: Dehydrohalogenation of 2-Bromobutane



When alkyl halides react with nucleophiles there is a continuous competition whether the elimination or substitution reaction will occur. This mainly depends upon a certain factor which will determine what type of reaction will take place.

RX + Base → Elimination
RX + Nucleophile → Substitution

Factors Responsible for Favouring Elimination/Substitution Reactions

- Nature of the substrate present in the reaction- Reaction will depend upon the type of haloalkane present (primary, secondary or tertiary).
- Size and strength of the base/nucleophile- If the nucleophile is highly reactive there is a possibility that the reaction taking place will be a substitution reaction (SN2). However, if the

nucleophile is bulky then due to steric hindrance substitution reaction is difficult. In such cases, elimination reaction takes place.

- Conditions involved in reaction (solvent used in the reaction)

Summary of Chemical Reactions

Type of Haloalkane	Elimination Reaction	Substitution Reaction & its Types
Primary	Not possible	Substitution Reaction Possible (SN_2)
Secondary	Possible- On the basis of base strength	Substitution Reaction Possible (SN_1 or SN_2)- On the basis of nucleophile strength
Tertiary	Possible-On the basis of alkene stability	Possible- SN_1

On the basis of carbocation
stability

Chemical Reactions of Haloalkanes- Reactions with Metals

Haloalkanes on reaction with metals form a special class of compounds – organometallic compounds. Alkyl Halides or R-X reacts with certain metals to produce compounds containing C-metal bonds.

Grignard Reagent

In the year 1910, a renowned scientist “Victor Grignard” discovered a special class of organometallic compounds/reagents known as a Grignard Reagent. The Grignard reagent is Alkyl magnesium halide (R-MgX). This reagent formation is possible when a haloalkane (in this case ethyl bromide) react with Magnesium in the presence of dry ether. This will result in the formation of R-MgX.

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

Formation of Grignard Reagent

C-Mg bond is polar and covalent in nature. This is due to the difference in electronegativity between the carbon and magnesium atom. Thus, the carbon atom will attract the electron towards itself resulting in the formation of partial positive charge (δ +) on magnesium atom and partial negative charge (δ -) on the carbon atom. However, Mg-X bond in the same compound is ionic in nature.

$$\overset{\delta-}{R} - \overset{\delta+}{Mg} - \overset{\delta-}{X}$$

Therefore, the Grignard reagent is highly reactive in nature. It reacts with an acidic proton bearing compound to produce hydrocarbon. Thus substances such as H_2O, $R - OH$, and $R - NH_2$ are enough acidic and can react with Grignard reagents to form hydrocarbon (RH).

For example, if ethyl magnesium bromide reacts with an alcohol to form the respective hydrocarbon. Anhydrous condition (dry ether) is used in this reaction in order to avoid traces of water.

$$\underset{\text{(Ethylmagnesium bromide)}}{CH_3CH_2-MgBr} + CH_3OH \xrightarrow{\text{Dry Ether}} \underset{\text{(Ethane)}}{CH_3CH_2-H} + Mg(OCH_3)Br$$

Formation of Hydrocarbon from Grignard Reagents

Wurtz Reaction

In this reaction, haloalkane reacts with sodium in presence of dry ether to form hydrocarbons with twice the number of carbon atoms originally present in the reactant.

$$2RX + 2Na \xrightarrow{\text{Dry Ether}} R-R + 2NaX$$

Wurtz Reaction

Solved Example for You

Q. Reaction of alkyl chloride with KOH (aqueous) produces alcohols. However, the same reaction with alcoholic KOH produces alkene as the reaction's major product. Justify

Solution: The aqueous solution of KOH breaks down into K^+ and OH^- due to ionization. OH^- act as the nucleophile and undergo nucleophilic substitution reaction with alkyl chlorides thereby forming alcohols. Additionally, the highly hydrating property of aqueous solution decreases the basic property of OH^-. Thus the reaction is unable to form an alkene.

However, the alcoholic KOH solution has alkoxide ions (RO^-). They demonstrate highly basic property in comparison to OH^-ions. Therefore, alcoholic KOH solution is able to preferentially remove a molecule from HCl from the substrate (alkyl chloride) and form an alkene.

Polyhalogen Compounds

Everyone is aware of DDT- a very common pesticide. Did you know DDT was sold as a wonder-chemical post World War II? It is because DDT was a very simple solution for all sorts of pest problems, be it small or large. It was in widespread use as a pesticide. DDT is nothing but one of the polyhalogen compounds. Polyhalogen compounds have a wide variety of usage. Let’s learn more about them.

Polyhalogen Compounds

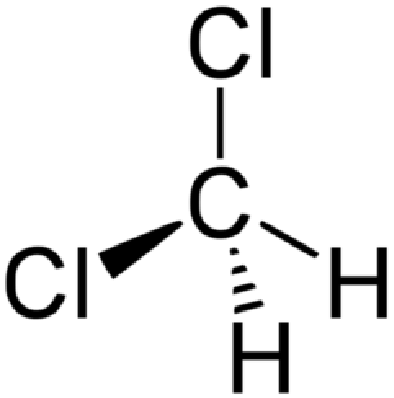
Polyhalogen compounds are Carbon compounds having more than one halogen (elements present in the group 17 of the modern periodic table) atom. Common uses of polyhalogen compounds are in agriculture and industrial sectors. They are popularly used for many purposes such as solvents, anaesthetics pesticides, etc.

Few very important polyhalogen compounds are methylene chloride, chloroform, carbon tetrachloride, iodoform, DDT, benzene hexachloride among many others. In this article, we will discuss some of the most prominent polyhalogen compounds.

1) Methylene chloride (Dichloromethane)

Dichloromethane, also known as methylene chloride, is one of the polyhalogen compounds present in form of solvent. It is popularly known for its uses in many purposes such as a paint remover, as a process solvent during drug manufacturing processes, as a propellant in aerosols, as a cleaning solvent, and as a finishing solvent.

Low levels of methylene chloride exposure in the air can cause slight hearing and vision impairment. High levels of methylene chloride exposure in the air can lead to nausea, dizziness, tingling, and numbness in an individual’s fingers and toes. Direct skin contact of humans with this solvent is highly injurious. It can cause harmful effects such as mild redness of the skin, intense burning, etc. Direct eye contact can lead to burning of the cornea.



Methylene chloride (Dichloromethane)

2) Chloroform (Trichloromethane)

Trichloromethane, also known as Chloroform, is a colourless polyhalogen compound present in liquid form. It has a characteristic sweet smell. The boiling point of chloroform is 334 K. However, chloroform can slowly oxidize by air and form a poisonous gas “phosgene” in the presence of light.

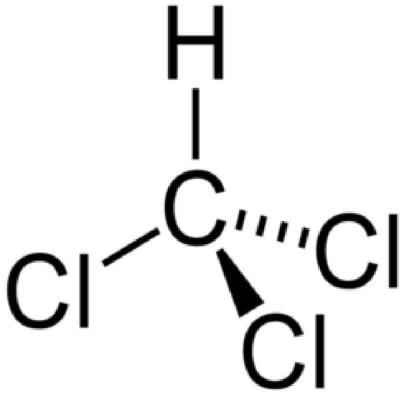
Therefore, it is necessary to store chloroform bottles away from sunlight. It should be completely filled to the brim in order to keep the air out of the bottle. Phosgene is the common name for the chemical carbonyl chloride, ($COCl_2$). However, the addition of little ethanol to chloroform can convert toxic phosgene to a nontoxic compound known as ethyl carbonate.

Chloroform act as a solvent for many substances such as fats, iodine, alkaloids, etc. One of the major use of chloroform in the present day for the manufacturing of Freon refrigerant R-22. Chloroform depresses the Central Nervous System. Initially, chloroform was used as the general anaesthetic for surgical purposes. However, now much safer options are available like ether.

Breathing 900 parts per million concentration of chloroform can lead to fatigue, dizziness, and headache. Chronic exposure of the compound can cause liver damage (due to the metabolism of chloroform and formation of poisonous gas phosgene) and kidney damage. Development of sores is one of the effects on immersion of skin in the chloroform.

Laboratory Uses of Chloroform

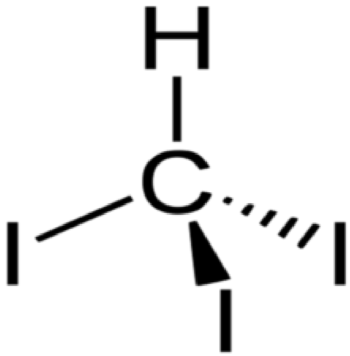
Chloroform act as a detection agent of primary amines during isocyanide test, also known as Carbylamine test. In the test, chloroform is heated with the mixture of amines with alcoholic NaOH. The reaction results in the formation of a foul-smelling isocyanide gas. It helps in the detection of aliphatic and aromatic primary amines.



Chloroform (Trichloromethane)

3) Iodoform (Triiodomethane)

The IUPAC name of Iodoform is triiodomethane. It is a pale yellow solid with the presence of a distinct smell. Initially, the polyhalogen compound was used as an antiseptic. However, the antiseptic property of the compound was due to the release of free iodine rather than iodoform which led to the release of objectionable smell. Therefore, now a day other iodine-containing formulations are in use rather than iodoform.



Iodoform (Triiodomethane)

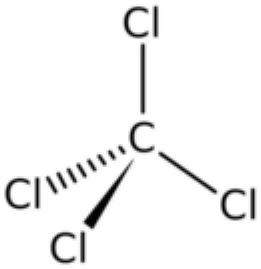
4) Carbon tetrachloride (Tetrachloromethane)

It is one of the most common polyhalogen compounds. The most common use of carbon tetrachloride (CCl_4) is in the manufacture of refrigerants. It also acts as propellants for aerosol cans. Additional use of this polyhalogen compound is for the synthesis of chemicals such as chlorofluorocarbons.

It is an important solvent in the pharmaceutical manufacturing process and for other general solvent purposes. Initially, in the mid of 1960's, carbon tetrachloride was widely available as cleaning fluid and degreasing agent in industries. It also acts as a cleaning agent, spot remover, and as a fire extinguisher in the home.

Evidence proves that carbon tetrachloride can cause liver cancer in humans. The common symptoms of carbon tetrachloride exposure are lightheadedness, nausea, dizziness, and vomiting that can lead to permanent damage to the nerve cells. It can also lead rapidly to coma, unconsciousness and sometimes death in severe cases. Overexposure to carbon tetrachloride can lead to irregular heart beating or sudden stop. It can irritate the eyes on contact.

The release of CCl_4 into the air can result in ozone depletion. Ozone depletion is one of the major environmental concerns today. Depletion of the ozone layer can lead to exposure of the UV rays which may further cause many problems such as eye diseases, different disorders, skin cancer, and disturbance of the immune system.

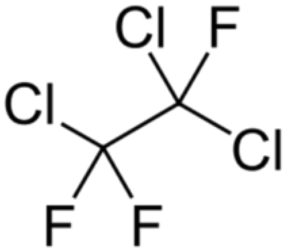


Carbon tetrachloride (Tetrachloromethane)

5) Freon (CFC's)

Freon is the collective term for chlorofluorocarbon derivatives of methane and ethane. These compounds are stable, non-corrosive, and non-toxic in nature. These derivatives are easily liquefiable gases. The most common Freon is Freon 12 (CCl_2F_2). Freon form from tetrachloromethane by a reaction process known as "Swarts reaction."

Freons can act as aerosol propellants. It also helps in air conditioning and refrigeration purposes. Total Freon production was approximately 2 billion pounds per year by the year 1974. Almost all types of freon gradually settle into the atmosphere without changing its form. This initiates radical chain reactions that cause the problem in the natural ozone balance of the atmosphere.



Freon (CFC's)

6) DDT (p,p´-Dichlorodiphenyltrichloroethane)

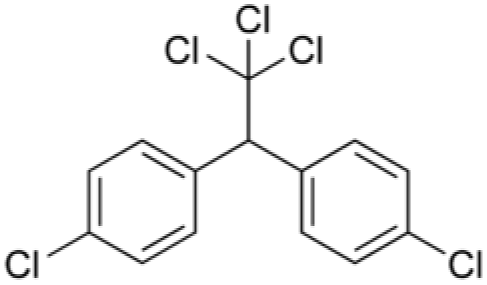
DDT is available in many forms including granules, powder, aerosols, etc. In 1873, DDT was prepared as the first chlorine-based organic insecticides. Paul Miller of Geigy Pharmaceuticals in Switzerland first found the efficacy of DDT as an insecticide in 1939. He received

Nobel Prize in Medicine and Physiology in 1948 for the discovery of DDT.

Post World War II there was an enormous increase in the use of DDT. It is because of the capacity of DDT to act against mosquitoes that cause malaria and lice that spreads typhus. However, everyone started observing the disadvantages of the overuse of DDT by late 1940s.

Gradually, insect started developing resistance against the compound. Moreover, it was highly toxic to fishes. Additionally, the chemical stability of DDT and its capacity of fat solubility increased the problem. Rapid metabolism of DDT is difficult by animals as a result of which accumulation and storage of DDT in the fatty tissues occur. Therefore constant ingestion of DDT can lead to a steady buildup of the compound over time. US government put a ban on DDT in the year 1973.

According to Stockholm Convention on Persistent Organic Pollutants, DDT was banned from using for agricultural purposes by the year 2001. However, it is still in use in developing and underdeveloped countries.



DDT (p,p'-Dichlorodiphenyltrichloroethane)

Here's a Solved Question for You

Q: Name the groups that will give a positive iodoform test?

Solution: Iodoform test is positive for the $CH_3 – C = O$ (acetyl) or $CH_3–CH\text{-}OH$ (alcohol) group.

Reactions of Haloarenes

Can you believe that marine organisms can produce haloarenes? Marine organisms that can use chloride and bromide available in the ocean waters are capable of producing haloarenes. They have been known to exhibit several medicinal properties. Thus, various reactions of haloarenes occur artificially as well as in nature.

Reactions of Haloarenes

Reactions of haloarenes or reactions of aryl halides are mainly of 3 types:

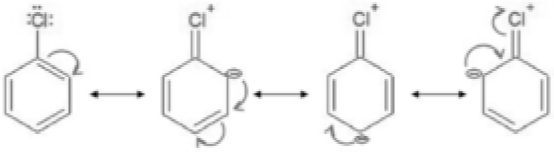
- Nucleophilic Substitution Reactions
- Electrophilic Substitution Reactions
- Reaction with Metals

I. Nucleophilic Substitution Reactions

Nucleophilic Substitution Reactions are difficult in case of haloarenes. However, haloarenes undergo nucleophilic substitution reaction under certain conditions. Key reasons for decreased or unreactive nature of haloarenes towards nucleophilic substitution reactions are as below:

Resonance Effect

In case of haloarenes, π – electrons present in the benzene ring undergo conjugation with the halogen atom present in the haloarene structure. This results in resonance and development of partial double bond in the C-X bond. The partial double bond cleavage of a haloarene is more difficult than a haloalkane. Thus, haloarenes cannot be cleaved by a nucleophile easily and they are less reactive towards a nucleophilic substitution reaction.



Example of Resonance Effect

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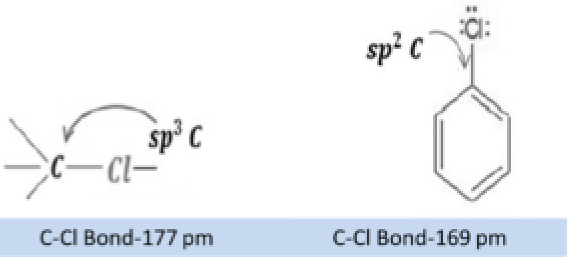
- Chemical Reactions and Stereochemistry
- Polyhalogen compounds

The Difference in Hybridization of Carbon Atom in C-X Bond

The member of the halogen group is attached to an sp_2 hybridized carbon atom in the case of haloarenes. However, the halogen is attached to the sp_3 hybridized carbon atom in haloalkanes. The s character is stronger in sp^2C in comparison to sp^3C. As a result, sp^2C is more electronegative than sp^3C.

Therefore, sp^2C has a greater capacity of withdrawing the electrons of the C-X bond and holding it tightly to itself. Thus, the bond length is shorter in case of haloarenes than haloalkanes. Shorter bond length results in a stronger bond. For instance, C—Cl bond length in haloalkane is 177pm whereas in haloarene it is 169 pm.



Difference in Hybridization of Carbon Atom in C-X Bond

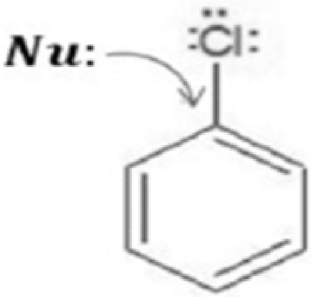
Phenyl Cation Instability

The breaking down of a C-X bond in haloarenes results in the formation of phenyl cation and X^-. The resultant phenyl cation is highly unstable because the positive charge is present on the electronegative sp^2 C atom. Moreover, it cannot obtain stability by electronic displacement effects such as resonance. Additionally, an S_N1 reaction is not possible due to unstable carbocation.

Therefore, instability of phenyl cation decreases the reactivity of the haloarene towards nucleophilic substitution reaction. Phenyl cation instability is quite similar to vinyl cations. In both the cases, the carbonation is present on the sp2 hybridized electronegative carbon atom. However, the stability of benzyl cation is quite similar to allyl cation. In both the cases, resonance effect help in the stabilization.

Possible Electronic Repulsion

A nucleophile approaching the electron-rich phenyl ring (arenes) in haloarenes can experience possible electronic repulsion.



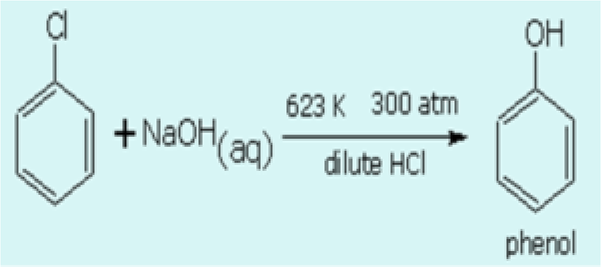
Electronic Repulsion

Conditions when Haloarenes are Reactive

We know that haloarenes are generally unreactive or less reactive towards nucleophilic substitution reactions. However, there are situations when haloarenes are reactive towards nucleophilic substitution reactions. Below example will further help to understand how certain haloarenes are reactive towards nucleophilic substitution reaction in certain drastic conditions.

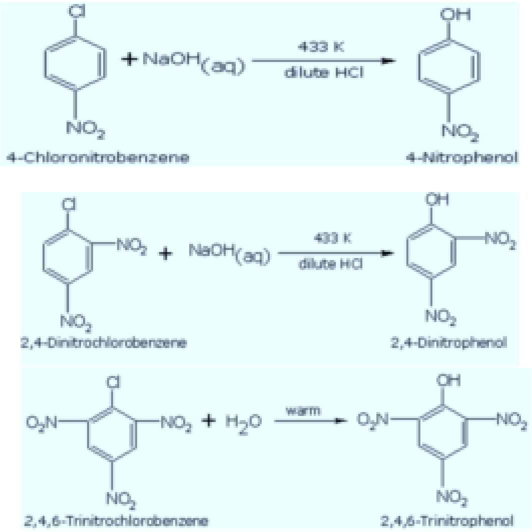
Replacement by Hydroxyl Members

For example, a haloarene such as a chlorobenzene can react to form phenol in drastic or extreme conditions. Chlorobenzene undergoes reaction to form alcohol under a temperature of 623K and a pressure of 300 atm. The haloarene reacts with NaOH in these conditions and forms phenol by substitution of chlorine group by OH group.



Replacement by Hydroxyl Member

However, if an electron withdrawing group is present in the haloarenes, these haloarenes become more reactive towards nucleophilic substitution reaction. This means if an electron withdrawing group such as $-NO_2$ is present in the ortho, para, and both ortho- and para- positions then the reactivity of the reaction increases in much lesser drastic conditions.



Increase of Reactivity Based on Position

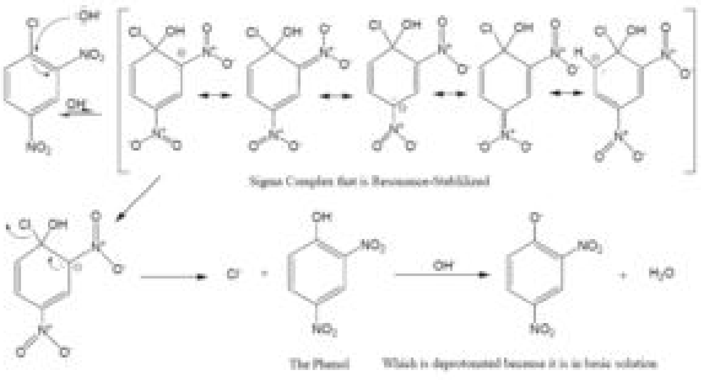
Mechanism of Aromatic Nucleophilic Substitution Reaction

A nucleophile approaches and attacks the C-X bond and the π –electrons move in a manner that the electron density delocalizes in the benzene ring at Ortho- and the Para position. If an electron withdrawing group is present in such a case at the Ortho and the Para positions of the benzene ring then it will stabilize the negative charge on the carbon atom by withdrawal.

Thus, the presence of electron withdrawing groups such as NO_2 at Ortho and Para position facilitate the attack of the nucleophile.

Furthermore, the stabilization of carbocation takes place by resonance as well as by the electron withdrawing group such as NO2.

A series of fast and slow step will occur in the reaction and result in the formation of a high resonance stabilized sigma complex. Finally, in the end, the π –electrons will be restored when the negative charge will delocalize by eliminating the Cl bond. Finally, the product will be formed. Read the below example to further understand the mechanism of nucleophilic substitution reaction.



Mechanism of Nucleophilic Substitution Reaction

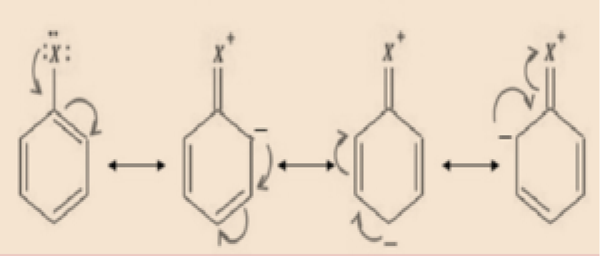
(Source Credit: Wikipedia)

II. Electrophilic Substitution Reactions

The type of reactions in which an electrophile substitutes another electrophile in any organic compound is known as electrophilic substitution reaction. An electrophile means an electron seeking species. Haloarenes will undergo the usual benzene ring reactions such as nitration, halogenation, Friedel-Crafts reactions and sulphonation.

We know that haloarenes are electron-rich compounds. Therefore, they can undergo electrophilic substitution reaction and the attacking species, in this case, will be an electrophile. The +M effect will result in the concentration of electron density at ortho −and para −positions.

However, electrophilic substitution reactions with respect to the haloarene reactions are slow in comparison to benzene reactions. This is because the halogen group present in haloarenes are deactivating because of the –I effect. Hence, electrons withdraw from the benzene ring.

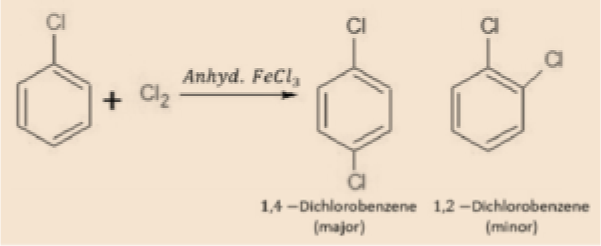


Electrophilic Substitution Reaction

Halogenation

The reactions of haloarenes take place when haloarene react with chlorine in the presence of a solvent (say ferric chloride). The chlorine molecule tends to become polar in nature and develops a slightly positive charge. Thus, the chlorine acts as an electrophile and will attack the electron-rich Ortho and Para position of the compound.

The reaction will result in the formation of both Ortho and Para compounds. However, Para isomer will be the major product and Ortho isomer will be the minor product of the reaction. In the below example chlorobenzene reacts in the presence of Lewis acid and form ortho and para substitutes of dihalobenzenes.

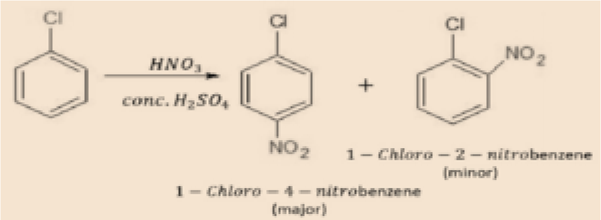


Halogenation Reaction

Nitration

The reaction starts with the formation of NO_2^+ from nitric acid on initiation with sulphuric acid. NO_2 contains an electrophilic centre because of the electronegative oxygen atoms present in the molecule itself. Again, the electrophile will attack the electron-rich ortho and para positions. The reaction will result in the formation of Para isomer and Ortho isomer as the major and the minor product respectively.

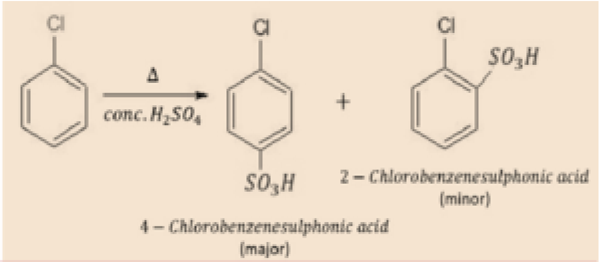
In the below example, nitration of halobenzene will result in the formation of ortho and para substituted products in the presence of nitric and sulphuric acid. The electrophile, in this case, is NO_2^+.



Nitration

Sulphonation

In sulphonation SO_3 acts as an electrophile. It attacks the electron-rich haloarene at Ortho and Para positions. The reaction results in the formation of Para and Ortho Chlorobenzenesulphonic acids, where Para isomer forms the major product and Ortho isomer forms the minor product.



Sulphonation

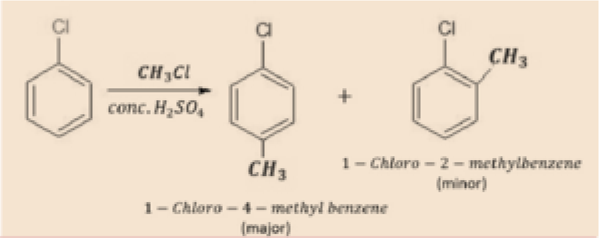
Friedel-Crafts Reaction

There are generally two types of Friedel-Crafts reaction

- Friedel-Crafts Alkylation Reactions
- Friedel-Crafts Acylation Reactions

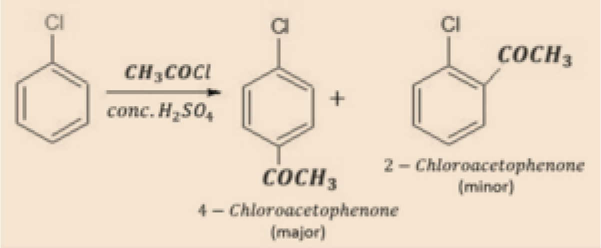
In this case, the electrophile is the alkyl and acetonic group because of the positive charge present in the carbon atom.

Friedel-Crafts Alkylation Reactions



Friedel-Crafts Alkylation Reactions

Friedel-Crafts Acylation Reactions



Friedel-Crafts Acylation Reaction

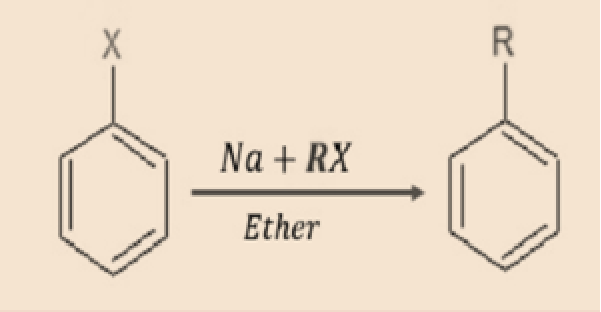
III. Reactions with Metals

Haloarenes undergo few reactions with metals. Two primary reactions are:

- Wurtz-Fittig Reaction
- Fittig Reaction

Wurtz-Fittig Reaction

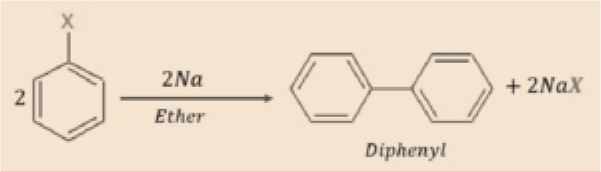
In this reaction, a mixture of alkyl halide reacts with an aryl halide in the presence of dry ether and sodium. The resultant product is alkyl arene.



Wurtz-Fittig Reaction

Fittig Reaction

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



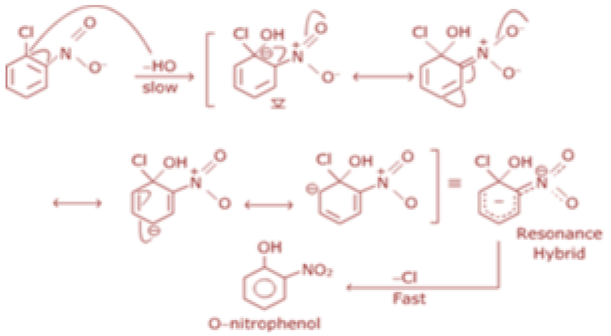
Fittig Reaction

Here’s a Solved Question for You

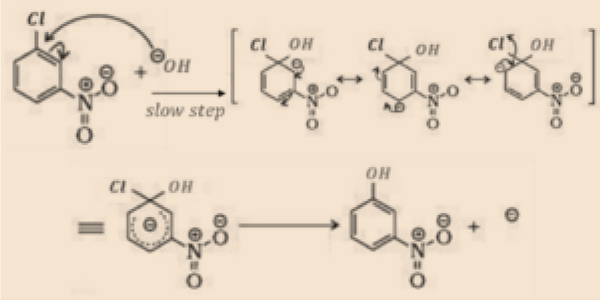
Q: Why does NO2 group is effective only at Ortho and Para positions but not at Meta position?

Solution: When the nitro group is present at Ortho or Para positions, the electron density from the arene structure is withdrawn. This facilitates the attack of a nucleophile group. Moreover, stabilization of carbonation by resonance occurs. The electron withdrawing or the –NO2 group stabilizes the negative charge present in O and P position. However, in case of Meta position any of the resonating structure do not accept the negative charge on carbon atom having the

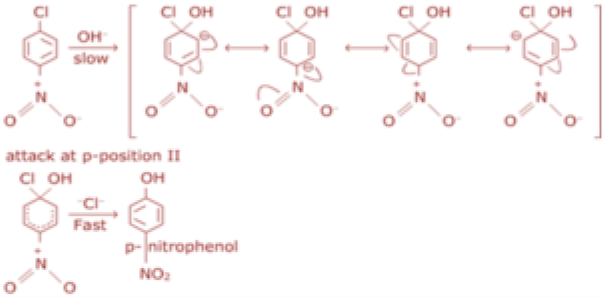
–NO2 group. As a result, the negative charge at Meta position is not stabilized. Therefore, there is no change seen in the reactivity of the nucleophilic substitution by the presence of –NO2 group.



Attack at Ortho-Position



Attack at Meta Position



Attack at Para-Position