Haloalkanes and Haloarenes

Haloalkanes

Haloalkanes are the halogen deivatives of hydrocarbons.

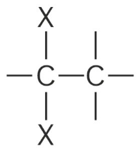
Classification of Haloalkanes

Monohalides (R–X): Monohalides are monohalogen derivatives of alkanes which have a general formula $C_nH_{2n+1}X$ and are known as alkyl halides.

R–X may be of three types:

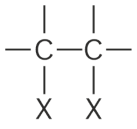
1.	Primary	$R-CH_2X$
2.	Secondary	R_2CHX
3.	Tertiary	R_3CX

Dihalides ($C_nH_{2n}X_2$): Dihalides are the di-halogen derivatives of alkanes and are of geminal and vicinal types.



$$-\underset{X}{\overset{X}{\mathrm{C}}}-\mathrm{C}-$$

Geminal



$$-\underset{X}{\mathrm{C}}-\underset{X}{\mathrm{C}}-$$

Vicinal

Example

(a) CH_3CHBr_2 (Ethylidine dibromide),

(b) $BrCH_2CH_2Br$ (Ethylene dibromide)

Trihalides ($C_nH_{2n-1}X_3$) or haloforms: Trihalides are tri-halogen derivatives of alkanes and are represented by a general formula CHX_3 (haloforms).

Tetrahalides: Tetrahalides are tetra-halogen derivatives of alkanes and arerepresented by a general formula CX_4 or CX_2Y_2.

Aromatic Halogen Compounds

When halogen atom is attached to aromatic hydrocarbons directly to the ring , the substance is known aryl halides. Their general formula is Ar—X.

Concept Ladder

In haloalkanes, the halogen atom is attached to the sp^3-hybridised carbon atom of an alkyl group whereas in haloarenes, the halogen atom is attached to sp^2-hybridized carbon atom of an aryl group.

Definitions

The monohalogen derivatives of alkanes are called alkyl halides or monohaloalkanes or simply haloalkanes.

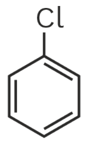
Concept Ladder

Haloalkynes or Alkynyl halides are the halogen derivatives of alkynes. The monohalogen derivatives of alkynes have the general formula $C_nH_{2n-3}X$ where X=F, Cl Br or I and n = 2, 3, 4....., etc.

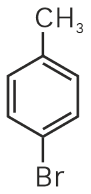
(a) Mono Halogen Derivatives

Examples

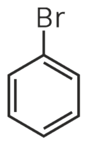
(i) Chlorobenzene



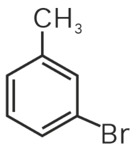
(ii) p-Bromotoluene



(iii) Bromobenzene



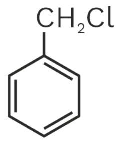
(iv) m-Bromotoluene



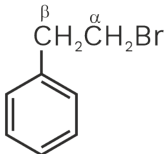
(b) Side chain Halogen Derivatives

Example

(i) Benzyl chloride



(ii) β-Phenylethyl bromide

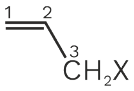


Allylic, Vinylic and Benzylic Halides

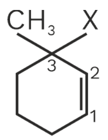
(a) Allylic Halides

Example

(i) 3-Haloprop-1-ene (1°)

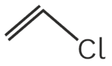


(ii) 3-Halo-3-methylcyclohex-1-ene (3°)

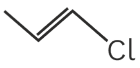


(b) Vinylic Halides

(i) Chloroethene

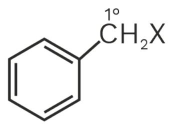


(ii) 1-Chloroprop-1-ene

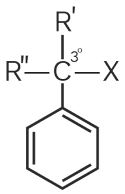


(c) Benzylic Halides

(i) Benzyl halide (1°)



(ii) A benzylic halide (3°)



Methods of preparation

Halogenation of alkanes

$$R-H+X_2 \xrightarrow{hv} R-X+HX$$

For example

$$CH_4+Cl_2 \xrightarrow[\text{or}520-650K]{hv} CH_3Cl+CH_2Cl_2+CHCl_3+CCl_4$$

$$\underset{\text{Propane}}{CH_3-CH_2-CH_3} \xrightarrow[298K]{Cl_2,hv} \underset{\text{1–Chloropropane (45\%)}}{CH_3-CH_2-CH_2-Cl} + \underset{\text{2-Chloropropane (55\%)}}{CH_3-CHCl-CH_3}$$

$$\underset{\text{Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[298\ K]{Cl_2,hv} \underset{\text{1–Chlorobutane(28\%)}}{CH_3CH_2CH_2CH_2Cl} + \underset{\text{2–Chlorobutane (72\%)}}{CH_3CH_2-CHCl-CH_3}$$

In general, the ease of subsitution of various hydrogens follows the sequence:

Allylic > 3° > 2° > 1° > CH_4

Reactivity order in halogens: $F_2 > Cl_2 > Br_2 > I_2$

Iodination is reversible, but it may be carried out in presence of an oxidising agent, such as, HIO_3, HNO_3, HgO, etc., which oxidises the HI as it is formed.

$$CH_4+I_2 \overset{hv}{\rightleftharpoons} CH_3I+HI\ ;\ 5HI+HIO_3 \longrightarrow 3I_2+3H_2O$$

Flourination: The best way to prepare alkyl fluorides is by halogen exchange. An alkyl chloride or bromide is heated in the presence of a metallic fluoride, such as AgF, Hg_2F_2, CoF_3 or SbF_3 to give alkyl fluorides.

$$\underset{\text{Bromomethane}}{CH_3Br}+AgF \longrightarrow \underset{\text{Fluoromethane}}{CH_3F}+AgBr$$

$$2CH_3CH_2Cl+Hg_2F_2 \longrightarrow 2\,CH_3CH_2\,F+Hg_2\,Cl_2$$

This reaction is called Swarts reaction.

When the organic halide contains two or three halogen atoms at the same carbon, CoF_3or the more easily available SbF_3 is used. For example,

$$\underset{\text{2, 2–Dichloropropane}}{3\,CH_3CCl_2CH_3}+2\,SbF_3 \longrightarrow \underset{\text{2,2–Difluoropropane}}{3\,CH_3CF_2CH_3}+2\,SbCl_3$$

from Alcohols : Generally alkyl halides are prepared from alcohols by replacement of —OH group by an halogen ion. This is usually by using HX or PX_5.

$$R-OH+X^- \longrightarrow R-X+OH^-$$

Concept Ladder

Vinylic and aryl hydrogen are so much unreactive that they do not participate in free radical halogenation. However, allylic and benzylic halides can be prepared from alkenes and arenes without any complication.

Definitions

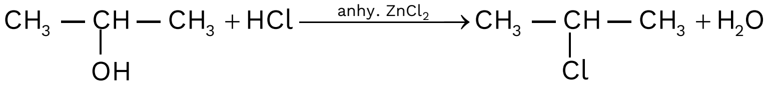
Swarts' reaction is generally used to get alkyl fluorides from alkyl chlorides or alkyl bromides. This is done by heating of the alkyl chloride/bromide in the presence of the fluoride of some heavy metals (silver fluoride or mercurous fluoride for example).

(a) By the action of Halogen acids :

$$R - OH + HX \xrightarrow{\text{Catalyst}} R - X + H_2O$$

(i) Using HCl :

$$CH_3CH_2OH + HCl(g) \xrightarrow{\text{anhy. } ZnCl_2} CH_3CH_2Cl + H_2O$$



$$CH_3-\underset{OH}{\underset{|}{CH}}-CH_3 + HCl \xrightarrow{\text{anhy. } ZnCl_2} CH_3-\underset{Cl}{\underset{|}{CH}}-CH_3 + H_2O$$

Anhydrous $ZnCl_2$ helps in the cleavage of C–O bond. Being a Lewis acid, it co-ordinates with the oxygen atom of the alcohol. As a result, C–O bond weakens and ultimately breaks to form carbocations, which form chlorides.

Concept Ladder

Order of reactivity of the halogen acids HI>HBr>HCl.
Order of reactivity of Alcohols:
$R_3COH > R_2CHOH > RCH_2OH$

$$(CH_3)_3C-OH + \underset{(\text{conc.})}{HCl} \xrightarrow[\text{temp}]{\text{Room}} (CH_3)_3C-Cl + H_2O$$

Yield is improved when vapours of alcohol and HCl are passed over alumina at 350°C.

(ii) Using HBr :

Alkyl bromides are obtained by refluxing the alcohol with constant boiling in HBr (40%) in presence of a little conc. H_2SO_4

$$CH_3CH_2OH + HBr \xrightarrow[\text{Reflux}]{H_2SO_4} CH_3CH_2-Br + H_2O$$

$$C_2H_5OH + KBr + H_2SO_4 \longrightarrow C_2H_5Br + KHSO_4 + H_2O$$

(iii) Using HI :

$$CH_3CH_2OH + HI \xrightarrow{\text{Reflux}} CH_3CHI + H_2O$$

$$CH_3OH + KI + H_3PO_4 \xrightarrow{\Delta} CH_3I + KH_2PO_4 + H_2O$$

Concept Ladder

In alkyl halide electro -negativity difference between the carbon and the halogen, the shared pair of electron lies closer to the halogen atom. As a result, the halogen carries a small negative charge, and carbon carries a small positive charge. So, C—X bond is always a polar covalent bond.

(b) By the action of Phosphorus Halides:

Phosphorus halides react with alcohols to form haloalkanes in excellent yield (80% or above).

$$ROH + PX_5 \longrightarrow R - X + POX_3 + HX$$

Here X can be either chlorine or bromine or iodine.

$$3ROH + PX_3 \longrightarrow 3R - X + H_3PO_3$$

Since, PI_3 and PBr_3 are not very stable compounds, these are generally prepared in situ by the action of red phosphorus on bromine and iodine respectively.

$$P_4 + 6X_2 \longrightarrow 4PX_3;\ R-OH \xrightarrow{P+Br_2} R-Br;\quad R-OH \xrightarrow{P+I_2} R-I$$

This method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides.

The method is generally useful for preparing lower alkyl bromides and iodides in laboratory.

Concept Ladder

Iodoalkanes or alkyl iodides are prepared by refluxing a suitable alcohol with constant boiling hydriodic acid (57%). HI may also be generated in situ by the action of 95% phosphoric acid on KI.

(c) By the action of Thionyl chloride : (Darzen's method)

Chloroalkanes are conveniently prepared by refluxing alcohol with thionyl chloride ($SOCl_2$) in presence of pyridine (C_5H_5N).

$$R-OH + SOCl_2 \xrightarrow[\text{Reflux}]{\text{Pyridine}} R-Cl + SO_2\uparrow + HCl\uparrow$$

Thionyl chloride method is preferred over hydrogen chloride or phosphorus chloride method for the preparation of chloroalkanes since both the by-products (SO_2 and HCl) in this reaction being gases escape, leaving behind chloroalkanes in almost pure state.

Previous Year's Question

The compound C_7H_8 undergoes the following reactions :

$$C_7H_8 \xrightarrow{3Cl_2/\Delta} A \xrightarrow{Br_2/Fe} B \xrightarrow{Zn/HCl} C$$

The product C is **[NEET]**

(1) m-bromotoluene
(2) o-bromotoluene
(3)3-bromo-2,4,6-trichlorotoluene
(4) p-bromotoluene.

3. From Silver salt of fatty acids :

This reaction is called as Borodine Hundsdiecker reaction and is a free radical reaction. This reaction gives the product with one carbon atom less than the fatty acid. The yield of the alkyl halide formation with this reactions is :

$$CH_3CH_2COOAg + Br_2 \xrightarrow{CCl_4,\text{Reflux}} CH_3CH_2-Br + CO_2 + AgBr$$

primary > secondary > tertiary.

Chloroalkanes can also be prepared by this method by using Cl_2 instead of Br_2 but the yields are poor.

With I_2, silver salts give esters instead of iodoalkanes.

$$2RCO_2Ag + I_2 \longrightarrow RCOOR + CO_2 + 2AgI$$

4. Halogen exchange reaction :

Iodoalkanes are easily prepared from corresponding chloroalkanes or bromoalkanes by heating with sodium iodide in acetone or methanal.

This reaction is called Frinkelstein Reaction.

$$RCl + NaI \xrightarrow[\Delta]{Acetone} RI + NaCl;\ \ X = Cl \text{ or } Br$$

Its a halide exchange reaction which involves a substitution of Cl/Br by I. The reaction was specially de signed to prepare iodo-alkanes which were not easily prepared using simple halogenation method. (Due to the reversibility of Iodination)

$$R - X + NaI \xrightarrow{Acetone} R - I + NaX\downarrow;\ \ X = Cl \text{ or } Br$$

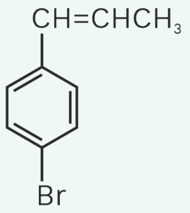
Reaction is supposed to be based on principle of greater solubility of NaI in acetone as compared to NaCl or NaBr because of greater covalent character in NaI. That is why despite of being a weaker reagent than Cl$^-$/ Br$^-$, I$^-$ still substitues them and the NaCl/NaBr formed precipitates out driving the equilibrium in forward direction.

Previous Year's Question

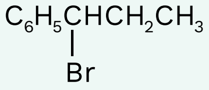
The reaction of $C_6H_5CH=CHCH_3$ with HBr produces **[NEET]**

(1) $C_6H_5CH_2CH_2CH_2Br$

(2)

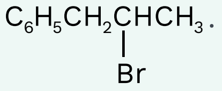


(3)



$C_6H_5\underset{\substack{|\\Br}}{CH}CH_2CH_3$

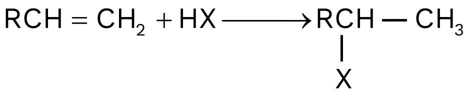
(4)



$C_6H_5CH_2\underset{\substack{|\\Br}}{CH}CH_3$.

from Alkenes :

Alkenes react with halogen acids to form haloalkanes. Order of reactivity : HI > HBr > HCl > HF.

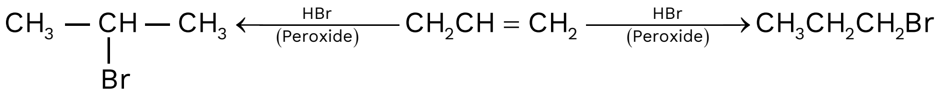


$$RCH = CH_2 + HX \longrightarrow R\underset{\substack{|\\X}}{CH} - CH_3$$

The unsymmetrical alkenes follows Markovnikov's rule during addition forming secondary or tertiary alkyl halides predominantly.

Concept Ladder

Peroxide effect is observed only for HBr. So HCl and HI when added to alkene give same product in presence of absence of peroxide.



$$CH_3 - \underset{\substack{|\\Br}}{CH} - CH_3 \xleftarrow[\text{(Peroxide)}]{HBr} CH_2CH = CH_2 \xrightarrow[\text{(Peroxide)}]{HBr} CH_3CH_2CH_2Br$$

(c) Allylic halogenation :When alkenes (except Ethylene) are heated with Cl_2 or

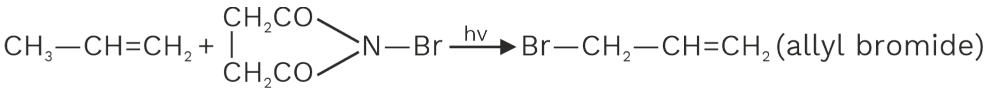
Br_2 at a high temperature of about 773 K, the hydrogen atom at the allylic carbon (i.e., carbon next to the double bond) is substituted by a halogen atom. For example,

Definitions

Reactions in which halogenation occurs at the allylic position of an alkene are called allylic halogenation reactions.

$$CH_3 - CH = CH_2 + Cl_2 \xrightarrow{773K} \underset{\text{3–Chloroprop–1–ene (Allyl chloride)}}{Cl - CH_2 - CH = CH_2}$$

However, a more specific reagent for allylic bromination is N-bromosuccinimide (NBS).



$$CH_3{-}CH{=}CH_2 + \begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!\!>\!N{-}Br \xrightarrow{hv} Br{-}CH_2{-}CH{=}CH_2 \text{ (allyl bromide)}$$

Allylic chlorination can also be carried out with sulphuryl chloride.

$$CH_3 - CH = CH_2 + SO_2Cl_2 \xrightarrow[\text{Traces of peroxide}]{475,\ hv} Cl - CH_2 - CH = CH_2 + HCl + SO_2$$

Previous Year's Question

When chlorine is passed through propene at 400°C, which of the following is formed? **[NEET]**

(1) PVC

(2) Allyl chloride

(3) Propyl chloride

(4) 1, 2-Dichloroethane

Physical properties of monohalides

- Lower members of monohalides(CH_3X, C_2H_5X) are colourless gases while higher members are colourless liquid up to C_{18}, members are colourless solids.
- Boiling point and density increase with increase in molecular weight.

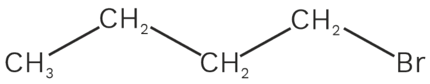
$$C_4H_9Cl > C_3H_7Cl > C_2H_5Cl > CH_3Cl$$

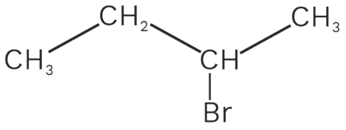
$$RI > RBr > RCl > RF$$

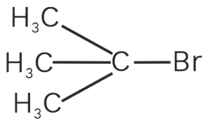
Likewise it happens in alkanes, branching also decrease B.P

Concept Ladder

CH_3Cl, CH_3Br, C_2H_5Cl, some chlorofluoromethanes are gases at room temperature. Higher chloro, bromo, iodo compounds are either liquids or solids. Many volatile halogen compounds have sweet smell.







Boiling Point ⟶ 375K 364K 346K

- Dipole moment: RCl > RF > RBr > RI

$$\underset{1.86D}{CH_3Cl} > \underset{1.847D}{CH_3Br} > \underset{1.83D}{CH_3Br} > \underset{1.636D}{CH_3I}$$

$\mu \rightarrow$

- Stability : RF > RBr > RCl > RI
- Solubility $\alpha \dfrac{1}{\text{Mol. wt.}}$

In general: $CH_3X > C_2H_5X > C_3H_7X > C_4H_9X$

Rack your Brain

n-Butyl bromide has higher boiling point than t-butyl bromide. Give reasons?

Q.1 Haloalkanes are less soluble in water, why?

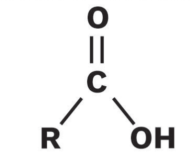
A.1 Haloalkanes are polar molecules, neither they form H-bond with water nor can thye break the H-bonds already existing between water molecules. As a result, the solubility of haloalkanes in water in very low.

ACIDITY & BASICITY

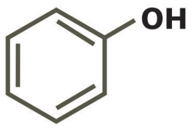
$H\text{-}A \rightleftharpoons H^+ + A^-$ | $K_a = \frac{[H^+][A^-]}{[HA]}$ | $pK_a = -\log_{10} K_a$

Key factors that effect the acidity

- $HF > H_2O > NH_3 > CH_4$ — **Electronegativity** - The more electronegative the anionic atom in the conjugate base, the better it is at accepting the negative charge.
- HI > HBr > HCI > HF — **Size** - The easier it is for the conjugate base to accommodate negative charge (lower charge density). The size of the group also weakens the bond H-X.
- RCOOH > ROH — **Resonance** - In the carboxylate ion ($RCOO^-$) the negative charge is delocalised across 2 electronegative oxygen atoms which makes it more stable than being localised on a specific atom as in alkoxide (RO-.)



>



> R — OH > R — NH_2 > R—H

Carboxylic acids $pK_a \approx 5$

Phenols $pK_a \approx 10$

Alcohols $pK_a \approx 16$

Amines $pK_a \approx 35$

Alkanes $pK_a \approx 60+$

Key factors that effect the basicity

- $CH_3^- > NH_2^- > OH^- > F^-$ — **Electronegativity** - The more electronegative the atom donating the electrons is, the less willing it is to share those electrons with a proton. so the weaker the base.
- $F^- > Cl^- > Br^- > I^-$ — **Size** - The larger the atom the weaker the H-X bond and the lower the electron density making it a weaker base..
- $RO^- > RCOO^-$ — **Resonance** - In the carboxylate ion ($RCOO^-$) the negative charge is delocalised across 2 electronegative atoms which makes it the electrons less available than when they localised on a specific atom as in the alkoxide (RO^-.)

General basicity trend of some common organic bases

$R-\ddot{\underset{\cdot\cdot}{N}}H$ Amide ions $pK_a \approx 35$ > $R-\ddot{\underset{\cdot\cdot}{O}}:$ Alkoxides $pK_a \approx 16$ > $R-\ddot{N}H_2$ Amines $pK_a \approx 9$

Chemical Properties of Monohalides

- Since the $\overset{\delta+}{C}-\overset{\delta-}{X}$ is polar, these are reactive compounds.
- The reactivity order is as follows:
  $R_3CX > R_2CHX > RCH_2X$
  $RI > RBr > RCl$
  $CH_3X > C_2H_5HX > C_3H_7X > ....$

Nucleophilic substitution reactions: Alkyl halides undergo nucleophilic substitution reactions as follows:

$$\overset{+\delta}{R}-\overset{-\delta}{X} + \underset{\substack{\text{Strong}\\ \text{Nucleophile}}}{\ddot{Z}} \longrightarrow R-Z + \ddot{X}$$

This reactions occurs by either S_N1 or S_N2 mechanism.

For example,

- $R-X \xrightarrow{\text{Aq.KOH}} R-OH + HX$
- $R-X \xrightarrow{\text{AgOH}} R-OH + AgX$
- $R-X \xrightarrow{\text{Alc.KCN}} R-CN + KX$

  R–CN is major product as KCN being ionic, provides CN^- ions. Therefore, attack occurs from the carbon atom side.
- $R-X \xrightarrow{\text{AgCN}} R-NC + AgX$

  Major product is R–NC as AgCN being covalent cannot give CN^- ions. Therefore, attack occurs from nitrogen atom to give R–NC.
- $R-X \xrightarrow{AgNO_2} \underset{\text{Nitroalkane}}{R-NO_2} + AgX$
- $R-X \xrightarrow{KNO_2} \underset{\text{Alkylnitrite}}{R-O-N=O} + KX$
- $R-X \xrightarrow{NaN_3} \underset{\text{Azides}}{R-N_3} + NaX$
- $R-X \xrightarrow{R'COOAg} R'COOH + AgX$
- $R-X \xrightarrow{R'ONa} R'-O-R + NaX$

The above reaction is called williamson synthesis.

Definitions

Reaction in which a stronger nucleophile displaces a weaker nucleophile are called nucleophilic substitution reaction and the atom or group which departs with its bonding pair of electrons is called the leaving group.

Concept Ladder

- Order of reactivity of haloalkanes:
  $RI > RBr > RCl > RF$
- Order of leaving tendency :
  $I^- > Br^- > Cl^- > F^-$

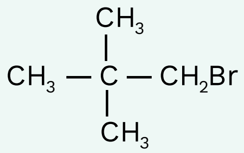
Previous Year's Question

In a SN_2 substitution reaction of the type

$$R-Br + Cl^- \xrightarrow{DMF} R-Cl + Br^-$$

which one of the following has the highest relative rate?

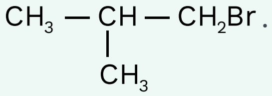
[NEET]

(1) 

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

(2) CH_3CH_2Br

(3) $CH_3CH_2CH_2Br$

(4) 

$CH_3-\underset{CH_3}{\underset{|}{CH}}-CH_2Br$.

SUBSTITUTION REACTION (S_N1)

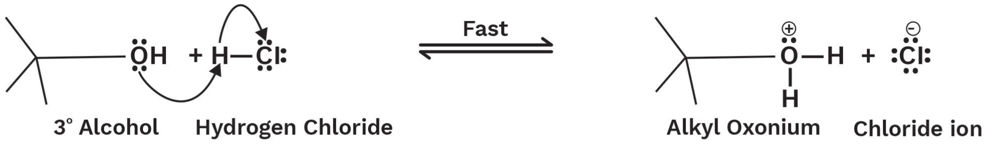
Yellow cat waits for the black cat to leave and then takes the pod. Similarly in S_N1 reaction one nucleophile waits for other nucleophile to move from substrate.

What Is S_N1 Reaction ?

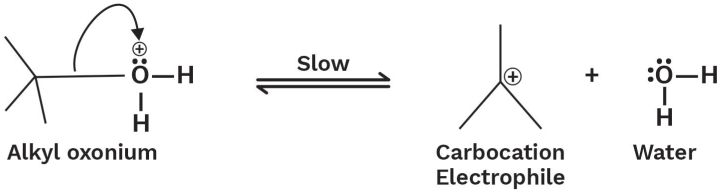
S_N1 indicates the unimolecular nucleophilic substitution reaction in organic chemistry. Their rate determining step of the mechanism depends on the decomposition of a single molecular species. So that, the rate of S_N1 reaction can be expressed as rate = K [R-LG]. Furthermore, S_N1 is a multi-step reaction, which forms an intermediate and several transition states during the reaction. This intermediate is a more stable carbocation and the reactivity of the molecule depends on the alkyl group.

S_N1 mechanism ($R—OH \longrightarrow R—X$)

Proton Transfer



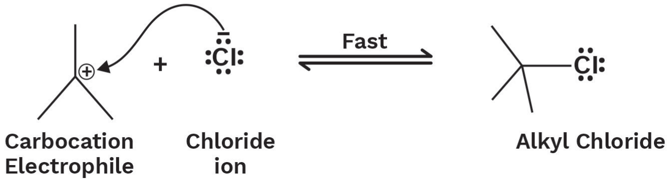
Dissociation Of Water



Rate- Determining Step

- Unimolecular
- Nucleophilic reaction
- "S_N1" mechanism

Capture Of Carbocation



Protic solvent ✓
3° or 2° carbon ✓
1° carbon ✗

SUBSTITUTION REACTION(S_N2)

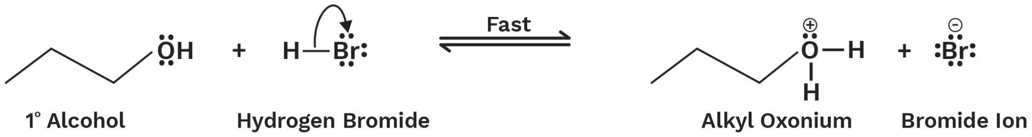
Yellow cat forces the black cat out from the pod. Similarly in S_N2, strong nucleophile kicks out the weaker nucleophile.

What Is S_N2 Reaction ?

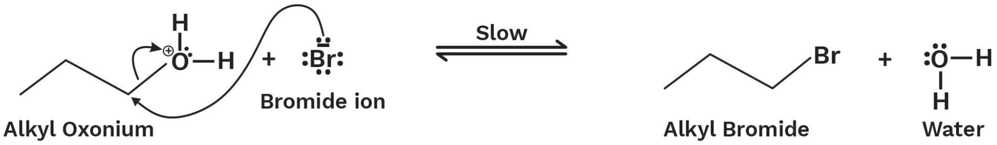
S_N2 indicates the bimolecular nucleophilic substitution reaction in organic chemistry. In this mechanism, separation of leaving group and formation of new bond happen synchronously. Therefore, two molecular species are involved in the rate determining step and this leads to the term bimolecular nucleophilic substitution reaction or S_N2. The rate of the S_N2 reaction can be expressed as rate = K [R-LG] [Nu-]. In inorganic chemistry, this reaction is also called associative substitution or interchange mechanism.

S_N2 mechanism ($R—OH \longrightarrow R—X$)

Proton Transfer



Nucleophile (halide) Seperates Water



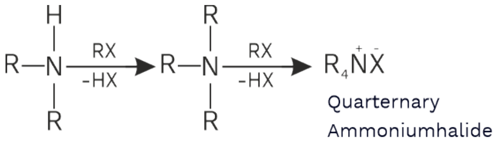
Here, nucleophile attacks from the opposite direction of the leaving group. Thus, S_N2 reaction always leads to an inversion of stereochemistry. This reaction works best with methyl and primary halides because bulky alkyl groups block the backside attack of the nucleophile. In addition, the stability of the leaving group as an anion and the strength of its bond to the carbon atom both affect the rate of reaction.

- $R-X \xrightarrow[C_2H_5OH/H_2O]{R'SNa} \underset{\text{Thioether}}{R'-S-R} + NaX$
- $R-X \xrightarrow{Na_2S} R-S-R + 2NaX$
- $R-X \xrightarrow[\text{Anhyd. } AlCl_3]{C_6H_6} C_6H_5-R + HX$

  The above reaction is called Friedel–Crafts reaction.

  $R-X \xrightarrow{\text{Moist } Ag_2O} R-OH$
- $2R-X + \underset{\text{Dry}}{Ag_2O} \longrightarrow \underset{\text{Ether}}{R-O-R} + 2AgX$
- $R-X + NaC\equiv CR' \longrightarrow \underset{\text{Alkyne}}{R-C\equiv C-R'} + NaX$

  $R-X \xrightarrow[-HX]{NH_3} R-NH_2 \xrightarrow[-HX]{X-R}$



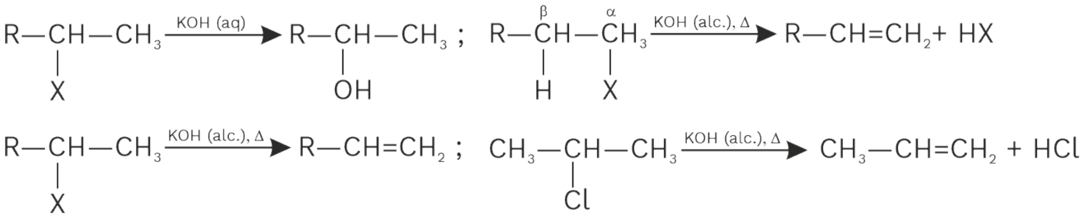
$$R-\underset{R}{\overset{H}{N}} \xrightarrow[-HX]{RX} R-\underset{R}{\overset{R}{N}} \xrightarrow[-HX]{RX} \underset{\text{Quarternary Ammoniumhalide}}{R_4\overset{+}{N}\overset{-}{X}}$$

Dehydrohalogenation

It involves α, β-elimination following E_1 and E_2 mechanisms.

- Here, α, β-elimination reaction takes place as follows:

  In case of tertiary and secondary halides, elimination dominates over substitution while in Primary-halides substitution is dominating. Low polarity of solvent, high temperature and strongness of base also favour elimination over substitution.



$$R-\underset{X}{CH}-CH_3 \xrightarrow{KOH\ (aq)} R-\underset{OH}{CH}-CH_3\ ;\ R-\underset{H}{\overset{\beta}{CH}}-\underset{X}{\overset{\alpha}{CH_3}} \xrightarrow{KOH\ (alc.),\ \Delta} R-CH=CH_2 + HX$$

$$R-\underset{X}{CH}-CH_3 \xrightarrow{KOH\ (alc.),\ \Delta} R-CH=CH_2\ ;\ CH_3-\underset{Cl}{CH}-CH_3 \xrightarrow{KOH\ (alc.),\ \Delta} CH_3-CH=CH_2 + HCl$$

Previous Year's Question

Which of the following undergoes nucleophilic substitution exclusively by S_N1 mechanism? **[AIPMT]**

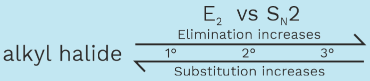
(1) Ethyl chloride
(2) Isopropyl chloride
(3) Chlorobenzene
(4) Benzyl chloride.

Rack your Brain

Ethyl iodide undergoes S_N2 reaction faster than ethyl bromide?

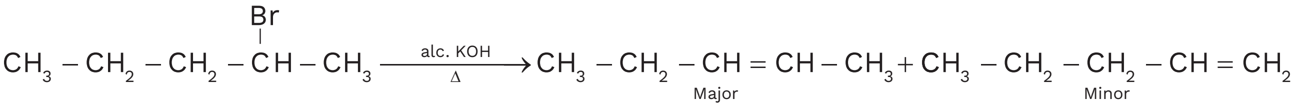
Concept Ladder

When elimination and substitution are competing reaction

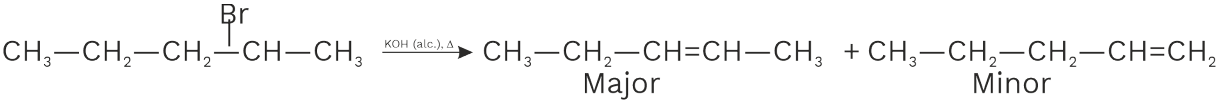


Saytzeff's Rule

According to Saytzeff's rule, removal of β-Hydrogen atom takes place from β-carbon atom having more number of alkyl groups, so that a more stable alkene is formed. e.g.,

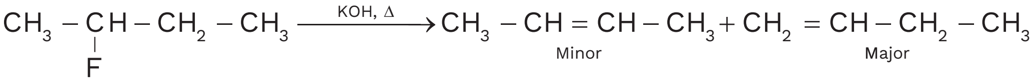


$$CH_3-CH_2-CH_2-\overset{\overset{Br}{|}}{C}H-CH_3 \xrightarrow[\Delta]{\text{alc. KOH}} \underset{\text{Major}}{CH_3-CH_2-CH=CH-CH_3} + \underset{\text{Minor}}{CH_3-CH_2-CH_2-CH=CH_2}$$

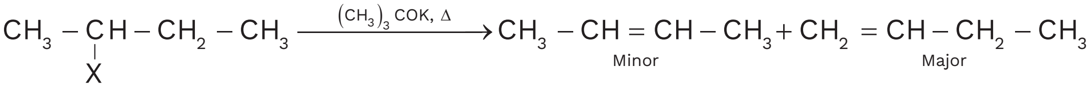


$$CH_3-CH_2-CH_2-\overset{\overset{Br}{|}}{C}H-CH_3 \xrightarrow{\text{KOH (alc.), }\Delta} \underset{\text{Major}}{CH_3-CH_2-CH=CH-CH_3} + \underset{\text{Minor}}{CH_3-CH_2-CH_2-CH=CH_2}$$

In case of a fluoro-alkane or other secondary halide, with very strong base like $(CH_3)_3COK$ or C_2H_5ONa, major product (Alkene) is according to Hoffmann's Rule. According to it, β-Hydrogen atom is eliminated from β-Carbon atom with less H-atom or less acidic β-H-atom which means less stable alkene is major product.



$$CH_3-\underset{\underset{F}{|}}{C}H-CH_2-CH_3 \xrightarrow{\text{KOH, }\Delta} \underset{\text{Minor}}{CH_3-CH=CH-CH_3} + \underset{\text{Major}}{CH_2=CH-CH_2-CH_3}$$



$$CH_3-\underset{\underset{X}{|}}{C}H-CH_2-CH_3 \xrightarrow{(CH_3)_3\text{COK, }\Delta} \underset{\text{Minor}}{CH_3-CH=CH-CH_3} + \underset{\text{Major}}{CH_2=CH-CH_2-CH_3}$$

Reaction with metals

(a) Reaction with Na (Wurtz reaction)

$$R-X+2Na+X-R \xrightarrow{\text{Dry ether}} R-R+2NaX$$

(b) Reaction with Zn (Frankland reaction)

$$R-X+Zn+X-R \xrightarrow{\Delta} R-R+ZnX_2$$

(c) Reaction with Mg

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

R may be $-CH_3$, $-C_2H_5$, $-C_6H_5$ etc.

Reactivity order for R–MgX is given as

$CH_3X > C_2H_5X > C_3H_7X$

R–I > R–Br > R–Cl

Previous Year's Question

Elimination reaction of 2-bromopentane to form pent-2-ene is

(A) β-Elimination reaction

(B) Follows Zaitsev rule

(C) Dehydrohalogenation reaction

(D) Dehydration reaction **[NEET]**

(1) (A), (B), (C)

(2) (A), (C), (D)

(3) (B), (C), (D)

(4) (A), (B), (D)

Grignard Reagent

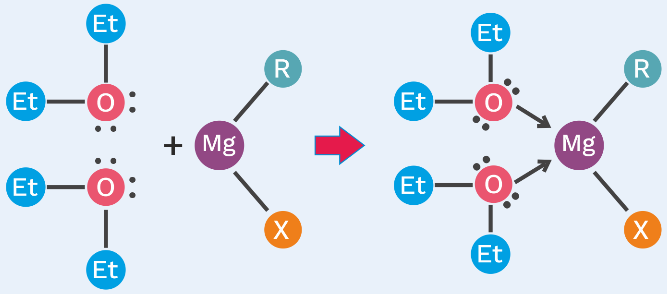
WHAT IS GRIGNARD REAGENT

If the metal attached to the carbon is magnesium, them it is called Grignard Reagent.

Victor Grignard first synthesized this compound

WHY GRIGNARD REAGENT IS PLACED IN DRY ETHER ?

Ether provides stability to Grignard reagent by completing the octet on Mg.



What Are Organo Metallics?

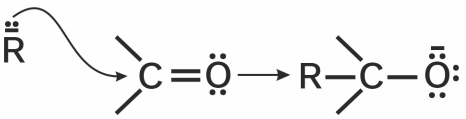
Organo metallic compounds are organic compounds in which metal atom is directly attached to Carbon atom

M-C

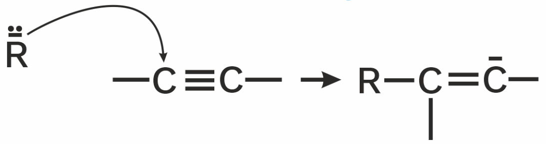
Chemical Reactivity Of Grignard Reagent

Grignard reagent produces nucleophile therefore it attacks at electrophilic centers

Attack On Aldehydes

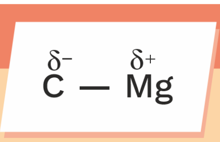


Attack On Alkynes



Reactivity

Carbon has high electronegativity than Mg.
so on breaking this bond produces a nucleophile



$\overset{\delta-}{C} - \overset{\delta+}{Mg}$

(d) Reaction with lead sodium alloy

$$4C_2H_5Br + 4Pb(Na) \longrightarrow \underset{\text{Tetraethyllead}}{(C_2H_5)_4Pb} + 4NaBr + 3Pb$$

- Tetraethyl lead (TEL) has anti-knocking properties used in petrol to avoid knocking.

(e) Reaction with lithium

$$R - X + 2Li \xrightarrow{\text{Ether}} R - Li + LiX$$

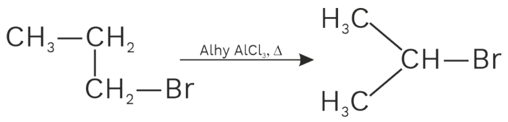
Reduction

$$R - X + 2[H] \xrightarrow{LiAlH_4} R - H + Hx$$

Heating effect

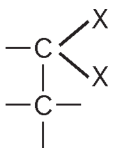
$$R - CH_2 - CH_2 \xrightarrow{560°C} R - CH = CH_2 + HX$$

Isomerination



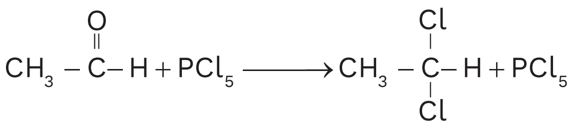
Dihalides

Gem or geminal halide or alkylidene halides



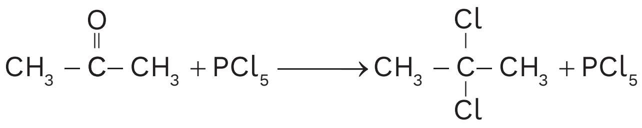
Methods of preparation of geminal halides

1. From aldehyde or ketone



$$CH_3 - \overset{\overset{\large O}{\|}}{C} - H + PCl_5 \longrightarrow CH_3 - \underset{\underset{\large Cl}{|}}{\overset{\overset{\large Cl}{|}}{C}} - H + PCl_5$$

Dichloroethane



$$CH_3 - \overset{\overset{\large O}{\|}}{C} - CH_3 + PCl_5 \longrightarrow CH_3 - \underset{\underset{\large Cl}{|}}{\overset{\overset{\large Cl}{|}}{C}} - CH_3 + PCl_5$$

2, 2 – Dichloropropane

Previous Year's Question

Grignard reagent is prepared by the reaction between

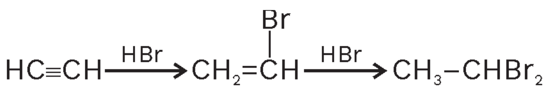
[NEET]

(1) magnesium and alkane
(2) magnesium and aromatic hydrocarbon
(3) zinc and alkyl halide
(4) magnesium and alkyl halide.

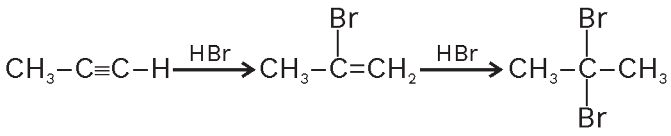
Concept Ladder

Organic lead (tetraethyl lead; TEL) is used as an antiknock agent in gasoline and jet fuels. TEL is absorbed rapidly from the skin as well as the lungs and gastrointestinal tract and is converted to triethyl lead in the body. This form of lead may be responsible for its toxic effects.

2. From alkyne



$$HC\equiv CH \xrightarrow{HBr} CH_2=\overset{Br}{\overset{|}{C}}H \xrightarrow{HBr} CH_3-CHBr_2$$

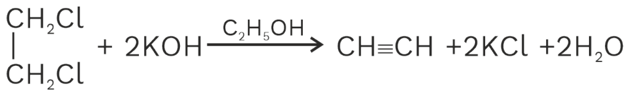


$$CH_3-C\equiv C-H \xrightarrow{HBr} CH_3-\overset{Br}{\overset{|}{C}}=CH_2 \xrightarrow{HBr} CH_3-\underset{Br}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-CH_3$$

Chemical properties of geminal halides (Alkylidene halides)

These are less reactive than the alkyl halides due to the fact that the presence of one-X-atom (E.W.G) makes the replacement of other X-atom slightly difficult.

1. Reaction with alcoholic KOH



$$\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix} + 2KOH \xrightarrow{C_2H_5OH} CH\equiv CH + 2KCl + 2H_2O$$

Previous Year's Question

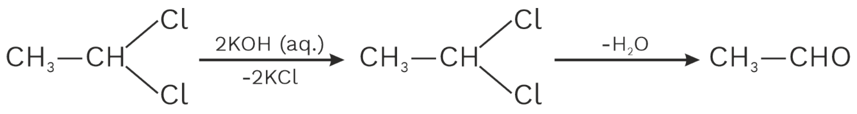
A compound of molecular formula C_7H_{16} shows optical isomerism, compound will be

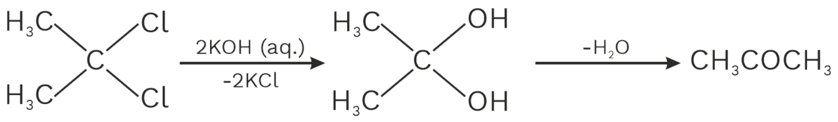
[NEET]

(1) 2,3-dimethylpentane
(2) 2,2-dimethylbutane
(3) 2-methylhexane
(4) none of these

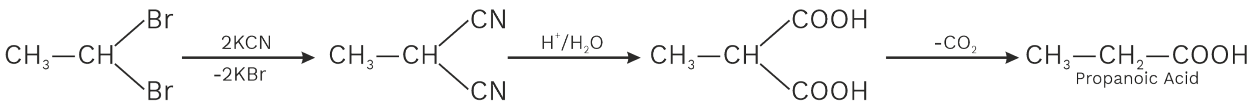
2. Reaction with aqueous KOH

Here, R–CHO, R–CO–R are formed

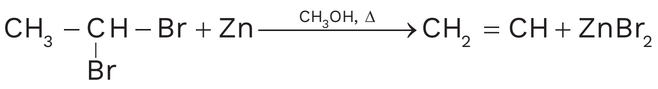




3. Reaction with KCN

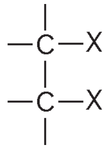


4. Reaction with Zn



$$CH_3-\underset{Br}{\underset{|}{C}}H-Br + Zn \xrightarrow{CH_3OH,\ \Delta} CH_2 = CH + ZnBr_2$$

Vic or vicinal dihalide or alkylene halides



$$-\overset{|}{\underset{|}{C}}-X \quad -\overset{|}{\underset{|}{C}}-X$$

Methods of preparation of vicinal dihalides

1. From alkenes

$CH_2=CH_2 + Br_2 \longrightarrow Br-CH_2-CH_2-Br$

2. From diols like glycol

$3HO-CH_2-CH_2-OH + 3H_3PO_3 \longrightarrow 3Br-CH_2-CH_2-Br + 3H_3PO_4$

$HO-CH_2-CH_2-OH \xrightarrow[-2H_2O]{2HCl} Cl-CH_2-CH_2-Cl$

Chemical properties of vicinal dihalides: They are as reactive as alkyl halides.

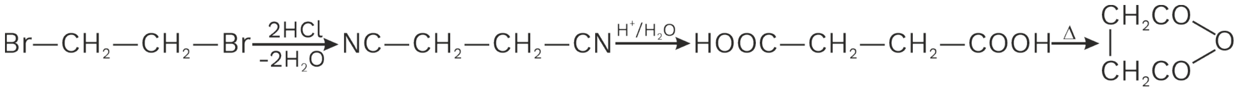
1. Reaction with KOH

$Cl-CH_2-CH_2-Cl + 2KOH \xrightarrow{\text{ethanol}, \Delta} CH\equiv CH + 2H_2O + 2KCl$

$Br-CH_2-CH_2-Cl + 2KOH \xrightarrow{\Delta} HO-CH_2-CH_2-OH$

Glycerol

2. Reaction with KCN



$$Br-CH_2-CH_2-Br \xrightarrow[-2H_2O]{2HCl} NC-CH_2-CH_2-CN \xrightarrow{H^+/H_2O} HOOC-CH_2-CH_2-COOH \xrightarrow{\Delta} \begin{matrix} CH_2CO \\ | \\ CH_2CO \end{matrix}\!\!>O$$

Succinic anhydride

3. Reaction with Zn

$Br-CH_2-CH_2-Br + Zn \xrightarrow{CH_3OH, \Delta} CH_2=CH_2 + ZnBr_2$

Trihalides or Haloforms (CHX_3)

Chloroform ($CHCl_3$)

- Chloroform was discovered by Justus Von Liebig and named by Jean-Baptiste Dumas.
- It has anesthetic nature which was discovered by James Young Simpson.

Methods of preparation

1. From chloral

$CCl_3CHO + NaOH \xrightarrow{\Delta} CHCl_3 + HCOONa$

Concept Ladder

Geminal dihalides have both halide groups attached to the same carbon atom whereas vicinal dihalides have their two halide groups attached to two adjacent carbon atoms in the same compound.

Previous Year's Question

Industrial preparation of chloroform employs acetone and **[AIPMT]**

(1) phosgene
(2) calcium hypochlorite
(3) chlorine gas
(4) sodium chloride

2. From ethyl alcohol or acetone

Ethyl alcohol (C_2H_5OH) or acetone (CH_3COCH_3) reacts with bleaching powder to give chloroform as follows:

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$H_2O + Cl_2 \longrightarrow HCl + [O]$$

$$CH_3CH_2OH \xrightarrow{[O]} CH_3CHO + H_2O$$

$$CH_3CHO \xrightarrow[-HCl]{3Cl_2} CCl_3CHO + H_2O$$

$$CH_3COCH_3 \xrightarrow[-HCl]{4Cl_2} \underset{2moles}{CCl_3COCH_3} \xrightarrow{Ca(OH)_2} 2CHCl_3 + (CH_3COO)_2Ca$$

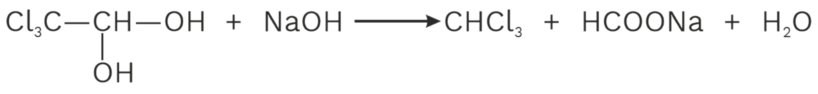
Concept Ladder

Bleaching powder is basic in nature. It gives calcium chloride, chlorine and water when bleaching powder reacts with hydrochloric acid.

3. From CCl_4

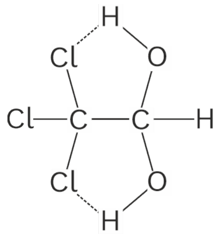
$$CCl_4 + 2[H] \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

4. From chloral hydrate



$$Cl_3C\!-\!\underset{\displaystyle OH}{\underset{|}{CH}}\!-\!OH + NaOH \longrightarrow CHCl_3 + HCOONa + H_2O$$

- Chloral hydrate is stable because of intramolecular hydrogen bonding in it which has butterfly-like structure.



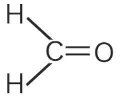
Rack your Brain

What are the harmful effect of chloral in human body?

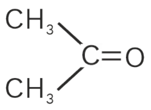
5. Haloform reaction

(A) It is given by >C=O having $-COCH_3$ group.

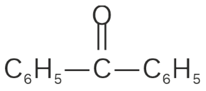
For example,



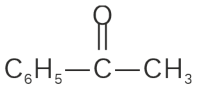
Does not show



show



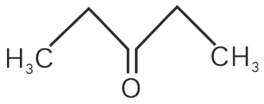
Does not show



show

Definitions

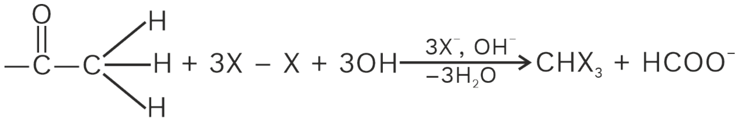
The reaction of a methyl ketone with chlorine, bromine, or iodine in the presence of hydroxide ions to give a carboxylate ion and a haloform is the haloform reaction.



Does not show

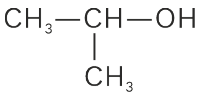
- Ethanal is the only aldehyde to show this reaction.

For example,



$$-\overset{\overset{\displaystyle O}{\|}}{C}-C\begin{smallmatrix}H\\-H\\H\end{smallmatrix} + 3X-X + 3OH \xrightarrow[-3H_2O]{3X^-,\ OH^-} CHX_3 + HCOO^-$$

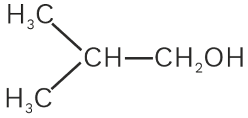
- $CH_3CHO + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + HCOONa + 3NaX + 3H_2O$
- $CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow CHI_3\downarrow + CH_3COONa + 3NaX + 3H_2O$

(B) Alcohol having  $CH_3-\underset{\underset{\displaystyle CH_3}{|}}{CH}-OH$ group shows haloform reaction.

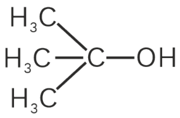
For example,

CH_3-CH_2-OH

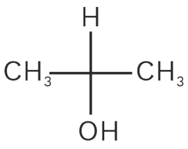
Shows



Does not show

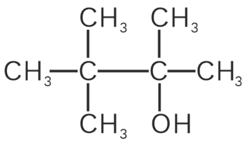


Does not show



$CH_3-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{}}-CH_3$

Show



$CH_3-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-CH_3$

Show

Previous Year's Question

An organic compound $A(C_4H_9Cl)$ on reaction with Na/diethyl ether gives a hydrocarbon which on monochlorination gives only one chloro derivative then, A is **[AIPMT]**

(1) t-butyl chloride
(2) s-butyl chloride
(3) iso-butyl chloride
(4) n-butyl chloride

For example,

$CH_3-CH_2-OH + 4I_2 + 6NaOH \longrightarrow CHI_3\downarrow + HCOONa + 5NaX$

$CHCl_3$

- Chloroform is a colourless liquid having a sweet smell.
- It is also a good solvent for resins, fats, etc.
- Its boiling point is 61°C.
- Soluble in organic solvents as oils but insoluble in H_2O.

$CHBr_3$

- $CHBr_3$ is a colourless liquid and its boiling point is 149.5°C.

CHI_3

- Its melting point is 119°C.
- It occurs as yellow, hexagonal plate like crystals.
- It can be used as antiseptic (due to the liberation of free I_2).

Test of Purity of $CHCl_3$

No precipitate is formed when chloroform reacts with silver nitrate. This is because, being covalent, $CHCl_3$ cannot furnish Cl^- ions.

Chemical properties of chloroform ($CHCl_3$)

1. Nitration

$$CHCl_3 + HO{-}NO_2 \longrightarrow CCl_3.NO_2 + H_2O$$

Chloropicrin (insecticide)

- It is used in the manufacture of tear gas, phenacyl chloride [$C_6H_5COCH_2Cl$].

2. Reduction

$$CHCl_3 \xrightarrow{6[H]Zn+H_2O} CH_4 + 3HCl$$

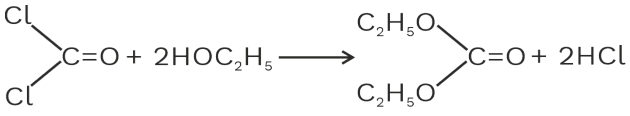
$$CHCl_3 \xrightarrow{2[H]Zn/HCl} CH_2Cl_2 + HCl$$

$$CHCl_3 + 4(H) \xrightarrow[\text{alc.HCl}]{\text{Zn}} CH_3Cl + 2HCl$$

3. Oxidation

$$CHCl_3 + \frac{1}{2}O_2 \xrightarrow{hv} \underset{\substack{\text{Phosgene}\\\text{(Poisonous)}}}{COCl_2} + HCl$$

- Chloroform is kept in dark, filled, tightly closed bottle with a small amount of C_2H_5OH (negative catalyst) to avoid oxidation or formation of phosgene. Ethyl alcohol (C_2H_5OH) converts phosgene into non-poisonous diethyl carbonate.



Diethyl carbonate

Concept Ladder

Iodoform is mainly used as an antiseptic, since it liberates free iodine. However it is not used now because of its bad smell.

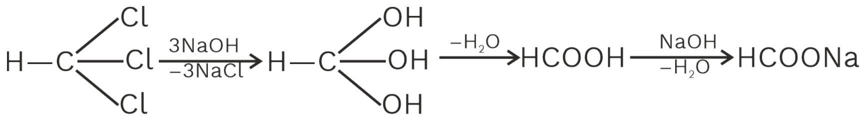
Rack your Brain

Chloroform is no longer used as an anaesthetic agent. Why?

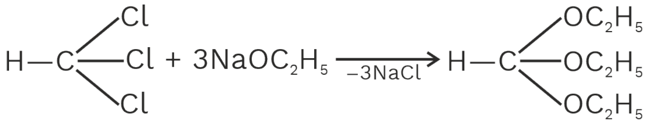
Concept Ladder

- $CHCl_3$ is mainly used in the production of Freon refrigerant, R-22.
- $CHCl_3$ is also used as a solvent for fats, alkaloids, iodine etc.
- $CHCl_3$ causes dizziness, headache and fatigue.
- Chronic chloroform exposure may damage liver and kidney.

4. Reaction with hot Sodium Hydroxide



5. Reaction with hot Sodium Ethoxide



Ethyl orthoformate

6. Carbylamine reaction: It is a test a primary amine. Here, the primary amine reacts with chloroform and base KOH, to give bad smelling isocyanide as follows:

$$R{-}NH_2 + CHCl_3 + 3KOH \longrightarrow R{-}NC + 3KCl + 3H_2O$$

- Here, the reaction intermediate is: CCl_2, that is, dichlorocarbene.
- If ethylamine is taken, product formed is ethyl isocyanide.

$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_2H_5NC + 3KCl + 3H_2O$$

- If aniline is taken, product formed is phenylisocyanide.

$$C_6H_5NH_2 + CHCl_3 + 3KOH \longrightarrow C_6H_5NC + 3KCl + 3H_2O$$

Previous Year's Question

Benzene reacts with n-propyl chloride in thepresence of anhydrous $AlCl_3$ to give

[AIPMT]

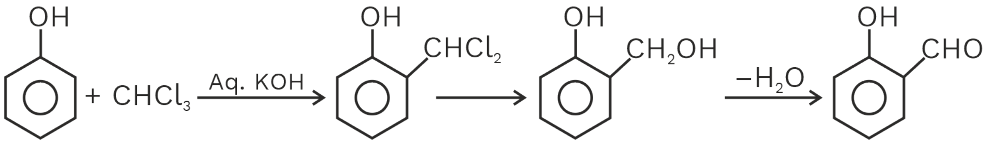
(1) 3-propyl-1-chlorobenzene
(2) n-propylbenzene
(3) no reaction
(4) isopropylbenzene

7. Reaction with Ag powder

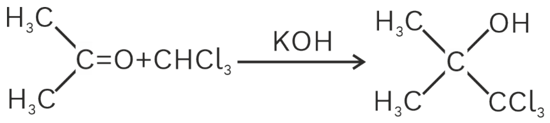
$$CHX_3 + 6Ag + CHX_3 \longrightarrow C_2H_2 + 6AgX$$

8. Reimer–Tiemann reaction:

Here reaction inter mediate is: CCl_2.



9. Reaction with acetone

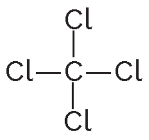


Chloretone

- Chloretone is used in hypnotic medicines.

CCl_4 or Pyrene

(Carbon Tetra-Chloride)



$$Cl-\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{C}}-Cl$$

Tetrahedral structure, sp3 hybridization, bond angle 109° 28' and μ is zero

Methods of preparation

1. $CH_4 + 4Cl_2 \xrightarrow[-4HCl]{hv} CCl_4$
2. $CHCl_3 + Cl_2 \xrightarrow{hv} CCl_4 + HCl$
3. $CS_2 + 2S_2Cl_2 \longrightarrow CCl_4 + 6S$
4. $C_3H_8 + 9Cl_2 \xrightarrow[70-100\text{atm}]{\Delta} CCl_4 + C_2Cl_6 + 8HCl$

Physical properties of pyrene

- It is a colourless, non-flammable, poisonous liquid having a boiling point of 350 K.
- Soluble in organic solvents as oils but insoluble in water and is a good solvent for fat, oil and wax.

Chemical properties of pyrene

1. Reaction with steam

$$CCl_4 \xrightarrow[\text{500°C under high pressure}]{H_2O} COCl_2 + 2HCl$$

2. Hydrolysis

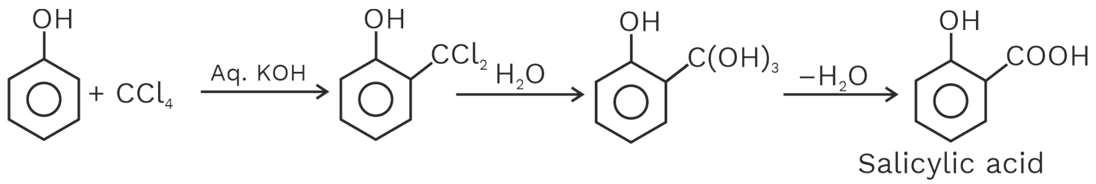
$$CCl_4 \xrightarrow[\text{Boiling KOH}]{\Delta} C(OH)_4 \xrightarrow[-2H_2O]{\Delta} CO_2$$

3. Reaction with HF

$$CCl_4 + 2HF \xrightarrow{SbF_5} \underset{\text{Freon}}{CF_2Cl_2} + 2HCl$$

- Freon-12 is used in air conditioners and refrigerators as a refrigerant.

4. Reaction with phenol



Previous Year's Question

Phosgene is a common name for **[AIPMT]**

(1) phosphoryl chloride
(2) thionyl chloride
(3) carbon dioxide and phosphine
(4) carbonyl chloride.

Concept Ladder

Carbon tetrachloride is released into the air, it goes in the upper atmosphere and depletes the ozone layer. Depletion of ozone layer increases the human exposure to ultraviolet radiations which may lead to increased skin cancer, eye diseases and disorders, and disruption of the immune system.

Uses of CCl_4:

(i) Under Pyrene it is used as a fire extinguisher.

(ii) Used as solvent for fats, oils, resins etc.

Teflon $(-CF_2-CF_2-)_n$

- Teflon is a polymer of tetrafluoroethylene.
- It is a chemically inert thermostatic plastic.
- It is used for electrical insulation and in gasket materials.

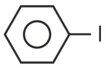
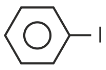
$$CHCl_3 \xrightarrow[HF]{SbF_3} CHF_2Cl \xrightarrow[-HCl]{800°C} CF_2 = CF_2$$

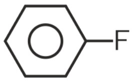
$$\underset{\text{Tetrafluoroethylene}}{nCF_2 = CF_2} \longrightarrow \underset{\text{Teflon}}{(-CF_2 - CF_2-)_n}$$

Chlorobenzene

Methods of preparation

From benzene

 can not be obtained by direct iodination as not only the reaction is reversible but also HI being a reductant can reduce  into Benzene. But if strong oxidants like HNO_3, HgO are used the reaction is possible as they oxidise HI into I_2.

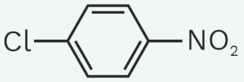
 can not be obtained as F is highly reactive and the reaction is violent also.

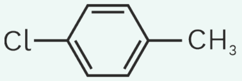
Concept Ladder

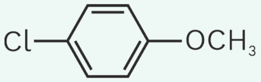
Teflon is the trading name for a commonly used polymer called Polytetrafluoroethylene. PTFE has unique and valuable qualities such as being chemical resistant, temperature resistant, low permeation and high corrosion resistant.

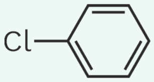
Previous Year's Question

Which of the following compounds undergoes nucleophilic substitution reaction most easily? **[NEET]**

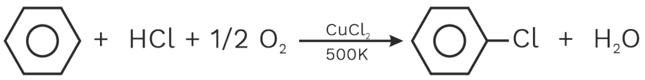
(1) 

(2) 

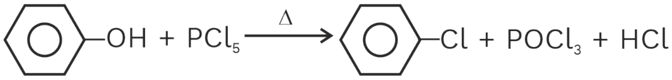
(3) 

(4) 

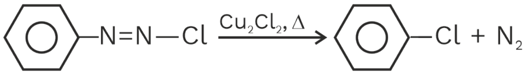
- Commercial method or Raschig method



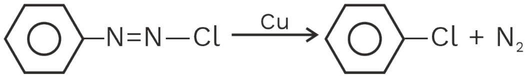
From alcohol



From benzene diazonium chloride or Sand Mayer's reaction



Gatterman reaction



Physical properties of Chlorobenzene

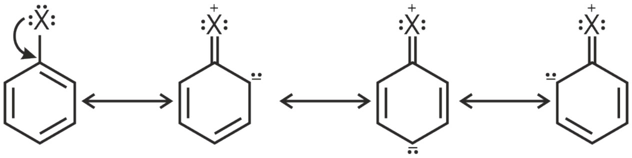
- It is colourless liquid with pleasant odour and a boiling point of 132°C.
- It is heavier than water and insoluble in it.

Chemical properties of Chlorobenzene

Due to benzene ring

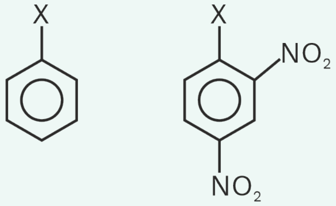
- The Cl^- atom present in the ring deactivates the ring but it is o- and p- directing. The rate of electrophilic substitution is slower than that of benzene.

  Here due to resonance electron density increases at o, p positions but due to –I effect –X atom has a tendency to withdraw electrons from benzene ring. It means due to deactivation in ring rate of electrophillic substitution decreases.



Previous Year's Question

The correct order of increasing reactivity of **[AIPMT]**



(I) (II)

$(CH_3)_3C—X$ (III)

$(CH_3)_2CH—X$ (IV)

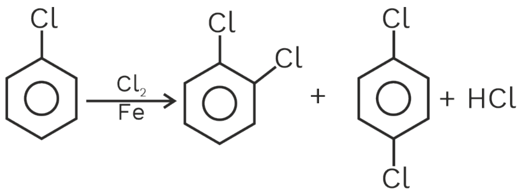
C—X bond towards nucleophile in the following compounds is

(1) I < II < IV < III
(2) II < III < I < IV
(3) IV < III < I < II
(4) III < II < I < IV

Concept Ladder

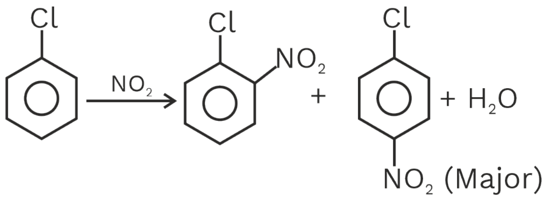
In haloarens and vinyl halides, the phenyl cation or the vinyl cation formed as a result of self ionization is not stabilized by resonance because the sp^2-hybridized orbital of carbon having the +ve charge is perpendicular to the p-orbital of the penyl ring or the vinyl group.

- **Halogenation**



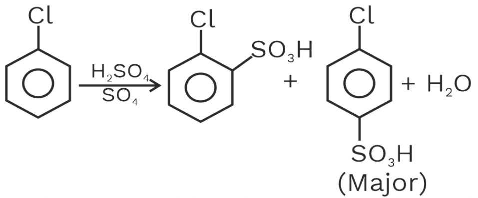
ortho, para dichlorobenzene

- **Nitration**



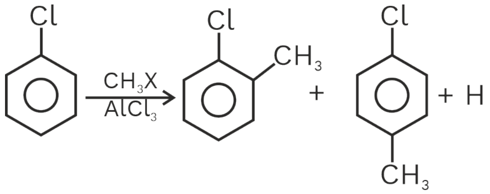
ortho, para nitrochlorobenzene

- **Sulphonation**



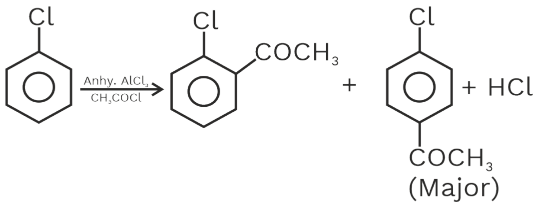
ortho, para chlorobenzene sulphonic acid

- **Friedel Crafts alkylation**



ortho, para methyl chlorobenzene

- **Acylation**



Here para product is major in all these cases.

Concept Ladder

In Chlorobenzene, Cl is attached to a sp^2-hybrid carbon atom. has greater s-character and more electronegative therefore chlorobenzene has less tendency to release electrons towards the Cl atom.

Rack your Brain

The C—Cl bond length in chlorobenzene is shorter than C—Cl bond length in CH_3—Cl?

Previous Year's Question

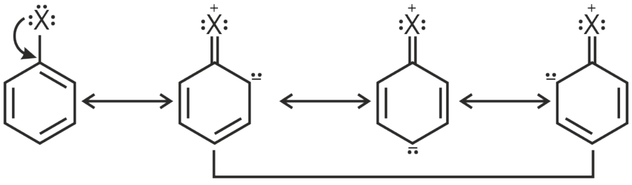
Benzene reacts with n-propyl chloride in the presence of anhydrous $AlCl_3$ to give

[NEET]

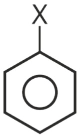
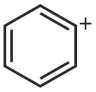
(1) 3-propyl-1-chlorobenzene
(2) n-propylbenzene
(3) no reaction
(4) isopropylbenzene

Reactions due to chlorine

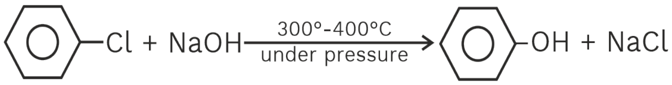
- Reactivity of chlorine atom in chlorobenzene The reactivity of Cl– atom in chlorobenzene is very low than R–X because C–Cl bond in chlorobenzene acquires a double bond character and is resonance stabilized, so more energy is required to break a double bond than a single bond.

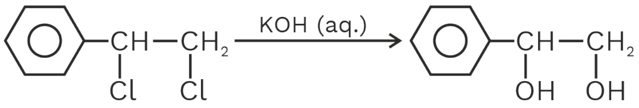


Resonance Stabilisation of C=X

In  C –X while in $R - CH_2 - X$ it means in haloarenes C–X bond length is shorten than in haloalkanes which is 169 and 177 PM respectively. It also decreases reactivity in haloarenes. Here  is very less stable so SN^1 reaction does not occur. The attack of electron rich Nucleophile is also inhibited by higher electron density at arenes.

- Substitution by –OH group

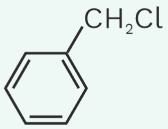




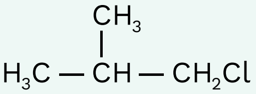
Previous Year's Question

Which of the following compounds will undergo racemisation when solution of KOH hydrolyses?

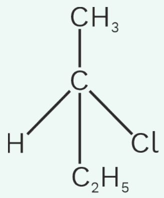
[NEET]

(i) 

(ii) $CH_3CH_2CH_2Cl$

(iii) 

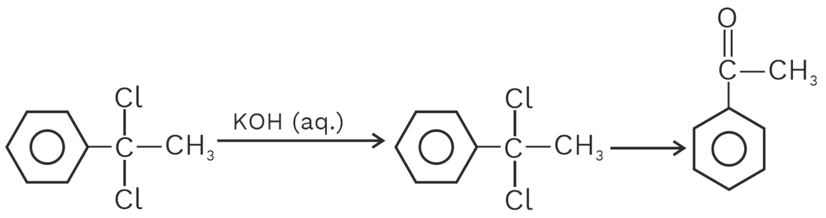
$$H_3C - \overset{\overset{\displaystyle CH_3}{|}}{C}H - CH_2Cl$$

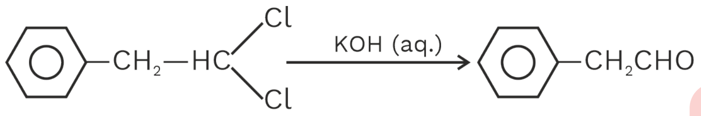
(iv) 

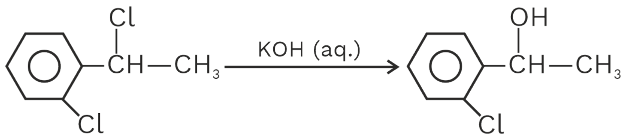
(1) (i) and (ii)
(2) (ii) and (iv)
(3) (iii) and (iv)
(4) (i) and (iv)

Concept Ladder

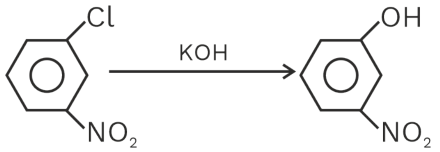
In haloarence presence of EWG such as $-NO_2$, $-CN$, etc. at o-and p-position (but not at m-position) w.r.t. the halogen greatly activates the halogen towards nucleophilic displacement.

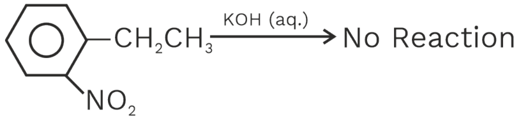




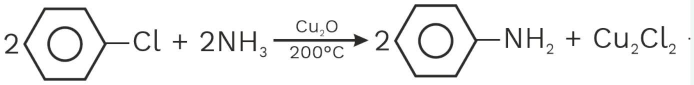


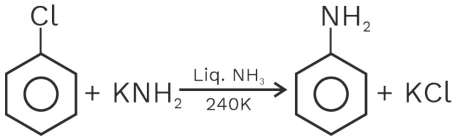
When a strong E.W.G group like $-NO_2$ is present at o, p position the substitution of –X becomes comparatively easier and reaction occurs.

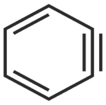




- Substitution by NH_2 group





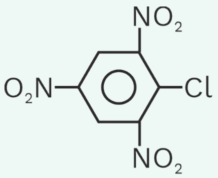
This reaction proceeds with Benzyne 

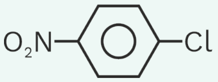
Rack your Brain

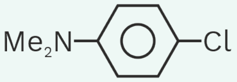
p-Chloronitrobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structure as well?

Previous Year's Question

Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative? **[AIPMT]**

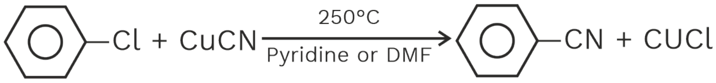
(1) 

(2) 

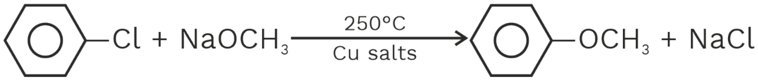
(3) 

(4) C_6H_5Cl

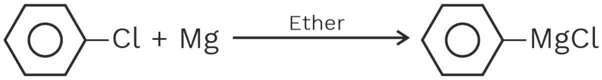
- Substitution by CN group



- Substitution by –OR group:

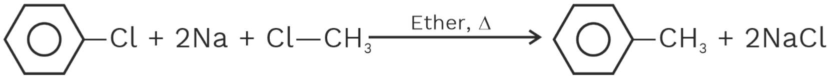


- Reaction with magnesium

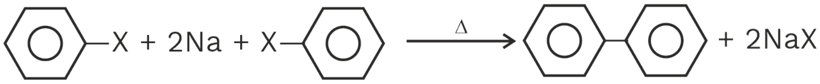


Grignard reagent

- Wurtz Fittig reaction

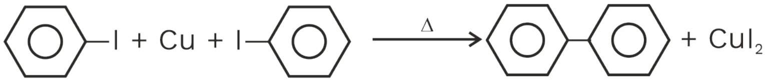


- Fittig reaction



Biphenyl

- Ullmann reaction

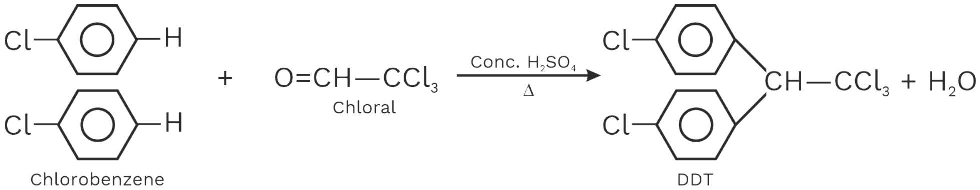


Biphenyl

- Reaction with chloral: Chloral on heating with chlorobenzene in presence of concentrated H_2SO_4 gives DDT (p,p-dichlorodiphenyl trichloroethane). It is non-biodegradable as both Cl atoms are linked with benzene ring.

Rack your Brain

Haloarence are less reactive towards nucleophilic substitution reactions?



Uses and Effects of Polyhalogen Compounds on Environment and Human Health

Iodoform

Freon

- Freon is used as a coolant in A.C and refrigerators. However, now its use has been abandoned since it damages the ozone layer.

DDT

- DDT is an off-white crystalline powder and has been a popular pesticide.
- It is highly toxic towards fish.
- It is not metabolized very rapidly by animals; it is deposited and is stored in the fatty tissues.
- Being non-biodegradable its residues accumulate in environment and are toxic to mammals etc.

Carbon tetrachloride

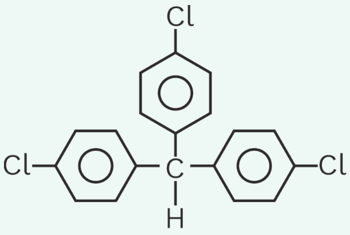
- Carbon tetrachloride or CCl_4 is mainly used in the synthesis of chloroflouro carbons.
- It may cause liver cancer in humans.
- It may cause headache, vomiting and nerve damage.
- It may lead to depletion of the ozone layer.

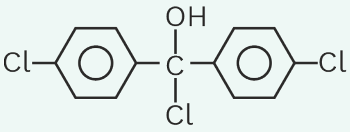
Benzene Hexachloride (B.H.C): It is commonly called as Gammexene or γ-Lindane or 6,6,6 [$C_6H_6Cl_6$]. It is a famous pesticide for killing of Thermites (white ants) from soil.

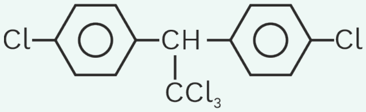
Previous Year's Question

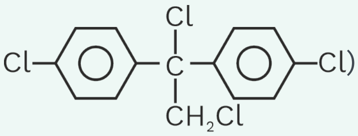
Trichloroacetaldehyde, CCl_3CHO reacts with chlorobenzene in presence of sulphuric acid and produces

[NEET]

(1)


(2)


(3)


(4)


Q.2 Aryl chlorides and bromides can be easily prepared by electrophilic substitution of arenes with chlorine and bromine respectively in the presence of Lewis acid catalysts. But why does preparation of aryl iodides requires presence of an oxidising agent?

A.2 Iodination reaction is reversible in nature. To carry out reaction in forward direction, HI formed during iodination is removed by oxidation. HIO_4 is used as an oxidising agent.

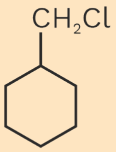
Q.3 Out of o-and p-dibromobenzene which one has higher melting point and why?

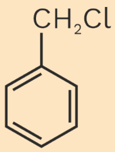
A.3 p-Dibromobenzene has higher melting point (M.P.) than its o-isomer. It is due to symmetry of p-isomer which fits in crystal lattice better than o-isomer.

Q.4 Which of the following compounds will have the highest melting point and why?

A.4 II, due to symmetry of para-positions; it fits into crystal lattice better than other isomers.

Q.5 Which of the following compounds would undergo S_N1 reaction faster and why?


(A)


(B)

A.5 (B) Undergoes S_N1 reaction faster than (A) because in case of (B), the carbocation formed after the loss of Cl^- is stabilised by resonance, whereas, no such stabilisation is possible in the carbocation obtained from (A).

Q.6 Allyl chloride is hydrolysed more readily than n-propyl chloride. Why?

A.6 Allyl chloride shows high reactivity as the carbocation formed by hydrolysis is stabilised by resonance while no such stabilisation of carbocation exists in the case of n-propyl chloride.

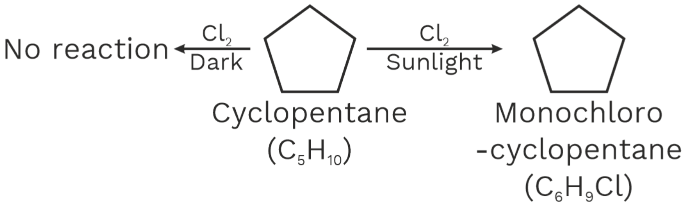
Q.7 Arrange each set of compounds in order of increasing boiling points
(i) Bromomethane, bromoform, chloromethane, dibromomethane.
(ii) 1 – Chloropropane, isopropyl chloride, 1 – chlorobutane.

A.7 (I) As molecular mass of compound increases, boiling point also increases. Therefore, correct order is:
chloromethane < bromomethane < dibromomethane < bromoform

(ii) Of molecules having same mass, it is size of molecule that determines boiling point. Branched compounds are comparatively more compact and hence have less surface area when compared to their straight chain compounds and therefore lower boiling point.
Order of boiling point :
iso-propyl chloride < 1-chloropropane < 1-chlorobutane

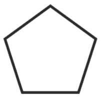
Q.8 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C5H9Cl in bright sunlight. Identify the hydrocarbon.

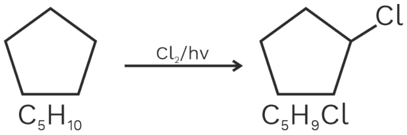
A.8 Hydrocarbon with molecular formula C_5H_{10} can either be a cycloalkane or an alkene. Since, compound does not react with Cl_2 in dark, therefore it cannot be an alkene but must be a cycloalkane. Since, cycloalkane reacts with Cl_2 in presence of bright sunlight to give a single monochloro compound, C_5H_9Cl, therefore, all ten hydrogen atoms of cycloalkanes must be equivalent. Thus, cycloalkane is cyclopentane.



Q.9 A hydrocarbon C_5H_{10} does not react with chlorine in dark but gives a single monochloro compound C_5H_9Cl in bright sunlight. Identify the hydrocarbon.

A.9 A number of structural isomers are possible for molecular formula C_5H_{10}. But, the given compound gives a single monochloro derivative when reacted with Cl_2 in sunlight suggests that, all the H-atoms in the compound are equivalent. This is possible only if the compound is a cyclic alkane.

therefore, the compound is 



Q.10 Which of the compounds will react faster in S_N1 reaction with the –OH ion?
$CH_3—CH_2—Cl$ or $C_6H_5—CH_2—Cl$

A.10 $C_6H_5—CH_2—Cl$

Q.11 Which compound in each of the following pairs will react faster in SN2 reaction with OH^-? (i) CH_3Br or CH_3I (ii) $(CH_3)_3CCl$ or CH_3Cl

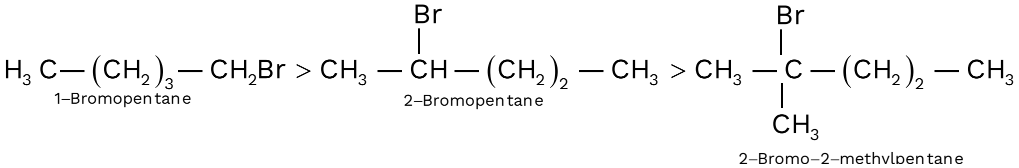
A.11 (i) Between CH_3I and CH_3Br, CH_3I will react faster via S_N2 mechanism. In S_N2 , C—X bond breaks and faster it breaks faster is the reaction. I^- is a better leaving group. Owing to its large size, C—I bond breaks faster than C—Br bond and hence reaction proceeds at a higher rate.

(ii) Order of reactivity in case of SN2 reaction depends upon minimal steric hindrance around carbon involved in C—X bond. Lesser will be the steric hindrance as felt by incoming nucleophile, and hence alkyl halide will be more reactive towards S_N2 reaction.

Based on the above, CH_3Cl will react faster than $(CH_3)_3CCl$.

Q.12 Arrange the compounds of each set in order of reactivity towards S_N2 displacement : 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

A.12 S_N2 reaction proceeds via formation of transition state where carbon atom is surrounded by 5 other atoms (groups). Thus, for such a transition state to form, steric interactions have to be minimum. So, the most preffered substrates for S_N2 reactions are 1° alkyl halides followed by 2° and 3° alkyl halides. Order of reactivity for S_N2 reactions : 1° > 2° > 3° > aryl halide.



$$H_3C-(CH_2)_3-CH_2Br > CH_3-\overset{Br}{\overset{|}{CH}}-(CH_2)_2-CH_3 > CH_3-\underset{CH_3}{\underset{|}{\overset{Br}{\overset{|}{C}}}}-(CH_2)_2-CH_3$$

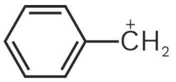
1–Bromopentane 2–Bromopentane 2–Bromo–2–methylpentane

Q.13 Out of $C_6H_5CH_2Cl$ and $C_6H_5CHClC_6H_5$, which is more easily hydrolysed by aqueous KOH?

A.13 $C_6H_5CHClC_6H_5$ is hydrolysed faster.

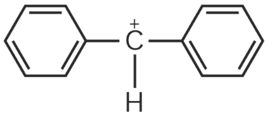
(a) Hydrolysis of an alkyl halide is an example of nucleophilic substitution reaction. In case of aryl halides this follows the SN1 pathway i.e., via the formation of carbocation.

(b) $C_6H_5CH_2Cl$ or benzyl chloride gives



(I) carbocation while

$C_6H_5CHClC_6H_5$ generates



(II)

(c) Out of I & II, carbocation II is more stable. Reason is presence of two phenyl rings attached to carbon carrying positive charge.

(d) As a result, delocalisation of +ve charge is greater and carbocation is more stable. Due to this, (II) is formed faster and corresponding halide is hydrolysed with greater ease as compared to benzyl chloride.

Q.14 p-Dichlorobenzene has higher m.p. and solubility than those of o- and m-isomers. Discuss.

A.14 The para-isomers have high melting points and solubility as compared to their ortho and meta isomers due to symmetry of para-isomers that fits into crystal lattice better than ortho and para isomers.

Q.15 What happens when n-butyl chloride is treated with alcoholic KOH.

A.15 $$\underset{\text{n–Butylchloride}}{CH_3 - CH_2 - CH_2 - CH_2 - Cl} \xrightarrow{\text{al. KOH}} \underset{\text{But–1–ene}}{CH_3 - CH_2 - CH = CH_2}$$

The reaction is an example of β-hydrogen elimination brought about by $C_2H_5O^-$

Q.16 How can the following conversions be carried out: Propene to propan-1 -ol?

A.16 $$\underset{\text{Propene}}{CH_3 - HC = CH_2} \xrightarrow[\text{peroxide}]{\text{HBr/}} CH_3 - CH_2 - CH_2Br \xrightarrow{\text{aq.KOH/}\Delta} \underset{\text{Propanol}}{CH_3 - CH_2 - CH_2 - OH}$$

Q.17 How can the following conversions be carried out: Ethanol to propanenitrile.

A.17 $$\underset{\text{Ethanol}}{H_3C - CH_2\,OH} \xrightarrow{SOCl_2} H_3C - CH_2Cl \xrightarrow{\text{KCN/Et OH—}H_2O} \underset{\text{Propanenitrile}}{CH_3 - CH_2OH}$$

Q.18 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform: Freon 12 (CCl_2F_2) is

A.18 (i) used in aerosol propellants
(ii) refrigeration
(iii) air-conditioning.

Q.19 Give the uses of freon 12, DDT, carbon tetrachloride and iodoform: DDT (p, p’-dichlorodiphenyltrichloroethane) is

A.19 (i) used as an insecticide,
(ii) mainly used against mosquitoes.

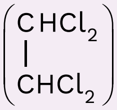
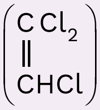
Q.20 alkyl halides, though polar, are immiscible with water. Explain why?

A.20 Only those compounds which can form hydrogen bonds with water are miscible with it. Alkyl halides, though polar due to the presence of electronegative halogen atom, are immiscible since they cannot form hydrogen bonds.

Chapter Summary

1. CCl_4 is used as a medicine for treatment against hookworms.
2. CF_4 is freon-14, CF_3Cl is freon-13, CF_2Cl_2 is freon-12 and $CFCl_3$ is freon-11.
3. Perfluorocarbons have a general formula C_nF_{2n+2}.

$$C_6H_{14} + 14F_2 \xrightarrow{573K, COF_2} C_6F_{14} + 14HF$$

4. Halothane ($CF_3CHClBr$) is used as an inhalative anaesthetic agent.
5. Chloretone is a hypnotic or sleep-inducing drug.
6. Westron is tetrachloroethane  $\left(\begin{array}{l} CHCl_2 \\ | \\ CHCl_2 \end{array}\right)$ while Westrosol is trichloroethylene  $\left(\begin{array}{l} CCl_2 \\ \| \\ CHCl \end{array}\right)$
7. The boiling point have the following order:
   alkyl iodides > alkyl bromides > alkyl chlorides > alkyl fluorides
   R–I > R–Br > R–Cl > R–F
8. The volatility has the following order:
   R–Cl > R–Br > R–I
9. Dipole moment has the following order:
   $CH_3Cl > CH_3F > CH_3Br > CH_3I$
10. The order of the boiling points in a group of isomeric alkyl halides is primary > secondary > tertiary
11. The order of the densities of alkyl halides is
    R–I > R–Br > R–Cl > R–F
    $CH_3Cl < CH_2Cl_2 < CHCl_3 < CCl_4$
12. The order of chemical reactivity of alkyl halides is
    RI > RBr > RCl
13. The order of reactivity of an alkyl halides is
    tertiary > secondary > primary
    This has been explained in terms of the inductive effect of alkyl groups, which increases the polarity of C–X bond and thereby making it more reactive.
14. It has been observed that presence of bulky groups in primary halides—inspite of higher positive ionization energy—causes steric hinderance and makes them less reactive towards SN^2 mechanism.
    The reactivity follows the order $CH_3X > C2H_5X > C_3H_7X$.
15. Antiseptic action of CHI3 is due to the liberation free I_2.
16. Perfluoro carbons (PFCs) have a general formula C_nH_{2n+2}.

$$C_7H_{16} + 16F_2 \xrightarrow[\text{Vapour phase } N_2C_0F_2]{\Delta\, 573K} C_7F_{16} + 16HF$$

Perfluoro heptane

These are colourless, odourless, non polar stable, non-toxic, substanies. They are stable to U.V or other radiations so don't deplete the U_3-layer. They can be used as lubricants, in medicines for skin care, medical diagnosis etc.

17. The halogen derivatives of the aromatic hydrocarbons in which the halogen atom is present in the side chain are called aryl alkyl halides or aralkyl halides.
For example, $Ar–CH_2–X$.

18. Bond strength and stability decreases as
$R–F > R–Cl > R–Br > R–I$

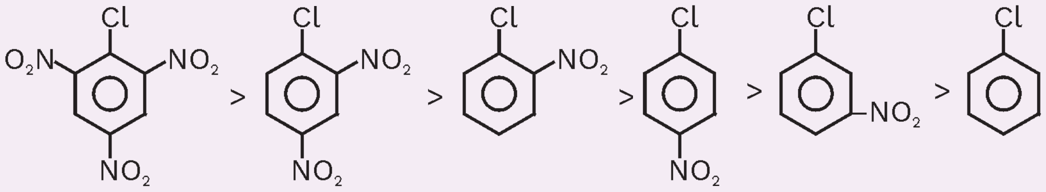
19. The relative nucleophilicity order for SN1 Reaction:

$$R\overline{S} > \overline{C}N > \overline{I} > R-\overline{O} > \overline{O}H$$

20. The Leaving group tendency for SN^2 Reaction:

$$p-CF_3C_6H_5SO_3^- > p-CH_3C_6H_4SO_3^- > I^- > Br^- > Cl^- > H_3\overset{+}{O} > F^- > CH_3COO^- > N^+R_3 > R-O^- > R_2N^- > N^-H_2$$

21. Decreasing order of Reactivity of Nucleophilic Substitution Reaction:



22. In Dorzen's method R–Br and R–I can not be obtained as $SOBr_2$ is un-stable and SOI_2 does not exist.