

# Chapter 1:

## Haloalkanes and Haloarenes

### Haloalkanes:

#### 1. Definition:

- Haloalkanes, also known as alkyl halides, are organic compounds containing one or more halogen atoms (fluorine, chlorine, bromine, or iodine) bonded to an alkyl group.
- The general formula of a haloalkane is R-X, where R is an alkyl group and X is a halogen atom.

#### 2. Classification:

- Haloalkanes are classified based on the number of halogen atoms bonded to the carbon atom:
- Primary ( $1^\circ$ ), where the carbon with the halogen atom is bonded to only one other carbon atom.
- Secondary ( $2^\circ$ ), where the carbon with the halogen atom is bonded to two other carbon atoms.
- Tertiary ( $3^\circ$ ), where the carbon with the halogen atom is bonded to three other carbon atoms.

#### 3. Physical Properties:

- Haloalkanes are generally polar due to the electronegativity difference between the carbon-halogen bond.
- They have higher boiling points compared to their parent alkanes due to the presence of polar bonds.
- Solubility decreases with increasing molecular weight due to decreased polarity.

## 4. Chemical Reactions:

- Substitution Reactions: The halogen atom in haloalkanes can be replaced by other nucleophiles through substitution reactions.
- Elimination Reactions: Haloalkanes can undergo elimination reactions to form alkenes when treated with strong bases.
- Reduction Reactions: Haloalkanes can be reduced to corresponding alkanes using reducing agents like lithium aluminum hydride ( $\text{LiAlH}_4$ ).
- Nucleophilic Substitution Reactions: Haloalkanes react with nucleophiles to undergo substitution reactions where the halogen atom is replaced by the nucleophile.

## 4. Uses:

- Haloalkanes find applications as solvents, refrigerants, pesticides, and pharmaceutical intermediates.
- Some haloalkanes are used as anesthetics and in the synthesis of plastics.

## Haloarenes:

### 1. Definition:

- Haloarenes are aromatic compounds containing one or more halogen atoms bonded directly to the aromatic ring.
- The general formula of a haloarene is  $\text{Ar-X}$ , where Ar represents an aromatic ring and X represents a halogen atom.

## 2.Properties:

- Haloarenes are less reactive than haloalkanes due to the resonance stabilization of the aromatic ring.
- They have lower boiling points compared to haloalkanes of similar molecular weight.
- Haloarenes are less soluble in water due to the non-polar nature of the aromatic ring.

## 3.Chemical Reactions:

- Electrophilic Substitution: Haloarenes undergo electrophilic aromatic substitution reactions where a halogen atom is replaced by an electrophile.
- Sandmeyer Reaction: It involves the conversion of aryl diazonium salts into haloarenes.
- Wurtz-Fittig Reaction: Haloarenes can be coupled with alkyl halides in the presence of sodium metal to form biaryl compounds.

## 4.Uses:

- Haloarenes find applications in organic synthesis, pharmaceuticals, agrochemicals, and dyes.
- Some haloarenes are used as intermediates in the production of plastics and fragrances.

# Haloalkanes and Haloarenes

## Haloalkanes

Haloalkanes are the halogen derivatives of hydrocarbons.

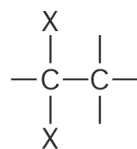
### Classification of Haloalkanes

**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.

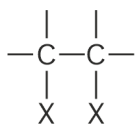
R-X may be of three types:

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

**Dihalides (C<sub>n</sub>H<sub>2n-2</sub>X<sub>2</sub>)** are the di-halogen derivatives of alkanes and are of geminal and vicinal types.



Geminal



Vicinal

Example

- (a)  $CH_3CHBr_2$  (Ethylidene dibromide),
- (b)  $BrCH_2CH_2Br$  (Ethylene dibromide)

**Trihalides (C<sub>n</sub>H<sub>2n-3</sub>X<sub>3</sub>) 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 are represented 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 as 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

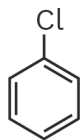


Haloalkynes or Alkynyl halides are the halogen derivatives of alkynes. The monohalogen derivatives of alkynes have the general formula  $C_nH_{2n-3}X$  where  $X = F, Cl, Br, I$  and  $n = 2, 3, 4, \dots$ , etc.

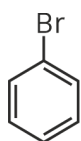
**(a) Mono Halogen Derivatives**

Examples

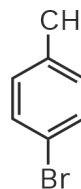
(i) Chlorobenzene



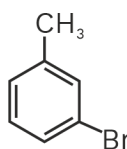
(iii) Bromobenzene



(ii) p-Bromotoluene

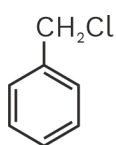


(iv) m-Bromotoluene

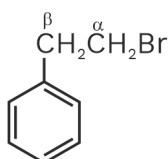
**(b) Side chain Halogen Derivatives**

Example

(i) Benzyl chloride



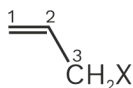
(ii) b-Phenylethyl bromide

**Allylic, Vinylic and Benzylic Halides**

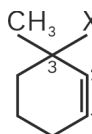
(a) Allylic Halides

Example

(i) 3-Halo-1-propene (1°)

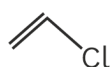


(ii) 3-Halo-3-methylcyclohex-1-ene (3°)

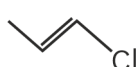


(b) Vinylic Halides

(i) Chloroethene

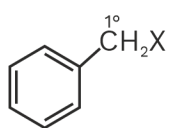


(ii) 1-Chloroprop-1-ene

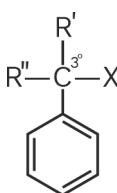


(c) Benzylic Halides

(i) Benzyl halide (1°)



(ii) A benzylic halide (3°)

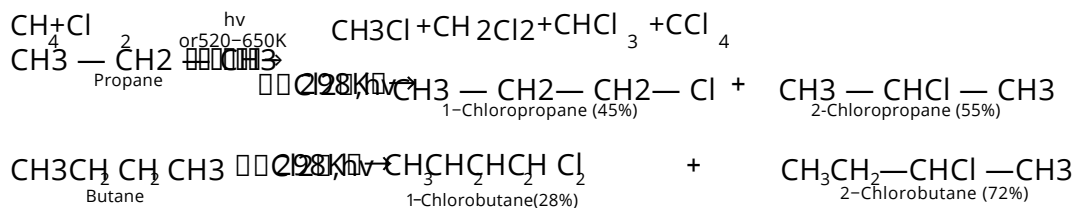


## Methods of preparation

### Halogenation of alkanes



#### For example

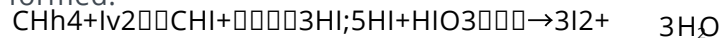


In general, the ease of substitution of various hydrogens follows the sequence:

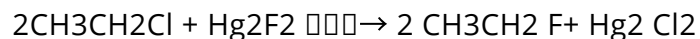
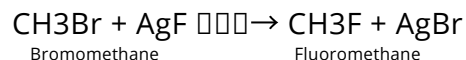


Reactivity order in halogens:  $\text{F}_2 > \text{Cl}_2 > \text{Br}_2 > \text{I}_2$

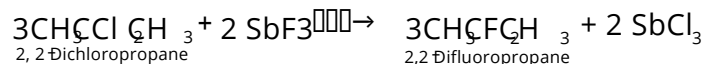
**Iodination** is reversible, but it may be carried out in presence of an oxidising agent such as  $\text{HIO}_3$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$ , etc. which oxidises the  $\text{HI}$  is formed.



**Fluorination:** 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  $\text{AgF}$ ,  $\text{Hg}_2\text{F}_2$ ,  $\text{CoF}_3$  or  $\text{SbF}_3$  to give alkyl fluorides.



**This reaction is called Swarts reaction.** When the organic halide contains two or three halogen atoms at the same carbon,  $\text{CoF}_3$  or the more easily available  $\text{SbF}_3$  is used. For example,



**from Alcohols:** Generally alkyl halides are prepared from alcohols by replacement of  $-\text{OH}$  group by an halogen ion. This is usually by using  $\text{HX}$  or  $\text{PX}_5$ .



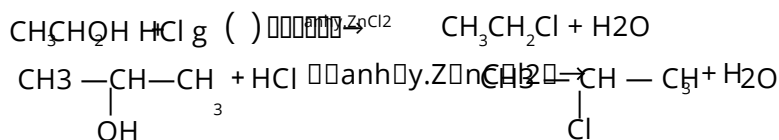
#### Concept Ladder



Vinyllic 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 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 :****(i) Using HCl :**

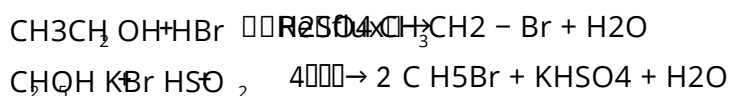
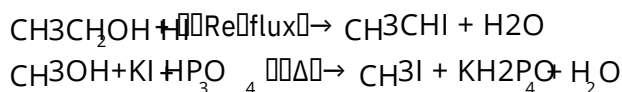
Anhydrous  $ZnCl_2$  helps in the cleavage of C-O bond. Being a Lewis acid, it co-ordinates with the oxygen atom of the alcohol. As a result, C-O bond weakens and ultimately breaks to form carbocations, which form chlorides.



Yield is improved when vapours of alcohol and HCl are passed over alumina at  $350^\circ\text{C}$ .

**(ii) Using HBr :**

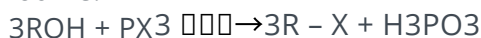
Alkyl bromides are obtained by refluxing the alcohol with constant boiling in HBr (40%) in presence of a little conc.  $H_2SO_4$

**(iii) Using HI :****(b) By the action of Phosphorus Halides:**

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



Here X can be either chlorine or bromine or iodine.

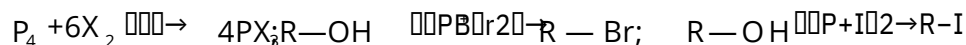
**Concept Ladder**

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

**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.

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.

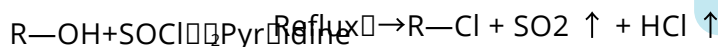


This method gives good yield of primary alkyl halides but poor yields of secondary and tertiary alkyl halides.

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

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

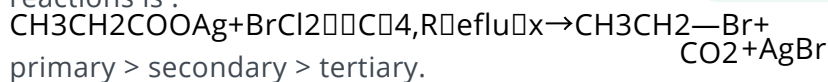
Chloroalkanes are conveniently prepared by refluxing alcohol with thionyl chloride ( $SOCl_2$ ) in presence of pyridine ( $C_5H_5N$ ).



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.

### 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 :



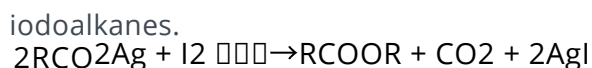
primary > secondary > tertiary.

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.

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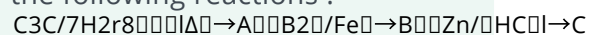
### Concept Ladder



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  $KI$ .

### Previous Year's Question

The compound  $C_7H_8$  undergoes the following reactions :



The product C is [NEET]

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



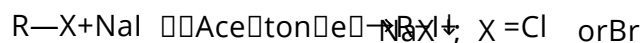
#### 4. Halogen exchange reaction :

Alkyl halides are easily prepared from corresponding chloroalkanes or bromoalkanes by heating with sodium iodide in acetone or methanol.

This reaction is called Finkelstein Reaction.



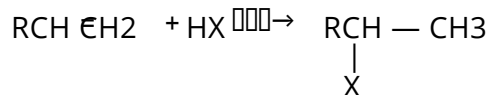
It is a halide exchange reaction which involves a substitution of Cl/Br by I. The reaction was specially designed to prepare iodo-alkanes which were not easily prepared using simple halogenation method. (Due to the reversibility of iodination)



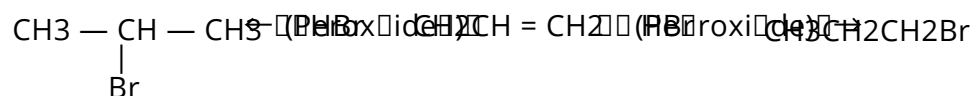
Reaction is supposed to be based on principle of greater solubility of NaI in acetone as compared to NaCl or NaBr because of greater covalent character in NaI. That is why despite of being a weaker reagent than Cl<sup>-</sup>/Br<sup>-</sup>, I<sup>-</sup> still substitutes them and the NaCl/NaBr formed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

#### from Alkenes :

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



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



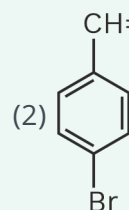
(c) Allylic halogenation : When alkenes (except Ethylene) are heated with Cl<sub>2</sub> or

#### Previous Year's Question



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

(1)  $C_6H_5CH_2CH_2CH_2Br$



(3)  $C_6H_5\underset{\text{Br}}{\text{CH}}\text{CH}_2\text{CH}_3$

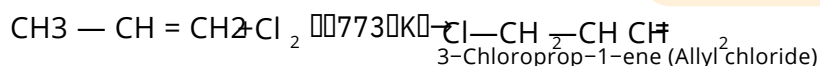
(4)  $C_6H_5\underset{\text{Br}}{\text{CH}_2}\text{CHCH}_3$

#### Concept Ladder

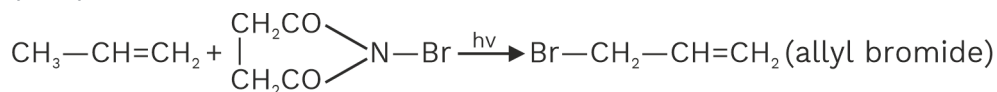


Peroxide effect is observed only for HBr. So HCl and HI when added to alkene give same product in presence or absence of peroxide.

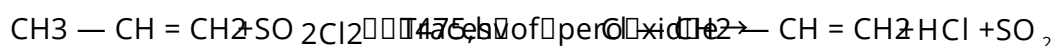
At a high temperature of about 773 K, the hydrogen atom at the allylic carbon (i.e., carbon next to the double bond) is substituted by a halogen atom. For example,



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



Allylic chlorination can also be carried out with sulphuryl chloride.



### Definitions

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

### 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

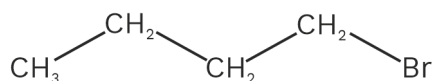
### Physical properties of monohalides

Lower members of monohalides ( $\text{CH}_3\text{X}$ ,  $\text{C}_2\text{H}_5\text{X}$ ) are colourless gases while higher members are colourless liquid up to  $\text{C}_{18}$ , members are colourless solids.

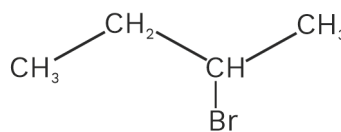
Boiling point and density increase with increase in molecular weight.



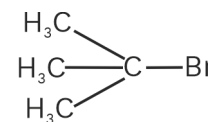
Likewise it happens in alkanes, branching also decrease B.P



Boiling Point  $\rightarrow$  375K

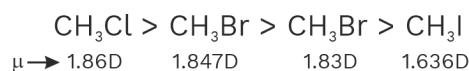


364K



346K

Dipole moment:  $\text{RCl} > \text{RF} > \text{RBr} > \text{RI}$



Stability :  $\text{RF} > \text{RBr} > \text{RCl} > \text{RI}$

Solubility  $\propto \frac{1}{\text{Mol.wt.}}$

In general:  $\text{CH}_3\text{X} > \text{C}_2\text{H}_5\text{X} > \text{C}_3\text{H}_7\text{X} > \text{C}_4\text{H}_9\text{X}$

### Concept Ladder



$\text{CH}_3\text{Cl}$ ,  $\text{CH}_3\text{Br}$ ,  $\text{C}_2\text{H}_5\text{Cl}$ , some chloro, fluoro, bromo, and iodo compounds are gases at room temperature. Higher chloro, bromo, and iodo compounds are either liquids or solids. Many volatile halogen compounds have sweet smell.

### Rack your Brain



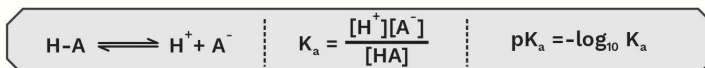
n-Butyl bromide has higher boiling point than t-butyl bromide. Give reasons?

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

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

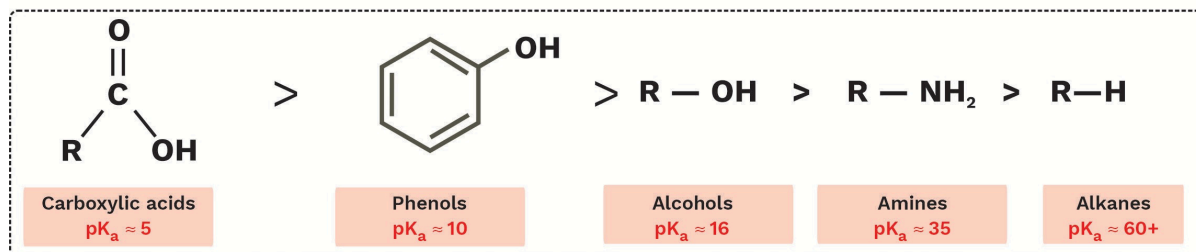
**1**

# ACIDITY & BASICITY



## Key factors that effect the acidity

- ➔  $\text{HF} > \text{H}_2\text{O} > \text{NH}_3 > \text{CH}_4$ 
}
**Electronegativity** - The more electronegative the anionic atom in the conjugate base, the better it is at accepting the negative charge.
- ➔  $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$ 
}
**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.
- ➔  $\text{RCOOH} > \text{ROH}$ 
}
**Resonance** - In the carboxylate ion ( $\text{RCOO}^-$ ) 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 ( $\text{RO}^-$ ).



## Key factors that effect the basicity

- ➔  $\text{CH}_3^- > \text{NH}_2^- > \text{OH}^- > \text{F}^-$ 
}
**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.
- ➔  $\text{F}^- > \text{Cl}^- > \text{Br}^- > \text{I}^-$ 
}
**Size** - The larger the atom the weaker the H-X bond and the lower the electron density making it a weaker base..
- ➔  $\text{RO}^- > \text{RCOO}^-$ 
}
**Resonance** - In the carboxylate ion ( $\text{RCOO}^-$ ) 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 ( $\text{RO}^-$ ).

## General basicity trend of some common organic bases



## Chemical Properties of Monohalides

y Since the  $\overset{\delta+}{\text{C}}-\overset{\delta-}{\text{X}}$  is polar, these are reactive compounds.

y The reactivity order is as follows:

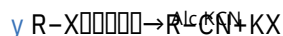
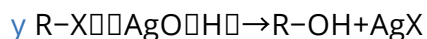


**Nucleophilic substitution reactions:** Alkyl halides undergo nucleophilic substitution reactions as follows:



This reaction occurs by either  $\text{S}_{\text{N}}1$  or  $\text{S}_{\text{N}}2$  mechanism.

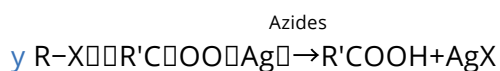
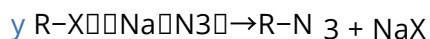
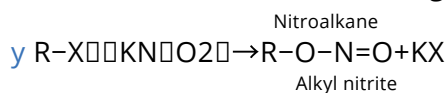
**For example,**



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



Major product is R-NC as AgCN being covalent cannot give  $\text{CN}^-$  ions. Therefore, attack occurs from nitrogen atom to give R-NC.



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:

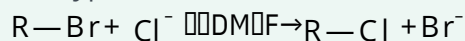


Order of leaving tendency:

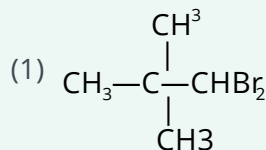


## Previous Year's Question

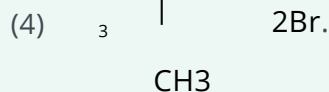
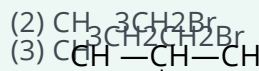
In a  $\text{S}_{\text{N}}2$  substitution reaction of the type



which one of the following has the highest relative rate?



[NEET]



## SUBSTITUTION REACTION ( $S_N1$ )



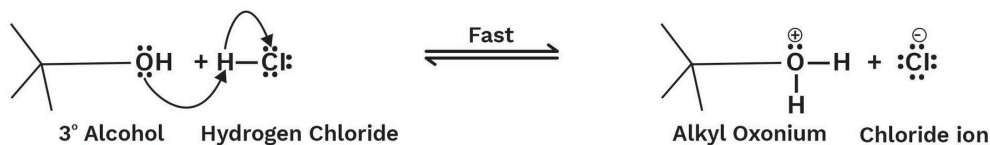
Yellow cat waits for the black cat to leave and then takes the pod. Similarly in  $S_N1$  reaction one nucleophile waits for other nucleophile to move from substrate.

### What Is $S_N1$ Reaction ?

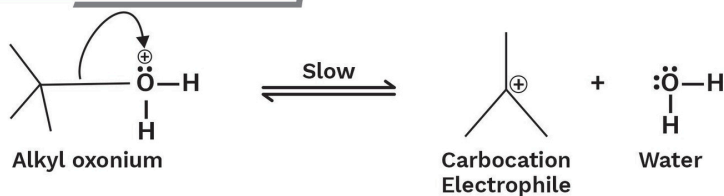
$S_N1$  indicates the unimolecular nucleophilic substitution reaction in organic chemistry. Their rate determining step of the mechanism depends on the decomposition of a single molecular species. So that, the rate of  $S_N1$  reaction can be expressed as rate =  $K [R-LG]$ . Furthermore,  $S_N1$  is 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



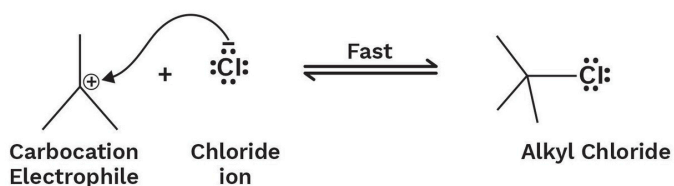
#### Dissociation Of Water



#### Rate- Determining Step

- Unimolecular
- Nucleophilic reaction
- " $S_N1$ " mechanism

#### Capture Of Carbocation



- Protic solvent
- 3° or 2° carbon
- 1° carbon

## SUBSTITUTION REACTION ( $S_N2$ )



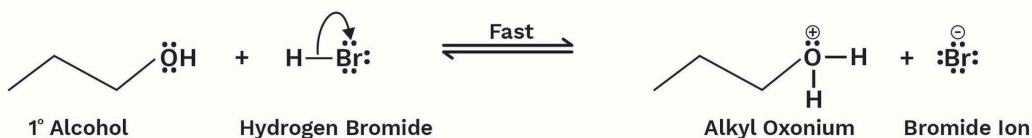
Yellow cat forces the black cat out from the pod. Similarly in  $S_N2$ , strong nucleophile kicks out the weaker nucleophile.

### What Is $S_N2$ Reaction ?

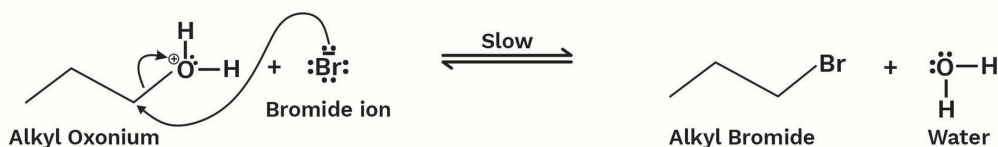
$S_N2$  indicates the bimolecular nucleophilic substitution reaction in organic chemistry. In this mechanism, separation of leaving group and formation of new bond happen synchronously. Therefore, two molecular species are involved in the rate determining step and this leads to the term bimolecular nucleophilic 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 ( $R-OH \longrightarrow R-X$ )

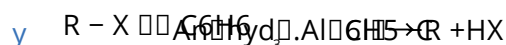
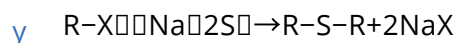
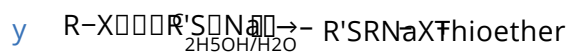
#### Proton Transfer



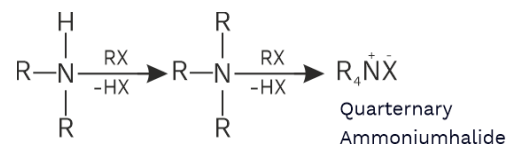
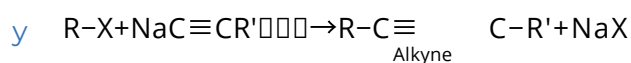
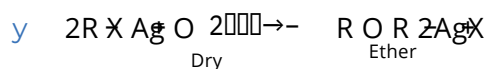
#### Nucleophile (halide) Separates Water



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.



The above reaction is called Friedel-Crafts reaction.

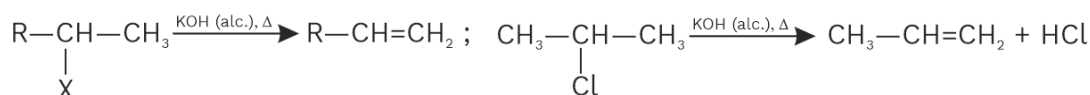
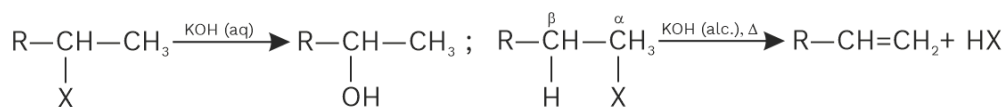


### Dehydrohalogenation

It involves  $\alpha$ ,  $\beta$ -elimination following  $E_1$  and  $E_2$  mechanisms.

Here,  $\alpha$ ,  $\beta$ -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.



### 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

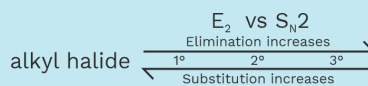


Ethyl iodide undergoes  $S_N2$  reaction faster than ethyl bromide?

### Concept Ladder



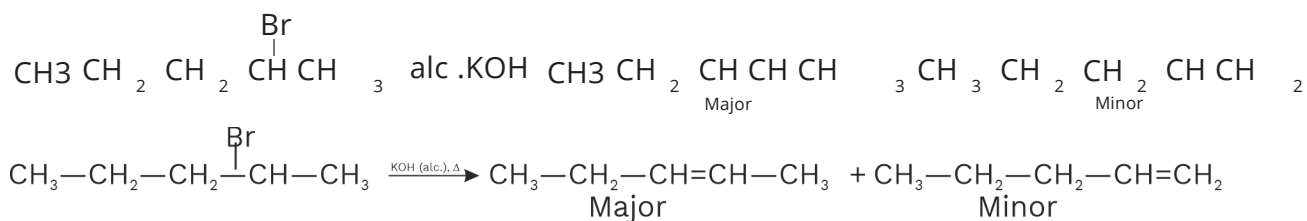
When substitution and elimination are competing reaction



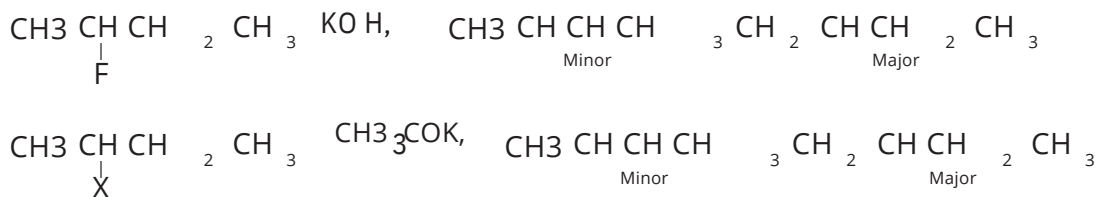


### Saytzeff's Rule

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



In case of a fluoro-alkane or other secondary halide,  $\text{KOH}$  or  $\text{KOC(CH}_3)_3$  is according to Hoffmann's Rule. According to it, b-Hydrogen atom is eliminated from b-Carbon atom with less H-atom or less acidic b-H-atom which means less stable alkene is major product.

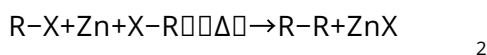


### Reaction with metals

(a) Reaction with Na (Wurtz reaction)



(b) Reaction with Zn (Frankland reaction)



(c) Reaction with Mg



R may be  $-\text{CH}_3$ ,  $-\text{C}_2\text{H}_5$ ,  $-\text{C}_6\text{H}_5$  etc.

**Reactivity order for R-MgX is given as**



### Previous Year's Question



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

- (A) b-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

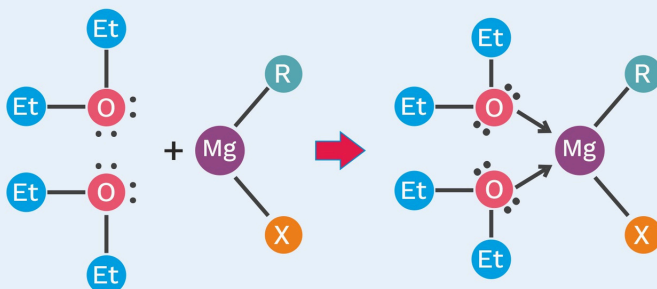
If the metal attached to the carbon is magnesium, then it is called Grignard Reagent.

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?

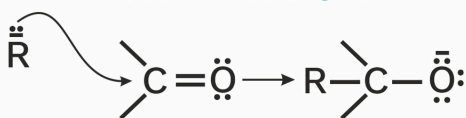
Organo metallic compounds are organic compounds in which metal atom is directly attached to Carbon atom

M-C

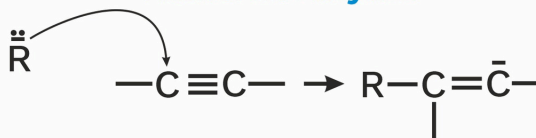
## Chemical Reactivity Of Grignard Reagent

Grignard reagent produces nucleophile therefore it attacks at electrophilic centers

### Attack On Aldehydes

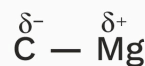


### Attack On Alkynes

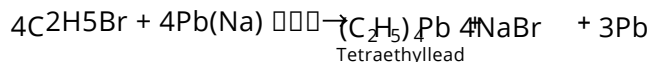


## Reactivity

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



(d) Reaction with lead sodium alloy



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

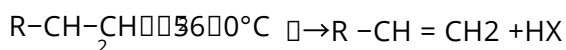
(e) Reaction with lithium



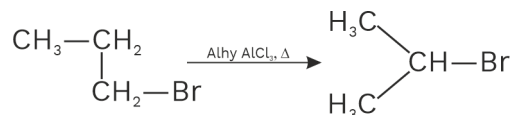
**Reduction**



**Heating effect**

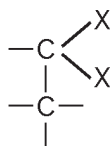


**Isomerisation**



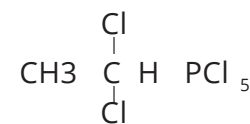
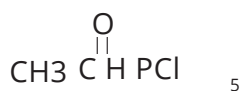
**Dihalides**

Gem or geminal halide or alkylidene halides

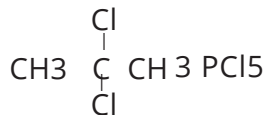
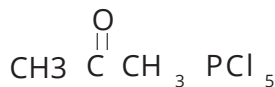


**Methods of preparation of geminal halides**

1. From aldehyde or ketone



Dichloroethane



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.



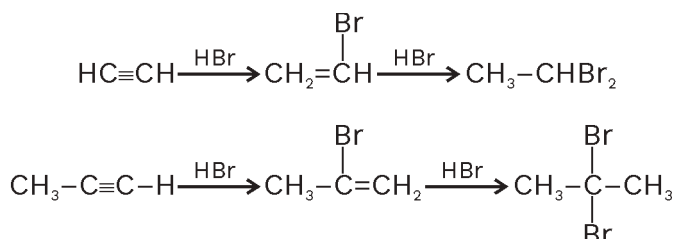
### Previous Year's Question

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

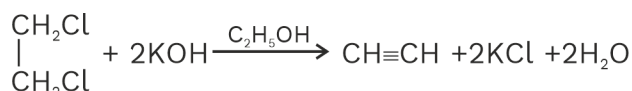
## 2. From alkyne



Chemical properties of geminal halides (Alkylidene halides)

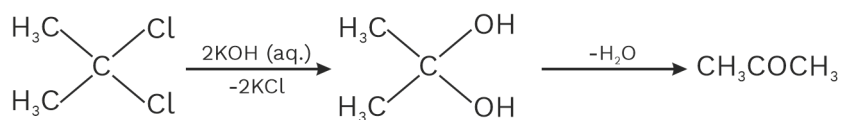
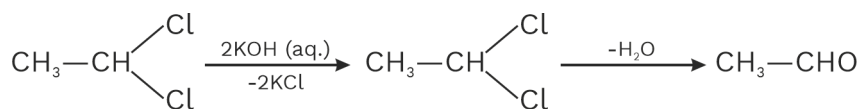
These are less reactive than the alkyl halides due to the fact that the presence of one-X-atom (E.W.G) makes the replacement of other X-atom slightly difficult.

### 1. Reaction with alcoholic KOH

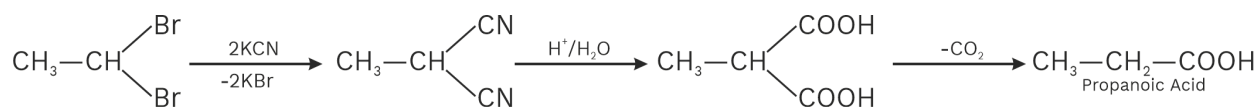


### 2. Reaction with aqueous KOH

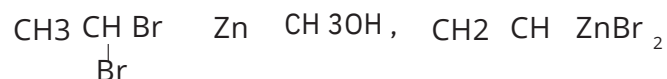
Here, R-CHO, R-CO-R are formed

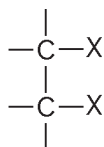
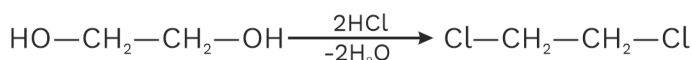


### 3. Reaction with KCN

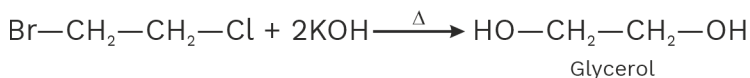
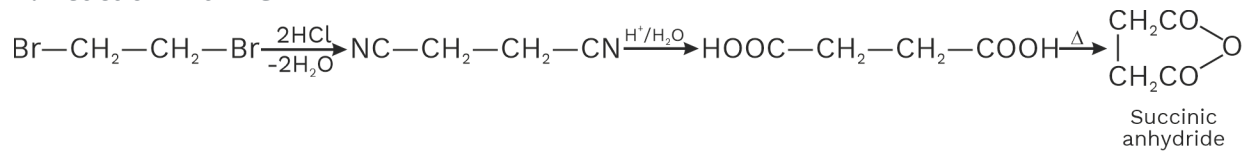
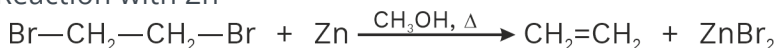


### 4. Reaction with Zn



**Vic or vicinal dihalide or alkylene halides****Methods of preparation of vicinal dihalides****1. From alkenes****2. From diols like glycol**

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

**1. Reaction with KOH****2. Reaction with KCN****3. Reaction with Zn****Trihalides or Haloforms (CHX<sub>3</sub>)****Chloroform (CHCl<sub>3</sub>)**

y Chloroform was discovered by Justus Von

Liebig and named by Jean-Baptiste Dumas.

y It has anesthetic nature which was discovered by James Young Simpson.

**Methods of preparation****1. From chloral****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.

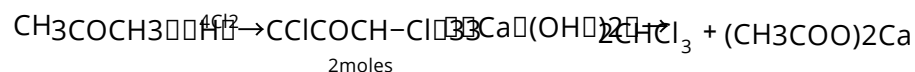
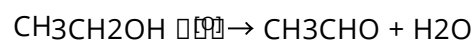
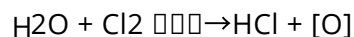
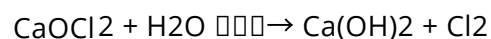
**Previous Year's Question**

Industrial preparation of chloroform employs acetone and [AIPMT]

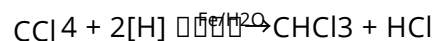
- (1) phosgene
- (2) calcium hypochlorite
- (3) chlorine gas
- (4) sodium chloride

2. From ethyl alcohol or acetone

Ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) or acetone (CH<sub>3</sub>COCH<sub>3</sub>) reacts with bleaching powder to give chloroform as follows:



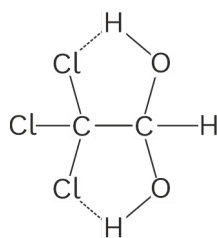
3. From CCl<sub>4</sub>



4. From chloral hydrate



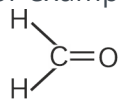
Chloral hydrate is a cyclic compound in which has butterfly-like structure.



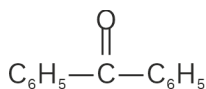
5. Haloform reaction

(A) It is given by >C=O having -COCH<sub>3</sub> group.

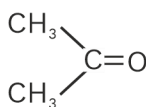
For example,



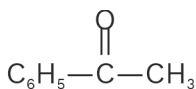
Does not show



Does not show



show



show

### Concept Ladder



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

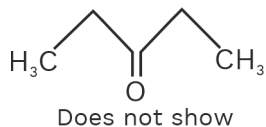
### Rack your Brain



What are the harmful effect of chloral in human body?

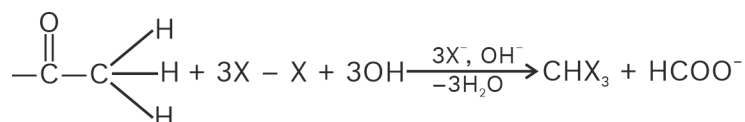
### Definitions

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.



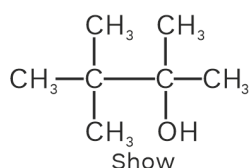
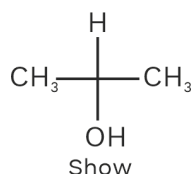
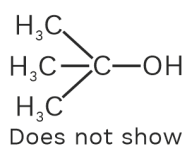
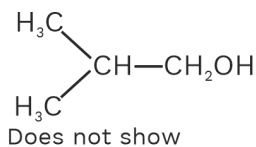
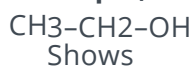
y Ethanal is the only aldehyde to show this reaction.

**For example,**

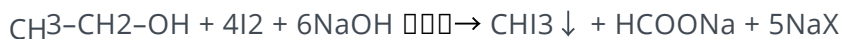


**(B)** Alcohol having  $\text{CH}_3-\underset{\text{CH}_3}{\text{CH}}-\text{OH}$  group shows haloform reaction.

**For example,**



**For example,**



**$\text{CHCl}_3$**

y Chloroform is a colourless liquid having a sweet smell.

y It is also a good solvent for resins, fats, etc.

y Its boiling point is  $61^\circ\text{C}$ .

y Soluble in organic solvents as oils but insoluble in  $\text{H}_2\text{O}$ .

**$\text{CHBr}_3$**

y  $\text{CHBr}_3$  is a colourless liquid and its boiling point is  $149.5^\circ\text{C}$ .

### Previous Year's Question



**Answer:** Organic compound A (C<sub>4</sub>H<sub>10</sub>O) 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

## CHI<sub>3</sub>

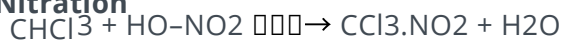
- y Its melting point is 119°C.
- y It occurs as yellow, hexagonal plate like crystals.
- y It can be used as antiseptic (due to the liberation of free I<sub>2</sub>).

### Test of Purity of CHCl<sub>3</sub>

No precipitate is formed when chloroform reacts with silver nitrate. This is because, being covalent, CHCl<sub>3</sub> cannot furnish Cl<sup>-</sup> ions.

### Chemical properties of chloroform (CHCl<sub>3</sub>)

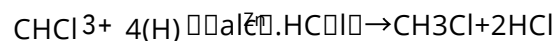
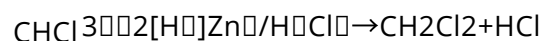
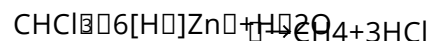
#### 1. Nitration



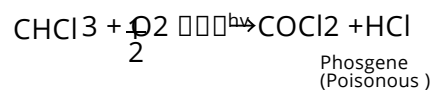
Chloropicrin (insecticide)

- y It is used in the manufacture of tear gas, phenacyl chloride [C<sub>6</sub>H<sub>5</sub>COCH<sub>2</sub>Cl].

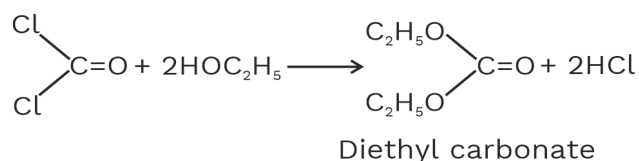
#### 2. Reduction



#### 3. Oxidation



y Chloroform is kept in dark, filled, tightly closed bottle with a small amount of C<sub>2</sub>H<sub>5</sub>OH (negative catalyst) to avoid oxidation or formation of phosgene. Ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) converts phosgene into non-poisonous 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



y CHCl<sub>3</sub> is mainly used in the production of Freon refrigerant, R-22.

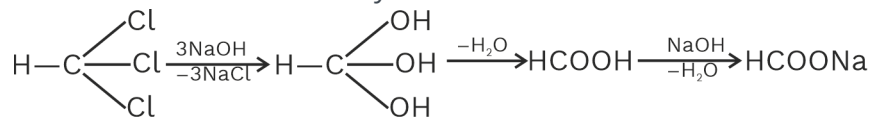
y CHCl<sub>3</sub> is also used as a solvent for fats, alkaloids, iodine etc.

y CHCl<sub>3</sub> causes dizziness, headache and fatigue.

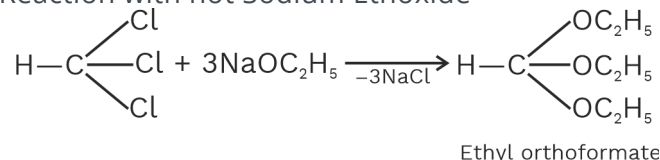
y Chloroform exposure may damage liver and kidney.



## 4. Reaction with hot Sodium Hydroxide



## 5. Reaction with hot Sodium Ethoxide

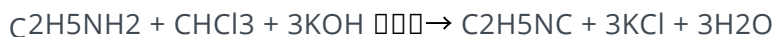


6. Carbylamine reaction: It is a test a primary amine. Here, the primary amine reacts with chloroform and base KOH, to give bad smelling isocyanide as follows:



Here, the reaction intermediate is:  $\text{CCl}_2$ , that is, dichlorocarbene.

If ethylamine is taken, product formed is ethyl isocyanide.



If aniline is taken, product formed is phenylisocyanide.

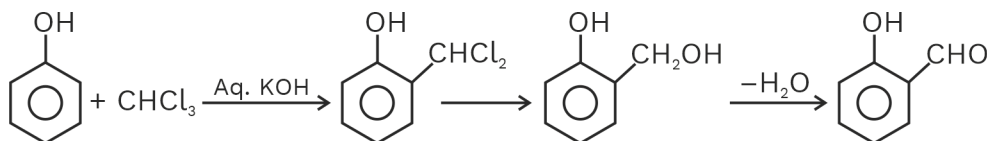


## 7. Reaction with Ag powder

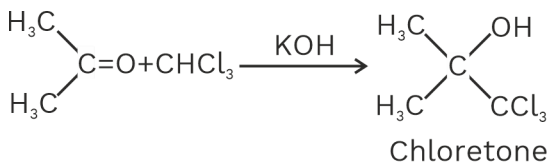


## 8. Reimer-Tiemann reaction:

Here reaction intermediate is:  $\text{CCl}_2$ .



## 9. Reaction with acetone



Chloretone is used in hypnotic medicines.

## Previous Year's Question



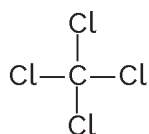
Benzene reacts with n-propyl chloride in the presence of anhydrous  $\text{AlCl}_3$  to give

[AIPMT]

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

## CCl<sub>4</sub> or Pyrene

(Carbon Tetra-Chloride)



Tetrahedral structure, sp<sup>3</sup> hybridization, bond angle 109° 28' and μ is zero

### Methods of preparation

- $\text{CH}_4 + 4\text{Cl}_2 \xrightarrow{\text{heat}} \text{CCl}_4 + 4\text{HCl}$
- $\text{CHCl}_3 + \text{Cl}_2 \xrightarrow{\text{heat}} \text{CCl}_4 + \text{HCl}$
- $\text{CS}_2 + 2\text{S}_2\text{Cl}_2 \rightarrow \text{CCl}_4 + 6\text{S}$
- $\text{CH}_3 + 9\text{Cl}_2 \xrightarrow{\text{heat}} \text{CCl}_4 + \text{C}_2\text{Cl}_6 + 8\text{HCl}$

### Physical properties of pyrene

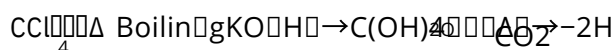
- It is a colourless, non-flammable, poisonous liquid having a boiling point of 350 K.
- Soluble in organic solvents as oils but insoluble in water and is a good solvent for fat, oil and wax.

### Chemical properties of pyrene

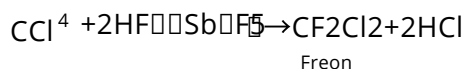
#### 1. Reaction with steam



#### 2. Hydrolysis

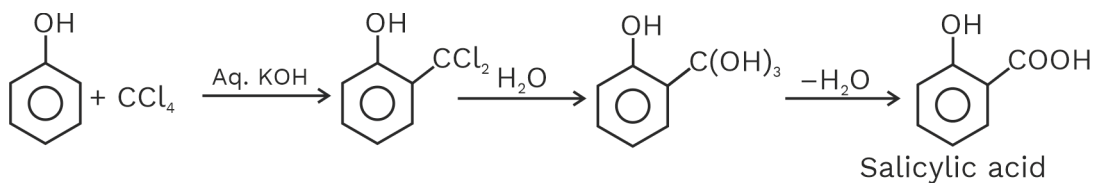


#### 3. Reaction with HF



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]

- phosphoryl chloride
- thionyl chloride
- carbon dioxide and phosphine
- 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<sub>4</sub>:**

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

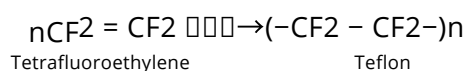
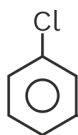
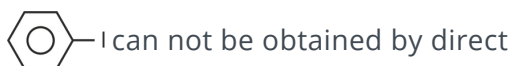
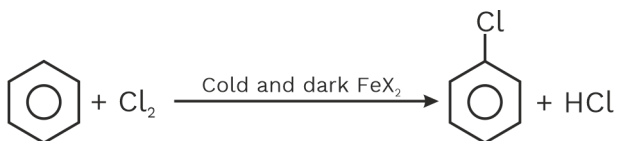
(ii) Used as solvent for fats, oils, resins etc.

**Teflon (-CF<sub>2</sub>-CF<sub>2</sub>-)<sub>n</sub>**

y Teflon is a polymer of tetrafluoroethylene.

y It is a chemically inert thermostatic plastic.

y It is used for electrical insulation and in gasket materials.

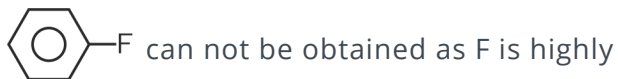
**Chlorobenzene****Methods of preparation****From benzene**

iodination as not only the reaction is reversible

but also HI being a reductant can reduce into Benzene. But if strong oxidants like HNO<sub>3</sub>, HgO are used the reaction is possible as they

oxidise HI into I<sub>2</sub>.

oxidise HI into I<sub>2</sub>.



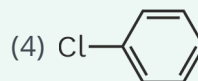
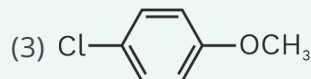
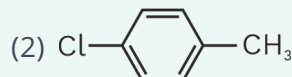
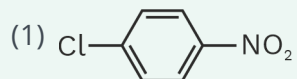
reactive and the reaction is violent also.

**Concept Ladder**

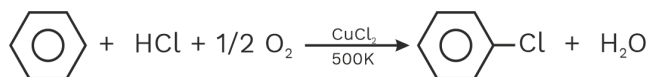
Teflon is the trading name for a commonly used polymer called Polytetrafluoroethylene. PTFE has unique and valuable qualities such as being chemical resistant, temperature resistant, low permeation and high corrosion resistant.

**Previous Year's Question**

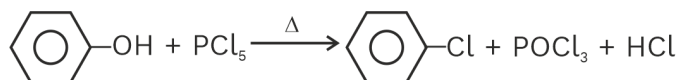
Which of the following compounds undergoes nucleophilic substitution reaction most easily? [NEET]



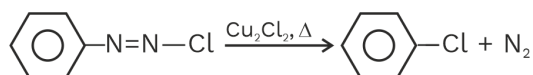
y Commercial method or Raschig method



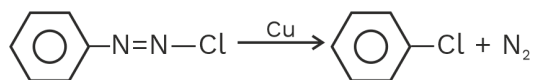
**From alcohol**



From benzene diazonium chloride or Sand Mayer's reaction



**Gatterman reaction**



**Physical properties of Chlorobenzene**

y It is colourless liquid with pleasant odour and a boiling point of 132°C.

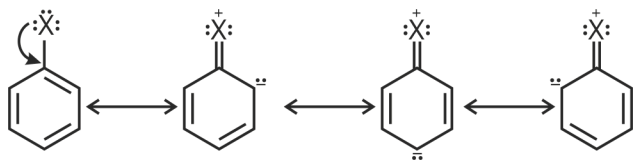
y It is heavier than water and insoluble in it.

**Chemical properties of Chlorobenzene**

Due to benzene ring

y 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.

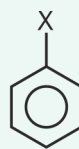
Here due to resonance electron density increases at o, p positions but due to -I effect -X atom has a tendency to withdraw electrons from benzene ring. It means due to deactivation in ring rate of electrophilic substitution decreases.



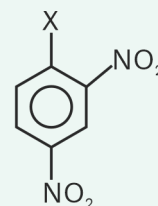
### Previous Year's Question



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



(I)



(II)



(III)

(IV)

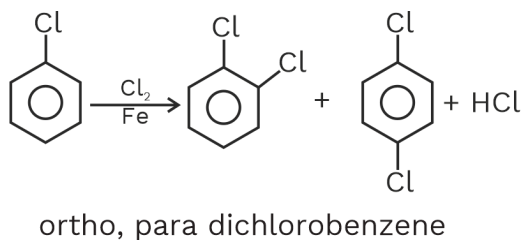
C-X bond towards nucleophile in the following compounds is (1) I < II < IV < III (2) II < III < I < IV (3) IV < III < I < II (4) III < II < I < IV

### Concept Ladder

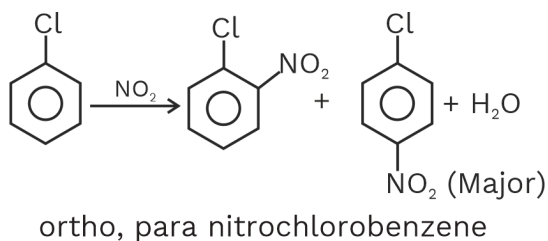


In haloarens and vinyl halides, the phenyl cation or the vinyl cation formed as a result of self ionization is not stabilized by resonance because the sp<sup>2</sup>-hybridized orbital of carbon having the +ve charge is perpendicular to the p-orbital of the phenyl ring or the vinyl group.

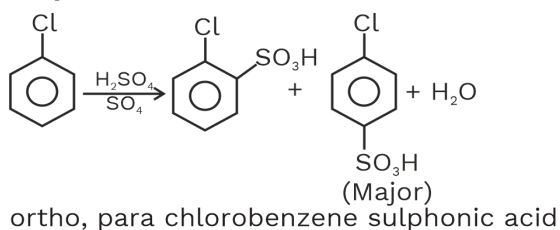
y **Halogenation**



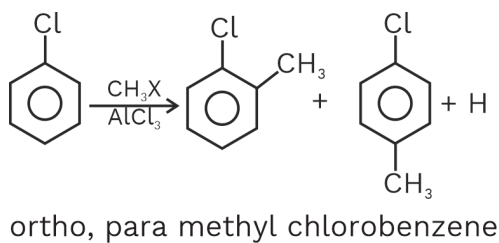
y **Nitration**



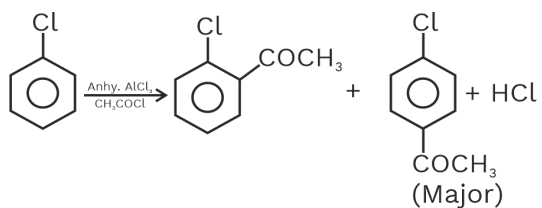
y **Sulphonation**



y **Friedel Crafts alkylation**



y **Acylation**



**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**

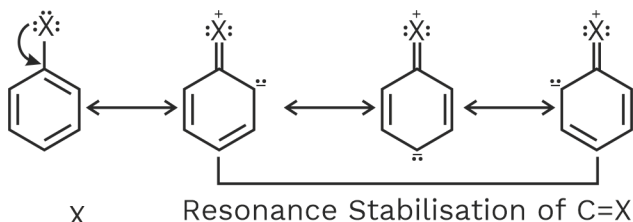
Benzene reacts with n-propyl chloride in the presence of anhydrous  $AlCl_3$  to give

[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.

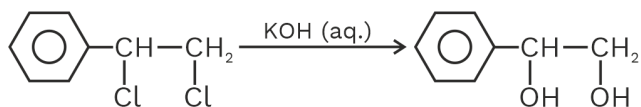
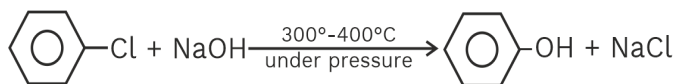


In haloarenes C-X bond length is shorter than in haloalkanes which is 169 and 177 PM respectively. It also decreases reactivity in

haloarenes. Here  $\text{C}_6\text{H}_5^+$  is very less stable so SN1 reaction does not occur. The attack of

electron rich Nucleophile is also inhibited by higher electron density at arenes.

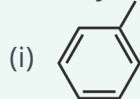
Substitution by -OH group



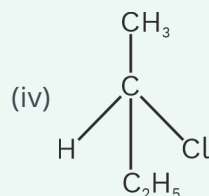
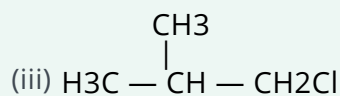
## Previous Year's Question



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



(ii)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$



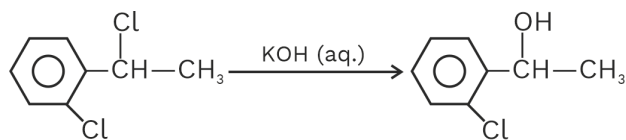
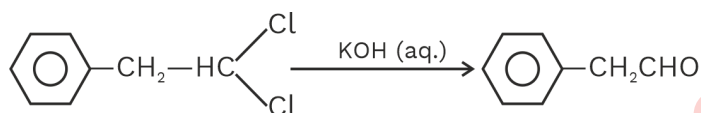
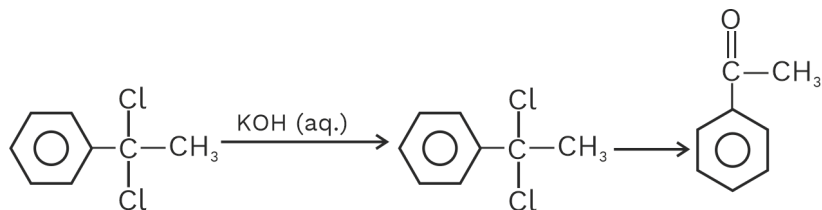
- (1) (i) and (ii)
- (2) (ii) and (iv)
- (3) (iii) and (iv)
- (4) (i) and (iv)

## Concept Ladder

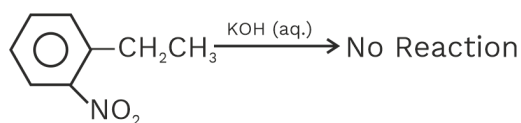
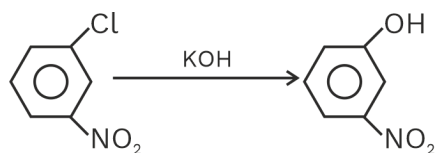


In haloarene presence of EWG such as  $-\text{NO}_2$ ,  $-\text{CN}$ , etc. at o- and p-position (but not at m-position)

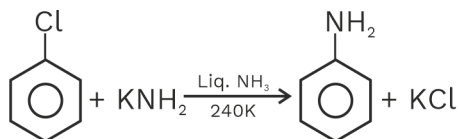
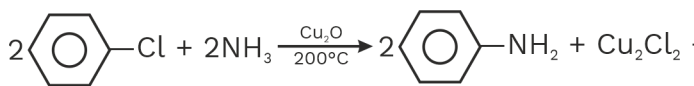
w.r.t. the halogen greatly activates the nucleophilic displacement.



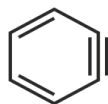
When a strong E.W.G group like  $-\text{NO}_2$  is present at o, p position the substitution of  $-\text{X}$  becomes comparatively easier and reaction occurs.



#### y Substitution by $\text{NH}_2$ group



This reaction proceeds with Benzene



#### Rack your Brain

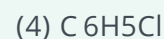
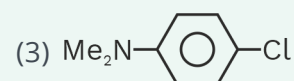
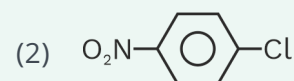
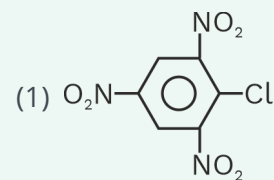


p-Chloronitrobenzene undergoes nucleophilic substitution faster than chlorobenzene. Explain giving the resonating structure as well?

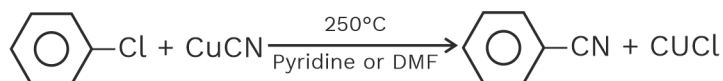
#### Previous Year's Question



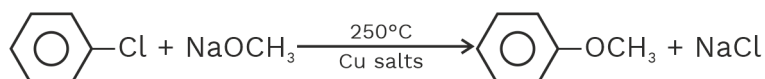
Which chloro derivative of benzene among the following would undergo hydrolysis most readily with aqueous sodium hydroxide to furnish the corresponding hydroxy derivative? [AIPMT]



y Substitution by CN group



y Substitution by -OR group:



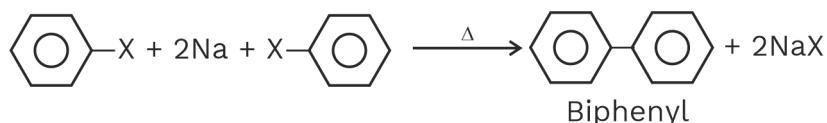
y Reaction with magnesium



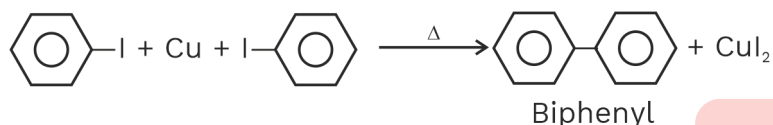
y Wurtz Fittig reaction



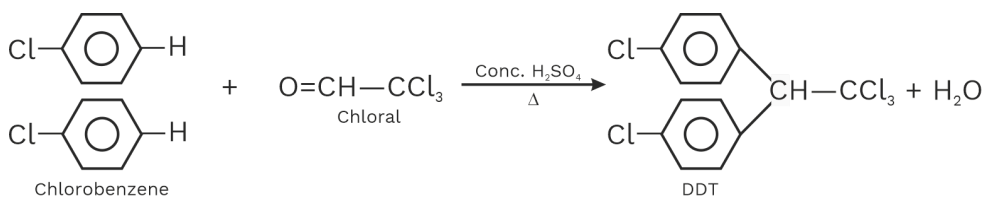
y Fittig reaction



y Ullmann reaction



y Reaction with chloral: Chloral on heating with chlorobenzene in presence of concentrated  $\text{H}_2\text{SO}_4$  gives DDT (p,p-dichlorodiphenyl trichloroethane). It is non-biodegradable as both Cl atoms are linked with benzene ring.



**Rack your Brain**



Halobenzene is a 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.
  - Residues accumulate in the environment and are toxic to mammals etc.
- Carbon tetrachloride** Carbon tetrachloride or  $\text{CCl}_4$

$\text{CCl}_4$  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  $\gamma$ -Lindane or 6,6,6 [ $\text{C}_6\text{H}_6\text{Cl}_6$ ]. It is a famous pesticide for killing of

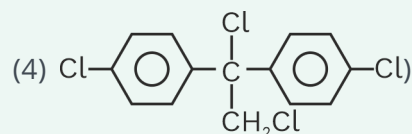
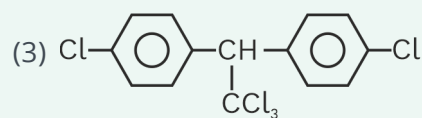
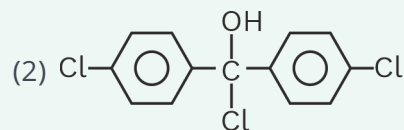
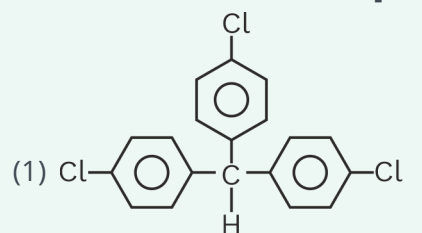
Termites (white ants) from soil.

## Previous Year's Question



$\text{CH}_3\text{CHO}$  reacts with chlorobenzene in presence of sulphuric acid and produces

[NEET]



**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.  $\text{HIO}_4$  as an oxidising agent.

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

**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.

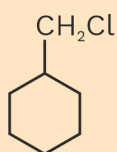
**A.3**

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

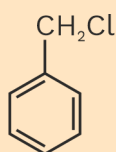
**4** II, due to symmetry of para-positions; it fits into crystal lattice better than other isomers.

**A.4**

**Q.5** Which of the following compounds would undergo  $\text{S}_{\text{N}}1$  reaction faster and why?



(A)



(B)

**A.5** (B) undergoes  $\text{S}_{\text{N}}1$  reaction faster than (A) because in case of (B), the carbocation formed after the loss of  $\text{Cl}^-$  is stabilised by resonance, whereas, no such stabilisation is possible in the carbocation obtained from (A).

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

**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.

**A.6**

**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.

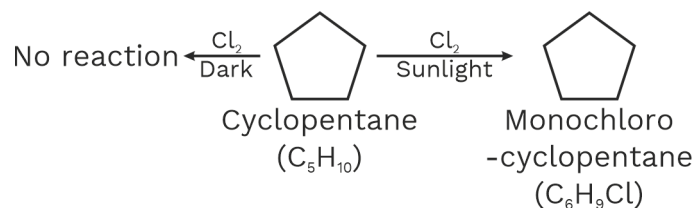
Order of boiling point :

iso-propyl chloride < 1-chloropropane < 1-chlorobutane

**Q.** 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.

**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, therefore, all ten hydrogen atoms of cycloalkanes must be equivalent. Thus, cycloalkane is cyclopentane.

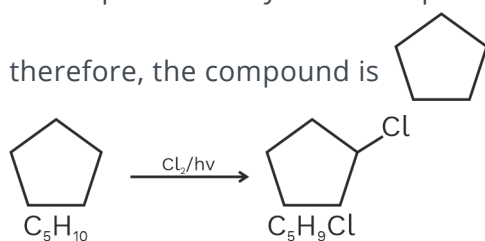
**A.8**



**Q.** 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.

**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.

**A.9** This is possible only if the compound is a cyclic alkane.



**Q.1** Which of the compounds will react faster in  $S_N1$  reaction with the  $-OH$  ion?  $CH_3-CH_2-Cl$  or  $C_6H_5-CH_2-Cl$

**0**  $C_6H_5-CH_2-Cl$

**A.1**

**Q.1** Which compound in each of the following pairs will react faster in  $S_N2$  reaction with  $OH^-$ ? (i)  $CH_3Br$  or  $CH_3I$  (ii)  $(CH_3)_3CCl$  or  $CH_3Cl$

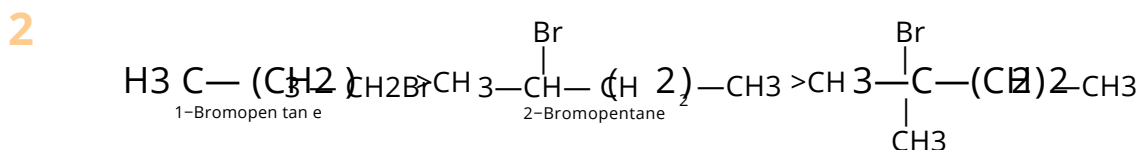
**1** (i) Between  $CH_3Br$ ,  $CH_3I$  will react faster via  $S_N2$  mechanism. In  $S_N2$ ,  $C-X$  bond breaks and faster it breaks faster is the reaction.  $I^-$  is a better leaving group. Owing to its large size,  $C-I$  bond breaks faster than  $C-Br$  bond and hence reaction proceeds at a higher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

**A.1**

**1** (ii) Order of reactivity in case of  $S_N2$  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.1** Arrange the compounds of each set in order of reactivity towards  $S_N2$  displacement : 2-Bromo-2-methylbutane, 1-Bromopentane, 2-Bromopentane

**2**  $S_N2$  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 preferred substrates for  $S_N2$  reactions are  $1^\circ$  alkyl halides followed by  $2^\circ$  and  $3^\circ$  alkyl halides. Order of reactivity for  $S_N2$  reactions :  $1^\circ > 2^\circ > 3^\circ >$  aryl halide.



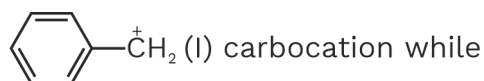
**Q.1** Out of  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  and  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$ , which is more easily hydrolysed by aqueous KOH?

**3**  $\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  is hydrolysed faster.  
(a) Hydrolysis of an alkyl halide is an example of nucleophilic substitution reaction. In case of aryl halides this follows the  $S_N1$  pathway i.e., via the formation of carbocation.

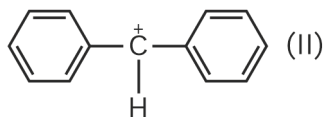
**A.1**

(b)  $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$  or benzyl chloride gives

**3**



$\text{C}_6\text{H}_5\text{CHClC}_6\text{H}_5$  generates



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

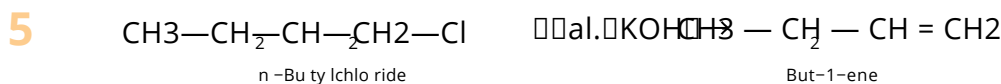
(d) As a result, delocalisation of +ve charge is greater and carbocation is more stable. Due to this, (II) is formed faster and corresponding halide is hydrolysed with greater ease as compared to benzyl chloride.

**Q.1** p-Dichlorobenzene has higher m.p. and solubility than those of o- and m-isomers. Discuss.

**4** 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 meta isomers.

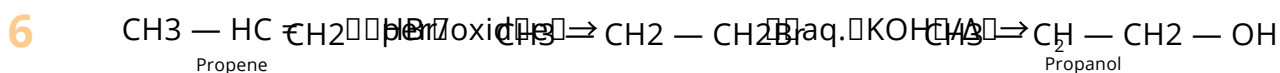
**A.1**

**Q.1** What happens when n-butyl chloride is treated with alcoholic KOH.

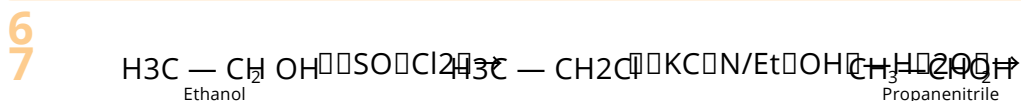


**A.1** The reaction is an example of  $\beta$ -hydrogen elimination brought about by  $\text{C}_2\text{H}_5\text{O}$

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



**A.1** How can the following conversions be carried out: Ethanol to propanenitrile.



**Q.18** Give the uses of freon 12, DDT, carbon tetrachloride and iodoform: Freon 12 ( $\text{CCl}_2\text{F}_2$ ) is

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

**Q.1** Give the uses of freon 12, DDT, carbon tetrachloride and iodoform: DDT (p, p'-dichlorodiphenyltrichloroethane) is

**9** (i) used as an insecticide,  
(ii) mainly used against mosquitoes.

**A.1**

**9**

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**Q.2** alkyl halides, though polar, are immiscible with water. Explain why?

**0** 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.

**A.20**

## Chapter Summary



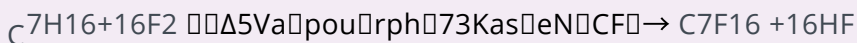
1.  $\text{CCl}_4$  is used as a medicine for treatment against hookworms.
2.  $\text{CF}_4$  is freon-14,  $\text{CF}_3\text{Cl}$  is freon-13,  $\text{CF}_2\text{Cl}_2$  is freon-12 and  $\text{CFCl}_3$  is freon-11.
3. Perfluorocarbons have a general formula  $\text{C}_n\text{F}_{2n+2}$ .



4. Halothane ( $\text{CF}_3\text{CHClBr}$ ) is used as an inhalative anaesthetic agent.
5. Chloretone is a hypnotic or sleep-inducing drug.

6. Westron is tetrachloroethane  $\begin{array}{c} \text{Cl} \quad \text{Cl} \\ | \quad | \\ \text{C} - \text{C} \\ | \quad | \\ \text{Cl} \quad \text{Cl} \end{array}$  while Westrosol is trichloroethylene  $\begin{array}{c} \text{Cl} \quad \text{Cl} \quad \text{Cl} \\ | \quad | \quad | \\ \text{C} = \text{C} - \text{C} \\ | \quad | \\ \text{H} \quad \text{Cl} \end{array}$

7. The boiling point have the following order:  
alkyl iodides > alkyl bromides > alkyl chlorides > alkyl fluorides  
 $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$
8. The volatility has the following order:  
 $\text{R-Cl} > \text{R-Br} > \text{R-I}$
9. Dipole moment has the following order:  
 $\text{CH}_3\text{Cl} > \text{CH}_3\text{F} > \text{CH}_3\text{Br} > \text{CH}_3\text{I}$
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  
 $\text{R-I} > \text{R-Br} > \text{R-Cl} > \text{R-F}$   
 $\text{CH}_3\text{Cl} < \text{CH}_2\text{Cl}_2 < \text{CHCl}_3 < \text{CCl}_4$
12. The order of chemical reactivity of alkyl halides is  
 $\text{RI} > \text{RBr} > \text{RCl}$
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—in spite of higher positive ionization energy—causes steric hinderance and makes them less reactive towards  $\text{S}_\text{N}2$  mechanism.  
The reactivity follows the order  $\text{CH}_3\text{X} > \text{C}_2\text{H}_5\text{X} > \text{C}_3\text{H}_7\text{X}$ .
15. Antiseptic action of  $\text{CHI}_3$  is due to the liberation free  $\text{I}_2$ .
16. Perfluoro carbons (PFCs) have a general formula  $\text{C}_n\text{H}_{2n+2}$ .



202



**Perfluoro heptane**

These are colourless, odourless, non polar stable, non-toxic, substances. They are stable to U.V or other radiations so don't deplete the O<sub>3</sub>-layer. They can be used as lubricants, in medicines for skin care, medical diagnosis etc.

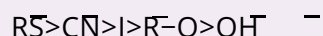
**17.** The halogen derivatives of the aromatic hydrocarbons in which the halogen atom is present in the side chain are called aryl alkyl halides or aralkyl halides.

For example, Ar-CH<sub>2</sub>-X.

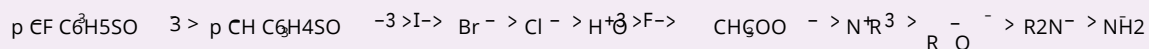
**18.** Bond strength and stability decreases as



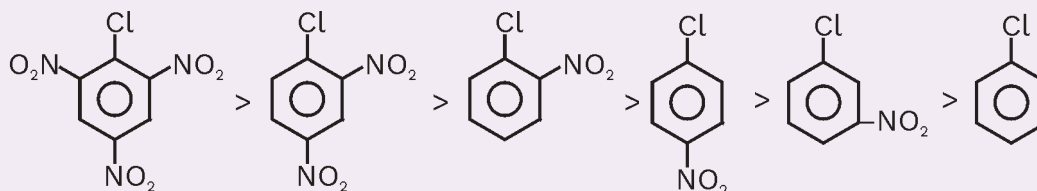
**19.** The relative nucleophilicity order for S<sub>N</sub>1 Reaction:



**20.** The Leaving group tendency for S<sub>N</sub>2 Reaction:



**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<sub>2</sub> is un-stable and SOI<sub>2</sub> does not exist.

