# **Alkyl and Aryl Halides**

# QUICK LOOK

# Difference in Reactivity of C-X bond in Alkyl Halides and Aryl Halides

Alkyl halides or halo alkanes are compounds in which a halogen is bonded to an alkyl group. They have the general formula RX (where R is alkyl group  $C_nH_{2n+1}$ )X is halogen atom.

$$\underset{\text{alkane}}{\text{RH}} \xrightarrow{-H, +X} \underset{\text{alkyl halide}}{\text{RX}}$$

Alkyl halides are classified as primary, secondary and tertiary alky halides depending on whether the halogen atom is attached to a primary, secondary or tertiary carbon atom respectively.

Aryl halides are much less reactive towards nucleophilic substitution reaction than haloalkanes. The less reactivity of aryl halides can be explained as follows:

 Withdrawal of Electrons by Benzene and Stabilization by Resonance: In aryl halide, the electron pair of halogen atom is in conjugation with π electrons of benzene ring. Thus halobenzene is a resonance hybrid of following structures:



The contributing structures II, III & IV indicate that C - X bond has partial double bond characters. As a resultant the C - X bond in halobenzene is shorter and hence stronger as compared to that in alkyl halides. Thus cleavage of C - X bond in halobenzene becomes difficult which makes it less reactive towards nucleophilic substitution.

- Different Hybrid States of Carbon Atom: In haloalkanes, the carbon atom bearing halogen is sp<sup>3</sup> hydridized while halogen bearing carbon atom is sp<sup>2</sup> hybrized in haloarenes. sp<sup>2</sup> hybrid orbital is smaller in size due to greater scharacter. As a result bond in haloarenes is smaller and is cleaved with difficulty.
- Polarity of C X Bond: The C X bond in halo alkanes is more polar than the C — X bond in haloarenes. Now greater the polarity of bond more is the reactivity.

Aromatic Halogen Compounds or Halo Arenes: are the halogen compounds which contain atleast one aromatic ring. Halogen derivatives of aromatic compounds are of two types.

 Aryl halides: In this type of compounds, the halogen atom is directly linked to the carbon of benzene nucleus *e.g.*



• Aralkyl halides: In this type of compounds halogen is linked to the carbon atom of the side chain.



**Nomenclature of Alkyl and Aryl Halides:** In the common system, aliphatic halogen derivatives are named as alkyl halides. The words n—sec—,tert—,neo—& amyl are usually used in writing the common names. In IUPAC nomenclature they are named as halo alkanes.

### Preparation

#### From alkanes

Alkanes react with halogens in the presence of light to give alkyl halides.

$$RH + Cl_2 \xrightarrow{hv} RCl + HCl$$

 $CH_4 + Cl_2 \xrightarrow{hv} CH_3Cl + HCl$ 

Alkyl halides formed further react with halogen to give di, tri and tetra halogen compounds.

From alkenes: Alkenes add halogen acids to give halides.For Example

$$\mathrm{CH}_2 = \mathrm{CH}_2 + \mathrm{HCl} \longrightarrow \mathrm{CH}_3 - \mathrm{CH}_2 \mathrm{Cl}$$

Markonikoff's rule: In the addition reactions of unsymmetrical alkenes the –ve part attaches to the carbon atom having lesser number of H-atoms. *e.g.* 

$$H_{3}C - CH = CH_{2} + HCl \longrightarrow H_{3}C - CH - CH_{3}$$

In case of HBr if peroxide is added antimarkonikoff's addition takes place which is also called Kharash effect or peroxide effect *e.g.* 

$$CH_3 - CH = CH_2 + HBr \xrightarrow{Peroxide} CH_3 - CH_2 - CH_2 - Br$$

- From silver salt of carboxylic acids RCOOAg + Br<sub>2</sub> → R → Br + CO<sub>2</sub> + AgBr This reaction is called Borodine Hunsdiecker reaction.
- Finkelstein reaction: Alkyl chlorides and bromides reacts with NaI in acetone to give alkyl iodides.
   R - Cl + NaI → R - I + NaCl

This reaction is possible because NaI is soluble in acetone but NaCl and NaBr are insoluble in acetone.

# **Physical Properties**

# Halo Alkanes

Boiling points: The boiling points of haloalkanes are in the order RCl < RBr < RI. It is because with increase in size and mass of halogen atom the magnitude of Vander Waal's forces of attraction increases. Among isomeric alkyl halides, the boiling point decreases with increase in branching in alkyl group. *e.g* the decreasing order of boiling point among the isomers of butane is

$$CH_{3}(CH_{2})CH_{2}Cl > H_{3}C - CH - CH_{2}CH_{3} > \bigcup_{\substack{l \\ Cl}} H_{3}C - CHCH_{2}Cl > (CH_{3})_{3}CCl \\ \bigcup_{\substack{l \\ CH_{3}}} H_{3}C - CHCH_{2}Cl > (CH_{3})_{3}CCl$$

For same halogen, the boiling point increases with increase in molecular mass. *e.g.* CH<sub>3</sub>Cl has lower boiling point than CH<sub>3</sub>CH<sub>2</sub>Cl. The boiling points of various halogen compounds increase with increase in number of halogen atoms. For *e.g.* boiling point of CCl<sub>4</sub> is more than boiling point of CHCl<sub>3</sub> which is further more than CH<sub>2</sub>Cl<sub>2</sub>.

#### **Halo Arenes**

 Boiling point: The boiling points of mono halogen derivatives of benzene follows the order: Iodo > Bromo > Chloro. The boiling points of isomeric dihalo benzenes are nearly the same. However their melting points are quite different. The melting point of para isomer is generally 70–100 degrees more than the melting points of ortho and meta isomers.



The higher melting point of p-isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice.

- Solubility: Haloarenes are insoluble in water, acids or base but are soluble in organic solvents. Haloarenes are insoluble in water because they cannot form hydrogen bonds with water molecules.
- Density: They are all heavier than water. Their densities follow the order: Iodo > Bromo > Chloro

**Chemical Properties:** Haloalkanes are highly reactive class of aliphatic compounds. Their reactivity is due to the presence of polar carbon – halogen bond in their molecule. In general for a given alkyl group, the order of reactivity decreases as: Iodides > Bromides > Chlorides. The explanation of above order is that reaction of alkyl halides involve cleavage of C–X bond. So higher the bond dissociation energy smaller reactivity & the bond dissociation energy decrease with increase in size of halogen atom.

#### The Chemical Reactions of Halo Alkanes are of 4 types

- Nucleophilic substitution reactions
- Dehydro halogenation reactions
- Reactions with metals
- Reduction reactions

Aryl halides being less reactive can be made to react under drastic conditions:

#### (i) Nucleophilic Substitution Reactions

 Replacement by Hydroxyl Group: On heating chlorobenzene with an aq. solution of NaOH at 623 K under 300 atm pressure, sodium phenoxide is formed which on subsequent acidification produces phenol.



 Replacement by Cyano Group: When heated with anhydrous CuCN in the presence of pyridine or dimethyl formamide at 470 K, bromo benzene gives cyanobenzene.

 Replacement by Amino Group: Halogen atom of haloarenes is replaced by amino group by reacting it with aq. NH<sub>3</sub>; and in presence of catalyst, Cu<sub>2</sub>O

$$2 \underbrace{\bigcirc}_{\text{Chloro benzene}} - \text{Cl} + 2\text{NH}_3 + \text{Cu}_2\text{O} \longrightarrow 2 \underbrace{\bigcirc}_{\text{Aniline}} - \text{NH}_2 + 2\text{C}$$

#### (ii) Reactions with Metals

 Action with Magnesium: Aryl bromides and iodides form Grignard's reagents with Mg in dry ether.



 Reaction with Sodium: Aryl halides react with sodium in the presence of ether. During reaction two phenyl rings unite. The reaction is called Fittig reaction.

$$2$$
 Cl + 2Na   
Bromobenzene   
Diphenly   
+ 2NaCl

However aryl halides when treated with halo alkane and sodium in dry ether undergo Wurtz fitting reaction.

 Reaction with Lithium: Aryl halides react with lithium metal to form the corresponding organometallic compound.



These organometallic compounds behave like Grignard reagents.

• **Reaction with Copper Powder:** Iodo benzene when heated with copper powder in a sealed tube gives diphenyl



• **Reduction:** An aryl halide is reduced to parent hydrocarbon by the action of nickel aluminium alloy in the presence of an alkali.



(iii) Ring Substitution Reactions: An aryl halide undergoes electrophilic substitution reactions in benzene ring. The presence of halogen atom in the ring directs the incoming substituent to the ortho and para position. Aryl halides are less reactive than benzene towards electrophilic substitution reactions. Some ring substitution reactions of aryl halides are given below:

 Halogenation: Halogentation takes place in the presence of iron or FeCl<sub>3</sub> or anhydrous AlCl<sub>3</sub> as a catalyst.



Nitration



1- chloro -4- nitro benzene



4- chloro benzene sulphonic acid

 Friedel Craft's Alkylation: With alkyl halide in presence of anhydrous AlCl<sub>3</sub>, alkylation takes place for *e.g.*



4- chloro toluene

 Friedel Craft's Acylation: Acylation of haloarenes can be carried out with the reaction of acyl chlorides in the presence of anhydrous AlCl<sub>3</sub>, for example



p-chloro acetophenone (minor)

**Poly Halogen Compounds:** Carbon compounds containing more than one halogen atom are usually referred to as polyhalogen compounds. Some important polyhalogen compounds are:

# **Dichloromethane (Methylene Chloride)**

**Preparation:** It is prepared industrially by direct chlorination of methane. The mixture so obtained is separated by fractional distillation.

**Properties:** It is a colourless, sweet smelling, volatile liquid boiling point = 313K. Because of its low boiling point and low inflammability, it is an effective extraction solvent used in pharmaceutical and food industries

# **Trichloro Methane (Chloroform)**

#### Preparation

• From methane: Chloroform is manufactured by chlorination of methane in presence of light or catalyst.

 $\begin{array}{ccc} \mathrm{CH}_{4} + \mathrm{Cl}_{2} & \longrightarrow & \mathrm{CH}_{3}\mathrm{Cl} + \mathrm{HCl} \\ \mathrm{CH}_{3}\mathrm{Cl} + \mathrm{Cl}_{2} & \longrightarrow & \mathrm{CH}_{2}\mathrm{Cl}_{2} + \mathrm{HCl} \\ \mathrm{CH}_{2}\mathrm{Cl}_{2} + \mathrm{Cl}_{2} & \longrightarrow & \mathrm{CHCl}_{3} + \mathrm{HCl} \\ \mathrm{CHCl}_{3} + \mathrm{Cl}_{2} & \longrightarrow & \mathrm{CCl}_{4} + \mathrm{HCl} \end{array}$ 

CHCl<sub>3</sub> can be separated by fractional distillation.

- From chloral hydrate NaOH + CCl<sub>3</sub>CHO Chloral → HCOONa + CHCl<sub>3</sub> Sodium formate + CHCl<sub>3</sub> Chloroform
- Laboratory method: In this method chloroform obtained from ethanol or acetone by reaction with a paste of bleaching powder and water.

 $CaOCl_{2} + H_{2}O \longrightarrow Ca(OH)_{2} + Cl_{2}$   $\overset{bleaching}{Powder}$   $CH_{3}CH_{2}OH + Cl_{2} \xrightarrow{Oxidation} CH_{3}CHO + 2HCl$ 

 $CH_{3}CHO+Cl_{2} \xrightarrow{Chlorination} CCl_{3}CHO+3HCl_{chloral}$   $Ca(OH)_{2}+2CCl_{3}CHO \xrightarrow{hydrolysis} 2CHCl_{3}+(HCOO)_{2}Ca_{chloroform}$ 

 From carbon tetra chloride: By partial reduction of carbontetrachloride with iron filings and water. CCl<sub>4</sub> + 2[H] → Fe/H<sub>2</sub>O △ CHCl<sub>3</sub> + HCl

**Uses of Chloroform:** As solvent in oils and varnishes, in medicine, As preservative, As laboratory reagent.

#### Tri iodo Methane (Iodoform)

#### Preparation

It is prepared by heating ethanol or acetone with sodium hydroxide & iodine or sodium carbonate & iodine in water.

 $CH_{3}CH_{2}OH + 6NaOH + 4I_{2} \xrightarrow{Heat} \rightarrow$ 

$$CHI_3 + HCOONa + 5H_2O + 5NaI$$

$$CH_3COCH_3 + 4NaOH + 3I_2 \xrightarrow{Heat}$$

**Uses:** It is used as antiseptic for dressing wounds. It is used to manufacture pharmaceuticals.

# Tetrachloro Methane (Carbon Tetra Chloride)

Preparation: CCI<sub>4</sub> is manufactured by following methods:
 (a) From methane: By chlorination of methane in the presence of sunlight.

 $CH_4 + 4Cl_2 \xrightarrow{hv} CCl_4 + 4HCl$ 

(b) From carbon disulphide: By reaction of chlorine with  $CS_2$  in presence of AlCl<sub>3</sub> as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow{AlCl_3} CCl_4 + \frac{S_2Cl_2}{Sulphur mono chloride}$$

**Uses:** As industrial solvent, for the manufacture of chloroform, as laboratory reagents, in dry cleaning, As a fire extinguisher.

**p** – **Dichloro Benzene:** It is prepared by chlorination of benzene. **Properties:** It is white volatile, solid m.p. = 325K, which readily sublimes.

**Uses:** As insecticide, as germicide, as soil fumigant, as deodrant and moth repellent.

#### Perfluoro Carbon (PFC's)

**Preparation:** They are prepared by controlled fluorination of alkanes in vapour phase. The reaction mixture is diluted with nitrogen in order to control the reaction

$$C_{7}H_{16} + 16F_{2} \xrightarrow{Vapour phase, N_{2}} \rightarrow C_{7}F_{16} + 16HF$$
Perflouroheptane

Teflon is a common perfluoro carbon.

**Properties:** They are non-toxic, non-inflammable, non-corrosive and extremely stable compounds.

Uses: As lubricants, For surface coating, As electrical insulator.

#### **Benzene Haxa Chloride**

These are popularly known as lindane and gammaxene. It is commercially prepared by the addition of chlorine to benzene in presence of ultraviolet light.

Uses: As a pesticide in agriculture.

 P-P'- Dichloro diphenyl tri chloro ethane (DDT): It is manufactured by condensation of chloro benzene with trichloro acetaldehyde (chloral) in the presence of sulphuric acid.



 Properties: It is a white powder insoluble in water but soluble in oils.

**Uses:** It is a powerful insecticide. However it is highly stable and is not easily decomposed in the environment. Therefore its long term effect could be potentially dangerous and its use is banned in many countries.

#### **Multiple Choice Questions**

# **Chemical Properties**

- 1. Which of the following halide is  $2^{\circ}$ ?
  - a. Isopropyl chloride
  - **b.** Isobutyl chloride
  - c. *n*-propyl chloride
  - d. n-butyl chloride
- 2. Acetone reacts with  $I_2$  in presence of NaOH to form:

a.	$C_2H_5I$	b.	$\mathrm{C_2H_4I_2}$
c.	CHI <sub>3</sub>	d.	CH3I

# **Poly Halogen Compounds**

- **3.** Full name of DDT is:
  - a. 1, 1, 1-trichloro-2, 2-bis(p-chlorophenyl) ethane
  - **b.** 1, 1-dichloro-2, 2-diphenyl trimethylethane
  - c. 1, 1-dichloro-2, 2-diphenyl trichloroethane
  - **d.** None of these
- 4. Benzene reacts with chlorine to form benzene hexachloride in presence of:
  - a. Nickel
    b. AlCl<sub>3</sub>
    c. Bright sunlight
    d. Zinc



# Introduction of Halogen Containing Compounds

6.	In $CH_3CH_2Br$ , % of Br is:		
	<b>a.</b> 80	<b>b.</b> 75	
	<b>c.</b> 70	<b>d.</b> 7	

- 7. Which of the following is a primary halide?a. Isopropyl iodide
  - **b.** Secondary butyl iodide
  - **c.** Tertiary butyl bromide
  - **d.** Neo hexyl chloride

- 8. The compound which contains all the four 1°, 2°, 3° and 4° carbon atoms is?
  - a. 2, 3-dimethyl pentane
    - b. 3-chloro-2, 3-dimethylpentane
    - c. 2, 3, 4-trimethylpentane
    - d. 3, 3-dimethylpentane

# **Preparation of Halogen Containing Compounds**

- **9.** What is the main product of the reaction between 2-methyl propene with HBr?
  - a. 1-bromo butane
  - **b.** 1-bromo-2 methyl propane
  - **c.** 2-bromo butane
  - d. 2-bromo-2 methyl propane
- 10. When ethyl alcohol (C<sub>2</sub>H<sub>5</sub>OH) reacts with thionyl chloride, in the presence of pyridine, the product obtained is?
  a. CH<sub>3</sub>CH<sub>2</sub>Cl+HCl
  - **b.**  $C_2H_5Cl + HCl + SO_2$

 $\mathbf{c.} \ \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{Cl} + \mathrm{H}_{2}\mathrm{O} + \mathrm{SO}_{2}$ 

- **d.**  $CH_3CH_2Cl + HCl + SO_2$
- 11.  $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl \text{ is an example of which}$ of the following types of reactions?
  - a. Substitution
  - **b.** Elimination
  - **c.** Addition
  - d. Rearrangement
- 12.  $R OH + HX \rightarrow R X + H_2O$

In the above reaction, the reactivity of different alcohols is:

- a. Tertiary > Secondary > Primary
- **b.** Tertiary < Secondary < Primary
- **c.** Tertiary < Secondary > Primary
- **d.** Secondary < Primary < Tertiary
- **13.** On heating diethyl ether with conc. HI, 2 moles of which of the following is formed?

<b>a.</b> Ethanol	<b>b.</b> Iodoform
<b>c.</b> Ethyl iodide	d. Methyl iodide

14. Ethanol is converted into ethyl chloride by reacting with:

- **a.**  $Cl_2$  **b.**  $SOCl_2$
- c. HCl d. NaCl
- 15. The starting substance for the preparation of  $CH_3I$  is:

a. CH <sub>3</sub> OH	<b>b.</b> $C_2H_5OH$
c. CH <sub>3</sub> CHO	<b>d.</b> $(CH_3)_2CO$

**16.** A Grignard's reagent may be made by reacting magnesium with:

a. Methyl amine	<b>b.</b> Diethyl ether
c. Ethyl iodide	d. Ethyl alcohol

- 17. Acetone is mixed with bleaching powder to give:a. Chloroformb. Acetaldehydec. Ethanold. Phosgene
- **18.** Ethylene reacts with bromine to form:
  - **a.** Chloroethane
  - **b.** Ethylene dibromide
  - c. Cyclohexane
  - d. 1-bromo propane
- 19. Best method of preparing alkyl chloride is:
  - **a.**  $\text{ROH} + \text{SOCl}_2 \longrightarrow$
  - **b.**  $ROH + PCl_5 \longrightarrow$
  - **c.**  $\operatorname{ROH} + \operatorname{PCl}_3 \longrightarrow$
  - **d.** ROH + HCl  $\xrightarrow{\text{anhy. ZnCl}_2}$
- 20. Which compound needs chloral in its synthesis?
  - **a.** D. D. T.
  - **b.** Gammexane
  - $\textbf{c.} \ \textbf{Chloroform}$
  - d. Michler's Ketone

#### **Properties of Halogen Containing Compounds**

- 21. Ethyl bromide can be converted into ethyl alcohol by:a. Heating with dilute hydrochloric acid and zinc
  - **b.** Boiling with an alcoholic solution of KOH
  - **c.** The action of moist silver oxide
  - d. Refluxing methanol
- 22. Reaction of ethyl chloride with sodium leads to:

a. Ethane	<b>b.</b> Propane
<b>c.</b> <i>n</i> -butane	d. <i>n</i> -pentane

- **23.**  $2CHCl_3 + O_2 \xrightarrow{X} 2COCl_2 + 2HCl$ 
  - In the above reaction, X stands for:
  - a. An oxidant
  - **b.** A reductant
  - **c.** Light and air
  - **d.** None of these
- 24. Phosgene is the common name for:
  - a.  $CO_2$  and  $PH_3$
  - b. Phosphoryl chloride
  - **c.** Carbonyl chloride
  - d. Carbon tetrachloride

- 25. When chloroform is treated with amine and KOH, we get?a. Rose odour smell
  - **b.** Sour almond like smell
  - **c.** Offensive odour
  - d. Sour oil of winter green like smell
- 26. Alkyl halides can be converted into Grignard reagents by:a. Boiling them with Mg ribbon in alcoholic solutionb. Warming them with magnesium powder in dry ether
  - **c.** Refluxing them with  $MgCl_2$  solution
  - **d.** Warming them with MgCl<sub>2</sub>
- **27.** The reactivity of ethyl chloride is:
  - **a.** More or less equal to that of benzyl chloride
  - **b.** More than that of benzyl chloride
  - c. More or less equal to that of chlorobenzene
  - d. Less than that of chlorobenzene
- **28.** Which of the following compound will make precipitate most readily with AgNO<sub>3</sub>?

a. CCl <sub>3</sub> CHO	<b>b.</b> CHCl <sub>3</sub>
<b>c.</b> $C_6H_5CH_2Cl$	<b>d.</b> CHI <sub>3</sub>

- 29. Grignard reagent is prepared by the reaction between:a. Zinc and alkyl halide
  - b. Magnesium and alkyl halide
  - c. Magnesium and alkane
  - d. Magnesium and aromatic hydrocarbon
- **30.** War gas is formed from:
- **a.**  $PH_3$  **b.**  $C_2H_2$
- c. Zinc phosphate d. Chloropicrin
- **31.** What happens when  $CCl_4$  is treated with AgNO<sub>3</sub>?
  - **a.** NO<sub>2</sub> will be evolved
  - b. A white ppt. of AgCl will be formed
  - **c.** CCl<sub>4</sub> will dissolve in AgNO<sub>3</sub>
  - d. Nothing will happen
- **32.** Ethylene difluoride on hydrolysis gives:
  - a. Glycol
  - **b.** Fluoroethanol
  - c. Difluoroethanol
  - d. Freon
- **33.** Ethyl chloride on heating with silver cyanide forms a compound X. The functional isomer of X is:

<b>a.</b> $C_2H_5NC$	<b>b.</b> $C_2H_5CN$
<b>c.</b> $H_3C - NH - CH_3$	<b>d.</b> $C_2H_5NH_2$

- 34. A compound A has a molecular formula  $C_2Cl_3OH$ . It reduces Fehling solution and on oxidation gives a monocarboxylic acid b. A is obtained by action of chlorine on ethyl alcohol. A is:
  - a. Chloral
  - **b.** CHCl<sub>3</sub>
  - c. CH<sub>3</sub>Cl
  - d. Chloroacetic acid
- **35.**  $C_2H_5Cl + KCN \longrightarrow X \xrightarrow{Hydrolysis} Y$ . 'X' and 'Y' are:
  - **a.**  $C_2H_6$  and  $C_2H_5CN$
  - **b.**  $C_2H_5CN$  and  $C_2H_6$
  - **c.**  $C_2H_5CN$  and  $C_2H_5CH_2NH_2$
  - **d.**  $C_2H_5CN$  and  $C_2H_5COOH$
- **36.** Dehydrohalogenation of an alkyl halide is:
  - a. An addition reaction
  - **b.** A substitution reaction
  - **c.** An elimination reaction
  - **d.** An oxidation reaction
- **37.** Chloroform for anesthetic purposes is tested for its purity with the reagent:
  - **a.** Silver nitrate
  - **b.** Lead nitrate
  - **c.** Ammoniacal  $Cu_2Cl_2$
  - **d.** Lead nitrate
- **38.** Chloroform is slowly oxidise by air in presence of light to form:
  - a. Formyl chloride
  - b. Phosgene
  - c. Trichloroacetic acid
  - **d.** Formic acid
- **39.** Vinyl chloride reacts with HCl to form:
  - **a.** 1, 1- dichloro ethane
  - **b.** 1, 2- dichloro ethane
  - **c.** Tetrachloro ethylene
  - **d.** Mixture of 1, 2 and 1, 1 dichloro ethane
- **40.** Reduction of acetyl chloride with H<sub>2</sub> in presence of Pd gives:

a.	CH <sub>3</sub> COCH <sub>3</sub>	b.	$C_2H_5OH$
c.	CH <sub>3</sub> COOH	d.	CH <sub>3</sub> CHO

- **41.** When methyl bromide is heated with Zn it gives? **a.**  $CH_4$  **b.**  $C_2H_6$ 
  - **c.**  $C_2H_4$  **d.**  $CH_3OH$

- 42. Iodoform on heating with KOH gives:
  a. CH<sub>3</sub>CHO
  b. CH<sub>3</sub>COOK
  c. HCOOK
  d. HCHO
- **43.**  $C_6H_6Cl_6$ , on treatment with alcoholic KOH, yields:
  - **a.**  $C_6H_6$  **b.**  $C_6H_3Cl_3$  **c.**  $(C_6H_6)OH$ **d.**  $C_6H_6Cl_4$
- 44. CHCl<sub>3</sub> and HF lead to the formation of a compound of fluorine of molecular weight 70. The compound is:a. Fluoroform
  - **b.** Fluorine monoxide
  - **c.** Fluorine dioxide
  - **d.** Fluromethanol
- **45.** In nucleophilic aliphatic substitution, the nucleophiles are generally
  - a. Acids
  - **b.** Bases
  - c. Salts
  - d. Neutral molecules
- 46. In which case formation of butane nitrile is possible?
  - **a.**  $C_3H_7Br + KCN$
  - **b.**  $C_4H_9Br + KCN$
  - c.  $C_3H_7OH + KCN$
  - **d.**  $C_4H_9OH + KCN$
- 47. In Wurtz reaction alkyl halide reacts with:
  - a. Sodium in ether
  - **b.** Sodium in dry ether
  - c. Sodium only
  - d. Alkyl halide in ether
- **48.** Chloroform reacts with concentrated  $HNO_3$  to give:
  - a. Water gas
  - **b.** Tear gas
  - **c.** Laughing gas
  - d. Producer gas
- 49. Chloroform, on warming with Ag powder, gives:
  - **a.**  $C_2H_6$  **b.**  $C_3H_8$ **c.**  $C_2H_4$  **d.**  $C_2H_7$
  - $c_{2}c_{2}c_{1}c_{4}$
- 50. Which metal is used in Wurtz synthesis?
  a. Ba
  b. Al
  c. Na
  d. Fe

- **51.** Alkyl halide can be converted into alkene by:
  - **a.** Nucleophilic substitution reaction
  - **b.** Elimination reaction
  - c. Both nucleophilic substitution and elimination reactio
  - d. Rearrangement
- 52. Alkyl halides react with dialkyl copper reagents to give:a. Alkenes
  - **b.** Alkyl copper halides
  - c. Alkanes
  - d. Alkenyl halides
- 53. Which of the following haloalkanes is most reactive?
  - **a.** 1-chloropropane
  - **b.** 1-bromopropane
  - **c.** 2-chloropropane
  - **d.** 2-bromopropane

# **Uses of Halogen Containing Compounds**

- 54. Freon (dichlorodifluoro methane) is used:
  - a. As local anaesthetic
  - **b.** For dissolving impurities in metallurgical process
  - c. In refrigerator
  - d. In printing industry

**55.** Which plastic is obtained from CHCl<sub>3</sub> as follows?

$\operatorname{CHCl}_3 \xrightarrow{\operatorname{HF}} X $	$\xrightarrow{800^{\circ}C} Y \xrightarrow{Polymerisation} Plastic$
a. Bakelite	<b>b.</b> Teflon
<b>c.</b> Polythene	<b>d.</b> Perspex

**56.** Which of the following is used in fire extinguishers?

• • ·· ··

<b>a.</b> CH <sub>4</sub>	<b>b.</b> CHCl <sub>3</sub>
<b>c.</b> $CH_2Cl_2$	<b>d.</b> $CCl_4$

**57.** Iodoform can be used as:

	a. Anaestnetic	<b>D.</b> Antiseptic
	c. Analgesic	d. Antifebrin
0	Which of the following is a	n ana asthatia?

00.	which of the	following is	s an anae	stnetic
	a. C.H.		b. (	CHCL

<b>a.</b> $C_2 II_4$	<b>b.</b> $\operatorname{chich}_3$
c. CH <sub>3</sub> Cl	<b>d.</b> $C_2H_5OH$

**59.** In fire extinguisher, pyrene is:

<b>a.</b> $CO_2$	<b>b.</b> $CCI_4$
<b>c.</b> CS <sub>2</sub>	<b>d.</b> CHCl <sub>3</sub>

- **60.** Use of chlorofluoro carbons is not encouraged because:
  - **a.** They are harmful to the eyes of people that use it
  - **b.** They damage the refrigerators and air conditioners
  - **c.** They eat away the ozone in the atmosphere
  - **d.** They destroy the oxygen layer

#### NCERT EXEMPLAR PROBLEMS

#### More than One Answer

- 61. Which of the following statements is incorrect?
  - **a.**  $C_2H_5Br$  reacts with alco. KOH to form  $C_2H_5OH$
  - **b.**  $C_2H_5Br$  when treated with metallic sodium gives ethane **c.**  $C_2H_5Br$  when treated with sodium ethoxide forms diethyl
  - ether
  - **d.**  $C_2H_5Br$  with AgCN forms ethyl isocyanide
- **62.** A sample of chloroform being used as an aesthetic is tested by:
  - a. Fehling solution
  - **b.** Ammoniacal Cu<sub>2</sub>Cl<sub>2</sub>
  - c. AgNO<sub>3</sub> solution
  - d. AgNO<sub>3</sub> solution after boiling with alcoholic KOH solution
- 63. Which of the following are correct statements about C<sub>2</sub>H<sub>5</sub>Br ?
  a. It reacts with metallic Na to give ethane
  b. It gives nitroethane on heating with aqueous ethanolic solution of AgNO<sub>2</sub>
  - **c.** It gives  $C_2H_5OH$  on boiling with alcoholic potash
  - d. It forms ethylacetate on heating with silver acetate
- 64. False statement is:
  - a. Chloroform is heavier than water
  - **b.**  $CCl_4$  is non-inflammable
  - c. Vinyl chloride is more reactive than allyl chloride
  - **d.** Br<sup>-</sup> is a good nucleophile as compared to I<sup>-</sup>
- **65.** In which one of the following conversions phosphorus pentachloride is used as a reagent:
  - **a.**  $H_2C = CH_2 \longrightarrow CH_3CH_2Cl$
  - **b.**  $H_3C O CH_3 \longrightarrow CH_3Cl$
  - c.  $CH_3CH_2OH \longrightarrow CH_3CH_2CI$
  - **d.** HC  $\equiv$  CH $\longrightarrow$  CH<sub>2</sub> = CHCl
- **66.** Which of the following is correct order of nucleophilicity in MeOH?

**a.**  $HO^- > HOO^$ **b.**  $CH_3CH_2\overline{O} > H\overline{O} > CH_3 - C - O^-$ 

c.  $HS^- > HO^- < \overline{N}H_2$ 

**d.** 
$$CH_3O \longrightarrow O^- > CH_3CO \longrightarrow O^-$$

**67.** Choose the correct statement (s):

**a.** In the  $S_N 1$ , transition state (rds) there is considerable positive charge on carbon, while there is little or no charge on carbon in the  $S_N 1$  transition state.

**b.** In  $S_N 1$  RT reacts with solvent rather than with stronger nucleophiles that may be present.

**c.**  $InS_N1$  as solvent polarity increases, intimate ion pair attraction increases, thus inversion increases.

**d.** As the nucleophilicity of solvent is decreasing, raacemisation is increasing.

- **68.** n-propyl bromide would give  $S_N 2$  reactions under which of the following conditions (s)?
  - a. NaN<sub>3</sub>, DMF
  - b. NaOH, DMF
  - c. CH<sub>3</sub>COO<sup>-</sup>Na<sup>+</sup>, CH<sub>3</sub>COOH
  - d. LDA, DMF
- **69.**  $PH-CH_2-CH-CH_3 \xrightarrow{Cl_2/hv}$  Which statements is/are correct about photochemical chlorination of the above

compound. a. The major product will be chiral carbon atom having

optically inactive compound

**b.** The intermediate free radical of the major product is resonance stabilised

c. The intermediate free radical is tertiary

- **d.** The intermediate free radical is planer, and stabilised by only hyperconjugation
- **70.** Which of the following statements about benzyl chloride is incorrect?

a. It is less reactive than alkyl halides

**b.** It can be oxidised to benzaldehyde by boiling with copper nitrate solution

c. It is a lachrymatory liquid and answers Beilstein's testd. It gives a white precipitate with alcoholic silver nitrate

71. Haloforms are trihalogen derivatives of:

a. Ethane	<b>b.</b> Methane
<b>c.</b> Propane	d. Benzene

- 72.  $C_6H_6 + Cl_2 \xrightarrow{\text{UV Light}}$  Product. In above reaction product is:
  - a. CCl<sub>3</sub>CHO
  - **b.**  $C_6H_6Cl_6$
  - **c.**  $C_6H_{12}Cl_6$
  - d.  $C_6H_9Cl_2$

**73.** Gem- dibromide is:

a. CH<sub>3</sub>CH(Br)OH(Br)CH<sub>3</sub>

- b. CH<sub>3</sub>CBr<sub>2</sub>CH<sub>3</sub>
   c. CH<sub>2</sub>(Br)CH<sub>2</sub>CH<sub>2</sub>
   d. CH<sub>2</sub>BrCH<sub>2</sub>Br
- 74. Silver acetate +  $Br_2 \xrightarrow{CS_2}$ . The main product of this reaction is:

- **75.** When ethyl alcohol and KI reacted in presence of Na<sub>2</sub>CO<sub>3</sub>, yellow crystals of..... are formed?
  - a.  $CHI_3$  b.  $CH_3I$  

     c.  $CH_2I_2$  d.  $C_2H_5I$

#### **Assertion and Reason**

**Note:** Read the Assertion (A) and Reason (R) carefully to mark the correct option out of the options given below:

- **a.** If both assertion and reason are true and the reason is the correct explanation of the assertion.
- **b.** If both assertion and reason are true but reason is not the correct explanation of the assertion.
- **c.** If assertion is true but reason is false.
- **d.** If the assertion and reason both are false.
- e. If assertion is false but reason is true.
- **76.** Assertion:  $CHCl_3$  is stored in transparent bottles.

**Reason:** CHCl<sub>3</sub> is oxidised in dark.

- 77. Assertion: Alkyl halides are soluble in organic solvents.Reason: p-dichlorobenzene possesses low melting point.
- 78. Assertion: CCl<sub>4</sub> is not a fire extinguisher.Reason: CCl<sub>4</sub> is insoluble in water.
- 79. Assertion: Aqueous hydrohalogen acids are used to prepare alkyl halides from alkenes.Reason: Hydrogen iodide readily reacts with alkenes to form alkyl halides.
- 80. Assertion: Alkyl halides form alkenes when heated above 300°C.
  Reason: CH<sub>3</sub>CH<sub>2</sub>I react slowly with strong base when

compared to  $CD_3CH_2I$ .

**81.** Assertion: Halogen acids react with alcohols to form haloalkanes.

Reason: Order of reactivity of halogen acids HCl> HBr > HI

- 82. Assertion: Electron withdrawing groups in aryl halides decrease the reactivity towards nucleophilic substitution.Reason: 2, 4-Dinitrochlorobenzene is less reactive than chlorobenzene.
- 83. Assertion: Aryl halides undergo electrophilic substitutions more readily than benzene.Reason: Aryl halide gives a mixture of o- and p- products.
- Assertion: Addition of Br<sub>2</sub> to cis-but-2-ene is stereo-selective.
   Reason: S<sub>N</sub>2 reactions are stereo-specific as well as stereo-selective.
- 85. Assertion: Nucleophilic substitution reaction on an optically active alkyl halide gives a mixture of enantiomers.Reason: The reaction occurs by S<sub>N</sub>1 mechanism.

#### **Comprehension Based**

#### Paragraph -I

The  $S_N 2$  reaction is disfavoured by hindered substrates, nonbasic nucleophiles, and protic solvents. You might therefore expect the reaction of a tertiary substrate such as  $(CH_3)_2$  CBr with neutral water to be among the slowest of substitution reaction. Remarkably, however, the opposite is true. The reaction is, in fact, quite rapid.

$$H_{3}C \xrightarrow[CH_{3}]{CH_{3}} Br \xrightarrow[H_{2}O]{H_{2}O} H_{3}C \xrightarrow[CH_{3}]{CH_{3}} OH + HBr$$

Perhaps even more surprising is that the reaction of the tertiary halide (CH<sub>3</sub>)<sub>3</sub> CBr with neutral water is more than I million times as fast as the corresponding reaction of the methyl halide CH<sub>3</sub>Br. What's going on here? Clearly, nucleophilic substitution reactions are occurring, yet the reactivity order seems backward. These reaction can't be taking place by the S<sub>N</sub>2 mechanism we've been discussing, and we must therefore conclude that they are occurring by an alternative substitution mechanism. This alternative mechanism is called the S<sub>N</sub>1 reaction (for substitution, nucleophilic, unimolecular). The observation of first-order kinetics for the S<sub>N</sub>1 reaction of (CH<sub>3</sub>)<sub>3</sub>CBr with water tells us that the alkyl halide in involved in a unimolecular rate-limiting step. In other words, 2-bromo-2methylpropane undergoes some manner of spontaneous, ratelimiting reaction without involvement of the nucleophile. But because the nucleophile must be involved at some point, there must be at least two steps in the reaction.

86. A reaction energy diagram for  $S_N 1$  reaction is given in the figure. The rate-limiting step is the spontaneous dissociation

#### of alkyl halide and is given by:



**87.** Reaction energy diagrams of two hypothetical reactions have been given. Select correct alternate based on them:



**a.** rate limiting step in A is first step while in B it is second step

**b.** both reactions are endothermic

**c.** A is exothermic while B is endothermic

d. A is endothermic while B is exothermic

**88.** Rate of  $S_N 1$  reaction is increased based on by following factors because:

**a.** good leaving groups (more stable anions) lower the energy of the transition state leading to carbocation formation thus increasing the reaction rate

**b.** a nonbasic nucleophile (like  $H_2O$ ) will prevent a competitive E2 reaction

**c.** polar solvents stabilize the carbocation intermediate by salvation, thereby increasing the reaction rate

**d.** all of the above

# Paragraph –II

Paul Walden, the brilliant son of a farmer succeeded in finding a concept that is now widely known as umbrella effect in  $S^2$ reactions. In an  $S_N2$  reaction, the configuration at the reaction centre is inverted as an umbrella turns inside out in a strong wind. An ideal  $S_N1$  reaction, on the other hand, yields nearly racemised product as it proceeds through planar carbocation.  $S_N2$  reactions proceed smoothly on primary alkyl halides, whereas tertiary halides are fit for  $S_N 1$  mechanism. However, evidences indicate that all the molecules of particular substrates do not necessarily react by a single mechanism. After all, the intention of the molecules is very clear; they want to follow the low energy path. If both paths have nearly the same energy barrier, they follow a mixed mechanism. For example, secondary alkyl halides follow a mixed mechanism; say 60% molecules react by and rest 40% by  $S_N 1$ . Stereo-chemical feature, as mentioned above, are noticeable only when the reaction is carried out on a particular enantiomer. Even the reaction centres, which are parts of suitably substituted rings, also exemplify the said features.

**89.** What is true about the product spread in the following reaction?

R  $C1 \xrightarrow{Nu}$  Substituted product R 100% R a. 40% S and 60% R b. 40% R and 60% S c. 100% S d. 50 - 50 % R/S

90. A reaction gives the following results.

$$H_3C$$
  $H_3C$   $H_3C$ 

What should be %age of back side attack assuming complete reactions?

<b>a.</b> 65%	<b>b.</b> 30%
<b>c.</b> 35%	<b>d.</b> 85%

**91.** There are two basic mechanism  $S_N1$  and  $S_N2$ . All except one of the following substrates give at least of these two reactions enthusiastically in the absence of catalyst. Identify the odd one that reacts sluggishly under both the mechanisms. What should be %age of back side attack assuming complete reactions?

**a.** 
$$R - CH_3 - X$$
  
**b.**  $R_3C - X$   
**c.**  $R_3C - CH_2 - X$   
**d.**  $R - CO - CH_2 - X$ 

92. Which of the following reactions cannot be used to study the stereo-chemical feature of  $S_N 2$  reactions?



# Match the Column

93. Match the following:

Column I	Column II	
(A) $CH_3 - CHBr - CD_3$ on	1. El reaction	
treatment with ale. KOH give		
$CH_2 = CH - CD_3$ as a major		
product.		
<b>(B)</b> $Ph - CHBr - CH_3$ reacts faster	<b>2.</b> E2 reaction	
than $Ph - CHBr - CH_3$		
(C) $Ph - CD_2 - CH_2Br$ on treatment	<b>3.</b> El cb reaction	
with $C_2H_5OD/C_2H_5O^-$ gives		
$Ph - CD = CH_2$ as the major		
product.		
<b>(D)</b> $Ph - CH_2 - CH_2Br$ and	4. First order	
$Ph - CD_2 - CH_2Br$ react	reaction	
with same rate.		
<b>a.</b> A $\rightarrow$ 2, B $\rightarrow$ 2, C $\rightarrow$ 3 $\rightarrow$ 4, D $\rightarrow$ 1,4		
<b>b.</b> $A \rightarrow 2$ , $B \rightarrow 4$ , $C \rightarrow 3$ , $D \rightarrow 1$		
c. $A \rightarrow 1$ , $B \rightarrow 3$ , $C \rightarrow 2$ , $D \rightarrow 4$		

**d.** 
$$A \rightarrow 4$$
,  $B \rightarrow 1$ ,  $C \rightarrow 3$ ,  $D \rightarrow 2$ 

**94.** Match the following:

Column I	Column II
(A) $CH_3CHCl \xrightarrow{Li}_{Cul} \rightarrow$	$1.(\mathrm{CH}_3)_2\mathrm{CHCH}_2\mathrm{CH}(\mathrm{CH}_3)_2$
$\xrightarrow{CH_3CH_2Cl} ?$	
$(\mathbf{B})_{(\mathrm{CH}_3)_2\mathrm{CHl}}\xrightarrow{\mathrm{Li}}_{\mathrm{Cul}} \rightarrow$	$2. \mathrm{CH}_{3} \mathrm{CH}_{2} \mathrm{CH}_{2} \mathrm{CH}_{3}$
$\xrightarrow{(CH_3)_2 CH_2 Br} ?$	
$(\mathbf{C}) \operatorname{CH}_3 \operatorname{CH}_2 \operatorname{C}(\operatorname{CH}_3)_2$	$3.(\mathrm{CH}_3)_3\mathrm{CCH}_2\mathrm{CH}_3$
$\operatorname{Br} \xrightarrow{\operatorname{Li}}_{\operatorname{Cul}} \xrightarrow{\operatorname{CH}_3\operatorname{CH}_2\operatorname{Br}} $	
$(\mathbf{D})(\mathrm{CH}_3)_3\mathrm{Cl}\xrightarrow[\mathrm{Cul}]{\mathrm{Cul}} \rightarrow$	$4. \mathrm{CH}_{3}\mathrm{CH}_{2}\mathrm{C}(\mathrm{CH}_{3})_{2}\mathrm{CH}_{2}\mathrm{CH}_{3}$
$\xrightarrow{\text{CH}_3\text{CH}_2-\text{Br}} \rightarrow$	
<b>a.</b> A $\rightarrow$ 2, B $\rightarrow$ 1, C $\rightarrow$ 4, D $\rightarrow$ 3	<b>b.</b> $A \rightarrow 2$ , $B \rightarrow 4$ , $C \rightarrow 3$ , $D \rightarrow 1$
$a \wedge 1 P \sim 2 C \sim 2 P \sim 4$	$d \wedge A P \rightarrow 1 C \rightarrow 2 D \rightarrow 2$

#### Integer

- **95.** The percent optical purity of partially racemized bromo compound.
- 96. The percent optical purity of partially racemized Alcohol.
- 97. Percentages of inversion.
- 98. Percentage of racemization.
- 99. Percentage of front-side attack.
- 100. Percentage of backside attack.

# ANSWER

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
а	с	а	с	а	b	d	b	d	d
11.	12.	13.	14.	15.	16.	17.	18.	19.	20.
а	а	с	b	а	с	а	b	а	а
21.	22.	23.	24.	25.	26.	27.	28.	29.	30.
с	с	с	с	с	b	b	d	b	d
31.	32.	33.	34.	35.	36.	37.	38.	39.	40.
d	а	b	а	d	с	а	b	а	d
41.	42.	43.	44.	45.	46.	47.	48.	49.	50.
b	с	b	а	b	а	а	b	d	с
51.	52.	53.	54.	55.	56.	57.	58.	59.	60.
b	с	d	с	b	d	b	b	b	с
61.	62.	63.	64.	65.	66.	67.	68.	69.	70.
a,b	c,d	b,d	c,d	b,c	b,d	a,b	a,b,c	a,b	а
71.	72.	73.	74.	75.	76.	77.	78.	79.	80.
b	b	b	а	а	d	с	e	e	с
81.	82.	83.	84.	85.	86.	87.	88.	89.	90.
с	d	e	b	а	а	а	a,c	b	а
91.	92.	93.	94.	95.	96.	97.	98.	99.	100.
с	b	a	а	83	58	70	30	15	85

#### **SOLUTION**

# **Multiple Choice Questions**

1. (a) Isopropyl chloride  $CH_3 - CH_1 - CH_3$  chlorine atom is Cl

attached to  $2^{\circ}$  carbon atom.

2. (c)  $.CH_3COCH_3 + 3I_2 + 4NaOH \longrightarrow$  $CHI_3 + 3Na + CH_3COONa + 3H_2O$ 







As  $-CCl_3$  is a *m*-directing group.

6. **(b)** % of Br = 
$$\frac{\text{Mass of Br}}{\text{Mass of organic compound}} \times 100$$
  
=  $\frac{80}{109} \times 100 = 73.39\%$   
or approx. 75%

7. (d) Neohexyl chloride is a primary halide as in it *Cl*-atom is attached to a primary carbon.

$$CH_{3} - CH_{2} - CH_{2} - CH_{2}CH_{2}CH_{3}$$

8. **(b)** 
$$\overset{1^{\circ}}{CH}_{3} - \overset{1^{\circ}}{\overset{CH}{CH}}_{3} - \overset{1^{\circ}}{\overset{CH}{CH}}_{3^{\circ}} - \overset{1^{\circ}}{CH}_{2} - \overset{1^{\circ}}{CH}_{3^{\circ}}_{2^{\circ}}$$

9. (d) 
$$CH_3 - CH_3 = CH_2 + HBr \longrightarrow CH_3 - CH_3 - CH_3$$
  
 $CH_3 - CH_3$   
 $CH_3 - CH_3$   
 $2$ -brown -2-methyl propan

Br

- 10. (d)  $C_2H_5OH + SOCl_2 \xrightarrow{Pyridine} C_2H_5Cl + SO_2 + HCl$
- 11. (a)  $C_3H_8 + Cl_2 \xrightarrow{\text{Light}} C_3H_7Cl + HCl$ This is an example of substitution reaction. Hydrogen atom of alkane is replaced by halogen atom.
- 12. (a)  $R OX + HX \longrightarrow R X + H_2O$ Reactivity order of alcohols for this reaction  $3^\circ > 2^\circ > 1^\circ$ Reactivity order of halogen acids R - I > R - Br > R - Cl
- 13. (c)  $C_2H_5 O C_2H_5 + 2HI \longrightarrow 2C_2H_5I + H_2O_{Ethyliodide}$
- 14. (b)  $C_2H_5OH + SOCl_2 \xrightarrow{Pyridine} C_2H_5Cl + SO_2 + HCl$
- 15. (a)  $CH_3OH + HI \xrightarrow{ZnCl_2} CH_3I + H_2O$
- **16.** (c)  $C_2H_5I + Mg \xrightarrow{Dry \text{ ether}} C_2H_5 Mg I$ Ethyl iodide Ethyl magnesium iodide
- 17. (a) Acetone forms chloroform when heated with bleaching powder.

 $CaOCl_{2} + H_{2}O \longrightarrow Ca(OH)_{2} + Cl_{2}$   $CH_{3}COCH_{3} + 3Cl_{2} \longrightarrow CCl_{3}COCH_{3} + 3HCl$   $2CCl_{3}COCH_{3} + Ca(OH)_{2} \longrightarrow 2CHCl_{3} + (CH_{3}COO)_{2}Ca$   $CH_{3}COCH_{3} + Ca(OH)_{2} \longrightarrow 2CHCl_{3} + (CH_{3}COO)_{2}Ca$ 

**18.** (b) When ethylene reacts with bromine, it forms ethylene dibromide.

$$\begin{array}{c} H_2C = CH_2 + Br_2 & \longrightarrow H_2C - CH_2 \\ \stackrel{|}{\operatorname{Bromine}} & \stackrel{|}{\operatorname{Br}} Br \\ & Br \\ \stackrel{|}{\operatorname{Br}} Br \\ \stackrel{|}{\operatorname{Ethylene}} \end{array}$$

19. (a) The chlorination of alcohol by SOCl<sub>2</sub> (thionyl chloride) is the best method for the preparation of alkyl halides as in this method all the other product are gaseous and thus halides are obtained on quite pure state

$$R - OH + SOCl_2 \xrightarrow{\Delta} R - Cl + HCl \uparrow + SO_2 \uparrow$$

- **20.** (a) DDT is formed by reaction of chloral with chloro benzene.
- 21. (c)  $Ag_2O + H_2O \longrightarrow 2AgOH$  $C_2H_5Br + AgOH \longrightarrow C_2H_5OH + AgBr$
- 22. (c)  $C_2H_5Cl + 2Na + ClC_2H_5 \frac{Dry}{Ether} + C_2H_5 C_2H_5 + 2NaCl$
- 23. (c)  $2CHCl_3 + O_2 \xrightarrow{\text{Light}} 2COCl_2 + 2HCl_{Phosgene}$
- 24. (c)  $COCl_2$  carbonyl chloride is commonly called as phosgene.
- 25. (c)  $C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow$  $C_2H_5 - N \equiv C + 3KCl + 3H_2O$ Ethylisocyanide(offensive odour)
- 26. (b)  $RX + Mg \xrightarrow{Dry ether} R Mg X$
- 27. (b)  $C_2H_5 Cl > C_6H_5 CH_2 Cl$ more reactive less reactive
- **28.** (d)  $CHI_3$  gives a yellow ppt. of *AgI*.

29. (b) 
$$RX + Mg \xrightarrow{Dry} R - Mg - X$$
 (X = Cl, Br, I)  
Grignard's reagent

- **30.** (d)  $\text{CHCl}_3 + \text{HO} \text{NO}_2 \longrightarrow \frac{\text{CCl}_3 \text{NO}_2}{\text{Chloropicrin (war gas)}} + \text{H}_2\text{O}$
- **31.** (d)  $CCl_4 + AgNO_3 \longrightarrow No reaction$

CCl<sub>4</sub> is a covalent compound. Therefore does not provide





**33.** (b) 
$$C_2H_5Cl + AgCN \rightarrow C_2H_5 - N \equiv C + AgCl$$
  
Ethyl isocyanide  
(X)

The functional isomer of ethyl isocyanide is ethyl cyanide  $C_2H_5 - C \equiv N$ .

34. (a)  $C_2Cl_3OH+$  Fehling sol.  $\longrightarrow Cu_2O$ A Red ppt It means -CHO group is present.

 $C_{2}Cl_{3}OH \xrightarrow{Oxidation} CCl_{3} - COOH$ Monocarboxylic acid
It means only one -CHO group is present.  $C_{2}H_{5}OH + Cl_{2} \longrightarrow CH_{3}CHO + 2HCl$   $CH_{3}CHO + 3Cl_{2} \longrightarrow CCl_{3}CHO + 3HCl$ Chloral

- **35.** (d)  $C_2H_5Cl + KCN \longrightarrow C_2H_5CN \xrightarrow{Hydrolysis} C_2H_5COOH$ Ethyl cyanide Propanoic acid (X) (Y)
- 36. (c) Alkyl halide gives alkene on elimination; reaction takes place in presence of alc. KOH. CH<sub>3</sub>CH<sub>2</sub>Br + Alc.KOH → CH<sub>2</sub> = CH<sub>2</sub> + KBr + H<sub>2</sub>O There are two types of elimination reactions.
  (a) E<sub>1</sub> → Unimolecular elimination
  (b) E<sub>2</sub> → Bimolecular elimination
- **37.** (a) If CHCl<sub>3</sub> sample contains phosgene (COCl<sub>2</sub>) then it will give a white ppt. When treated with cold AgNO<sub>3</sub>.
- **38.** (b)  $\operatorname{CHCl}_3 + \operatorname{O}_2 \longrightarrow \operatorname{COCl}_2 + \operatorname{HCl}_{\operatorname{Phosgene}}$
- **39.** (a)  $CH_2 = CH Cl + HCl \longrightarrow CH_3 CHCl_2$
- 40. (d)  $CH_3COCl + H_2 \xrightarrow{Pd} CH_3CHO + HCl$
- 41. (b)  $CH_3Br + Zn + BrCH_3 \xrightarrow{\Delta} C_2H_6 + ZnBr_2$
- 42. (c)  $CHI_3 + 4KOH(aq.) \longrightarrow HCOOK + 3KCl + 2H_2O$ Potassium formate
- (b) C<sub>6</sub>H<sub>6</sub>Cl<sub>6</sub> + 3KOH → C<sub>6</sub>H<sub>3</sub>Cl<sub>3</sub> + 3KCl + 3H<sub>2</sub>O Thus Benzene hexahalides decomposes when heated with alc. KOH and yield trichloro benzene.
- 44. (a) We know that  $CHCl_3 + HF \longrightarrow CHF_3 + 3HCl$ . Thus in this reaction the compound obtained in fluoroform (CHF<sub>3</sub>). As we know molecular weight of CHF<sub>3</sub> = 70.
- 45. (b)  $R X + OH^{-}_{Nucleophile} \longrightarrow R OH + X^{-}$

- 46. (a) C<sub>3</sub>H<sub>7</sub>Br+KCN→C<sub>3</sub>H<sub>7</sub>CN+KBr
   In IUPAC system the carbon of functional group also take in numbering. So C<sub>3</sub>H<sub>7</sub>CN is butane nitrile.
- **47.** (a) Alkyl halides give alkane when react with sodium in ether. This is called Wurtz reaction.

 $R - Cl + 2Na + R - Cl \xrightarrow{ether} R - R + 2NaCl$ 

- 48. (b) When chloroform reacts with HNO<sub>3</sub> product formed are chloropicrin or tear gas and water.
   CHCl<sub>3</sub> + HNO<sub>3</sub> → CCl<sub>3</sub>NO<sub>2</sub> + H<sub>2</sub>O chloroform conc.
- **49.** (d) We know that

 $\underset{chloroform}{\text{HCCl}_{3}} + 6\text{Ag} + \underset{chloroform}{\text{Cl}_{3}}CH \xrightarrow{\text{heat}} HC \equiv CH + 6\text{AgCl}$ 

Thus in this reaction acetylene (HC  $\equiv$  CH) is produced.

**50.** (c) 
$$CH_3Br + 2Na + Br - CH_3 \xrightarrow{Dry} CH_3CH_3 + 2NaBr$$

51. (b) Alkyl halide is best converted to alkene by mean of elimination reaction in form of dehydrohalogenation.  $R-CH_2-CH_2-X \xrightarrow{dehydrohalogenation} R-CH = CH_2$ 

52. (c) 
$$R_2CuLi + R'X \longrightarrow R - R' + R - Cu + LiX$$

**53.** (d) The alkyl halides are highly reactive, the order of reactivity is

Iodide > bromide > chloride > (nature of the halogen atom).

Tertiary > secondary > primary.

Thus 2-bromopropane is the given option.

- 54. (c) Freon  $(CCl_2F_2)$  is an odourless, non-corrosive, non toxic gas which is stable even at high temperatures and pressures. It has low b.Pt, low specific heat and can be easily liquified by applying pressure at room temperature. It is therefore, widely used in refrigerant (cooling agent) in refrigerators and air conditioners.
- 55. (b)  $2CHCl_3 \xrightarrow{HF} 2CHF_2Cl \xrightarrow{800^{\circ}C} -2HCl}$  $CF_2 = CF_2 \xrightarrow{Polymari} (-CF_2 - CF_2 -)_r$
- **56.** (d) Its vapours are non inflammable (*i.e.* do not catch fire). Hence used as fire extinguishers under the name pyren.
- **57.** (b) Iodoform is used as an antiseptic for dressing wounds. When it comes in contact with skin (organic matter), Iodine is set free which responsible for antiseptic action.

- **58.** (b) Inhalation of CHCl<sub>3</sub> vapours produces loss of consciousness and is therefore, used as a general anaesthetic agent in surgery.
- 59. (b) CCl<sub>4</sub> is stable to red heat. Its vapours are highly non-inflammable *i.e.* do not catch fire. It is because of this property CCl<sub>4</sub> is used as a fire extinguisher. But now a day's its use as a fire extinguisher is restricted because with water vaporous. It forms highly poisonous phosgene gas

$$CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl_{Phosgene}$$

**60.** (c) Chlorofluorocarbon is used in air-conditioning and in domestic refrigerators for cooling purposes. Its main drawback is this; it is responsible for ozone depletion.

# **NCERT Exemplar Problems**

#### More than One Answer

- 61. (a,b)  $C_2H_5Br + alc.KOH \longrightarrow C_2H_4 + H_2O + KBr$   $C_2H_5Br + 2Na + Br - C_1H_5 \longrightarrow C_2H_5 - C_2H_5 + 2NaBr$ Butane
- **62.** (c,d) Before using the sample of chloroform as an anaesthetic, it is tested by treating with aq. solution of AgNO<sub>3</sub>. A pure sample does not give ppt with aq. AgNO<sub>3</sub>.
- 63. (b,d)  $C_2H_5Br + alc. AgNO_2 \longrightarrow C_2H_5 NO_2 + AgBr$   $C_2H_5Br + CH_3COOAg \longrightarrow CH_3 - COO - C_2H_5 + AgBr$ Ester
- **64.** (c,d) Vinyl chloride is less reactive than allyl chloride due to resonance effect. Order of nucleophilicity amongst the halide ion are as  $I^- > Br^- > Cl^-$ .
- 65. (b,c)  $CH_3 O CH_3 + PCl_5 \longrightarrow 2CH_3Cl + POCl_3$   $CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + HCl + POCl_3$ So, both reaction carried out by  $PCl_5$
- 66. (b,d)  $H = \ddot{O} \cdot \vec{O}^{-}$  is more nucleophilic than HO<sup>-</sup>.
- **67.** (a,b) Increase in solvent polarity reduces the intimate in pair attraction thus, increases racemisation. Nucleophilicity of solvent decreases, racemisation decreasing.
- **68.** (**a**,**b**,**c**) LDA being a strong and bulky base gives elimination reaction even in primary halide.
- **69.** (**a**,**b**) Free radical mechanism

$$PH-CH_2-CH-CH_3$$
  
 $CH_3$ 

give three types of FR.

**70.** (a) Benzyl chloride are far more reactive than alkyl halide towards nucleophilic substitution reaction due to the reason that the carbocation formed after the removal of halide ion is stabilized by resonance.



- **71.** (b)  $CH_4 \xrightarrow{-3H}_{+3X} CHX_3$  (X = Cl, Br, I)
- 72. **(b)**  $C_6H_6 + 3Cl_2 \xrightarrow{U.Vlight} C_6H_6Cl_6$ Benzene
- **73.** (b) Gem-dihalides are those in which two halogen atoms are attached on the same carbon atom.
- 74. (a)  $CH_3COOAg + Br_2 \xrightarrow{CS_2} CH_3Br + AgBr + CO_2$

75. (a) 
$$C_2H_5OH \xrightarrow{KI}_{Na_2CO_3}CHI_3$$

#### **Assertion and Reason**

- (d) CHCl<sub>3</sub>is stored in dark bottles of prevent oxidation of CHCl<sub>3</sub>in presence of sunlight.
- 77. (c) Due to symmetrical nature and more-closer packing pdichlorobenzene has highest melting point.
- **78.** (e)  $CCl_4$  is used as a fire extinguisher. The dense, non combustible vapours cover the burning substance and prevents the availability of oxygen round burning material.
- **79.** (e) Dry gaseous hydrohalogen acids are better electrophile. Also in aqueous solution,  $H_2O$  acting as nucleophile may produce alcohol.
- 80. (c) CH<sub>3</sub>CH<sub>2</sub>Ireacts more rapidly with strong base in comparison to CD<sub>3</sub>CH<sub>2</sub>I. The elimination of HI (or DI) in presence of strong base shows E<sub>2</sub>elimination. The rate determining step involves the breaking up of C—H (or C—D) bond. The C—D bond being stronger than C—H and thus elimination is faster in case of CH<sub>3</sub>CH<sub>3</sub>I.
- 81. (c) For a given alcohol the order of reactivity of halogen acids follows the sequence HI > HBr > HCl. It is because of the fact that I<sup>-</sup> is a stronger nucleophile than Br<sup>-</sup> which in turn is a stronger nucleophile than Cl<sup>-</sup>.

82. (d) Halobenzenes become reactive to nucleophilic substitution reactions when electron withdrawing groups (nitro, cyano) are present at ortho/para position. This is evident from the milder conditions required for hydrolysis in 2, 4-dinitrochlorobenzene than chlorobenzene.



- **83.** (e) Halogens are somewhat deactivating but o, p-directing. As a result, aryl halides undergo the usual electrophilic substitution reactions less readily than benzene.
- 84. (b) A reaction is said to be stereo selective if a particular stereoisomer can give two or more stereo-isomeric products but gives one of them in greater amount than the other or even to the exclusion of the other. So, addition of Br<sub>2</sub> to cis-but-2-ene is stereo-selective since it gives only  $(\pm)$  2, 3-dibromobutane.
- 85. (a) In  $S_N 1$  mechanism, recemization takes place, which is due to inverting nucleophilic displacement of halogen atom from the alkyl halide by the halide in solution.

#### **Comprehension Based**

# **86.** (a) AB

- **87.** (a) Rate limiting step in A is first step while in B it is second step
- **88.** (a,c) Good leaving groups (more stable anions) lower the energy of the transition state leading to carbocation formation thus increasing the reaction rate, Polar solvents stabilize the carbocation intermediate by salvation, thereby increasing the reaction rate
- 89. (b) This is a typical multiple choice question. You cannot accurately calculate the exact answer, but can easily pick-up the most appropriate answer. It's a secondary substrate and thereby follows a mixed mechanism; say 60% molecules s through S<sub>N</sub>1 and the rest 'R' configuration, we have; 60 'R S<sub>N</sub><sup>1</sup> → 30'R'+30'S', 40R' S<sub>N</sub><sup>2</sup> → 40'S'. Total molecules with 'S' configuration is higher (70 here).

This is always true for any combination of  $S_N1$  and  $S_N2$  mechanisms. But 'S' molecules can never be 100%.

90. (a) Percentage of backside attack = Percentage of inversion + $\frac{1}{2}$  (Percentage of racemisation) 70% racemisation and rest

30% inversion gives 65% backside attack.

- **91.** (c) The substrate through is a primary halide but it is excessively branched at the - $\beta$ position. Such substrate fails miserably in S<sub>N</sub>2 reaction even though it's a primary halide. Being a primary halide it does not react actively in S<sub>N</sub>1 mechanism as well. However, it reacts quite fluently by S<sub>N</sub>1 mechanism in presence of Ag<sup>+</sup> catalyst.
- **92.** (b) In choice (b) one centre other than the reaction center carries two identical substituent's *i.e.* two methyl groups. As a result, neither the reactant nor the product of the reaction can give rise to stereo-isomers; the stereo-chemical feature of  $S_N 2$  reaction thus cannot be verified. The compound in choice (c), on the other hand will give the cis form. Thus shows the stereo-chemical feature of  $S_N 2$  reaction.

#### Match the Column

93. (a)  $A \rightarrow 2$ ,  $B \rightarrow 2$ ,  $C \rightarrow 3 \rightarrow 4$ ,  $D \rightarrow 1,4$ 

94. (a)  $A \rightarrow 2$ ,  $B \rightarrow 1$ ,  $C \rightarrow 4$ ,  $D \rightarrow 3$ 

Integer

**95.** (83) Bromide =  $\frac{30^{\circ}}{36^{\circ}}(100\%) = 83\%$ 

**96.** (58) Alcohol = 
$$\frac{-6.0^{\circ}}{-10.3^{\circ}}(100\%) = 58\%$$

- **97.** (70) Percentage inversion =  $\frac{58\%}{83\%}(100\%) = 70\%$
- **98.** (30) Percentage racemisation = 100% 70% = 30%
- 99. (15) Percentage of front-side attack

$$=\frac{1}{2}(30\%)=15\%$$

100. (85) Percentage of backside attack

$$= 70\% + \frac{1}{2}(30\%) = 85\%$$

\* \* \*