Unit 14: Haloalkanes and Haloarenes

26. Classify the following compounds in the form of alkyl, allylic, vinyl, benzylic halides. (i) $CH_3 – CH = CH – Cl$ (ii) $C_6H_5CH_2I$
(iii) $CH_3 - CH(Br) - CH_3$ (iv) $CH_2 = CH – Cl$

(i) $CH_3 – CH = CH – Cl$- allyl chloride → allylic
(ii) $C_6H_5CH_2I$ - Benzyl iodide → Benzylic Halides
(iii) $CH_3 - CH(Br) - CH_3$ - 2-bromo propane → alkyl
(iv) $CH_2 = CH – Cl$ – Vinyl chloride → Vinyl

27. Why chlorination of methane is not possible in dark?

Methane does not react with chlorine in dark. Reaction of methane with chlorine proceeds by free radical mechanism. The initiation step in the free radical chain reaction is $Cl_2 \rightarrow 2Cl$. This step requires chain more energy. The excess energy is provided by heat or light.

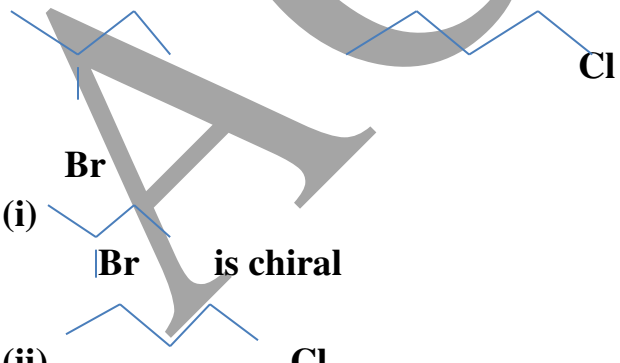
28. How will you prepare n propyl iodide from n-propyl bromide?

n-propyl iodide from n-propyl bromide. n-propyl bromise on heating with concentrated solution of sodium iodide in acetone gives n-propyl Iodide. This reaction is called **Finkelstein reaction.**

$$CH_3CH_2CH_2Br + NaI \xrightarrow[\text{acetone}]{\Delta} CH_3CH_2CH_2I + NaBr$$

n-propyl bromide n-propyl iodide

29. Which alkyl halide from the following pair is i) chiral ii) undergoes faster SN_2 reaction?



(i) Br is chiral

(ii) Cl

30. How does chlorobenzene react with sodium in the presence of ether? What is the name of the reaction?

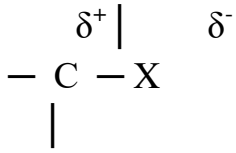
Haloarenes react with sodium metal in dry ether, two aryl groups combine to give biaryl products is reaction is called **fittig reaction.**

$C_6H_5Cl + 2Na + Cl - C_6H_5 \xrightarrow{\text{Ether}} C_6H_5 - C_6H_5 + 2NaCl$

Chlorobenzene $\xrightarrow{\Delta}$ Biphenyl

31. Give reasons for polarity of C-X bond in halo alkane.

Carbon halogen bond is a polar bond as halogens are more electro negative than carbon. The carbon. The carbon atom exhibits a partial positive charge (δ+) and halogen atom a partial negative charges (δ-)



32. Why is it necessary to avoid even traces of moisture during the use of Grignard reagent?

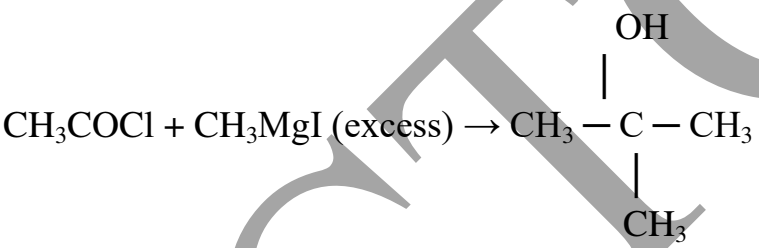
The Grignard carbon is highly basic and reacts with acidic protons of polar solvents like water to form an alkane so all reagents should be pure and dry.

$RMgX + H_2O \rightarrow RH + Mg(OH)X$

Grigard Alkane

33. What happens when acetyl chloride is treated with excess of CH_3MgI?

When acetyl chloride is treated with excess of CH_3 MgI , tertiary alcohols are formed.



t- Butyl alcohol

34. Arrange the following alkyl halide in increasing order of bond enthalpy of RX CH_3Br, CH_3F, CH_3Cl, CH_3I.

The bond strength of C-X bond decreases form C-F to C-I in CH_3X.

Increasing order of bond enthalpy.

$CH_3I < CH_3Br < CH_3Cl < CH_3F$

35. What happens when chloroform reacts with oxygen in the presence of sunlight?

Chloroform undergoes oxidation in the presence of light and air to form phosgene (carbonyl chloride).

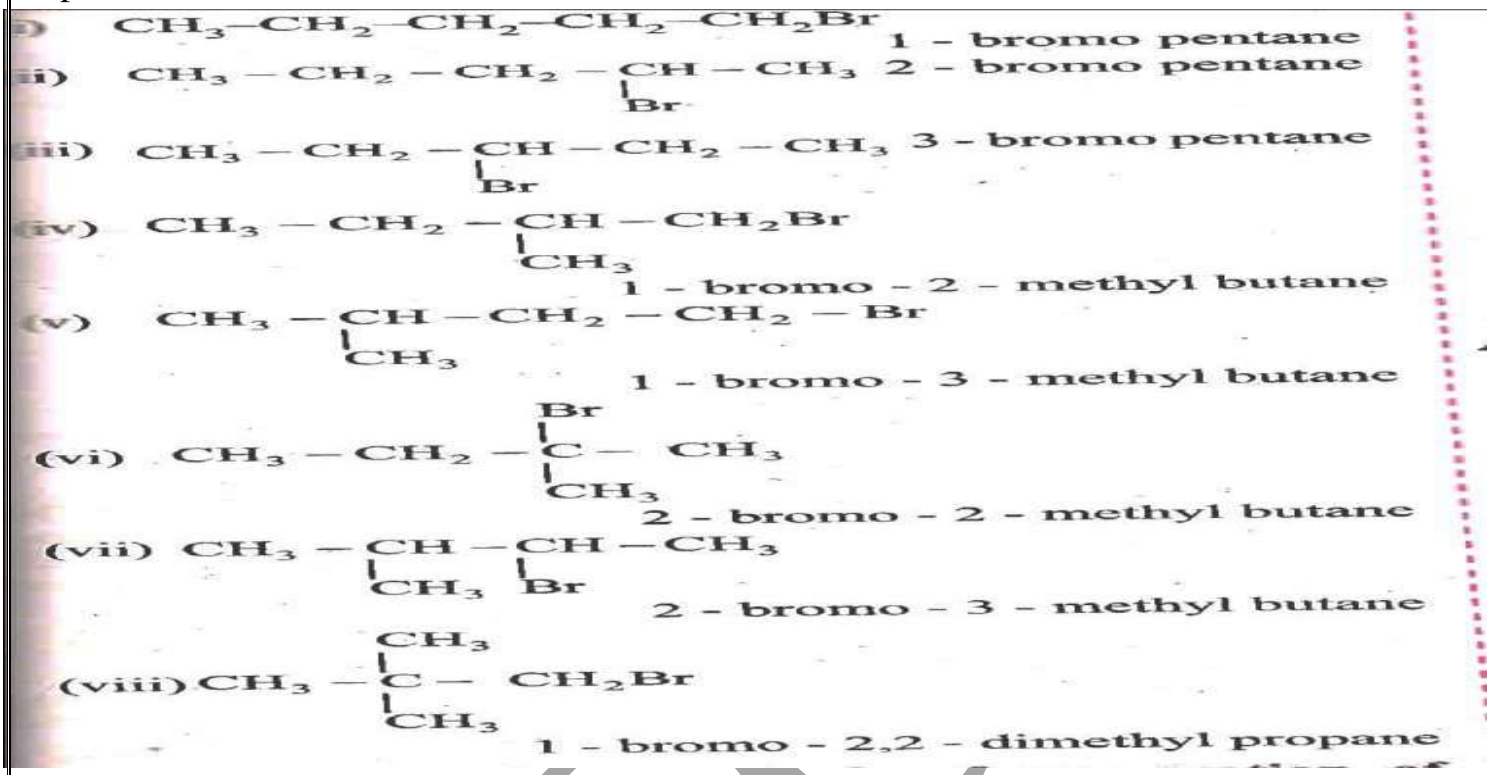
$CHCl_3 + ½\ O_2 \xrightarrow{Air/light} COCl_2 + HCl$

Chloroform Phosgene

Since phosgene is very poisonous, its presence makes chloroform unfit for use as **anaesthetic.**

36. Write down the possible isomers of $C_5H_{11}Br$ and give their IUPAC and common names.

All possible isomers of $C_5H_{11}Br$. There are 8 isomers that have the molecule formula $C_5H_{11}Br$.



37. Mention any three methods of preparation of haloalkanes from alcohols.

- **Reaction with HCl(lucas reagent)**

$$CH_3CH_2OH + HCl \xrightarrow[\Delta]{Anhydrous ZnCl2} CH_3CH_2Cl + H_2O$$

Ethanol chloro ethane

- **Reaction with PCl_5**

$$CH_3CH_2OH + PCl_5 \rightarrow CH_3CH_2Cl + POCl_3 + HCl$$

Ethanol chloro ethane

- **Reaction with $SOCl_2$**

$$CH_3CH_2OH + SOCl_2 \xrightarrow{pyridine} CH_3CH_2Cl + SO_2 + HCl$$

Ethanol chloro ethane

38. Compare SN_1 and SN_2 reaction mechanisms.

SN^1	SN^2
It is **Unimolecular Nucleophilic substitution** reaction.	It is a **bimolecular Nucleophilic substitution** reaction.
Its mechanism occurs in **two steps**.	It is a **one step** process.
It follows **second order** kinetics.	It follows **first order** kinetics.
It involves the **formation of an intermediate.**	It involves the **formation of transition state.**
Rate =k[Alkyl halide]	**Rate =k[Alkyl halide][nuclophile]**
Products have both retained and inverted configuration.	**Products have inverted configuration.**
Carbocation rearrangement occurs.	No carbocation rearrangement occurs
Reactivity: methyl <1°< 2°<3°	**Reactivity:** methyl >1°>2°>3°

39. Reagents and the conditions used in the reactions are given below. Complete the table by writing down the product and the name of the reaction.

Reaction	Product	Name of the reaction
$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{pyridine}} ?$	———	———
$CH_3CH_2Br + AgF \longrightarrow ?$	———	———
$C_6H_5Cl + Na \xrightarrow{\text{ether}} ?$	———	———

Ans.

Reaction	Product	Name of the reaction
$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{pyridine}} ?$	Chloro ethane $CH_3CH_2Cl + SO_2 + HCl$	Darzens reactions
$CH_3CH_2Br + AgF \longrightarrow ?$	Fluoro ethane $CH_3CH_2F + AgBr$	Swarts reaction
$C_6H_5Cl + Na \xrightarrow{\text{ether}} ?$	Biphenyl $C_6H_5 - C_6H_5$	Fittig

40. Discuss the aromatic Nucleophilic substitutions reaction of chlorobenzene.

Halo arenes do not undergo nucleophilic substitution reaction readily. This is due to C–X bond in aryl halide is short and strong and also the aromatic ring is a centre of high electron density.

The halogen of haloarenes can be substituted by OH– , NH_2 –, or CN– with appropriate nucleophilic reagents at high temperature and pressure.

For Example

$$C_6H_5Cl + NaOH \xrightarrow[300\ atm]{350°C} C_6H_5OH + NaCl$$

Chlorobenzene Pheno1

This reaction is known as **Dow's Process.**

41. Account for the follo following (i) t-butyl chloride reacts with aqueous KOH by SN_1 mechanism while n-butyl chloride reacts with SN_2 mechanism. (ii) p-dichloro benzene has higher melting point than those of o-and m-dichloro benzene.

i) This is because rate of SN_2 reaction is directly proportional to delta inversely proportional to steric crowding. Tert-butyl chloride has vast steric crowding and thus it is more stable for SN_1 reaction rather then SN_2 reaction.

ii)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 and consequently strong intermolecular attractive force which requires more energy for melting.

p –Dihalo benzene > o- Dichloro benzene > m-Dichloro benzene

42. In an experiment ethyl iodide in ether is allowed to stand over magnesium pieces. Magnesium dissolves and product is formed a) Name the product and write the equation for the reaction.

b) Why all the reagents used in the reaction should be dry? Explain

c) How is acetone prepared from the product obtained in the experiment.

a) The product formed is ethyl magnesium iodide.(Grignard reagent)

$$C_2H_5I + Mg \xrightarrow{dry\ ether} C_2H_5MgI$$

b) The Grignard carbon is highly basic and reacts with acidic protons of polar solvents like water to form an alkane so all reagents should be pure and dry.

$$RMgX + H_2O \rightarrow RH + Mg(OH)X$$

Grigard Alkane X

43. **Write a chemical reaction useful to prepare the following: i) Freon-12 from Carbon tetrachloride ii) Carbon tetrachloride from carbon disulphide.**

i) Freon – 12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalylic amount of antimony patachloride. This is called **Swartz reaction.**

$$CCl_4 + 2HF \xrightarrow{SbCl5} 2HCl + CCl_2F_2$$

Carbon Tetrachloride — Freon - 12

ii) Carbon disulphide reacts with chlorine gas in the presence of anhydrous $AlCl_3$ as catalyst giving carbon tetrachloride.

$$CS_2 + 3Cl_2 \xrightarrow{anhydrous\ AlCl3} CCl_4 + S_2Cl_2$$

carbon disulphide — carbon tetrachloride

44. **What are Freons? Discuss their uses and environmental effects**

i) Freons are a used as refrigerants in refrigerators and air conditioners.

(ii) It is used as a propellant for aerosols and foams.

(iii) It is used as propellant for foams to spray out deodorants, shaving creams, and insecticides.

45. Predict the products when bromo ethane is treated with the following i) KNO_2 ii) $AgNO_2$

i) Haloalkanes react with alcoholic solution of $NaNO_2$ or KNO_2 to form alkyl nitrites.

$CH_3CH_2Br + KNO_2 \rightarrow CH_3CH_2–O–N=O + KBr$

Bromoethane Ethyl nitrite

ii) Haloalkanes react with alcoholic solution of $AgNO_2$ to form nitro alkanes.

$CH_3CH_2Br + AgNO_2 \rightarrow CH_3CH_2NO_2 + AgBr$

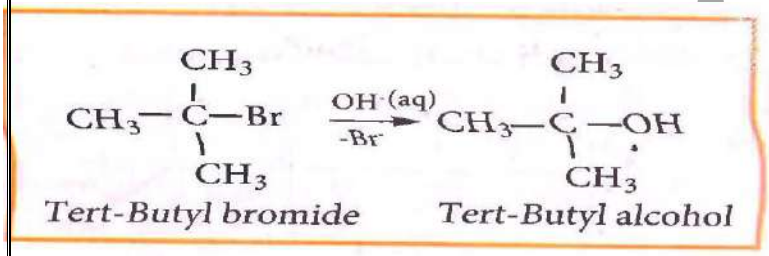
Bromo ethane Nitro ethane

46. **Explain the mechanism of SN_1 reaction by highlighting the stereochemistry behind it.**

S_N1 stands for Unimolecular Nucleophilic Substitution. The rate of the following S_N1 reaction depends upon the concentration of alkyl halide (RX) and is independent of the concentration of the nucleophile (OH^-)

Hence Rate of the reaction = k[alkyl halide]

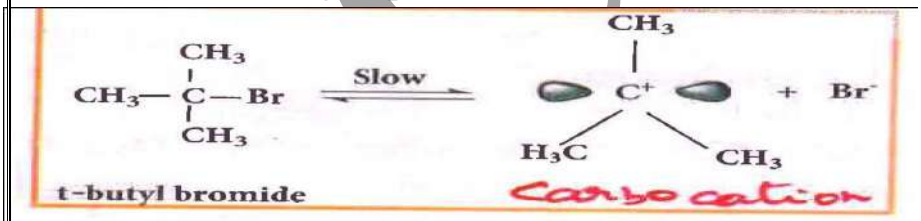
SN1 reaction mechanism by taking a reaction between tertiary butyl bromide with aqueous KOH.



This reaction takes place in two steps as shown below

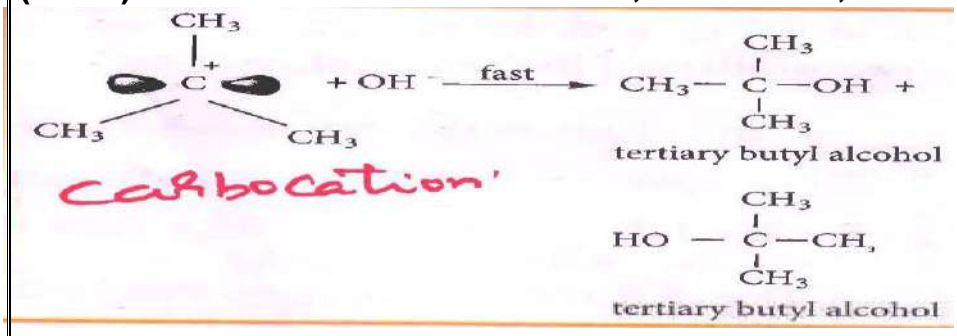
Step - 1 Formation of carbocation

The polar C - Br bond breaks forming a carbocation and bromide ion. This step is slow and hence it is the rate determining step.



The carbocation has 2 equivalent lobes of the vacant 2p orbital, so it can react equally rapidly from either face.

Step – 2 The nucleophile immediately reacts with the carbocation. This step is fast and hence does not affect the rate of the reactions.

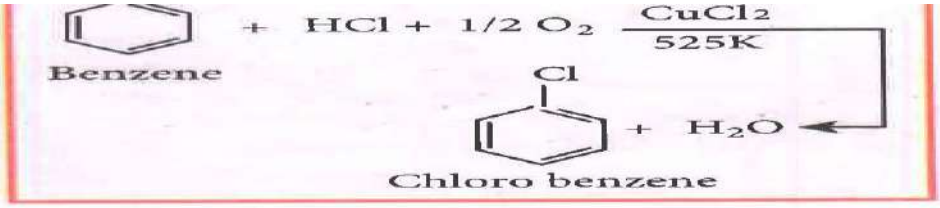


As shown above, the Nucleophilic reagent OH- can attack carbocation from both the sides.

47. Write short notes on the the following

i) Raschig process ii) Dows Process iii) Darzens process

i) **Raschig process**: Chloro benzene is commercially prepared by passing a mixture of benzene vapour, air and HCl over heated cupric chloride .This reaction is called Raschig process.



ii) Dows process:

$$C_6H_5Cl + NaOH \xrightarrow[300\ atm]{350^{\circ}C} C_6H_5OH + NaCl$$

Chlorobenzene Pheno1

This reaction is known as **Dow's Process.**

ii) Darzens process

$$CH_3CH_2OH + SOCl_2 \xrightarrow{pyridine} CH_3CH_2Cl + SO_2 + HCl$$

Ethanol chloro ethane

48. Starting from CH3MgI, How will you prepare the following?

i) Acetic acid ii) Acetone iii) Ethyl acetate iv) Iso propyl alcohol

v) Methyl cyanide

i) **Acetic acid :**Solid carbon dioxide reacts with Grignard reagent to form addition product which on hydrolysis yields carboxylic acids.

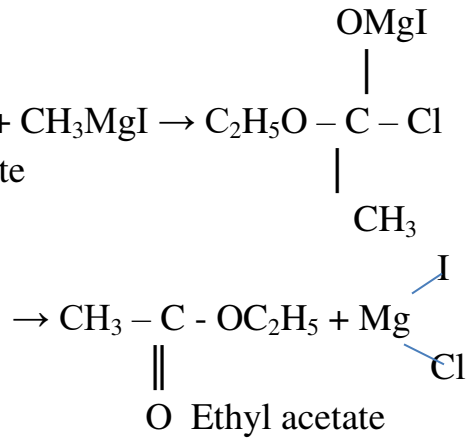
$$O = C = O + CH_3MgI \rightarrow CH_3 - \underset{\underset{O}{\|}}{C} - OMgI \xrightarrow{H2O\ H+} CH_3 - COOH + Mg(OH)I$$

Acetic acid

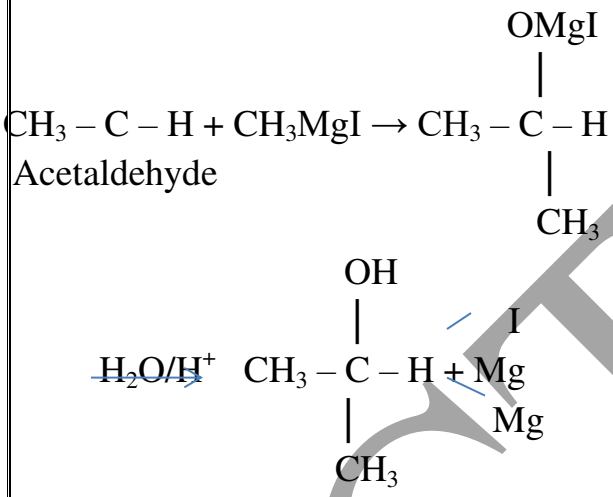
ii) Acetone: $CH_3 - I + Mg \xrightarrow{\text{dry ether}} CH_3MgI$

Iodomethane Methyl magnesium iodide

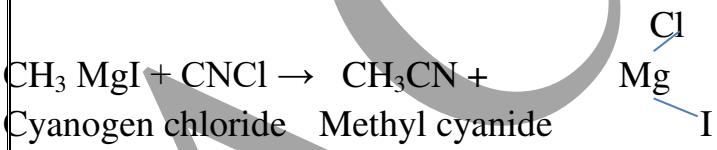
ii) Ethyl acetate: Ethyl chloro formate reacts with Grignard reagent to form esters.



iv) Iso propyl alcohol : Aldehydes other than formaldehyde, react with Grignard reagent to give addition product which on hydrolysis yields secondary alcohol.



v) Methyl cyanide : Grignard reagent reacts with cyanogen chloride to form alkyl cynide



49. Complete the following reactions

i) $CH_3 - CH = CH_2 + HBr$ Peroxide

ii) $CH_3 - CH_2 - Br$ + NaSH alcohol

H_2O

iii) $C_6H_5Cl + Mg$ THF iv) $CHCl_3 + HNO_3$ Δ v) $CCl_4 + H_2O$ Δ

i) The addition of HBr to an alkene in the presence of organic peroxide, gives the anti Markovniko's product. Is effect is called peroxide effect.

$CH_3 - CH = CH_2 + HBr$ Peroxide $CH_3 – CH_2 – CH_2 – Br$

Propene $(C_6H_5CO)_2O_2$ 1- bromopropane

ii) Haloalkanes react with sodium or potassium hydrogen sulphide to form thio alcohols.

$CH_3 - CH_2 - Br + NaSH \xrightarrow{alcohol} CH_3CH_2SH + NaBr$

Bromo ethane $H_2O\ \Delta$ **Ethane thiol**

ii) Chloroform reacts with nitric acid to form chloropicrin. (Trichloro nitro methane) Δ

$CHCl_3 + HNO_3 \rightarrow CCl_3NO_2 + H_2O$

Chloroform **Chloropicrin**

iv) Carbon tetrachloride reacts with hot water or with hot water vapour producing the poisonous gas, phosgene.

$$CCl_4 + H_2O(g) \xrightarrow{\Delta} COCl_2 + 2H_2O$$

Carbon tetrachloride **Phosgene**

50. Explain the preparation of the following compounds

i) DDT ii) Chloroform iii) Biphenyl iv) Chloropicrin v) Freon-12

i) DDT: DDT can be prepared by heating a mixture of chlorobenzene with chloral (Trichloro acetaldehyde) in the presence of con.H2SO4.

ii)Chloroform : The reaction of methane with excess of chlorine in the presence of sunlight will give carbon tetrachloride as the major product.

$CH_4 + 4Cl_2 \xrightarrow{h\gamma}$ **$CCl4$ +** $4HCl$

Methane carbon tetrachloride

iii) Biphenyl:

$C_6H_5Cl + 2Na + Cl - C_6H_5 \xrightarrow[\Delta]{Ether} C_6H_5 - C_6H_5 + 2NaCl$

Chlorobenzene **Bipheyl**

iv) Chloropicrin: Chloroform reacts with nitric acid to form chloropicrin.(Trichloro nitro methane)

$$CHCl_3 + HNO_3 \xrightarrow{\Delta} CCl_3NO_2 + H_2O$$

Chloroform **Chloropicrin**

v) Freon-12: Freon-12 is prepared by the action of hydrogen fluoride on carbon tetrachloride in the presence of catalylic amount of antimony pentachloride. It is called Swartz reaction.

$$CCl_4 + 2HF \xrightarrow{SbCl_5} 2HCl + CCl_2F_2$$

Carbon tetrachloride Freon - 12

51. An organic compound (A) with molecular formula C_2H_5Cl reacts with KOH gives compounds (B) and with alcoholic KOH gives compound (C). Identify (A), (B), and (C)

$CH_3CH_2Cl + KOH_{(Aq)} \rightarrow CH_3CH_2OH$

(A) (B)

Chloroethane Ethanol

+

Alc KOH A CH_3CH_2Cl Chloroethane

↓ B CH_3CH_2OH Ethanol

$CH_2 = CH_2$ C $CH_2 = CH_2$ Ethene

(C)

Ethene

52. Simplest alkene (A) reacts with HCl to form compound (B).Compound (B) reacts with ammonia to form compound (C) of molecular formula C_2H_7N.Compound (C) undergoes carbylamine test. Identify (A), (B), and (C).

$CH_2 = CH_2 + HCl \rightarrow CH_3 - CH_2Cl$

(A) (B)

Ethene Chloroethane

$CH_3CH_2Cl + NH_3 \rightarrow CH_3CH_2NH_2$

(B) (C)

Chloroethane Ethyl amine

A $CH_2 = CH_2$ Ethene

B CH_3CH_2Cl Chloroethane

C $CH_3CH_2NH_2$ Ethylamine

53. A hydrocarbon C_3H_6 (A) reacts with HBr to form compound (B). Compound (B) reacts with aqueous potassium hydroxide to give (C) of molecular formula C_3H_6O.what are (A) (B) and (C). Explain the reactions.

$CH_3 - CH = CH_2 + HBr \rightarrow CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$

(A) (B)

Propene 2 – bromo propane

↓KOH aq

$CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$

Iso propyl alcohol

54. Two isomers (A) and (B) have the same molecular formula $C_2H_4C_{l2}$.Compound (A) reacts with aqueous KOH gives compound (C) of molecular formula C_2H_4O.Compound (B) reacts with aqueous KOH gives compound (D) of molecular formula $C_2H_6O_2$

$\underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3$ (A) 1,1, - dichloro ethane

$\underset{\displaystyle Cl}{\underset{|}{CH}} - CH_3$

$CH_2 - CH_2 \xrightarrow[aq\ KOH]{}$ $CH_2OH - CH_2OH$

| | (B) 1,2, dichloro ethane (D) ETHYLENE GLYCOL

Cl Cl

Cl OH

| |

$CH - CH_3 \xrightarrow[aq\ KOH]{} CH - CH_3 \xrightarrow[-H_2O]{} CH_3CHO$

| |

Cl OH (C)

(A) Acetaldhyde

1,1, - dichloro ethane

Cl

|

(A) $CH - CH_3$ - 1,1, - dichloro ethane

|

Cl

(B) $CH_2 - CH_2$

| | - 1,2, dichloro ethane

Cl Cl

(C) CH_3CHO - Acetaldhyde

(D) $CH_2 - CH_2$

| | - Ethyleneglycol

OH OH