UNIT-14 HALOALKANES AND HALOARENES

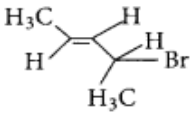
MY REVISION TIMELINE:-

SUMMARY:-

- When one or more hydrogen atoms of aliphatic or aromatic hydrocarbons are replaced by the corresponding number of halogens like fluorine, chlorine, bromine or iodine, the resultant compounds are either called haloalkanes or haloarenes.
- Classification of organic halogen compounds:
  - Based on no. of halogens
    - Mono halo compounds
    - Poly halo compounds
  - Based on the hybridisation of carbon attached with halogen
    - Compounds containing C_{sp^3} – X bond
      - Alkyl halides or haloalkanes
      - Allylic halides
      - Benzylic halides
      - Alicyclic halides
    - Compounds containing C_{sp^2} – X bond
      - Vinylic halides
      - Arylic halides or halo arenes
- Haloalkanes are mono halogen derivatives of alkanes. It is represented as R-X where R is C_nH_{2n+1} and X is F, Cl, Br or I
- Organo metallic compounds: Organic compounds in which there is a direct carbon-metal bond.
- Haloarenes are compounds in which the halogen is directly attached to the benzene ring.
- Poly halogen compounds are compounds containing more than one halogen atoms.

TEXTBOOK EVALUATION

Multiple choice questions:-

1. The IUPAC name of  is

(a) 2-Bromopent – 3 – ene **(b) 4-Bromopent – 2 – ene**
(c) 2-Bromopent – 4 – ene (d) 4-Bromopent – 1 – ene

2. Of the following compounds which has the highest boiling point?
(a) n-Butyl chloride (b) Isobutyl chloride
(c) t-Butyl chloride (d) n-propyl chloride

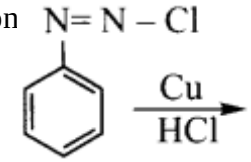
3. Arrange the following compounds in increasing order of their density.
(A) CCl_4 (B) $CHCl_3$ (C) CH_2Cl_2 (D) CH_3Cl

(a) D<C<B<A (b) C<B<A<D
(c) A<B<C<D (d) C<A<B<D

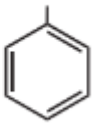
4. With respect to the position of – Cl in the compound $CH_3 – CH = CH – CH_2 – Cl$, it is classified as
(a) Vinyl **(b) Allyl**
(c) Secondary (d) Aralkyl

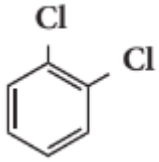
5. What should be the correct IUPAC name of diethyl chloromethane?
(a) 3-Chioropentane (b) 1-Chloropentane
(c) 1-Chloro- 1, 1, diethylmethane (d) 1-Chloro- 1 –ethylpropane

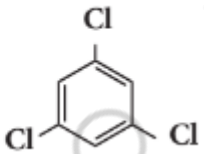
6. C-X bond is strongest in
(a) Chloromethane (b) lodomethane
(c) Bromomethane **(d) Fluoromethane**

7. In the reaction 

i. $X + N_2$, X is

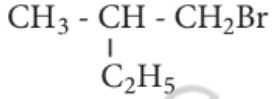
a) 
b) 

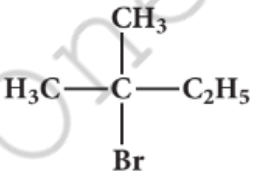
c) 

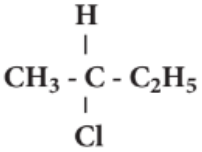
d) 

Option b)

8. Which of the following compounds will give racemic mixture on nucleophilic substitution by OH^- ion?

i) 

ii) 

iii) 

(a) (i) (b) (ii) and (iii)
(c) (iii) (d) (i) and (ii)

9. The treatment of ethyl formate with excess of RMgX gives

a) R- C(=O) - R b) R- CH(OH) - R

c) R- CHO d) R- O – R

Option c)

10. Benzene reacts with Cl_2 in the presence of $FeCl_2$ and in absence of sunlight to form –
(a) Chlorobenzene (b) Benzyl chloride
(c) Benzal chloride (d) Benzene hexachloride

11. The name of $C_2F_4Cl_2$ is
(a) Freon – 112 (b) Freon – 113
(c) Freon – 114 (d) Freon – 115

12. Which of the following reagent is helpful to differentiate ethylene dichloride and ethylidene chloride?
(a) Zn / methanol (b) KOH / ethanol
(c) Aqueous KOH (d) $ZnCl_2$ / Cone. HCl

13. Match the compounds given in Column I with suitable items given in Column II.

	Column I (Compound)		**Column II (Uses)**
A	Iodoform	1	Fire extinguisher
B	Carbon tetra chloride	2	Insecticide
C	CFC	3	Antiseptic
D	DDT	4	Refrigerants

(a) A→2,B→4,C→1,D→3 (b) A→3,B→2,C→4,D→1
(c) A→1,B→2,C→3,D→4 **(d) A→3,B→1,C→4,D→2**

14. Assertion: in mono haloarenes, electrophilic substitution occurs at ortho and para positions.
Reason: Halogen atom is a ring deactivator.
(a) If both assertion and reason arc true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

15. Consider the reaction, $CH_3CH_2CH_2Br + NaCN \rightarrow CH_3CH_2CH_2CN + NaBr$ This reaction will be the fastest in
(a) ethanol (b) methanol
(c) DMF (N, N' – dimethyl formamide) (d) water

16. Freon-12 is manufactured from tetrachloromethane by
(a) Wurtz reaction **(b) Swarts reaction**
(c) Haloform reaction (d) Gattermann reaction

17. The most easily hydrolysed molecule under S_N1 condition is
(a) allyl chloride (b) ethyl chloride
(c) isopropyl chloride **(d) benzyl chloride**

18. The carbocation formed in S_N1 reaction of alkyl halide in the slow step is
(a) sp^3 hybridised **(b) sp^2 hybridised**
(c) sp hybridised (d) none of these

19. The major products obtained when chiorobenzene is nitrated with HNO_3 and cone. H_2SO_4
(a) 1-chloro-4-nitrobenzene (b) 1-chloro-2-nitrobenzene
(c) 1-chloro-3-nitrobenzene (d) 1-chloro- 1 –nitrobenzene

20. Which one of the following is most reactive towards nucleophilic substitution reaction?

a) 

b) 

c) 

d) 

Option d)

21. Ethylidene chloride on treatment with aqueous KOH gives
(a) acetaldehyde (b) ehtylene glycol
(c) formaldehyde (d) glyoxal

22. The raw material for Rasching process is
(a) chlorobenzene (b) phenol
(c) benzene (d) anisole

23. Chloroform reacts with nitric acid to produce
(a) nitro-toluene (b) nitro-glycerine
(c) chloropicrin (d) chioropicric acid

24. Acetc $\xrightarrow[(ii)\ H_2O/H^{+1}]{(i)\ CH_3MgI}$ X, X is
(a) 2-propanol **(b) 2-methyl-2-propanol**
(c) 1 –propanol (d) acetonol

25. Silver propionate when refluxed with Bromine in carbon tetrachloride gives
(a) propionic acid (b) chloroethane
(c) bromoethane (d) chloropropane

Write brief answers to the following questions:-

26. Classify the following compounds in the form of alkyl, allylic, vinyl, benzylic halides.
(a) CH_3-CH = CH-Cl - Vinylic
(b) $C_6H_5CH_2I$ - Benzylic
(c) $CH_3 - \underset{\displaystyle Br}{\underset{|}{CH}} - CH_3$ - Alkyl
(d) CH_2 = CH – Cl - Vinylic

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

The **chlorination of methane** is carried out by **free radical mechanism** and formation of free radicals needs high energy which can be supplied by **light energy**.

$\mathbf{Cl\text{-}Cl \xrightarrow{h\nu} 2Cl}$

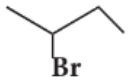
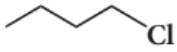
This reaction is not possible in **dark**.

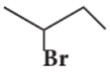
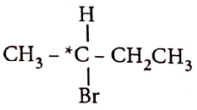
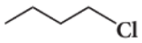
28. How will you prepare n propyl iodide from n-propyl bromide?

n-propyl bromide on heating with a **concentrated solution** of **sodium iodide** in dry acetone gives n-propyl iodide. This S_N^2 reaction is called **Finkelstein reaction**.

$$\underset{n\text{–propyl bromide}}{CH_3-CH_2-CH_2Br} + NaI \xrightarrow{\text{Acetone}} \underset{n\text{–propyl iodide}}{CH_3-CH_2-CH_2I} + NaBr$$

29. Which alkyl halide from the following pair is i) chiral ii) undergoes faster S_N2 reaction?

- The **chiral molecule** is  or 2-bromobutane 
-  undergoes S_N2 reaction faster because it is a **primary alkyl halide** or 1-chlorobutane CH_3-CH_2-CH_2Cl.

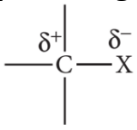
30. How does chlorobenzene react with sodium in the presence of ether? What is the name of the reaction?

Reaction name: **Fittig reaction**

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + 2Na + ClC_6H_5 \xrightarrow[\Delta]{\text{Ether}} \underset{\text{Biphenyl}}{C_6H_5-C_6H_5} + 2NaCl$$

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

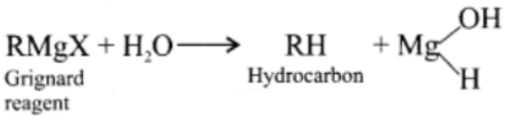
- Carbon halogen bond is a polar bond as **halogens** are **more electronegative** than carbon.
- The **carbon** atom exhibits a partial positive change **(δ^+)** and **halogen** atom acquires a partial negative change. **(δ^-)**



- The C –X bond is formed by overlap of sp3 orbital of carbon atom with **half filled p-orbital** of the halogen atom.
- The **atomic size** of halogen increases from fluorine to iodine, which increases the C – X bond length. Larger the size, greater is the bond length, and weaker is the bond formed. The bond strength of C–X decreases from C – F to C – I in CH_3X.

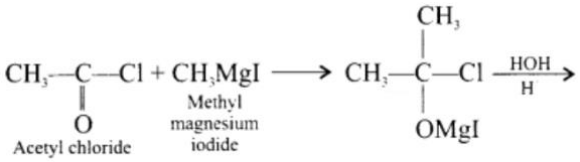
32. Why is it necessary to avoid even traces of moisture during the use of Grignard reagent?

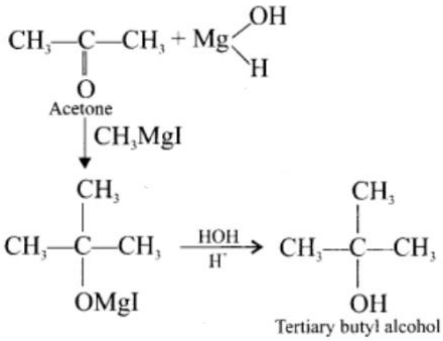
Grignard reagents are **highly reactive substances**. They react with any source of proton to form hydrocarbons. Even **water** is sufficiently acidic to convert it into the corresponding hydrocarbon. So it is necessary to avoid **even traces of moisture** with the Grignard reagent as they are **highly reactive**.



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

First it forms **acetone** which further reacts with excess CH_3MgI to give **tertiary alcohol**.





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

$CH_3I < CH_3Br < CH_3Cl < CH_3F$

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**.

$$\underset{\text{Chloroform}}{CHCl_3} + \frac{1}{2}O_2 \xrightarrow[\text{light}]{\text{air}} \underset{\text{Phosgene}}{COCl_2} + HCl$$

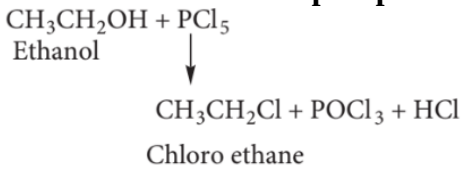
36. Write down the possible isomers of $C_5H_{11}Br$ and give their IUPAC and common names.

Isomer	IUPAC name	Common name
$CH_3—CH_2—CH_2—CH_2—CH_2Br$	1-bromopentane	n-pentyl bromide or n-amyl bromide
$CH_3—CH(Br)—CH_2—CH_2—CH_3$	2-bromopentane	sec-pentyl bromide or sec-amyl bromide
$CH_3—CH_2—CH(Br)—CH_2—CH_3$	3-bromopentane	-
$CH_3—CH(CH_3)—CH_2—CH_2Br$	1-bromo-3-methylbutane	Isopentyl bromide or iso amylbromide
$CH_3—CH_2—CH(CH_3)—CH_2Br$	1-bromo-2-methylbutane	-
$CH_3—C(CH_3)_2—CH_2Br$	1-bromo -2,2-di methyl propane	Neo pentyl bromide or neo amyl bromide
$CH_3—CH(Br)—CH(CH_3)—CH_3$	2-bromo-3-methylbutane	-
$CH_3—CH_2—C(Br)(CH_3)—CH_3$	2-bromo-2-methylbutane	t-pentyl bromide or t-amyl bromide

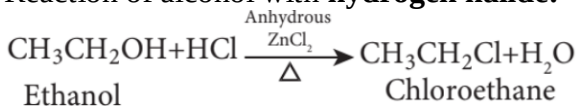
37. Mention any three methods of preparation of haloalkanes from alcohols.

Haloalkanes are prepared from alcohols by

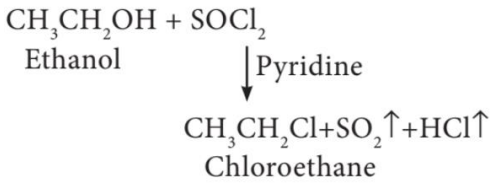
- Reaction of alcohol with **phosphorous halide**:



- Reaction of alcohol with **hydrogen halide:**

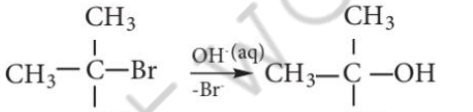


- Reaction of alcohol with **thionyl chloride:**

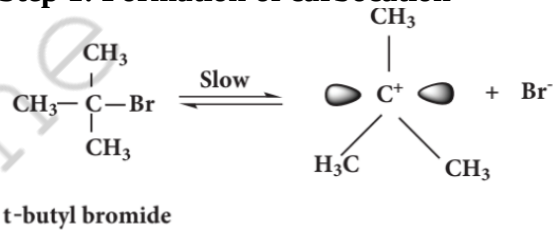


38. Compare S_N1 and S_N2 reaction mechanisms.

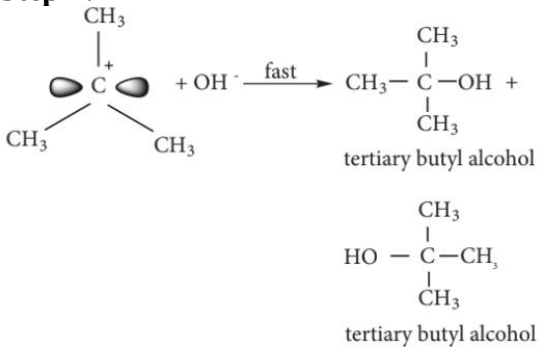
- **S_N1 mechanism:**
  - It is a **unimolecular nucleophilic substitution** reaction of first order.
  - It takes place in **two steps**.
  - It leads to **racemisation**.
  - It mostly take place in **tertiary alkyl halides**.
  - The rate of the reaction depends only on the **concentration of one of substrate** and so it is a first order reaction.
  - Example:



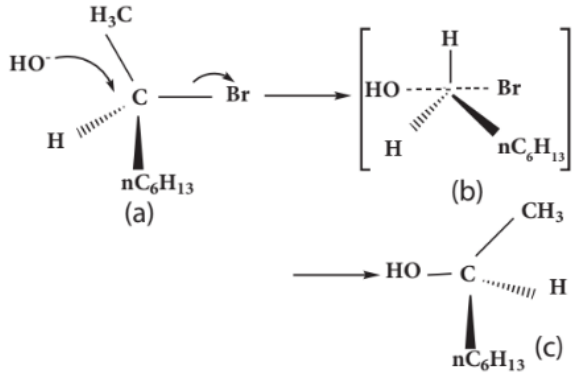
Step 1: Formation of carbocation



Step 2:



- **S_N2 mechanism:**
  - It is a **bimolecular nucleophilic substitution** reaction of second order.
  - It takes place in **one step**.
  - It leads to **invertion of configuration**.
  - It mostly take place in **primary alkyl halides**.
  - The rate of the reaction depends on the **concentration of both the substrate** as well as the nucleophile and so it is a second order reaction.
  - Example:



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
$CH_3CH_2OH + SOCl_2 \xrightarrow{\text{pyridine}} ?$	$CH_3CH_2Cl + SO_2 + HCl$ Ethyl chloride	**Darzen's halogenation**
$CH_3CH_2Br + AgF \longrightarrow ?$	$CH_3CH_2F + AgBr$ Ethyl fluoride	**Swartz reaction**
$C_6H_5Cl + Na \xrightarrow{\text{ether}} ?$	$C_6H_5C_6H_5 + 2NaCl$ Biphenyl	**Fittig reaction**

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–, NH2–, or CN– with appropriate nucleophilic reagents at high temperature and pressure.
- This reaction is known as **Dow's process**.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + NaOH \xrightarrow[300\ atm]{350^oC} \underset{\text{Pheno1}}{C_6H_5OH} + NaCl$$

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + 2NH_3 \xrightarrow[50\ atm]{250^0C} \underset{\text{Aniline}}{C_6H_5NH_2} + NH_4Cl$$

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + CuCN \xrightarrow[\text{Pyridine}]{250^0C} \underset{\text{Phenyl cyanide}}{C_6H_5CN} + CuCl$$

41. Account for the following

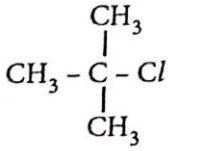
(i) t-butyl chloride reacts with aqueous KOH by SN1 mechanism while n-butyl chloride reacts with S_N2 mechanism.

(ii) p-dichloro benzene has higher melting point than those of o-and m-dichloro benzene.

- t-butyl chloride is a **tertiary halide**, so it undergoes S_N1 mechanism. In the first step (slow) a **carbocation** is formed. It is a two-step process reaction. n-butyl chloride is a primary halide, so it undergoes S_N2 mechanism. Here an **intermediate transition state** is formed. It is a one step process.

$CH_3CH_2CH_2CH_2Cl$ - Primaryhalide

n - butyl chloride - $[S_N2]$



Tertiary halide $[S_N1]$

t - butyl chloride

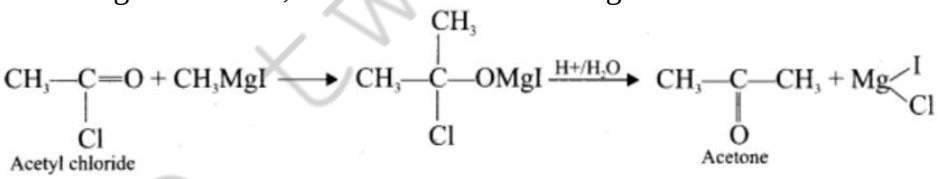
- The p-isomer has a symmetrical structure. Its molecular have **closely packed crystal lattice**. So inter molecular attractive forces are **stronger**. So greater energy is required to break its lattice.

42. In an experiment ethyliodide 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?

- $CH_3 - CH_2I + Mg \xrightarrow{\text{dry ether}} \underset{\text{Ethyl magnesium iodide (Grignard reagent)}}{CH_3 - CH_2MgI}$
- If the reagents are wet, H_2O will react with RMgX to form alkanes.
- 

43. Write a chemical reaction useful to prepare the following:

i) Freon-12 from Carbon tetrachloride

ii) Carbon tetrachloride from carbon disulphide

- Freon- 12 is prepared by the action of **hydrogen fluoride** on carbon tetrachloride in the presence of catalytic amount of **antimony pentachloride**. This is called "**swartz reaction**".

$\underset{\text{Carbon tetrachloride}}{CCl_4} + 2HF \xrightarrow{Sbcl_5} 2HCl + \underset{\text{Freon - 12}}{CCl_2F_2}$

- Carbon disulphide reacts with chlorine gas in the presence of anhydrous $AlCl_3$ as catalyst to give carbon tetrachloride.

$\underset{\text{carbon disulphide}}{CS_2} + 3Cl_2 \xrightarrow[AlCl_3]{\text{anhydrous}} \underset{\text{carbon tetrachloride}}{CCl_4} + S_2Cl_2$

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

The chloro fluro derivatives of methane and ethane are called **freons.**

Uses:

- Freons are used as **refrigerants** in refridgerators and air conditioners.
- It is used as **propellant** for **aerosols** and **foams**.
- It is used as **propellant** for foams to spray out **deoderants**, **shaving creams** and **inseticides**.

Environmental effects:

CFC's are the exhaust of supersonic air craft's and jumbo jets flying in the upper atmosphere. They slowly pass from **troposphere to stratosphere**. They stay for a very long period of **50-100** years. In the presence of uv radiation, CFC's break up into chlorine free radical.

$$CF_2Cl_2 \xrightarrow{h\upsilon} CF_2Cl + Cl.$$

$$CFCl_3 \xrightarrow{h\upsilon} CFCl_2 + Cl^{\cdot}$$

$$Cl^{\cdot} + O_3 \rightarrow ClO + O_2$$

$$ClO^{\cdot} + O \rightarrow Cl + O_2$$

Due to this formation of ozone layer takes place. It is estimated that for every chlorine atom generated in stratosphere **1,00,000 molecules of ozone are depleted**.

45. Predict the products when bromoethane is treated with the following

i) KNO_2 ii) $AgNO_2$

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

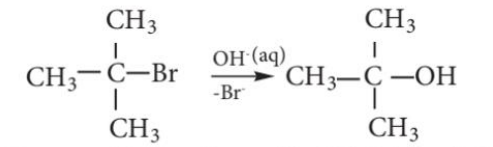
  Bromoethane Ethyl nitrite

- $CH_3CH_2Br+AgNO_2 \rightarrow CH_3CH_2NO_2+ AgBr$

  Bromo ethane Nitro ethane

46. Explain the mechanism of S_N1 reaction by highlighting the stereochemistry behind it.

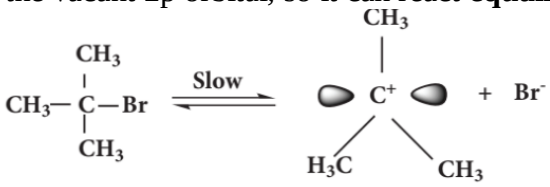
- It is a **unimolecular nucleophilic substitution** reaction of first order.
- It takes place in **two steps**.
- It leads to **racemisation**.
- It mostly take place in **tertiary alkyl halides**.
- The rate of the reaction depends only on the **concentration of one of substrate** and so it is a first order reaction.
- Example:



Tert-Butyl bromide Tert-Butyl alcohol

Step 1: Formation of carbocation

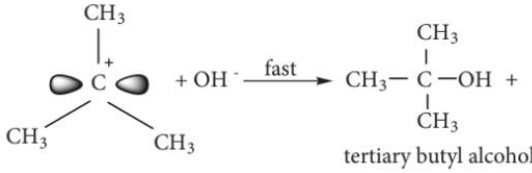
The polar C-Br bond breaks first **forming a carbocation and bromide ion**. This step is slow and hence it is the rate determining step. The carbocation has two equivalent lobes of the vacant 2p orbital, so it can react **equally fast form either face**.



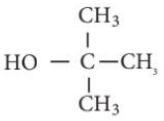
t-butyl bromide

Step 2:

The nucleophile immediately reacts with the carbocation. This step is **fast** and hence does not affect the rate of the reaction. The nucleophile OH can attack carbocation from both the sides.



tertiary butyl alcohol



tertiary butyl alcohol

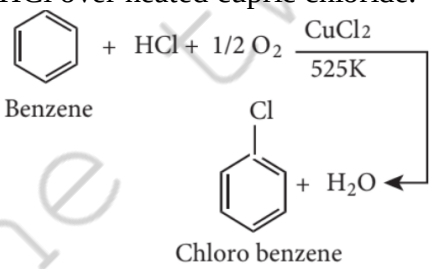
47. Write short notes on the the following

i) Raschig process

ii) Dow's Process

iii) Darzen's process

- Chlorobenzene is commercially prepared by passing a mixture of benzene vapour in air and HCl over heated cupric chloride.



Chloro benzene

- Chlorobenzene is boiled with Sodium hydroxide to get Phenol. This reaction is called Dow's process.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + NaOH \xrightarrow[300\ atm]{350^oC} \underset{\text{Pheno1}}{C_6H_5OH} + NaCl$$

- Ethanol reacts with SOCl, in the presence of pyridine to form chloroethane. This reaction is called Darzen's process.

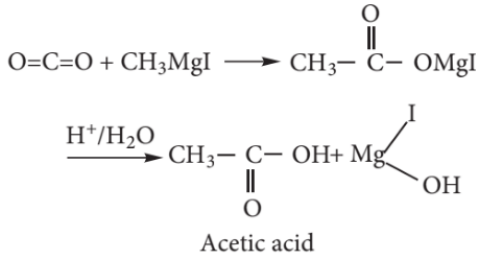
$$\underset{\text{Ethanol}}{CH_3CH_2OH} + SOCl_2 \xrightarrow{\text{Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

48. Starting from CH_3MgI, How will you prepare the following?

i) Acetic acid ii) Acetone iii) Ethyl acetate

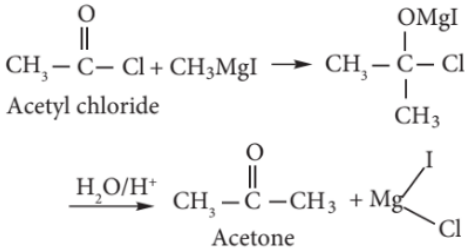
iv) Iso propyl alcohol v) Methyl cyanide

- **Acetic acid**



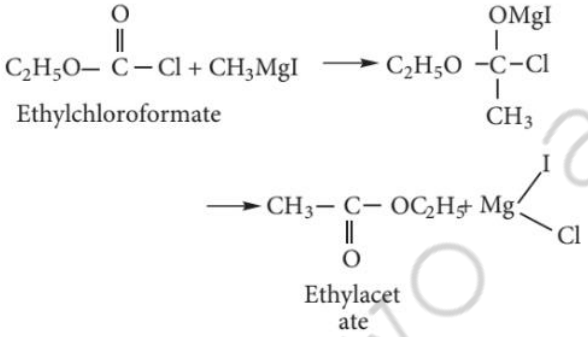
Acetic acid

- **Acetone**



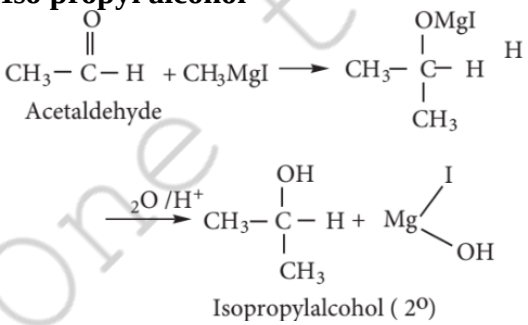
Acetone

- **Ethyl acetate**



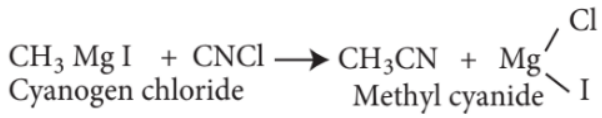
Ethylacetate

- **Iso propyl alcohol**



Isopropylalcohol (2º)

- **Methyl cyanide**



49. Complete the following reactions

$$\underset{\text{Prop-1-ene}}{CH_3-CH=CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-bromopropane}}{CH_3-CH_2-CH_2Br}$$

$$\underset{\text{Bromoethane}}{CH_3-CH_2Br} + NaSH \xrightarrow[H_2O]{\text{alcohol}} \underset{\text{Ethanethiol}}{CH_3-CH_2SH} + NaBr$$

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + Mg \xrightarrow{THF} \underset{\text{Phenyl magnesium chloride}}{C_6H_5MgCl}$$

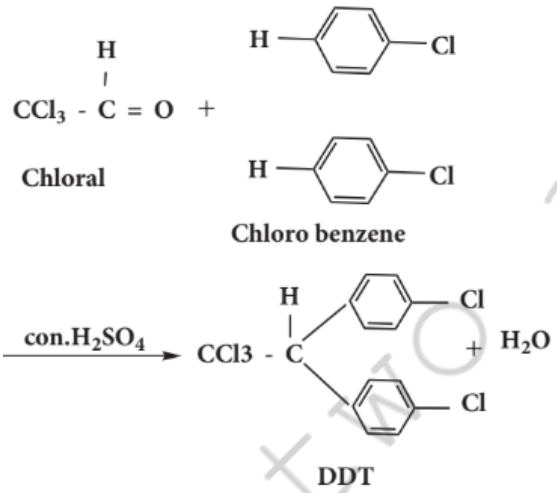
$$\underset{\text{Chloroform}}{CHCl_3} + HNO_3 \xrightarrow{\Delta} \underset{\text{Trichloronitromethane (chloropicrin)}}{CCl_3NO_2} + H_2O$$

$$\underset{\text{Carbon tetra-chloride}}{CCl_4} + H_2O(g) \xrightarrow{\Delta} \underset{\text{Phosgene}}{COCl_2} + 2H_2O$$

50. Explain the preparation of the following compounds

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

- **DDT**



- **Chloroform**

Step – 1: Oxidation

$$CH_3CH_2OH + Cl_2 \rightarrow CH_3CHO + 2HCl$$

Ethyl alcohol Acetaldehyde

Step – 2: Chlorination

$$CH_3CHO + 3Cl_2 \rightarrow CCl_3CHO + 3HCl$$

Acetaldehyde Trichloro acetaldehyde

Step – 3: Hydrolysis

$$2CCl_3CHO + Ca(OH)_2 \rightarrow 2CHCl_3 + (HCOO)_2Ca$$

Chloral chloroform

- **Biphenyl**

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

Chlorobenzene — Biphenyl

- **Chloropicrin**

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

Chloroform — Chloropicrin

- **Freon-12**

$$CCl_4 + 2HF \xrightarrow{Sbcl_5} 2HCl + CCl_2F_2$$

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)

$$\underset{\text{Ethylchloride}}{\underset{(A)}{CH_3CH_2Cl}} \xrightarrow{\text{aq.KOH}} \underset{(B)}{\overset{\text{Ethanol}}{CH_3CH_2OH}} + KCl$$

$$CH_3CH_2Cl \xrightarrow[\Delta]{\text{alc.KOH}} \underset{(C)}{\overset{\text{Ethene}}{CH_2 = CH_2}} + KCl + H_2O$$

Elimination
Dehydrohalogenation

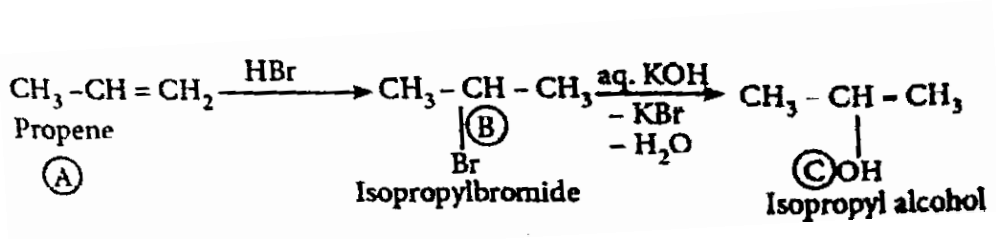
Compound	Name
A	Ethyl chloride
B	Ethyl alcohol
C	Ethylene

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_2N. Compound (C) undergoes carbylamine test. Identify (A), (B), and (C).

$$\underset{\substack{\text{Simplest alkene}\\ \text{Ethylene}\\ (A)}}{CH_2 = CH_2} \xrightarrow{HCl} \underset{\substack{(B)\\ \text{Ethylchloride}}}{CH_3CH_2Cl} \xrightarrow{NH_3} \underset{\substack{(C)\\ \text{Ethylamine}}}{CH_3CH_2NH_2} \xrightarrow[KOH]{CHCl_3} \underset{\substack{\text{Methyl}\\ \text{carbylamine}}}{CH_3NC}$$

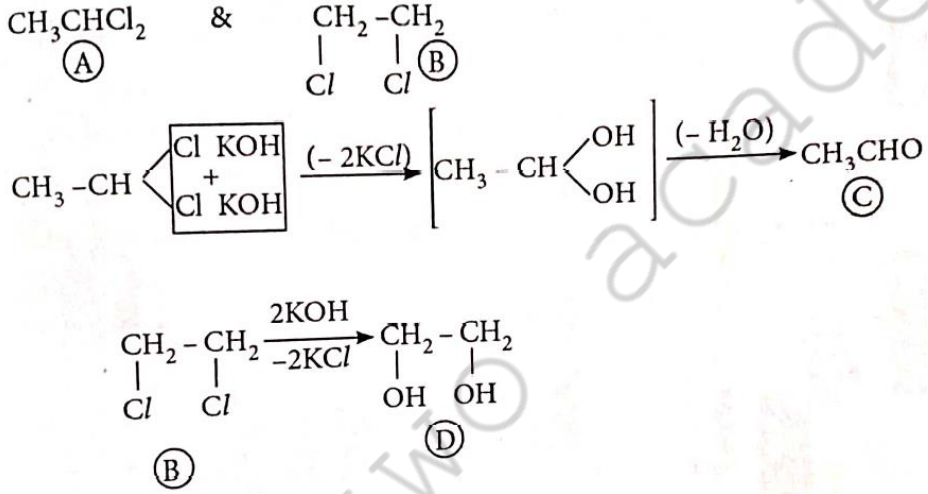
Compound	Name
A	Ethylene
B	Ethyl chloride
C	Ethylamine

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_8O. What are (A) (B) and (C). Explain the reactions.



Compound	Name
A	Propene
B	Isopropyl bromide
C	Isopropyl alcohol

54. Two isomers (A) and (B) have the same molecular formula $C_2H_4Cl_2$. Compound (A) reacts with aqueous KOK, gives compound (C) of molecular formula C_2H_4O. Compound (B) reacts with aqueous KOH, gives compound (D) of molecular formula $C_2H_6O_2$. Identify (A), (B), (C) and (D).



Compound	Name
A	Ethylidene chloride
B	Ethylene dichloride
C	Acetaldehyde
D	Ethylene glycol