Q. No. 2 Part (i)

REACTIONS OF DIL-HCL

- **Li_2O** : Li_2O reacts with dil. HCl to form salt and water.

$$Li_2O + 2HCl \longrightarrow 2LiCl + H_2O$$

- **Na_2O_2** : Na_2O_2 reacts with dil. HCl to form salt and hydrogen peroxide (H_2O_2). At high temp. H_2O_2 decomposes to $H_2O + O_2$.

$$Na_2O_2 + 2HCl \longrightarrow 2NaCl + H_2O_2$$

$$2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2$$

- **KO_2** : KO_2 reacts with dil. HCl to form salt, hydrogen peroxide and oxygen. At high temp. H_2O_2 decomposes to give H_2O and O_2.

$$2KO_2 + 2HCl \longrightarrow 2KCl + H_2O_2$$

$$2H_2O_2 \xrightarrow{\Delta} 2H_2O + O_2$$

Q. No. 2 Part (ii)

ATOMIC RADII OF ELEMENTS OF PERIOD 3:

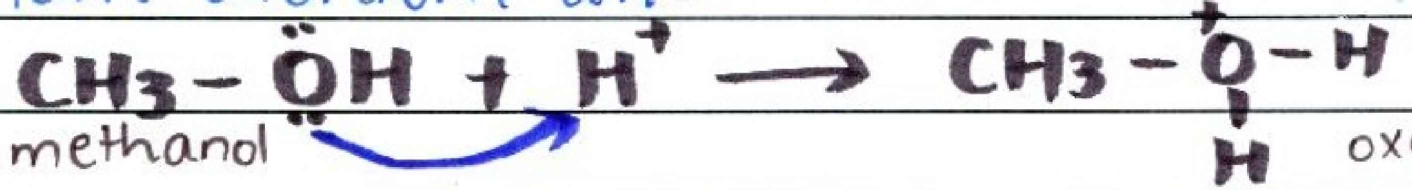
As we move from left to right in period 3, number of shells remain **constant** and thus **shielding effect remains constant**. But **effective nuclear charge increases** due to increase in atomic number. Due to this greater effective nuclear charge, electrons are pulled closer towards the nucleus. As a result atomic **radii decrease** as we move from Na to Cl. However atoms of nobles gases have greater radii than preceding halogens due to interelectronic repulsion. Thus order of atomic radii in period 3 is:

Na > Mg > Al > Si > P > S > Cl But, **Cl < Ar**

Q. No. 2 Part (iii)

MECHANISM:

STEP 1: Acid/Base reaction. Protonation of alcohlic -OH group to make it a better leaving group. This reaction is fast and reversible. Oxygen of -OH group attacks H^+ to form oxonium ion.

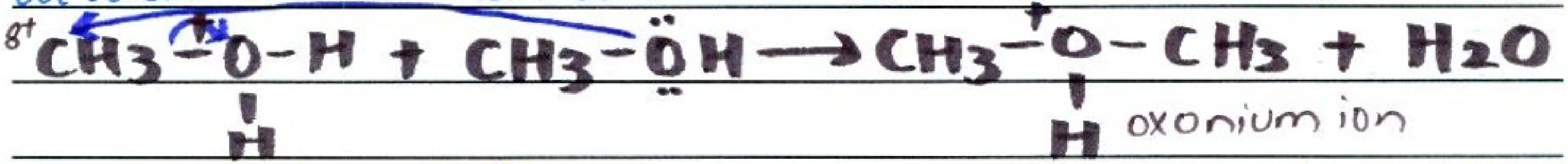


$$CH_3-\ddot{O}H + H^+ \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{+}{O}}-H$$

methanol

oxonium ion

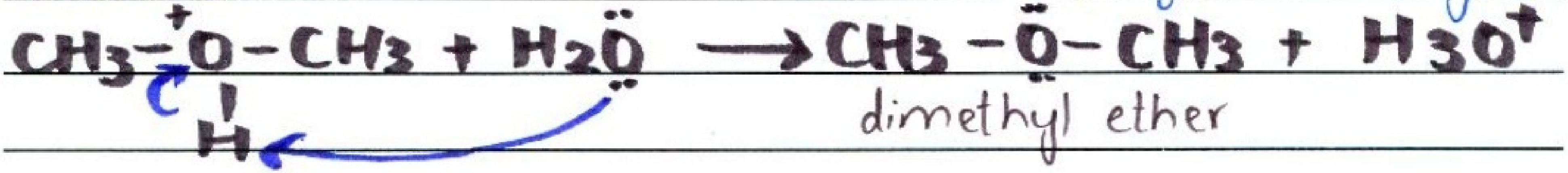
STEP 2: Oxygen atom of -OH group of other methanol attacks oxonium ion to form another oxonium ion intermediate



$$^{\delta+}CH_3-\underset{\underset{H}{|}}{\overset{+}{O}}-H + CH_3-\ddot{O}H \longrightarrow CH_3-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_3 + H_2O$$

oxonium ion

STEP 3: Attack of H_2O on oxonium ion to form dimethyl ether.



$$CH_3-\underset{\underset{H}{|}}{\overset{+}{O}}-CH_3 + H_2\ddot{O} \longrightarrow CH_3-\ddot{O}-CH_3 + H_3O^+$$

dimethyl ether

Q. No. 2 Part (iv) **PREPARATION OF BaO**

BaO is prepared either by heating barium with O_2 or by heating $BaCO_3$ at high temperature.

$$2Ba + O_2 \xrightarrow{\Delta} 2BaO$$

$$BaCO_3 \xrightarrow{\Delta} BaO + CO_2$$

BaO IS HEATED IN O_2:

When BaO is heated in O_2, at high temperature, Barium peroxide is formed.

$$2BaO + O_2 \xrightarrow{\Delta} 2BaO_2$$

REACTION OF BaO_2 WITH DIL. H_2SO_4

BaO_2 reacts with dil. H_2SO_4 to form Barium sulphate and hydrogen peroxide.

$$BaO_2 + H_2SO_4 \longrightarrow BaSO_4 + H_2O_2$$

Q. No. 2 Part (v) **REACTION OF V_2O_5**

- **HCl :** V_2O_5 reacts with HCl to form vanadium oxydichloride and Cl_2.

$$V_2O_5 + 6HCl \longrightarrow 2VOCl_2 + Cl_2 + 3H_2O.$$

- **HNO_3** = V_2O_5 reacts with HNO_3 to form metavanadic acid.

$$V_2O_5 + 2HNO_3 \longrightarrow 2HVO_3 + N_2O_5.$$

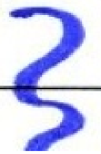
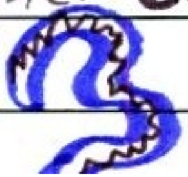
- **SO_2** = V_2O_5 oxidizes SO_2 to SO_3. This reaction occurs in contact process synthesis of H_2SO_4.

$$SO_2 + V_2O_5. \longrightarrow SO_3 + V_2O_4$$

$$V_2O_4 + \tfrac{1}{2}O_2 \longrightarrow V_2O_5$$ (**V_2O_5 as catalyst**)

Net $$SO_2 + \tfrac{1}{2}O_2 \xrightarrow{V_2O_5} SO_3$$

Q. No. 2 Part (vi)

SECONDARY STRUCTURE	TERTIARY STRUCTURE :
• The coiling and zigzagging of polypeptide chains result in secondary structure of protein.	• The folding and twisting of polypeptide chains result in tertiary structure of proteins.
• Polypeptide chains acquire α-helix or β-pleated sheets structure in secondary structure.	• Polypeptide chains acquire globular structure in tertiary structure.
• Secondary structure results due to H-bonding.	• Tertiary structure occurs due to H-bonding and ionic bonds.
Example: **Keratin / Actin**	Example: **Enzymes**
 	

Q. No. 2 Part (vii)

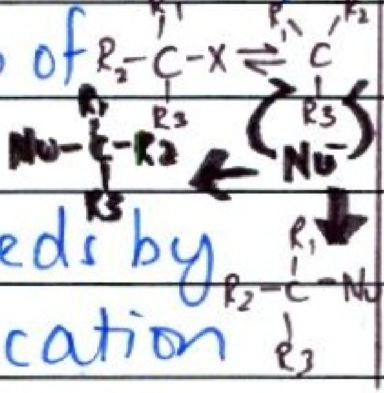
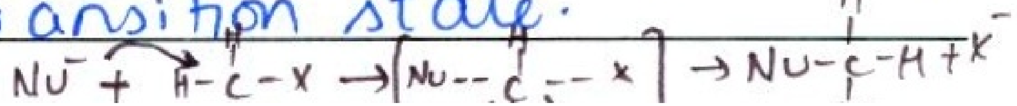
SIMILARITIES OF MEMBERS OF HOMOLOGOUS SERIES:

- All members of homologous series have same elements and functional group. e.g: all members of homologous series of alcohol has $-OH$ functional group.
- All members have same general formula. e.g: alkenes have C_nH_{2n}
- They have similar chemical properties and can be prepared by similar methods.

DIFFERENCE:

- Members of homologous series have slight different physical properties like melting point, boiling point, densities due to increase in hydrocarbon chain.

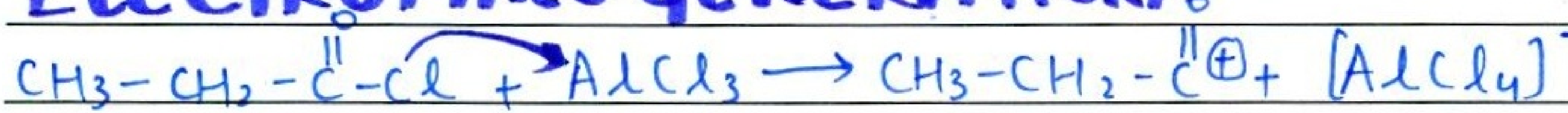
Q. No. 2 Part (viii)

S_N^1	S_N^2
• It is a unimolecular nucleophilic substitution reaction and is two step reaction.	It is a bimolecular nucleophilic substitution reaction and is one step reaction.
• In S_N^1, alkyl halide ionize reversibly to form carbocation and halide ion, before the attack of nucleophile.	In S_N^2, nucleophile directly attack on α- Carbon, followed by departure of halide ion.
• In S_N^1 50% inversion, 50% retention of configuration. 	In S_N^2 100% inversion of configuration takes place.
• Reaction proceeds by forming carbocation intermediate.	• Reaction proceeds by forming Transition state.  $Nu^- + H-\overset{H}{C}-X \rightarrow [Nu--\overset{H}{C}--X] \rightarrow Nu-\overset{H}{C}-H + X^-$

Q. No. 2 Part (ix)

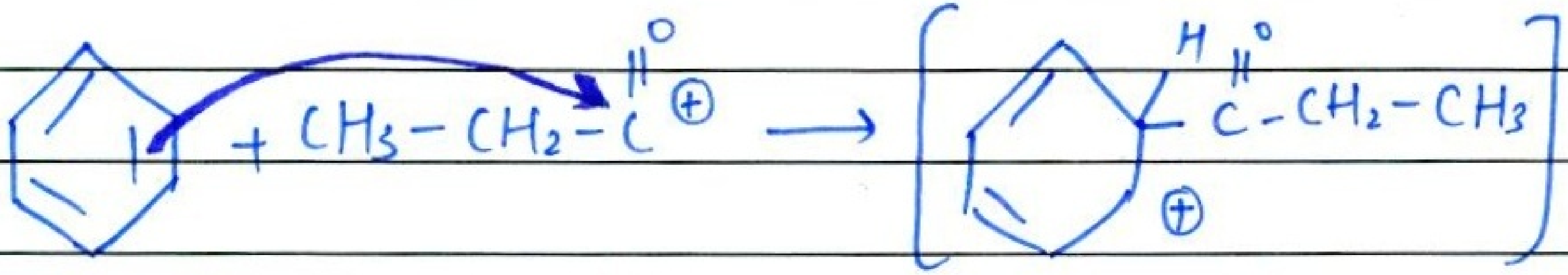
MECHANISM:

ELECTROPHILE GENERATION.



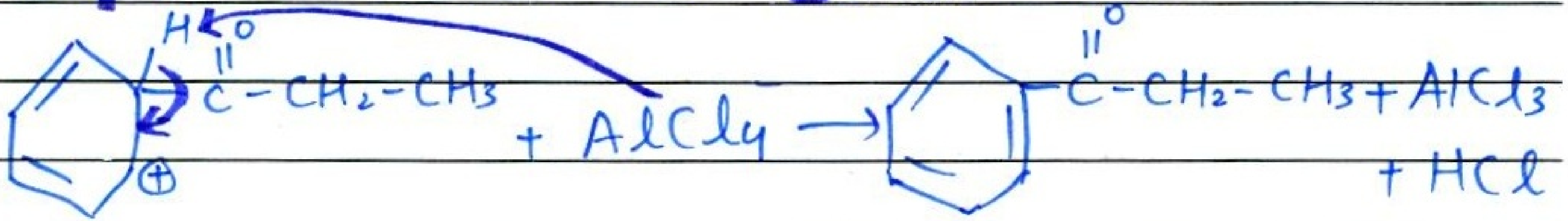
$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-Cl + AlCl_3 \longrightarrow CH_3-CH_2-\overset{O}{\overset{\|}{C}}^{\oplus} + [AlCl_4]^-$$

ATTACK OF ELECTROPHILE



Benzene.

REGENERATION OF CATALYST



Q. No. 2 Part (x) S_N2 REACTION MECHANISM

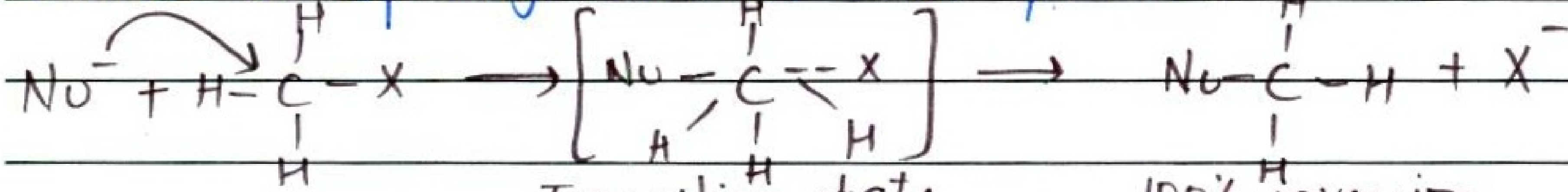
KINETIC EVIDENCE:

Experiments show that S_N2 reaction depends on the concentration of both alkyl halide and nucleophile. Thus, it is 2nd order reaction. It is bimolecular nucleophilic substitution reaction.

$$\text{Rate} = K[R-X][Nu^-]$$

STEREOCHEMICAL EVIDENCE:

In S_N2 reaction, back side attack of nucleophile on α - carbon along with complete inversion of configuration takes place. Carbon atom in transition state is sp^2 hybridized and planar.



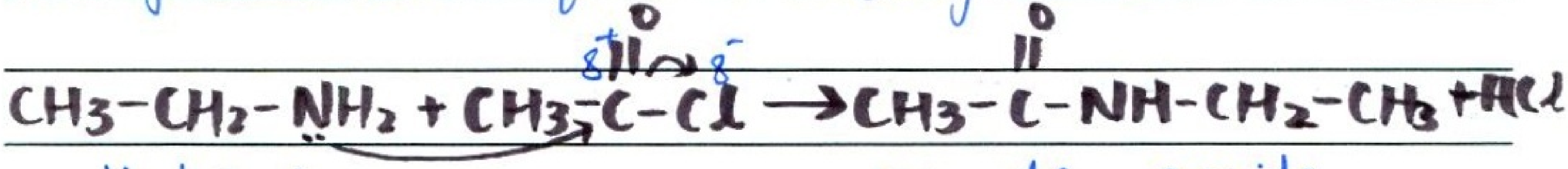
Transition state

100% inversion.

Q. No. 2 Part (xi)

REACTIONS OF $CH_3-CH_2-NH_2$

- **ACETYL CHLORIDE**: Ethyl amine reacts with acetyl chloride to form secondary amide.



$$CH_3-CH_2-\ddot{N}H_2 + CH_3-\overset{\overset{O}{\|}}{C}-Cl \rightarrow CH_3-\overset{\overset{O}{\|}}{C}-NH-CH_2-CH_3 + HCl$$

ethyl amine secondary amide.

- **ACETELDEHYDE**: Ethyl amine reacts with aceteldehyde to form Schiff's base (imine).

$$\begin{matrix}CH_3\\H\end{matrix}\!>C=\boxed{O + H_2}N-CH_2-CH_3 \rightarrow \begin{matrix}CH_3\\H\end{matrix}\!>C=N-CH_2-CH_3 + H_2O$$

aceteldehyde imine.

- **HNO_2/HCl**: Ethyl amine reacts with HNO_2/HCl to form diazonium compound.

$$CH_3-CH_2-NH_2+HNO_2 \xrightarrow[0-5°C]{HCl} CH_3-CH_2-\overset{+}{N}\equiv N\overset{-}{Cl}+2H_2O$$

ethyl amine. diazonium compound.

Q. No. 2 Part (xii) **PREPARATION OF DIMETHYL ETHER:**

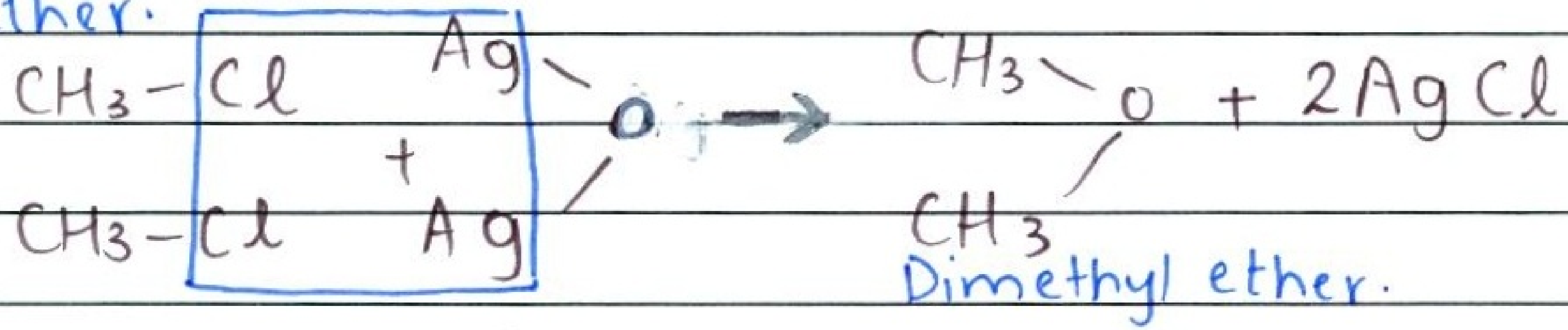
- **WILLIAMSON'S SYNTHESIS:** Methanol reacts with sodium to form sodium methoxide which reacts with methyl chloride to form dimethyl ether.

$$2CH_3-OH + 2Na \longrightarrow 2CH_3-\overset{-}{O}\overset{+}{Na} + H_2.$$

$$CH_3\overset{-}{O}\overset{+}{Na} + \overset{\delta+}{CH_3}-\overset{\delta-}{Cl} \longrightarrow CH_3-O-CH_3 + NaCl.$$

sodium methoxide methyl chloride dimethyl ether.

- **ALKYL HALIDE:** Two molecules of methyl chloride react with dry Ag_2O to form dimethyl ether.



Dimethyl ether.

Q. No. 2 Part (xiii)

REACTION OF 1- PROPANOL.

• $SOCl_2$

$CH_3-CH_2-CH_2-OH + SOCl_2 \longrightarrow CH_3-CH_2-CH_2-Cl + SO_2 + HCl.$

1-propanol — propyl chloride.

• Conc. H_2SO_4/ 180°C

$CH_3-CH_2-CH_2-OH + Conc.H_2SO_4 \xrightarrow[180°C]{} CH_3=CH=CH_2 + H_2O$

1-propanol — 1-propene.

• $K_2Cr_2O_7$/ H_2SO_4

$CH_3-CH_2-CH_2-OH + [O] \xrightarrow[50°C]{K_2Cr_2O_7/H_2SO_4} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-H$

1-propanol — propanal

$CH_3-CH_2-CHO + [O] \xrightarrow[50°C]{K_2Cr_2O_7+H_2SO_4} CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH$

propanal — propanoic acid.

Q. No. 2 Part (xiv) **APPLICATIONS OF IODOFORM:**

(1) Iodoform test is used to distinguish ethanol from methanol. Ethanol reacts with NaOH/I_2 to form yellow ppt. of CHI_3 whereas methanol don't.

$CH_3-CH_2-OH + 4I_2 + 6NaOH \rightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$.

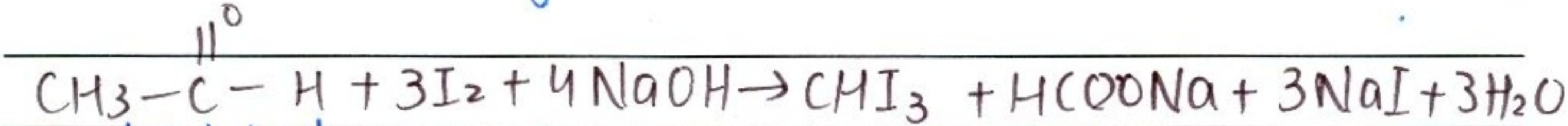
ethanol

Yellow ppt.

$CH_3-OH + 4I_2 + 6NaOH \rightarrow$ **No Yellow ppt.**

methanol

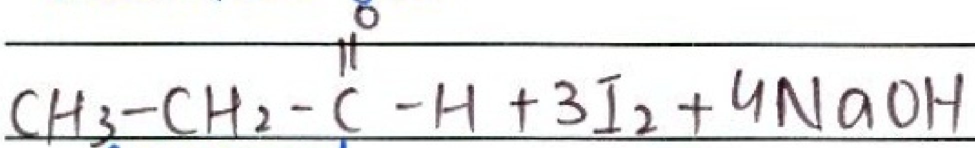
(2) Iodoform test is used to distinguich aceteldehyde from other aldehydes.



$CH_3-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \rightarrow CHI_3 + HCOONa + 3NaI + 3H_2O$

Aceteldehyde

Yellow ppt.



$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-H + 3I_2 + 4NaOH \rightarrow$ **No Yellow ppt**

Propanal.

Q. No. 3 (Page 1) **POLYMERIZATION:**

The process in which small organic molecules known as monomer combined to form large organic molecule is called polymerization. The larger molecules thus produced are called polymers.

TYPES OF POLYMERIZATION:

- Addition polymerization
- Condensation polymerazation.

Condensation Polymerization: (Step-growth)

In condensation polymerization, monomers combine to produce polymers which usually eliminates water or CH_3-OH.

Example:

polyesters, polyamides.

Nylon-6,6 is the most common polyamide. It involves combination of adipic acid and hexamethylence diamine at 2000°C. Nylon-6,6 derives its name from its two starting materials adipic acid and hexamethylene diamine. Both consist of 6 carbon atom.

Nylon-6,6 was prepared as synthetic fiber and for stocking and wearing apparell. It was introduced in New York Public Affairs

Q. No. 3 (Page 2) in 1939. Nylon 6-6 is used in the preparation of fibres for clothing and carpeting, filaments for fishing lines and ropes and bristles for brushing.

$$\underset{\text{Adipic acid}}{HOOC(CH_2)_4COOH} + \underset{\text{Hexamethylene diamine.}}{H_2N(CH_2)_6NH_2}$$

$$\Big\downarrow \text{ Heating (2000°C)}$$

$$-OC(CH_2)_4CONH(CH_2)_6NH-$$

$$\Big\downarrow \text{ Polymerization}$$

$$\underset{\text{Nylon-6,6}}{\left[O(CH_2)_4CONH(CH_2)_6NH \right]_n}.$$

ADDITION POLYMERIZATION (Chain-Growth).

Addition polymers are combination of alkene monomers to produce single huge molecule only.

These reactions are catalyzed by peroxides and acids and require **1000 atm. pressure and 2000°C temp.**

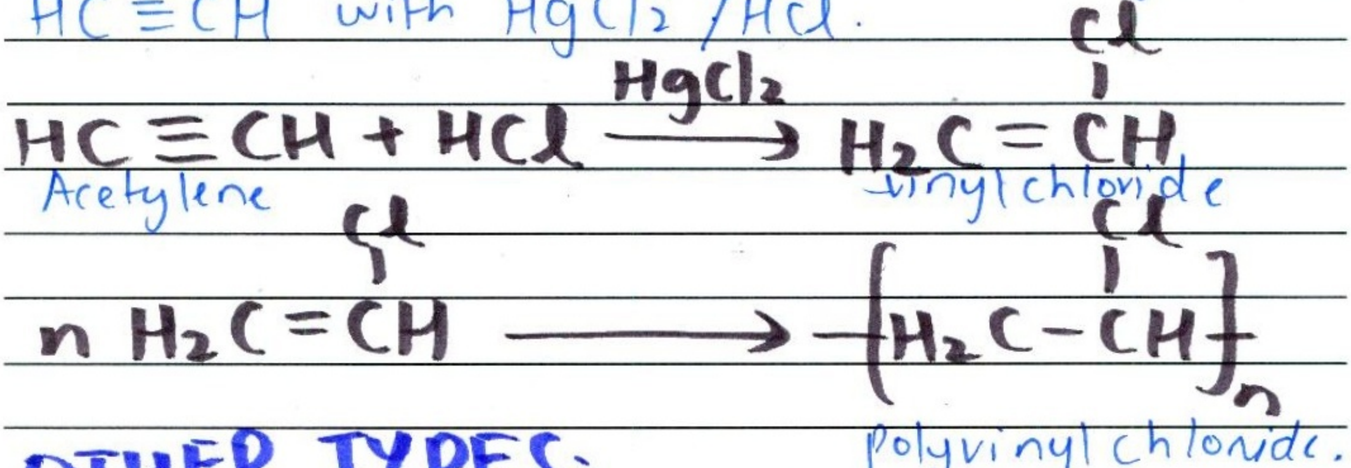
Much lower temp. and pressure can be used with Zeiglar catalysts which are **Trialkylaluminium $Al(R)_3$ and Titanium Tetrachloride $TiCl_4$**

Q. No. 3 (Page 3) The backbone of polymer is formed by Carbon atoms originally forming double bonds. No molecule is lost. Molecules simply add into one another.

Example:
polyvinylchloride and polyethylene.

PVC: Polyvinylchloride is formed by combination of vinyl chloride. PVC is used as immitation of leather, corrugated roofing material, gramophone records.

vinyl chloride is formed by reaction of HC≡CH with $HgCl_2$ / HCl.



$$\underset{\text{Acetylene}}{HC \equiv CH} + HCl \xrightarrow{HgCl_2} \underset{\text{vinyl chloride}}{H_2C = \overset{Cl}{\overset{|}{C}}H}$$

$$n\, H_2C = \overset{Cl}{\overset{|}{C}}H \longrightarrow \underset{\text{Polyvinyl chloride.}}{\left[H_2C - \overset{Cl}{\overset{|}{C}}H \right]_n}$$

OTHER TYPES:
Polymers formed by combination of same momomers are called homopolymers. e.g: polyethylene. Polymers formed by combination of different monomers are called copolymers. Thermoplastic polymers soften on heating and hard on cooling. e.g: polythene
Themosetting polymer get hard on heating and cannot be soft. e.g: Bakelite

HALOGEN AS OXIDIZING AGENT:

Halogen act as powerful oxidizing agent due to their high electron affinity and tendency to accept electrons. Therefore they themselves reduce and oxidize other substances.

Oxidizing property of halogens can be shown by following equation.

$$\frac{1}{2}X_2 + e^- + H_2O \longrightarrow X^- + \text{Energy.}$$

RELATIVE POWER:

As electron affinity decreases from F to I. So, oxidizing strength also decreases in this direction. The relative power of oxidizing strength of halogen decreases in the following direction.

$$F_2 > Cl_2 > Br_2 > I_2$$

As F_2 has highest oxidizing power, it can ~~reduce~~ oxidize all halide ion to corresponding halogens. In other words, it can displace all halogen from their halides.

F_2 has highest oxidizing power due to these reasons:-

- Low bond dissociation energy of F_2.
- High hydration energy due to small F^-
- High heat of vaporization.

- High standard reduction potential.

PROOFS:

F_2 can oxidize all halides to halogens.

$F_2 + 2NaCl \longrightarrow 2NaF + Cl_2$.

$F_2 + 2NaBr \longrightarrow 2NaF + Br_2$

$F_2 + 2NaI \longrightarrow 2NaF + I_2$.

In other words:

$F_2 + 2X^- \longrightarrow 2F^- + X_2$

where $[X = Cl, Br, I]$

Cl_2 can oxidize only Br^- and I^-

$Cl_2 + 2NaBr \longrightarrow 2NaCl + Br_2$

$Cl_2 + 2NaI \longrightarrow 2NaCl + I_2$

In other words:

$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2$

where $[X = Br, I]$

Br_2 can oxidize only I^-

$Br_2 + 2NaI \longrightarrow 2NaBr + I_2$

I_2 cannot oxidize anyone.

Therefore strength of oxidizing power is proved as:

$F_2 > Cl_2 > Br_2 > I_2$.

Q. No. 5 (Page 1)

TRENDS IN PERIOD 3 ELEMENT:

• IONIZATION POTENTIAL:

The minimum amount of energy required to remove 1 mole of loosely held electrons from 1 mole of gaseous atoms to form 1 mole of unipositive ion.

$$X_{(g)} \longrightarrow X^{+}_{(g)} + 1e^{-}$$

FACTORS:

Ionization energy depends on following factors.

- Atomic size
- Shielding effect.
- Nature of orbital
- Effective nuclear charge.

TREND IN PERIOD 3:

As we move from left to right in period 3, due to decrease in atomic size and increase in nuclear charge ionization energy increases, but there are certain anamolous trends.

ANAMOLOUS TRENDS:

Ionization energy of Mg and P are higher than Al and S respectively.

- Mg and Al

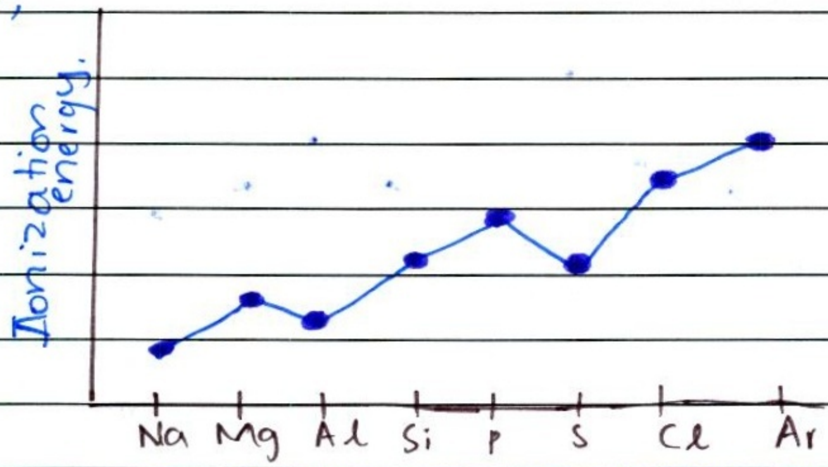
In case of Mg ($1s^2 2s^2 2p^6 3s^2$), it is difficult to remove electron from completely filled low energy 3s orbital. In Al ($1s^2 2s^2 2p^6 3s^2 3p^1$) it is easier to remove electron from partially filled 3p orbital. Thus ionization energy of Mg is higher than Al.

- **P and S :**

In S ($1s^2 2s^2 2p^6 3s^2 3p_x^2 3p_y^1 3p_z^1$), there is a pair of electron in 1 orbital of 3p wherea in posphorus ($1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$), it is no paired electron in 3p orbital. Due to presence of paired electrons in S, their repulsion increases and removal of electron becomes easy.

Also, in P 3p subshell is half filled while in S it is partially filled. Half-filled p-subshell in P enhances I.E.

Thus,



MELTING AND BOILING POINT:

Melting and boiling point is strength of intermolecular forces.

TREND IN PERIOD 3:

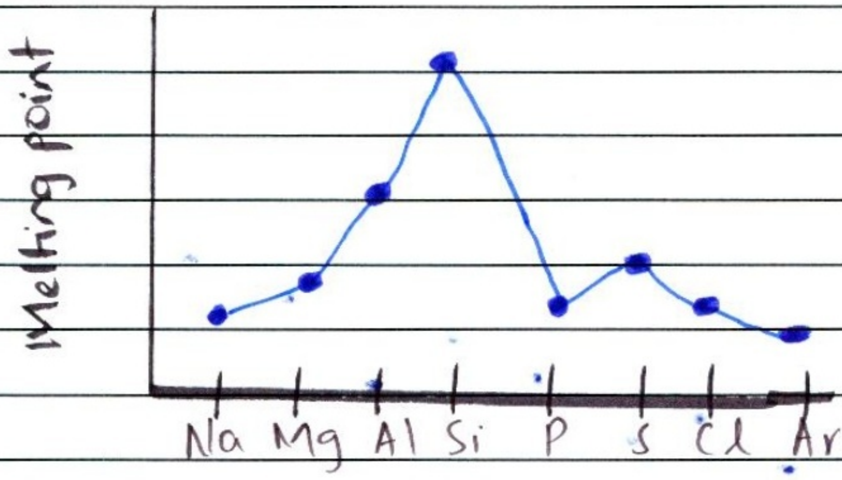
In period 3, melting and boiling point increases up to middle i.e, Group IVA and then decrease.

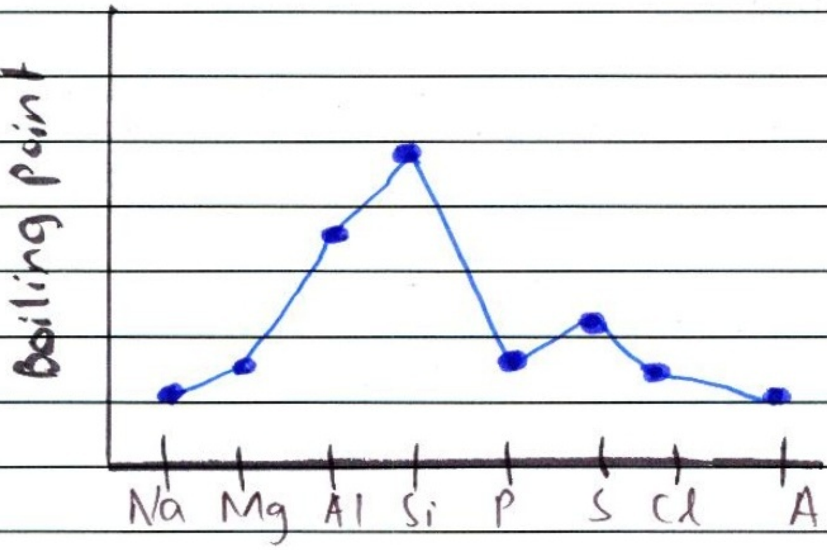
Q. No. 5 (Page 3)

REASON:

- Melting and boiling point increase upto Group III-A due to increase in number of binding electrons and silicon has giant covalent structure
- P, S, Cl, Ar have low melting and point, ~~thus~~ due to the reason that they have simple covalent structure existing as molecules.
- S_8 has higher boiling/melting point than P_4.

$Na < Mg < Al < Si > P_4 < S_8 > Cl_2 > Ar$.

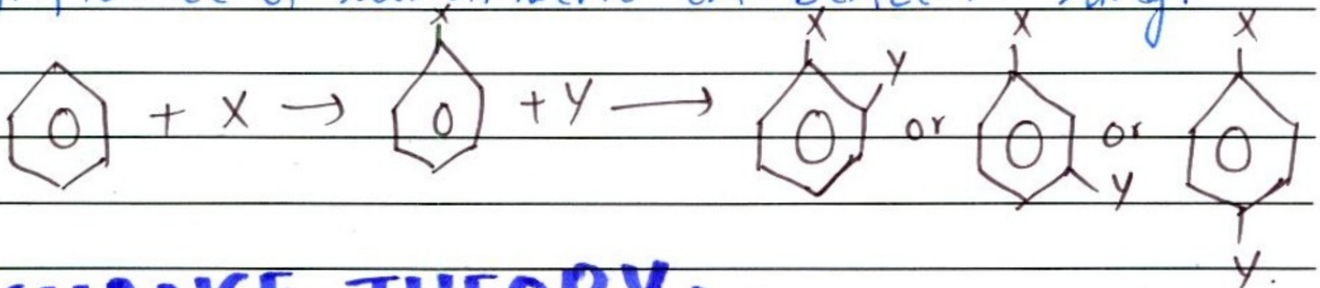




DIRECTIVE INFLUENCE OF SUBSTITUENTS (ORIENTING EFFECT).

When electrophilic substitution reaction takes place on benzene ring only one kind of monosubstitude benzene is formed as all 6 positions are equivalent. But when second substitutent is inserted its position depends on nature of first substituent.

The second substituent is inserted at ortho, meta and para position depending on 1st substituent. This is called directive influence of substituent on benzene ring.



CHANCE THEORY:

According to chance theory, the proportion of disubstituded product will be 40% ortho, 40% meta and 20% para.

However results do not agree with chance theory.

CLASSIFICATION OF SUBSTITUENTS.

Substituents are classified as:

- Ortho-para directing groups
- Meta directing groups.

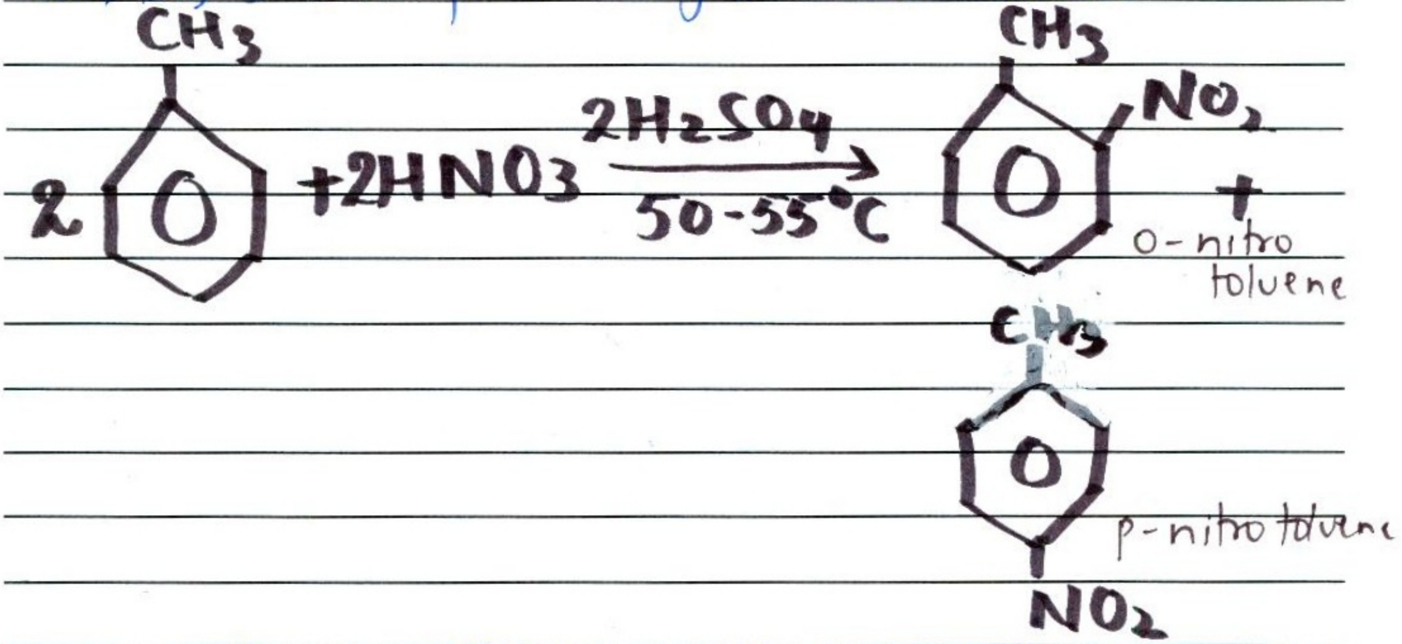
ORTHO-PARA DIRECTING GROUPS:

These groups donate electrons towards benzene ring at ortho and para positions. As a result, ortho and para position become electron rich and second substituent is inserted at ortho and para position. Therefore, these are called ortho-para directing groups. These activate benzene ring.

Examples:

−OH, −OR, −R, $-NH_2$, −Cl, −Br, −I e.t.c.

Cl, Br, I are partially deactivators.

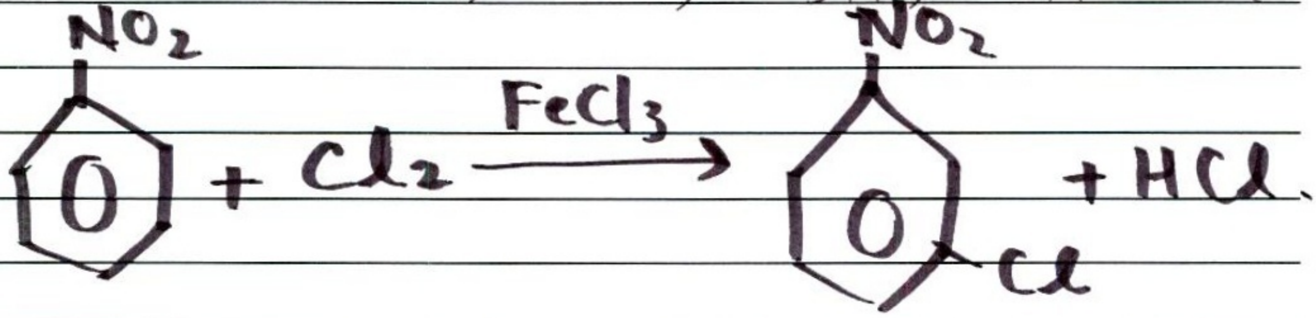


META DIRECTING GROUPS:

These groups withdraw electrons from benzene ring at ortho and para position. Therefore, ortho and para position become electron deficient as compared to meta position. Thus new substituent enters at meta position. These are known as meta directing groups. These deactivate benzene ring.

Example:

$-COOH$, $-NO_2$, $-SO_3H$, $-CHO$ e.t.c.



m- chloronitro benzene.