**Q. No. 2 Part (i)**

## $Fe^{+2}$ as a Catalyst:

The reaction between $S_2O_8^{-2}$ and $I^-$ can be catalysed in the presence of $Fe^{+2}$.

Reaction:- $S_2O_8^{-2} + 2I^- \xrightarrow{Fe} 2SO_4^{-2} + I_2$

Mechanism:-

1. $Fe^{+2}$ reduces persulphide ion, itself oxidesed.

$$S_2O_8^{-2} + 2Fe^{+2} \longrightarrow 2SO_4^{-2} + 2Fe^{+3}$$

2. $Fe^{+3}$ is reduced back to $Fe^{+2}$ by $I^-$ ions.

$$2Fe^{+3} + 2I^- \longrightarrow I_2 + 2Fe^{+2}$$

Since $Fe^{+2}$ is regenerated in the step 2, $Fe^{+2}$ acts as a catalyst

---

**Q. No. 2 Part (ii)**

## Acidic nature of $SO_3$

As $SO_3$ is acidic, it reacts with bases to form sulphates.

(i) $SO_3 + 2NaOH \longrightarrow Na_2SO_4 + H_2O$

$SO_3$ reacts with sodium hydroxide to form sodium sulphate.

(ii) $SO_3 + CaO \longrightarrow CaSO_4$

$SO_3$ reacts with Calcium oxide to form calcium sulphate.

**Q. No. 2 Part (iii)**

(a) $2NaOH + Cl_2O \longrightarrow 2NaOCl + H_2O$
Sodium chlorite

(b) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$
phosphorous acid

(c) $Na_2O_2 + 2H_2O \longrightarrow 2NaOH + H_2O_2$
hydrogenperoxide

---

**Q. No. 2 Part (iv)**

$KMnO_4$ acts as a strong oxidising agent

(i) With $FeSO_4$

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$[FeSO_4 + H_2SO_4 + [O] \longrightarrow Fe_2(SO_4)_3 + H_2O] \times 5$

$2KMnO_4 + 8H_2SO_4 + 5FeSO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$

(ii) With Mohr. Salt

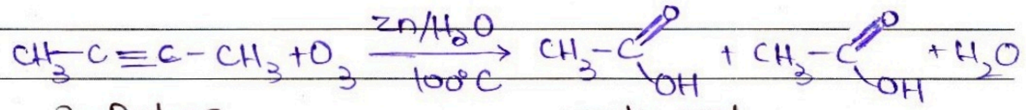
$2KMnO_4 + 7H_2SO_4 + 10(NH_4)_2SO_4 \cdot FeSO_4 \cdot 6H_2O \rightarrow K_2SO_4 + MnSO_4 + 68H_2O$
$+ 10(NH_4)_3SO_4 + 5Fe_2(SO_4)_3$

$KMnO_4$ oxidises $Fe^{+2}$ to $Fe^{+3}$

**Q. No. 2 Part (ix)**

**Ozonolysis** of **2-Butyne** can be used to prepare two molecules of acetic acid.

Alkynes react with ozone followed reaction with Zn and boiling $H_2O$ to produce carboxylic acids.

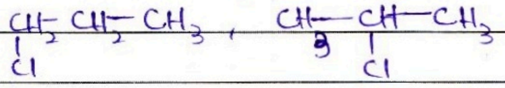


$$CH_3-C\equiv C-CH_3 + O_3 \xrightarrow[100°C]{Zn/H_2O} CH_3-C(=O)OH + CH_3-C(=O)OH + H_2O$$

2-Butyne acetic acid

**Q. No. 2 Part (v)** **Structural Isomerism**

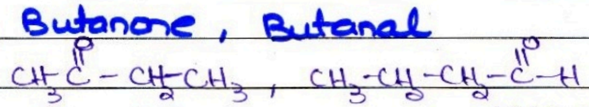
**(a) 1-Chloro propane , 2-Chloropropane**



$$\underset{|\atop Cl}{CH_2}-CH_2-CH_3 \ , \ CH_3-\underset{|\atop Cl}{CH}-CH_3$$

Position isomerism as -Cl group is present at different position with same molecular formula

**(b) Butanone , Butanal**



$$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_3 \ , \ CH_3-CH_2-CH_2-\overset{O}{\overset{\|}{C}}-H$$

Functional Group Isomerism (Aldehyde and ketone)

**(c) Diethyl ether and methyl propyl ether**

$C_2H_5-O-C_2H_5$ , $CH_3-O-CH_2-CH_2-CH_3$

Metamerism is present. (unequal distribution of Carbon atom on either side of functional group)

**Q. No. 2 Part (vi)** **Types of Protein**

**(a) Simple Protein:** Proteins which produce amino acids and their derivatives only on hydrolosis.
E.g Globulins, Histones

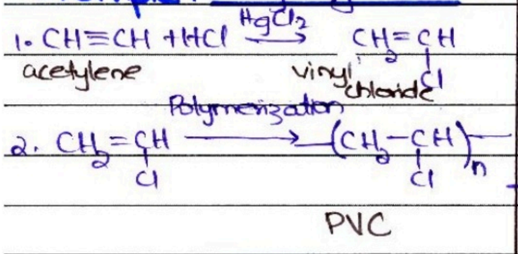
**(b) Conjugated Proteins:** Proteins which are conjugated or attatched to a non-protein group called "Prosthetic group".
E.g Mucoproteins, Nucleuproteins

**(c) Derived Proteins:** Proteins which are derived from simple and conjugated proteins.
Eg Proteans, proteosis, peptides.

**Q. No. 2 Part (vii)**

| **Pollutant** | **Sources** | **Impact** |
|---|---|---|
| Oxides of Nitrogen ($NO_x$) | - Bacterial action in soil<br>- Forest fires | - Decreased visability due to yellauish color of $NO_2$<br>- Causes cancer |
| Oxides of Sulphur ($SO_x$) | - Roasted sulphide ores<br>- Volcanic activity | - loss of green color in plants<br>- Acid rain |

**Q. No. 2 Part (viii)**

| **Addition Polymerization** | **Condensation Polymerization** |
|---|---|
| 1. Polymerization in which alkene monomers combine to form single large molecule only | 1. Polymerization in which monomers combine with elimination of small molecule like $H_2O$, $CH_3OH$ |
| 2. Also called "chain growth polymers" | 2. Also called "Step-growth polymers". |
| **Example:** Polyvinylchloride. | **Ex:** Nylon-6,6 |
|  1. $CH\equiv CH + HCl \xrightarrow{HgCl_2} \underset{Cl}{\underset{\vert}{CH_2=CH}}$ <br> acetylene, vinyl chloride <br> 2. $CH_2=\underset{Cl}{\underset{\vert}{CH}} \xrightarrow{Polymerization} -\!(CH_2-\underset{Cl}{\underset{\vert}{CH}})_n\!-$ <br> PVC | $HOOC(CH_2)_4COOH + H_2N(CH_2)_6NH_2$ <br> adipic acid, hexamethylene diamin <br> ↓ heat at 2000°C <br> $-\!(OC(CH_2)_4CONH(CH_2)_6NH)_n\!-$ <br> Nylon, 6-6 |

**Q. No. 2 Part (x)**

**Basic strength of amines:**

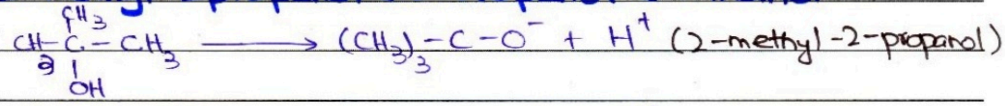
Secondary amine > Primary amine > Tertiary amine

- Presence of electron-donating alkyl groups increases the basicity of amines by pushing electrons towards the nitrogen atom. Hence, secondary amines are more basic than primary amines.
- However, even though electron density is increased in tertiary amines by presence of three alkyl groups, the presence of three bulky groups hinders the approach of proton towards nitrogen atoms. Hence, basic strength of tertiary amines is lowest.

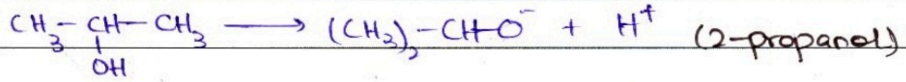
**Q. No. 2 Part (xi)**

Increasing order of reactivety towards cleavage of O—H:-

**2-Methyl-2propanol< 2-Propanol < Ethanol**



$CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_3 \longrightarrow (CH_3)_3-C-O^- + H^+$ (2-methyl-2-propanol)



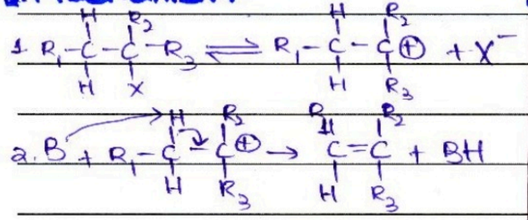
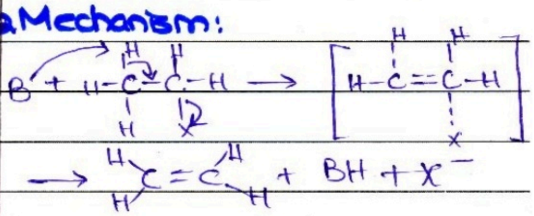
$CH_3-\underset{OH}{CH}-CH_3 \longrightarrow (CH_2)_2-CH-O^- + H^+$ (2-propanol)

$CH_3-CH_2-OH \longrightarrow CH_3-CH_2-O^- + H^+$ (ethanol)

Cleavage of O—H bonds involves formation of alkoxide ion ($RO^-$). The presence of electron-donating R-group unstablises the ion, reducing reactivety.

∴ Ethanol with least R-group is most reactive while 2-methyl-2-propanol with 3-R-groups is least reactive

**Q. No. 2 Part (xii)**

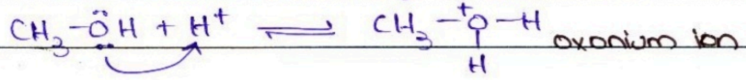
| **E₁** | **E₂** |
|---|---|
| 1. It is unimolecular elimination reaction. | 1. It is biomoleacular elimination reaction |
| 2. **Mechanism:**  | 2. **Mechanism:**  |
| 3. Tertiary alkyl halides are preffered because of formation of carbocation | 3. Primary alkyl halides are preffered to facilitate the attack of base. |
| 4. First-order reaction. Rate = k[R—X] | 4 Second-order reaction Rate = k[R—X][B] |

**Q. No. 2 Part (xiii)**

$$2CH_3OH \xrightarrow[140°C]{H_2SO_4} CH_3OCH_3 + H_2O$$

Mechanism :-

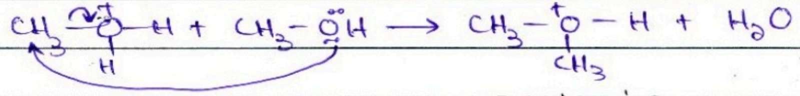
1. Proton-abstraction by oxygen atom:



$$CH_3-\ddot{O}H + H^+ \rightleftharpoons CH_3-\overset{+}{O}(H)-H$$

oxonium ion

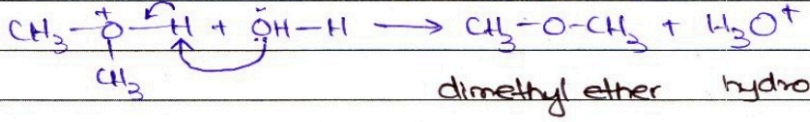
2. Nucleophillic attack:



$$CH_3-\overset{+}{O}(H)-H + CH_3-\ddot{O}H \longrightarrow CH_3-\overset{+}{O}(CH_3)-H + H_2O$$

oxonium ion

3. Proton abstraction (Formation of ether)



$$CH_3-\overset{+}{O}(CH_3)-H + \ddot{O}H-H \longrightarrow CH_3-O-CH_3 + H_3O^+$$

dimethyl ether hydroxonium ion

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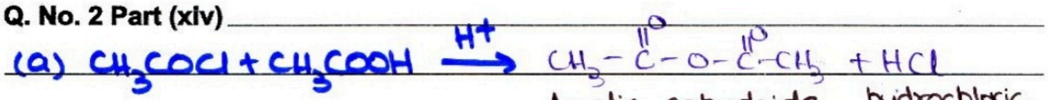
**Q. No. 2 Part (xiv)**

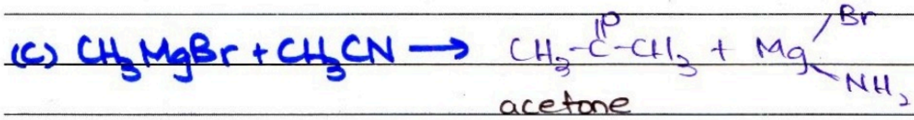


(a) $CH_3COCl + CH_3COOH \xrightarrow{H^+} CH_3-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-CH_3 + HCl$

Acetic anhydride hydrochloric acid

(b) $CH_3COOC_2H_5 + LiAlH_4 \longrightarrow CH_3CH_2OH + CH_3CH_2OH$

ethanol ethanol



(c) $CH_3MgBr + CH_3CN \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + Mg\begin{smallmatrix}Br\\NH_2\end{smallmatrix}$

acetone

aminomagnesiumbromide

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

# MASS SPECTROMETRY

**Prinaple:** Mass spectrometry involves formation of gaseous ions of istopes of element and organic molecule, then separate according to m/z ratio and measurement of intensity in the form of spectrum.

## Application:

1. Mass spectrometer is a device extensively used for detection and identification of isotopes of an element and measurement of relative abundance
2. It is also used to identify structure of organic compounds.
3. It is used to calculate relative atomic mass of an element.

## Working:

1. Vapourization: Sample is usually injected as a gas, but if solid or liquid is introduced, it is evaporated in vapourization chamber.
2. Ionization: Conversion of gaseous atoms and molecules to gaseous positive ions by bombardment of high speed electrons (70 eV)
3. Acceleration: The cations are accelerated by applying an electric field of negative potential (500-2000 V)

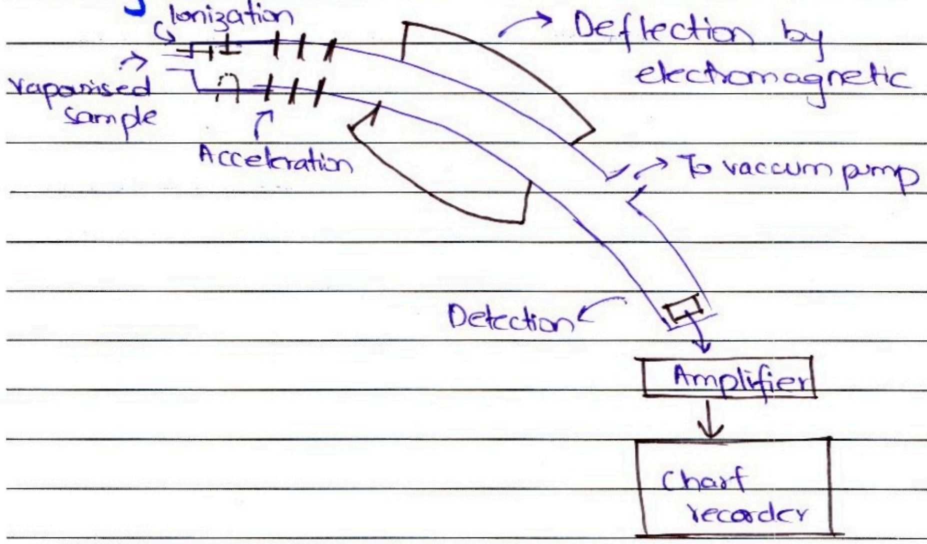
**Q. No. 3 (Page 2)**

4. Deflection: Cations are deflected by applying variable magnetic field according to m/z ratio. The angle of deflection of cations ~~depen~~ is inversely proportional to m/z ratio.

5. Detection:

Ions of a particular m/z ratio are collected and amplified by an electron multiplier which can count the number of ions striking it.

**Diagram:**



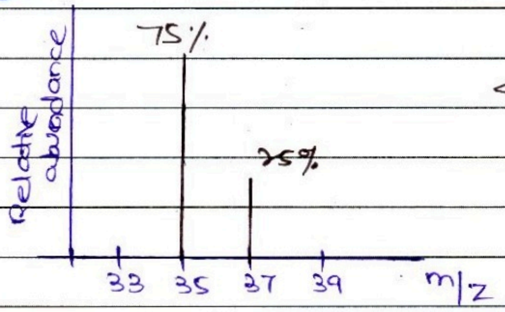
**Relative Atomic Mass:**

- Number of peaks indicate the possible number of isotopes of element
- Height of peaks is proportional to the relative abundance of isotope

**Q. No. 3 (Page 3)**

- The relative atomic mass of an element is the average of the masses of isotopes.

**Example:**



<< Istopes of chlorine

Chlorine has 2 istopes in the ratio 3:1.

Relative atomic mass of chlorine $= \frac{75\% \times 35 + 25\% \times 37}{2}$

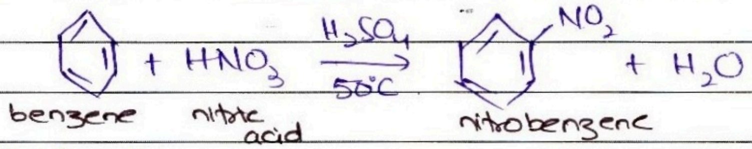
$= 35{\cdot}2$

Q. No. 4 (Page 1)

# NITRATION

**Def:** Substitution of $-NO_2$ group to benzene ring is called nitration reaction.

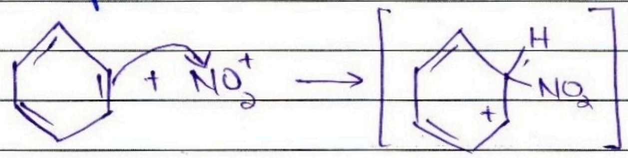
## General Reaction:



## Mechanism:

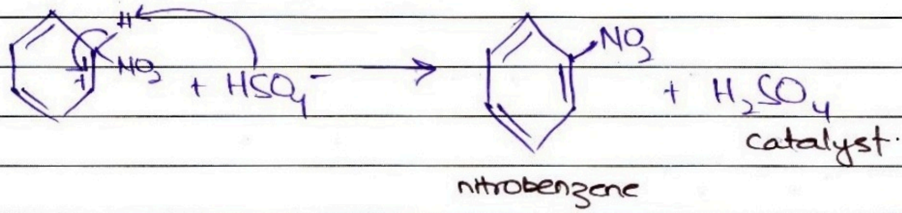
1. $HNO_3 + H_2SO_4 \rightleftharpoons \underset{\text{electrophille}}{NO_2^+} + HSO_4^- + H_2O$

## 2. Nucleuophillic attack:



phenonium ion (intermediate)

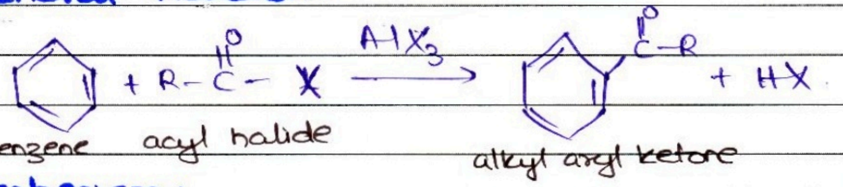
## 3. Regeneration of Catalyst:



# FRIEDEL CRAFT ACYLATION

**Def:** Substitution of acyl group $\left(R-\overset{O}{\overset{\|}{C}}-\right)$ to benzene ring is called fiedal craft acylation.

**General Reaction:**

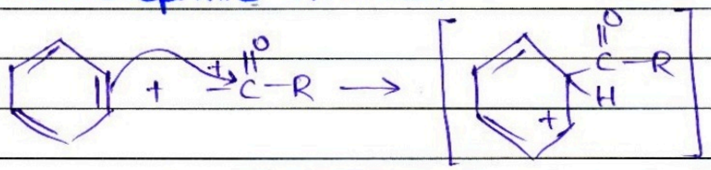


**Mechanism:**

**(1) Generation of strong electrophile:**

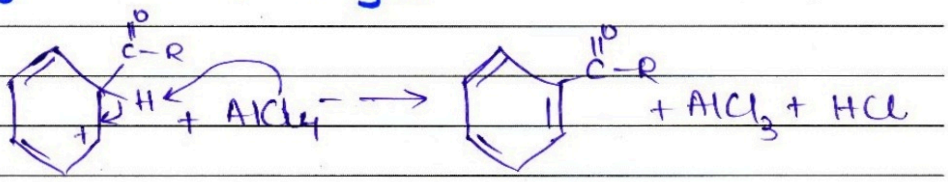
$$R-\overset{O}{\overset{\|}{C}}-X + \underset{\text{catalyst}}{AlCl_3} \longrightarrow R-\overset{O}{\overset{\|}{C}}^{+} + AlCl_4^{-}$$

**(2) Nucleophilic Attack:**



phenonium ion (Intermediate)

**(3) Regeneration of Catalyst:**

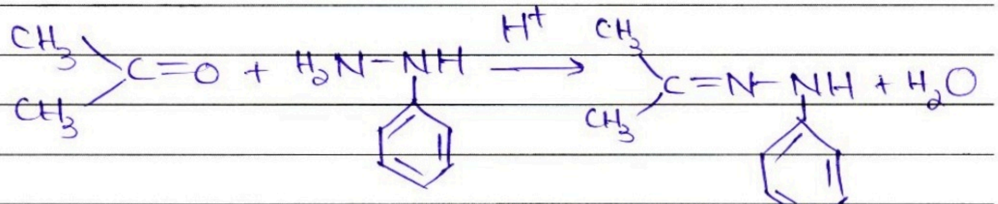


**Q. No. 4 (Page 3)**

~~ACID CATALYSED REACTION OF CARBONYL COMPOUNDS WITH AMMONIA DERIVATIVES~~

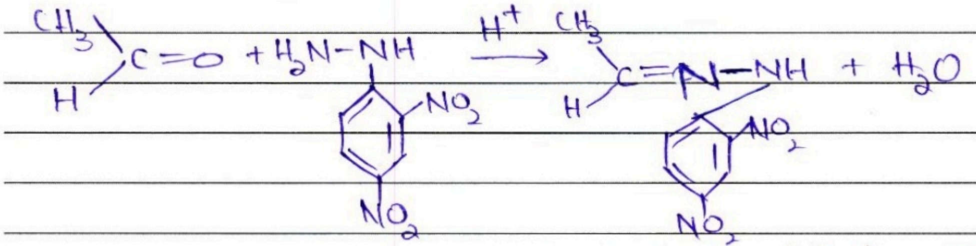
# REACTION OF CARBONYL COMPOUNDS WITH AMMONIA DERIVATIVES :-

(1) Acetone and Phenyl hydrazine



Acetone phenyl hydrazone

(2) Acetaldehyde and 2,4 - DNPH

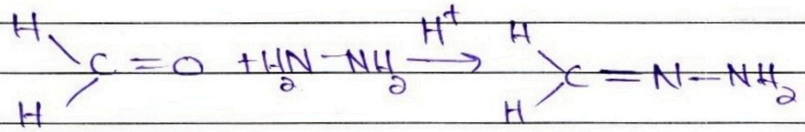


2,4- dinitrophenyl hydrazone

2,4 - dinitrophenyl hydrazone forms yellow/orange precipitate. This is an identifyng test for aldehydes and ketones.

**Q. No. 5 (Page 2)**

(3) Formaldehyde and Hydrazine



Formaldehyde hydrozone

**Q. No. 5 (Page 3)**

# ACIDIC STRENGTH OF ALCOHOLS, PHENOLS AND CARBOXYLIC ACIDS

**Order of Acidic Strength:**

RCOOH > Phenol > Alcohol

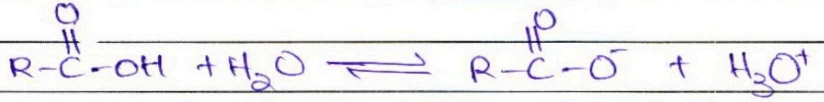
**$P_{K_a}$ Values**

RCOOH ($P_{ka} \approx 5$) is strongest acid while phenol ($P_{ka} \approx 10$) is stronger acid than alcohol ($P_{ka} \approx 16-20$) which is weakest acid.

**Conjugate bases:**

$$R-OH + H_2O \rightleftharpoons \underset{\text{alkoxide}}{R-O^-} + H_3O^+$$

$$C_6H_5-OH + H_2O \rightleftharpoons \underset{\text{phenoxide}}{C_6H_5-O^-} + H_3O^+$$



$$R-\overset{\overset{O}{\|}}{C}-OH + H_2O \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^- + H_3O^+$$

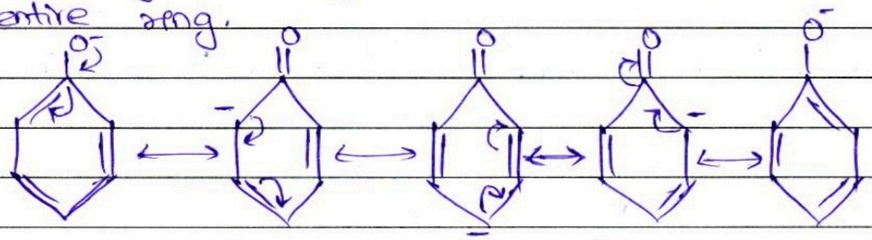
carboxylate ion

**Resonant Structures:**

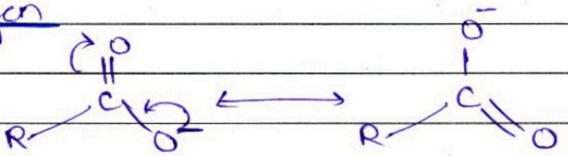
Alkoxide has no resonant structures. The negative charge on oxygen atom is localised, hence its unstable and least acidic.

**Q. No. 6 (Page 2)**

Phenoxide is more stable than alkoxide since the negative charge is delocalised over the entire ring.

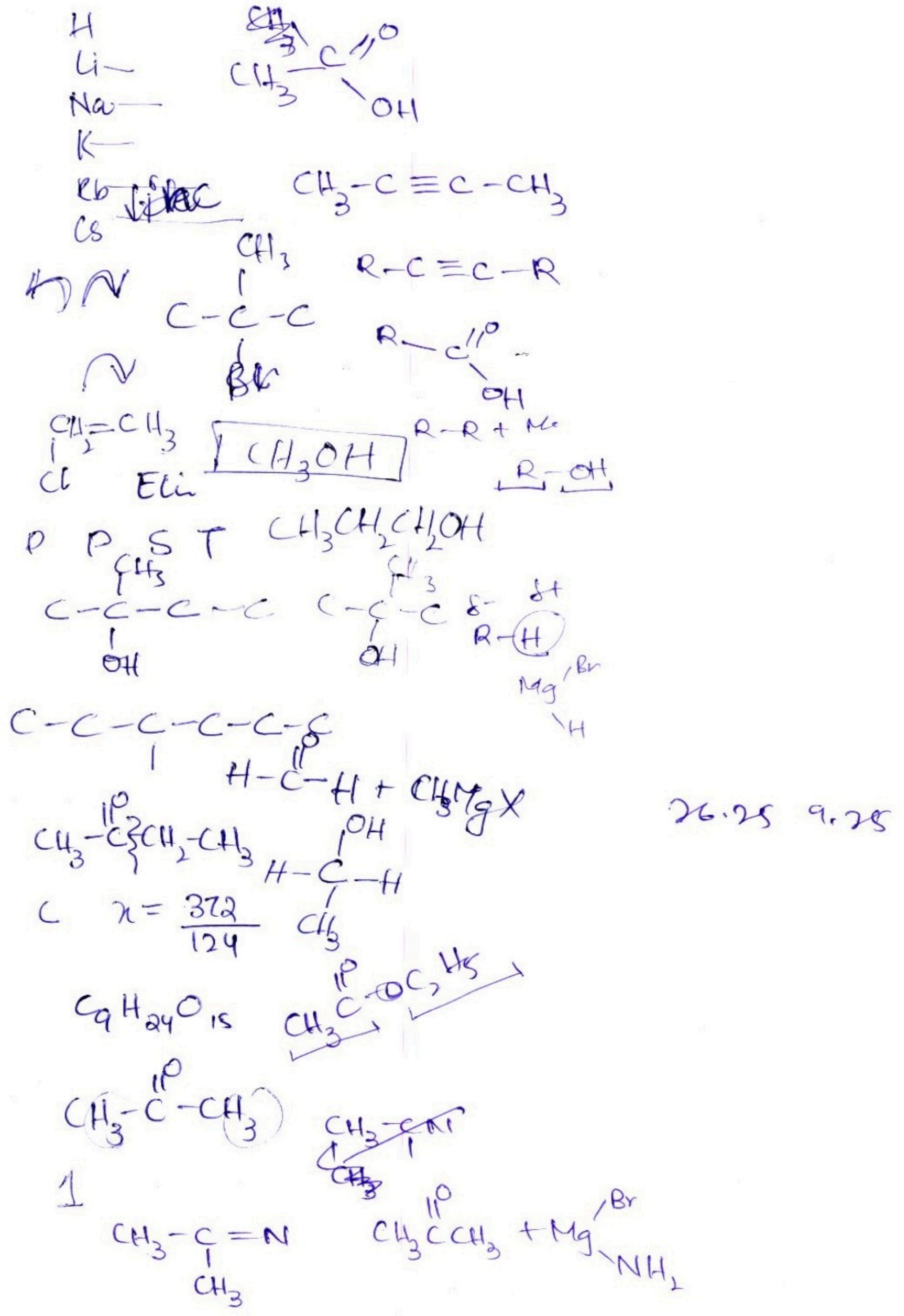


Carboxylate ion is most stable conjugate base because negative charge spreads from oxygen to oxygen



Both these structure are equivalent resonance contributors, hence RCOOH is strongest acid. While in phenoxide, the resonant structures are minor contributors.

**Q. No. 6 (Page 3)**


H
Li
Na
K
Rb
Cs
CH3-C(=O)OH
CH3-C≡C-CH3
R-C≡C-R
R-C(=O)OH
CH2=CH3
Cl
Eli
CH3OH
R-R + Mg
R-OH
P P S T
CH3CH2CH2OH
δ- δ+
R-H
Mg Br H
H-C(=O)-H + CH3MgX
26.25 9.25
CH3-C(=O)-CH2-CH3
H-C(OH)(CH3)-H
C x = 372/124
C9H24O15
CH3C(=O)-OC2H5
CH3-C(=O)-CH3
1
CH3-C(CH3)=N
CH3C(=O)CH3 + Mg Br NH2