Inter (Part-II) 2016

Chemistry	Group-I	PAPER: II
Time: 20 Minutes	(OBJECTIVE TYPE)	Marks: 17

Note: Four possible answers, A, B, C and D to each question are given. The choice which you think is correct, fill that circle in front of that question with Marker or Pen ink in the answer-book. Cutting or filling two or more circles will result in zero mark in that question.

1-1- Which compound is more soluble in water:

(a) C_2H_5OH √ (b) C_6H_5OH

(c) CH_3COCH_3 (d) n-Hexanol

2- The reaction between fat and NaOH is called:

(a) Esterification (b) Hydrogenolysis

(c) Saponification √ (d) Fermentation

3- Oxidation of NO in air produces:

(a) N_2O (b) N_2O_3

(c) N_2O_4 √ (d) N_2O_5

4- Ammonium nitrate fertilizer is not used for which crop:

(a) Paddy rice √ (b) Cotton

(c) Wheat (d) Sugarcane

5- Synthetic rubber is made by polymerization of:

(a) Chloroprene √ (b) Chloroform

(c) Acetylene (d) Divinyl acetylene

6- Peroxyacetylnitrate is an irritant to human beings and it affects:

(a) Eyes √ (b) Ears

(c) Stomach (d) Nose

7- Which of the following is a typical transition metal:

(a) Si (b) Y

(c) Ra (d) Co √

8- The mineral $CaSO_4 . 2H_2O$ has the general name:

(a) Dolomite (b) Gypsum √

(c) Calcite (d) Epsom salt

9- The carbon atom of a carboxyl group is hybridized:

(a) sp
(b) sp^2 √
(c) sp^3
(d) dsp^2

10- Which of the following derivative cannot be prepared directly from acetic acid:

(a) Acetamide √
(b) Acetyl chloride
(c) Acetic anhydride
(d) Acetic acid

11- During nitration of benzene, the active nitrating agent is:

(a) NO_3
(b) NO_2^+ √
(c) NO_2^-
(d) HNO_3

12- Tincal is a mineral of:

(a) Al
(b) B √
(c) Si
(d) C

13- In t^0-Butyl alcohol, the tertiary carbon is bonded to:

(a) One hydrogen atom
(b) No hydrogen atom √
(c) Three hydrogen atoms
(d) Two hydrogen atoms

14- Which halogen occurs naturally in a positive oxidation state:

(a) Fluorine
(b) Chlorine
(c) Bromine
(d) Iodine √

15- For which mechanism, the first step involved is the same:

(a) E1 and E2
(b) E2 and S_N2
(c) S_N1 and E2
(d) E1 and S_N1 √

16- Newspaper can be recycled again and again by how many times:

(a) 2
(b) 3
(c) 4
(d) 5 √

17- Choose the correct statement:

(a) Na^+ is smaller than Na atom √
(b) Na^+ is larger than Na atom
(c) Cl^- is smaller than Cl atom
(d) Cl^- ion and Cl atom are equal in size

Inter (Part-II) 2016

Chemistry	Group-I	PAPER: II
Time: 3.10 Hours	(SUBJECTIVE TYPE)	Marks: 83

Section-I

2. Write short answers to any EIGHT (8) questions: (16)

(i) What is Lanthanide contraction?

Ans The decrease in size (as radii of atoms or ion or of atomic volume) with increasing atomic number of metals of lanthanides series is called Lanthanide contraction.

(ii) Name various classes of hydrides.

Ans The binary compounds of hydrogen with other elements are called hydrides. According to the nature of bonding, hydrides may be broadly classified into three classes: ionic, covalent and intermediate.

(iii) Why 2% gypsum is added in cement?

Ans Gypsum plays a very important role in controlling rate of hardening of cement. During manufacturing of cement, a small (2%) amount of gypsum is introduced during final grinding process. Gypsum is added to control the "setting of cement".

(iv) What happens when :

1. Li_2CO_3 is heated. 2. Na_2CO_3 is heated.

Ans **1. Li_2CO_3 is heated:**

When Li_2CO_3 is heated as lithium has low electropositive character, thus its carbonate are not so stable and, therefore, decompose giving lithium oxide.

$$Li_2CO_3 \rightarrow Li_2O + CO_2$$

2. Na_2CO_3 is heated:

Anhydrous sodium carbonate melts at 851°C, however, it gradually decompose in temperature range you have specified:

$$Na_2CO_3 \longrightarrow Na_2O + CO_2$$

(v) Aqueous solution of borax is alkaline. Give reason.

Ans Borax when dissolved in water ionizes as:

$$Na_2B_4O_7 \longrightarrow 2Na^+ + B_4O_7^{2-}$$

Hydrolysis of $B_4O_7^{2-}$ ions occurs as follows:

$$B_4O_7^{2-} + 7H_2O \longrightarrow 4H_3BO_3 + 2OH^-$$

So, a strong alkali (NaOH) is formed which is highly ionized. On the other hand, boric acid (H_3BO_3) is ionized to a little extent, because it is a weak acid. Hence, solution of borax as a whole is alkaline in nature.

(vi) Write two uses of sodium silicate.

Ans Uses of Sodium silicate:

1. It is used as a filler for soap in soap industry.
2. It is used in textile as a fire proof.

(vii) What are Freons and Teflon?

Ans Freons:

Fluorine is used for the preparation of freons. Freon is the commercial name of low molecular mass chlorofluorocarbons, CCl_2F_2, $CClF_3$. These are being used as refrigerants and aerosol propellants.

Teflon:

Fluorine is used to prepare Teflon $(-CF_2 - CF_2-)_n$. It is a polymerized tetrafluoro ethylene compound. It is a valuable plastic which resists the action of oxidants, acids and alkalies.

(viii) Describe two uses of helium.

Ans Following are two uses of helium:

1. Helium is used in weather balloons, in welding and in traffic signal light.
2. A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers.

(ix) Why the elements of group VI A other than oxygen show more than two oxidation states?

Ans Except oxygen the other members of the group show a covalency of +2, +4, and +6, for example, SCl_2, SCl_4, SCl_6. +2 oxidation state is shown due to 2 unpaired electrons in the p-orbitals. +4 oxidation state is shown when 1 electron from p-orbital is promoted to the next vacant d-orbital, while +6 oxidation state is shown when another electron from s-orbital is also promoted to the next vacant d-orbital.

(x) Write down two chemical equations. Which show that H_2SO_4 is dehydrating agent?

Ans

1. With oxalic acid to forms CO_2 and CO.

$$\begin{matrix}COOH\\|\\COOH\end{matrix} \xrightarrow{\text{conc. } H_2SO_4} CO_2 + CO + H_2O$$

2. With formic acid to form CO.

$$HCOOH \xrightarrow{\text{conc. } H_2SO_4} CO + H_2O$$

(xi) Complete and balance the following chemical equation: $KMnO_4 + FeSO_4 + H_2SO_4 \rightarrow$.

Ans

$$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 5Fe(SO_4)_3 + 8H_2O$$

(xii) Describe chromyl chloride test for chloride radical. Also write chemical equation in support of your answer.

Ans Chromyl Chloride Test:

When solid potassium dichromate is heated with solid metal chloride in the presence of concentrated sulphuric acid, chromyl chloride is produced.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

Chromyl chloride

3. Write short answers to any EIGHT (8) questions: (16)

(i) How octane number of gasoline is improved? Explain with example.

Ans The octane number of gasoline is improved by a process called reforming. It involves the conversion of straight chain hydrocarbons into branched chain by heating in the absence of oxygen and in the presence of a catalyst.

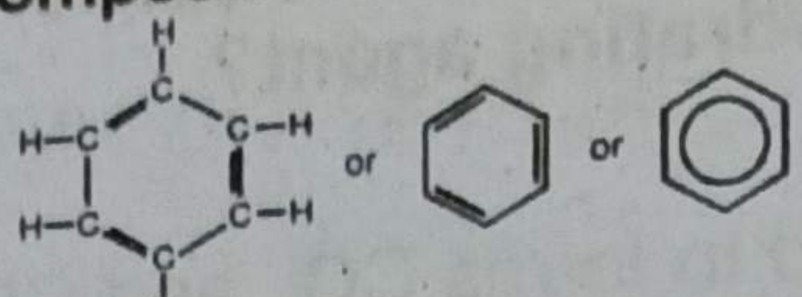
$$CH_3-(CH_2)_6-CH_3 \xrightarrow[\text{Catalyst}]{\text{Heat}} CH_3-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-CH_2-\overset{\displaystyle CH_3}{\overset{|}{CH}}-CH_3$$

n-octane 2,2,4-Trimethylpentane

(ii) What are aromatic compounds? Explain with example.

Ans These carbocyclic compounds contain at least one benzene ring, six carbon atoms with three alternate double and single bonds.

These bonds are usually shown in the form of a circle. Typical example of aromatic compounds are given below:



Benzene

(iii) Explain Markownikov's rule with suitable example.

Ans The rule states that in the addition of an unsymmetrical reagent to an unsymmetrical alkene, the negative part of the adding reagent goes to that carbon, which has least number of hydrogen atoms.

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

Propene 2-Bromopropane

(iv) Convert ethyne into acetaldehyde.

Ans

$$CH \equiv CH + H - OH \longrightarrow CH_2 = CHOH$$

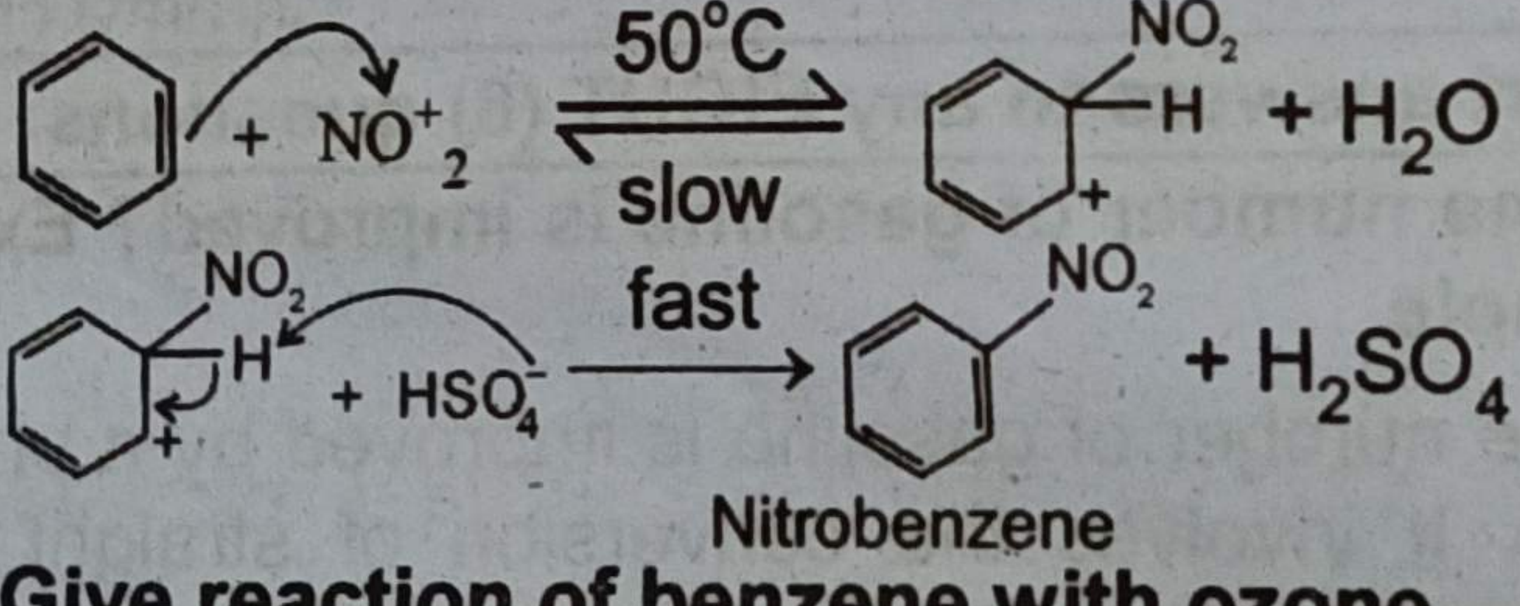
$$CH_2 = CHOH \xrightarrow{\text{Rearrangment}} CH_3 - CHO$$

(acetaldehyde)

(v) Give mechanism of nitration of benzene.

Ans Mechanism:

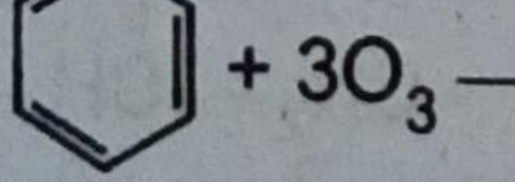
$$HONO_2 + H_2SO_4 \underset{}{\overset{50\text{-}55^\circ C}{\rightleftharpoons}} NO_2^+ + HSO_4^- + H_2O$$



Nitrobenzene

(vi) Give reaction of benzene with ozone.

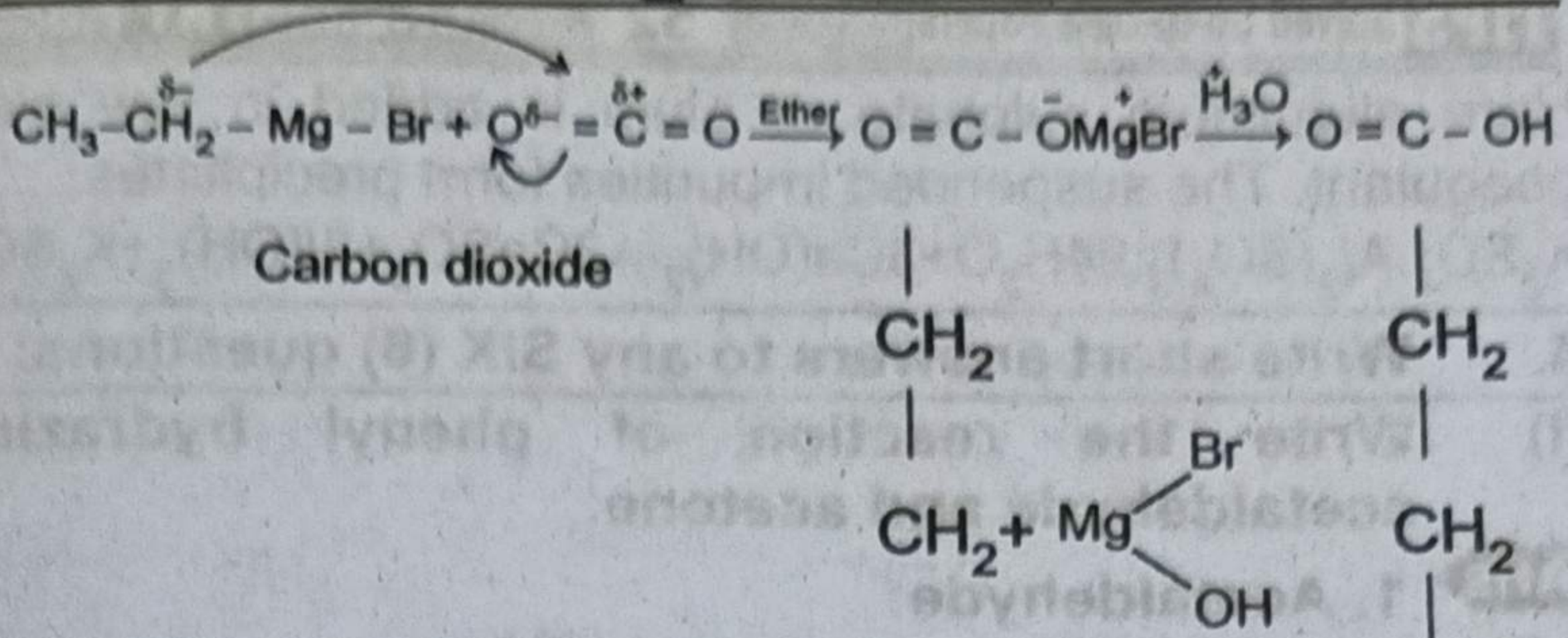
Ans Benzene reacts with ozone and gives glyoxal through benzene triozonide.



Benzene triozonide Glyoxal

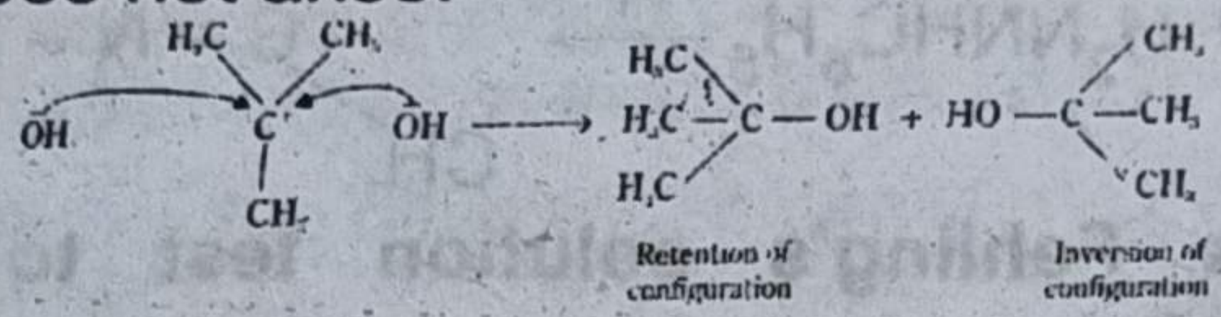
(vii) Give reaction of Grignard's reagent with CO_2 followed by hydrolysis in acid medium.

Ans With CO_2



(viii) Give mechanism of S_N1 reaction.

Ans In S_N1 mechanism, the nucleophile attacks when the leaving group had already gone, so the question of the direction of the attack does not arise.



(ix) Convert acetone into ethyl alcohol.

Ans $CH_3 - \overset{\overset{O}{\|}}{C} - CH_3 + 4[O] \rightarrow CH_3COOH + CO_2 + H_2O$

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

$2CH_3COOH + 2H_2O \rightarrow CH_3 - CH_3 + 2CO_2 + 2NaOH + H_2$

$CH_3 - CH_3 + Cl_2 \rightarrow CH_3 - CH_2Cl + HCl$

$KOH + CH_3 - CH_2Cl \rightarrow CH_3 - CH_2OH + KCl$

(x) Water has higher boiling point than ethanol. Explain.

Ans Water has higher boiling point than ethanol because water has strong hydrogen bonding than ethanol.

(xi) What is chemical oxygen demand?

Ans The amount of oxygen consumed in the chemical oxidation of dissolved organic matter in given water sample is called chemical oxygen demand. It is denoted as COD.

(xii) Explain purification of water by use of coagulating agent.

Ans The process in which suspended and colloidal particles are removed as precipitates using a coagulant is called coagulation.

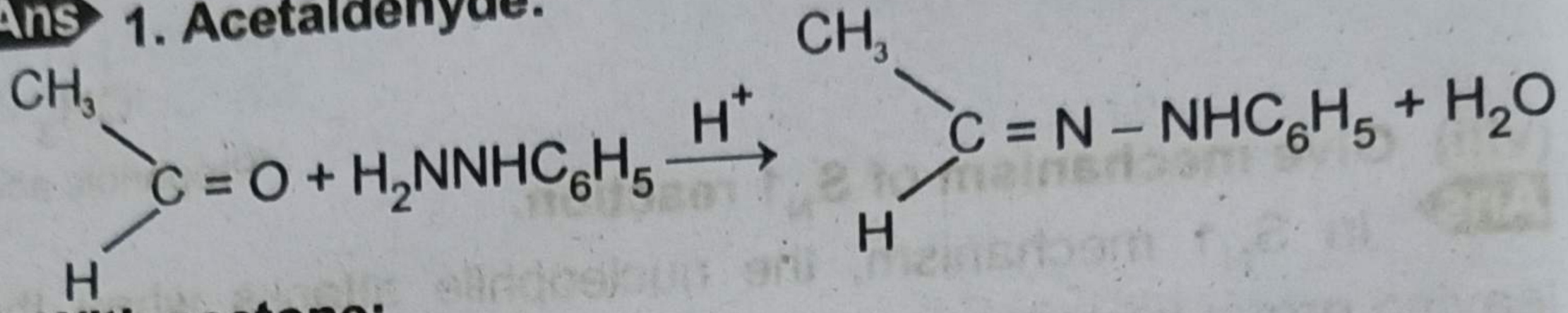
Here aluminium sulphate or alum is added in raw water as a coagulant. The suspended impurities form precipitates.

$$K_2SO_4.Al_2(SO_4)_3.24H_2O + 3Ca(OH)_2 \rightarrow 3CaSO_4 + 2Al(OH)_3 + K_2SO_4 + 24H_2O$$

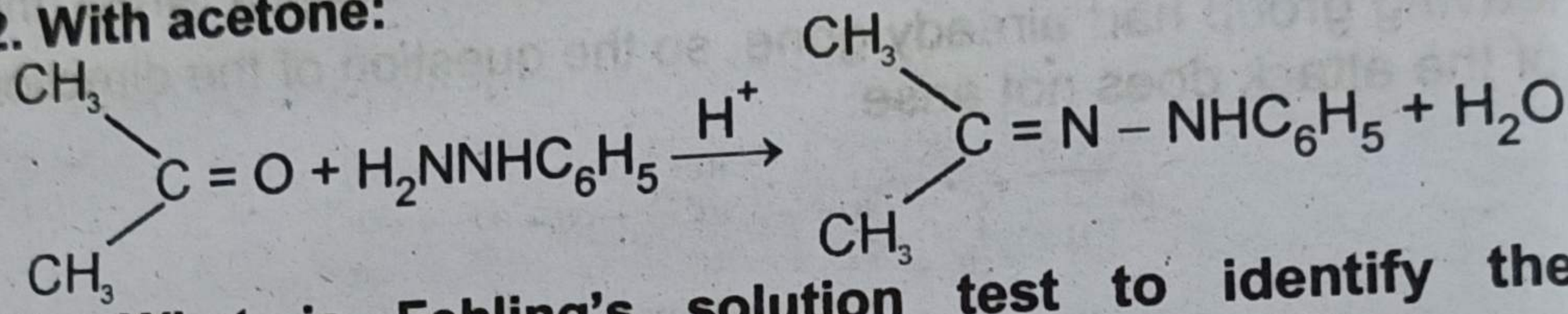
4. Write short answers to any SIX (6) questions: (12)

(i) Write the reaction of phenyl hydrazine with acetaldehyde and acetone.

Ans 1. Acetaldehyde:



2. With acetone:



(ii) What is Fehling's solution test to identify the aldehyde?

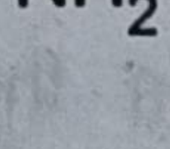
Ans Fehling's Solution Test:

Aliphatic aldehdyes form a brick-red precipitate with Fehling's solution. To an aldehyde solution, add Fehling's solution and boil. A brick red precipitate of cuprous oxide is formed. Ketones do not give this test.

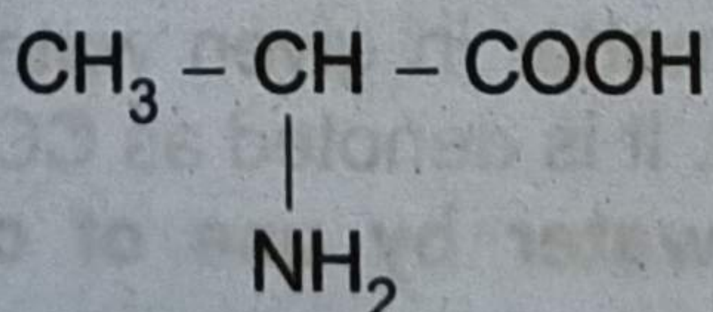
$$R - CHO + 2Cu(OH)_2 + NaOH \longrightarrow \underset{\text{Brick-red ppt}}{R - COONa + Cu_2O} + 3H_2O$$

(iii) Write the formulae of glycine and alanine.

Ans Glycine:



Alanine:



(iv) How amino acid is prepared by strecker method?

Ans When hydrogen cyanide is added to an aldehyde in the presence of ammonia, α-amino acid is obtained.

$$RCHO + HCN + NH_3 \longrightarrow R - \underset{\displaystyle NH_2}{\underset{|}{CH}} - CN$$

α-amino nitrile upon acidic hydrolysis yields an α-amino acid.

$$R - \underset{\displaystyle NH_2}{\underset{|}{CH}} - CN \xrightarrow{H_3O^+} R - \underset{\displaystyle NH_2}{\underset{|}{CH}} - COOH$$

(v) Define saponification number, give example.

Ans It is defined as the number of milligrams of potassium hydroxide required to saponify one gram of the fat or oil. For example, one mole of glycerol tripalmitate (mol. wt. = 836) requires 168,000 mg of KOH for saponification. Therefore, one gram of fat will require 168000/836 mg of KOH. Hence the saponification number of glycerol tripalmitate is 208.

(vi) What is difference between DNA and RNA?

Ans Following are the differences between DNA and RNA:

RNA	DNA
1. RNA contains sugar ribose.	1. DNA contains the sugar 2-deoxyribose.
2. RNA contains the bases adenine, cytosine guanine and uracil.	2. DNA contains bases adenine, cytosine, guanine and thyamine.
3. RNA is single stranded.	3. DNA is always double stranded.

(vii) Define iodine number.

Ans The extent of unsaturation in a fat or an oil is expressed in terms of its iodine number. It is defined as the number of grams of iodine which will add to 100 grams of a fat or an oil. The value of iodine number depends on the number of double bonds present in the acid component of the glycerides. The glycerides with no double bonds have zero iodine number.

(viii) What reaction takes place in decomposition zone during manufacturing of cement?

Ans Here the temperature goes up to 800°C. In this zone, the limestone ($CaCO_3$) decomposes into lime (CaO) and CO_2.

$$CaCO_{3(s)} \xrightarrow[800^\circ C]{} CaO_{(s)} + CO_{2(g)}$$

(ix) **Which type of woody raw material is used in paper industry?**

Ans **Woody Raw Material:**

1. Poplar (hard wood)
2. Eucalyptus (hard wood)
3. Douglas fir (soft wood)

Section-II

NOTE: Attempt any Three (3) questions.

Q.5.(a) Write two similarities and two dissimilarities of hydrogen with IA group of element (Alkali Metals). (4)

Ans **Position of Hydrogen:**

Although it is not a metal but in most of the modern versions of periodic table, hydrogen is placed at the top of the group IA.

Similarities:

1. Some of the properties of hydrogen resemble with those of alkali metals. Like alkali metals, hydrogen atom has one electron in 1s subshell, which it can lose to form H^-.
2. Both hydrogen and alkali metals have a strong tendency to combine with electronegative elements such as halogens.

Dissimilarities:

1. Hydrogen is also markedly different from alkali metals. For example, hydrogen is a non-metal in true sense. It does not lose electron as easily as most of the alkali metals do.
2. Unlike alkali metals, molecular hydrogen exists in open atmosphere.

(b) Complete and balance the following equations: (4)

(i) $Li_2O + H_2O \rightarrow$ **(ii)** $Na_2O_2 + H_2O \rightarrow$

(iii) $Mg(OH)_2 \xrightarrow{heat}$ **(iv)** $NaNO_3 \xrightarrow{heat}$

Ans (i) $Li_2O + H_2O \longrightarrow 2LiOH_{(aq)}$

(ii) $2Na_2O_2 + 2H_2O \longrightarrow 4NaOH_{(aq)} + O_{2(g)}$

(iii) $Mg(OH)_{2(s)} \xrightarrow{heat} MgO + H_2O$

(iv) $2NaNO_3 \xrightarrow{heat} 2NaNO_2 + O_2$

Q.6.(a) Write a note on aluminium silicate. (4)

Ans Many important silicate rocks contain aluminium. The weathering of these rocks results in the disintegration of the complex silicates which they contain. The boiling and freezing of water in the rocks, and the chemical action of water and CO_2 convert these compounds into potassium carbonate, sand and clay. The following reaction explains the weathering of potassium feldspar.

$$K_2O.Al_2O_3.6SiO_2 + H_2CO_3 + H_2O \longrightarrow K_2CO_3 + 4SiO_2 + Al_2O_3.(SiO_2)_2.2H_2O$$

Pure clay, which has the formula shown above, is white and is called kaolin. It is used to make porcelain and china wares. Ordinary clay contains compounds of iron and other metals and it has a yellow or reddish-yellow colour.

Impure clays can be more easily fused because they contain oxides of iron, calcium, magnesium and other metals which form easily fusable silicates with sand. Such clays are used to make bricks, tiles, and stonewares. Due to the presence of ferric oxide, the articles of this clay turn reddish when heated in a kiln.

Stoneware is usually glazed to give it a less porous surface by throwing salt upon the articles while they are hot. This treatment produces sodium aluminate and sodium aluminium silicate, which melt readily and cover the entire surface. When the article cools, the covering solidifies, producing a compact, smooth, waterproof surface. China wares are made from a mixture of kaolin, bone ash, and feldspar; the mixture fuses when heated and fills the pores between the grains of kaolin.

The use of clay in making pottery and other ceramic articles depends upon the plasticity of the paste. When soaked in water, the clay progressively hydrates, and the paste becomes more plastic. When the clay is heated, the water of hydration is lost and a hard rock like mass is formed.

(b) Write any four applications of the noble gases. (4)

Ans **Applications of the Noble Gases:**

1. Helium is used in weather balloons, in welding and in traffic signal light.
2. A mixture of 80% helium and 20% oxygen is used for breathing by the sea divers.

3. Helium is used as a cooling medium for nuclear reactors.
4. Neon is largely used in making neon advertising signs, in high voltage indicators and TV tubes.

Q.7.(a) Explain sp^3 mode of hybridization with an example. (4)

Ans sp^3 Hybridization:

In order to explain the bonding and shapes of molecules in which carbon is attached with four atoms, all these four atomic orbitals are mixed together to give rise to four new equivalent hybrid atomic orbitals having same shape and energy. This mode of hybridization is called tetrahedral or sp^3 hybridization.

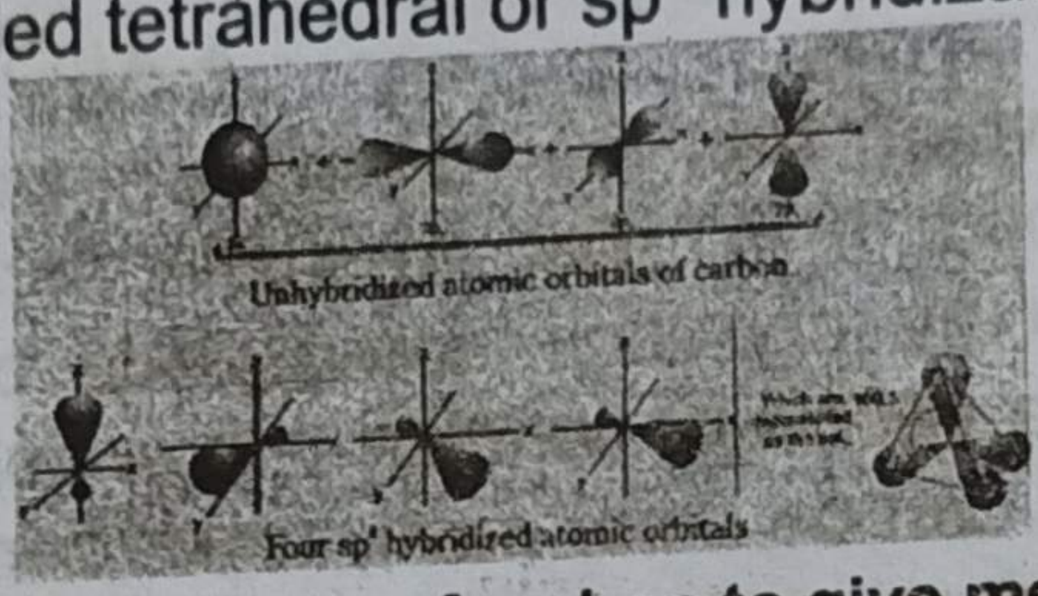


Fig. (a) sp^3 hybridization of carbon to give methane (CH_4).

All these four sp^3 hybrid orbitals are degenerate (having equal energy) and are directed at an angle of 109.5° in space to give a tetrahedral geometry.

When a carbon atom forms single bonds with other atoms, these hybrid orbitals overlap with the orbitals of these atoms to form four sigma bonds. This type of hybridization explains the bonding and shapes of all those compounds in which carbon atom is saturated.

In the formation of methane, the four hybrid atomic orbitals of carbon overlap separately with four 1s atomic orbitals of hydrogen to form four equivalent C–H bonds. The shape of methane thus formed is very similar to the actual methane molecule. All the four hydrogen atoms do not lie in the same plane.

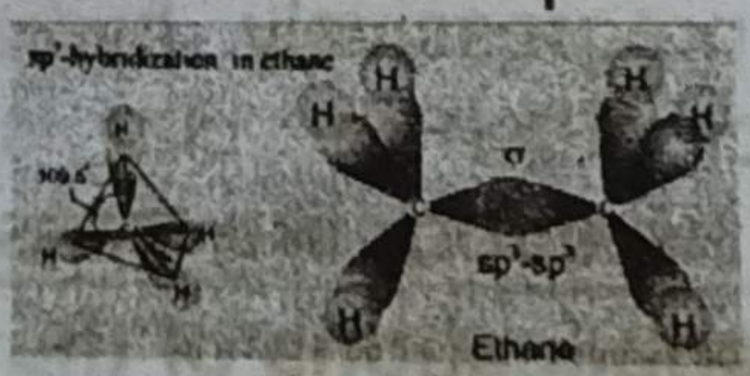


Fig. (b)

In ethane, CH_3–CH_3, the two tetrahedrons of each carbon are joined together as shown in the above figure. Further addition of a carbon atom with ethane will mean the attachment of another tetrahedron.

Before excitation, the carbon should make two covalent bonds releasing an adequate amount of energy. After excitation, however, it will form four covalent bonds releasing almost double the amount of energy. This excess energy is more than that needed to excite the carbon atom. So, a tetravalent carbon atom is expected to be more stable than a divalent carbon atom.

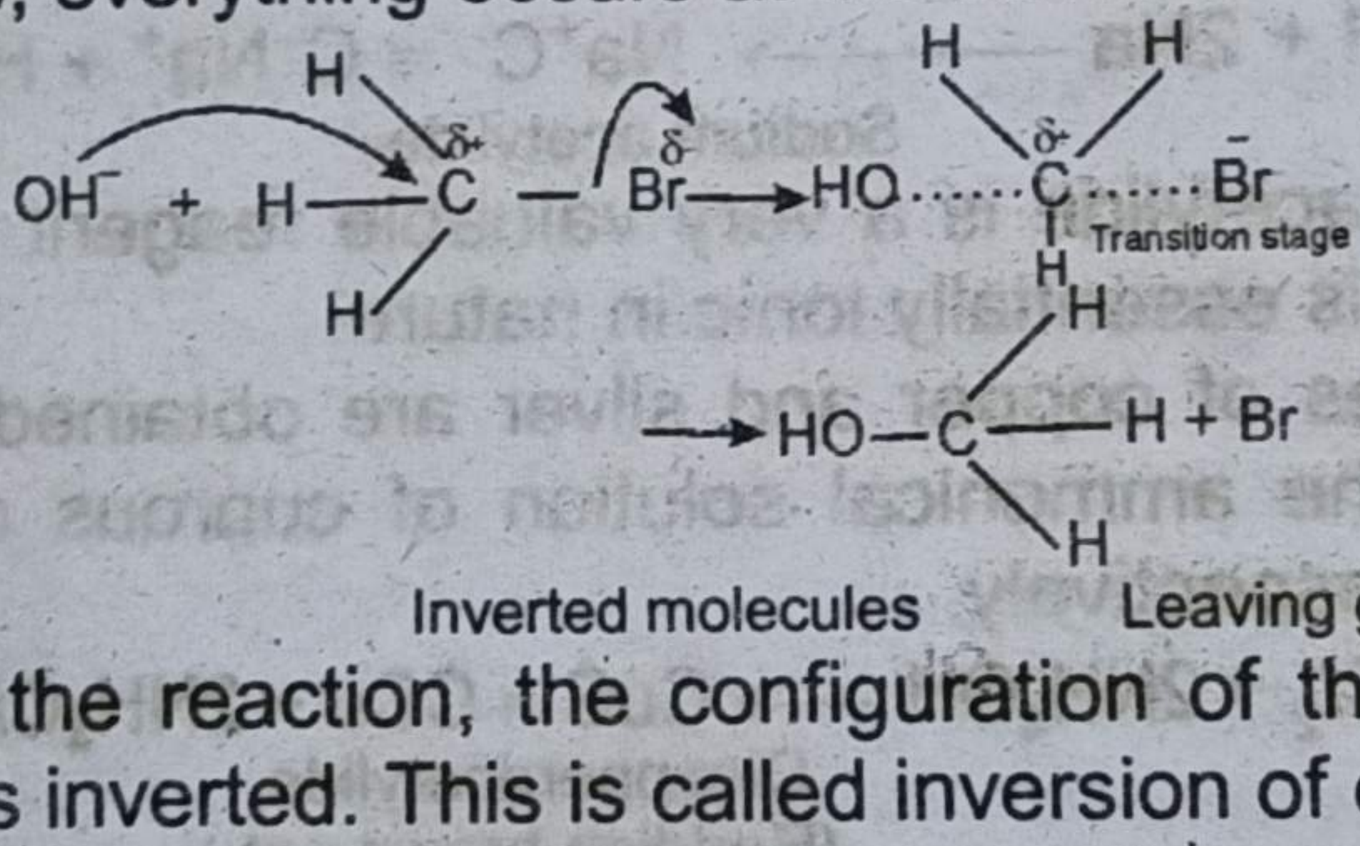
(b) Explain nucleophilic substitution bimolecular (S_N2) mechanism of alkyl halides. (4)

Ans Nucleophilic Substitution Bimolecular (S_N2):

This is a single-step mechanism. As soon as the nucleophile starts attacking, the electrophilic carbon of the substrate, the bond with which the leaving group is attached, starts breaking. In other words, the extent of bond formation is equal to the extent of bond breakage.

Another important feature of this mechanism is the direction of the attack of the attacking nucleophile. It attacks from the side which is opposite to the leaving group.

In order to give to the nucleophile enough room to attack, the substrate carbon atom changes its state of hybridization from tetrahedral sp^3 to planar sp^2. The attack of the nucleophile, change in the state of hybridization and the departure of the leaving group, everything occurs at the same time.



During the reaction, the configuration of the alkyl halide molecule gets inverted. This is called inversion of configuration.

Molecularity of a reaction is defined as the number of molecules taking part in rate-determining step. Since, in this mechanism, the reaction takes place in only one step which is also a rate-determining step and two molecules are participating in this step, so it is called a bimolecular reaction.

Kinetic studies of the reactions involving S_N2 mechanism have shown that the rates of such reactions depend upon the concentrations of alkyl halide as well as the attacking nucleophile.

Mathematically, the rate can be expressed as:

$$\text{Rate} = k\,[\text{Alkyl Halide}]^1\,[\text{Nucleophile}]^1$$

Since, the exponents of the concentration terms in the above expression are unity, so the order of a typical S_N2 reaction will be 1 + 1 = 2.

Among the alkyl halides, the primary alkyl halides always follow S_N2 mechanism whenever they are attacked by nucleophiles.

Q.8.(a) Discuss acidic nature of alkynes with examples. (4)

Ans Acidic Nature of Alkynes:

In ethyne and other terminal alkynes like propyne, the hydrogen atom is bonded to the carbon atom with sp-s overlap. An sp hybrid orbital has 50% s character in it and renders the carbon atom more electronegative than sp^2 and sp^3 hybridized carbons. As a result, the sp hybridized carbon atom of a terminal alkyne pulls the electrons more strongly making the attached hydrogen atom slightly acidic.

$$H-C\equiv C^{\delta-}-H^{\delta+}$$

When 1-alkyne or ethyne is treated with sodamide in liquid ammonia or passed over molten sodium, alkynides or acetylides are obtained.

$$R-C\equiv CH + NaNH_2 \xrightarrow{\text{liq. } NH_3} R-C\equiv C^-Na^+ + NH_3$$

$$HC\equiv CH + 2Na \longrightarrow \underset{\text{Sodium acetylide}}{Na^+C^-\equiv C^-Na^+} + H_2$$

Sodium acetylide is a very valuable reagent for chemical synthesis and is essentially ionic in nature.

Acetylides of copper and silver are obtained by passing acetylene in the ammonical solution of cuprous chloride and silver nitrate, respectively.

$$HC\equiv CH + Cu_2Cl_2 + 2NH_4OH \longrightarrow \underset{\substack{\text{Dicopperacetylide}\\ \text{(Reddish-brown ppt.)}}}{CuC\equiv CCu} + 2NH_4Cl + 2H_2O$$

$$HC\equiv CH + 2AgNO_3 + 2NH_4OH \longrightarrow \underset{\substack{\text{Disilver acetylide}\\ \text{(white ppt.)}}}{AgC\equiv CAg} + 2NH_4NO_3 + 2H_2O$$

Silver and copper acetylide react with acids to regenerate alkynes.

$$AgC\equiv CAg + H_2SO_4(\text{dil.}) \longrightarrow HC\equiv CH + Ag_2SO_4$$

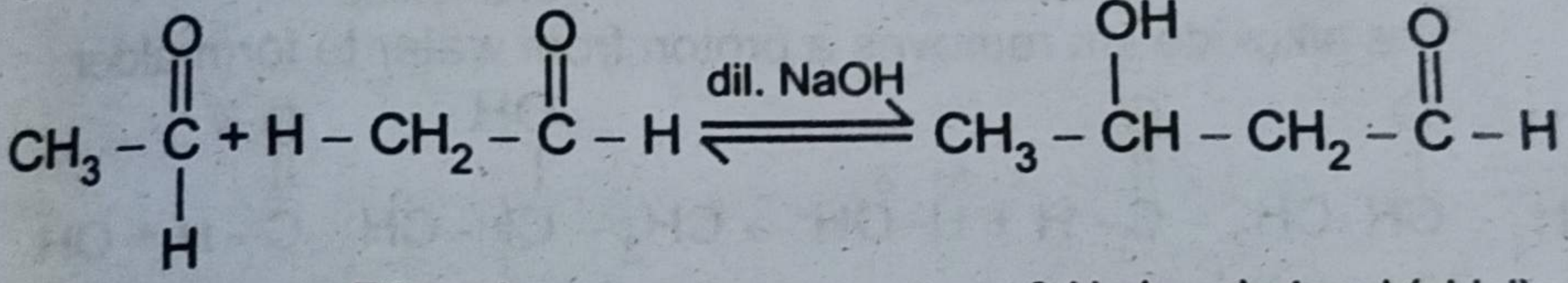
$$AgC\equiv CAg + 2HNO_3(\text{dil.}) \longrightarrow HC\equiv CH + 2AgNO_3$$

These alkynides are used for the preparation, purification, separation and identification of alkynes.

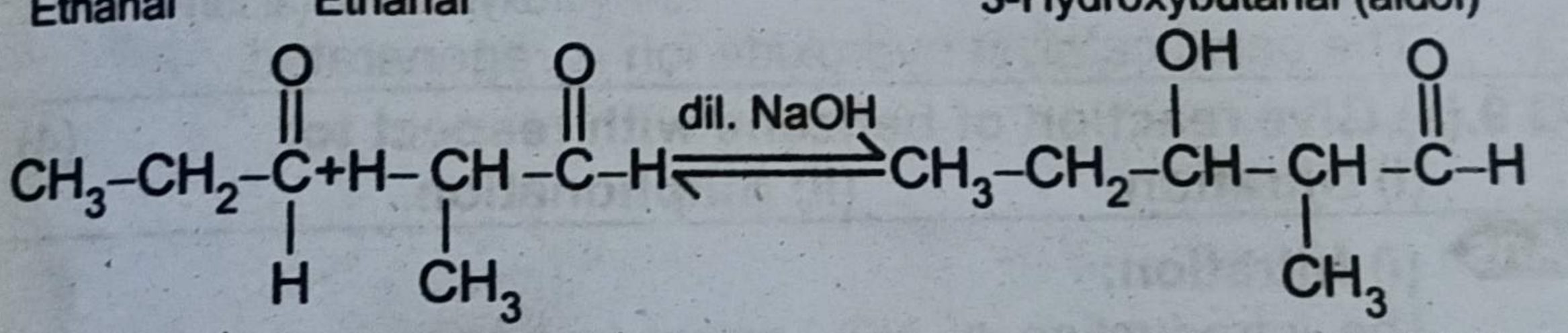
(b) What are aldols? Explain aldol condensation reaction mechanism for condensation of ethanal. (4)

Ans Aldol Condensation:

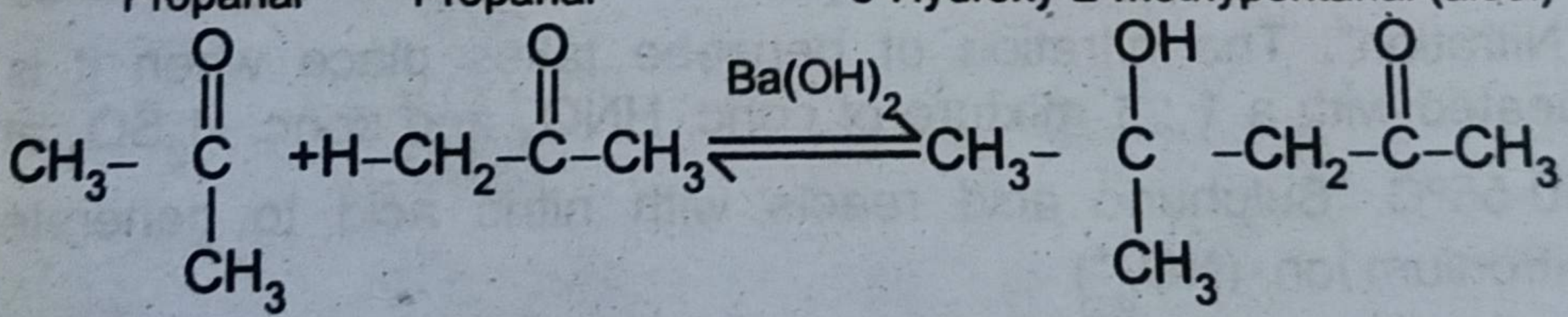
Aldehydes and ketones possessing α-hydrogen atoms areact with a cold dilute solution of an alkali to form addition products known as aldols. The name 'aldol' is given to the product because it contains both aldehyde and alcohol functional groups. Note that the name aldol condensation is reserved for the reaction that starts with two identical carbonyl compounds. Two molecules of the same carbonyl compound condense to form an aldol.



Ethanal Ethanal 3-Hydroxybutanal (aldol)

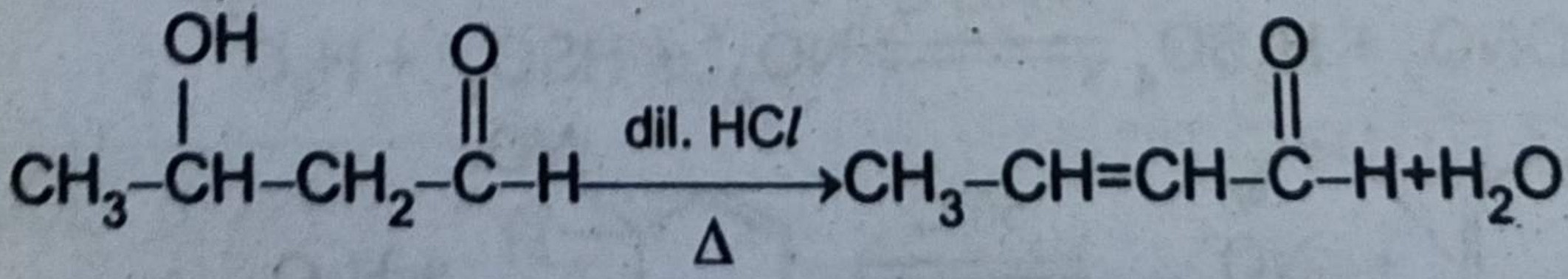


Propanal Propanal 3-Hydroxy-2-methypentanal (aldol)



Propanone Propanone 4-Hydroxy-4-methyl-2-pentanone

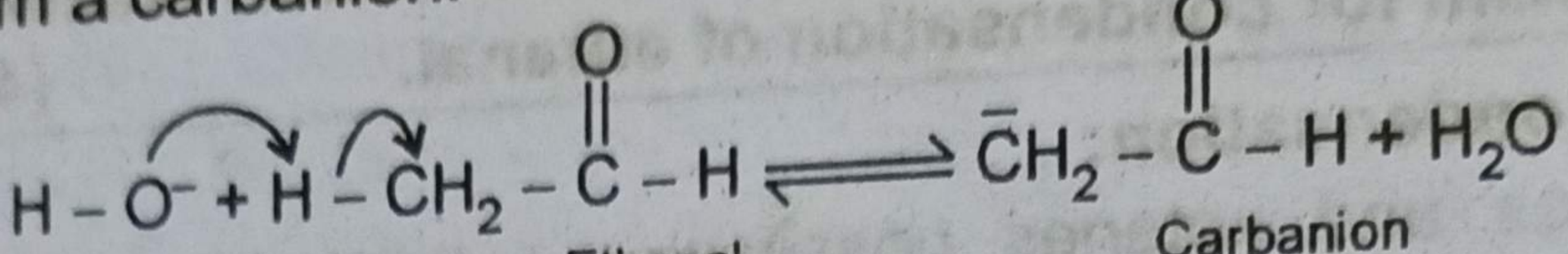
The aldol compound readily loses water on heating in the presence of dilute acid to form an unsaturated carbonyl compound. A carbon-carbon double bond is formed between the α-and β-carbon atoms.



3-Hydroxybutanal Crotonaldehyde

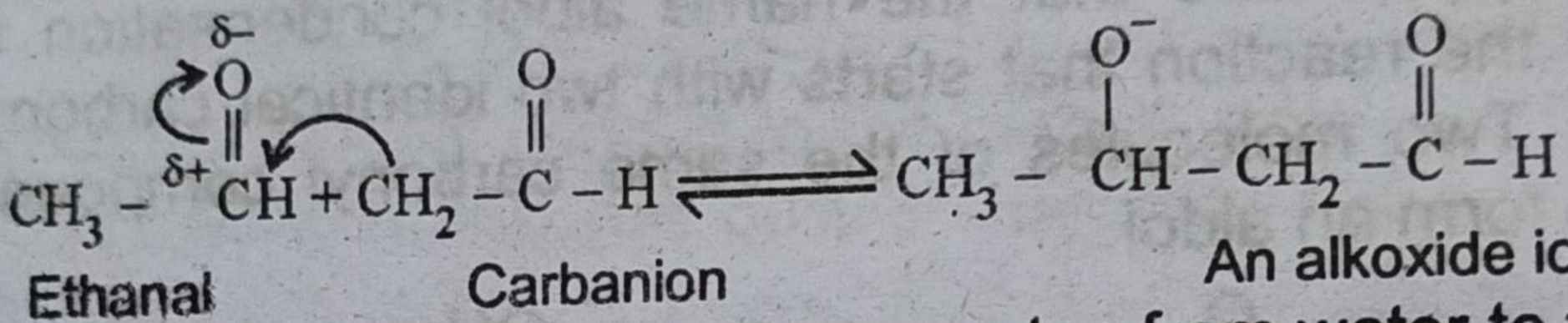
Mechanism of Aldol Condensation:

The hydroxide ion acts as a base. It removes a proton from α-carbon of one molecule of the carbonyl compound to form a carbanion.



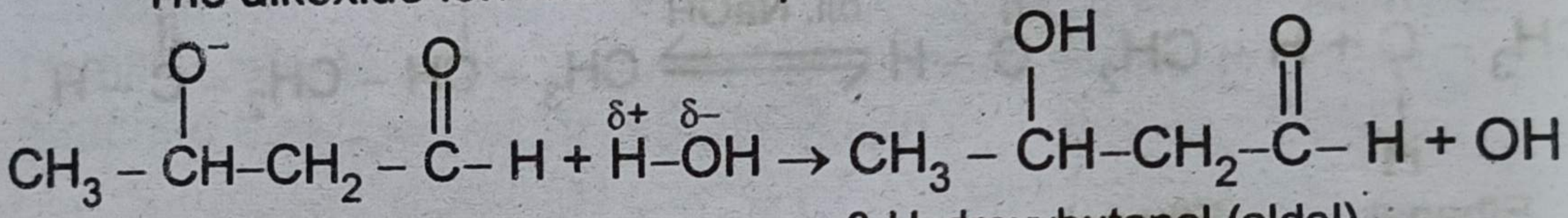
Hydroxide ion Ethanal Carbanion

The carbanion acts as a nucleophile. It attacks the electrophilic carbonyl carbon atom of the unchanged second molecule to form an alkoxide ion.



Ethanal Carbanion An alkoxide ion

The alkoxide ion removes a proton from water to form aldol.



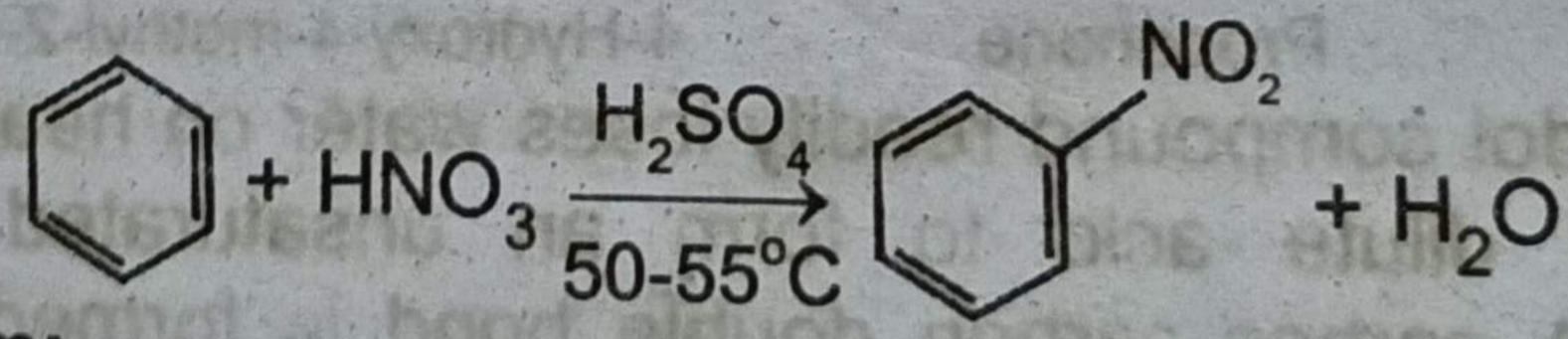
Alkoxide ion 3-Hydroxybutanal (aldol)

The basic catalyst hydroxide ion is regenerated.

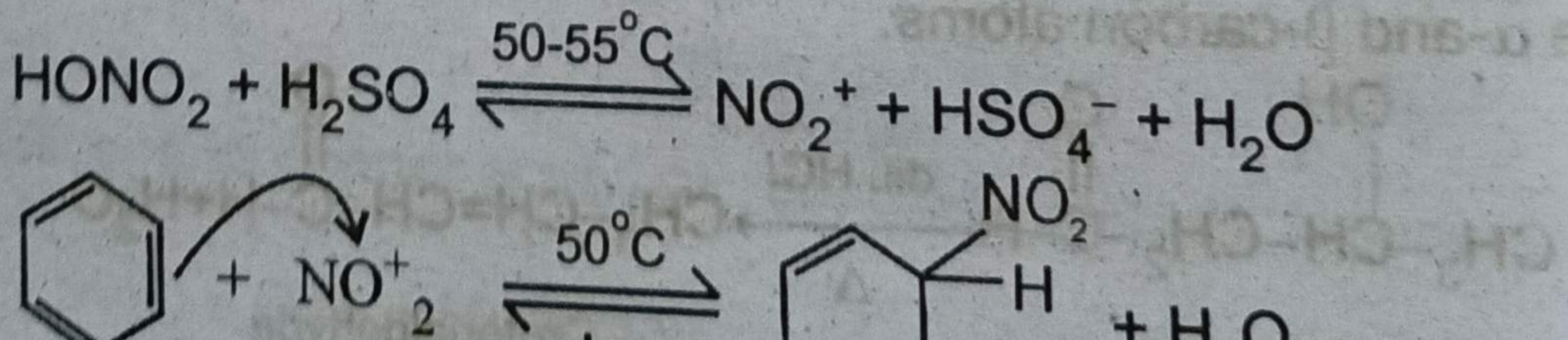
Q.9.(a) Give reaction of benzene with respect to: (4)
(i) Nitration. (ii) Sulphonation.

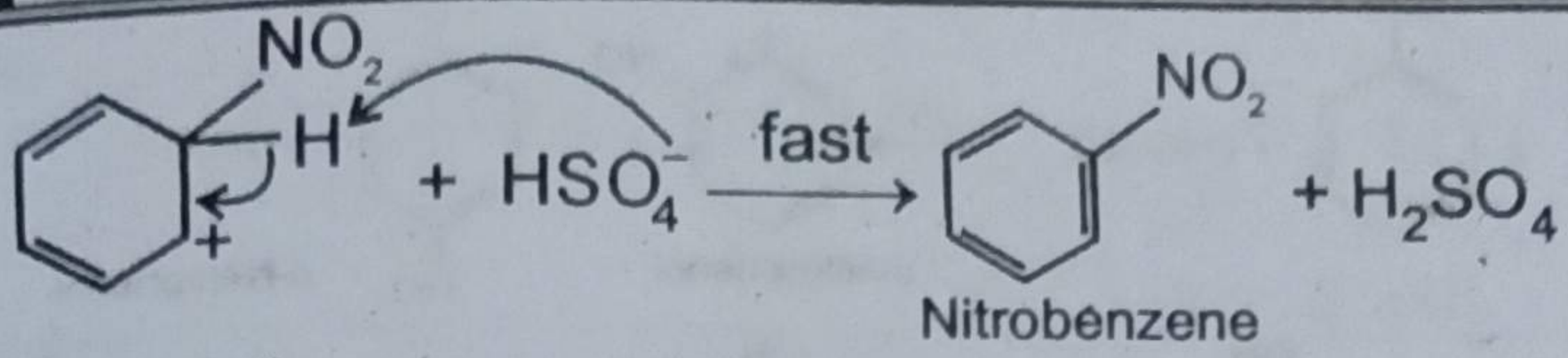
Ans (i) Nitration:

The introduction of NO_2 group in benzene ring is called "Nitration". The nitration of benzene takes place when it is heated with a 1 : 1 mixture of conc. HNO_3 and conc. H_2SO_4 at 50-55°C. Sulphuric acid reacts with nitric acid to generate nitronium ion, (NO_2^+)



Mechanism:

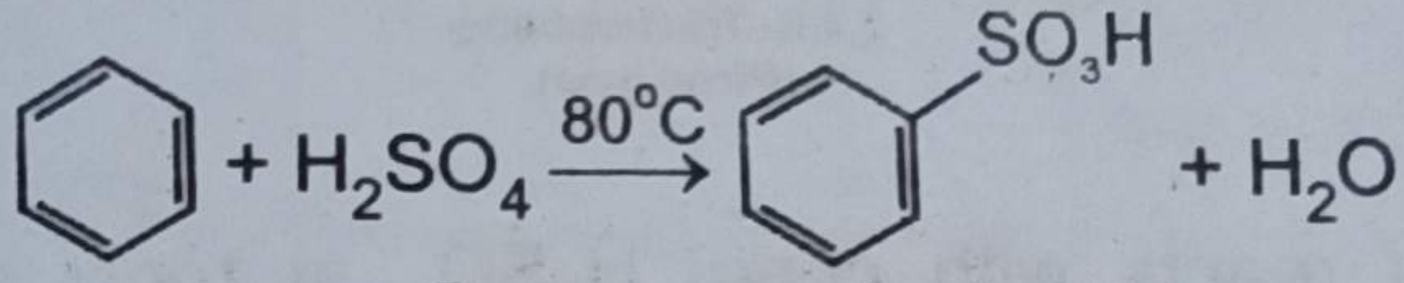




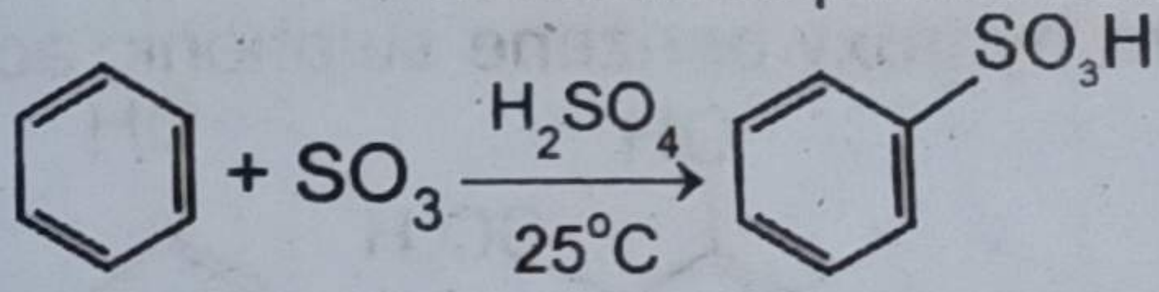
Nitrobenzene

(ii) Sulphonation:

The introduction of sulphonic acid group in benzene ring is called Sulphonation. When benzene is heated with fuming H_2SO_4 or conc. H_2SO_4, it yields benzene sulphonic acid.



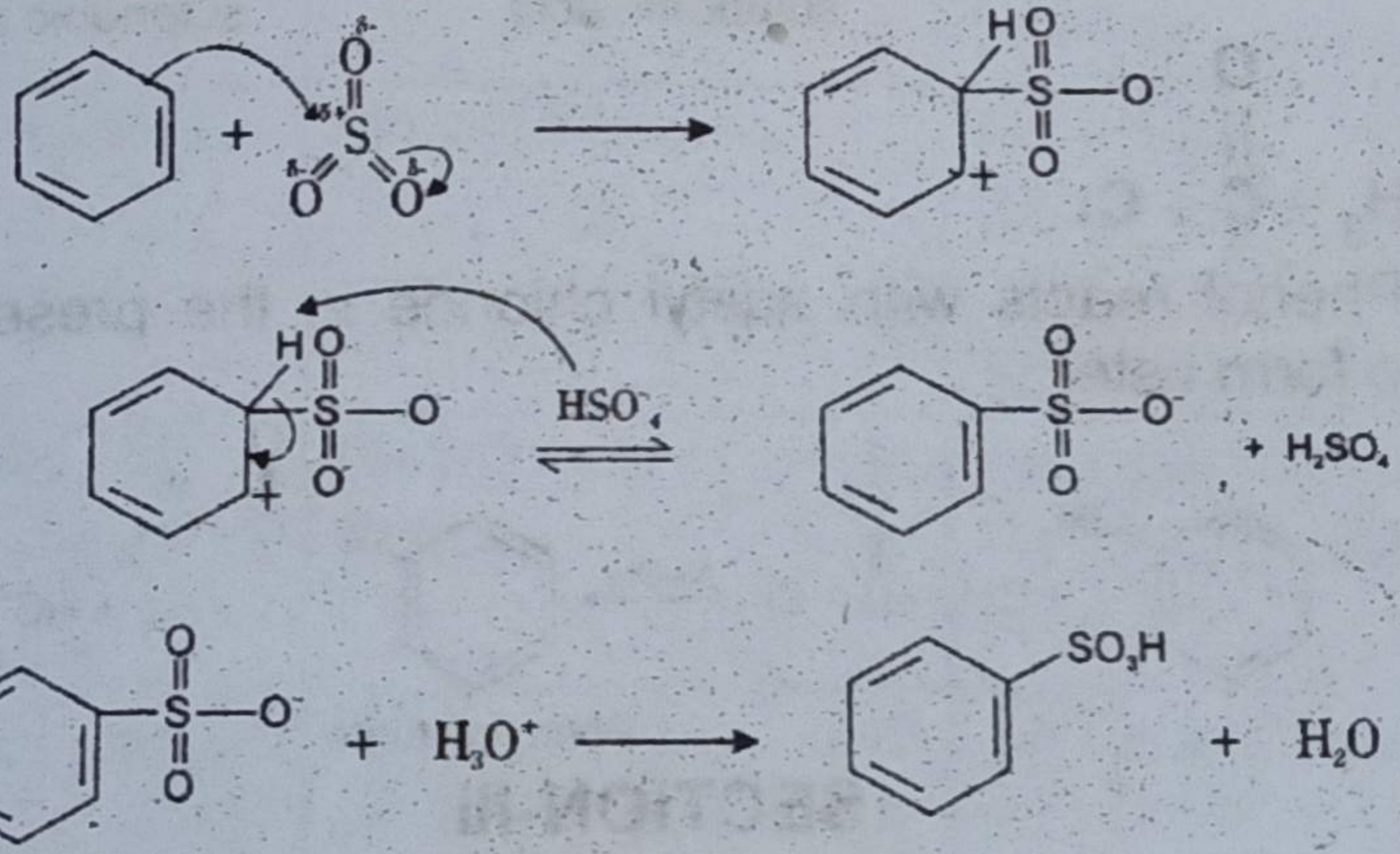
Benzenesulphonic acid



Mechanism:

When sulphuric acid alone is used, the actual electrophile in this reaction is SO_3.

$$H_2SO_4 + H_2SO_4 \rightleftharpoons H_3O^+ + SO_3 + HSO^-_4$$

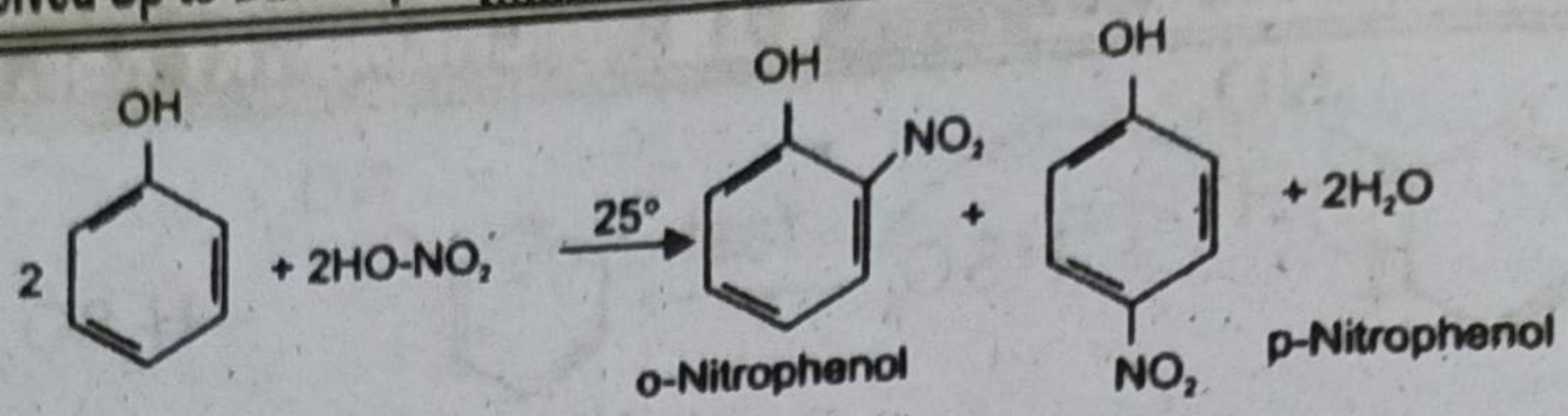


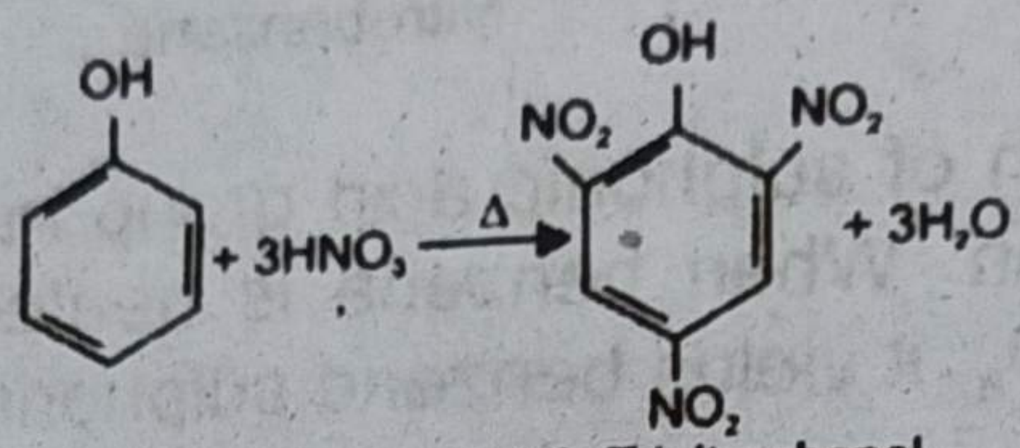
(b) Give the reaction of phenol with: **(4)**

(i) HNO_3 **(ii) H_2SO_4** **(iii) $CH_3 - \overset{\overset{O}{\|}}{C} - Cl$**

Ans **(i) HNO_3:**

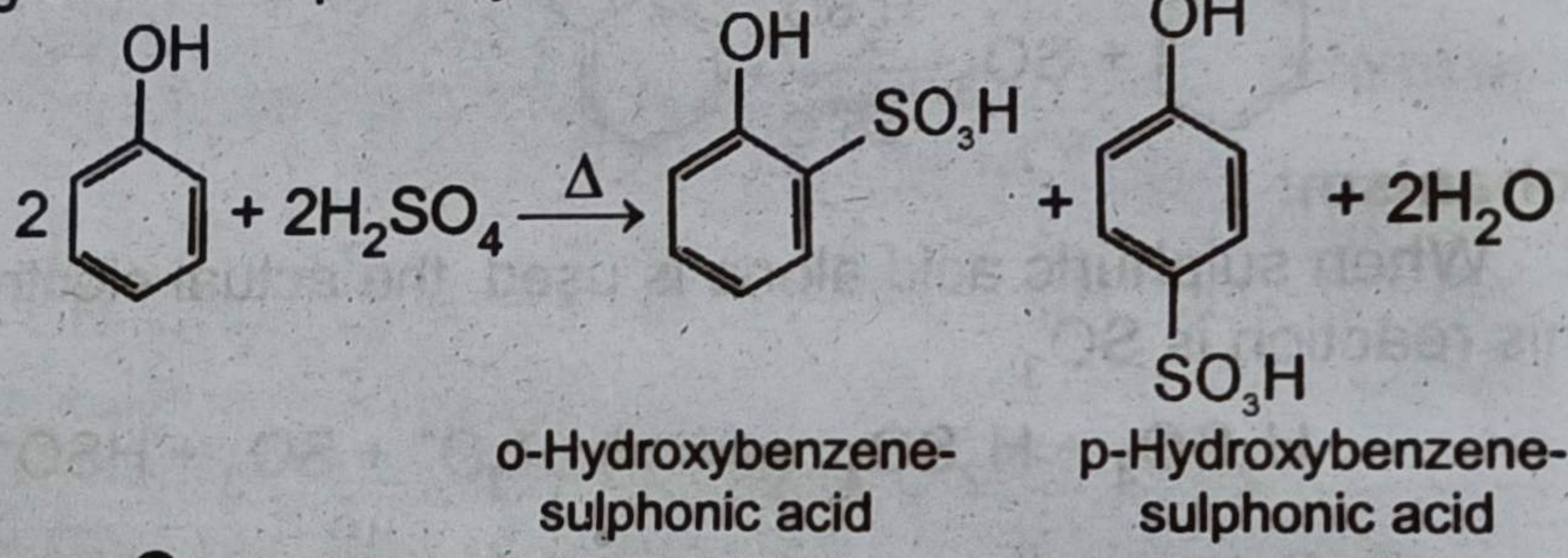
Phenol reacts with dil. and conc. HNO_3 at different temperatures as follows:





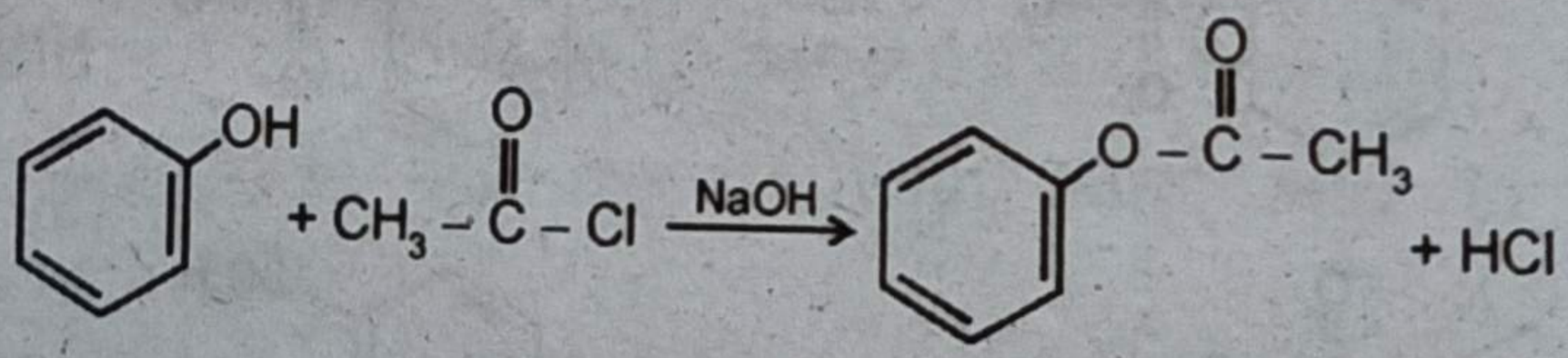
(ii) H_2SO_4:

Phenol reacts with conc. H_2SO_4 at room temperature giving ortho and para hydroxy benzene sulphonic acids.



(iii) $CH_3 - \overset{\overset{O}{\|}}{C} - Cl$:

Phenol reacts with acetyl chloride in the presence of a base to form ester.



SECTION-III

(Practical Part)

NOTE: Attempt any Three (3) questions.

A- Write complete qualitative analysis for Al^{+3} in systematic way.

Ans **(5)**

Experiment	Observation	Inference
Dry Test: 1. Note the colour of salt.	White salt.	Cu^{2+}, Cr^{3+}, Fe^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+} are absent.
2. Note the smell of salt.	No smell of NH_3.	NH_4^+ is absent.
Flame Test: 3. Made a paste of salt with conc. HCl and burnt it on flame with Pt wire.	No characteristic flame.	Na^+, K^+, Cu^{2+}, Ca^{2+}, Ba^{2+}, Sr^{2+} are absent.
Filter Ash Test: 4. Dipped a filter paper strip in a solution of salt and $Co(NO_3)_2$ solution and burnt it.	Blue ash.	May be Al^{3+}.
Wet Tests: 5. O.S + dil. HCl.	No precipitates.	Group-I (Ag^+, Hg_2^{2+}, Pb^{2+}) is absent.
6. O.S + dil. HCl + H_2S gas.	No precipitates.	Group-II (Cd^{2+}, Bi^{2+}, Hg^{2+}, Pb^{3+}, Cu^{2+}, Sn^{2+}, As^{3+}, Sb^{3+}) is absent.
7. O.S + $NH_4Cl_{(s)}$ + boil + cool + $NH_4OH_{(excess)}$.	Gelatinous white ppt.	Group-III (Fe^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}) is present.
8. Note the colour of salt and precipitates.	White salt and white gelatinous precipitates.	Al^{3+} is indicated.
Confirmatory Tests: 9. O.S + $NaOH_{(sol)}$.	White gelatinous ppt. soluble in excess NaOH.	Al^{3+} is confirmed.
10. O.S + $Na_3PO_{4(sol)}$	White ppt. ($AlPO_4$)	Al^{3+} is confirmed.

11. Lake Test: O.S + few drops of litmus solution + dil. HCl + NH_4OH.	Blue precipitates float over colourless solution.	Al^{3} is confirmed.

B- Write complete qualitative analysis for Na^{+} in systematic way. (5)

Ans

Experiment	Observation	Inference
Dry Test: 1. Noted the colour of salt.	White salt.	Cu^{2+}, Cr^{3+}, Fe^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+}, Mn^{2+} are absent.
2. Noted the smell of salt.	No smell of NH_3.	Hg_2^{2+} is absent.
Flame Test: 3. Made a paste of salt with conc. HCl and burnt on flame with Pt wire.	Golden yellow flame.	May be Na^{+}.
Filter Ash Test: 4. Dipped a filter paper strip in a solution of salt and $Co(NO_3)_2$ and burnt it on the flame.	No characteristics ash.	Sn^{+}, Al^{+}, Zn^{2+}. Mg^{2+} are absent.
Wet Tests: 5. O.S + dilute HCl.	No precipitates.	Group-I (Ag^{+}, Hg_2^{2+}, Pb^{2+}) is absent.
6. O.S + dilute HCl + $H_2S_{(gas)}$.	No precipitates.	Group-II (Cd^{2+}, Hg^{2+}, Bi^{3+}, Pb^{2+}, Cu^{2+}, Sn^{2+}, As^{3+}, Sb^{3+}) is absent.
7. O.S + $NH_4Cl_{(s)}$ + boil + cool + $NH_4OH_{(excess)}$.	No precipitates.	Group-III (Fe^{2+}, Fe^{3+}, Cr^{3+}, Al^{3+}) is absent.
8. O.S + $NH_4Cl_{(s)}$ + boil + cool + $NH_4OH_{(excess)}$ + $H_2S_{(gas)}$	No precipitates.	Group-IV (Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}) is absent.

9. O.S + $NH_4Cl_{(s)}$ + boil + Cool + $NH_4OH_{(excess)}$ + $(NH_4)_2CO_3$.	No precipitates.	Group-V (Ca^{2+}, Ba^{2+}, Sr^{2+}) is present. As first five groups are absent to Group VI is present.
10. Salt + $NaOH_{(sol)}$ + boil.	No smell of NH_3.	Hg_2^{2+} is absent.
11. O.S + CH_3COOH + Sod. Cobaltinitrite $Na_3[Co(NO_2)_6]$ solution.	No yellow ppt.	K^+ is absent.
12. O.S + $NH_4Cl_{(s)}$ + NH_4OH + $(NH_4)_2HPO_{4(sol)}$.	No white precipitates.	Mg^{2+} is absent.
13. O.S + KOH + Pot. pyroantimonate $K_2H_2Sb_2O_{7(sol)}$ and scratch the walls of test tube.	White ppt. ($Na_2H_2Sb_2O_7$).	Na^+ is indicated.
Confirmatory Tests: 14. O.S + Zinc urinyl acetate solution.	Yellow ppt.	Na^{2+} is confirmed.
15. Applied flame test.	Golden yellow flame.	Na^{2+} is confirmed.

C- Write complete qualitative analysis for NO3–1 in systematic way. (5)

Ans Nitrate (NO_3^{1-})

	Experiments	Observations	Inferences
1.	Salt + dil. H_2SO_4 and heat.	No reaction.	Dil. H_2SO_4 group (HCO_3^{1-}, CO_3^{2-}, NO_2^{1-}, S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$) is absent.
2.	Salt + conc. H_2SO_4 and warm.	A colourless gas is evolved smelling like HNO_3.	Conc. H_2SO_4 group (Cl^{1-}, Br^{1-}, I^{1-}, NO_3^{1-}, $C_2O_4^{2-}$, CH_3COO^{1-}) is present.

3.	Add paper pellet to expt. no. 2 and note the colour of the gas evolved.	Brown gas with pungent odour.	NO_3^{1-} is present.
4.	Pass the gas through $FeSO_4$ soln.	$FeSO_4$ is turned black (NO_2 gas).	NO_3^{1-} is present.
5.	Salt soln. +$AgNO_3$ soln.	No ppt.	S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$, $C_2O_4^{2-}$, Cl^{1-}, Br^{1-}, I^{1-} and PO_4^{3-} are absent.
6.	Salt soln. + $BaCl_2$ soln.	No ppt.	SO_3^{2-}, $C_2O_4^{2-}$, PO_4^{3-} and SO_4^{2-} are absent.
7.	Salt soln. + $FeSO_4$ + conc. H_2SO_4.	Black ring ($FeSO_4$. NO) is formed.	NO_3^{1-} is confirmed.
8.	Salt soln. + diphenylamine drops.	Deep blue colouration.	NO_3^{1-} is confirmed.
9.	Salt + Cu. turnings + conc. H_2SO_4 and heat.	Brown fumes of NO_2 are given.	NO_3^{1-} is confirmed.
10.	Salt + MnO_2 + conc. H_2SO_4 and heat.	Brown fumes of NO_2.	NO_3^{1-} is confirmed.

D- How phenolic functional group is confirmed by different tests? (5)

Ans Test for Phenols:

1. Neutral $FeCl_3$ Test:

Take 5 cm^3 $FeCl_3$ solution in a test tube and add few drops of NH_4OH until precipitate is obtained. Shake the solution and filter it. Discard the residue. Add few crystals of compound in the filtrate. A blue, green, red, purple (Violet) ppt. or shade shows the presence of phenol. Yellow or any other colour shows the absence of phenols. The colour of Phenols with $FeCl_3$ is due to the formation of adduct with Fe^{3+} ions.

2. Phthalein Test:

Take 0.2 g of organic substance and 0.2 g of phthalic anhydride (or phthalic acid) in a dry test tube. Add 5 cm^3 of

conc. H_2SO_4 in it and heat for two minutes. Pour the contents of the test tube into 30 cm^3 of water containing about 2 cm^3 of dil. NaOH taken in the beaker. A pink, red or purple colour shows the presence of phenol while green fluorescence shows the presence of dihydric phenols. If some other colour is formed, it indicates that phenols are absent.

E- Write the material required equation and procedure for aspirin preparation. (5)

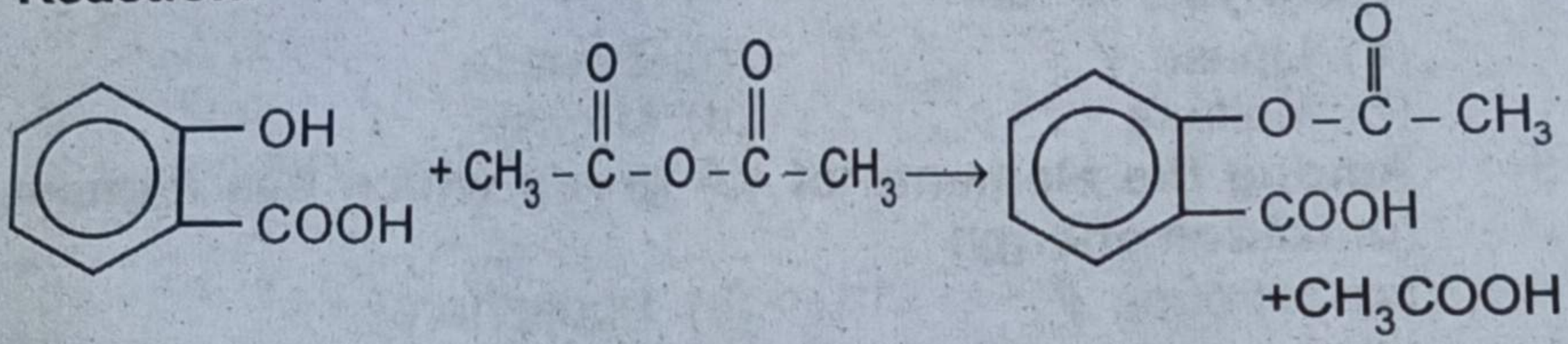
Ans Theory:

Aspirin is formed by the acetylating of salicylic acid. The addition of acetyl group-$COCH_3$ to an organic molecule is called acetylation. Acetylation takes place in acidic medium.

Material Required and Apparatus:

Ethyl alcohol 20 cm^3, sodium carbonate 20 g, Iodine 10 g.

Reaction:



Calicylix acid

Acetyl-salicylic acid (Aspirin)

Procedure:

Take 10 cm^3 of acetic acid and 10 cm^3 of acetic anhydride in round bottom flask. It is called acetylating mixture. Add 10 g of salicylic acid in it. Boil this mixture under reflux for 30 minutes. Stop heating and pour about 200 cm^3 of ice cold water in it. Stir the mixture vigorously. White crystals of aspirin will be formed, filter these crystals. Dry the crystals and show to the examiner.