QP Code :**70168**

[Time : 3 Hours] **[Total Marks : 100]**

Please check whether you have got the right question paper.

N.B. : 1. All Questions are compulsory.

2. Figures to the right indicate full marks.

3. Use of log-table/nonprogrammable calculator is allowed.

4. Answers for the same question as far as possible should be written together.

1. (A) Select the correct option and complete the following sentences. (any **twelve**) **12**

(i) Substances with higher reduction potentials are strong **oxidising agents.**

(ii) All metals lying above in electrochemical series can liberate H_2 gas by reaction with **acids**.

(iii) In galvanic cell, electrons are given off**by anode** electrode.

(iv) A system with zero degrees of freedom is known as **non variant**.

(v) The eutectic temperature of lead silver system is**576K**

(vi) All metals lying below in electrochemical series can liberate H_2 gas by reaction with **bases**.

(vii) In first transition series **Cr** element has its 3d level exactly half filled.

(viii) Solution containing hydrated Ti3+ is **purple** in colour

(ix) Ni among following Shows ferromagnetism

(x) The complex $[NiCN]_4^{2-}$ has **square planar** structure

(xi) Fe 2+ salts show blue colour with **K- ferricyanide**.

(xii) The molecular formula of chromium carbonyl is **$Cr(CO)_6$**

(xiii) Due to presence of electron withdrawing group strength of carboxylic acid **increases**.

(xiv) Aromatic carboxylic acid on heating with soda lime forms **arene**.

(xv) Carboxylic acid is prepared from grignard reagent by action of **CO_2**.

(xvi) **Detergents** are salts of sulfonic acids.

(xvii) Naphthalene on reaction with concentrated H_2SO_4 at 160^oC forms **2 – naphthalene sulphonic acid**.

(xviii) Nitro Benzene on reaction with oleum forms **m – nitro sulphonic acid**.

(B) State whether the following statements are true or false. (any **three**) **3**

(i) Any uni-univalent type salt can be used to prepare salt bridge - **FALSE**

(ii) Aqueous salt solution is a classic example of single phase system. **FALSE**

(iii) With increase in covalent character, acidic character of transition compounds increases - **True**

(iv) Ionisation isomerism is a form of stereoisomerism in coordination compounds- **False**

(v) Acetic acid is stronger than chloro acetic acid - **FALSE**

(vi) In IPSO substitution – SO_3H group is replaced by NO_2 group - **TRUE**

(C) Match the column. (any **five**) **5**

(i)	Salt bridge	(f)	**to minimize liquid junction potential**
(ii)	Clpyeron equation	(e)	$dP/dT = \frac{\Delta H_f}{T(V_{liq.} - V_{vapour})}$
(iii)	SCN^-	(b)	Ambidentate ligand
(iv)	Mo	(d)	Half filled state
(v)	Acyl nucleophilic substitution	(g)	Forms tetrahedral intermediate
(vi)	Reaction of different esters	(a)	Crossed Claisen condensation

2. Attempt any **four** of the following. **20**

(A) Differentiate between concentration and chemical cells. **5**
Any three differences – 3 marks
Example of type – 2 mark.

(B) Explain any two applications of Nernst equation in the study of galvanic cells? **5**
Any two applications with example – 2 ½mark each

(C) The emf of a cell Zn | $ZnSO_4$ || $CuSO_4$|Cu at 25°C is 0·3 V and the temperature coefficient of emf is -1·4 x 10^{-4} V per degree. Calculate the heat of reaction per mole for the reaction that taking place inside the cell. **5**

$\Delta H = nF\left[T\left(\frac{dE}{dT}\right)_P - E\right]$ - 2 marks

$= 2\,x\,96500\,[\,298(1\cdot 4x10^{-4}) - 0\cdot 03]$..... correct substitution – 2mks

= -24843J = -24.843KJ .... - 1 mk.

(D) Justify the number of phases and components present in the following system – **5**

$CaCO_3$ (solid) ⇌CaO (solid) + CO_2 (gas)

The number of phases with justification - 2½ mks.

The number of components with justification - 2½ mks.

(E) Derive Gibbs phase rule thermodynamically.
Correct derivation – 5 mks.

(F) The boiling point of a given solvent is 352·2K at 1·013 x 10^5 N m^{-2}. Calculate the boiling point of the given solvent at 0·63 x 10^5 N m^{-2}. (molar heat of vaporization of a solvent at 352.2 K is 31·8 kJ mol^{-1}; R= 8·314 JK^{-1} mol^{-1})

Given -

T_2 = 352.2K P_2= 1.013 x 10^5 N m^{-2} P_1 =0.63 x 10^5 N m^{-2}

T_1= ?

ΔH_v = 31.8 kJ mol^{-1} = 31.8 X 10^3J mol^{-1}, R= 8.314 JK^{-1} mol^{-1} -- 1mk

$\log P_2/P_1 = \frac{\Delta H_{vap}}{2\cdot 303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$ - 1 mks.

Correct substitution of respective values – 2 marks

T_1 = 1/0.002963 = 337.49= 337.5 K Correct answer – 1 mks

3. Attempt any **four** of the following. **20**

(A) Explaination of two terms - 2 marks each **05**
One example each ½ mark each

(B) Names of oxides of Titanium and Vanadium –1 ½ mark each =03 **05**
Any two properties of oxide of Titanium and Vanadium -½ mark each =02

(C) Any five evidences of formation of coordination compounds- 1 mark each **05**

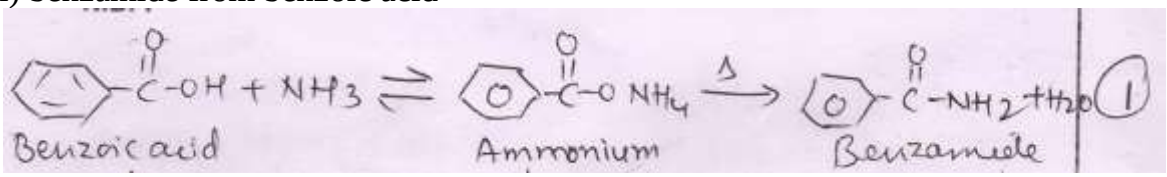
(D) Colour property of transition metals- Explanation with examples on the basis of i. **05**
Presence of unpaired electrons
ii. d-d transition of electrons
iii.Splitting of d orbitals and absorption of of light of certain wavelength

(E) **Werner's Theory –** postulates 03 marks
Examples 02 marks

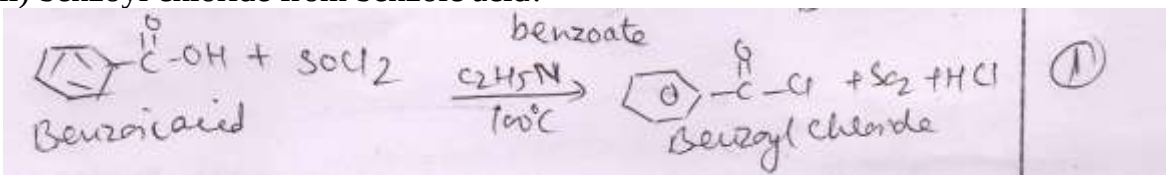
(F) Note on variable oxidation state of transition metals- Brief account -03 marks
Examples w.r.t. oxidation states - 02 marks

4. Attempt any **four** of the following. **20**

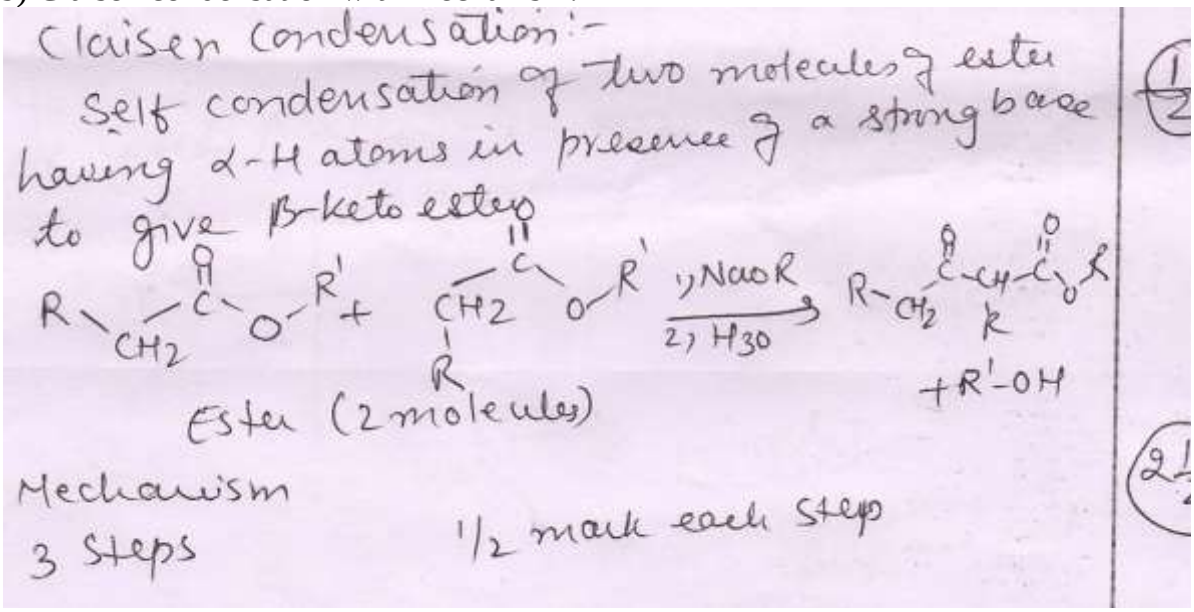
(A) a) How will you prepare—
i) benzamide from benzoic acid-



ii) benzoyl chloride from benzoic acid?

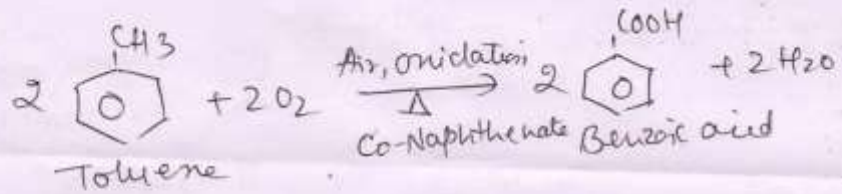


b) Claisen condensation with mechanism.



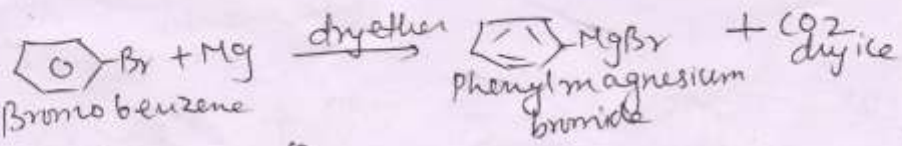
(B) a) Benzoic acid preparation -

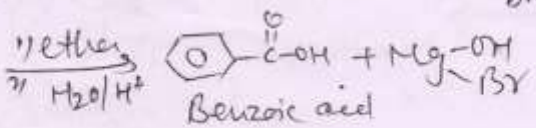
a



(½)

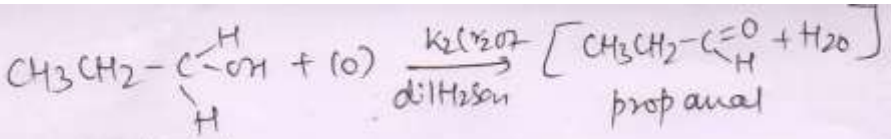
b

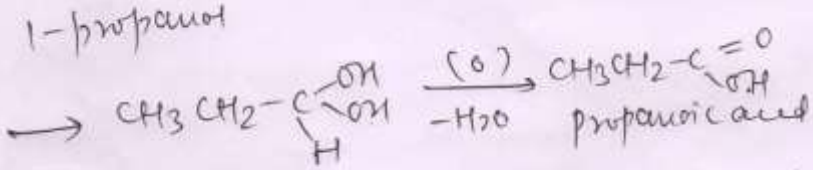




(1½)

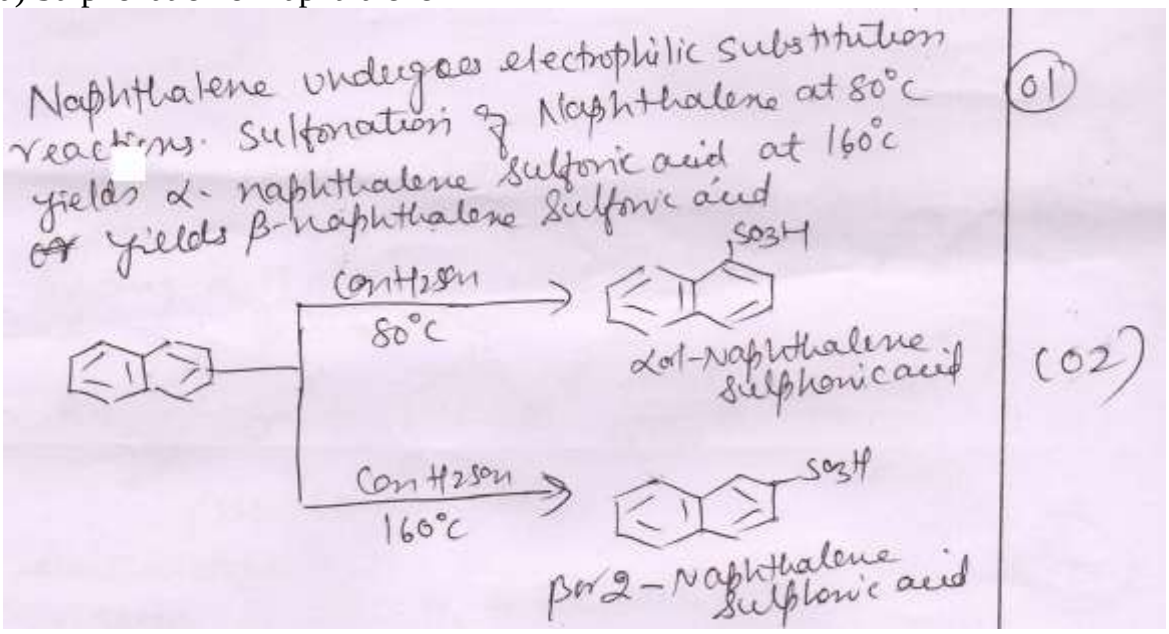
b)





(02)

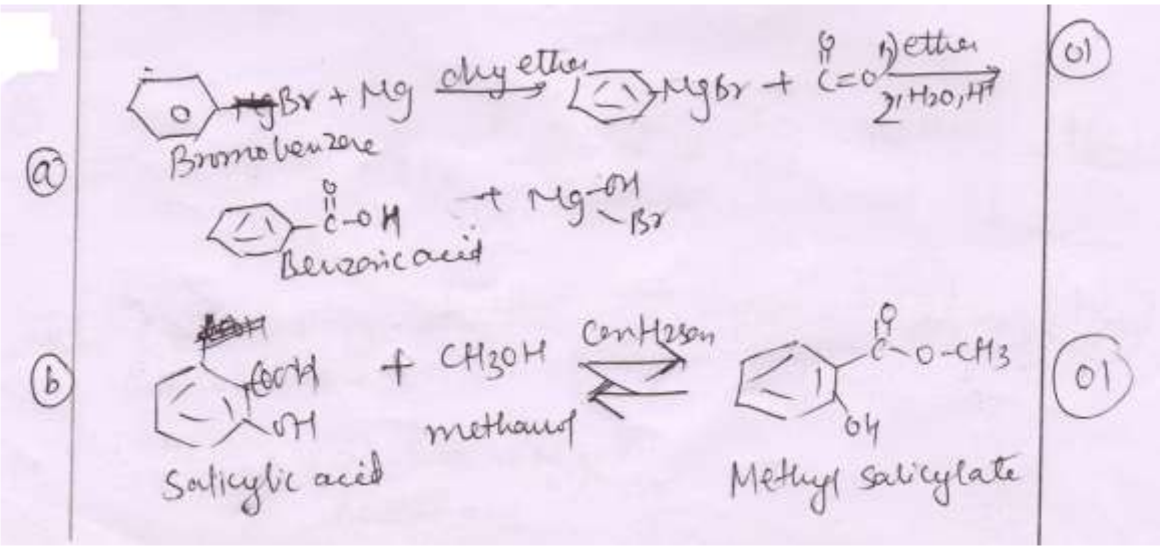
(C) a) Sulphonation of naphthalene



(01)

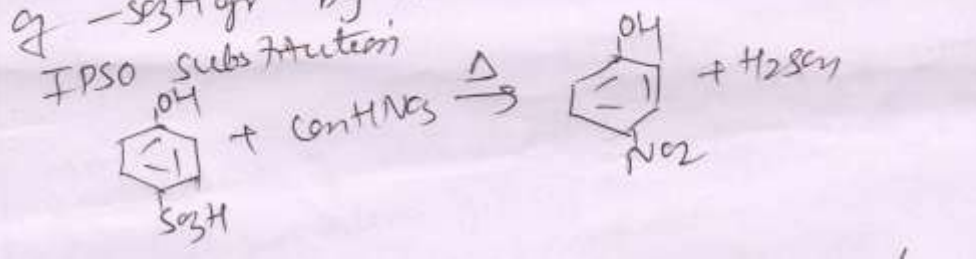
(02)

b)



(D) a)

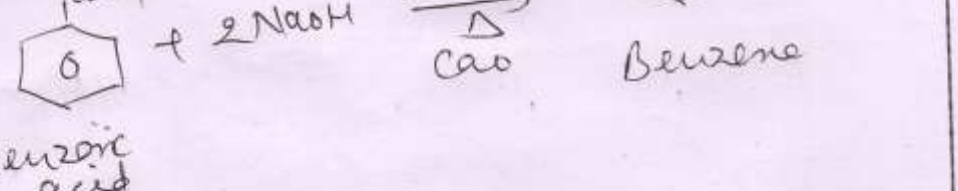
IPSO substitution
Aromatic ring in which $-SO_3H$ group is attached undergoes electrophilic substitution reaction in the same way as the ring carrying strongly electron attracting gr. (02)
It deactivates the ring & is meta directing.
This type of electrophilic attack in aromatic sulfonic acids which results in replacement of $-SO_3H$ gr by H-atom is known as IPSO substitution (01)



b)

Decarboxylation

When carboxylic acid is heated strongly with soda lime, it eliminates CO_2 to give alkane or arene. (01)



Benzoic acid — Benzene (01)

Acid strength of

(E) a)

Effect of substituents on Acid strength of Aliphatic acids (02)

1) presence of electron withdrawing substituents or like F, Cl, Br, CN, NO_2 (−I effect)
∴ helps to release proton ∴ strength of acid increase
Explanation with example

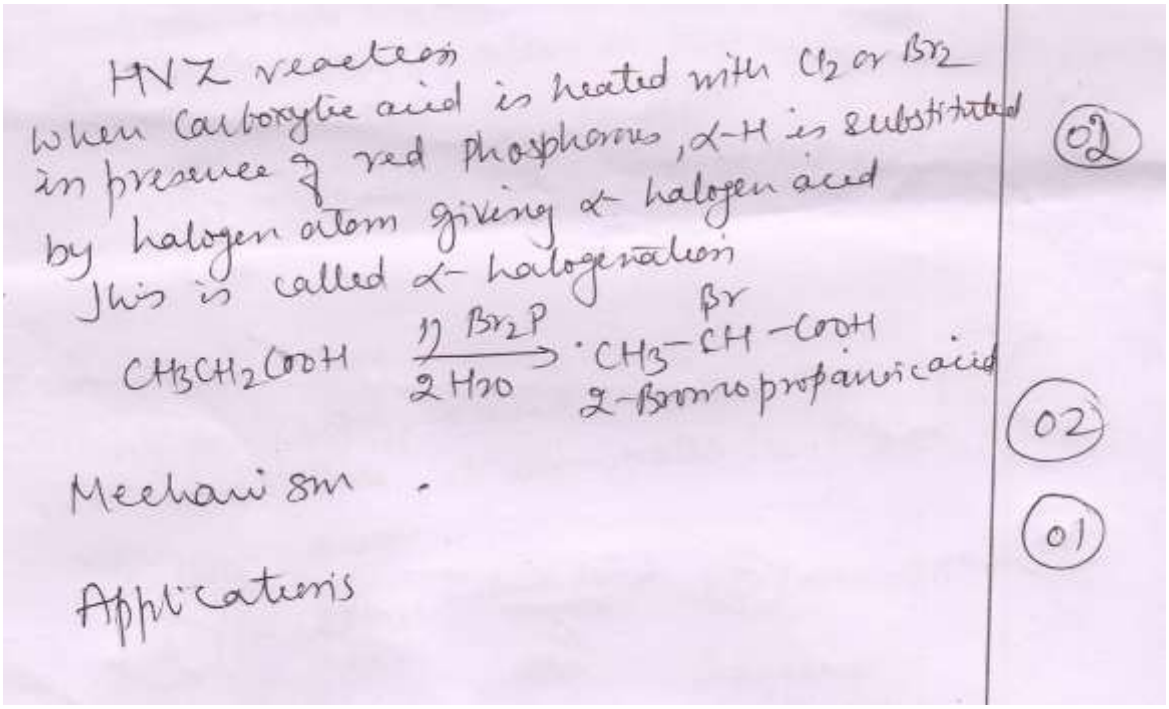
2) presence of electron donating or +I effect
∴ release of proton is difficult
Explanation with example

Marks 02

b)

2-methyl butanoic acid (01)

(F)



5. Attempt any **four** of the following. **20**

(A) What are the advantages and disadvantages of Quinhydrone electrode in the determination of pH? **5**

Any three advantages – 3 mks
Any 2 disadvantages – 2 mks.

(B) Ether boils at 306K at 1.00 x 10^5 Pa pressure. At what temperature will it boil at a pressure of 9.85 x 10^3 Pa? Given that the molar enthalpy of vaporization of ether is 2.74 x 10^4 J mol^{-1}.

Given that ΔH_{vap} = 2.74 x 10^4 J mol^{-1}. - **1mk**

T_2 = 306K; T_1 = ?

p_2 = 1.00 x 10^5 Pa p_1 = 9.85 x 10^3 Pa

Substituting these values in Clausius – Clapeyron equation—

$\log {}^{p_2}/_{p_1} = \frac{\Delta H_{vap}}{2{\cdot}303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$ - **1mk**

$\log {}^{1.00 \text{ x } 10^5 \text{Pa}}/_{9.85\ x\ 10^3 Pa} = \frac{2.74 \text{ x } 10^4 \text{ J mol}^{-1}}{2{\cdot}303R}\left[\frac{306-T_1}{T_1 306}\right]$ -**2mk**

$\therefore T_1$ = 252K -**1mk**

(C) Representation in tabular form 04 marks
Names of elements with special stability 01 mark

(D)

1) Fischer Esterification — 01

Acid catalyzed esterification is known as Fischer esterfication — 1½

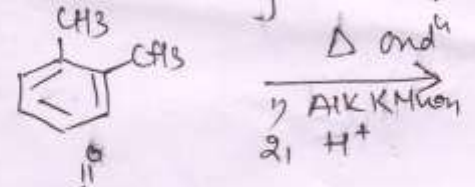
Any Examples

2) Ammonolysis — 01

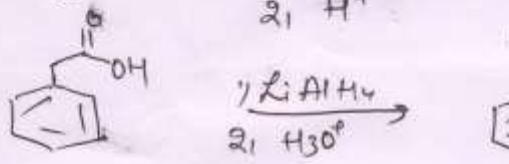
Ester when heated with ammonia, acid amide and an alcohol is obtained. This is called ammonolysis — 1½

(E)

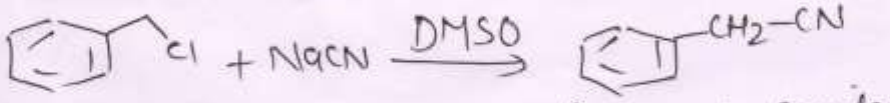
Any Examples

a) 

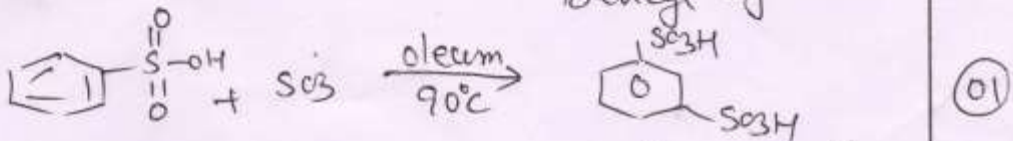
O-Toluic acid — 01

b) 

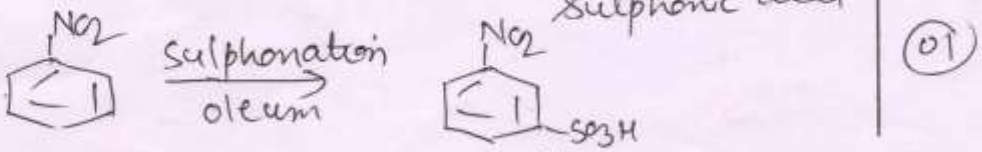
Benzyl alcohol — 01

c) 

Benzyl cyanide — 01

d) 

m-benzene di-sulphonic acid — 01

e) 

m-nitro benzene sulphonic acid — 01