## B.Sc. 4<sup>th</sup> Semester (Honours) Examination, 2022, (CBCS) Subject: Chemistry (Organic Chemistry- IV) Paper: CC-10

**Time: 2 Hours** 

Full Marks: 40

1. Answer any *five* questions from the following:

 $5 \times 2 = 10$ 

 a) Explain why the following compound does not undergo Pinacol-Pinacolone Rearrangement.



- b) Ethylene and acetylene do not show C-C multiple bond stretching frequency in IR. Why?
- c) What is the full form of TMS? Why it is used as the reference compound in <sup>1</sup>H-NMR?
- d) Convert Salicyldehyde to Catechol with mechanism.
- e) Aromatic protons are more deshielded than ethlenic protons although both cases the protons are attached to sp<sup>2</sup> hybridized C-atoms- Explain.
- f) Explain why a polar solvent usually shifts the  $\pi$  to  $\pi^*$  transition to longer wavelength.
- g) The IR spectrum of Ethylacetoacetate shows absorption at 1748 cm<sup>-1</sup>, 1724 cm<sup>-1</sup>, 1650 cm<sup>-1</sup>.- Explain.
- h) Give the synthetic equivalents of the following ions.

2. Answer any *two* questions from the following:

(a) (i) Give the synthesis of the following compound with mechanism using a rearrangement reaction as the key step.



 $2 \times 5 = 10$ 

(ii) Alkyl halides produce mainly cyanides with aq. ethanolic KCN but with AgCN, isocyanides are the major products. Explain. 2

- (b) (i) How can you distinguish *cis*-stilbene and *trans*-stilbene by UV-spectroscopy? 2
  - (ii) Calculate the  $\lambda_{max}$  for the following compounds:



(c) (i) The position of the UV absorption maxima of aniline in aq solution are different from those of benzene but are almost identical with those in a solution of pH 1.- Explain.
(ii) Distinguish between o-hydroxybenzaldehyde and p-hydroxybenzaldehyde using IR spectroscopy.

(d) (i) Identify the product with mechanistic details:



(ii) How the following reagents are used to protect the functional group in organic synthesis?Give example.



3. Answer any <i>two</i>	questions from the following:	$2 \times 10 = 20$
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(a) Show retrosynthesis of the following compounds with forward synthesis.  $2.5 \times 4 = 10$ 

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(b) (i) Phenols can be converted to anisole using diazomethane. But aliphatic alcohols cannot be converted to the corresponding methyl ether by this method. Explain.
(ii) Complete the following reaction
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(iii) Two possible disconnections (a & b) of a target molecule are shown below. Obtain a pair of suitable synthons from each disconnection and indicate the umpolung synthon, if any. Give a synthetic equivalent for each synthon.



(iv) Alkaline hydrolysis of benzonitrile affords the salt of an acid but in presence of hydrogen peroxide, an amide is formed.- Explain.

(c) (i) Identify the products with mechanism of step A to B and C to D.

$$\frac{i)Mg/Hg \text{ in } dry \text{ ether}}{ii)H_3O^+} A \xrightarrow{C. H_2SO_4} B \xrightarrow{LAH} C \xrightarrow{C. H_2SO_4} D$$

(ii) Write down the Gabriel's Phthalimide synthesis for the preparation of EtNH<sub>2</sub>. Why the primary amine like Et<sub>3</sub>C-NH<sub>2</sub> cannot be prepared by the above method?

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(iii) Explain why the diazocoupling reaction with phenol should be best carried out at pH 9. What will happen if the diazonium coupling reation with phenol is carried out at pH > 10?

(d) (i) How many signals will you expect in <sup>1</sup>H-NMR spectrum of o-dinitrobenzene? Assign the signals and arrange them in increasing order of their Chemical Shifts. State the splitting pattern of the signals. 3 (ii) When p-aminophenol is made to react with benzene diazonium chloride in alkaline and acid medium separately, different products are obtained. Explain.

(iii) Convert p-bromonitrobenzene to m-bromobenzoic acid with plausible mechanism. 4

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