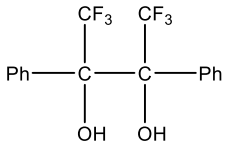
B.Sc. 4th Semester (Honours) Examination, 2022, (CBCS)
Subject: Chemistry
(Organic Chemistry- IV)
Paper: CC-10

Time: 2 Hours **Full Marks: 40**

1. Answer any ***five*** questions from the following: **5 × 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 ^{1}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^2 hybridized C-atoms- Explain.

f) Explain why a polar solvent usually shifts the π to π* transition to longer wavelength.

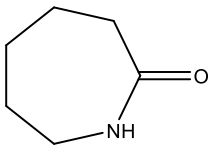
g) The IR spectrum of Ethylacetoacetate shows absorption at 1748 cm $^{-1}$, 1724 cm $^{-1}$, 1650 cm $^{-1}$.- Explain.

h) Give the synthetic equivalents of the following ions.

i) $^{\ominus}COOH$ ii) $^{\oplus}CH_2CH_2OH$ iii) $^{\ominus}CH_2COOH$ iv) $^{\ominus}Ph$

2. Answer any ***two*** questions from the following: **2 × 5 = 10**

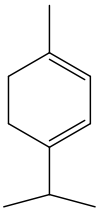
(a) (i) Give the synthesis of the following compound with mechanism using a rearrangement reaction as the key step. 3

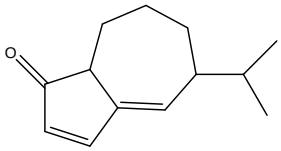


(ii) Alkyl halides produce mainly cyanides with aq. ethanolic KCN but with AgCN, isocyanides are the major products. Explain. 2

(b) (i) How can you distinguish *cis*-stilbene and *trans*-stilbene by UV-spectroscopy? 2

(ii) Calculate the λ_{max} for the following compounds: 3

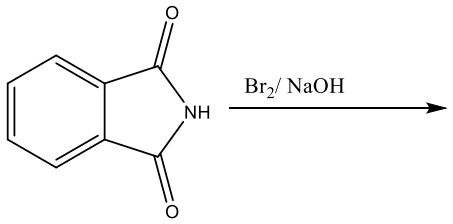
(I) 

(II) 

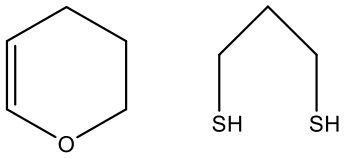
(c) (i) The position of the UV absorption maxima of aniline in aq solution are different from those of benzene but are almost identical with those in a solution of pH 1.- Explain. 3

(ii) Distinguish between o-hydroxybenzaldehyde and p-hydroxybenzaldehyde using IR spectroscopy. 2

(d) (i) Identify the product with mechanistic details: 3

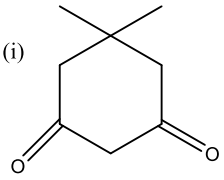


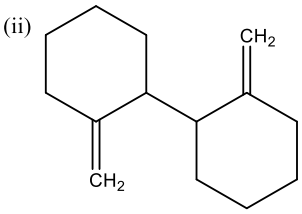
(ii) How the following reagents are used to protect the functional group in organic synthesis? Give example. 2

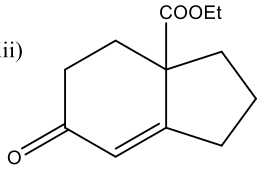


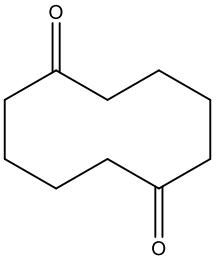
3. Answer any ***two*** questions from the following: **2 × 10 = 20**

(a) Show retrosynthesis of the following compounds with forward synthesis. 2.5 × 4 = 10

(i) 

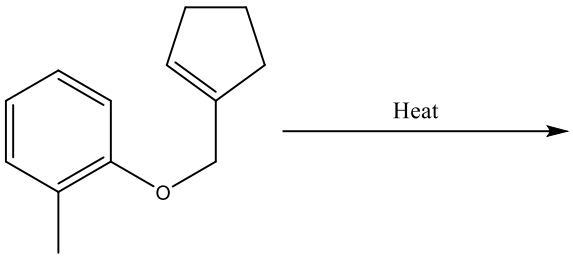
(ii) 

(iii) 

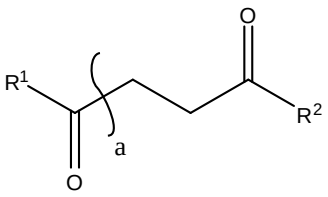
(iv) 

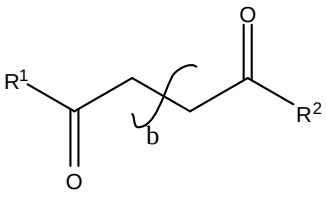
(b) (i) Phenols can be converted to anisole using diazomethane. But aliphatic alcohols cannot be converted to the corresponding methyl ether by this method. Explain. 2

(ii) Complete the following reaction 2



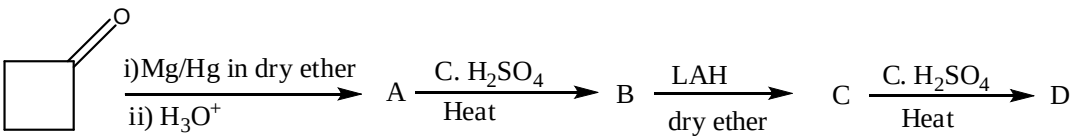
(iii) Two possible disconnections (a & b) of a target molecule are shown below. Obtain a pair of suitable synthons from each disconnection and indicate the umpolung synthon, if any. Give a synthetic equivalent for each synthon. 4





(iv) Alkaline hydrolysis of benzonitrile affords the salt of an acid but in presence of hydrogen peroxide, an amide is formed.- Explain. 2

(c) (i) Identify the products with mechanism of step A to B and C to D. 4



(ii) Write down the Gabriel's Phthalimide synthesis for the preparation of $EtNH_2$. Why the primary amine like $Et_3C\text{-}NH_2$ cannot be prepared by the above method? 3

(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? 3

(d) (i) How many signals will you expect in ^{1}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. 3

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