B.Sc. 4th Semester (Honours) Examination, 2019

Subject : Chemistry

Paper : CC-10

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

The figures in the margin indicate full marks.

*Candidates are required to give their answers in their own words
as far as practicable.*

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

   (a) Define synthon and synthetic equivalent with one example for each.

   (b) What are the products you expect on reduction of nitrobenzene with

      (i) Zn-dust, ammonium chloride, methanol

      (ii) Zn-dust, methanol, sodium hydroxide?

   (c) Explain the terms bathochromic shift and hypsochromic shift in U.V. spectroscopy.

   (d) Give the products:

      (i)

      (ii) $N_2CHCO_2Et \xrightarrow{h\gamma}$? $\longrightarrow$?
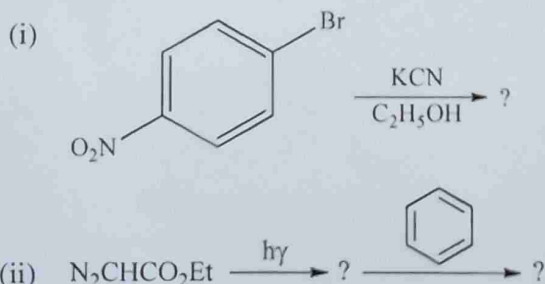
   (e) Define magnetically equivalent protons and chemically equivalent protons in light of NMR spectroscopy with one example for each.

   (f) Identify M, N, O and P.
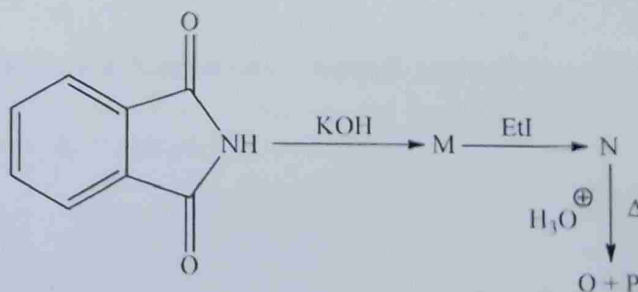
   (g) Name the factors that affect chemical shift positions of protons in different organic compound in ^{1}H NMR spectrum.

(h) Explain why cyclobutane ring formation is difficult as compared to either cyclopropane or cyclopentane ring formation.

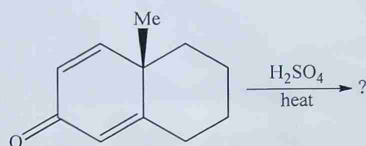2. Answer *any two* questions from the following: 5×2=10

(a) (i) Predict the product(s) when an unsymmetrical ketone, having enolisable α-Hs, in an acid medium, is made to react with a secondary amine. Explain your prediction.

1+2=3

(ii) Draw the product of the following reaction and mention the steps involved: 2

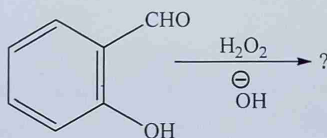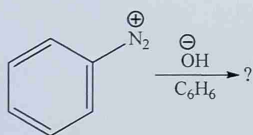$$\xrightarrow[\text{heat}]{\text{H}_2\text{SO}_4} \quad ?$$

(b) (i) What happens when cyclohexanone is treated initially with hydroxylamine hydrochloride and subsequently with phosphorus pentoxide? Predict the product(s) with mechanism. 1+2=3
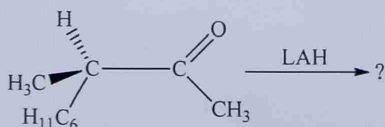
(ii) Predict the product in each of the following reactions: 1+1=2

$$\xrightarrow[\text{C}_6\text{H}_6]{\overset{\ominus}{\text{OH}}} \quad ?$$

$$\xrightarrow[\overset{\ominus}{\text{OH}}]{\text{H}_2\text{O}_2} \quad ?$$

(c) (i) Predict the major product formed in the following reaction and explain its formation using Felkin–Anh model. 3
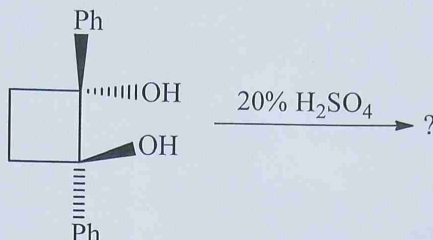

$$\xrightarrow{\text{LAH}} \quad ?$$

(ii) Why is excess of diazomethane used in Arndt-Eistert synthesis? 2
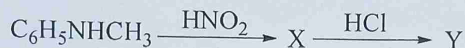
(d) (i) Identify the product(s) formed in the following reaction given below. Justify your prediction with proper mechanism. 1+2=3

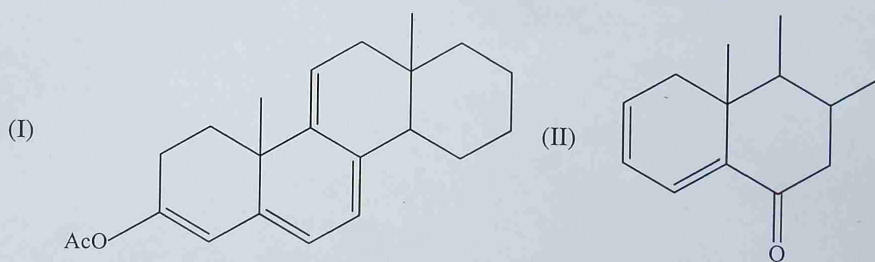$$\text{(cyclobutane with Ph, OH groups)} \xrightarrow{20\% \ H_2SO_4} \ ?$$

(ii) Complete the following: 1+1=2

$$C_6H_5NHCH_3 \xrightarrow{HNO_2} X \xrightarrow{HCl} Y$$

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

(a) (i) Predict the λ_{max} for the following compounds using Woodward's rule: 2+2=4

(I)   (II)

AcO

(ii) The molar extinction coefficient (ε) value for acetyl acetone in water is much less compared to the (ε) value measured in isooctane though their λ_{max} value in water (274 nm) and in isooctane (272 nm) are comparable. [$\varepsilon_{water} \sim 2000$; $\varepsilon_{isooctane} \sim 12000$] 3

(iii) How can you distinguish the following pairs of molecules by UV spectroscopy? (I)1,3– Butadiene and Butanone, (II) *p*-nitrophenol and *m*-nitrophenol (in faintly basic medium) 1½+1½=3
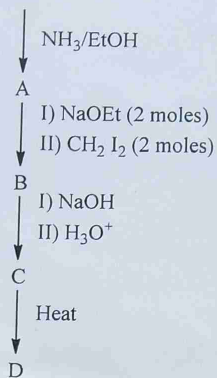
(b) (i) Using retrosynthetic analysis, suggest a possible synthetic route for the following target molecules. [Both backward and forward routes are to be shown with required reagents and conditions.] 3+3=6

(I)   (II) $Me_3C \ CH_2 \ CO_2 \ Et$
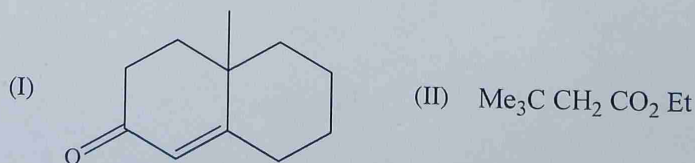
(ii) Identify the products given below:

Acetone (1 mole) + Ethylcyanoacetate (2 moles)   4

$\downarrow$ $NH_3/EtOH$

A

$\downarrow$ I) NaOEt (2 moles)
  II) $CH_2 I_2$ (2 moles)

B

$\downarrow$ I) NaOH
  II) H_3O^+

C

$\downarrow$ Heat

D

(c)   (i) Is it possible to distinguish an aromatic compound from an anti-aromatic one using ^1H NMR spectroscopy? Explain.   1½

(ii) How many ^1H NMR signals do you expect in the spectrum of *o*-dinitro benzene? Draw their pattern and assign their position in the spectrum with respect to the structure. ½+1+½+½=2½

(iii) Identify the compound (x) having molecular formula $C_4H_8O_2$ from the spectroscopic data given below. You have to relate each data with your predicted structure.

UV : 206 nm   2+1+1+2=6

IR : 1736 cm^{-1}

^1H NMR(δ) :   0·95 (3H, t, J = 7·0 Hz),

1·67 (2H, sextet, J = 7 Hz),

4·12 (2H, t, J = 7 Hz),

8·07 (1H, S)

(d)   (i) Carbon tetrachloride is gradually added into neat ethyl alcohol. Comment on the changes that may be observed in the IR absorption of O–H stretching frequency.   2

(ii) Distinguish between the members of the following pairs using IR spectroscopy: 2+2=4
(I) Vinyl acetate and methyl acrylate
(II) Cyclohexanone and 2-ethyl cyclopentanone

(iii) Does the O – H absorption peak in IR spectrum shift if 'H' is replaced by 'D'? Justify your view.
                                                                           2

(iv) Can IR spectroscopy be a handy tool to study the progress of the following reaction? Justify your answer.
                                                                    ½+1½=2