

[This question paper contains 9 printed pages]

Your Roll No

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M.Tech./II Sem.
CHEMICAL SYNTHESIS AND PROCESS
TECHNOLOGIES

Paper-203 Spectroscopy-II and Heterocyclic Chemistry
(Chemical Synthesis and Process Tech)

Time 3 Hours

Maximum Marks 70

*(Write your Roll No. on the top immediately
on receipt of this question paper)*

Use separate answer sheet for section A and B.

SECTION-A

Attempt all the questions

- 1 Attempt any *six* of the following (answer should not be more than 2-3 lines) 2×6
- (a) Ethyl benzene gives base peak at m/z 91, while propyl benzene gives two peaks at m/z 91 and m/z 92 Explain
- (b) An unknown compound has a molecular ion peak at m/z 110 with relative intensity of 100% The relative intensity of $M+1$ peak is 6.5% and that of

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M+2 is about 4.7% Calculate molecular formula of the compound

- (c) Methyl carbon of acetonitrile appears at 17.9 ppm in ^{13}C NMR, while methyl carbon of methyl chloride appears at 28.7 ppm, even though cyano group has higher electronegativity than cyano group (dipole moment of acetonitrile is 3.92D, while methyl chloride has dipole moment of 1.85D) Explain
- (d) A compound shows M^+ peak at 186 (100%), M+2 peak at 188 (19.5%), and M+4 peak at 190 (9.5%) It shows only one signal in the ^1H NMR Identify the compound
- (e) How will you distinguish between isomeric alcohols of molecular formula $\text{C}_5\text{H}_{12}\text{O}$ by MS
- (f) How will you differentiate between propyne and but-2-yne by ^{13}C NMR
- (g) How will you differentiate between *o*-tolyl-methanol and *p*-tolyl-methanol by MS
- (h) How many signals do you expect for 2,2,4-trimethyl-1,3-pentanediol in ^{13}C NMR
- (i) An aromatic hydrocarbon shows molecular ion peak at m/z 121 Find out molecular formula of the compound

- 2 IR, ^1H NMR, ^{13}C NMR and mass spectral of an unknown compound are given in chart A. Deduce the structure of the compound, assign the peaks, and show the mass spectral fragmentation 12

Or

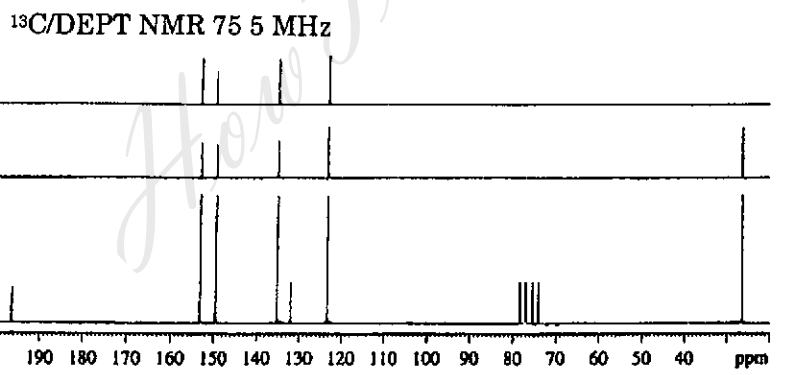
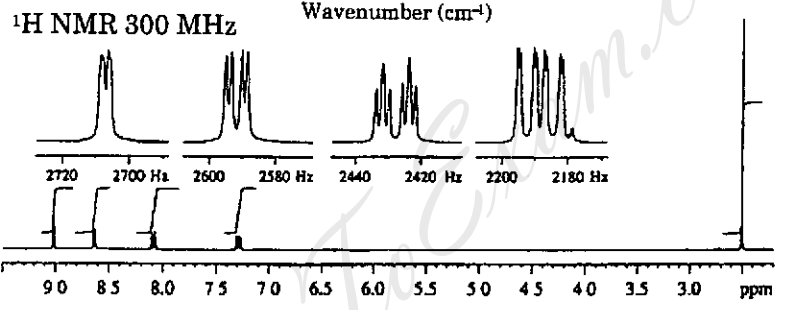
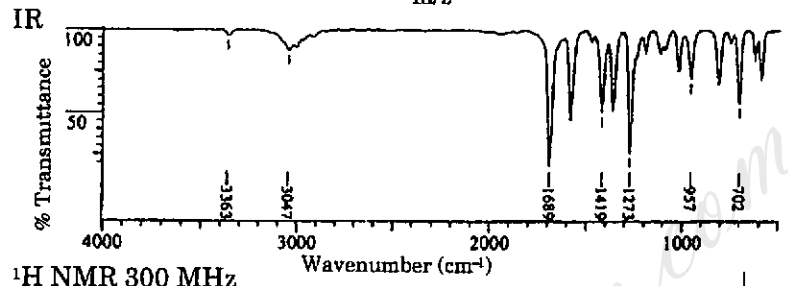
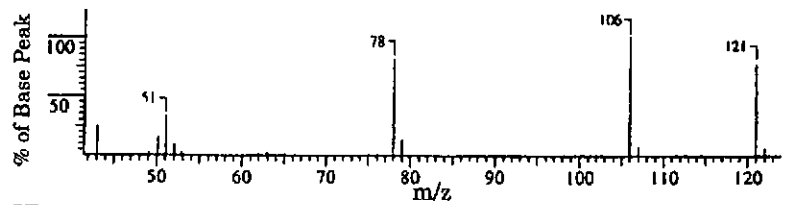
- (a) A compound of MF $\text{C}_{13}\text{H}_{20}\text{O}_2\text{N}_2$ gave following spectral data IR 3500, 3400, 1735 (cm^{-1}), ^1H NMR 1.15 (t, 6H), 2.4-2.8-1.9 (m, 6H), 3.70 (brs, 2H), 4.10 (t, 2H), 6.8 (d, $J = 8\text{Hz}$, 2H), 7.8 (d, $J = 8\text{Hz}$, 2H), ^{13}C NMR 13.7 (+), 46.4 (-), 53.2 (-), 66.2 (-), 115 (+), 120.5 (Cquart), 130.4 (+), 151.2 (Cquart), 167.2 (Cquart), MS (m/z) 236 (M^+), 235, 207, 164, 150, 121. Find out structure of the compound and assign all the peaks 8
- (b) A compound of MF $\text{C}_7\text{H}_7\text{NO}$ gave following spectral data ^1H NMR 2.83 (m, 2H), 3.82 (t, 1H), 7.52 (d, $J = 8\text{Hz}$, 2H), 8.66 (d, $J = 8\text{Hz}$, 2H), ^{13}C NMR 48.8 (-), 57.3 (+), 123.2 (+), 149.7 (+), 152.7 (Cquart), MS (m/z) 121 (M^+) Find out structure of the compound 4

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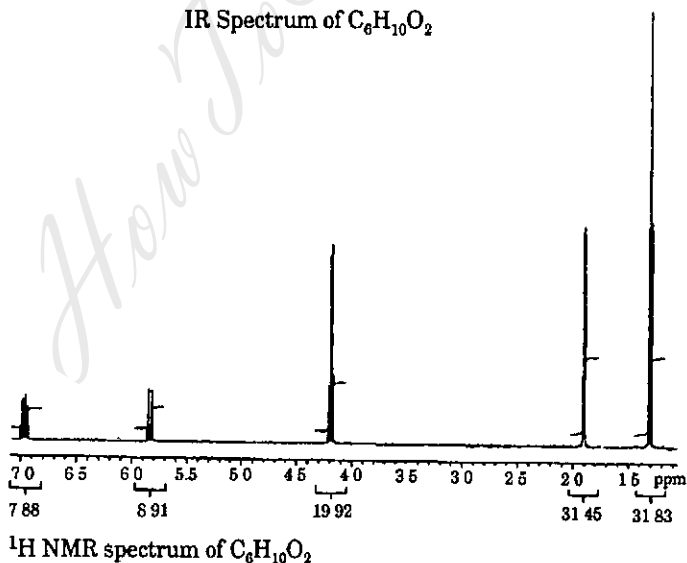
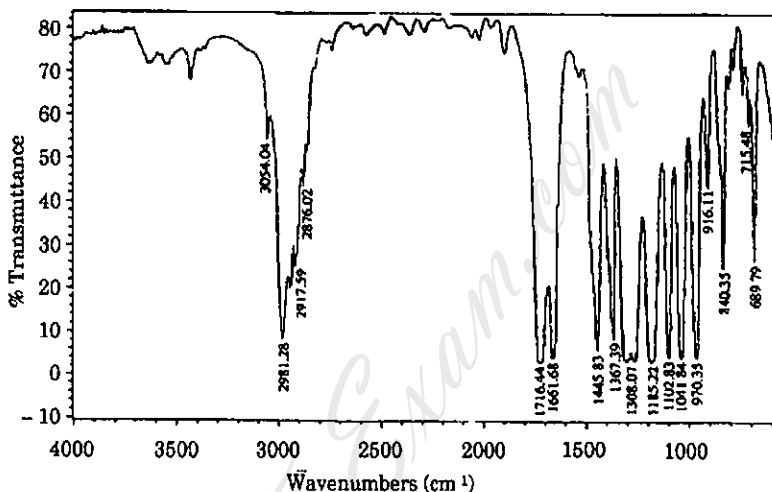
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CHART A



- 3 The molecular formula of an organic compound is $C_6H_{10}O_2$. 1H , ^{13}C , COSY and HETCOR NMR spectra are given below. In addition to this IR spectrum is also given below. Find out the structure and assign all the peaks.

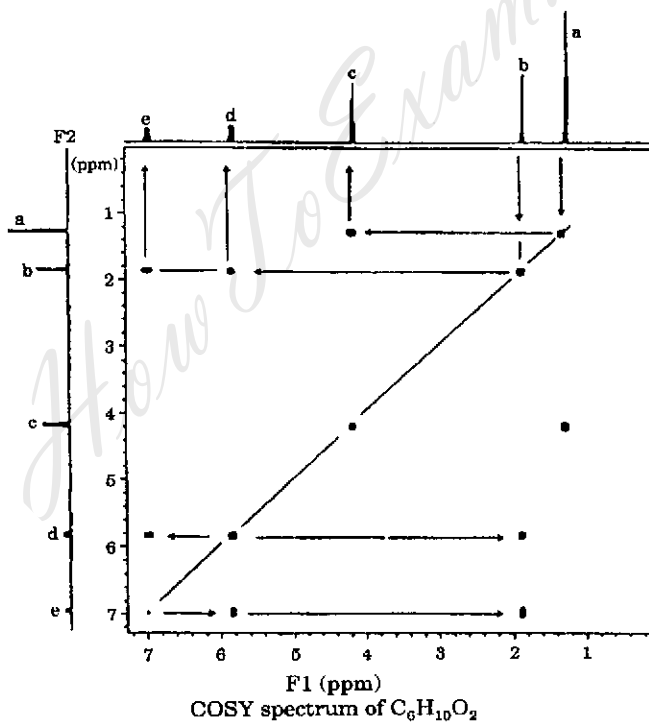
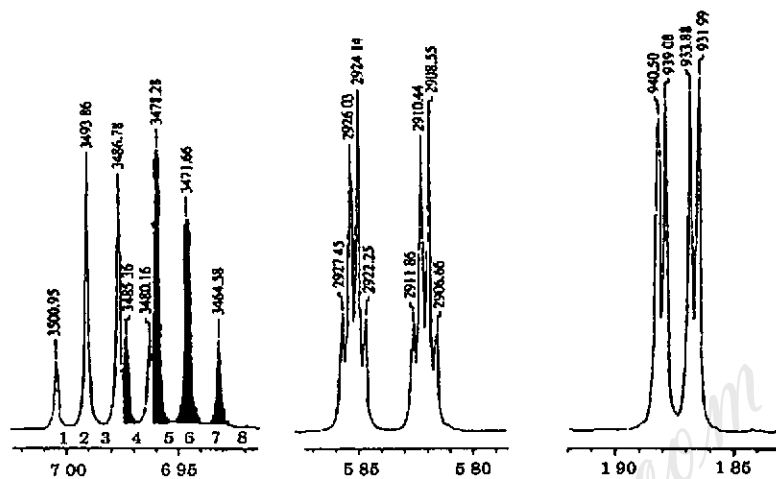
1×11=11

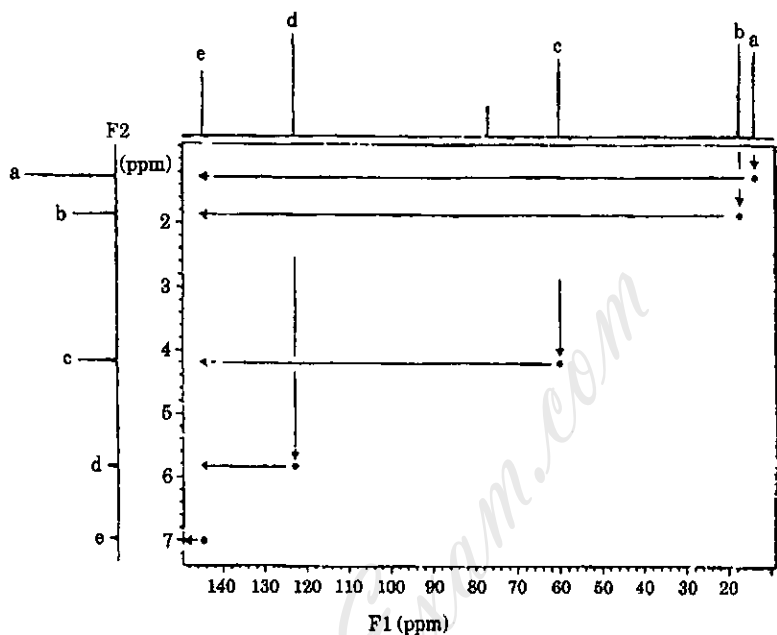


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HETCOR spectrum of $C_6H_{10}O_2$

Or

(a) Write short notes on any *three* of the following

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- (i) HSQC
- (ii) HMBC
- (iii) ROESY
- (iv) FID

(b) Discuss the hyperfine splitting of diethyl ether radical.

2×1=2

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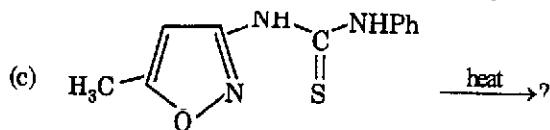
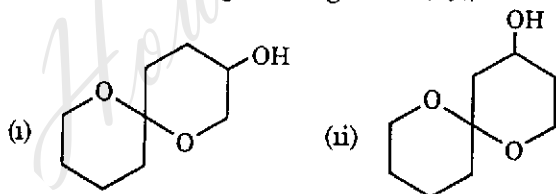
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SECTION-B

Answer three questions in all

Question No 4 is compulsory.

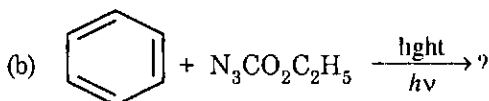
- 1 (a) Discuss the mechanism of
(i) Hoch Campbell reaction
(ii) Davis Pizzini reaction
(b) Discuss the use of the azalactone route L-DOPA 11
- 2 (a) How can 1,3-dipolar cycloaddition be used for the synthesis of isoxazoles
(b) What is Boulton-Katritzky rearrangement? Identify the product of the reaction of benzofuroxan with ethyl acetoacetate and morpholine. Discuss the mechanism of this reaction 11
- 3 (a) Discuss a synthesis of Serotonin
(b) What are 'anomeric effect' and 'double anomeric effect'? Predict the most favourable conformations for the two compounds given below



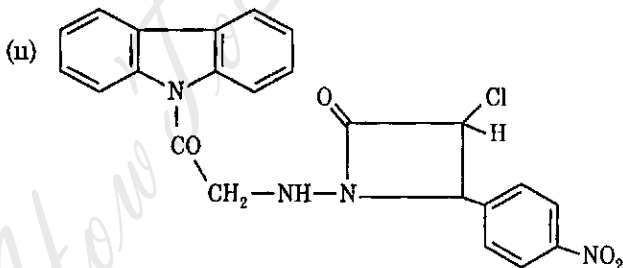
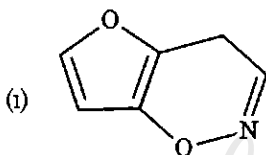
Explain the reaction and name the product

- (d) How can Valium be synthesised? 11

- 4 (a) Discuss the limitations of the Corey Tramontano synthesis of methoxatin. How can these be overcome?



- (c) Discuss the Corey-Chaykovsky reaction using both dimethyl sulphide and dimethyl sulphoxide
- (d) How can the following be named systematically



- (e) Put down the chemical structure for

(i) Trans-1,2-dimethyl-3-phenyl aziridine

(ii) 4H-[1,3]-Thiazino [3,4,-a] azepine

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