

This question paper contains 9 printed pages.]

Your Roll No.

4342

A

M.Tech./II Sem.
CHEMICAL SYNTHESIS AND PROCESS
TECHNOLOGIES
Paper-203 : Spectroscopy-II and Heterocyclic
Chemistry

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 : Spectroscopy-II

Attempt all the questions.

1. (a) Write down the structures of some molecular ions. Locate the charge at the most preferable position. 3
 - (i) 1- Butene
 - (ii) trifluoroethanol
 - (iii) Pyridine
- (b) What is the statement of the even-electron rule? 1
- (c) What is the statement of Stevenson's rule? 1

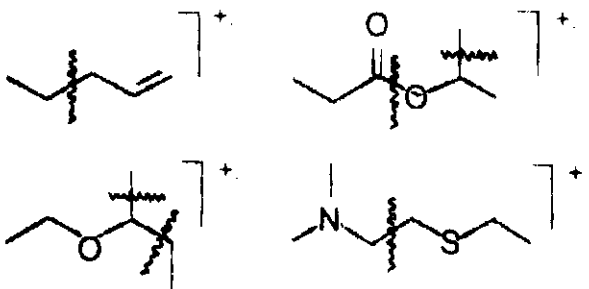
[P.T.O.]

(d) Where will the charge reside according to Stevenson's rule?

Write down the structures of the preferred fragment ions upon

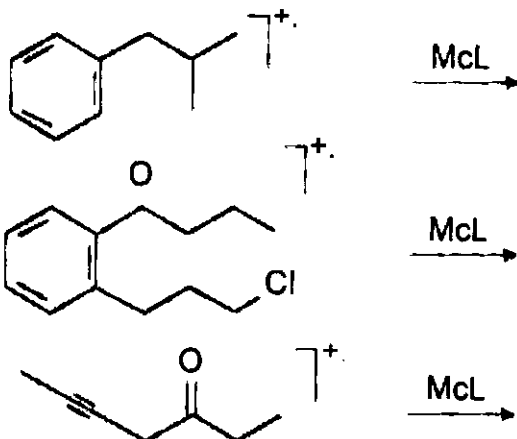
cleavage of the bonds indicated below :

4



2. Write short note on methods of ionization in mass spectroscopy. 4

3. Decide which of the following molecular ion can undergo McLafferty rearrangement. Even two pathways might occur for one ionic species. 4



4. Once an M.Sc. Student ROSEY got an unlabelled bottle containing an organic compound with ten probable structures (given below, Figure 1) and was asked to identify the correct structure of that

compound. In order to identify the compound, she initially run simple ^1H NMR (shown below, **Figure 2**) and concluded five isomeric structures out of ten structures as her probable choices. What were those structures? Then she performed 2D Homonuclear correlation NOESY and COSY experiments and recorded the spectra (shown below, **Figure 3**) of that compound. She also performed Heteronuclear correlation HMQC and found that the two resonances between δ 9.0 and 10.0 ppm do NOT show ANY short range C-H coupling. After careful analysis of 2D correlation spectra, she ended with one structure out those five choices. What was her choice?

Chemical Shifts are approximate.

3 + 5

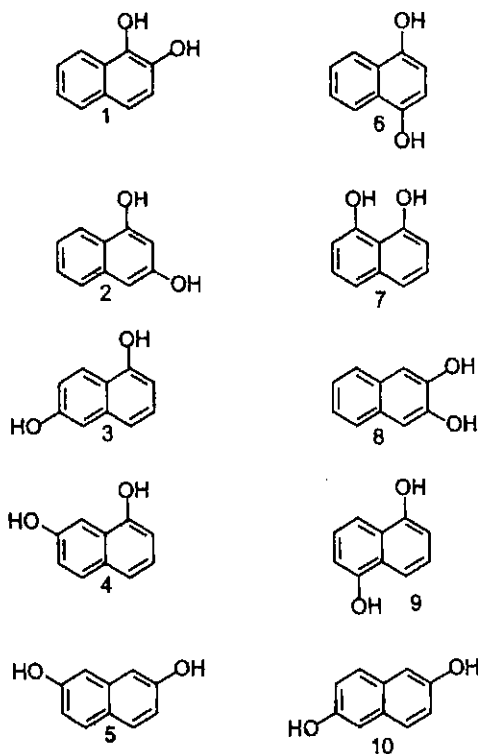


Figure 1 : Probable structures of compound

[P.T.O.]

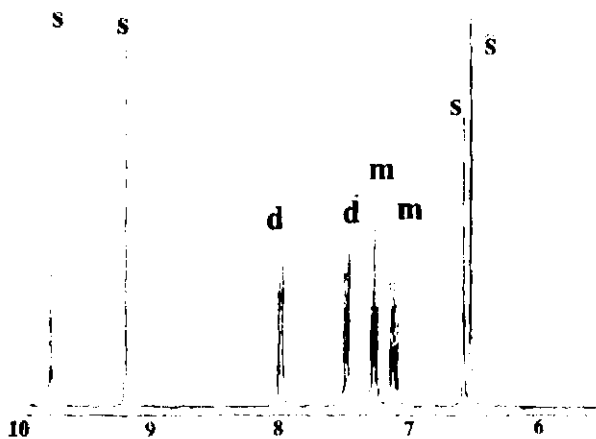
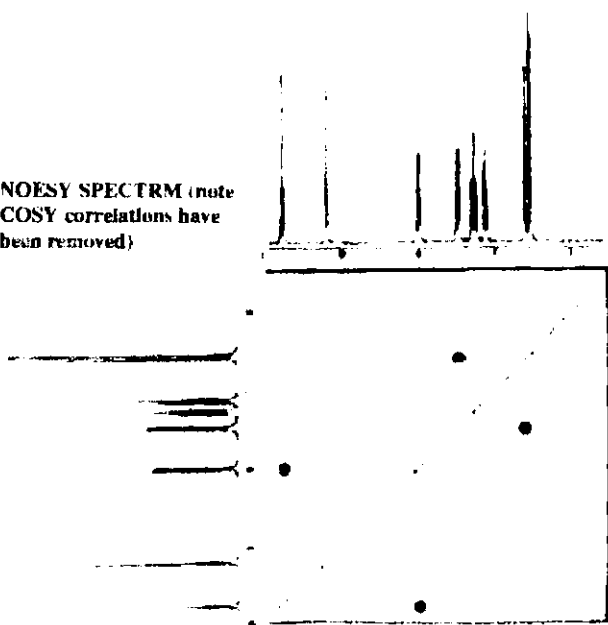


Figure 2 : ¹H NMR Spectrum of the compound

NOESY SPECTRUM (note
COSY correlations have
been removed)



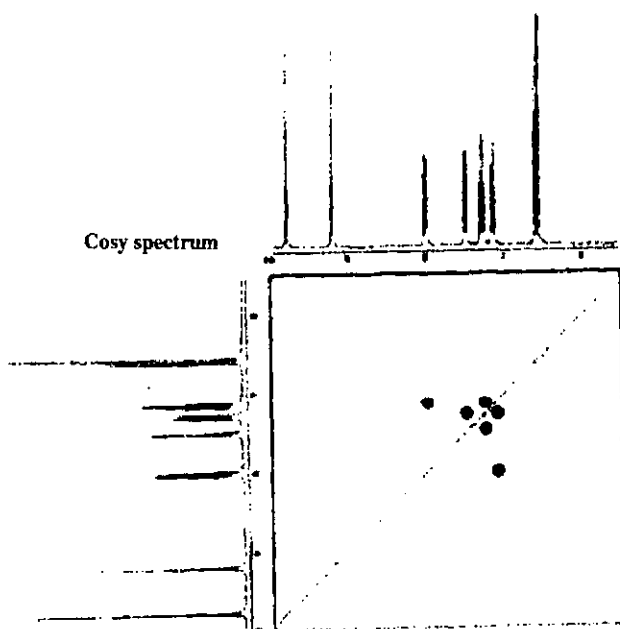


Figure 3 : NOESY and COSY Spectrum of the compound

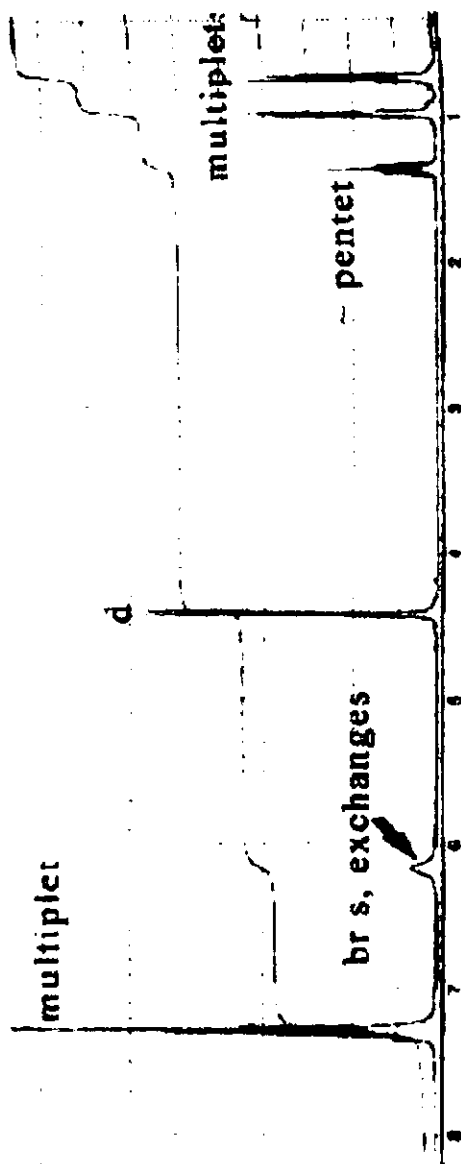
5. A compound with $C_{11}H_{13}NO$. Calculate the DBE of this compound. 1

The IR spectrum contains characteristic peaks at 3300 (one peak), 1698, 703 and 689 cm^{-1} .

Which one of the following functional group is present in this compound? 1

- (a) alcohol (b) aldehyde (c) acid (d) amine (e) ether
 (f) ester (g) alkyne (h) ketone (i) amide (j) anhydride

The ^1H NMR spectrum of the compound is shown below:



When D_2O is added or the sample is heated, the resonance at 6.2 ppm disappears and that at 4.41 ppm becomes a singlet.

The ^{13}C NMR spectrum: δ 173.4 (s), 138.5(s), 128.6 (d), 127.7(d), 127.3(d), 43.8(t), 14.7 (d), 7.2 (t).

The two multiplets in the 1H NMR at δ 0.72 and 0.97 ppm also show long range HMQC (10Hz) to the ^{13}C resonance at 173.4 ppm but to nothing else.

Draw structure of this compound.

8

SECTION -B : Heterocyclic Chemistry

Answer three questions in all.

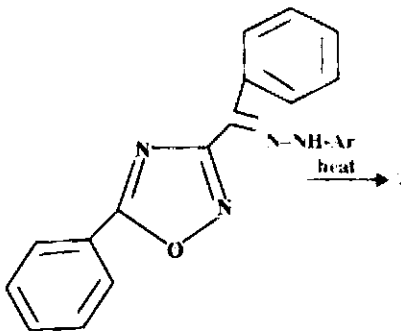
Question No. 4 is compulsory.

- I. (a) Discuss the differences in products obtained from the Fischer indolisation of ortho, meta and para substituted phenyl hydrazones.
- (b) Discuss the mechanisms of the following reactions :
 - (i) Leimgruber Batcho synthesis
 - (ii) Reissert synthesis
 - (iii) Japp Klingemann reaction

11

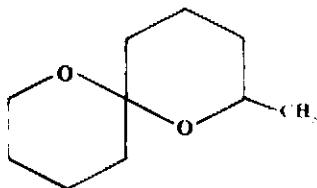
[P.T.O.]

2. (a) Discuss a synthesis of Sumatriptan, the anti-migraine drug.
 (b) Discuss a synthesis of (+) chuangxin mycin.
 (c) How can Librium be synthesised? 11
3. (a) Discuss 'Umpolung' in relation to the Gairnor & Weinreb synthesis of Methoxatin.
 (b) Discuss 'ring inversion' and pyramidal inversion in 1, 3, 5-trimethyl-hexahydro-1, 3, 5-triazine using evidence from $^1\text{H-NMR}$ (dynamic: variable temperature) experiments. 11
4. (a)

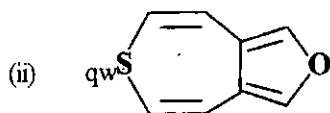
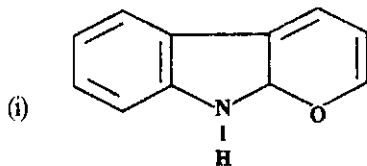


Identify the product and name the reaction.

- (b) Name & describe the effect which would determine the preferred conformation of:



- (c) Give the systematic name of the following : (using the Hantzsch
Widman nomenclature)



- (d) Put down the structure of: Imidazo [1,5,-b] pyridazine 13