Topic : Structural Elucidation Problems.

Assignment

Submitted By,

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II nd M.Sc chemistry.

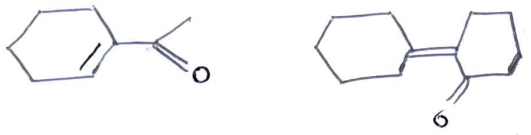
UNIVERSITY QUESTION PAPERS.

Topic : structural elucidation problems:

D 31434 - 3rd sem Jan 2004.

Part-A — UV

(1) Calculate the λ_{max} for the following :-



Part-B

(21) A compound of molecular formula $C_9H_{10}O$ has the following spectral characteristics:-

UV (EtOH) : λ_{max} 260 nm (305)
285 nm (80)

IR (KBr) : 1720 cm^{-1}.

^1H nmr ($CDCl_3$) : δ 2.1 (s, 3H).
3.6 (s, 2H).
7.2 (m, 5H).

Suggest a suitable structure for the above compound and predict the mass spectral fragmentation pattern

C 25782 - M.Sc (Final) Mar/Apr 2003.

Part-C

(30) Find the structure of compound A $C_5H_8O_2$ which shows:

IR: no major peaks above 3000, 1725 (s), 1680 m, 1600 m, 980 - s cm^{-1}. ^1H NMR : δ 1.85 d, J = 6 Hz ; 3H ; 3.55, s, 3H; 5.72, d, J = 16 Hz, 1H; 6.75, m, 1H. EIMS : m/z (%) :

M^+ 100(20), 75(40), 69(100); 59(10), 47

C 26012 – 3rd sem, Apr 2003.

(29) A compound whose mass spectrum showing the molecular ion at m/e 146, has 2 additional intens peaks at m/e 131 and 103. There appears a strong absorption band in its IR near 1650 cm^{-1}. Its ^1H nmr spectrum exhibits the following signals, δ 2.3 (s, 3H), 6.7 (d, J = 16 Hz, 1H), 7.4 (broad m, 5H), 7.5 (d, J = 16 Hz, 1H) overlapping with the previous signal. Its ^{13}C NMR exhibits signals at δ 24 (q), 127 (d), 128 (d, 2C), 129 (d, 2C), 130 (d), 135 (s), 144 (d), and 198 (s). Deduce the structure and stereochemistry of the compound after assigning the structural features responsible for each of the absorptions.

Part C

C 18814 – M.Sc Final, Mar/Apr 2002.

(3) 2 isomeric aliphatic ketones show M^+ ion at m/z 86 one has a base at m/z 43; the other at m/z 57. Identify the ketones. only one shows a peak at m/z 58. which one and why?

Part A

Part C

(30) (b) Identify the structure of compound A $C_{11}H_{14}O_2$ from the following data :-

(i) IR (cm^{-1}) : 2960, 2920, 2880, 1695, 1605, 1260, 835 cm^{-1}.

(ii) ^1H NMR (δ) : 1.05 (t, 3H); 1.52 (sextet, 2H); 1.8 (quintet, 2H); 4.05 (t, 2H); 6.98 (d, 2H), 7.82 (d, 2H); 9.88 (s, 1H)

EIMS (m/z) : M^+ 178, 177, 149, 135, 105, 73.

compound A is easily oxidised to an acid $C_{11}H_{14}O_3$. On boiling with aqueous HI it generates n-butyl iodide.

C 18820 – M.Sc (Final), Mar/Apr 2002.

Section C

(30) (a) An organic compound of molecular formula $C_{12}H_{17}O_2N$ displays the following spectral characteristics. Propose the most probable structure that is consistent with the data and predict important fragments that may arise in its mass spectrum.

UV : λ_{max} 300 nm (100).

IR : 1120 cm^{-1} (s), 1630 cm^{-1} (m); 1660 cm^{-1} (cm), 1695 cm^{-1} (s), 3500 cm^{-1} (m, doublet).

^1H nmr : 1·5 (s, 6H), 2·8 (s, 2H), 3·6 (s, 3H).

(δ scale) 4·2 (s, 2H which disappears on D_2O wash)

7·6–7·8 (m, 4H).

C 12598 – M.Sc (Final), Mar/Apr 2001.

(33) (c) Arrive at the structure of the organic compound whose spectral data are listed below:

UV : 203 nm (40).

IR : 3150 cm^{-1} (broad); 1718 cm^{-1} (strong).

Mass : M^+ at 104.

^1H nmr : 1·25 (t, 3H).

(δ scale) : 3.65 (q, 2H)

4.15 (s, 2H)

10.10 (s, 1H).

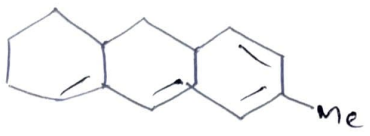
Predict the ^{13}C nmr spectra for this compound.

C 12604 – M.Sc Final, Mar/Apr 2001.

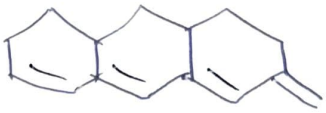
① How A may be distinguished from B spectroscopically (33)

Part A

A.



B.



② Depict the molecular ion M^+ peak profile of Ph–Br and $C_6H_4Br_2$.

Part B

(22) compound A shows a $[M^+]$ peak at 170 and a $[M+2]$ at 172 in the ratio 1:1. Its IR spectrum has a sharp peak at 500 cm^{-1}. The ^1H NMR shows a peak at 2.1 ppm (3H, singlet) and a doublet of doublets at 6.9 (4H). What is the structure of A?

M.Sc (Final), Mar/Apr 2000.

Part A

⑤ Formulate the fragmentation, fragments and structure of the base peak seen in the EIMS of

$PhCH_2OMe$ (m/z 122, 91 (100%), 31, 30).

154 – M.Sc (Final), Mar / Apr 2000.

Part. B

(32) Bring out the importance of isotopic peaks in interpreting the structure of organic compounds.

Part. C

(33) (c) A compound of mol. formula C_9H_8O exhibits the following spectral characteristics. Deduce the structure and stereo chemistry of the compound.

UV_{nm} : 284 (intense), 308 (very weak).

$IR_{cm^{-1}}$: 1690

H_{nmr} : 6.7 (1H, dd, J = 16 Hz & 8 Hz), 7.4 (5H, m).

(δ scale) : 7.45 (1H, d, J = 16 Hz), 9.75 (1H, d, J = 8 Hz)

^{13}C nmr : 128.2 (d), 128.3 (d), 128.8 (d), 131 (d).

(δ scale) : 134 (s), 152 (d), 193 (d).

Mass m/e : 132, 131 (base peak), 103.

M.Sc (Final), Mar / Apr 1999.

Part. A

(5) Provide the structure, mode of formation & m/z value for the base peak in the MS of,

Part c

(33) (b) Logically analysing the spectral data, arrive at the structure of the organic compound with molecular formula $C_9H_{10}O$ and exhibiting λ_{max} (300nm, ϵ, 90), Prominent ν_{max} at 1690 cm^{-1} and ^1H NMR signals at δ 7.2 (m, 5H), 3.6 (s, 2H) and 2 (s, 3H). Justify your answer.

D 26248 - M.Sc (Final), Mar/Apr 1996.

(33) (a) The spectroscopic data of an unknown organic compound are given below. Deduce its structure & interpret the spectra.

Part c

IR : diagnostically important bands at 1600 & 1680 cm^{-1} in addition to other bands.

Mass : 134 (M^+, 10); 119 (5); 105 (100); 77 (20).

PMR : δ, 1.0 (t); 2.5 (quart); 7.0 (5) (intensity ratio 3:2:5).

(b) A terpenic compound $C_{10}H_{16}O$ upon reaction with $FeCl_3$ gave thymol (2-Isopropyl-5-methyl phenol). The spectroscopic details of the original compound are given below. Deduce its structure & interpret the spectra.

UV (ethanol) : λ_{max} 237 nm (ϵ 15,000).

IR : the most significant feature is a strong band at 1700 cm^{-1}.

JMR : (δ) 0.9 (d, 6H) ; 1.2 (m, 2H) ; 1.3 (m, 1H) ;
1.9 (s, 3H) ; 2.1 (t, 2H) ; 3.0 (m, 1H) ; 5.5 (s, 1H).

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STRUCTURAL ELUCIDATION PROBLEMS

Shifana Shermily
II nd Msc. chemistry.

D 3162

A compound with the molecular composition C_7H_6O shows in its ^{1}HNMR spectrum peaks at δ: 9.8 s, 1H; 7.2, s, 5H. It reacted with hydroxylamine and the product so obtained was reacted next with P_2O_5 to obtain another compound C_7H_5N which showed a peak at ~ 2210 cm^{-1} in its IR and the signal at δ: 7.3, s, 5H in its ^{1}H NMR spectrum. What are these two compounds.

C 28436

2. (a) Discuss the use of δ values and J values in deriving structural information from NMR spectra the structure determination of organic compounds.

(b) Find the structure of a compound $C_4H_7NO_2$ which shows: IR: 3005, 2870, 1605, 1550, 1355, 805 cm^{-1}: NMR δ: 2.5, singlet (3H); 7.2, doublet, (2H); 8.2, doublet of a doublet (2H); 7.05, double (2H). Upon reduction, it forms a compound that dissolves in dil. Hcl.

D 52712

3. (a) Find the structure of A (C_8H_9NO) from the following partial spectral data:
IR: 3210 (b) 1685 (m); ^{1}HNMR: 2.4 s, 3H; 6.8 - 7.5 multiple, 5H: 8l b, 1H. Mass spectrum shows a strong peak at m/z 105.

(b) Explain the use of ^{1}H NMR spetroscopy in the structure elucidation of organic compounds.

D 52

4. (a) p-$MeOC_6H_4Me$ shows in its ^{1}H NMR spectrum two peaks at δ 2.34, s, 3H; and at δ, 3.75, s, 3H. Assign these two signals.

(b) How can an aldehyde be distin... ¹HNMR spectrum and (ii) by spectrum?

C 63175

5. (a) Explain how chemical shift values aid in the structure determination of organic compounds.

(b) Deduce the structure of the compound C_8H_8O which shows: IR: 3010, 2950w, 2820w, 1695, 1510, 1005, 750, 690cm⁻¹ : ¹H NMR (400MHz) δ: 3.66 singlet (2H); 7.06, multiplet (5H); 7.14, multiplet, (2H); 9.71, singlet (1H). Mass spetrum shows an intense peaks at m/z 91 & 65. ^{13}C NMR has peaks at 198, 136, 130, 124, 122 & 50ppm.

D 9186

6. A compound shows a stretching band in its IR at 1710cm⁻¹ & its ¹H NMR spectrum shows a peak at δ 9.8. Identify the functional group responsible for the above.

D 2832

7. Identify the structure of compound C whose spectral data are presented hereunder: UV (ethanol): 277 nm (ε = 11600); IR (neat) 3050, 2980, 2830, 2735, 1698, 1601, 1515cm⁻¹ and other peaks; ¹H NMR ($CDCl_3$) δ 9.6 (s, 1H), 7.5 (d, J = 7.5 Hz, 2H) 6.7 (d, J = 7.5 Hz, 2H) 3.6 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 57.5 (CH_3), 117.2 (CH), 131.4 (CH), 132.8 (C), 164.3 (C), 192.4 (C); MS (EI) 136 (M^+, 56%), 135 (100%), 107, 92, and other peaks. The compound gave a positive test with schiffs reagent.

D 1703

8. Identify the structure of compound A using:

Mol formula : $C_8H_{10}O_2$

IR bands : 3000, 2951, 2936, 1509, 1464, 1233, 1060, 827cm⁻¹

¹H NMR peaks : δ 3.75, s, 6H & 6.83, s, 4H

^{13}C NMR peaks (off resonance splitting in parantheses).

56(q), 114(t) and 153(s) ppm.
Electron impact MS: 138 Base peak, 123, 95, 41
Heating with hydriodic acid gave MeI and an alkali soluble compound.

D

9. Identify the structure of compound D whose spectral data are presented hereunder:
UV (ethanol): transparent above 220 nm; IR (neat) 2970, 1742 cm^{-1} and other peaks; ^1H NMR ($CDCl_3$) δ 4.7 (s, 4H), 2.1 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 21.1 (CH_3), 63.2 (CH_2), 172.4 (C); MS (EI) 146 (M^+, <1%) 86 (10) 43 (100), other peaks. The compound gave appositive iodoform test.

D28446

10. (a) An organic compound with MF $C_3H_5O_2Cl$ exhibits the following spectral data:
IR: 1710, 2800, 3250 cm^{-1}
NMR: δ, 2.8, E, 2H, J = 6.9 H_2
3.8, E, 2H, J = 6.9 H_2.
12.1, 1H, exchangeable with D_2O.
M.S: m^+, 108, 110 (3:1)
Arrive at a suitable structure and assign the data.

(b) A compound with molecular formula C_3H_6O can exit in two tautomeric forms A & B. which have the following prominent IR absorption bonds at: (i) 1710 cm^{-1}, (ii) – 3250 cm^{-1}, 1630 cm^{-1}. Give the structure for A and B based on the above data.

11. An organic compound $C_{10}H_{18}O$, upon reduction followed by dehydrogenation gave 3,5-dimethyphenol. The original compound had

a strong IR band at 1,720 cm^{-1}, its NMR spectrum had the following signals.

δ 1.02, singlet, 12H

1.53, singlet, 2H

2.06, singlet, 4H.

Identify the compound.

10. Identify the compound $C_9H_{10}O_2$ from the following spectral data. Interpret the data.

Mass spectrum : m/e : 108 (100); 91 (80); 43 (81)

IR : 1745 cm^{-1} (In addition to other bands).

NMR : δ 1.96 (s, 3H), 5.00 (s, 2H); 7.22 (s, 5H).