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ST—14/15—2022

FACULTY OF SCIENCE

M.Sc. (Second Year) (Third Semester) EXAMINATION

MAY/JUNE, 2022

(CBCS/New Pattern)

CHEMISTRY

(CH-511/531)

(Advance Spectro & Copic Methods)

(Tuesday, 28-06-2022)

Time : 2.00 p.m. to 5.45 p.m.

Time— 3.45 Hours

Maximum Marks—75

N.B. :— (i) All questions are compulsory.

(ii) Figures to the right indicate full marks.

(iii) Multiple Choice Questions (MCQs) should be attempt only once on page number three of answer-book with complete answer.

1. Attempt any *three* of the following : 15

(a) Trans-isomer is found to absorb at longer wavelength with higher value of extinction coefficient as compared to cis-isomer. Explain.

(b) Explain the effect of intermolecular and intramolecular hydrogen bonding on the position of absorption frequency of a compound.

(c) Differentiate among ortho, meta and *p*-xylene on the basis of proton decoupled CMR spectra.

(d) Mass spectra of *p*-cresol displays the following peaks :

m/e 107, 79, 77.

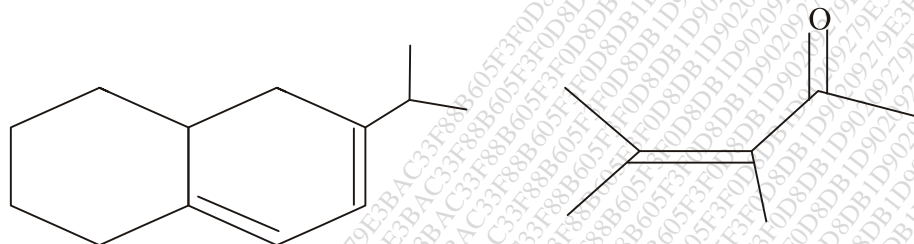
(e) α -Hydroxy-3-nitroacetophenone shows two carbonyl stretching frequencies.

P.T.O.

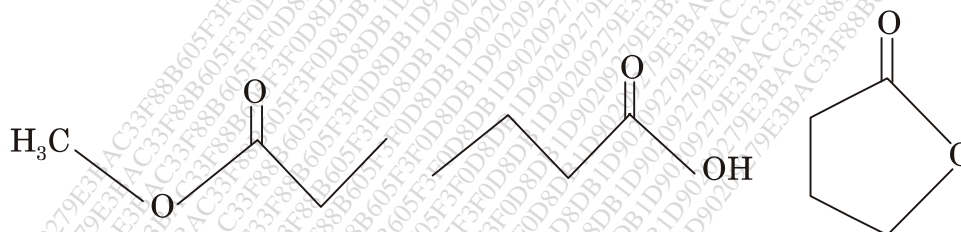
2. Attempt any *three* of the following :

15

(a) Calculate the λ_{\max} for the following compounds :



(b) Explain the $>C=O$ absorption frequency in IR-spectra for the following compounds :



(c) Deduce the structure of compound using $^1\text{H-NMR}$ data :

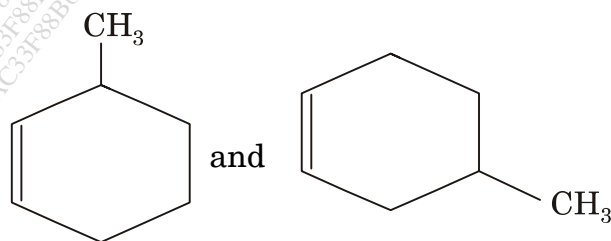
M.F. $\text{C}_4\text{H}_7\text{O}_2\text{Br}$

$^1\text{H-NMR}$ (δ_{ppm}) : 2.88 (*t*, 2H)

3.53 (*t*, 2H)

3.68 (*s*, 3H)

(d) Distinguish the following compounds on the basis of Mass-Spectroscopy.



(e) Deduce the structure of a compound using ^{13}C -NMR data :

Mol. formula : $\text{C}_5\text{H}_{12}\text{O}$

CMR (δ_{ppm}) : 14(*q*), 22(*t*), 28(*t*) 32(*t*), 62(*t*).

3. Solve the following :

(a) Deduce the structure of compound based on the following data : 8

Molecular formula : $\text{C}_6\text{H}_{10}\text{O}_2$

IR (cm^{-1}) : 3000, 1735

^1H -NMR (δ_{ppm}) : 6.97(*dq.*, $J = 6.8$ & 15.2 Hz, 1H)

5.83(*d*, $J = 15.2$ Hz, 1H)

4.17 (*q*, $J = 7.2$ Hz, 2H)

1.87 (*d*, $J = 6.8$ Hz, 3H)

1.27 (*t*, $J = 7.2$ Hz, 3H)

^{13}C -NMR (δ_{ppm}) : 170, 144, 123, 60, 18, 14.

Or

A compound with molecular weight 116 gave the following spectra information :

(i) UV : 283 $\text{m}\mu \in_{\text{max}}$ 22

(ii) IR(cm^{-1}) : 3000 – 2500 (broad), 1715, 1342

(iii) ^1H -NMR (δ_{ppm}) : 2.12 (S, 3H)

: 2.6 (*t*, 2H)

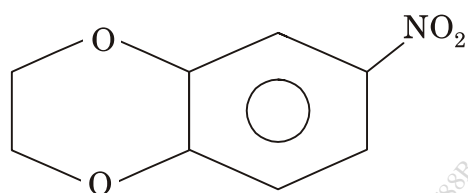
: 2.25 (*t*, 2H)

: 11.10 (S, 1H)

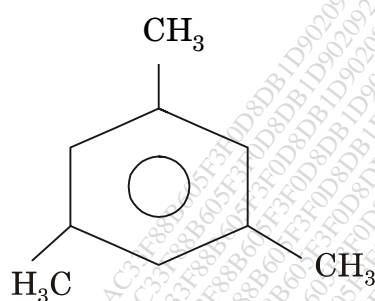
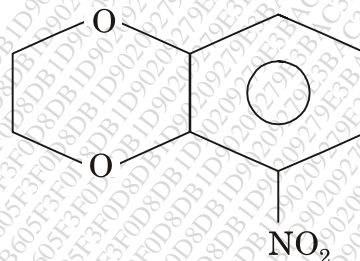
Find the structural formula of the compound.

P.T.O.

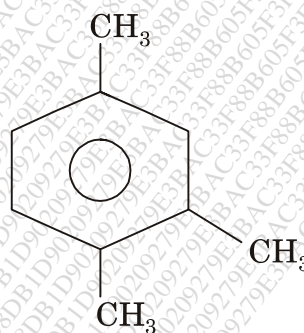
(b) Distinguish between the following pairs using the PMR-Spectra. 7



and

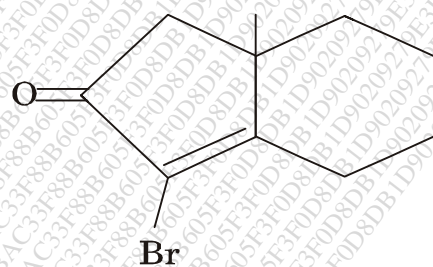


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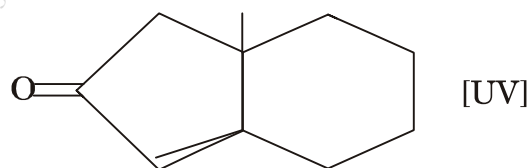


Or

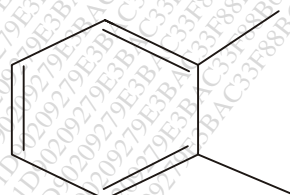
Distinguish between the following pairs using the indicated method.



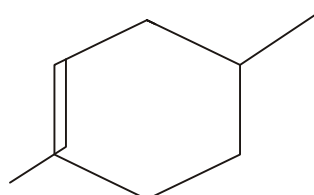
and



[UV]



and



[IR]

4. Solve the following :

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(a) A compound with M.F. $C_{10}H_{15}NO$ displays the following spectral data :

IR (cm^{-1}) : Broad peak at 3300 cm^{-1}

1H -NMR (δ_{ppm}) 7.1 (2H, *d*, $J = 7.3\text{ Hz}$)

6.8 (2H, *d*, $J = 7.3\text{ Hz}$)

4.05 (1H, *q*, $J = 6.6\text{ Hz}$)

3.8 (3H, *S*)

2.4 (3H, *S*)

1.45 (1H, *S*)

1.35 (3H, *d*, $J = 6.61$)

^{13}C -NMR (δ_{ppm}) : 159, 131, 129, 110, 60.5, 56, 33, 21

Or

An organic compound with the following data :

M.F. = $C_{10}H_{13}O_2N$.

I.R. (cm^{-1}) : Broad band between $3600 - 3400\text{ cm}^{-1}$, 1725 cm^{-1}

1H -NMR (δ_{ppm}) : 1.33 (*t*, $J = 6\text{ Hz}$, 9mm)

2. 11 (*S*, 9 mm)

4.15 (*q*, $J = 6\text{ Hz}$, 6 mm)

6.85 (*d*, $J = 9\text{ Hz}$, 6 mm)

7.40 (*d*, $J = 9\text{ Hz}$, 6 mm)

8.0 (*S*, 3 mm)

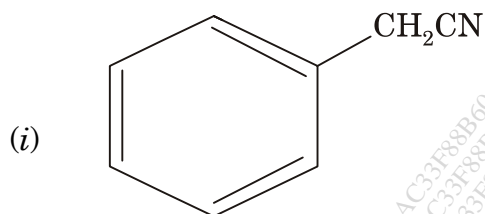
^{13}C -NMR (δ_{ppm}) : 14, 29, 60, 113, 118, 130, 151, 166.

Deduce the structure.

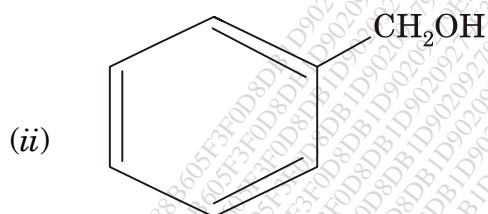
P.T.O.

(b) Explain the genesis of the ions :

7



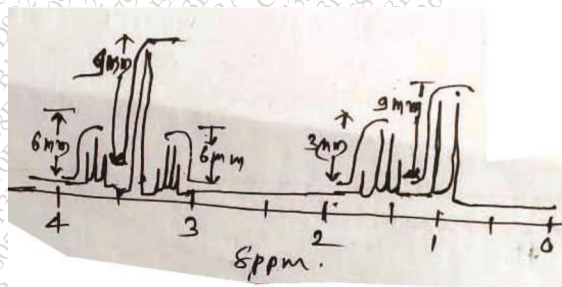
$m/e = 117, 91, 90, 77, 65$



$m/e = 108, 107, 106, 105, 77, 79$

Or

A compound $C_5H_{11}OCl$ shows the following NMR spectrum. Deduce its structure :



5. (a) Select the correct answer from the following Multiple Choice Questions and rewrite complete answer : 5

(i) NMR-spectroscopy is used for determining structures in which of the following materials ?

(a) Radioactive materials

- (b) Insoluble Chemical Compounds
(c) Liquid
(d) Gases.
- (ii) Mass spectrometer separates ions on the basis of which of the following ?
(a) Mass (b) Charge
(c) Molecular weight (d) Mass to charge ratio
- (iii) Which of the following molecules will *not* show IR-spectra ?
(a) H₂ (b) HCl
(c) CH₄ (d) H₂O
- (iv) Number of vibrational degrees of freedom in C₆H₅CH₃ are :
(a) 39 (b) 15
(c) 18 (d) 40
- (v) Which one of the following is the correct basic value of λ_{\max} for homoannular diene ?
(a) 214 nm (b) 217 nm
(c) 253 nm (d) 215 nm

(B) Write short notes on (any *two*) :

10

- (a) Deuterium exchange reactions in ¹H-NMR spectroscopy.
(b) Chromophore and Auxochrome
(c) MacLafferty rearrangement.