This question paper contains **7** printed pages]

AI—12—2017

FACULTY OF SCIENCE

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

OCTOBER/NOVEMBER, 2017

(CBCS Pattern)

CHEMISTRY

(CH-531)

(Advanced Spectroscopic Methods)

(Friday, 10-11-2017) **Time : 2.00 p.m. to 5.00 p.m.**

Time—3 *Hours* *Maximum Marks*—75

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

(*ii*) Figures to the right indicate full marks.

(*iii*) Multiple Choice Qustions (MCQ) should be attempted only *once* on page number three of answer-book with complete answer.

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

(*a*) $h \rightarrow \sigma^*$ transition in methyl chloride is 172 mu and methyl iodide is 258 mu. Explain.

(*b*) Why are water and ethanol not commonly used as solvents in IR-spectroscopy ?

(*c*) Explain Hooke's law in IR.

(*d*) Pentanoic acid gives m/z 60 in mass spectrum. Explain.

(*e*) In PMR spectrum, aldehydic proton appears in the far region (δ = 9 – 10 ppm)

P.T.O.

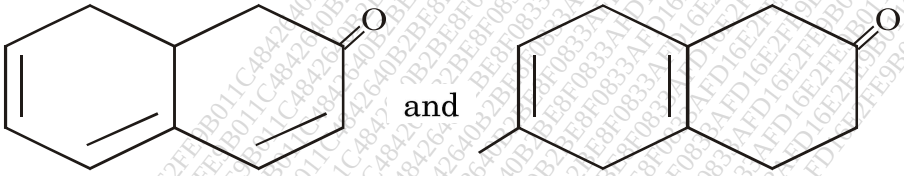
2. Attempt any *three* of the following : 15

(*a*) Explain the effect of the following substitutents on the observable primary and secondary absorption band of benzene :

(*i*) $—NH_2$

(*ii*) —COOH.

(*b*) Using the Woodward-Fieser rules, predict λ_{max} of the following compound :



(*c*) What will be the force constant for the bond in CO, if fundamental vibrational frequncy is 6.4296×10^{13} s^{-1} ? Given : C = 12.011, O = 15.999.

(*d*) Ethyl butanoate in its mass spectrum shows two characteristic peaks at m/e 88 and an abundant peak at m/e 71. Explain the fragmentation.

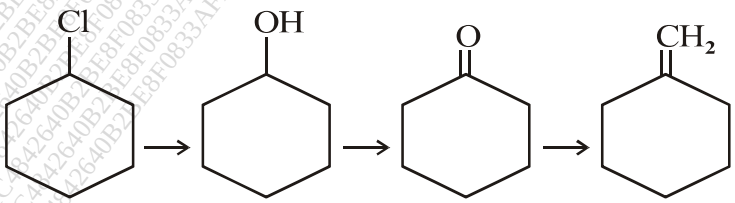
(*e*) Assign the structure of the compound using given PMR data :

MF : C_8H_9Br

$\delta_{(ppm)}$: 2.7 (2H), 3.4(2H), 7.22 (5H).

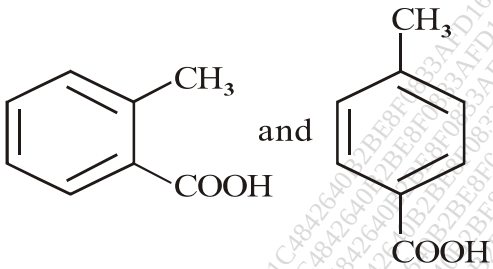
3. Solve the following :

(*a*) How will you follow the following sequence of reaction using IR-spectrosocpy ? 7

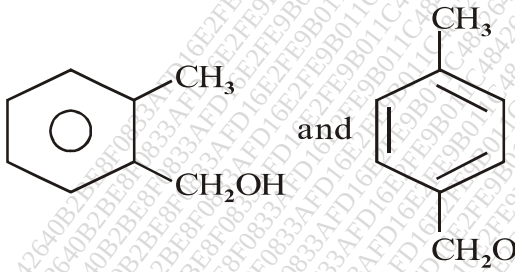


Or

Distinguish between the following pairs by using the indicated spectral method : 7



[Mass]



[Mass]

(*b*) Deduce the structure of the compound using the following spectral data : 8

MF : $C_7H_4O_4NCl$

UV : 280 nm, $\in$ = 8000

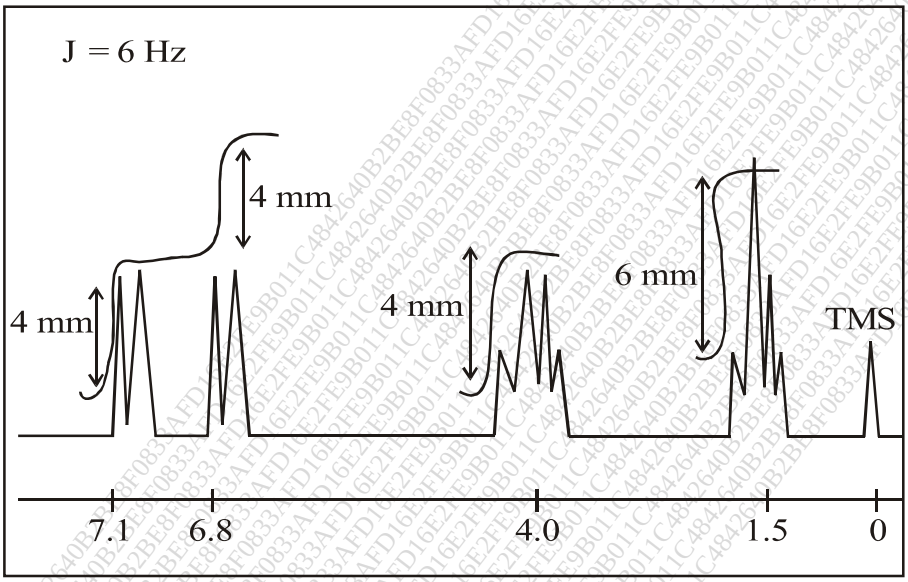
IR : 3300 cm^{-1}, 2700 cm^{-1},
1720 cm^{-1}, 1620 cm^{-1},
1540 cm^{-1}, 920 cm^{-1}

PMR : (δ) : 5.5 (broad singlet 7 mm)
7.9 (doublet 7 mm, J = 7.5 Hz)
8.4 (doublet of doublet 7 mm, J = 7.5 and 2.5 Hz)
8.65 (doublet, 7 mm, J = 2.5 Hz)

P.T.O.

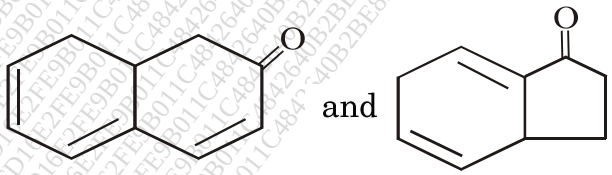
Or

A compound having molecular formula C_8H_9OBr shows the following NMR spectrum. Deduce its structure : 8



4. Solve the following :

(*a*) Distinguish between the following pairs by using the indicated spectral methods : 7



Or

An organic compound with molecular formula $C_{11}H_{14}O_2$ shows the following spectral data. Assign structure and justify the spectral data : 7

PMR (δPPM) : 7.18—7.38(5 H, *m*)

5.71(2H, *q*)

4.50(2H, *s*)

4.06(4H, *t*)

2.63(1H, *s*)

^{13}C NMR : δ(PPM) : 58.5(*t*), 65(*t*)

72.5(*t*), 127.8(*d*), 127.9(*d*),

128.0(*d*), 128.5(*d*), 134.4(*d*),

137.8(*s*).

(*b*) Compound with MF $C_{10}H_{14}$ shows the following sepctral data : 8

UV : λ_{max} 265 nm (ε_{max} 450)

IR : 3030, 2970, 1600, 1515, 1465 and 813 cm^{-1}

PMR : (δppm) : δ1.2(d, 6H, J = 7 Hz)

δ2.3(*s*, 3H)

δ2.8(heptet, 1H, J = 7Hz)

δ7.1(*m*, 4H).

^{13}C NMR (δppm) : 21.3(*q*), 24.2(*q*)

39(*d*), 126(*d*), 128(*d*)

139(*s*), 145(*s*).

Rationalize the spectral data and assign the structure to the compound.

Or

A compound with MF C_6H_5NO displays the following spectral data : 8

UV : 265 nm

P.T.O.

IR : 2720, 1710, 1600, 1500, 850 cm^{-1}

PMR : δ 7.24(*d*, 10 mm)

8.70(*d*, 10 mm)

10.40(*s*, 5 mm).

5. (A) Select the correct answer from the following multiple choice questions and rewrite complete answer : 5

(*i*) The methyl proton signal in the NMR spectrum of anisole is expected around :

(*a*) 0.9δ (*b*) 1.5δ

(*c*) 2.5δ (*d*) 3.9δ

(*ii*) Quadruple splitting observed in IR .....

(*a*) $FeSO_4.7H_2O$ (*b*) $Na_2[Fe(CN)_5.NO]$

(*c*) Only (*a*) (*d*) Both (*a*) and (*b*)

(*iii*) In the α-cleavage of acetone, the m/z ratio is :

(*a*) 35 (*b*) 43

(*c*) 45 (*d*) 20

(*iv*) In IR spectrum, due to the presence of strong hydrogen bonding, the absorption band shifts to :

(*a*) Higher wave number

(*b*) Lower wave number

(*c*) Both

(*d*) No effect

(*v*) Electromagnetic radiations used in ^{13}C NMR spectroscopy is :

(*a*) IR (*b*) Microwave

(*c*) Radio (*d*) None of these

(B) Write short notes on (any *two*) : 10

(*i*) MacLafferty rearrangement

(*ii*) Spin-spin coupling in PMR

(*iii*) Stretching and bending vibrations in IR-spectroscopy.