



NBW-003-036403 Seat No. _____

M. Sc. (Pharma Organic Chemistry) (Sem. IV)
(CBCS) Examination

April / May - 2017

POC - 403 : Modern Analytical Techniques

Faculty Code : 003

Subject Code : 036403

Time : $2\frac{1}{2}$ Hours]

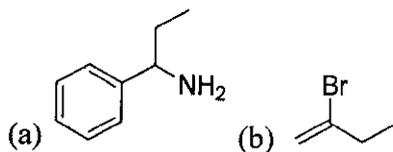
[Total Marks : 70

Instructions :

- (1) All questions are **compulsory** and carry **equal** marks.
- (2) Draw diagrams and scheme of reaction wherever necessary.
- (3) Standard chemical shift chart and IR frequencies provided at the end of Paper.

1 Answer any **seven** out of the following **ten** questions : **14**

- (1) Explain Stevenson's Rule with example in mass spectroscopy.
- (2) Identify the types of protons in the following compounds:



- (3) Give application of flame photometry.
- (4) Define optical rotation and optical activity.
- (5) Differentiate ethanol and dimethyl ether by CMR spectroscopy.

- (6) What is ee ? Give the formula for calculation of ee.
- (7) What is nitrogen rule in mass spectroscopy? Give its example.
- (8) Indicate the number of signals and multiplicity off-resonance decoupled ^{13}C NMR spectra of the following compounds :
 - (a) 2-Bromopropane
 - (b) Nitrobenzene.
- (9) Why ester shows absorption peak at high wave number than ketone ?
- (10) What is a vibration in a molecule ?

2 Answer any **two** out of the following **three** questions : **14**

- (1) Write a brief note on Polarimetry.
- (2) Which types of burner used in flame photometry ? Discuss in detail.
- (3) Explain fundamental bands in IR spectroscopy.

3 Answer the following questions : **14**

- (1) Discuss instrumentation of Mass spectroscopy with schematic diagram.
- (2) Explain Spin-Spin splitting in ^1H NMR Spectroscopy with suitable examples.

OR

3 Answer the following questions : **14**

- (1) Calculate the chemical shift value of carbon of following compounds :
 - (a) 2-fluoropentane
 - (b) 3-bromotoluene
 - (c) p-xylene.
- (2) Explain the instrumentation of Emission spectroscopy with schematic diagram.

4 Answer any **two** out of the following **three** questions : 14

- (1) Explain Diels-Alder and McLafferty rearrangement in Mass spectrometry.
- (2) Discuss instrumentation of IR spectroscopy with schematic diagram.
- (3) Deduce the structure of compound from the given spectral data :

MF : $C_{10}H_{10}O$; IR : 3030, 2950, 1710, 1480, 1380, 750 and 700 cm^{-1} .

PMR : τ ppm 7.8 (s, 3H), 3.8 (d, 1H, $J = 16.5\text{ Hz}$), 3.2 (d, 1H, $J = 16.5\text{ Hz}$), 2.2-2.8 (m, 5H) CMR (Proton noise decoupled): 8 signals

5 Answer any **two** out of the following **four** questions : 14

- (1) Answer the following questions :
 - (a) Explain fermi resonance and overtone in detail.
 - (b) How will you distinguish *ortho*, *meta* and *para*-xylene on the basis of IR spectroscopy ?
- (2) Describe ionization techniques used in Mass spectrophotometer.
- (3) Explain α -, β - and γ -Effects in CMR spectroscopy.
- (4) An organic compound with MF : $C_{10}H_{14}O$ furnished the following spectral data :

UV : 277 nm; IR: 3520, 3020, 2960, 2875, 1622, 1458, 1383, 1385, 1222, 852 and 804 cm^{-1} .

PMR : δ 1.2 (6H, d), 2.2 (3H, s), 3.2 (1H, m), 4.2 (1H, s), 6.6 (1H, dd, $J = 8\text{ Hz}$), 6.9 (1H, dd, $J = 8\text{ Hz}$) and 7.2 (1H, dd, $J = 2\text{ Hz}$).

CMR (Off-resonance decoupled) : Three singlet, four doublet and two quartet. Deduce the structure of the compound and explain the spectral data.

CHARACTERISTIC INFRARED ABSORPTION BANDS OF FUNCTIONAL GROUPS

Class of Compounds	Absorption, cm ⁻¹	Intensity	Assignment	Class of Compounds	Absorption, cm ⁻¹	Intensity	Assignment
Alkanes and Alkyls	2850-3000 1450-1470 1370-1390 1365 + 1395 (two bands) 715-725	s s m m w	C-H stretch C-H bend CH ₃ C-H bend -(CH ₂) ₂ or -(CH ₃) ₂ bend -(CH ₂) _n bend	Carboxylic Acids	2500-3500 1710-1715 1680-1710	s, broad s, broad s	O-H stretch C=O stretch C=O stretch
Alkenes	3020-3140 1640-1670 RCH=CH ₂ 910 + 990 (two bands) RR'C=CH ₂ cis-RCH=CHR' trans-RCH=CHR' RCH=CR'R''	w-m vw-m m+s s m-s, broad s s	=C-H stretch C=C stretch =C-H bend =C-H bend =C-H bend =C-H bend	Esters	aliphatic 1160-1210 acetates -1240 aromatic 1250-1310 R-C(O)-O-R 1735-1750 C=C-C(O)-O-R or 1715-1730 Ar-C(O)-O-R R-C(O)-O-Ar 1760-1790	s-vs s s s	O=C-O-C stretch C=O stretch C=O stretch C=O stretch
Alkynes	R-C≡C-H 3265-3335 2100-2140 610-700 R-C≡C-R' 2190-2260	a. sharp m s, broad vw-w	≡C-H stretch C≡C stretch ≡C-H bend C≡C stretch	Acyl Chlorides	R-C(O)-Cl 1785-1815 Ar-C(O)-Cl 1770-1800	s s	C=O stretch C=O stretch
Alkyl halides	R-F 1000-1350 R-Cl 750-850 R-Br 500-680 R-I 200-500	vs s s s	C-F stretch C-Cl stretch C-Br stretch C-I stretch	Anhydrides	R-C(O)-O-C(O)-R -1750 -- -1815 Ar-C(O)-O-C(O)-Ar -1720 -- -1775 (both two bands)	s,s s,s	C=O symmetric & asym. stretch
Alcohols	3300-3400 C-C-CH ₂ -OH 1035-1050 R-CH ₂ -OH (1°) or 1050-1085 C=C-CH(R)-OH RR'CH-OH (2°) or C=C-CRR'-OH RR'R''C-OH (3°) Ar-O-H 1180-1260	s, broad m-s m-s m-s m-s m-s	O-H stretch C-O stretch C-O stretch C-O stretch C-O stretch C-O stretch	Nitriles	R-C≡N 2240-2260 C=C-C≡N or 2220-2240 Ar-C≡N	m-s s	C≡N stretch C≡N stretch
Ethers	R-O-R' 1085-1150 Ar-O-R 1020-1075 and 1200-1275 (two band)	s m-s	C-O-C stretch =C-O-C sym. & asym. stretch	Amines	R-NH ₂ ~3400 + ~3500 (two bands) 1580-1650 RR'N-H 3310-3335	w w-m w	N-H symmetric & asym. stretch N-H bend N-H stretch
Aldehydes	2700-2725 R-CH=O 1720-1740 C=C-CH=O or Ar-CH=O 1685-1710	m s s	H-C=O stretch C=O stretch C-O stretch	Amides	R-C(O)-NH ₂ 3200-3400 and 3400-3500 (two bands) 1650-1690 1590-1655 R-C(O)-NH-R 3400-3500 1640-1690 1510-1560 R-C(O)-NR'R'' 1630-1680	w-m s, broad m-s w-m s, broad m-s m-s	N-H symmetric & asym. stretch C=O stretch N-H bend N-H stretch C=O stretch N-H bend C=O stretch
Ketones	RR'C=O 1710-1720 C=C-C(O)-R 1665-1685 Ar-C(O)-R 1675-1695 four member 1770-1780 cyclic five member 1740-1755 cyclic six member 1710-1720 cyclic	s s s s s s	C=O stretch C=O stretch C=O stretch C=O stretch C=O stretch C=O stretch	Nitro Compounds	R-NO ₂ ~1550 and ~1370 C=C-NO ₂ or Ar-NO ₂ ~1525 and ~1335 (both two bands)	s s s s	N-O symmetric & asym. stretch N-O symmetric & asym. stretch
				Aromatic Compounds	3010-3100 1450-1600 (two to four bands) monosubstituted 730-770 and 690-710 (two bands) o-disubstituted 735-770 m-disubstituted 750-810 and 690-710 p-disubstituted 810-840	m m-s sharp s s s s s s	Ar C-H stretch ring C=C stretch C-H bend C-H bend C-H bend C-H bend C-H bend C-H bend

Intensity abbreviations: vw = very weak, w = weak, m = medium, s = strong, vs = very strong

Standard chemical shift value (ppm from TMS)

¹³C chemical shifts for some linear and branched-chain alkanes

Alkane	C-1	C-2	C-3	C-4	C-5
Methane	-2.5				
Ethane	5.7				
Propane	15.8	16.3	15.8		
Butane	13.4	25.2	25.2	13.4	
Pentane	13.9	22.8	34.7	22.8	13.9
Hexane	14.1	23.1	32.2	32.2	23.1
Heptane	14.1	23.2	32.6	29.7	32.6
Octane	14.2	23.2	32.6	29.9	29.9
Isobutene	24.5	25.4			
Isopentane	22.2	31.1	32.0	11.7	
Neopentane	31.7	28.1			
2,3-Dimethylbutane	19.5	34.3			
2,2,3-Trimethylbutane	27.4	33.1	38.3	16.1	
3-Methylpentane	11.5	29.5	36.9	(18.8, 3-CH ₃)	

Acyclic olefinic carbons	
Substituent carbon C	Correction
α	+10.6
β	+7.2
γ	-1.5
α'	-7.9
β'	-1.8
γ'	-1.5
z (cis)	-1.1

Increments* (ppm) for substituents Y on alkanes

Substituent Y	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH ₃	+9	+6	+10	+8	-2
HC=CH ₂	+20		+6		-0.5
C≡CH	+4.5		+5.5	+2	-3.5
COOH	+21	+16	+3	+2	-2
COO ⁻	+25	+20	+5	+3	-2
COOR	+20	+17	+3	+2	-2
COCl	+33	+28		+2	
CONH ₂	+22		+2.5		-0.5
COR	+30	+24	+1	+1	-2
CHO	+31		0		-2
Phenyl	+23	+17	+9	+7	-2
OH	+48	+41	+10	+8	-5
OR	+58	+51	+8	+5	-4
OCOR	+51	+45	+6	+5	-3
NH ₂	+29	+24	+11	+10	-5
NH ₃ ⁺	+26	+24	+8	+6	-5
NHR	+37	+31	+8	+6	-4
NR ₂	+42		+6		-3
NH ₃ ⁺	+31		+5		-7
NO ₂	+63	+57	+4	+4	
CN	+4	+1	+3	+3	-3
SH	+11	+11	+12	+11	-4
SR	+20		+7		-3
F	+68	+63	+9	+6	-4
Cl	+31	+32	+11	+10	-4
Br	+20	+25	+11	+10	-3
I	-6	+4	+11	+12	-1

Increments in the shifts of the aromatic carbon atoms of monosubstituted benzenes (ppm from benzene at 128.5 ppm)

Substituent	C-1	C-2 (<i>ortho</i>)	C-3 (<i>meta</i>)	C-4 (<i>para</i>)
H	0.0	0.0	0.0	0.0
CH ₃	+9.3	+0.7	-0.1	-2.9
CH ₃ CH ₂	+15.6	-0.5	0.0	-2.6
CH(CH ₃) ₂	+20.1	-2.0	0.0	-2.5
HC≡CH ₂	+9.1	-2.4	+0.2	-0.5
C ₆ H ₅	+12.1	-1.8	-0.1	-1.6
F	+35.1	-14.3	+0.9	-4.5
Cl	+6.4	+0.2	+1.0	-2.0
Br	-5.4	+3.4	+2.2	-1.0
I	-32.2	+9.9	+2.6	-7.3
OH	+26.6	-12.7	+1.6	-7.3
OCH ₃	+31.4	-14.4	+1.0	-7.7
CHO	+8.2	+1.2	+0.6	+5.8
COCH ₃	+7.8	-0.4	-0.4	+2.8
COOH	+2.9	+1.3	+0.4	+4.3
CN	-16.0	+3.6	+0.6	+4.3
NO ₂	+19.6	-5.3	+0.9	+6.0
NH ₂	+19.2	-12.4	+1.3	-9.5
NHCOCH ₃	+11.1	-9.9	+0.2	-5.6
COOCH ₃	+2.0	+1.2	-0.1	+4.8