



Seat No. : _____

XY-110

April-2013

M.Sc. (Sem.-II)

408 : Chemistry

(Organic Chemistry)

Time : 3 Hours]

[Max. Marks : 70

1. (a) (1) Predict the number of signals with approximate δ values expected in the proton decoupled ^{13}C NMR spectrum of ethyl benzene. **4**
(2) Discuss the mass fragmentation of 1-butanol in detail **3**

OR

- (a) (1) Give a brief idea on ^{13}C chemical shifts of olefinic, ketonic and aromatic carbon by giving appropriate examples. **4**
(2) Write a note on High resolution mass spectroscopy. **3**
(b) (1) What is McLafferty rearrangement ? Explain it by a specific example of 2-Octanone. **4**
(2) Write a note on FAB technique for ionization. **3**

OR

- (b) Deduce the structure of the compound from the following spectral data with suitable explanation. **7**

MF : $\text{C}_6\text{H}_8\text{O}_4$

UV : 210 nm

IR (KBr) : 3010, 2865, 1740, 1650, 1230 cm^{-1}

^1H NMR : (δ) δ 3.9(6H, singlet), 6.1 (2H, singlet) (ppm)

^{13}C NMR : (δ) 51.5, 133.6, 169.4

HRMS : 144.0423

2. (a) (1) Explain the modified Jablonski diagram. **4**
(2) Explain Norrish type I reaction mechanism. **3**

OR

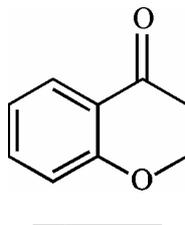
- (a) (1) Write a note on photo isomerisation of olefins by Schenck mechanism. **4**
(2) Explain photo dimerization of 1, 3-butadiene. **3**
(b) Give any two synthesis and four important reactions for Thiazole or Pyrazole. **7**

OR

- (b) Give any two synthesis and four important reactions for Pyrazine or Quinazoline. **7**

3. (a) Discuss the principle, mechanism and synthetic applications of the following reactions (any **two**) : 7
- (1) Buchwald Hartwig reaction
 - (2) Birch Reduction
 - (3) Suzuki Reaction
- (b) Discuss the principle, mechanism and synthetic applications of the following Reactions (any **two**) : 7
- (1) Knoevenagel Reaction
 - (2) Dickmann Reaction
 - (3) Mannich Reaction
4. (a) Discuss selectivity, mechanism and utility of the following reagents (any **two**) : 7
- (1) DIBAL-H
 - (2) Dess-Martin peridionane
 - (3) Lithium diisopropylamide (LDA)
- (b) Discuss selectivity, mechanism and utility of the following reagents (any **two**) : 7
- (1) Dicyclohexyl carbodiimide (DCC)
 - (2) Phase transfer catalysis
 - (3) Gilman's reagent Lithium Dimethylcuprate.
5. Answer the following questions : 14
- (1) Compound I has a molecular formula of C_7H_{16} . In ^{13}C NMR, compound I gave 3 peaks and in 1H NMR it also gave 3 peaks, a doublet, a triplet and a multiplet. Provide a structure for compound I.
 - (2) In mass spectrum of n-Methylbenzylamine, peaks are formed at m/z 120, 91 and 77. Justify the origin of these signals.
 - (3) Bromine possesses two isotopes (^{79}Br and ^{81}Br) in an approximate 1 : 1 ratio. In the mass spectrum of Br_2 , how many peaks will the parent ion contain ?
 - (4) What is quantum yield ?
 - (5) Give one requirement for the selection of photosensitiser ?
 - (6) Give one synthesis of Imidazole.

- (7) Write two applications of Mitsunobu reaction.
- (8) In the preparation of Grignard reagent which compound is used as initiator ?
- (9) Which ingredients are used in Michael addition ?
- (10) What is the specialty of n-Butyl lithium reagent ?
- (11) Which reagent is used in Jones oxidation ?
- (12) What is Pfitzner-Moffatt Oxidation ?
- (13) How will you distinguish isomeric 1-Hexylamine and Triethylamine by mass spectroscopy ?
- (14) Predict the approximate CMR values of the following compound :



35M390-4

SELECTED SPECTRAL DATA

Characteristic Infrared Absorption Frequencies

Bond Type	Stretching, cm ⁻¹	Bending, cm ⁻¹
C-H alkanes	2960-2850 (s)	1470-1350 (s)
C-H alkenes	3080-3020 (m)	1000-675 (s)
C-H aromatic	3100-3000 (v)	870-675 (y)
C-H aldehyde	2900, 2700 (m, 2 bands)	
C-H alkyne	3300(s)	
C≡C alkyne	2260-2100 (v)	
C≡N nitrite	2260-2220 (v)	
C=C alkene	1680-1620 (v)	
C=C aromatic	1600-1450 (v)	
C=O ketone	1725-1705 (s)	
C=O aldehyde	1740-1720 (s)	
C=O α,β-unsaturated ketone	1685-1665 (s)	
C=O aryl ketone	1700-1680 (s)	
C=O ester	1750-1735 (s)	
C=O acid	1725-1700 (s)	
C=O amide	1690-1650 (s)	
O-H alcohols (not hydrogen bonded)	3650-3590 (v)	
O-H alcohols (hydrogen bonded)	3600-3200 (s, broad)	1620-1590 (v)
O-H acids	3000-2500 (s, broad)	1655-1510 (s)
N-H amines	3500-3300 (m)	
N-H amides	3500-3350 (m)	
C-O alcohols, ethers, esters	1300-1000 (s)	
C-N amines, alkyl	1220-1020 (w)	
C-N amines, aromatic	1360-1250 (s)	
NO ₂ nitro	1560-1515 (s)	
	1385-1345 (s)	

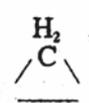
s = strong absorption w = weak absorption
 m = medium absorption v = variable absorption

Typical chemical shifts for Types of Hydrogen Atoms, Seen in Proton Magnetic Resonance Spectra

Type of Hydrogen Atom	δ*	Type of Hydrogen Atom	δ*
RCH ₃	0.9	R ₂ C=CH ₂	5.0
RCH ₂ R acyclic	1.3	RCH=CR ₂	5.3
acyclic	1.5	ArH	7.3
R ₃ CH	1.5-2.0	O RCH	9.7
R ₂ C=C CH ₃ R'	1.8	RNH ₂	1-3
O RCCH ₃	2.0-2.3	ArNH ₂	3-5
ArCH ₃	2.3	O RCNHR	5-9
RC≡CH	2.5	ROH	1-5
RNHCH ₃	2-3	ArOH	4-7
RCH ₂ X (X = Cl, Br, I)	3.5	O RCOH	10-13
O ROCH ₃ , RCOCH ₃	3.8		

35M390-5

COMMON FRAGMENTS LOST

Molecular Ion Minus	Fragment Lost Inference structure
1	H·
2	2H·
15	CH ₂ ·
16	O (ArNO ₂ , amine oxides, sulfoxides); ·NH ₂ (carboxamides, sulfonamides)
17	HO·
18	H ₂ O (alcohols, aldehydes, ketones)
19	F·
20	HF
26	CH≡CH, ·CH≡N
27	CH ₂ =CH·, HC≡N (aromatic, nitrites, nitrogen heterocycles)
28	CH ₂ =CH ₂ ·, CO, (quinones) (HCN+H)
29	CH ₃ CH ₂ · (ethyle ketones, ArCH ₂ CH ₂ CH ₃), ·CHO
30	NH ₂ CH ₃ ·, CH ₂ O (ArOCH ₃), NO (ArNO ₂), C ₂ H ₄
31	·OCH ₃ (methyl esters), ·CH ₂ OH, CH ₃ NH ₂
32	CH ₃ ,OH,S
33	HS· (thiols), (·CH ₃ and H ₂ O)
34	H ₂ S (thiols)
35	Cl·
36	HCl, 2H ₂ O
37	H ₂ Cl (or HCl + H)
38	C ₃ H ₃ , C ₃ N, F ₂
39	C ₃ H ₃ , HC ₂ N
40	CH ₃ C≡CH
41	CH ₃ =CHCH ₂ ·
42	CH ₂ =CHCH ₃ , CH ₂ =C=O, H ₂ C  CH ₂ , NCO, NCNH ₂
43	C ₃ H ₇ · (propyl ketones, ArCH ₂ -C ₃ H ₇), CH ₃ C(=O)· (methyl ketones, CH ₃ CG(=O), where G= various functional groups), CH ₂ =CH-O· (CH ₃ · and CH ₂ =CH ₂), HCNO
44	CH ₂ =CHOH,CO ₂ (esters, anhydrides) N ₂ O, CONH ₂ , NHCH ₂ CH ₃
45	CH ₃ CHOH, CH ₃ CH ₂ O (ethyl esters), CO ₂ H, CH ₃ CH ₂ NH ₂
46	(H ₂ O and CH ₂ =CH ₂), CH ₃ CH ₂ OH, ·NO ₂ (ArNO ₂)
47	CH ₃ S·
48	CH ₃ SH, SO(sulfoxides), O ₃
49	·CH ₂ Cl
51	·CHF ₂

35M390-6

52	C_4H_4, C_2N_2
53	C_4H_6
54	$CH_2 = CH - CH = CH_2$
55	$CH_2 = CHCHCH_3$
56	$CH_2 = CHCH_2CH_3, CH_3CH = CHCH_3, 2CO$
57	C_4H_8 (butyl ketones), C_2H_5CO (ethyl ketones, $EtC=OG$, G = various structural units)
58	$NCS, (NO + CO), CH_3COCH_3, C_4H_{10}$

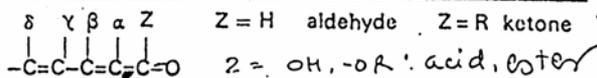
Chemical Shifts for Carbon Atoms in Carbon - 13 Nuclear Magnetic Resonance Spectra

Type of Carbon Atom	δ^*	Type of Carbon Atom	δ^*
RCH_2CH_3	13-16	$RCH = CH_2$	115-120
RCH_2CH_2	16-25	$RCH = CH_2$	125-140
R_3CH	25-38	$RC \equiv N$	117-125
$\begin{array}{c} O \\ \\ CH_3CR \end{array}$	~30	ArH	125-150
$\begin{array}{c} O \\ \\ CH_2COR \end{array}$	~20	$\begin{array}{c} O \\ \\ RCOR' \end{array}$	170-175
RCH_2Cl	40-45	$\begin{array}{c} O \\ \\ RCOH \end{array}$	177-185
RCH_2Br	28-35	$\begin{array}{c} O \\ \\ RCH \end{array}$	190-200
RCH_2NH_2	37-45	$\begin{array}{c} O \\ \\ RCR' \end{array}$	205-220
RCH_2OH	50-64		
$RC \equiv CH$	67-70		
$RC \equiv CH$	74-85		

✓ WOODWARD RULES FOR CONJUGATED DIENE
 ABSORPTION
 $\pi \rightarrow \pi^*$ Transitions

Acyclic diene or heteroannular diene (transoid)	214 nm
Homoannular diene (cisoid)	253 nm
Increment for each:	
Double bond extending conjugation	30 nm
If double bond conjugation is cis	40 nm
Exocyclic double bond	05 nm
Increment for each substituents:	
Alkyl group or ring residue (R)	05 nm
Chlorine (Cl) or Bromine (Br)	05 nm
Alcohol (OH) or Alkoxy (OR)	06 nm
Ester (OCOR)	00 nm
Amine (NR ₂)	60 nm
Thioether (SR)	30 nm

✓ WOODWARD RULES FOR $\alpha\beta$ -UNSATURATED
 ALDEHYDES AND KETONES ABSORPTION
 $\pi \rightarrow \pi^*$ Transitions



$\alpha\beta$ - Unsaturated aldehyde	208 nm
$\alpha\beta$ - Unsaturated acyclic or six carbon ring ketone	215 nm
$\alpha\beta$ - Unsaturated five carbon ring ketone	202 nm
Increment for each:	
Double bond extending conjugation	30 nm
If double bond conjugation is cis	40 nm
Exocyclic double bond	05 nm
Increment for each substituents:	
Alkyl group or ring residue (R)	α 10 nm β 12 nm γ, δ 18 nm
Chlorine (Cl)	α 15 nm β, γ, δ 12 nm
Bromine (Br)	α 25 nm β 30 nm γ, δ 25 nm
Alcohol (OH)	α 35 nm β 30 nm γ 30 nm δ 50 nm
Alkoxy (OR)	α 35 nm β 30 nm γ 17 nm δ 31 nm
Ester (OCOR)	$\alpha, \beta, \gamma, \delta$ 06 nm
Amine (NH ₂ , NHR, NR ₂)	β 95 nm
Thioether (SR)	β 85 nm

