Seat No. : _____

AR-127

May-2016

M.Sc., Sem.-II

408 : Chemistry

(Organic Chemistry)

Time : 3 Hours] **[Max. Marks : 70**

Instructions : (1) **All** the questions are compulsory.
(2) Figures to the right indicate full marks.

1. (a) Answer the following questions : **7**

(1) Give any four differences between 13_C NMR and 1_H NMR.

(2) Discuss fast Atomic Bombardment (FAB) technique used in mass spectroscopy.

OR

(1) Indicate the number of signals alongwith approximate position observed in 13_C NMR spectrum for the following compounds :

(i) Phenyl acetic acid

(ii) Methyl cyclohexane

(iii) 2, 4, 4 – trimethyl 1-pentene

(2) Do the mass fragmentation for the following molecules :

(i) 2-Hexanone

(ii) Benzamide

(b) Answer the following : **7**

Deduce the structure of the compound from the following spectral data with suitable explanation.

Mol. wt : 136

IR : 2810, 2700, 1683, 1600, 1511, 1315, 1260, 1160, 1024, 833 cm^{-1}

1_H NMR : δ = 3.8 (S, 3H)

δ = 6.95 (d, 2H)

δ = 7.6 (d, 2H)

δ = 9.8 (S, 1H)

13_C NMR : δ = 55.6, 114.5, 130.2, 132.1, 164.5, 191

Mass : $\frac{m}{z}$ = 136, 135, 119, 107, 92, 65, 64, 63, 51

OR

An organic compound exhibits the following spectral data interprete the spectral data and deduce the structure of the compound.

Molecular Formula : $C_8H_8O_2$

IR : 1764, 1593, 1493, 1371, 1193, 1031, 925, 749, 692 cm^{-1}

1_H NMR : $\delta = 2.3$ (S, 3H)

: $\delta = 7.15$ (d, 2H)

: $\delta = 7.25$ (t, 1H)

: $\delta = 7.4$ (t, 2H)

13_C NHR : $\delta = 20.8, 121.7, 125.6, 129.8, 151.1, 169.2$

Mass : $\frac{m}{z} = 136, 95, 94, 66, 65, 63, 51, 50, 43$

2. (a) Answer the following : **7**

(1) Draw Jablonski diagram and explain the term – Fluorescence and Phosphorescence.

(2) Explain Norrish type II reaction mechanism with suitable examples.

OR

(1) What is Paterno-Buchi reaction ? Discuss Paterno-Buchi reaction with relevant evidences.

(2) On the basis of molecular orbital structure at a carbonyl group, explain photo reduction of benzophenone in presence of toluene.

(b) Answer the following : **7**

Give any two synthesis and four important reactions for Thiazole or Cinnoline.

OR

Give any two synthesis and four important reactions for pyrazole or Quinoxaline.

3. (a) Answer the following : **7**

(1) How will you prepare methyl vinyl ketone (Michael acceptor) by Mannich reaction ? Give complete mechanism of Michael addition reaction with one application.

(2) How will you prepare phosphorous ylide ? Explain mechanism of reaction in which phosphorus ylide react with carbonyl compounds.

OR

(1) What precautions will you take in selecting a base for Darzen's glycidic ester condensation ? Explain the conversion of cyclohexanone to cyclohexane carboxaldehyde and acetophenone to 2-phenyl propionaldehyde using this reaction.

(2) Using Villsmeyer – Haack reaction give the mechanism for the preparation of 2, 4-dimethoxy benzaldehyde and P-N, N-dimethyl aminobenzaldehyde using suitable starting material.

(b) Discuss the principle, mechanism and three synthetic applications of the following reactions. **7**

(1) Suzuki reaction

(2) Mitsunobu reaction

OR

Discuss the principle, mechanism and three synthetic applications of the following reactions :

(1) Sonogashira reaction

(2) Birsch reduction

4. Answer the following : **7**

(a) Discuss selectivity, mechanism and three utilities of the following reagents.

(1) N, N-Dicyclohexyl carbodimide (DCC)

(2) Gilman's reagent (Lithium dialkyl cuprate)

OR

Discuss selectivity, mechanism and three utilities of the following reagents :

(1) Grignard reagent

(2) DIBAL-H

(b) Discuss selectivity, mechanism and three utilities of the following reagents. **7**

(1) 2, 3-Dichloro –5, 6-Dicyanobenzo Quinone (DDQ)

(2) 1, 3-dithiane

OR

Discuss selectivity, mechanism and three utilities of the following reagents :

(1) Phase transfer catalysis

(2) Sodium borohydride

5. Answer the following questions : **14**

(1) What is Fermi resonance ?

(2) Predict the approximate CMR values of 4-methyl-2-pentanone

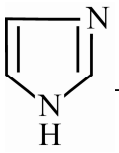
(3) What do you understand by Nitrogen rule ?

(4) What is McLafferty rearrangement ?

(5) Give structures of the following compound :

(i) Benzo (h) isoquinoline

(ii) 2H, 6H-1 5, 2-dithiazine

(6)  $\xrightarrow[CHCl_3]{Br_2}$ (?)

(7) What is Quantum Yield ?

(8) What is Knoevenagel condensation ?

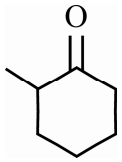
(9) What is carbopolladation ?

(10) Which reagent is used in Jones oxidation ?

(11) What is Dieckmann condensation ?

(12) Write structure of Dess-Martin periodinane with one application.

(13) On which factors the selectivity of enzyme depend ?

(14)  $\xrightarrow[(ii)\ CH_2 = CH - CH_2\ Br]{(i)\ LDA\ |\ DMF}$ (?)

COMMON FRAGMENTS LOST

Molecular Ion Minus	Fragment Lost Inference structure
1	$H\cdot$
2	$2H\cdot$
15	$CH_3\cdot$
16	O ($ArNO_2$, amine oxides, sulfoxides); $\cdot NH_2$ (carboxamides, sulfonamides)
17	$\cdot HO\cdot$
18	H_2O (alcohols, aldehydes, ketones)
19	$F\cdot$
20	HF
26	$CH\equiv CH$, $\cdot CH\equiv N$
27	$CH_2=CH\cdot$, $HC\equiv N$ (aromatic, nitrites, nitrogen heterocycles)
28	$CH_2=CH_2\cdot$, CO, (quinones) (HCN+H)
29	$CH_3CH_2\cdot$; (ethyle ketones, $ArCH_2CH_2CH_3$), $\cdot CHO$
30	$NH_2CH_2\cdot$, CH_2O ($ArOCH_3$), NO ($ArNO_2$), C_2H_6
31	$\cdot OCH_3$,(methyl esters), $\cdot CH_2OH$, CH_3NH_2
32	CH_3OH,S
33	$HS\cdot$ (thiols), ($\cdot CH_3$ and H_2O)
34	H_2S (thiols)
35	$Cl\cdot$
36	HCl, $2H_2O$
37	H_2Cl (or $HCl + H$)
38	C_3H_2, C_2N, F_2
39	C_3H_3, HC_2N
40	$CH_3C\equiv CH$
41	$CH_3=CHCH_2\cdot$
42	$CH_2=CHCH_3$, $CH_2=C=O$, CH_2, NCO, $NCNH_2$
43	$C_3H_7\cdot$ (propyl ketones, $ArCH_2$–C_3H_7), $CH_3\overset{O}{\overset{\|}{C}}\cdot$ (methyl ketones, $CH_3\overset{O}{\overset{\|}{C}}G$, where G= various functional groups), $CH_2=CH$–$O\cdot$ ($CH_3\cdot$ and $CH_2=CH_2$), HCNO
44	$CH_2=CHOH$,CO_2 (esters, anhydrides) N_2O, $CONH_2$, $NHCH_2CH_3$
45	CH_3CHOH, CH_3CH_2O (ethyl esters), CO_2H, $CH_3CH_2NH_2$
46	(H_2O and $CH_2=CH_2$), CH_3CH_2OH, $\cdot NO_2$ ($ArNO_2$)
47	$CH_3S\cdot$
48	CH_3SH, SO(sulfoxides), O_2
49	$\cdot CH_2Cl$
51	$\cdot CHF_2$

52 C_4H_4, C_2N_2

53 C_4H_5

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_9· (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_3	16–25	$RCH = CH_2$	125–140
R_3CH	25–38	$RC \equiv N$	117–125
$CH_3\overset{O}{\overset{\|}{C}}R$	~30	ArH	125–150
$CH_2\overset{O}{\overset{\|}{C}}OR$	~20	$R\overset{O}{\overset{\|}{C}}OR'$	170–175
RCH_2Cl	40–45	$R\overset{O}{\overset{\|}{C}}OH$	177–185
RCH_2Br	28–35	$R\overset{O}{\overset{\|}{C}}H$	190–200
RCH_2NH_2	37–45	$R\overset{O}{\overset{\|}{C}}R'$	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 αβ – UNSATURATED ALDEHYDES AND KETONES ABSORPTION

$\pi \rightarrow \pi^*$ Transitions

δ γ β α Z Z = H aldehyde Z = R ketone

$-C=C-C=C-C=O$ Z = OH, -OR : acid, ester

αβ – Unsaturated aldehyde		208	nm
αβ – Unsaturated acyclic or six carbon ring ketone		215	nm
αβ – 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)	α, β, γ, δ	06	nm
Amine (NH_2, NHR, NR_2)	β	95	nm
Thioether (SR)	β	85	nm