* B B G - 0 0 3 - 1 0 1 6 0 0 7 *

BBG-003-1016007 Seat No. _____

B. Sc. (Sem. VI) (CBCS) (W.E.F. 2016) Examination

July - 2021

Chemistry : C - 602

(Organic Chemistry & Spectroscopy) (New Course)

Faculty Code : 003

Subject Code : 1016007

Time : $2\frac{1}{2}$ Hours] [Total Marks : **70**

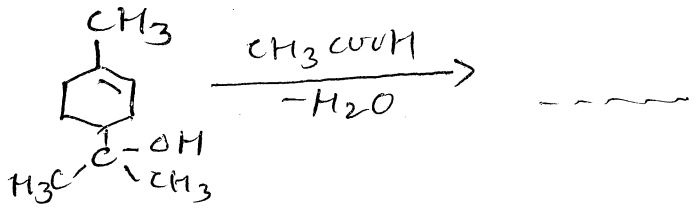
Instructions : (1) Answer any five out of ten questions.
(2) All questions carry equal marks – 14 marks.
(3) Figures given in right side indicate individual marks of that question.

1 (a) Answer the following questions. **4**
(i) Write the structure of P-cymene.
(ii) Write the structure of Baygon.
(iii) Give full name of HMTA.
(iv) Complete the reaction.

$C_9H_{15}CHO + Ag_2O \rightarrow .....$

(b) Give structure of carbendazine and uses. **2**
(c) Give synthesis of P.E.T.N. **3**
(d) Give synthesis of α-Terpineol by Parkin method. **5**

2 (a) Answer the following questions. **4**
(i) Write the structure of parathion.
(ii) Define Explosive.
(iii) Complete it : HMTA $\xrightarrow{\text{Nitration}}$ .....
(iv) Complete it :



(b) Give synthesis of Levulinic acid. **2**

(c) Give synthesis of Musk Amberette. **3**

(d) Give synthesis of Musk Ketone and TNT. **5**

3 (a) Answer the following questions. **4**

(i) Write the structure of Ninhydrin.

(ii) Write Lead Sulphide Test.

(iii) Define basic amino acid and give one example.

(iv) Write structure of Valine.

(b) Give synthesis of Phthalic acid from potassium phthalate. **2**

(c) Give synthesis of Glycyl alanine from Phthalic Anhydride. **3**

(d) Give constitution of Thyronin. **5**

4 (a) Answer the following questions. **4**

(i) Write the structure of β-amino acid.

(ii) Write Ninhydrin Test.

(iii) Write the structure of Histidine.

(iv) Complete the reaction :

$$\alpha-\text{amino acid} \xrightarrow{LiAlH_4} \overset{?}{\text{.....}}$$

(b) Complete the reaction. **2**

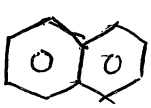
$$R-\underset{\underset{NH_2}{|}}{CH}-COOH + C_6H_5NCO \longrightarrow \overset{A}{\text{.....}} \xrightarrow{-H_2O} \overset{B}{\text{.....}}$$

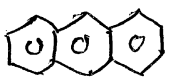
(c) Explain physical properties of Amino acid. **3**

(d) Give synthesis of Thyroxin. **5**

5 (a) Answer the following questions. **4**

(i) Draw chair form of cyclohexane and mention axial, equatorial position.

(ii)  Acidic $KMnO_4$ → A

(iii)  conc. HNO_3 / V_2O_5 + air → A

(iv) What is parent peak ? Define.

(b)  2

(c) Give synthesis of phenanthrene from Fittig Reaction. 3

(d) Explain conformational analysis of 1,3 disubstituted cyclohexane. 5

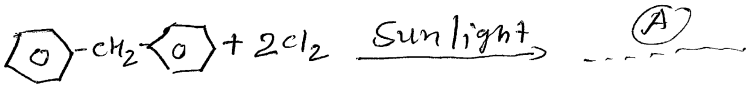
6 (a) Answer the following questions. 4

(i) Draw the Twisted boat form of cyclohexane.

(ii) What is cation radical ?

(iii) Arrange cation stability order.

$R_2CH^+, CH_3^+, R_3C^+, RCH_2^+$

(iv) 

(b) Define Hydrogen transfer rearrangement with example. 2

(c) Give only names of main parts of mass spectrometer and explain FAB technique. 3

(d) Give Addition Reaction of Antracene (minimum four). 5

7 (a) Answer the following questions. 4

(i) Which of the following nuclei are easily observed in NMR spectroscopy.

(a) ^1H (b) 19_F

(c) 31_P (d) All

(ii) How many NMR signal would you expected in 1,1-dimethyl cyclopropane ?

(iii) Give structural formula of C_3H_6O compound which give rise to only two NMR signal.

(iv) Carbonyl group (>C=O) peak identify from

(a) UV spectra (b) IR spectra

(c) NMR (d) TLC

(b) Define Equivalent and Nonequivalent proton. 2

(c) Give difference between chemical shift δ and coupling constant "J". 3

(d) Explain spin-spin coupling with example. 5

8 (a) Answer the following questions. 4

(i) How many types of protons are present in the compound $CH_3 \cdot CH = CH_2$?

(ii) How many NMR signal we get from this compound ?
$CH_3 \cdot CH_2CH_2COOCH_3$

(iii) Give structure formula of compound which give rise to only two NMR signal $C_5H_{10}Br_2$.

(iv) In NMR spectra which information we get from splitting of signal ?

(b) Give structural formula of compound which give rise to only two NMR signal. 2

(i) $C_8H_{18}O$

(ii) $C_3H_8O_2$

(c) Distinguish $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$ by NMR spectra. 3

(d) Explain factors affecting on chemical shift in NMR spectra. 5

9 (a) Answer the following questions. 4

(i) What is spectroscopy ? Define.

(ii) How many signal would you expected in NMR-spectrum of 1, 2-dibromopropane ?

(iii) Arrange chemical shift δ ppm in ascending order : Benzene, Methan, Ethiline, Cyclopropane.

(iv) Give the no. of signal and splitting of each signal
$CH_3 \cdot CF_2 \cdot CH_2 \cdot OCH_3$.

(b) If experiment done in 60 MHz NMR instrument specific proton give signal at 120 Hz from TMS calculate chemical shift in both unit δ and τ ppm. 2

(c) Assign the structure formula from the following NMR-data M.F. = $C_5H_{10}O_4$. 3

NMR

(i) a singlet δ = 4.2 ppm 1H

(ii) b singlet δ = 3.8 ppm 3H

(iii) c singlet δ = 3.7 ppm 6H

(d) Assign the structure formula from the following data : **5**
M. F. = $C_8H_8Br_2$
U.V. : Above 220 nm gives U.V. bonds
IR = 3080, 1640, 1510, 1405, 1215, 930, 760 and 710 CM^{-1}
NMR
a doublet δ = 4.0 ppm 1H
b doublet δ = 4.1 ppm 1H
c two doublet δ = 5.1 ppm 1H
d singlet δ = 7.4 ppm 5H

10 (a) Answer the following questions. **4**
(i) What is chemical shift ? Define.
(ii) Give expected IR frequency of Acetiline.
(iii) In aqueous solution which solvent is used as a reference compound in NMR spectra ?
(iv) Give structure formula of compound which give rise only one NMR-signal :
$C_5H_8Cl_4$

(b) Give structure formula from following data : **2**
M.F. $C_3H_6O_2$
a Singlet 1.98 δ ppm 3H
b Singlet 3.7 δ ppm 3H

(c) Give structure formula from following data : **3**
M.F. : $C_5H_9O_2Cl$
a Triplet δ ppm = 1.5 3H
b Doublet δ ppm = 2.35 2H
c Singlet δ ppm = 11.25 1H
d Quintet δ ppm = 1.8 2H
e Quintet δ ppm = 3.5 1H

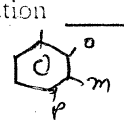
(d) Give structure formula from following data : **5**
M.F. : $C_6H_{14}O$
UV : Above 220 nm, transparent
IR : 3200(b), 2950, 2850, 1460, 1430, 1385, 1080 CM^{-1}.
NMR
a Triplet τ = 8.8 δ ppm 6H
b Quintet τ = 8.5 δ ppm 4H
c Multiplet τ = 8.3 δ ppm 1H
d Doublet τ = 6.1 δ ppm 2H
e Singlet τ = 5.5 δ ppm 1H

IR- Data

	Type of Vibrartion	Frequency(cm^{-1})	Intensity
[1]	**Hydrocarbon :-**		
	C-H Stretching vibration		
	(a) Alkane Stretch vib $\xrightarrow{CH_3/CH_2}$	2990-2850	a,s
	(b) Alkene Stretch vib $\xrightarrow{>C=CH_2}$	3100-3000	m
	(c) Alkyne Stretch vib $\xrightarrow{-C\equiv C-H}$	3300	S.V.
	(d) Aromatic Stretch vib $\xrightarrow{Ar-H}$	3030	m
[2]	**C-H Bending Vibration :-**		
	(a) (i) CH_3 - Bending	1450	s
	(ii) CH_2 - Bending	1465	m
	(iii) CH - Bending	1340	w
	(b) Isoprobyl $-CH(CH_3)_2$	1375, 1385 (Doublet)	s
	(c) Tert-butyl $-C(CH_3)_3$	1365, 1390 (Doublet)	m
	(d) Alkene bending vib	1420-690	m
	(e) Alkene CiS $H_2C=CH$	690 Trans 970	
	(f) Alkyne bending vib	630	s
	CH_2 Roking (More then four CH_2 group)	720 & 625	m
[3]	**C-C Multiple Bond :-**		
	(a) C = C Alkene stretch vib	1680-1600	m.v
	(b) C ≡ C Alkyne stretch vib	2250-2100	m.v
	(c) C = C Aromatic ring scalatal vib	1600,1580 / 1500,1450	m
[4]	**C=O Carbonyl group**		
	(a) (i) C=O Acid	1700	(s)
	(ii) O-H(Stretch) $C(=O)-OH$ Acid broad	2700-3200	(w)
	(b) Ketone	1715	(s)
	(c) (i) Aldehyde	1745	(s)
	(ii) C-H Strech vib $\xrightarrow{CHO}$	2820, 2750 (Doublet)	(s)
	(d) (i) Ester	1750-1735	(s)
	(ii) Aromatic or unsaturated	1730-1715	(s)
	(e) Acid Halide	1800	(s)
	(f) Anhydride	1810, 1760 (Doublet)	(s)

Type of Vibrartion	Frequency(cm^{-1})	Intensity
[5] $CONH_2$ Amide :		
(i) C=O Stretch Vib ⟶	1650	(s)
(ii) Due to NH_2 Group also at ⟶	3400	s
[6] C-O		
(i) Alconols, Acids, Anhydrides ⟶	1300-1000	m
(ii) Ether ⟶ R - O - R ⟶	1200-1100	m
(iii) Ester ⟶ COOR ⟶	1245, 1045 (Doublet)	m
[7] O-H		
(i) Free -OH (Alcohola.Phenls) ⟶	3650-3600	(s)
(ii) H-bonded (Inter -Molecular) ⟶	3500-3200	(m)
(iii) Carboxyls Acid (Broad) ⟶	3400-2700	(w)
[8] N-H (Amine)		
(i) Primary amine -> NH_2 Free ⟹	3500, 3400 (Doublet)	(m)
(ii) N-H bending ⟶	1650-1550	m
(iii) Secondry amine =NH ⟶	3500-3100	m
[9] C-N		
Strech vib Aromatic ⟶	1350-1200	m
Aliphatic ⟶	1200-1000	m
C=N ⟶ Amines of oximes ⟶	1690-1640	(w)
C≡N ⟶ Nitriles ⟶	2260-2240	(m)
[10] NO_2 Nitrogroup ⟶	1550-1350	(s)
S-H -> Marcaptans ⟶	2550	m
S=O ⟶ (i) Sulfoxides ⟶	1050	(s)
(ii) Sulfones,Sulfony,Chlorides SO_2Cl ⟶	1375-1300	(s)
(iii) Sulfats,Sulfonmides Ar-So_2NH_2 ⟶	1200-1140	(s)
[11]		
C-F ⟶ Floride ⟶	1400-1000	(s)
C-Cl ⟶ Chloride ⟶	800-600	s
C-Br ⟶ Bromide ⟶	617	s
C-I ⟶ Iodide ⟶	500	s

Substitution
- Mono (Two bonds) ==> 700 & 650
- Ortho (Single) ==> 750 ± 20
- Meta (Two bonds) ==> 710 & 750
- Pera (Single) ==> 820 ± 20



N.M.R. CHEMICAL SHIFTS

In δ ppm

Type	Type of Proton	Chemical Shifts in δ p.p.m.
Primary	R- $\underline{CH_3}$	0.9 (1.0)
Secondary	R_2 - $\underline{CH_2}$	1.3 (1.5)
Tertiary	R_2 - $\underline{CH}$	1.5 (1.8)
Vinylic	C = C - $\underline{H}$	4.6 - 5.9
Acetytinic	C≡C - $\underline{H}$	2-3
Aromatic	Ar - $\underline{H}$	7-8
Benzylic	 C - $\underline{H}$	Ar - C - H 2.2-3
Allylic	C = C - $\underline{CH_3}$	1.7
Flourides	$\underline{HC}$ - F	4-4.5
Chlorides	$\underline{HC}$ - Cl	3-4
Bromides	$\underline{HC}$ - Br	H - C - X 2.5-4 — 2-4.5
Iodides	$\underline{HC}$ - I	2-4
Alcohols	$\underline{HC}$ - OH	3.4-4
Ethers	$\underline{HC}$ - OR	H - C - OR(H) 3.3-4
Esters	R - C(=O)H - OCH_3	RCOO - $\underline{CH_3}$ 3.7-4.1
Acids	$\underline{HC}$ - COOH	2.6-3
Carbonyl compounds	$\underline{HC}$ - C = O	2-2.7
Carboxylic	R - $\underline{COOH}$	10-12
Aldehyde	R - $\underline{CHO}$	9-10
Hydroxylic	R - $\underline{OH}$	1-5.5 (depend on H-bond)
Phenolic	Ar - $\underline{OH}$	4-12
Enolic	C = C - $\underline{OH}$	15-17
Amino	R - $\underline{NH_2}$	1-5
CYN.	$\underline{CH}$ - CN	2.7