

B.Sc. Semester - 6 (CBCS) Examination

March/April -2020

ORGANIC CHEMISTRY AND SPECTROSCOPY (CORE)

Time: 2:30 Hours

Marks: 70

Instructions:

1. All questions are compulsory.
 2. Figures to the right indicate marks.
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- Q. 1 (A) Answer the following question. (4)
(1) Explain Gabriel phthalimide synthesis for preparation of amino acids.
- Q.1 (B) Answer the following questions. (Any two) (10)
(1) Write any five chemical properties of amino acid due to amino group.
(2) What are amino acids? Classify them in detail.
(3) Synthesize alanylglycine dipeptide by Fischer's method.
- Q. 2 (A) Answer the following question. (4)
(1) Write synthesis of PETN from acetaldehyde and give its uses.
- Q. 2 (B) Answer the following questions. (Any two) (10)
(1) Write synthesis of (I) Musk Ambrette from m-cresol and (II) Baygon from catechol.
(2) Write synthesis of Citral from 1,3-dibromo-3-methylbutane.
(3) Explain constitution of α -Terpineol in detail.
- Q. 3 (A) Answer the following question. (4)
(1) Explain Fischer Indole Synthesis in detail.
- Q. 3 (B) Answer the following questions. (Any two) (10)
(1) Explain Friedlander's Synthesis in detail.
(2) Write any five substitution reactions of Anthracene.
(3) Conversion: Anthracene from Naphthalene.
- Q. 4 (A) Answer the following question. (4)
(1) NMR spectra of an organic compound in 60 MHz instrument requires 330 Hz secondary magnetic field. What value of secondary field will be required if the NMR of the compound is taken in 100 MHz
(2) A molecule with molecular formula $C_4H_{12}Si$ gives the following signal in NMR. Deduce the constitution. a) $12H$ s 10τ .
- Q. 4 (B) Answer the following questions. (Any two) (10)
(1) Give difference between Chemical shift δ and coupling constant j .
(2) Explain anisotropic effect in ethene, acetylene and 18-Annulene.
(3) A molecule contains $C\% = 54.5$, $H\% = 2.28$, and F . The Vapour Density is 66 and gives a singlet at 7.8δ . Deduce its constitution. (Mol.wt=2 Vapour Density)
- Q. 5 (A) Answer the following question. (4)
(1) Explain factors affecting stability of conformations.
- Q. 5 (B) Answer the following questions. (Any two) (10)
(1) Discuss conformations of cyclohexane.
(2) Discuss important features of mass spectra of alkanes.
(3) A compound has the following spectral properties. Deduce its structure.
M.F. $C_8H_8Br_2$, Gives UV band above 220 nm, IR: 3080, 1640, 1510, 1405, 1215, 930, 760 and 710 cm^{-1} , NMR:
a) $5H$ s 7.4δ b) $1H$ d 4.1δ c) $1H$ d 4.1δ d) dd $1H$ 5.1δ

Spectral Data

U.V.

Empirical rules for Dienes:

	(A) homoannular $\lambda = 253$ nm	(B) heteroannular $\lambda = 253$ nm
Increments for double bond extending conjugation	30	30
Exocyclic double bond	5	5
Alkyl substitution or ring residue	5	5
Homocyclic Diene components	39	39
Polar Groups:		
-OCOCH ₃	0	0
-OR	6	6
-Cl, -Br	5	5
-NR ₂	60	60

(C) Simple Diene:

Parent $\lambda = 217$ nm

Polar Groups	
Alkyl substitution or ring residue	5 nm
-Cl, Br	17
-OH	5
-OR	5
-NR ₂	60
-SR	30

(D) Empirical rules for Enone and Dienones:

λ

(a) Z=C

(1) 6 membered ring or acyclic 215

(2) 5 membered ring 202

(b) Z=H 207

(c) Z= OH or OR 193

(d) Acyclic dienone 245

Increment for:

double bond extending conjugation 30

alkyl group or ring residue α 10

β 12

γ or higher 18

Exocyclic double bond position 5

Homocyclic diene component 39

Polar Groups	α	B	γ	δ' other
-Cl	15	12	-	-
-OH	35	30	50	50
-OR	35	30	17	31
-NR ₂	-	93	-	-
-O	-	75	-	-
-NHCOR	-	95	-	-
-OCOCH ₂	6	6	-	6

-SR	-	85	-	-
-Br	25	30	-	-
-NO ₂	-	95	-	-
(e) Empirical rules for Benzoyl derivatives:				
Parent Chromophor:			mm	
Z= Alkyl or ring residue			246	
Z= H			250	
Z = -OH or OR			230	
Increment for each substituent:		Q	M	R
Alkyl or ring residue		3	3	10
		7	7	25
		11	20	78
		0	0	10
		2	2	15
		13	13	58
		20	20	45
		-	-	73
		20	20	85
Infra Red Data				
Alkane (stretching)	-C-H		2960-2850	
Alkene	=C-H		3200-3100	
Alkyne	≡C-H		3300-3200	
Aromatic	Ar-C-H		3100-3010	
Aromatic Ring	C=C		1600-1500	
Alkene	>C=C<		1680-1610	
Alkyne	-C≡C-		2260-2100	
Alkene (Bending)	-C-H		1340	
	-C(C ₂ H ₃) ₃		1470-1430	
			1380-1385	
	-C(CH ₂) ₃		1365	
Aldehyde	-C-H		2820-2720	
Aldehyde	>C=O		1740-1720	
Ketone	>C=O		1725-1710	
Carboxylic acid	>C=O		1725-1705	
Ester	>C=O		1750-1730	
Amide	>C=O		1670-1640	
			1860-1810 &	
Anhydride	>C=O		1790-1740	
Alcohols, ethers, esters, carboxylic acids, anhydride	C-O		1300-1000	
Alcohols, Phenols:				
Free	-OH		3650-3600	
H-bonded	-OH		3500-3200	
Carboxylic acid				
Free	-OH		3500-3650	
H-bonded	-OH		2500-3200	
Amines				
stretching	-N-H		3330-3500	
bending	-N-H		1640-1550	

Nitrile	-C≡N	2280-2210
Ether	-O-	1150-1070
Alkene bending		
disubstituted cis		690
disubstituted trans		960-970
Aromatic substitution: C-H out of plane bending		
No. of adjacent H atom		Range (cm)
		750
		&
5		700
4		750
3		780
2		830
1		850

NMR

Type	Type of proton	Chemical shifts (approximate) in δ ppm
Primary	R-CH ₃	0.9-1.0
Secondary	R ₂ -CH ₂	1.3-1.5
Tertiary	R ₃ -CH	1.5-1.8
Vinyllic	C=C-H	4.6-5.9
Acetylinic	C≡C-H	2.0-3.0
Aromatic	Ar-H	7.0-8.0
Benzylic	Ar-C-H	2.2-3.0
Allylic	C=C-CH ₃	1.7-1.8
Flourides	HC-F	4.0-4.5
Chlorides	HC-Cl	3.0-4.0
Bromides	HC-Br	2.5-4.0
Iodides	HC-I	2.0-4.0
Alcohols	HC-OH	3.4-4.0
Ethers	HC-OR	3.3-4.0
Esters	R-COO-CH ₃	3.7-4.1
Acids	HC-COOH	2.6-3.0
Carbonyl Compounds	HC-C=O	2.0-2.7
Carboxylic acid	R-COOH	10.0-12.0
Aldehyde	R-CHO	9.0-10.0
Hyroxylic	R-OH	1.0-5.5
Phenolic	Ar-OH	4.0-12.0
Enolic	C=C-OH	15.0-17.0
Amino	R-NH ₂	1.0-5.0
Cyano	HC-CN	2.6-2.8
