M-003-001506-N Seat No. _____

B. Sc. (Sem. V) (CBCS) Examination

October / November – 2016

C-502 : Organic Chemistry & Spectroscopy

(New Course)

Faculty Code : 003
Subject Code : 001506-N

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

Instructions : (1) Total three questions; all questions are compulsory.
(2) The figures to the right side, indicate the marks of the questions/sub-question.

1 Answer the following : **20**

(1) Give the reaction of coniine react with HI at 300°C temp.

(2) Give synthesis of imidazole.

(3) Complete the following reaction :

$$CH \equiv C - CHO \quad + \quad NH_2OH \rightarrow$$

(4) Give structure and use of Saccharin.

(5) Give the reaction of three moles of benzene treated with PCl_3 in the absence of air.

(6) Give structure and use of Orange-II.

(7) Complete the following reaction :

$$HS - CH_2 - CH_2 - NH_2 \quad + \quad HO - CH_2 - CH_2 - OH \rightarrow$$

2-Mercapto ethyl amine 1,2-Ethane diol

(8) Complete the following reaction :

$$\text{Papaverin} \xrightarrow{\text{cold \& dil. } KMnO_4} \xrightarrow{\text{hot \& dil. } KMnO_4}$$

(9) Give synthesis of Thiazole.

(10) Complete the following reaction :

$$\text{Glucose} \xrightarrow{3\text{PhNHNH}_2}$$

(11) Give point group of Cis and Trans planer H_2O_2.

(12) Give the structure of the molecule having D_{2h} point group. Give its symmetry elements.

(13) What is Inversion centre ?

(14) Define : Symmetry element.

(15) Arrange the following carbonyl compounds in the decreasing order of their λ_{max} :

C_6H_5CHO, C_6H_5COOH, $C_6H_5COCH_3$

(16) Arrange the following carbonyl compounds in the decreasing order of their $\nu_{C=O} cm^{-1}$ value :

C_6H_5CHO, HCHO, $C_6H_5COCH_3$

(17) Give characteristic infra red absorption frequencies of the Nitrile compound.

(18) Give type of bending vibration.

(19) Define : Chromophor and Auxochrome.

(20) Define : Bathochromic shift and Hyperchromic effect.

2 (A) Answer the following : (any **three**) : **6**

(i) Give synthesis of Pyrimidine.

(ii) Give any two methods of preparation of $LiAlH_4$.

(iii) Give two synthetic uses of Hoffmann rearrangement.

(iv) Give conversion of D(–) Fructose from D(+) Glucose.

(v) Give synthesis and use of Dulcin.

(vi) Explain Zeisel method.

(B) Answer the following : (any three) **9**

(i) Explain epimerization with a suitable reaction.

(ii) Give synthesis of Crysodine-G.

(iii) Give the reaction mechanism of Leuckart – Wallach reaction.

(iv) Explain Emde's degradation method.

(v) Explain Killani reaction with a suitable example.

(vi) (a) Give the reaction of ethylene glycol react with 1,2-dibromoethane.

(b) Give the reaction of acetylene react with diazomethane.

(c) Give the reaction of maleic anhydride react with hydrazine hydrate.

(C) Answer the following : (any **two**) **10**

(i) Give synthesis and uses of :

(a) Adrenaline

(b) Ibuprofen.

(ii) Explain : Mutarotation.

(iii) Prove that Nicotine is β-pyridyl-α-pyrrolidine alkaloid.

(iv) Prove that D(+) Glucose contain pyranose ring system.

(v) Explain Arndt-Eistert reaction with mechanism.

3 (A) Answer the following : (any **three**) **6**

(i) Explain the $n \rightarrow \pi^*$ electronic transition in UV spectra.

(ii) Give point group of Ethylene and m-Dichlorobenzene.

(iii) Give structure of the molecule having D_{4h} point group. Give its symmetry elements.

(iv) Explain : Fermi resonance.

(v) Define : Improper rotational axis.

(vi) Explain Overton in IR spectra.

(B) Answer the following : (any **three**) **9**

(i) Construct multiplication table for C_{2h} point group.

(ii) Explain the effect of polar solvent on $\pi \rightarrow \pi^*$ transition band of carbonyl group.

(iii) Prove that the $S_n^n = \sigma_h$ in eclipsed ethane.

(iv) How will you distinguish cis and trans isomers with the help of UV spectra ?

(v) Explain : Finger print region.

(vi) Assign the structure to a compound having following characteristics :

M.F. : C_9H_8

I.R. : 3050, 2930, 2890, 2210, 1595, 1490, 1450, 1380, 1020, 750, 700 cm^{-1}

(C) Answer the following : (any **two**) **10**

(i) Construct the multiplication table for C_{3v} point group and explain with suitable example.

(ii) Discuss the factor affecting the position of carbonyl group in infra red spectroscopy.

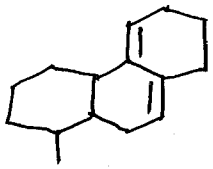
(iii) What is plain of symmetry ? Explain different types of plain of symmetry.

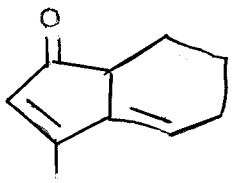
(iv) Assign the structure to a compound from the following spectral result :

M.F. : C_9H_8

I.R. : 3310 (m), 3045 (m), 2960 (m), 2190 (m), 1610 (m), 1570 (m), 1505 (m), 1460 (m), 1320 (m), 1030 (m), 760 (s), 710 (s) cm^{-1}.

(v) Calculate λ_{max} for following compound :

(a) 

(b) 

Spectral Data

U.V. :

Empirical rules for Dienes :

	(A) Homoannular λ = 253 nm.	(b) Heteroanuular λ = 215 nm.
Increments for double bond extending conjugation	30 nm.	30 nm.
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 λ = 217 nm.

Polar groups :

Alkyl subst for ring residue	5 nm
–Cl, -Br	17
–OH	5
–OR	5
$-NR_2$	60
–SR	30

(D) Empirical Rules for Enones 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 :	
	Doyble bond extending conjugation	30
	Alkyl group of ring residue	α 10
		β 12
	γ or higher	18
	Exocyclic double bond position	5
	Homocyclic diene component	39

Polar groups	α	β	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	-	-

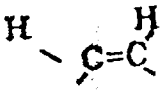
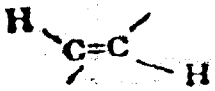
(e) Empirical Rules for Benzoyl Derivative :

Parent Chromophor :	mm
Z = alkyl or ring residule	246
Z = H	250
Z = -OH or -OR	230

Increment for each substituent :	Q	M	R
Alkyl or ring residue	3	3	10
-OH; $-OCH_3$ -OR	7	7	25
-O	11	20	78
-Cl	0	0	10
-Br	2	2	15
$-NH_2$	13	13	58
$-NHCOCH_2$	20	20	45
$-NHCH_3$	-	-	73
$-N(CH_2)_3$	20	20	85

Infra - Red Data

Alkene (strcteching)	–C–H	2850-2960(v)
Alkene	=C–H	3100-3200(m)
Alkyene	≡C–H	3200-3300(s)
Aromatic	ArC–H	3010-3100(m)
Aromatic ring	C=C	1500-1600(v) (two to three)
Alkene	>C=C<	1610-1680(v)
Alkyene	–C≡C –	2100-2260(s)
Alkene (Bending)	–C-H	1340(w)
	$-C(C_2H_3)_3$	1430-1470(m) & 1380-1385(s)
	$-C(CH_2)_3$	1365 (8)
Aldehyde	–C–H	2820-2000(w)&2650 2760(s)
Adehyde	C=O	1740-1720(s)
Ketone	C=O	1725-1710(s)
Carboxylic acid	C=O	1725-1705(s)
Ester	C=O	1750-1730(s)
Amide	C=O	1670-1640(s)
Anhydride	C=O	1810-1860(s)&1740-1790
Alecohols, Ethers, esters Carboxylic acids, Anhydride	C-O	1300-1000(s)

Alcohols, phenols :		
Free	O-H	3650-3600(sh)
bonded	O-H	3500-3200(b)
Carboxylic acids free		
Free	O-H	3500-3650(m)
H-bonded	O-H	2500-3200(b)
amines (stretch)	N-H	3330-3500(m)
Bnding	-N-H	1640-1550(m)
Nitrile	-C=N	2210-2280(s)
Ether	-O-	1070-1150(s)
Alkene bending		-690(s)
disulstituted Cis.		
disulstituted Trans.		960-970(s)

Aromatic substitution :	
Type C-H out of plane bending	
No. of adjacent H atom.	range cm
5	750(s) & 700(s)
4	750
3	780
2	830
1	850