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RO-003-001506

Seat No. _____

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

February - 2019

Chemistry - 502

(Organic Chemistry & Spectroscopy)

(Old Course)

Faculty Code : 003

Subject Code : 001506

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

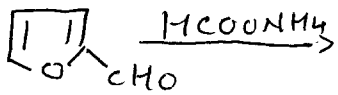
Instructions : (1) Total three questions, all are compulsory.

(2) The figures to the right side indicate the marks of the sub-questions.

1 Answer the following : **20**

(1) Complete it : Nicotine $\xrightarrow[KMnO_4]{\text{Oxidation}}$ .....

(2) Write structure of α-picoline.

(3) Complete it : 

(4) Give IUPAC name of

(i) $CH_3COCH_2CH_3$

(ii) CH_3COCl

(5) Give the example of Aldopentose.

(6) Complete it : P-methoxy anilne $\xrightarrow[\Delta]{\text{Urea}}$ .....

(7) Complete it : Isobutyl benzene $\xrightarrow[CH_3COCl]{\text{Anhy. } AlCl_3}$ .....

(8) Complete it : Diphenyl amine + Sulphur $\xrightarrow[\text{High Temp.}]{I_2}$ .....

(9) Complete it : Coniine $\xrightarrow{\text{Zn dust}}$ .....

(10) Give structure and uses of saccharin.

(11) Define law of inversion.

(12) Give point group of PCl_5.

(13) Give point group of H_3BO_3.

(14) Give useful range of IR spectra.

(15) Give the name of various components of U.V. spectrophotometer (instrument).

(16) Give possible transition in Aniline in U.V. spectra.

(17) Write approximately IR frequency of Acitic Anhydride.

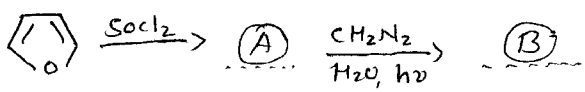
(18) Why β-kerotine is coloured ?

(19) Which material is used for prism in IR spectra ?

(20) Give one example of D_2d point group and its symmetry elements.

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

(1) Give one synthesis of Dulcin.

(2) 

(3) Explain reaction of Fructose with HCl.

(4) Give synthesis of catachol from Veratric acid.

(5) Give one synthesis of Dioxane.

(6) Give synthesis of pyrimidine from 1,3-diamino propane.

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

(1) Give synthesis of Ibuprofen.

(2) Prove that–CH_2 group is present between isoquinoline and benzene ring in papaverine.

(3) Give synthesis of Coniine by Bergmann method.

(4) Give synthesis of Morpholine from ethylene oxide.

(5) Give synthesis of saccharin from Anthranilic acid.

(6) Give synthesis of Adrenaline.

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

(1) Give synthesis and uses of Orange-II.

(2) Give the conversion of D-Glucose into D-Fructose and D-Fructose to D-Glucose.

(3) Explain Hoffman rearrangement with examle.

(4) Explain constitution of papaverine.

(5) Explain constitution of Nicotine.

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

(1) Explain $\pi - \pi^*$ electronic transition in U.V. spectra.

(2) Explain law of multiplication with example.

(3) For NH_3 molecule prove that :

$C_3 \times \sigma va \neq \sigma va \times C_3$

(4) Write expected IR frequency of p-amino benzaldehyde.

(5) Calculate theoretical number of vibrational degree of freedom in HCN and Aniline.

(6) Explain Auxochrome in U.V. Spectra.

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

(1) Write difference between C_n and S_n.

(2) Find out point group of Cis planner H_2O_2 and construct multiplication table for it.

(3) Explain Bathochromic and Hipsocromic shift in U.V. spectra.

(4) Distinguish phenyl acetic acid and p-Toluec acid by IR spectra.

(5) Explain steric hindrance in Diphenyl compound.

(6) Assign the structure to a compound from the following spectral data :

M.F. = $C_6H_{14}O$

IR = 2990, 2850, 1465, 1450 and 1200-1100 cm^{-1}.

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

(1) Discuss the factor affecting on the bands of carbony (C = O) group in IR spectra.

(2) Explain law of association for NH_3 molecule.

$A(B \times C) = (A \times B)C$ where $A = C_3$, $B = \sigma v_1$, $C = \sigma v_3$

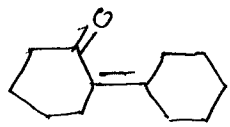
(3) What are P. Q. R. branches of spectra ? Derive their equation.

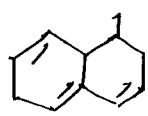
(4) Assign the structure to a compound from the following spectral data :

M.F. = $C_5H_7NO_2$

IR = 2990, 2840, 2250, 1735, 1465, 1455 and 1210 cm^{-1}.

(5) Calculate λ_{max} for the following compound :

(i) 

(ii) 

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, -OH	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 :

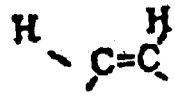
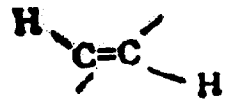
Parent Chromophor :

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

Increment for each substituent :	O	M	P
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	$-C\equiv C^2$.	2100-2260(s)
Alkene (Bending)	–C-H	1340(w)
	$-C(C_2^3H_3)_3$	1430-1470(m) & 1380-1385(s)
	$-C(CH_2)_3$	1365 (s)
Aldehyde	–C–H	2820-2900(w)&2850-2760(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
Alcohols, 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	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 disulstituted Cis.		-690(s)
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**