SEAT No._____ No. of Printed Pages : 4+2

[92 & A-61]

SARDAR PATEL UNIVERSITY

B.Sc. EXAMINATION (VTH SEMESTER)

SUBJECT TITLE : ORGANIC CHEMISTRY

COURSE CODE: US05CCHE01

DATE: 09-04-2018 **TIME: 02:00 P.M. TO 05:00 P.M.**

DAY: MONDAY **TOTAL MARKS: 70**

Q-1 Choose the correct option for the following : **[10]**

(i) Which of the following compound is use in the treatment of tuberculosis ?

(a) Nicotinic acid (b) Niacin

(c) Isoniazid (d) Thiamine

(ii) Which of the following reagent will react with pyrrole to give 2-formylpyrrole ?

(a) HCOOH (b) H_2O_2

(c) H_2SO_4 (d) $CHCl_3$/KOH

(iii) How many CMR signals would you expect from m-Xylene ?

(a) 5 (b) 7

(c) 6 (d) 9

(iv) Which of the following compound have smallest delta value ?

(a) CH_3Cl (b) RCH_2Cl

(c) R_2CHCl (d) RCH_3

(v) Which of the following is the monomeric unit of Neoprene ?

(a) Chloroprene (b) Isoprene

(c) Adipic acid (d) Methyl methacrylate

(vi) Which one is a more stable diene ?

(a) 1,4 – Pentadiene (b) Alkene

(c) 1,3 – Butadiene (d) 1,2 – Butadiene

(vii) The best method to prepare polyisobutylene is :

(a) Free polymerization (b) Coordination polymerization

(c) Cationic polymerization (d) Anionic polymerization

(viii) Which of the following compound is used as diluent in detergent ?

(a) CMC (b) Sodium tripolyphosphate

(c) Sodium silicate (d) Sodium perborate

(ix) Which of the following insecticides is transmitted into the human body through cow's milk ?

(a) B.H.C (b) Baygon

(c) D.D.T (d) Ferbum

(x) _____is used for electroplating of metal.

(a) Linalool (b) Musk xylene

(c) Heliotropin (d) Vanillin

[P.T.O.]

Q-2 Answer the following : (Any Ten) **[20]**

(i) Hydrogenation of pyrrole increase the basic strength by a factor of 10^{11}.

(ii) Give the synthesis of 2-Aminopyridine by a well-known reaction ?

(iii) Give the synthesis of 2,5-Diphenyl furan from ethyl acetate and ethyl benzoate using needed aliphatic inorganic reagents.

(iv) Why TMS is use as a standard for reference point in NMR Spectroscopy ?

(v) Give various aspects of NMR Spectroscopy.

(vi) Differentiate between Enantiotopic proton and Diastereotopic proton.

(vii) Give synthesis of Vulcanized rubber.

(viii) Explain Syndiotactic and Atactic arrangement with example.

(ix) Write the chemical structure of monomer and polymer for following:

(a) Plexiglass **(b)** Nylon-6

(x) Differentiate between Stomach insecticides and Contact insecticides.

(xi) Give the synthesis and applications of detergent use for scouring of wool.

(xii) Give only the large scale synthesis of Coumarin and give characteristics of good vehicle.

Q-3 Answer the following : **[10]**

Give the synthesis of 1-Azaphenanthrene from 2-Amino naphthalene using Skraup synthetic route. Why electrophilic substitution reaction in pyrrole takes place chiefly at the 2-position but not at the 3-position. Also discuss why nucleophilic substitution reaction in pyridine is preferred at the 2- and 4- position but not at the 3-position.

OR

Q-3 Answer the following : **[10]**

Arrange the increasing basicity order for the Pyridine, Aliphatic amine, Pyrrole and give detail explanation of your answer. Also give the synthesis of **(i)** 3-Carbethoxy-2,4,5-trimethyl pyrrole from appropriate α-amino ketone and acetoacetic ester by Knorr-Pyrrole synthetic route and **(ii)** Give the detail step mechanism of 2-Acetyl pyrrole by Hauben-Hoesch reaction.

Q-4 Answer the following :

(a) Deduce the structure of compound having following spectral data. Label all kinds of protons/carbons and give appropriate explanation for the structure.

(i) Molecular formula: C_9H_{10} **[04]**

IR (CM^{-1}) : 3100,2950,1650,1600,1500,1450,1375,890,760-770.

NMR (δ,ppm) : **(a)** 7.4, 5H, Complex **(b)** 5.35,1H, Singlet

(c) 5.1, 1H, Singlet **(d)** 2.10, 3H, Singlet.

(ii) Molecular formula: $C_4H_{10}O_2$ **[03]**

CMR (δ,ppm) : **(a)** 15.0, Quartet **(b)** 61.6,Triplet

(c) 66.6, Triplet **(d)** 72.1, Triplet.

(b) How will you differentiate geometric isomers by using CMR Spectroscopy ? **[03]**

OR

Q-4 Answer the following:

(a) Write a note on phenomenon of the splitting of NMR signals indicating clearly how the multiplicity of splitting reflects the number of protons adjacent to the absorbing protons. **[04]**

(b) Deduce the structure of compound having following spectral data. Label all kinds of protons/carbons and give appropriate explanation for the structure. **[06]**

(i) Molecular formula: $C_4H_8O_3$

NMR (δ,ppm) : **(a)** 1.27, 3H, Triplet **(b)** 3.66, 2H, Quartet

(c) 4.13, 2H, Singlet **(d)** 10.95, 1H, Singlet.

(ii) Molecular formula: $C_4H_6O_2$

CMR (δ,ppm) : **(a)** 22.3, Triplet **(b)** 27.9,Triplet

(c) 68.9, Triplet **(d)** 178.2, Singlet.

(iii) Molecular formula: C_7H_9N

CMR (δ,ppm) : **(a)** 14.3, Quartet **(b)** 28.2,Triplet

(c) 123.4, Doublet **(d)** 149.8, Doublet

(e) 152.8, Singlet.

[P.T.O.]

Q-5 Answer the following :

(a) Give detail account for the addition of HBr to 1,3-Butadiene at higher temperature yields 1-Bromo-2-butene as a major product but at lower temperature it becomes a minor product with potential energy diagram. **[04]**

(b) Give the mechanism for polymerization of styrene in presence of sodium metal and naphthalene. **[03]**

(c) What is sacrificial hyperconjugation ? Why propylene is 2.7 K.cal more stable than ethylene. **[03]**

OR

Q-5 Answer the following :

(a) What is Coordination polymerization ? Explain the importance of Ziegler-Natta catalyst in coordination polymerization and discuss its advantages over free-radical polymerization in the preparation of polyethylene. **[04]**

(b) What are plastics ? Give their classification and discuss its properties. **[03]**

(c) Draw the structure of following dienes and classify them into appropriate class. **(i)** 2,4-Hexadiene **(ii)** 1,2- Butadiene **(iii)** 1,4 - Pentadiene **[03]**

Q-6 Answer the following :

(a) What is meant by detergent ? Discuss detail classification of detergent on the basis of ionization into water. **[04]**

(b) Give the synthesis and applications of following from cheapest raw materials. **[06]**

(i) Compound used as insecticidal additive to seed disinfectants.

(ii) Compound which occurs in the essential oils of bergamot.

OR

Q-6 Answer the following :

(a) What is fixative ? What is the main function of fixative ? Discuss in detail about animal fixative. **[04]**

(b) Give the synthesis and applications of following from cheapest raw materials. **[06]**

(i) Optical brightening agent of Stilbene class derivative.

(ii) Compound use as insecticide of Organo phosphorus class.

N. M. R. Chemical Shifts

Type of proton		Chemical shift δ ppm	Type of Proton		Chemical shift δ ppm
Primary	RCH_3	0.9	Alcohols	HC–OH	3.4–4
Sec.	R_2CH_2	1.3	Ethers	HC–OR	3.3–4
Tert.	R_3CH	1.5	Esters	RCOO–CH	3.7–4.1
Vinylic	C=C–H	4.6–5.9	Esters	HC–COOR	2–2.2
Acetylenic C	C≡C–H	2–3	Acids	HC–COOH	2–2.6
Aromatic	Ar–H	6–8.5	Carbonyl	HC–C=O	2–2.7
Benzylic	Ar–C–H	2.2–3	Aldehydic	RCHO	9–10
Allylic	C=C–CH_3	1.7	Hydroxylic	R–OH	1–5.5
Chlorides	HC–Cl	3–4	Phenolic	Ar–OH	4–12
Bromides	HC–Br	2.5–4	Enolic	C=C–OH	15–17
Iodides	HC–I	2–4	Carboxylic	R–COOH	10.5–12
			Amino	R–NH_2	1–5

CH_3–Cl	δ 3.0
R–CH_2–Cl	δ 3.4
R_2CH–Cl	δ 4.0

CH_3–C–Cl	δ 1.5
R–CH_2–C–Cl	δ 1.7
R_2CH–C–Cl	δ 1.6

Characteristic Infrared Absorption Frequencies

Bond	Compound type	Frequency range, cm^{-1}
C–H	Alkanes	2850–2960
		1350–1470
	tert-Butyl: unsymmetrical doublet	1370 (*s*) 1395 (*m*)
	isopropyl "split"	1370 and 1385
	Methyl and methylene groups confirmed by a band	1430–1470
		1170
C–H	Alkenes	3020–3080 (*m*)
		675–1000
	$RCH=CH_2$ 910–920 cm^{-1} and 990–1000	*cis*-RCH=CHR 675–730 (*variable*)
	$R_2C=CH_2$ 880–900	*trans*-RCH=CHR 965–975
C–H	Aromatic rings	3000–3100 (*m*)
		675–870
	monosubstituted 690–710 cm^{-1} and 730–770	*m*-disubstituted 690–710 and 750–810
	o-disubstituted 735–770	*p*-disubstituted 810–840
C–H	Alkynes	3300
C=C	Alkenes	1640–1680 (*v*)
C≡C	Alkynes	2100–2260 (*v*)
C=C	Aromatic rings	1500, 1600 (*v*)
C–O	Alcohols, ethers, carboxylic acids, esters	1080–1300
	1° ROH about 1050 cm^{-1}	3° ROH about 1150 cm^{-1}
	2° ROH about 1100	Ar–OH about 1230
		Alkyl ethers 1060–1150 cm^{-1}
	Aryl and vinyl ethers 1200–1275 cm^{-1} (and, weaker, at 1200–1075 cm^{-1})	
C=O	Aldehydes, ketones, carboxylic acids, esters	1690–1760
O–H	Monomeric alcohols, phenols	3610–3640 (*v*)
	Hydrogen-bonded alcohols, phenols	3200–3600 (*broad*)
	Carboxylic acids	2500–3000 (*broad*)
N–H	Amines	3300–3500 (*m*)
C–N	Amines	1180–1360
C≡N	Nitriles	2210–2260 (*v*)
$-NO_2$	Nitro compounds	1515–1560
		1345–1385

¹³C NMR chemical shifts

Type of Carbon	Chemical shift (δ) ppm.
RCH_3	0 – 35
R_2CH_2	15 – 40
RCH_2Br	20 – 40
R_3CH	25 – 50
RCH_2Cl	25 – 50
RCH_2NH_2	35 – 50
RCH_2OH	50 – 65
–C≡C–	65 – 90
>C=C<	100 – 150
	110 – 175
>C=O	190 – 220

alkane sp^3 C' 0 – 65 ppm

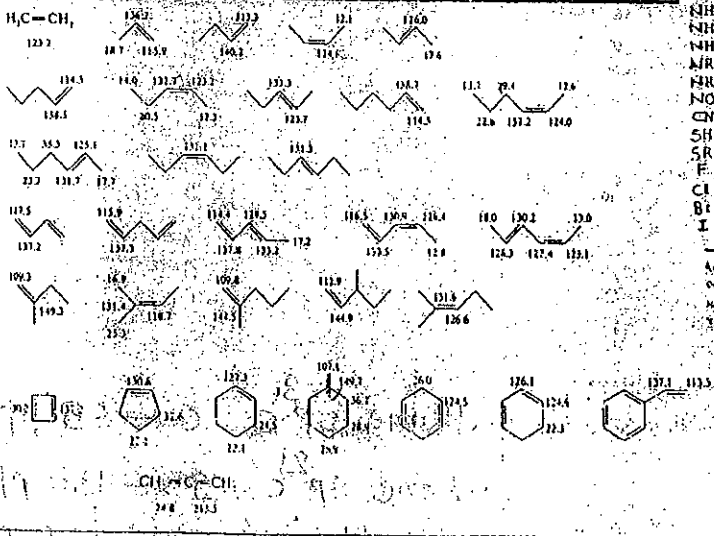
alkene sp^2 C' 95 – 150 ppm

aromatic C' 110 – 135 ppm

alkyne sp C' 70 – 100 ppm

Substituent	(Aromatic carbon)	C-1	C-2	C-4	C of Substituent (ppm from TMS)
H	0.0	0.0	0.0	0.0	
CH_3	+9.3	+0.3	−0.1	−2.9	21.3
CH_2CH_3	+15.6	−0.5	0.0	−2.6	29.2 (CH_2), 15.8 (CH_3)
$CH(CH_3)_2$	+20.1	−2.0	0.0	−2.5	34.4 (CH), 24.1 (CH_3)
$C(CH_3)_3$	+22.2	−3.4	−0.4	−3.1	34.5 (C), 31.4 (CH_3)
$CH=CH_2$	+9.1	−1.4	+0.2	−0.5	137.1 (CH), 115.3 (CH_2)
$C\equiv CH$	−5.8	+6.9	+0.3	+0.4	84.0 (C), 77.8 (CH)
C_6H_5	+12.1	−1.8	−0.1	−1.6	
CH_2OH	+13.3	−0.4	−0.6	−0.4	64.5
CH_2OCCH_3 (O)	+7.7	−0.0	−0.0	−0.0	20.9 (CH_3), 66.1 (CH_2), 170.5 (C=O)
OH	+26.6	−12.7	+1.6	−7.3	
OCH_3	+31.4	−14.4	+1.0	−7.7	54.8
OC_6H_5 (O)	+29.0	−9.4	+1.6	−5.3	
$OCCH_3$ (O)	+22.4	−7.1	−0.4	−3.7	21.0 (CH_3); 169.7 (C=O)
CHO (O)	+8.2	+1.2	+0.6	+5.8	191.0
CCH_3 (O)	+7.8	−0.4	−0.4	+2.8	24.6 (CH_3), 195.7 (C=O)
CC_6H_5 (O)	+9.1	+1.5	−0.2	+3.8	196.4 (C=O)
CCF_3 (O)	−5.6	+1.0	+0.7	+6.7	
COH (O)	+2.9	+1.3	+0.4	+4.5	161.0
$COCH_3$ (O)	+9.0	+1.2	−0.1	+4.8	31.0 (CH_3), 166.8 (C=O)
CO (O)	+4.46	+2.9	+0.6	+5.0	168.5
CNH_2 (O)	+3.0	−1.2	0.0	+3.4	
C≡N	−16.0	+3.6	+0.6	+4.3	119.5
NH_2	+13.2	−12.4	+1.3	−9.5	
$N(CH_3)_2$	+22.4	−15.7	+0.8	−11.8	40.3
$NHCCH_3$ (O)	+11.2	−9.9	+0.2	−5.6	
NO_2	+19.9	−5.3	+0.9	+6.0	
N=C=O	+3.7	−3.6	+1.2	−2.6	125.5
F	+35.1	−14.3	+0.9	−4.5	
Cl	+6.4	+0.2	+0.4	−2.0	
Br	−5.5	+3.4	+2.2	−1.0	
I	−32.3	+9.9	+2.4	−7.3	
CF_3	+2.6	−3.2	+0.4	+3.4	
SH	+2.3	+0.6	+0.7	−2.2	
SCH_3	+10.2	−1.4	+0.4	−3.4	15.9
SO_2NH_2	+15.3	+2.9	+0.4	+3.3	
$S(CH_3)_2$	+13.4	+4.4	−1.4	−0.1	

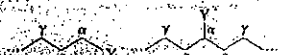
Alkene and Cycloalkene Chemical Shifts (ppm from TMS)



Branched Hydrocarbons

^{13}C Atoms	Shift (ppm) (δ)
α	+9.1
β	+9.4
γ	−2.5
δ	+0.3
ε	+0.1
1° (3°)	−1.1
1° (4°)	−3.4
2° (3°)	−2.5
2° (4°)	−7.2
3° (2°)	−3.7
3° (3°)	−9.5
4° (1°)	−1.5
4° (2°)	−8.4

Incremental Substituent Effects (ppm) on Replacement of H by Y in Alkanes. Y is Terminal or Internal (+ left, − right)



Terminal Internal

	α		β		γ
	Terminal	Internal	Terminal	Internal	
CH_3	+ 9	+ 6	+ 10	+ 8	− 2
$CH=CH_2$	+20		+ 6		−0.5
$C\equiv CH$	+ 4.5		+ 5.5		−3.5
COOH	+21	+16	+ 3	+ 2	− 2
COO⁻	+25	+20	+ 5	+ 3	− 2
COOR	+20	+17	+ 3	− 2	− 2
COCl	+33	+25		+ 2	
$CONH_2$	+22		+ 2.5		−0.5
COR	+30	+24	+ 1	+ 1	− 1
CHO	+31		0		− 2
Phenyl	+23	+17	+ 9	+ 7	− 2
OH	+48	+41	+10	+ 8	− 5
OR	+58	+51	+ 8	+ 5	− 4
OCOR	+51	+45	+ 6	+ 5	− 3
NH_2	+29	+24	+11	+10	− 5
NH_3^+	+26	+24	+ 8	− 6	− 5
NHR	+37	+31	+ 8	− 6	− 4
NR_2	+42		+ 6		− 3
NR_3^+	+31		+ 5		− 2
NO_2	+63	+57	+ 4	+ 4	
CN	+ 4	+ 1	+ 3	+ 3	− 3
SH	+11	+11	+12	+11	− 1
SR	+20		+ 7		− 3
F	+63	+63	+ 9	+ 6	− 4
Cl	+31	+32	+11	+10	− 4
Br	+20	+25	+11	+10	− 3
I	− 6	+ 4	+11	+12	− 1

Add these increments to the shift values of the appropriate carbon on in Table 5.2 or to the shift value calculated from Table 5.1.

Source: Welti, F.W., Marchand, A.P., and Welti, S. (1983). *Interpretation of Carbon-13 NMR Spectra*, 2nd ed. London: Heyden.