



**RY-003-001607**

Seat No. \_\_\_\_\_

**B. Sc. (Sem. VI) (CBCS) Examination**

**March - 2019**

**Chemistry : Paper - 602**

*(Organic Chemistry & Spectroscopy)*

*(Old Course)*

**Faculty Code : 003**

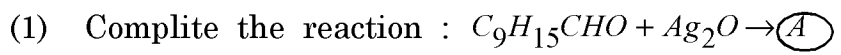
**Subject Code : 001607**

Time :  $2\frac{1}{2}$  Hours]

[Total Marks : 70

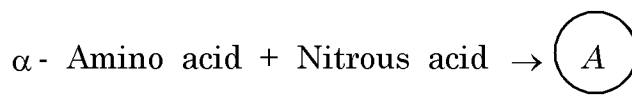
- Instructions :**
- (1) Total five questions, all are compulsory.
  - (2) The figure to the right side indicate the marks of the sub-question.

**1** Answer the following questions : **20**

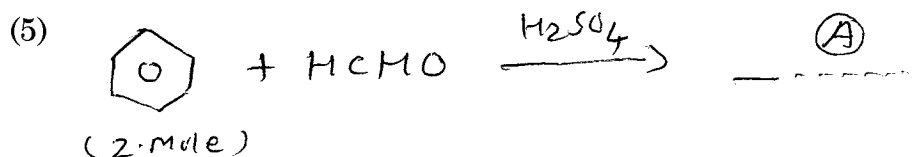


(2) Write the structure of Musk xylene

(3) Complete the reaction



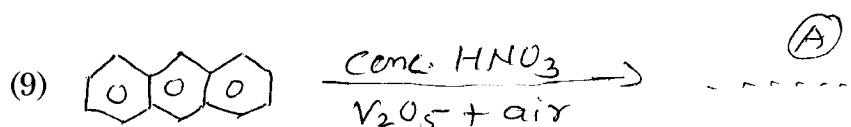
(4) Write the structure of Ninhydrin.



(6) Give structure and uses of PARATHION.

(7) Write structure of hippuric acid.

(8) Write Ninhydrine test.



(10) Draw Sawhorse and New mann projection structure of Ethane.

(11) Define equivalent and non-equivalent protons.

(12) In IR spectra aldehyde (-CHO group), CH stretching frequency in  $\text{cm}^{-1}$  observed approximately at.....

(13) How many NMR signals would you expect in Neopentane.

(14) How many minimum carbon required for Mc-Lafferty rearrangement ?

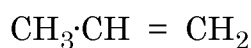
(15) Give structure formula of following compound which give rise only Two NMR signal (i)  $\text{C}_4\text{H}_6\text{O}_4$ .

(16) Which information we get from IR - spectra.

(17) In NMR spectra which information we get from Intensity of signal.

(18) Define Base Peak in Mass Spectra.

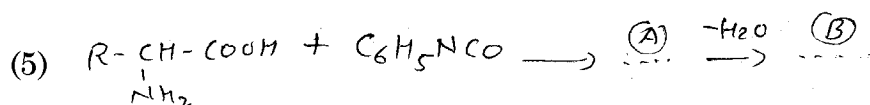
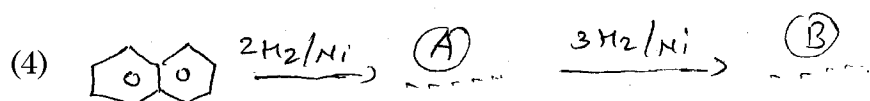
(19) Give No. of Signal in the compound



(20) Predict the number of NMR signals in Cis - 1, 2 cyclopropane.

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

- (1) Give structure and uses of carbendazine.
- (2) Give synthesis of Geranic acid.
- (3) Give synthesis of phthalic acid from potassium phthalate.



- (6) Give Nitration reaction of Diphenyl.

(b) Answer any three from following : 9

- (1) Give synthesis and uses of Baygon.
- (2) Give synthesis of Glycyl alanine from Phthalic Anhydride.
- (3) Explain physical properties of Amino acid.
- (4) Give synthesis of Naphthaline by Hawarth method.
- (5) Give synthesis and uses of P.E.T.N.
- (6) Explain conformations of cyclopentane.

(c) Answer any two from the following : 10

- (1) Explain constitution of Thyronine.
- (2) Give synthesis of  $\alpha$ -Terpinol from P-Toluic acid.
- (3) Explain constitution of Citral.
- (4) Explain chemical properties of Anthracene.
- (5) Give synthesis of (i) RDX (ii) TNT.

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

- (1) Explain principle of Mass Spectroscopy.
- (2) Define Equivalent and Non equivalent protons.
- (3) Define : Geminal proton and Vicinal proton.
- (4) Give No. of Signal, Splitting of each signal and  $\delta_{\text{ppm}}$  value of the compound.



- (5) Give the structure for the compound  $\text{C}_8\text{H}_{18}\text{O}$  giving only one NMR signal.
- (6) Give structure formula of compounds which give rise to only two NMR signal
  - (i)  $\text{C}_3\text{H}_6\text{O}$
  - (ii)  $\text{C}_4\text{H}_{10}\text{O}_2$

(b) Answer any three from the following : 9

- (1) Distinguish the following compound by NMR spectra.  
*n*-Propyl benzene and isopropyl benzene.
- (2) Discuss importance of TMS in NMR spectroscopy
- (3) Explain Mc Lafferty rearrangement.
- (4) How will you distinguish the stereoisomers of 1,3 dibromo. 1, 3 - dimethyl cyclo butane with the help of NMR spectra.
- (5) Explain deuterium labelling.
- (6) Assign the structure from the following spectral data.

M.F. =  $\text{C}_8\text{H}_{14}\text{O}_3$  NMR =

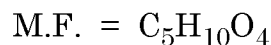
*a* septet  $\delta = 2.73$  ppm 2H

*b* doublet  $\delta = 1.2$  ppm 12H

(c) Answer any two from the following :

10

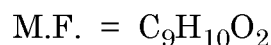
- (1) Explain Enantiometric and Diastereomeric protons.
- (2) Explain spin-spin coupling with example.
- (3) Assign the structure to a compound from the following spectral data.



NMR	Signal	Splitting	$\delta_{\text{ppm}}$	Intensity
	a	Singlet	$\delta = 4.8 \text{ ppm}$	4.3 squares
	b	Singlet	$\delta = 3.8 \text{ ppm}$	13.2 squares
	c	Singlet	$\delta = 3.7 \text{ ppm}$	25.8 squares

- (4) Assign the structure from the following data.

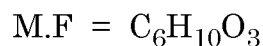
IR = 1745, 1240, 1045, 749 and 697  $\text{cm}^{-1}$



NMR

- a Singlet  $\tau = 2.72 \text{ ppm}$  5H
- b Singlet  $\tau = 7.00 \text{ ppm}$  2H
- c Singlet  $\tau = 6.3 \text{ ppm}$  3H

- (5) Assign the structure from the following data.




IR = 3400–3500  $\text{cm}^{-1}$ , 2990, 2810, 1725,

1025  $\text{cm}^{-1}$

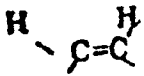
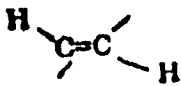
NMR =

- a Triplet  $\delta_{\text{ppm}} = 1.0$  3H
- b Singlet  $\delta_{\text{ppm}} = 2.1$  3H
- c Quartet  $\delta_{\text{ppm}} = 2.5$  2H
- d Singlet  $\delta_{\text{ppm}} = 2.4$  1H
- e Singlet  $\delta_{\text{ppm}} = 3.2$  1H

# NMR-Data : Chemical Shift

Type	Type of Proton	Chemical Shifts in $\delta$ p.p.m.
Primary	$\longrightarrow$ R- $\underline{\text{C}}\text{H}_3$	$\longrightarrow$ 0.9 (1.0)
Secondary	$\longrightarrow$ R <sub>2</sub> - $\underline{\text{C}}\text{H}_2$	$\longrightarrow$ 1.3 (1.5)
Tertiary	$\longrightarrow$ R <sub>2</sub> - $\underline{\text{C}}\text{H}$	$\longrightarrow$ 1.5 (1.8)
Vinylic	$\longrightarrow$ C = C - $\underline{\text{H}}$	$\longrightarrow$ 4.6 - 5.9
Acetylinic	$\longrightarrow$ C $\equiv$ C - $\underline{\text{H}}$	$\longrightarrow$ 2-3
Aromatic	$\longrightarrow$ Ar - $\underline{\text{H}}$	$\longrightarrow$ 7-8
Benzylic	 - C - $\underline{\text{H}}$ $\longrightarrow$ Ar - C - H	$\longrightarrow$ 2.2-3
Allylic	$\longrightarrow$ C = C - $\underline{\text{C}}\text{H}_2$	$\longrightarrow$ 1.7
Flourides	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{F}$	$\longrightarrow$ 4-4.5
Chlorides	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{Cl}$	$\longrightarrow$ 3-4
Bromides	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{Br}$	$\longrightarrow$ 2.5-4
Iodides	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{I}$	$\longrightarrow$ 2-4
Alcohols	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{OH}$	$\longrightarrow$ 3.4-4
Ethers	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{OR}$	$\longrightarrow$ 3.3-4
Esters	R - $\overset{\text{O}}{\parallel}{\text{C}} - \text{OCH}_3 \longrightarrow \text{RCOO} \cdot \underline{\text{C}}\text{H}_3$	$\longrightarrow$ 3.7-4.1
Acids	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{COOH}$	$\longrightarrow$ 2.6-3
Carbonyl compounds	$\longrightarrow$ $\underline{\text{H}}\text{C} - \text{C} = \text{O}$	$\longrightarrow$ 2-2.7
Carboxylic	$\longrightarrow$ R - $\text{COO}\underline{\text{H}}$	$\longrightarrow$ 10-12
Aldehyde	$\longrightarrow$ R - $\underline{\text{C}}\text{HO}$	$\longrightarrow$ 9-10
Hydroxylic	$\longrightarrow$ R - $\underline{\text{O}}\text{H}$	$\longrightarrow$ 1-5.5 (depend on H-bond)
Phenolic	$\longrightarrow$ Ar - $\underline{\text{O}}\text{H}$	$\longrightarrow$ 4-12
Enolic	$\longrightarrow$ C = C - $\underline{\text{O}}\text{H}$	$\longrightarrow$ 15-17
Amino	$\longrightarrow$ R - $\underline{\text{N}}\text{H}_2$	$\longrightarrow$ 1-5
CYN.	$\longrightarrow$ $\underline{\text{C}}\text{H} - \text{CN}$	$\longrightarrow$ 2.7

## Spectral Data

Infra - Red Data		
Alkene (stretching)	-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 <sup>2</sup>	2100-2260(s)
Alkene (Bending)	-C-H	1340(w)
	-C(C <sub>2</sub> H <sub>3</sub> ) <sub>3</sub>	1430-1470(m) & 1380-1385(s)
	-C(CH <sub>2</sub> ) <sub>3</sub>	1365 (s)
Aldehyde	-C-H	2820-2000(w)&2650 2760(s)
Aldehyde	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		
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)
disubstituted Cis.		
disubstituted Trans.		960-970(s)
Aromatic substitution :		
Type C-H out of plane bending		
No. of adjacent H atom.		range cm
5	———— Mono subst. ————>	750(s) & 700(s)
4	ortho " ————>	750 ± 20
3		
2	Meta (two bends) ————>	710 & 750
1	para sub. ————>	820 ± 20