



B.Sc. (Semester – V) Examination, October/November 2018
CHEMISTRY (Paper – III) (6 Units)
Organic Chemistry

Duration : 2 Hours

Max. Marks : 80

Instructions : 1) All questions are **compulsory**.

2) Answers to the two Sections should be written in **separate** answer books.

3) Tables of NMR and CMR values are attached at the end.

SECTION – I

(40 Marks)

I. Answer **any four** of the following questions :

16

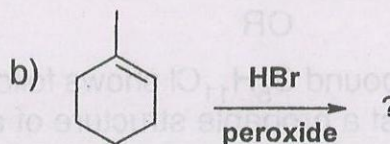
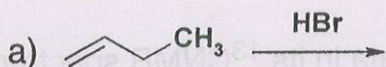
i) Define the following terms :

Molecular ion peak, Anisotropic effect, Deshielded proton, Base peak.

ii) What is Herzog Meyer's method ? How is this method used in the structure elucidation of Nicotine ?

iii) Distinguish between ortho-dichlorobenzene, meta-dichlorobenzene and para-dichlorobenzene by both ^1H NMR and ^{13}C NMR spectroscopy.

iv) Predict the major product for the following and name the product :



v) a) A molecule having molecular formula $\text{C}_3\text{H}_8\text{O}$, shows three signals in its ^1H NMR spectrum and shows in its spectra IR 3600cm^{-1} . Elucidate its correct structure.

b) Explain Isotope effect of ethyl bromide in Mass spectrometry.

vi) Explain α -cleavage fragmentation of acetone.

2. A) i) A compound $\text{C}_3\text{H}_7\text{Cl}$ shows following data in its ^1H NMR spectrum :
Suggest a probable structure of a compound and assign the peaks.
 δ 1.71 (doublet, 6H) and δ 4.38 (multiplet, 1H).

4

ii) Give synthesis of Veratric acid.

2

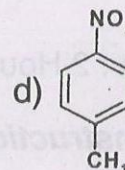
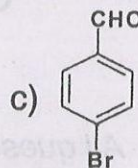
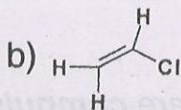
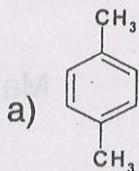
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P.T.O.



- A) iii) Indicate the number of ^1H NMR signals for the following compounds :

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- iv) Explain E2 elimination reaction with the help of an illustration.

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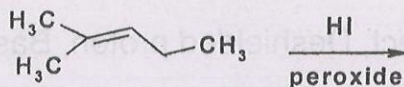
- B) i) A compound $\text{C}_4\text{H}_8\text{Br}_2$ shows following data in its ^1H NMR spectrum. Suggest a probable structure of a compound and assign the peaks :

δ 1.97 (singlet, 6H) and δ 3.84 (singlet, 2H).

4

- ii) Define Anti-Markownikoff's addition rule. Predict the major product for the following :

2



3. A) i) Explain the mechanism and stereochemistry of addition of Br_2 to trans-2-Butene.

4

- ii) Give an evidence to prove presence of active methylene group in tropinone.

2

OR

- A) iii) A compound $\text{C}_5\text{H}_{11}\text{Cl}$ shows following data in its ^{13}C NMR spectrum. Suggest a probable structure of a compound and assign the peaks : δ 22.1 (quartet), δ 22.8 (doublet), δ 41.8 (triplet) and δ 43.2 (triplet).

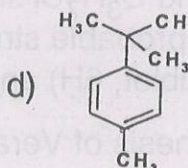
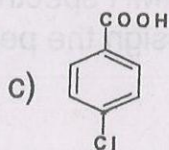
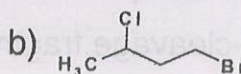
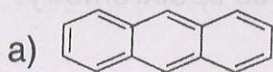
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- iv) Give $\text{S}_{\text{N}}\text{i}$ reaction leading to retention of configuration.

2

- B) i) Indicate the number of ^{13}C NMR signals for the following in its proton decoupled spectrum :

4



- ii) Give synthesis of papaverine from homoveratryl amine and homoveratroyl chloride.

2



SECTION - II

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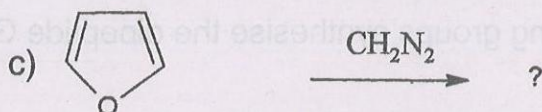
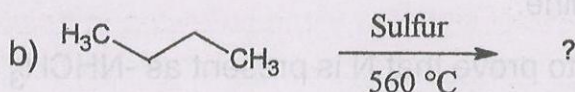
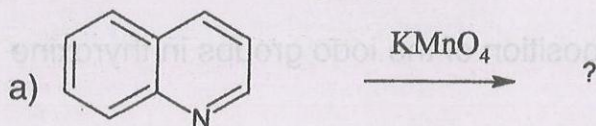
4. Answer **any four** of the following :

16

- Compare the relative reactivity of furan, thiophene and pyrrole towards electrophilic aromatic substitution and arrange them in order of increasing reactivity. Explain your answer.
- Give a synthesis for Thyroxine.
- Write equations for the reaction of phenylalanine with :
 - Acetyl chloride
 - Ethyl bromide
- Using equations, explain Bischler-Napieralski synthesis.
- Write the name and structure of the amino acid obtained when the tripeptide Phenylalanyl Alanyl Glycine is treated with :
 - Edman's reagent
 - Enzyme carboxypeptidase.
- Where does electrophilic substitution occurs in pyridine ? Explain giving all resonance contributing structures.

5. A) i) Complete the following equations :

3



ii) Give analytical evidence to prove Vitamin A contains a β -ionone nucleus.

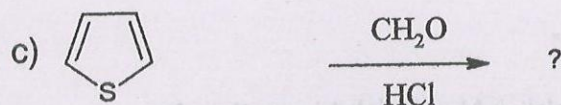
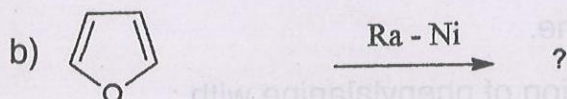
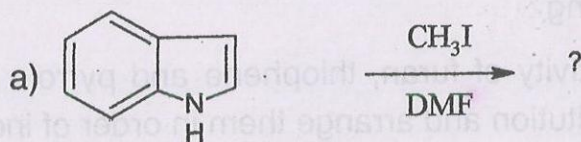
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OR



A) iii) Complete the following equations :

3



iv) Vitamin C is converted to dehydro-Vitamin C and then back to Vitamin C. Explain using representative equations. What inference can be made from this ?

3

B) i) With the help of resonance contributing structures, explain where nucleophilic aromatic substitution occurs in quinoline.

4

ii) Explain the molecular orbital picture of furan.

2

6. A) i) Differentiate between globular and fibrous proteins. Give examples of each.

3

ii) How will you prove the position of the iodo groups in thyroxine ?

3

OR

iii) Write a synthesis for alanine.

3

iv) Give analytical evidence to prove that N is present as $-\text{NHCH}_3$ group at the end of the side chain in adrenaline.

3

B) i) Using protecting and activating groups synthesise the dipeptide Gly-Ala. Explain showing all steps.

4

ii) What are ribonucleotides ? Give the structure of Guano sine - 3' - phosphate

2

TABLE - 1
Approximate Proton Chemical Shifts in NMR

TYPE OF PROTON	CHEMICAL SHIFT, DELTA, PPM (δ)
Cyclopropane	0.2 - 0.8
1° Alkyl, RCH_3	0.8 - 1.0
2° Alkyl, RCH_2R	1.2 - 1.4
3° Alkyl R_3CH	1.4 - 1.7
Alkyl, $\text{R}_2\text{C}=\text{C}-\text{CH}_3$	1.6 - 1.9
$\begin{array}{c} \\ \text{R} \end{array}$	
Benzylic, ArCH_3	2.2 - 2.5
Alkyl chloride RCH_2Cl	3.6 - 3.8
Alkyl bromide, RCH_2Br	3.4 - 3.6
Alkyl iodide, RCH_2I	3.1 - 3.3
Ether, ROCH_2R	3.3 - 3.9
Alcohol, HOCH_2R	3.3 - 4.0
Ketone, RCCH_3	2.1 - 2.6
$\begin{array}{c} \\ \text{O} \end{array}$	
Aldehyde, RCH	9.5 - 9.6
$\begin{array}{c} \\ \text{O} \end{array}$	
Vinyl, $\text{R}_2\text{C}=\text{CH}_2$	4.6 - 5.0
Vinyl $\text{R}_2\text{C}=\text{CH}$	5.2 - 5.7
$\begin{array}{c} \\ \text{R} \end{array}$	
Aromatic, ArH	6.0 - 9.5
Acetylenic, $\text{RC}=\text{CH}$	2.5 - 3.1
Alcohol hydroxyl, ROH	0.5 - 6.0 ^a
Carboxylic, RCOH	10 - 13 ^a
$\begin{array}{c} \\ \text{O} \end{array}$	
Phenolic, ArOH	4.5 - 7.7 ^a
Amino $\text{R}-\text{NH}_2$	1.0 - 5.0 ^a

The chemical shifts of these groups vary in different solvents and with temperature and concentration.

TABLE - 2
Typical¹³ CMR Chemical Shifts and Units

Alkanes	1 - 60
C - O and C - N	30 - 80
$\text{C} \equiv \text{C}$	70 - 95
$\text{C} = \text{C}$	100 - 150
Aromatic C	110 - 135
C = O in acids, ester, amides	150 - 180
C = O in aldehydes and ketones	195 - 250