T.Y. BSc
Sem VI

Subject: Chemistry P III
Organic Chemistry

QP Code : 77213

(17)

(2½ Hours) **[Total Marks : 75**

N.B. : (1) **All** questions are **compulsory.**
(2) **Figures** to the **right** indicate **full** marks.
(3) Use of **log-tables/non-programmable calculators** is permitted.

Answer **any three** of the following :-

(A) An organic compound has molecular formula $C_4H_8O_2$. Determine the index of its hydrogen deficiency and deduce its structural formula from the following spectral data. Also write name of the compound. **5**
IR (cm^{-1}) : 3300-2700 very broad, 1712, 1415, 1220
PMRδ (ppm) : 0.9 (3H)triplet, 1.8 (2H)sextet, 2.3 (2H) triplet, 10.5-11.2 (1H) broad signlet.

(B) An organic compound has molecular formula C_7H_8O. Determine the index of its hydrogen deficiency and deduce its structural formula from the following spectral data. Also write name of the compound. **5**
IR(cm^{-1}) : 3325, 3065, 2875,1470,1018, 736,698
PMRδ (ppm) : 2.5 (1H)broad singlet, 4.6 (2H)singlet, 7.3 (5H) multiplet

(C) (a) Three samples are expected to be of 2-butanol, butanone and ethoxyethane. Explain how you will choose the correct ones using their I.R. spectra. **3**

(b) How will you distinguish between the following pairs of compounds on the basis of the λmax values in their u.v.spectra ? **2**
(i) Butanal and crotonaldehyde
(ii) 1, 3- Pentadiene and 1, 4-pentadiene.

(D) (a) Three samples having molecular formula $C_5H_{11}Cl$ are expected to be isomeric monochloropentanes; viz. 1-chloropentane, 2,-chloropentane and 3-chloropentane. How will you choose the correct ones using their PMR-spectra ? **3**

(b) Why are ethylenic protons more deshielded than expected ? **2**

(E) What are base peak and molecular ion peak ? Explain their significance in mass-spectrometry of organic compounds. **5**

(F) (a) Give the mass-spectrometric fragmentation pattern of 2-methylbutane. **3**

(b) Two nitrogenous organic compounds A & B form molecular ion peaks at m/e 59 and m/e 60 respectively. How will you distinguish between them in terms of the number of nitrogen atoms present, on the basis of the nitrogen rule ? **2**

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2. Answer any three of the following :-

(A) (a) Explain inter-system crossing with the help of a neat and labelled Jablonski diagram.

(b) Explain di-π-methane rearrangement of 1,4-dienes with its mechanism

(B) Explain photochemical conversion of benzophenone to benzpinacol in stepwise manner.

(C) (a) Write the reactions for preparation of following from their monomers and give thier uses

(i) PVA (ii) PET

(b) What is polymerisation ? How are polymers classified on the basis of physical properties ?

(D) (a) Explain free radial mechanism of addition polymerisation of vinyl chloride.

(b) Draw the structure and write uses of following

(i) PAN (ii) Nylon - 66

(E) (a) What are biodegradable polymers? Give two suitable examples with structures.

(b) Explain the following terms with one example

(i) Fillers (ii) Stabilizers

(F) (a) Explain the different stereoisomers of vinyl polymers on the basis of tacticity.

(b) Identify the monomers in the following polymers.

1) $-\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_5-NH-\right]_n$ 2) $-\left[CH_2-\underset{C_6H_5}{\underset{|}{CH}}\right]-$

3. Answer any three of the following :-

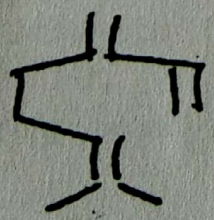
(A) (a) Write the products obtained when citral is treated with the following reagents :

(i) alkaline $KMnO_4$ (ii) aqueous K_2CO_3

(b) What are steroids ? Give the structure of cholesterol.

(B) (a) Give the synthesis of camphor from α-pinene

(b) Write the products of ozonolysis of :



(C) Explain the use of Hofmann exhaustive methylation and degradation in the structural determination of alkaloids with a suitable example. 5

(D) (a) How will you account for the presence of following in nicotine ? 3

(i) Pyridine ring

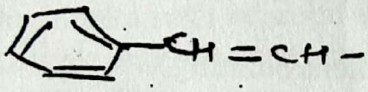
(ii) $\geq N\text{-}CH_3$ group 2

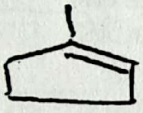
(b) How is methly heptenone converted to citral ? 5

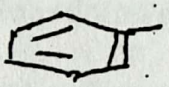
(E) Complete the following reactions :

(i) $O_2N-CH_2-CH_2-COOCH_3 \xrightarrow[250^\circ C]{H_2, Pd} ?$

(ii) $H_3C-C\equiv C-CH_3 \xrightarrow[\text{Catalyst}]{\text{Lindlar}} ?$

(iii)  $\xrightarrow{NaBH_4} ?$

(iv)  $\xrightarrow[ii)\ H_2O_2, NaOH]{i)\ B_2H_6} ?$

(v)  $\xrightarrow{CAN} ?$

(F) (a) Explain the use of selenium dioxide in synthetic organic chemistry with suitable examples. 3

(b) What is Wilkinson's catalyst ? Mention its use in synthesis. 2

Answer **any three** of the following :-

(A) What are α-amino acids ? Explain their configuration with an example. Write the preparation of α-amino acids by 5

(i) Strecker's Synthesis (ii) Amidomalonate synthesis

(B) Explain Merrifield's solid phase synthesis to prepare dipeptides. Write its advantages. 5

(C) Explain the terms nucleotides and nucleosides. Draw one structure of each. Explain the double helix structure of DNA. 5

(D) What are conjugated proteins? Name any two conjugated protiens ? Name any two conjugated proteins. Explain (i) Pleated sheet structure of proteins (ii) Colloidal nature of proteins. 5

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(E) (a) What is the action of the following on n-butyl lithium.
(i) HCHO (ii) CO_2 (iii) CH_3OH

(b) What is Reformatsky reaction ? Give an example.

(F) (a) Using a suitable Grignard reagent give the preparation of :
(i) 2-phenylethanol (ii) I-methylcyclohexanol

(b) Give the preparation of lithium dialkyl cuprate.

5. (A) Fill in the blanks with appropriate choice.

(a) _____ transitions produce weak absorption bands at higher wavelengths.
($\sigma \rightarrow \sigma^*/n \rightarrow \sigma^*/\pi \rightarrow \pi^*/n \rightarrow \pi^*$)

(b) Unsymmetrical in-plane bending vibrations are called _____ vibrations.
(rocking / scissoring / wagging / twisting)

(c) Presence of electron withdrawing groups brings about _____ of neighbouring protons.
(Shielding/deshielding/upliftment/bonding)

(d) The highest peak in a mass spectrum is called _____ peak.
(base/lofty/sharp/towering)

OR

(A) State true or false.

(p) Quartz sample cells are used for u.v.spectroscopy.

(q) For non-linear polyatomic molecules, the number of possible modes of vibration = 3n - 5

(r) Shift of a proton from one position to another is called chemical shift in NMR spectroscopy.

(s) In mass spectrometry of organic compounds; for fragment ions normally m/e = m

(B) Fill in the blanks iwth appropriate option :-

(a) Cis neoprene rubber is obtained by polymerisation of 2-Chloro-1,3 butadiene in presence of _____
(i) Peroxide (ii) Ziegler-Natta Catalyst
(iii) Benzoylchloride (iv) Grubb's Catalyst

(b) The substances which are added to a polymer to reduce its brittlenes and to increase its flexibility are called _____.
(i) fillers (ii) stabilizers
(iii) plasticizers (iv) Elastomers

(c) By free radical polymerisation of tetrafluoroethene in presence of peroxide, polymer obtained is _____.
(i) PVC (ii) teflon
(iii) PVA (iv) PAN

(d) _____ have high tensile strength.
(p) Thermoplastics (q) Resins
(r) Fibers (s) Elastomers

OR

(B) State whether the following are true or false. 4
(p) When free radical polymerisation of isoprene is carried out in presence of a peroxide, trans polyisoprene is obtained.
(q) Urethanes are esters of carbamic acid.
(r) Bakelite is an epoxy resin.
(s) Dibutyl phthalate is used as stabilizer for polymers. 4

(C) Fill in the blanks iwth appropriate option :-
(a) Rosenmund reduction makes use of _____ catalyst
(i) Ruthenium (ii) Rhodium
(iii) Palladium

(b) _____ is a fat soluble vitamin
(i) Ascorbic acid (ii) Tocopherol
(iii) Riboflavin

(c) Citral contains _____ isoprene unit/s
(i) One (ii) Two
(iii) Three

(d) In nicotine, the pyridine ring is attached to a _____ ring.
(i) Pyrollidine (ii) Pyrrole
(iii) Pyrazine

OR 4

(C) Fill in the blanks iwth appropriate option :-
(p) Metachloroperbenzoic acid is used for _____ of alkenes.
(i) epoxidation (ii) hydroxyation
(iii) Chlorination

(q) A molecule of thyroxine contains _____ iodine atoms
(i) two (ii) three
(iii) four

(iii) Geraniol is obtained as product of _____ of citral
(p) oxidation (q) reduction
(r) ozonolysis

(iv) Atropine is a _____ alkaloid
(p) Belladona (q) Cinchona
(r) Opium

6 (22)

(D) Match the following :

Column I	Column II
(a) Cytosine	Basic amino acid
(b) Adenine	Pyrimidine base
(c) Alanine	Purine base
	Neutral amino acid
	Acidic amino acid

OR

(D) State true or false

(p) Lead acetate is an organometallic compound.

(q) Haemoglobin is a conjugated protein.

(r) RNA contains uracil.
