CSM – 17/21

Chemistry

Paper – II

Time : 3 hours

Full Marks : 300

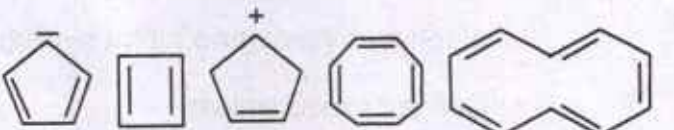
The figures in the right-hand margin indicate marks.

Candidates should attempt Q. No. 1 from Section – A and Q. No. 5 from Section – B which are compulsory and any ***three*** *of the remaining questions, selecting at least* ***one*** *from each Section.*

SECTION – A

1. Answer any **three** questions of the following :

   (a) (i) Classify the following examples into aromatic, anti-aromatic and non-aromatic. Justify your answer. 10



(a) (b) (c) (d) (e)

(ii) Predict the aromaticity of kekulene and fulvenes. 10

(b) (i) Define primary and 3D structure of protein. 10

(ii) Write the name of polymer that is formed by the reaction of adipic acid and hexamethylenediamine. Explain the reaction mechanism of the same. 10

(c) (i) Name the reaction in which alkene is synthesized from carbonyl compound. Explain its mechanism. 10

(ii) Write down the name reaction in which products are formed by the reaction of aldehydes having no alpha hydrogen. Define its mechanism. 10

(d) (i) The following data was obtained in the

determination of average molecular weight of a polymer : 10

Molecular weight	Weight (g)
80,000	1.0
50,000	3.0
30,000	5.0
10,000	6.0

Calculate :

(A) Number average molecular weight

(B) Weight average molecular weight

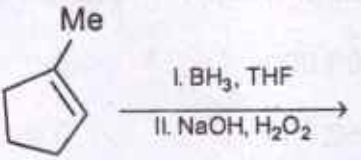
(C) Polydispersity index of the polymer

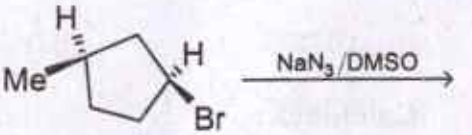
(ii) Briefly describe Membrane osmometry method for the determination of number average molecular weight. 10

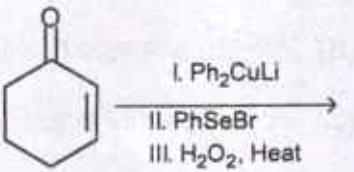
2. Answer any **three** questions as directed :

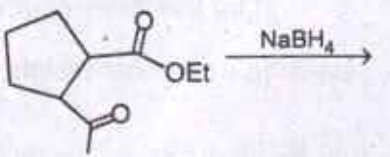
(a) Indicate the products formed in the following reactions. Give the mechanism in each case

and draw the appropriate stereochemistry if desired : 5×4 = 20

(i) 

(ii) 

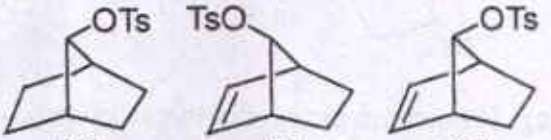
(iii) 

(iv) 

(b) Answer the following questions : 5×4 = 20

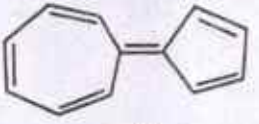
(i) Among the norbornane derivatives the

acetolysis of (C) is 10^{11} times faster than (A). While the acetolysis of (B) isomer is only 10^4 times faster than (A). Explain.



(A) (B) (C)

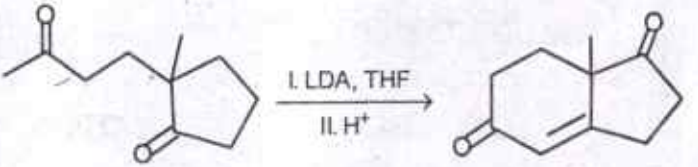
(ii) The value of the barrier of rotation for the marked bond in A is only 14 kcal/mole. What could be the reason for this low barrier of rotation in this molecule ?



A

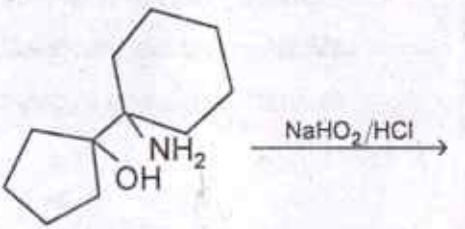
(iii) Addition of triplet carbene to cis-2-butene leads to a cis and trans products, whereas a singlet carbene gives only a cis product. Give mechanistic explanation.

(iv) Comment on the selectivity shown in the following reaction :

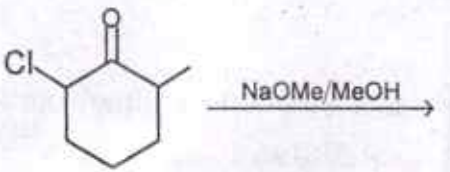


(c) Predict the product of the following reactions and outline the mechanism involved in their transformation : 5×4 = 20

(i)



(ii)



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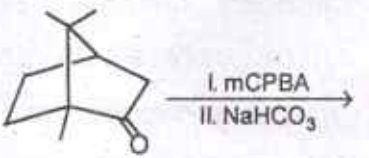
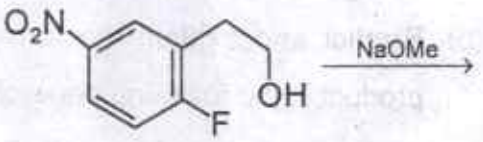


(iv) 

(d) What do you know of electronic transition as applied to :

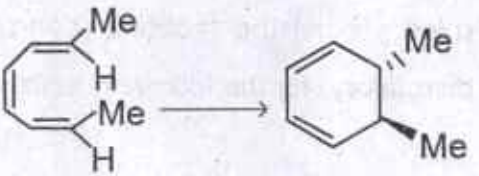
(i) Fluorescence and Phosphorescence 10

(ii) Charge-transfer complexes 5

(iii) Which solvents are generally used in U. V.-visible spectroscopy and why ? 5

3. Attempt any **two** questions as directed :

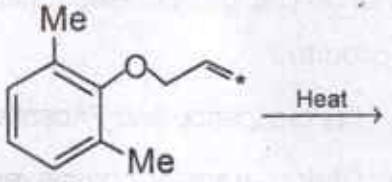
(a) (i) Using Frontier orbital approach, predict whether the following transformation is thermally or photochemically allowed : 10

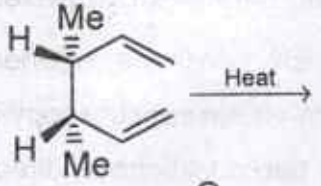


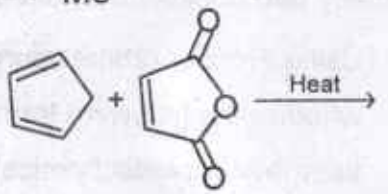
(ii) How are the natural products formed by Witting reactions ? Show the synthesis of vinyl halides and ethers by the reactions. 20

(b) Predict and explain the formation of the product in the following pericyclic reactions :

10×3 = 30

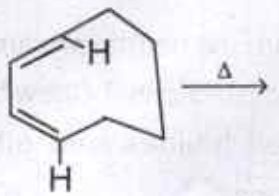
(i) 

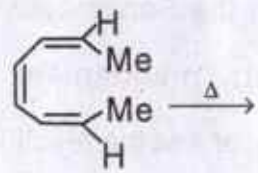
(ii) 

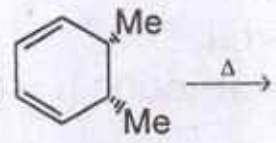
(iii) 

(c) By means of Woodward-Hoffmann selection rules predict the motions (conrotatory or disrotatory) for the following reactions :

10×3 = 30

(i) 

(ii) 

(iii) 

4. Answer any **three** questions as directed :

(a) (i) What are salient features of Aldol condensation ? 5

(ii) Explain cross-Aldol condensation between two different carbonyl compounds. 5

(iii) Give the product of the following reactions : 10

I. $CH_3 - CHO + CH_3 - CO - CH_3 \xrightleftharpoons{OH^-}$

II. $CH_3 - CHO + CH_3 - CHO \xrightleftharpoons{OH^-}$

(b) (i) Explain the Sandmeyer reaction and give its mechanism. Write the applications of the reaction. 10

(ii) Give the mechanism of the followings : 10

I. $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-COOC_2H_5 + (C_6H_5)_3C^- \rightleftharpoons CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}-COOC_2H_5 + (C_6H_5)_3CH$

II. $C_6H_5COOC_2H_5 + CH_3COOC_2H_5 \xrightarrow[2.\ H^{\oplus}]{1.\ C_2H_5ONa} C_6H_5COCH_2COOC_2H_5 + C_2H_5OH$

(c) (i) Give the reaction and product of the following : 10

When reduction of aliphatic and mixed aliphatic-aromatic carbonyl compounds takes place and when reduction of keto-acids takes place.

(ii) Show the reaction and mechanism of Dieckmann reaction. 10

(d) (i) Name the following reaction and give the whole reaction and mechanism : 10
The condensation of aldehydes and ketones with compounds having active methylene group in presence of basic catalyst and form α, β-unsaturated compounds.

(ii) Perkin reaction has many useful synthetic applications. Explain any four reactions. 10

(e) (i) Explain the Reimer-Tiemann Reaction, its mechanism and reaction conditions. 10

(ii) Show the mechanism and applications of Reformatsky reaction. 10

SECTION – B

5. Answer any **three** questions of the following :

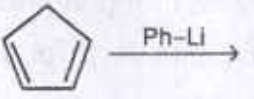
(a) (i) Which of the following annulenesis are aromatic ? Justify your answer. 10

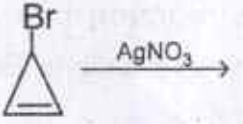
(A) 8-Annulene

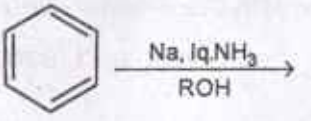
(B) 10-Annulene

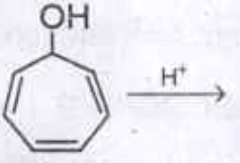
(C) 12-Annulene

(ii) Give the products of the following reactions and explain their aromaticity : 10

(i) 

(ii) 

(iii) 

(iv) 

(b) (i) Which method is generally used to prepare silicone and silicates ? Explain its mechanism and applications. 10

(ii) Which catalyst is used to synthesize syndiotactic polypropylene ? Describe its mechanism and applications. 10

(c) Explain the following reaction and give two applications : 20

(i) Skraup synthesis

(ii) Von Richter reactions

(d) (i) Define isoelectric point of amino acid. Draw the Zwitter ions form of the following amino acids : 10

(A) Valine

(B) Phenylalanine

(C) Glutamine

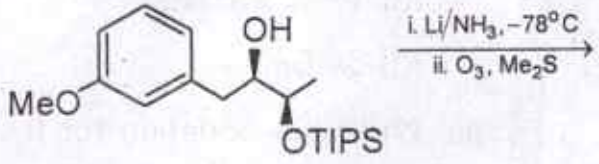
(ii) Write the equation for the trans-amination reaction between alanine and oxaloacetate. Name the products that are formed. 10

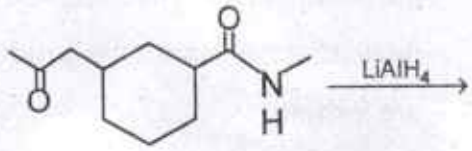
(e) (i) Give an account of end group analysis method used for determination of

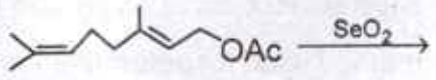
molecular weight of polymer. Calculate molecular weight of polypropylene whose DP value is 2000. 10

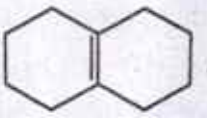
(ii) Explain how thermal transitions in polymers are measured by using DSC technique. How does hydrogen bonding effects Tg and Tm of polymers ? Among Nylon 66 and Kevlar fibers, which is more crystalline and why ? 10

6. Answer any **six** questions of the following : 10×6 = 60

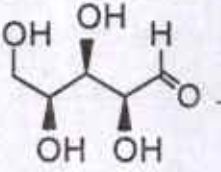
(a) 

(b) 

(c) 

(d) 

(e) 

(f) 

(g) How N-bromosuccinamide is prepared ? Show its reaction conditions. How it is used as a brominating and oxidizing agent ? Show the degradation of amino acids with N-bromosuccinamide.

7. Attempt any **three** of the following :

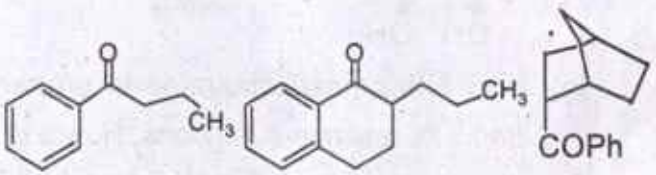
(a) (i) The UV spectrum of propanone shows two absorption maxima at 190 (ε = 1100) and 279 (ε = 15) nm, explain which among them is due to n-π^* transition. 5

(ii) Define the terms : Zero field splitting and Kramers degeneracy in ESR. 5

(iii) Write a mechanism for the formation of cyclobutane from the photolysis of cyclopentanone. 10

(b) (i) Differentiate between the photochemical and thermal reactions. 5

(ii) Arrange these compounds in increasing order for the ease of Norrish type-II reaction with the explanation. 8



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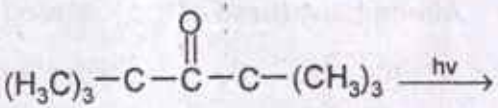
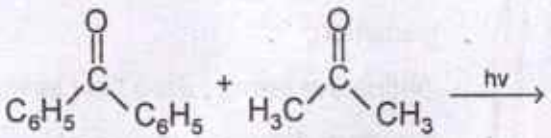
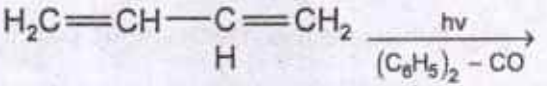
(iii) Complete the following photochemical reaction : 7



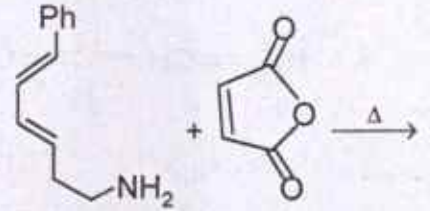
(c) (i) Predict the product of the following reaction : 5

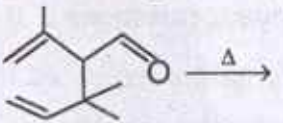


(ii) Suggest a mechanism for the following reaction : 5

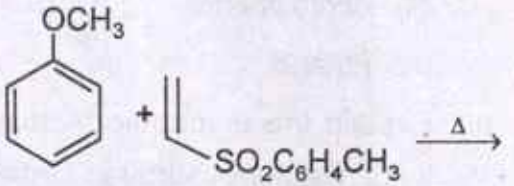


(iii) Predict the outcomes in the following reactions : 10

I. 

II. 

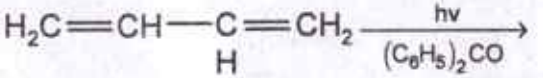
(d) (i) Identify the type of reaction and predict the product/s in the following reaction : 6

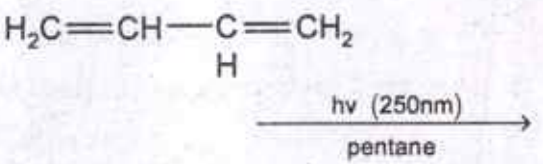


(ii) Write the mechanism for the following type of reactions : Norrish type-1,

Norrish type-II and Paterno Buchi reaction. 6

(iii) What are the mechanistic paths in the following reactions : 8

I. 

II. 

8. Answer any **six** questions of the following :

(a) (i) Write the expected I. R. peaks for the following compounds : 1×5 = 5

(I) p-nitrophenol

(II) Acetic anhydride

(III) Aceto phenol

(IV) Ethanol

(ii) Explain the electronic factors which influence the absorption frequency of I. R. spectra. 5

(b) (i) Write detailed note on spin-spin coupling in N. M. R. spectroscopy. 5

(ii) What is meant by term chemical shift in N. M. R ? Name the varoius factors on which the value of chemical shift depend and discuss one in detail. 5

(c) (i) What do you understand by term "double resonance" in N. M. R. ? How it is helpful in simplifying the spectra ? 5

(ii) Which of the following atoms do not exhibit N. M. R. peaks : 5

^{12}C, ^{16}O, ^{14}N, ^{15}N, ^{2}H, ^{19}F, ^{13}C, ^{31}P

How many kinds of ^{1}Hs are there in :

$CH_3 - CH_2 - CH_3$, $CH_2 = CH_2$, $CH_3 - CH = CH_2$, $C_6H_5 - CH_3$

(d) (i) Write notes of the following for N.M.R. : 5

Nuclear over-hauser effect

Deuterium exchange reactions

(ii) How many N.M.R. signals are expected in each of the following compounds ? 5

Propane, isobutene, ethanol, cyclobutane, ethyl methyl ether, butanol, caprolactum, glycol, α-alanine.

(e) (i) What are important features of the mass spectra of Hydrocarbons ? Give examples. 5

(ii) Discuss nitrogen rule in mass spectrometry. 5

(f) (i) What are general fragmentation modes in mass spectrometry ? Explain all. 5

(ii) Describe the fragmentation of 2-pentene and benzene mass spectra. 5

(g) (i) Show the graph of mass spectrum of 1-butanol and 2-butanol. Explain the fragmentation modes also. 5

(ii) Determine the structure of the compound whose m/e values in the mass spectrum are 100, 85, 75, 57, 43 (base), 41, 29 and 27. 5

(h) (i) Write notes on following mass spectra : Meta stable peaks, molecular ion peak and relative abundance of the parent and fragmentations. 5

(ii) Define following in UV spectra- Bathochromic effect, Hypsochromic effect, Hyperchromic effect, Hypochromic effect, K-band, B-band, R-band, E-band. 5