

(8 pages)

MAY 2016

P/ID 40127/PCHG

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Time : Three hours

Maximum : 100 marks

PART A — (10 × 2 = 20 marks)

Answer ALL questions.

1. What is the connection between axial halo ketone rule and octant rule?
2. Compare the chemical shifts of hydrogen's in the following compounds :  $CH_3OCH_3$ ,  $(CH_3)_3N$ ,  $(CH_3)_4C$ .
3. A compound with molecular formula  $C_9H_9Br_3$  exhibits only one proton NMR signal. What is this compound.
4. Indicate the position at which azulene undergoes electrophilic substitution. Explain why?
5. Account for the tub shape of cyclo octatetraene.
6. [18]- Annulene exhibits two proton NMR signals. Why?
7. Compare the inter system crossing efficiency of benzophenone and 1,3- butadiene.

8. Cyclohexene is a hydrogen donor in photochemical reduction reactions. Explain.
9. Indicate how 2,4,5 - trialkylimidazole can be prepared.
10. Suggest a method of synthesising 2-methyl-4-phenyloxazole.

PART B — (4 × 20 = 80 marks)

Answer ALL questions.

11. (a) (i) Explain how  $^{13}\text{C}$  NMR spectrum can be used to distinguish ortho, meta and para - dibromobenzenes.  
  
(ii) The molecular ion peak of compound *X* and the (M+2) ion peak of this compound are equally intense. The  $^1\text{H}$  NMR spectrum of *X* has two signals, both are singlets, at  $7.5\ \delta(5\text{H})$  and  $4.5\ \delta(2\text{H})$ . IR spectrum of *X* has bands at  $690$  and  $770\ \text{cm}^{-1}$ .

X reacts with sodium cyanide to give Y, Y has a sharp band at  $2215\text{ cm}^{-1}$  in its IR spectrum and the  $^1\text{H}$  NMR spectrum again has only two singlets ( $7.3\delta, 5\text{H}; 3.7\delta, 2\text{H}$ ).

Lithium aluminum hydride reduction of Y gives Z, whose  $^1\text{H}$  NMR spectral features are listed below:

$7.3\delta$ , multiplet, 5H;  $2.9\delta$ , triplet, 2H;  $2.6\delta$ , triplet, 2H;  $1.1\delta$ , singlet, 2H  
Identify X, Y and Z.

Answer the following questions regarding X, Y and Z.

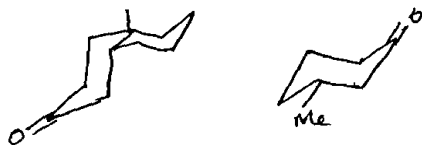
- (1) How many signals can you get in the  $^{13}\text{C}$  NMR spectrum of Y?
- (2) At What  $\frac{m}{2}$  values, the molecular ion and  $(m+2)$  ion peaks will appear in the mass spectrum of X?
- (3) What prominent peaks can you expect in the IR spectrum of Z? (5 + 15)

Or

- (b) (i) Explain why the  $\lambda_{\text{max}}$  predicted by Woodward Fieser rules are solvent dependent for enones? Comment on solvent correction procedure while calculating the  $\lambda_{\text{max}}$  for enones.

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- (ii) What is Karplus equation? Explain its use with illustrations.
- (iii) Predict the sign of the cotton effect curves for the following compounds.



- (iv) Indicate how IR spectroscopy is useful in “carbonyl” chemistry. (5 + 5 + 4 + 6)

12. (a) (i) Comment on the aromaticity or otherwise of cyclopentadiene, cyclopentadienyl cation and cyclopentadienyl anion.
- (ii) 1,3,5 - Cycloheptatriene reacts with one mole of bromine at 0°C in  $CCl_4$  to give a 1,6 - addition product. What is this compound? This dibromo compound on heating readily loses HBr giving  $C_7H_7Br$ .  $C_7H_7Br$  is not soluble in non polar solvents, but soluble in water. Why?

When treated with silver nitrate,  $C_7H_7Br$  gives a dense precipitate. Account for this reaction.

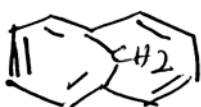
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[P.T.O.]

- (iii) What are nonbenzenoid aromatic compounds? Give examples.
- (iv) What are pyrenes? Are they aromatic? Explain.
- (v) Heptalene adds to bromine, and reacts with acid. The molecule is not planar. Account for these observations.  
(6 + 6 + 3 + 2 + 3)

Or

- (b) (i) Most of [10]-annulenes are not aromatic. But the following compound is aromatic. Explain.

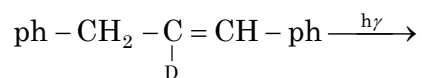


- (ii) 16-Annulenes readily take up two electrons to form anion. Explain.
- (iii) With adequate examples, illustrate the use of Huckel's rule to explain aromaticity. Explain how "ring current effect" concept provides a more suitable definition for aromaticity.
- (iv) Comment on the bond length, stability and ease of generation associated with cyclo butadiene.
- (v) Compare the aromaticity of pyrrole, pyridine and benzene. (3 + 3 + 6 + 4 + 4)

13. (a) (i) What is the photolysis product of 2-propanone in propan-2-ol? What is the intermediate radical formed in this reaction?
- (ii) What is orbital correlation diagram? Explain the steps involved in constructing this diagram. Illustrate how the diagram is helpful in explaining the pericyclic processes, whether they are thermally allowed or not.
- (iii) Show that bullvalene has a three fold axis of symmetry. Describe the fluxional behaviour associated with bullvalene.
- (iv) Chair like transition states are proposed to account for the stereo chemical outcome during cope rearrangement. Illustrate this point with a specific example. (3 + 7 + 5 + 5)

Or

- (b) (i) Write the product in the following reaction. How does the nature of the product formed help to explain the mechanism of di- $\pi$ -methane rearrangement?



- (ii) Describe the scope, mechanism and limitation of paterno Buchi reaction. Explain the synthetic uses of this reaction.

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- (iii) Claisen rearrangement is a [3,3]-sigmatropic migration process. Can a para - Claisen rearrangement be described to involve [3,5]-sigmatropic migration? Explain your answer.
- (iv) Discuss the conditions under which Norrish Type I and Norrish Type II reactions take place. List out the secondary processes occurring in this type of reactions. (5 + 6 + 4 + 5)

14. (a) (i) What happens when  $\alpha$  - acylamido Ketones are treated with phosphorous pentoxide?
- (ii) Discuss the general methods of preparing flavones and iso flavones.
- (iii) Ethyl isothiurea reacts with sodium salt of formyl acetic ester to give a compound A. A reacts with phosphorous oxychloride to yield B. B, on treatment with ammonia gives C. C on HBr treatment yields D. Identify A to D.
- (iv) Indicate how estrone can be converted to testosterone. (2 + 10 + 4 + 4)

Or

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- (b) (i) What are anthocyanins? How can they be prepared?
- (ii) Indicate any one method of synthesising vitamin A.
- (iii) Discuss the role of Blanc's rule and Barbier Wieland degradation in establishing the structure of cholesterol.

(4 + 8 + 8)

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