

**CHEMISTRY****Paper II**

*Time Allowed : Three Hours*

*Maximum Marks : 200*

**QUESTION PAPER SPECIFIC INSTRUCTIONS**

**Please read each of the following instructions carefully before attempting questions.**

There are **EIGHT** questions in all, out of which **FIVE** are to be attempted.

Question Nos. **1** and **5** are compulsory. Out of the remaining **SIX** questions, **THREE** are to be attempted selecting at least **ONE** question from each of the two **Sections A** and **B**.

Attempts of questions shall be counted in sequential order. Unless struck off, attempt of a question shall be counted even if attempted partly. Any page or portion of the page left blank in the Question-cum-Answer Booklet must be clearly struck off.

All questions carry equal marks. The number of marks carried by a question/part is indicated against it.

Answers must be written in **ENGLISH** only.

Unless otherwise mentioned, symbols and notations have their usual standard meanings.

Assume suitable data, if necessary and indicate the same clearly.

Neat sketches may be drawn, wherever required.

## SECTION 'A'

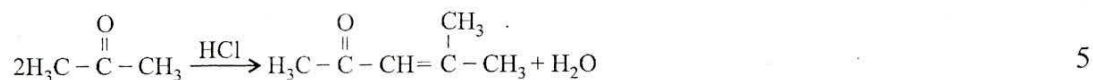
1. Answer the following : 5×8=40

1.(a) Name a sandwich compound which is aromatic in character. Draw its structure. 5

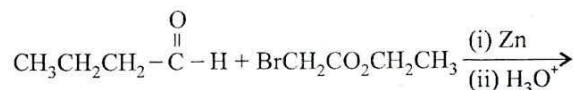
1.(b) What are sydnones ? Draw a representative structure. 5

1.(c) With a suitable example show 'Norrish Type-II' cleavage reaction. 5

1.(d) Show the mechanism for the following reaction :

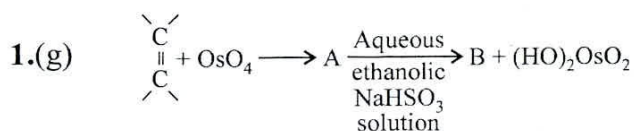


1.(e) Mention the product in the given reaction :



Also provide mechanism of the above reaction. 5

1.(f) How 2,3-dimethyl-2,3-butanediol can be converted to 3,3-dimethyl-2-butanone ? Suggest the mechanism of the involved reaction. 5



Identify A and B. 5

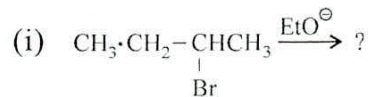
1.(h) Explain why di-t-butoxycarbene is unreactive. 5

2.(a) (i) The rate of hydrolysis of  $(\text{CH}_3)_3\text{CBr}$  in 50% aqueous methanol is thousand times faster than that in pure methanol – explain. 5

(ii) Mention the product(s) in the following reaction. Elucidate your answer.

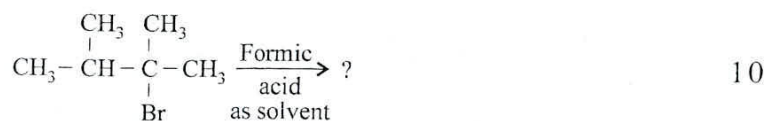


2.(b) Write down the names and the structures of the predominant products for the following elimination reactions :

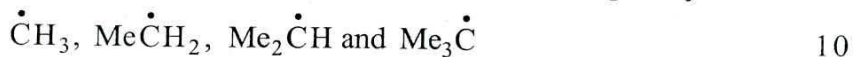


- 2.(c) (i) Give the mechanistic steps for the synthesis of aniline from benzamide. 5  
 (ii) Why does  $\text{LiAlH}_4$  usually fail to reduce a C – C multiple bond? Why does such a bond in conjugation with an aromatic system on one side and a carbonyl group on the other side get reduced by  $\text{LiAlH}_4$ ? 5

2.(d) Give the mechanistic steps and mark the major product of the following reaction :



3.(a) Write down the stability order of the following alkyl radicals. Explain your answer.



3.(b) Which of the following is(are) aromatic?

- (i) Cyclopropenyl cation
- (ii) Cyclopropenyl anion
- (iii) Cyclopropenyl free radical

Justify your answer.

10

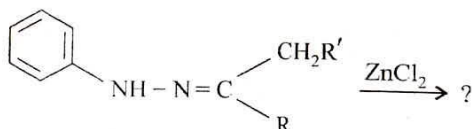
3.(c) Account for the observed dipole moment and aromaticity in azulene. 10

3.(d) Cis-2-butene + Singlet carbene  $\longrightarrow$  ?

Cis-2-butene + Triplet carbene  $\longrightarrow$  ?

Mention the product(s) in each of the above cases. Substantiate your answer. 10

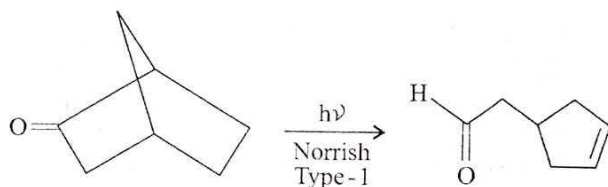
4.(a) Mention the product(s) in the following reaction. Suggest the mechanism of this reaction. What is the popular name of this reaction?

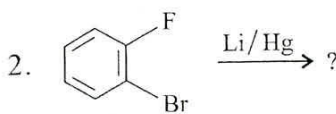


[R', R = alkyl, aryl or hydrogen]

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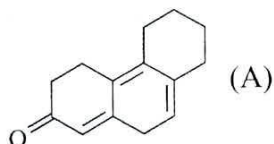
4.(b) Write down the mechanism of the following reaction :



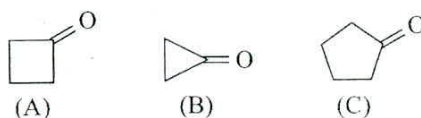
- 4.(c) (i) Between [14] Annulene and [16] Annulene – which one is aromatic and why? 5
- (ii) Write the structure of the product formed in the following reactions :
1.  $\text{H}-\ddot{\text{N}}+\text{CH}_2 \xrightarrow{\text{CH}_2} ?$
  2.  5
- 4.(d) With a suitable free-energy profile diagram illustrate and explain what is meant by 'thermodynamically controlled product' and 'kinetically controlled product'. 10

### SECTION 'B'

5. Attempt the following :
- 5.(a) Illustrate 'McLafferty Rearrangement' with a suitable example. 5
- 5.(b) Calculate  $\lambda_{\text{max}}$  of the given compound (A) by the use of Woodward-Fieser rule. 5



- 5.(c) Write the names and draw the structures of two purins and three pyrimidines that occur in RNA and/or DNA. 5
- 5.(d) Which of the following will show a microwave rotational spectrum and why?  $\text{H}_2$ ,  $\text{HCl}$ ,  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and  $\text{CH}_3\text{Cl}$  5
- 5.(e) The rotational spectrum of  $\text{CO}$  shows a series of lines placed  $3.84235 \text{ cm}^{-1}$  apart. Calculate the moment of inertia of  $\text{C}=\text{O}$  bond. [ $h = 6.626 \times 10^{-27} \text{ erg sec.}$ ] 5
- 5.(f) Show all the possible fundamental modes of vibration of  $\text{CO}_2$  molecule. 5
- 5.(g) Explain the E.S.R. spectrum of the methyl radical. 5
- 5.(h) In  $^1\text{H}$  NMR spectrum of a compound at 200 MHz, a signal at 1058 Hz was observed. Calculate the chemical shift ( $\delta$ ) for this proton. 5
- 6.(a) (i) Arrange  $\nu_{\text{max}}$  ( $\text{C}=\text{O}$ ) of the given compounds in decreasing order and give suitable explanation of your answer. 5



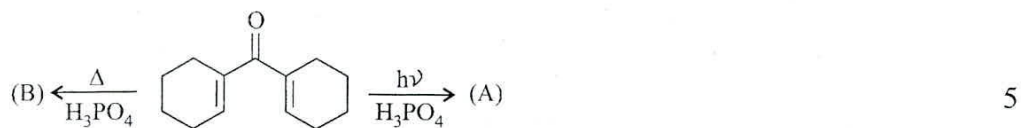
- (ii) What are silicones? Mention some of its uses. 5
- 6.(b) What is cross-linking in the context of polymers? Suggest one method for obtaining polyvinyl alcohol. 10

6.(c) What is a peptide bond? What is the difference between a peptide, oligopeptide and protein? 10

6.(d) (i) What is borazine? Why is it called 'Inorganic benzene'? 5

(ii) What is Zeigler-Natta catalysis? What is the active form of this catalyst? 5

7.(a) (i) Give stereochemistry of the product of the given reaction:



(ii) Complete the following reaction:



7.(b) (i) 'In electronic spectra a bathochromic shift is often associated with increasing conjugation' — Explain. 5

(ii) Aniline on treatment with sodium nitrite and HCl in cold generates a product (X) which on treatment with  $\beta$ -naphthol gives (Y). Provide the structures of X and Y. Name the concerned reaction. 5

7.(c) Write a short note on 'Crossover Experiment' with special emphasis on the elucidation of reaction mechanism. 10

7.(d) Predict the reaction between ethene and allyl cation in the light of Woodward-Hoffmann rules. 10

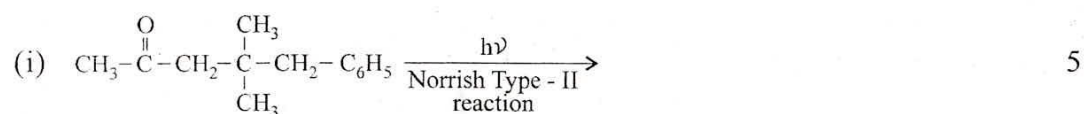
8.(a) Write a short note on 'Determination of molecular weight by viscosity measurements'. 10

8.(b) Starting from benzene, how will you prepare the following employing Friedel-Crafts reaction?

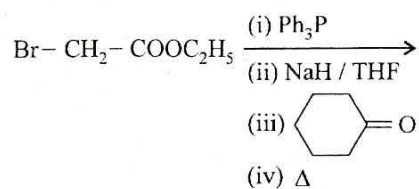
(i) 4-oxo-4-phenylbutanoic acid.

(ii) Isobutyl benzene. 10

8.(c) Complete the given reactions and give its mechanism:

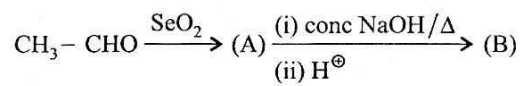


8.(d) (i) Complete the given reaction and give its mechanism :



5

(ii) Complete the following reaction sequence and give mechanism for the formation of (B) into (C) :



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