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.*

*Questions no. **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.

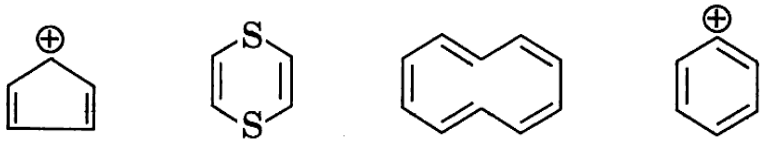
Assume suitable data, if necessary, and indicate the same clearly.

Neat sketches may be drawn, wherever required.

SECTION A

Q1. Answer the following : ***5×8=40***

(a) Classify the following compounds as aromatic, antiaromatic and non-aromatic. Explain your answer. *5*

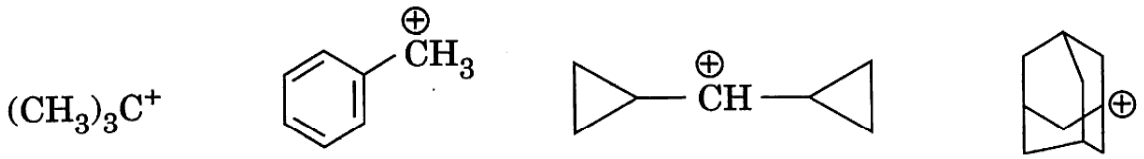


A B C D

(b) Discuss the role of crossover experiments in determining the reaction mechanism. *5*

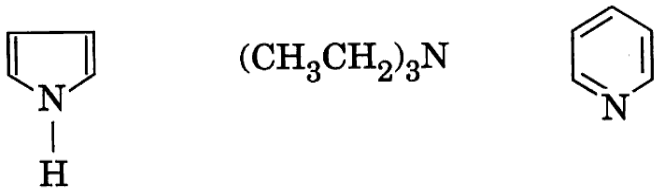
(c) Quinuclidine reacts much faster with ethyl iodide than triethyl amine in S_N2 reaction. Explain. 5

(d) Arrange the following carbocations in decreasing order of their stability. Give reason in support of your answer. 5



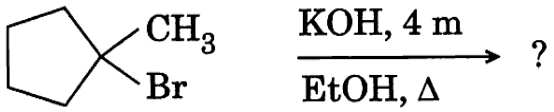
A B C D

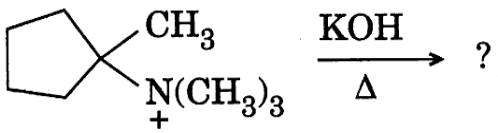
(e) Arrange the following in decreasing order of basicity. Give explanation to justify your answer. 5



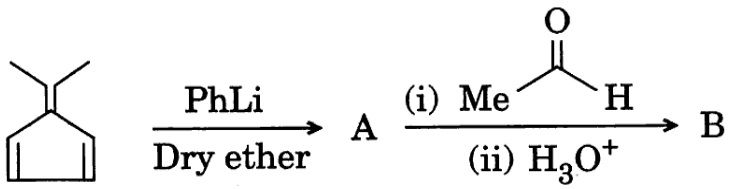
A B C

(f) Write the products formed in the following reactions : 5

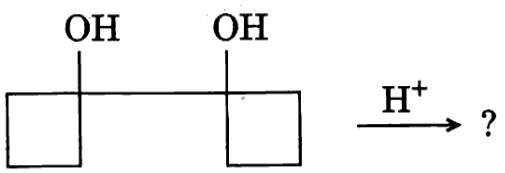
(i) 

(ii) 

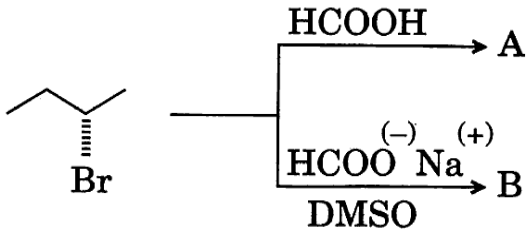
(g) Write the products formed in the following reaction sequence : 5



(h) Write the product and mechanism of the reaction : 5

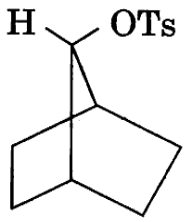


Q2. (a) (i) Write the outcome of the reaction and predict the reaction to S_N1 or S_N2 in each case. *5*



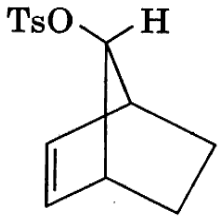
(ii) Show the products of the following reactions : *5*

(I)



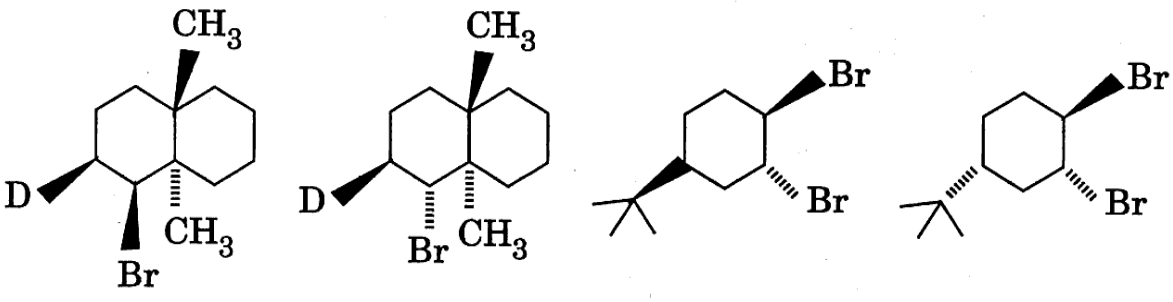
$OAc^{(-)}$ → ?

(II)



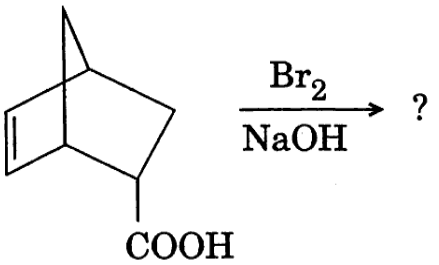
$OAc^{(-)}$ → ?

(b) On attempted E_2 reaction, A reacted much faster than B, while C reacted much faster than D. Explain with writing the product of the reaction in each case. *10*

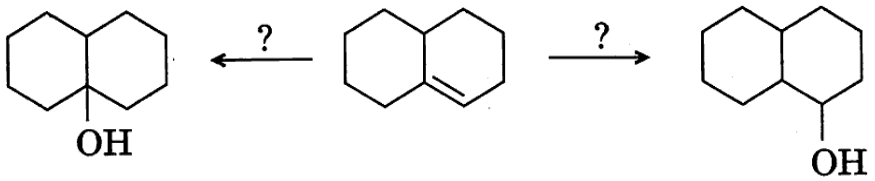


A B C D

(c) (i) What product can one expect from the following reaction ? Depict the stereochemical outcome at every step. 5

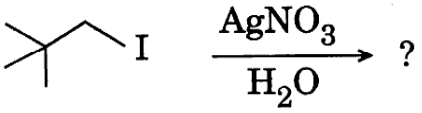


(ii) What reagents are needed to bring the transformation ? 5



(d) Write a short note on aromatic character of sydnones. 10

Q3. (a) Write the structure of the product formed. 10

(i) 
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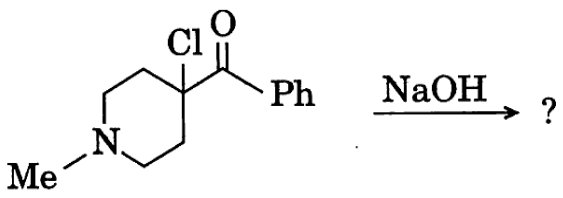
(ii) 
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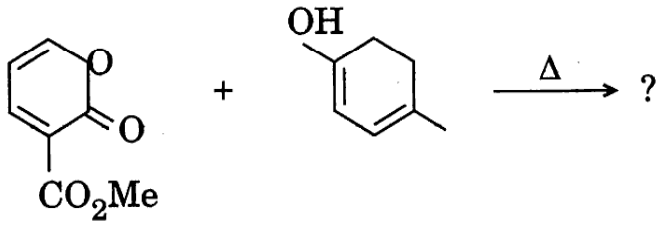
(b) Complete the following pericyclic reactions : 10

(i) 
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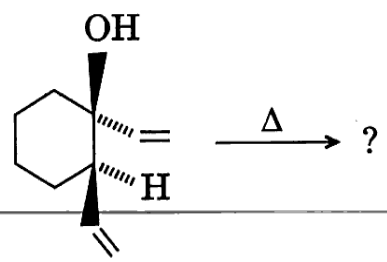
(ii) 
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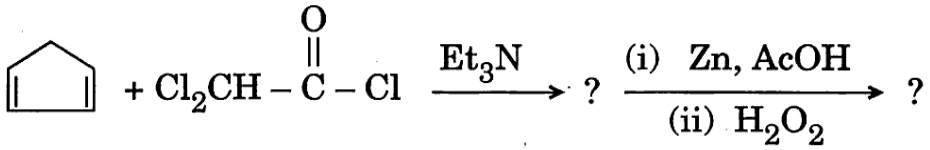
(c) (i) Explain correlation diagrams for electrocyclic interconversion of 1,3-butadiene and cyclobutene. *5*

(ii) One of the cyclobutenes on heating reacts very fast while the other reacts at extremely slow rate. Explain. *5*

A B

(d) Write the products in the following reactions : *10*

(i) 

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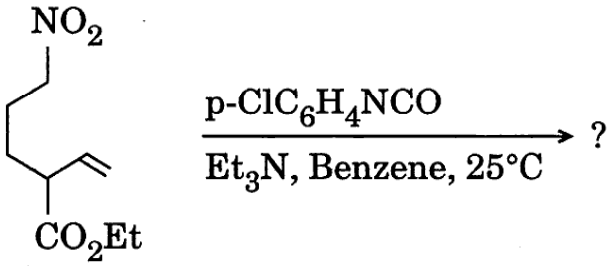
(ii) 

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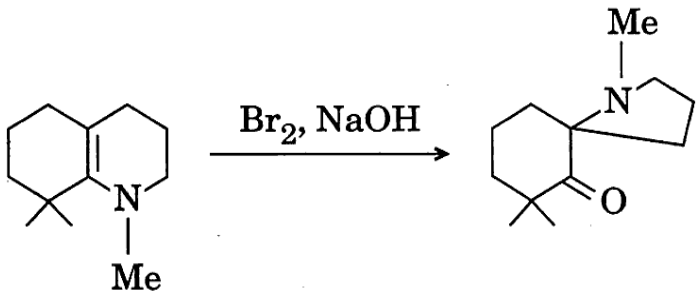
Q4. (a) Suggest a mechanism for the following reactions : *10*

(i) 

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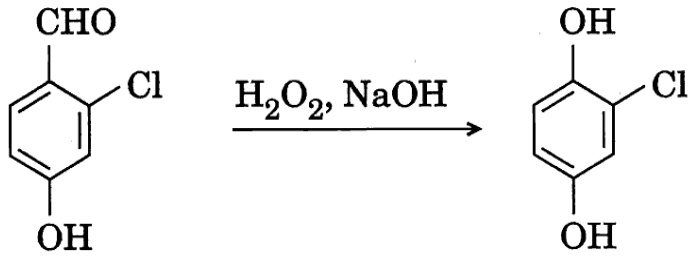
(ii) 

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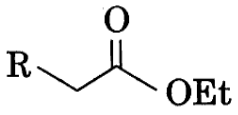
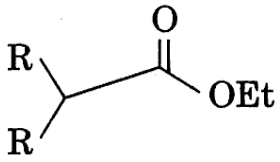
(b) Claisen-ester condensation is possible with substrates of type A but not possible with type B. Explain by writing the mechanism. *10*

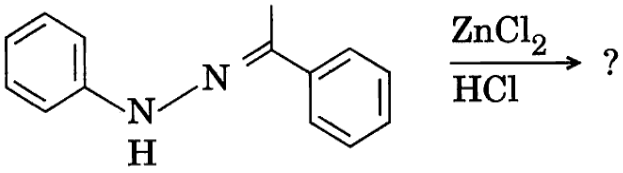


A



B

(c) Discuss the mechanism of the reaction by writing the product. *10*



(d) What are stabilized and unstabilized ylids ? How does E-Z selectivity in Wittig reaction depend upon the nature of ylid ? Explain. *10*

SECTION B

Q5. Attempt the following : *5×8=40*

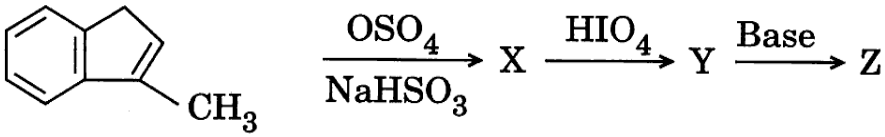
(a) Write the names of monomers of the following polymers and classify them as addition or condensation polymers : *5*

(i) Teflon

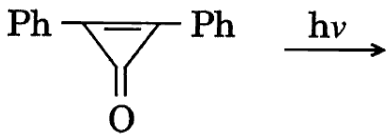
(ii) Bakelite

(b) Name the products obtained on complete hydrolysis of DNA and give their structures. *5*

(c) Write the structure of X, Y and Z. *5*



(d) Formulate the product(s) and give the mechanism for the following reaction : *5*



(e) A compound contains two types of protons which exhibit signals at 139·2 Hz and 430·2 Hz downfield from TMS in a spectrometer operating at 60 MHz. What will be their relative position when measured on a 100 MHz instrument ? *5*

(f) Explain the following variations in λ_{max} (in nm) of CH_3Cl (173), CH_3Br (204), CH_3I (258). *5*

(g) Why is a bathochromic shift observed with increasing conjugation in electronic spectra ? Explain. *5*

(h) What is McLafferty rearrangement in Mass Spectrometry ? Mass spectrum of 1-phenyl butanone exhibits m/z (mass by charge) 105 as a base peak and m/z 120 as one of the major peaks. Explain. *5*

Q6. (a) Calculate $\overline{M}_n$ and $\overline{M}_w$ for a polymer that consists of 10% by weight of a macromolecule of molecular weight 10,000 and 90% by weight of a macromolecule with molecular weight 1,00,000. *10*

(b) How will you determine the molecular weight of a polymer solution using Ostwald viscometer ? *10*

(c) State whether *true* or *false*. If false, give the correct statement. *2×5=10*

(i) Polyvinyl alcohol can be prepared by polymerization of vinyl alcohol.

(ii) CH_4 can be polymerized.

(iii) C_2H_2 and aniline cannot be polymerized.

(iv) Polymers have sharp melting point.

(v) Ziegler-Natta catalyst is used for the preparation of syndiotactic polymer.

(d) What is an oligopeptide ? How is it different from a polypeptide ? What is the secondary structure of protein ? *10*

Q7. (a) An organic liquid with molecular formula $C_6H_{10}O$ gave the following spectral data :

UV : ν_{max} 230 nm (ε 12600), 329 nm (ε 41)

IR : ν_{max} 2950 – 2860 (m), 1695 (s), 1620 (m), 1460 (m) cm^{-1}

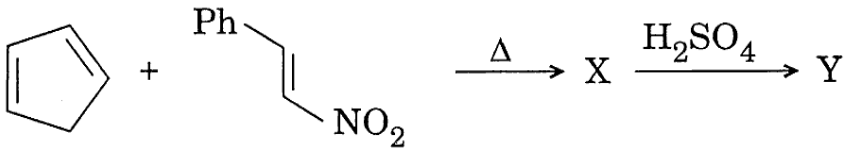
NMR : δ 1·9 (s, 3H), 2·1 (s, 6H), 6·15 (s, 1H)

Write the possible structure of compound with suitable justification. Predict its ^{13}C-NMR spectrum. *20*

(b) How can the NMR spectrum distinguish between the isomers — p-xylene and ethyl benzene ? Justify your answer. *10*

(c) Give the ESR spectra of Naphthalene negative ion, Anthracene negative ion and Triphenyl methyl radical. *10*

Q8. (a) Complete the reactions and give appropriate mechanisms of the following : *10×3=30*

(i) 

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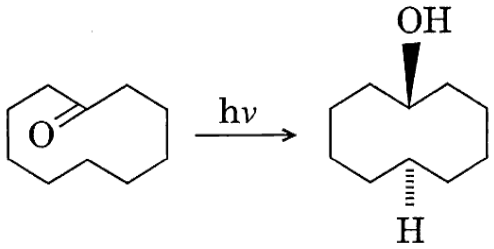
(ii) 

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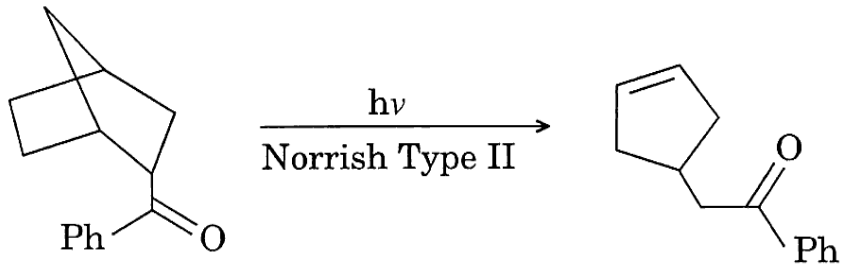
(iii) 

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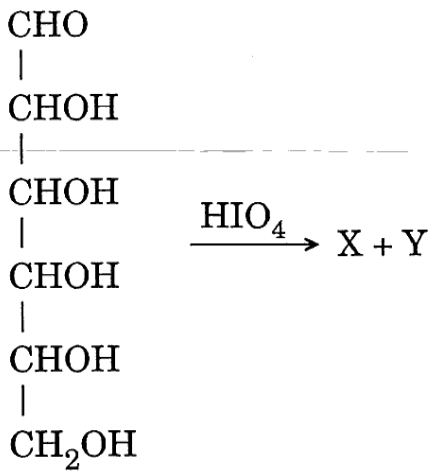
(b) (i) Explain how many molecules of formaldehyde and formic acid are formed in the reaction. *5*



(ii) Identify the X. *5*