

MSC I - Sem. I - Oct. 2016

Chemistry - paper III. - org. chem.

QP Code : 77447

(2½ Hours)

[Total Marks : 60

- N. B. : (1) All questions are compulsory.
(2) Figures to the right indicate full marks.

1. (A) Answer any two of the following :-

- (a) Draw Frost Musulin diagram for cyclooctatetraene. Show the distribution of electrons in MOs and comment on its aromaticity.
- (b) Draw the π MO diagrams with distribution of electrons in reactants of Diels - Alder reaction. Explain the interaction of FMOs. 4
- (c) Show the interaction of allyl cation and allyl anion with their π MO diagrams. Predict the product of the reaction. 4
- (d) Explain the following :- 4
- (i) Homo aromatic compounds
- (ii) Thermochemical criteria of aromaticity.

(B) Answer any one of the following :-

- (a) Explain the aromaticity of :- 4
- (i) Pyridine
- (ii) Furan.
- (b) Explain the significance of HOMO-LUMO gap in the UV absorption of ethene and butadiene with π MO diagrams. 4

2. (A) Answer any two of the following :-

- (a) What is specific and general base catalysis? Explain any one of them using a suitable example. 4
- (b) Compare, giving reasons, the acidity of: 4
- (i) o-Nitrobenzoic acid and p-Methylbenzoic acid.
- (ii) o-Hydroxybenzoic acid and p-Hydroxybenzoic acid.
- (c) With the help of a potential energy diagram, explain, in detail, the Transition State Theory. 4
- (d) Giving appropriate examples, distinguish between E_1 and E_{1CB} mechanisms on the basis of - 4
- (i) Nature of substrate
- (ii) Nature of leaving group

(B) Answer any **one** of the following :-

(a) Explain :-

- (i) Cross-over experiments help in detection of the mechanism of a reaction.
- (ii) Nitration of benzene does not follow the primary kinetic isotope effect.

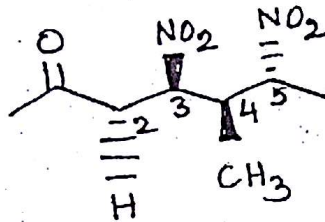
(b) Distinguish between kinetic and thermodynamically controlled products in a reaction.

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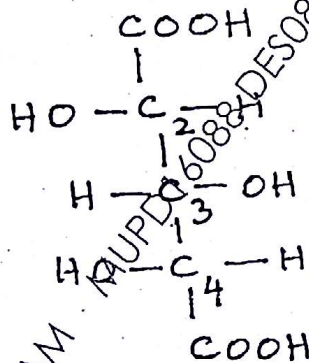
3. (A) Answer any **two** of the following :-

(a) Answer the following :-

- (i) Assign appropriate configurational nomenclature to the specified centres in the molecule -



- (ii) Assign configurational nomenclature to C-2, C-3 and C-4 :-



(b) Answer the following :-

- (i) Explain the principle of planar and axial chirality on the basis of elongated tetrahedron approach.
- (ii) Identify the principal axis of symmetry in naphthalene. Why is it called the principal axis of symmetry?

(c) Discuss the stereochemistry of ansa compounds. Using suitable examples, explain how configurational descriptors are assigned to such molecules.

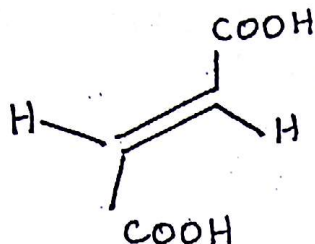
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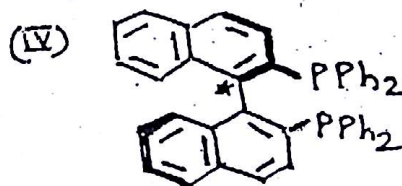
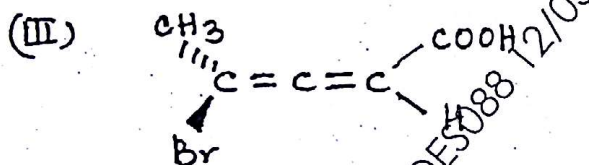
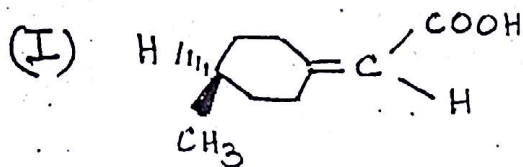
- (d) What are diastereotopic ligands and faces? Draw the R_e and S_i faces of acetophenone. 4

Identify the R_e and S_i faces in the following molecule –



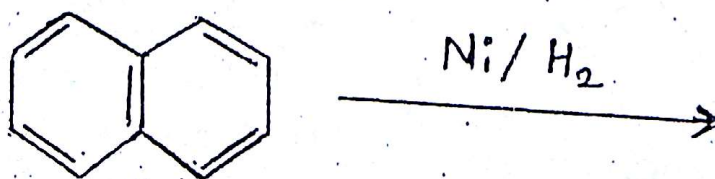
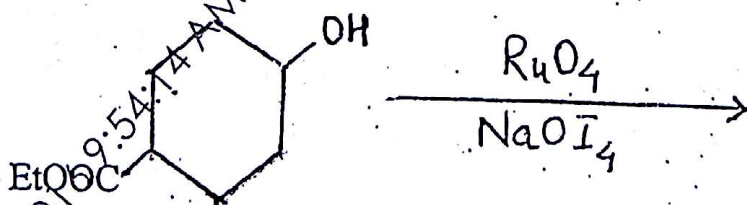
(B) Answer any one of the following :-

- (a) Explain the stereochemistry of tri- and tetra coordinated sulphur compounds. 4
- (b) Establish the stereochemical descriptors of the following molecules. 4



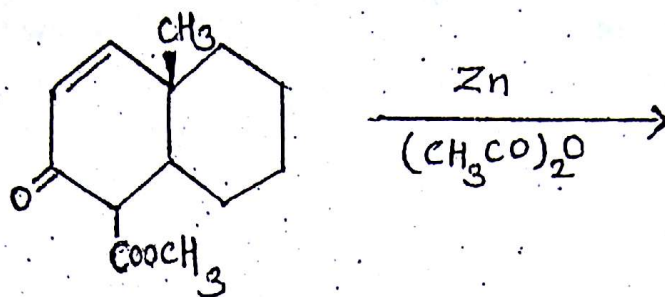
4. (A) Answer any two of the following :-

- (a) Predict the products in the following reactions: 4

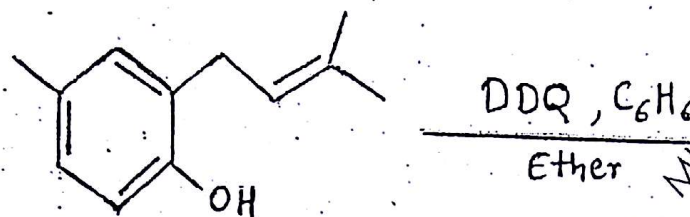


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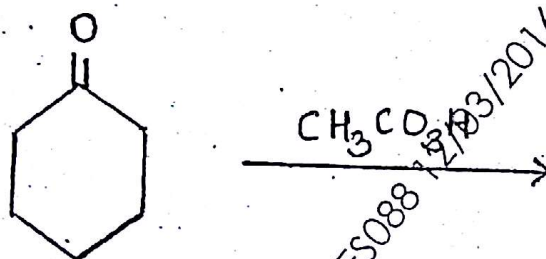
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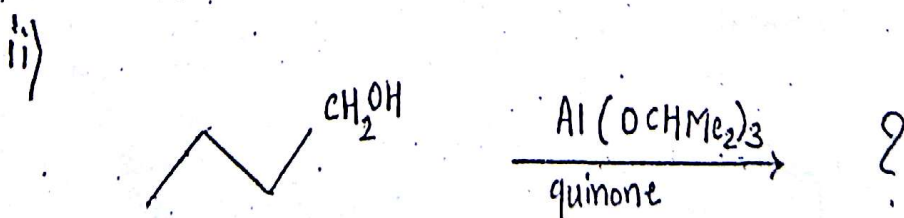
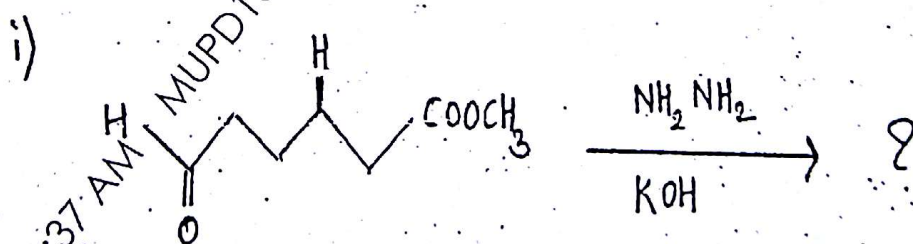
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(b) Complete the following reaction, name it and give its mechanism. 4



(c) Complete the following reactions and name them : 4

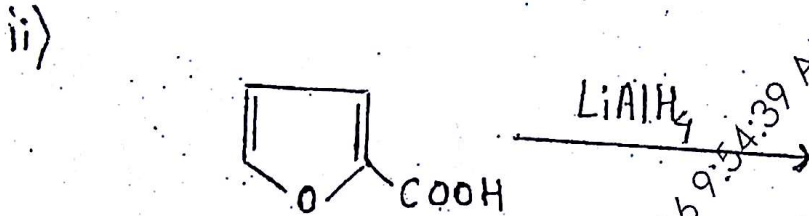
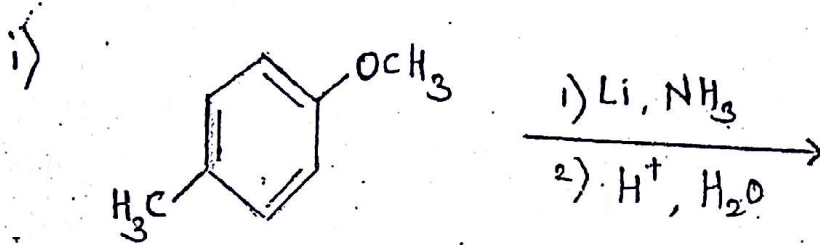


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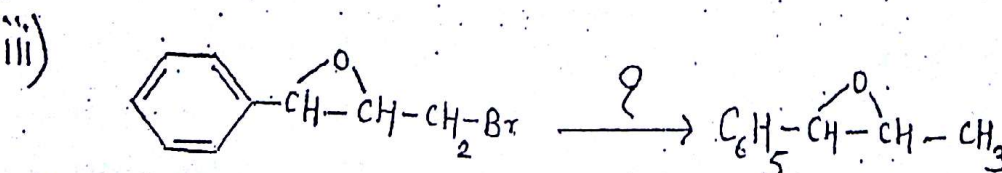
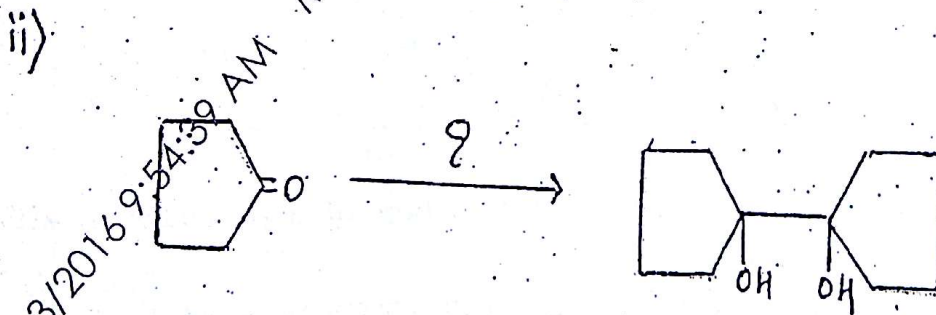
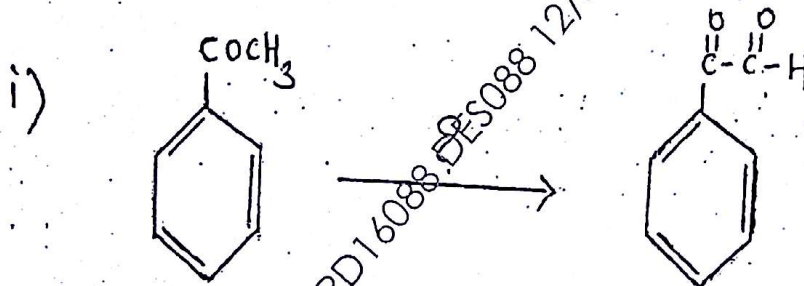
- (d) What is Swern oxidation? Explain using suitable example and give its mechanism. 4

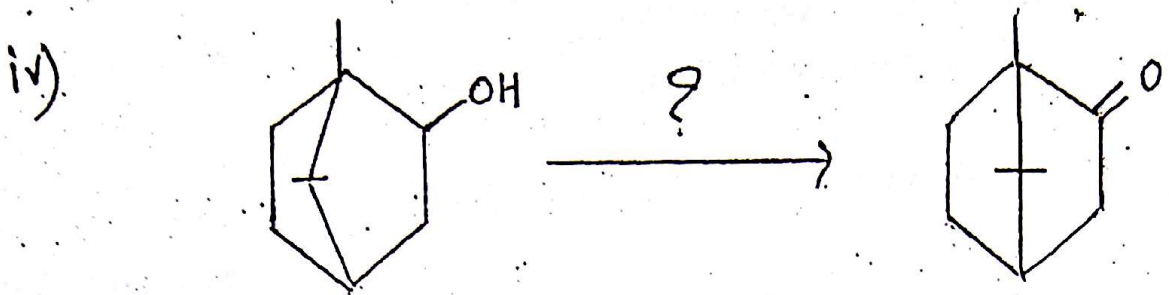
(B) Answer any one of the following :-

- (a) Complete the following reactions and give mechanism of any one. 4



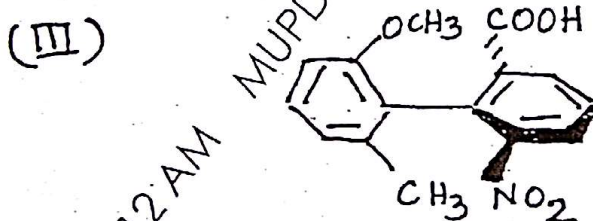
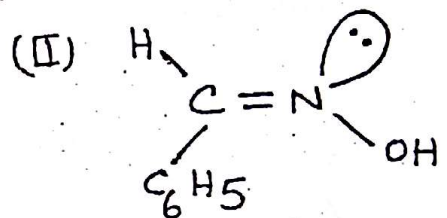
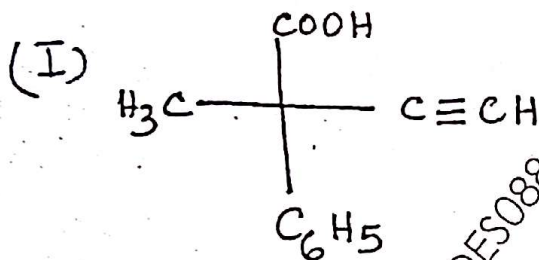
- (b) Complete the following equations 4





5. Answer any four of the following :-

- What are hard and soft acids?
- Draw the Frost Musulin diagram with electron distribution for
 - Cyclopentadienyl anion
 - Cyclopentadienyl cation.
- Discuss the stereochemistry of E_2 elimination reaction.
- What is Chugaev reaction? Give an example.
- Using suitable examples, explain proper and improper axes of symmetry.
- Assign configurational descriptors to the following molecules



- Discuss the mechanism of oxidation of aryl methanes with CrO_2Cl_2 reagent.
- What is Dakin Reaction? Give its mechanism and one application.