M.Sc Sem I April 2017

Chemistry III

QP Code : 03713

(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 π MOs of diene and dienophile showing electron distribution. Label FMOs and show the interaction of diene and dienophile. 4

(b) Draw Frost Musulin diagram for benzene. Show distribution of electrons in MOs and comment on its aromaticity. 4

(c) Draw the π MO diagram for allyl cation and allyl anion. Show the interaction of their FMOs. Predict the product of the reaction between the two ions. 4

(d) Explain the following :- 4

(1) Antiaromatic compounds

(2) Use of ^{1}H-NMR to detect aromaticity.

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

(a) Compare the aromaticity of [14] and [18] annulenes. 4

(b) Explain the dimerization of ethylene to cyclobutane using FMOs. 4

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

(a) Complete and name the mechanism of each of the following two reactions- 4

(i) $CH_3-\underset{\displaystyle CH_3}{\underset{|}{CH}}-CH_2-Br \xrightarrow[CH_3OH]{CH_3O^-}$

(ii) $CH_3-\underset{\displaystyle H}{\underset{|}{\overset{\displaystyle OH}{\overset{|}{C}}}}-CH_2-\overset{\displaystyle O}{\overset{\|}{C}}-H \xrightarrow{OH^-}$

(b) Sulphonation of naphthalene gives two different products depending upon the temperature of the reaction. Explain. 4

(c) How do the following help in determining the mechanism of a reaction? 4

(i) Trapping of intermediates

(ii) Isotopic labelling studies

(d) Explain the following :- 4

(i) Transition State Theory

(ii) Principle of Microscopic Reversibility

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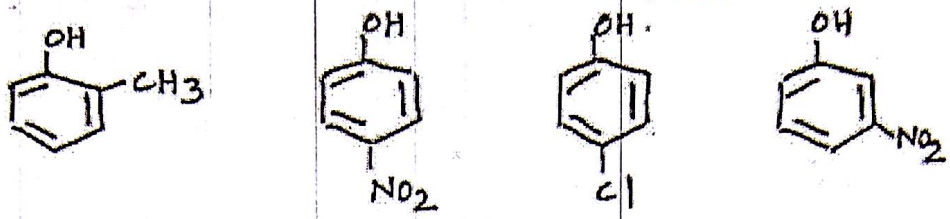
(B) Answer any **one** of the following :-

(a) Assign, giving reasons, the correct pKa value to the following molecules- 4



pKa values : 9.26, 8.35, 7.14, 10.28

(b) Give examples and explain the significance of : 4

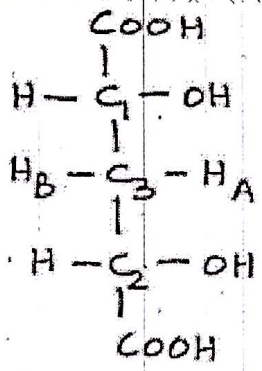
(i) Primary Kinetic Isotope Effect

(ii) Secondary Kinetic Isotope Effect

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

(a) Discuss the stereochemistry of biphenyls. Give examples to explain how configurational descriptors are assigned to such molecules. 4

(b) Answer the following with respect to the given molecule : 4



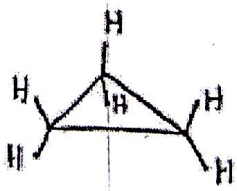
(i) Relationship between H_A and H_B

(ii) Stereochemical descriptors of H_A and H_B

(iii) Nature of C_3.

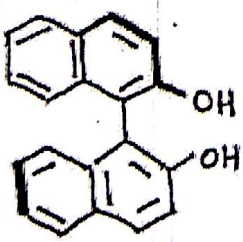
(c) (i) Identify the axes of symmetry in the following molecules : 4

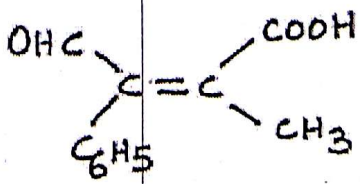
(I) 

(II) 

(ii) Explain the two-dimensional chiral simplex approach for axial andplanar chirality.

(d) (i) Give the configurational nomenclature of the following molecules- 4

(I) 

(II) 

(ii) What are spirans? Give examples to represent the different configurational descriptors of spirans. 4

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

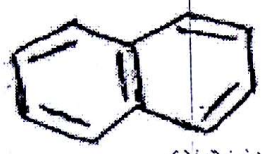
(a) Explain, using substitution-addition criteria :-
(i) Homotopic ligands and faces
(ii) Enantiotopic ligands and faces. 4

(b) Give examples of tetra co-ordinated compounds of
(i) Sulphur
(ii) Nitrogen
Discuss their configurational stability. 4

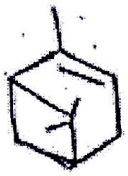
4. (A) Answer any **two** of the following :-

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

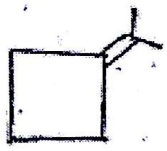
(i)



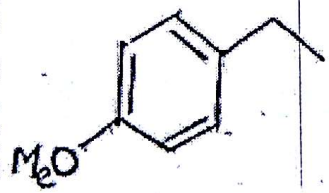
$\xrightarrow[130-140\,^{\circ}C]{Na,\ Isoamyl\ alcohol}$?



$\xrightarrow[\text{Dicyclohexano-18-Crown-6}]{KMnO_4 / C_6H_6}$?

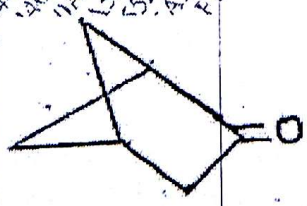


$\xrightarrow[H_2O]{O_3}$?



$\xrightarrow[AcOH]{DDQ}$?

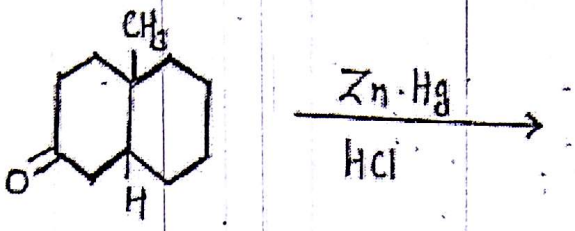
(b) Complete the following reaction, name it and give its mechanism : 4



$\xrightarrow{CH_3CO_3H}$?

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

i)



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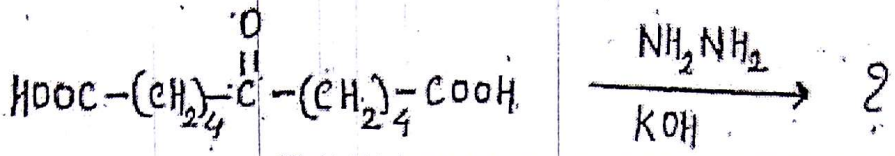
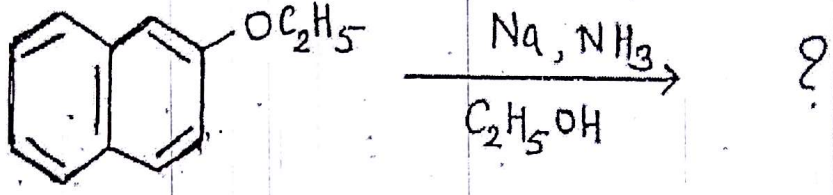


(d) Give the synthetic applications of DMSO reagent. 4

(B) Answer any **one** of the following : 4

(a) Complete the following reactions and give the mechanism of any **one** : 4

i)



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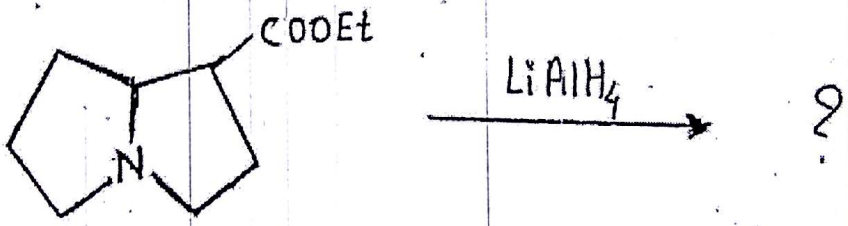
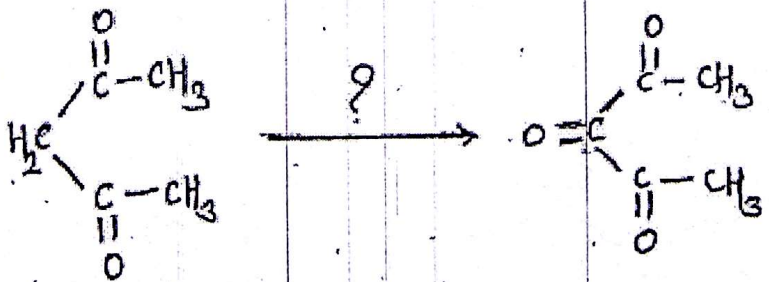


(b) Complete the following equations : 4

i)



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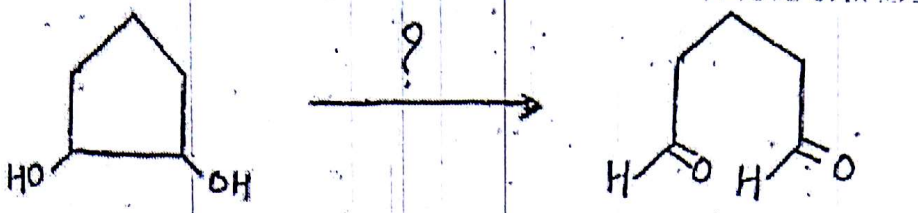
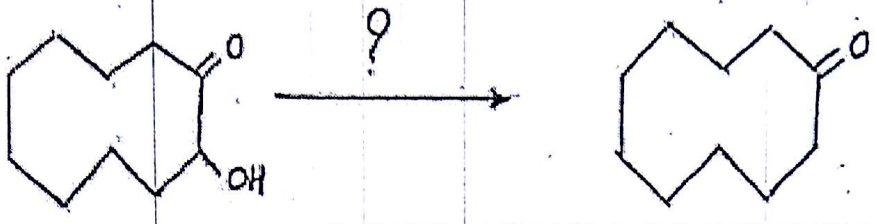
ii)



iii)



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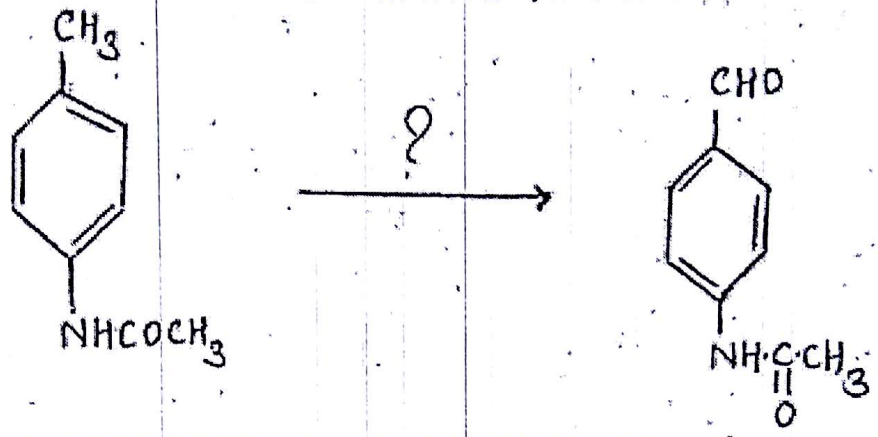


5. Answer any **four** of the following :- **12**

(a) Discuss the aromaticity of pyrrole.

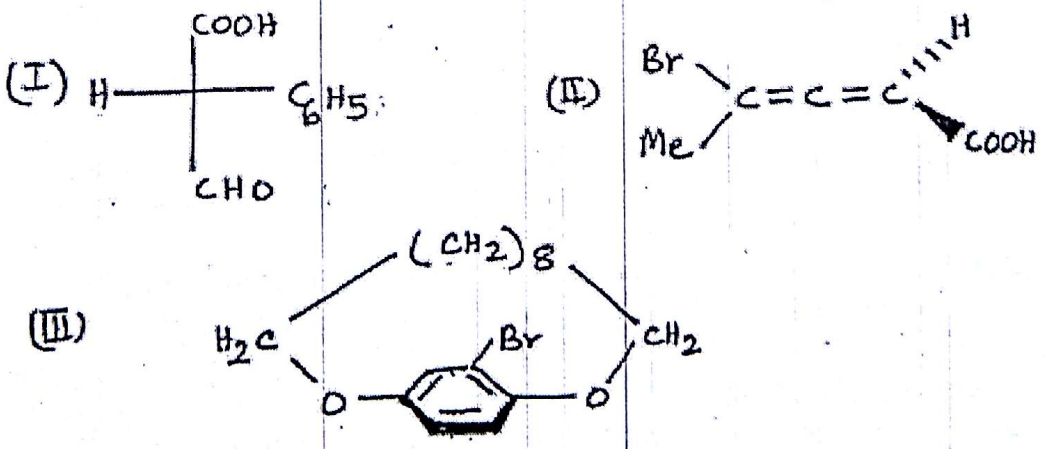
(b) What are hard and soft nucleophiles?

(c) What are the characteristic features of specific acid catalysis reactions? Give an example.

(d) What are E_i reactions? Give two examples.

(e) Explain the Rotation - Reflection axis of symmetry with a suitable example.

(f) Assign the configurational nomenclature to the following molecules-



(g) What is Oppenauer oxidation? Explain its mechanism.

(h) Illustrate the uses of the following reagents in organic syntheses, with one example each :

(i) Red Al

(ii) DIBAL H

(iii) L-Selectride