

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

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

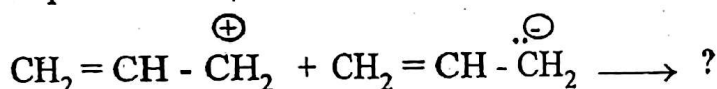
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- (a) Compare the aromaticity of [14] and [18] annulenes. 4  
 (b) Explain the following : 4  
 (i) Cyclooctatetraene prefers to remain in a tub shape.  
 (ii) Furan is aromatic.  
 (c) Explain the thermochemical criteria and NMR characteristics of aromatic compounds. 4  
 (d) 'Nucleophiles interact with the LUMO of an aldehyde and attack takes place at the C-atom of the aldehyde'. Explain using  $\pi$ -M.O. diagram of the carbonyl group of an aldehyde. 4

(B) Answer any one of the following : -

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- (a) Complete the following reaction. Draw the  $\pi$ -M.O. orbital diagrams of the reactants and explain the interaction of their FMOs



- (b) 'Dimerization of ethene takes place via a photochemical pathway'. Explain on the basis of HOMO - LUMO interaction using a  $\pi$ -M.O. diagram. 4

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

- (a) Explain in detail the thermodynamic and kinetic control of any one organic reaction with mechanism and potential energy diagram. 4  
 (b) Choose the stronger base from the following pairs and explain your choice. 4

(i)



and



(ii) p-nitroaniline and p-toluidine.

- (c) Explain and give one example of :

4

- (i) General acid catalysis.  
 (ii) General base catalysis.

- (d) Explain how primary and secondary kinetic isotope effects are used in determining reaction mechanism with one example each. 4

(B) Answer any one of the following :-

(a) Illustrate the use of the following techniques in determining reaction mechanism with one example each.

(i) Crossover experiments

(ii) Product analysis.

(b) Explain the following :-

(i) Benzoic acid dissolves in  $\text{NaHCO}_3$  solution but phenol does not.

(ii) Salicylic acid is a stronger acid than p-hydroxybenzoic acid.

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

(a) Explain the following terms with one example each.

(i) erythro and threo isomers.

(ii) stereogenic centre.

(iii) pro-pseudoasymmetric centre.

(b) (i) Differentiate between  $C_n$  and  $S_n$  axes of symmetry.

(ii) Draw the structure of tetrachloroallene, mark all axes of symmetry and label the principal axis of symmetry.

(c) What is prochirality? Draw structures of molecules containing:

(i) a prochiral axis and (ii) a prochiral plane

Assign appropriate stereochemical descriptors to one pair of enantiotopic ligands in each.

(d) Explain the optical activity of the following with one example each.

(i) cyclophanes.

(ii) alkylidene cycloalkanes.

(B) Answer any one of the following :-

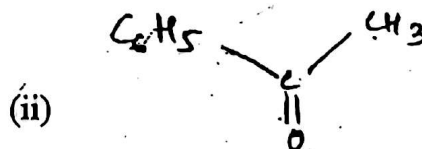
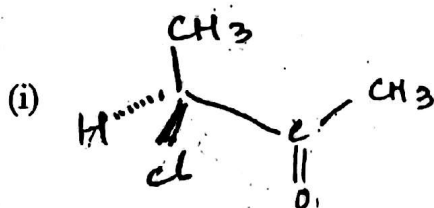
(a) (i) Explain any one principle of axial chirality.

(ii) Write the structures of

(I) (R) - BINAP

(II) (S) - 6,6' - dinitrobiphenyl - 2,2' - dicarboxylic acid.

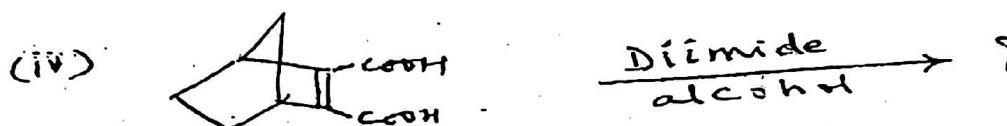
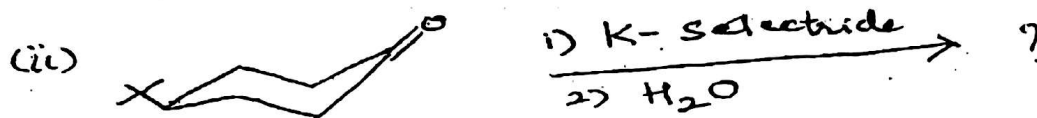
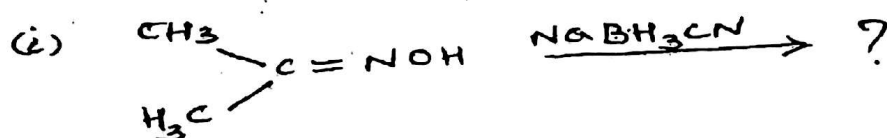
(b) What are enantiotopic and diastereotopic faces? Assign stereochemical descriptors to the top and bottom faces of



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

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(a) Predict the products in the following reactions.

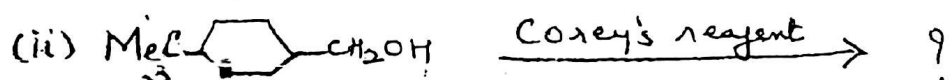
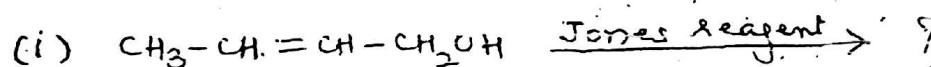


(b) Explain the mechanism of Baeyer Villiger oxidation and give two applications of the reaction.

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(c) Give the composition of Corey's and Jones' reagents and complete the following reactions.

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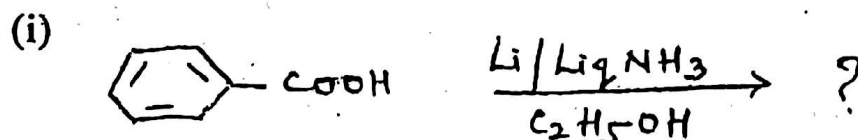
(d) Give the mechanism of Wolff-Kishner reduction on octan-2-one. What is Huang - Minlon modification of the reaction?

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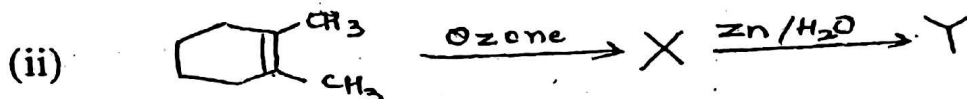
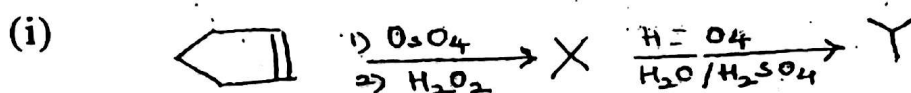
(B) Answer any one of the following :-

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

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(b) Predict the products X and Y in the following reactions.



5. Answer any four of the following :-

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(a) Draw Frost Musulin diagrams with electron distribution for :

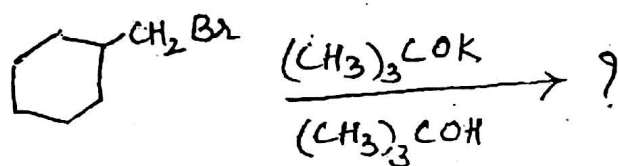
(i) Cyclopentadienyl anion.

(ii) Cyclopropenyl cation.

(b) What are soft nucleophiles and soft electrophiles ? Give one example of each.

(c) What is Chugaev reaction ? Explain its mechanism.

(d) Complete the following reaction and give the mechanism.

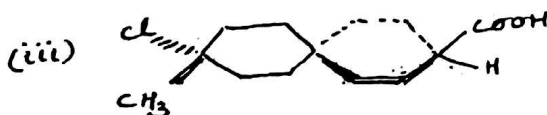
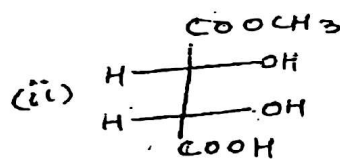
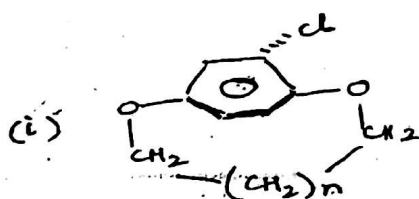


(e) Explain with suitable examples the chirality of :

(i) Quarternary phosphonium compounds.

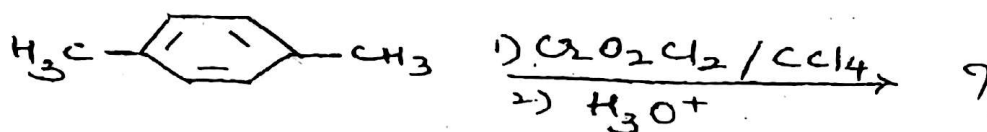
(ii) Silanes.

(f) Assign stereochemical descriptors to the following.

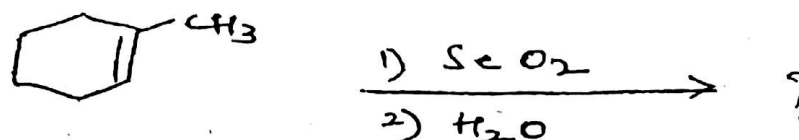


(g) Predict the products in the following reactions

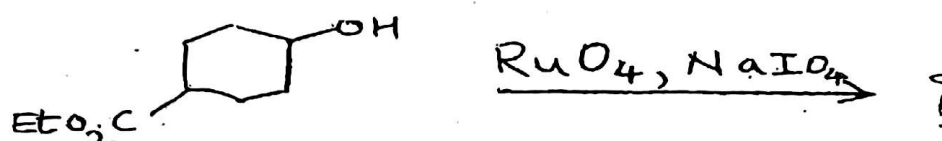
(i)



(ii)



(iii)



(h) What is Raney-Nickel? Predict the products X and Y in the following reaction.

