

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

(A) Answer any two of the following :-

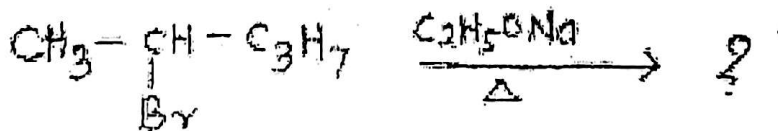
- (a) Draw the MO diagrams for the allyl cation and allyl anion. Show the interaction of their FMOs and predict the product of the reaction between the two ions. 4
- (b) Compare the aromaticity of [10] annulene and [18] annulene. 4
- (c) Draw the Frost Musulin diagram for cyclooctatetraene showing the distribution in the MOs. Comment on the shape of the molecule and its aromaticity. 4
- (d) Answer the following :-
- (i) What are antiaromatic compounds ? Give an example. 4
- (ii) Explain the use of <sup>1</sup>H-NMR to prove aromaticity of a compound.

(B) Answer any one of the following :-

- (a) Explain the significance of the HOMO-LUMO gap in the UV absorption of ethene and butadiene with  $\pi$  MO diagrams. 4
- (b) Draw the Frost Musulin diagrams for the tropylium cation and cyclobutadiene. Show the distribution of electrons in their MOs and comment on their aromaticity. 4

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

- (a) Complete the following reaction and explain its mechanism with stereochemistry. 4



- (b) Explain the use of the following techniques in determining mechanism of the reactions specified. 4
- (i) Cross-over experiments in rearrangement reactions.
- (ii) Detection and trapping of intermediates in aromatic  $\text{S}_\text{N}$  on chlorobenzene.
- (c) Arrange the following in increasing order of acidity and justify your answer. 4
- Benzoic acid, benzyl alcohol, phenol, p-chlorobenzoic acid.

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(d) Answer the following :-

- (i) Compare the basicity of p-toluidine and p-chloroaniline  
 (ii) 'Piperidine is more basic than pyridine'. Explain.

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(B) Answer any one of the following :-

(a) With the help of an energy profile diagram explain:

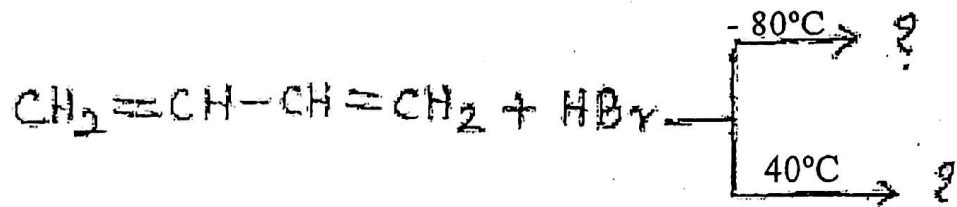
- (i) Hammond's postulate  
 (ii) Transition state theory.

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(b) Answer the following :-

- (i) Predict the products of the following reaction and comment on their stabilities.

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- (ii) Write a complete equation to represent Chugaev reaction.

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

(a) Explain 'atropisomerism' with reference to biphenyls. Write the structures of a pair of enantiomeric biphenyls with their configurational descriptors.

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(b) Answer the following :-

- (i) Explain 'improper' axis of symmetry in a molecule with a suitable example.  
 (ii) Differentiate between an asymmetric and a pseudoasymmetric centre in a molecule with suitable examples.

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(c) Explain the substitution and symmetry criteria for differentiating between homotopic and enantiotopic ligands with suitable examples.

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(d) Explain enantiomerism in the following compounds with suitable examples.

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- (i) N - oxides  
 (ii) Phosphines

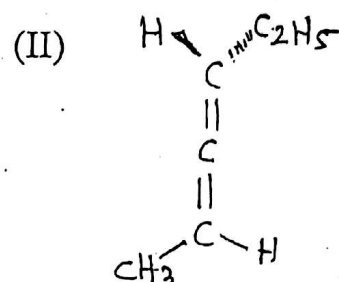
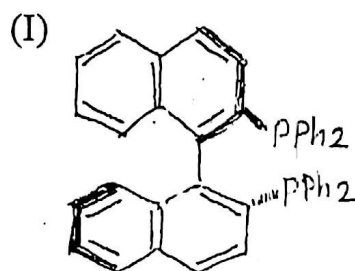
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(B) Answer any **one** of the following :-

(a) Answer the following

(i) Assign configurational descriptors to the following :

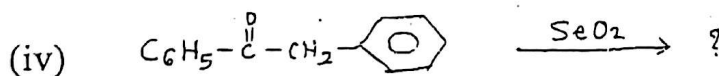
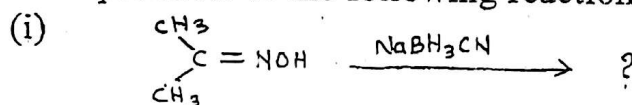


(ii) Write the structure of a molecule with enantiotopic faces and assign stereochemical descriptors to these faces.

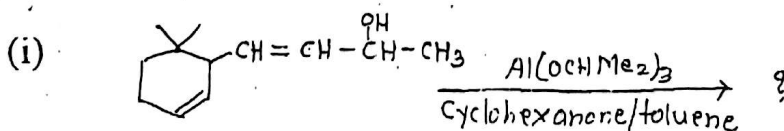
(b) Explain the principle of planar chirality with reference to cyclophanes. Write the structure of a chiral paracyclophane with its stereochemical descriptor.

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

(a) Predict the products of the following reactions :

(b) Give the general mechanism of metal hydride reduction. Illustrate the chemoselectivity of  $\text{NaBH}_4$  with two examples.

(c) Complete the following reactions and name them.

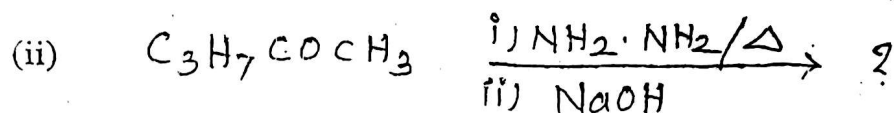
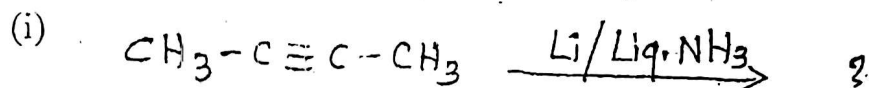


(d) What is Swern oxidation? Explain its mechanism with a suitable example.

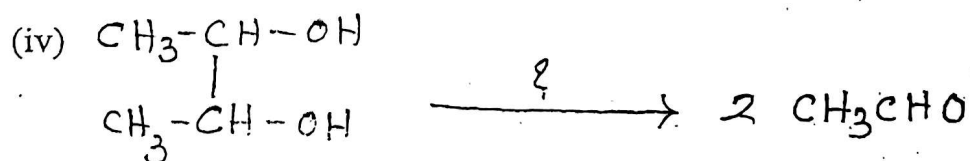
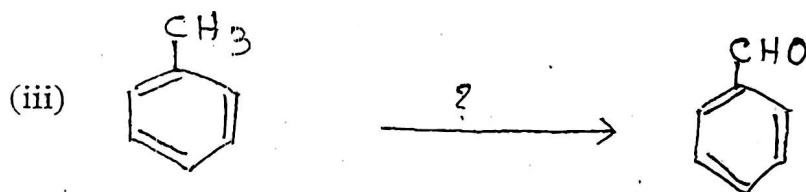
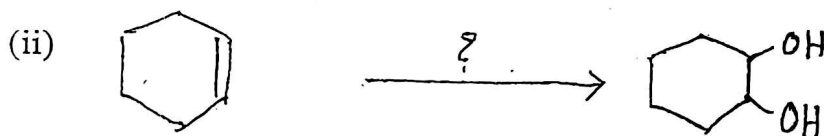
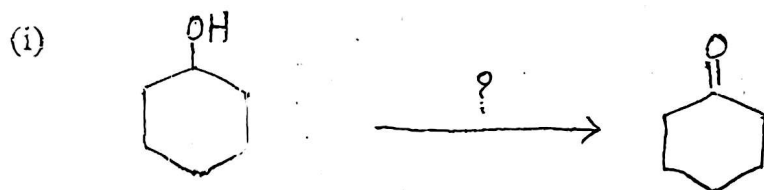
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(B) Answer any one of the following :-

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



(b) Suggest suitable reagents for the following: 4



5. Answer any four of the following :-

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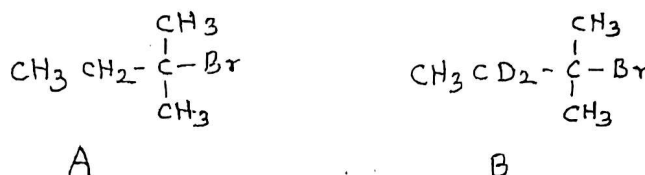
(A) Explain whether the followings ions are aromatic or not :  
cyclopropenyl cation, cyclopropenyl anion, cyclopentadienyl anion.

(B) Comment on the aromaticity of pyridine and furan.

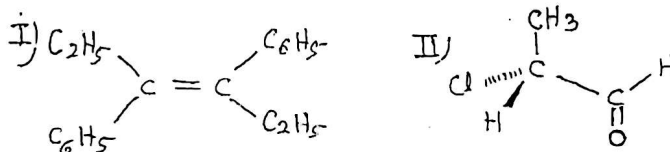
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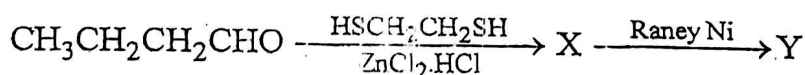
- (C) The rate of elimination of HBr from compound A is 1.4 times faster than from compound B. What is the type of kinetic isotope effect displayed and how is the mechanism ( $E_1$  or  $E_2$ ) proved ?



- (D) What is specific acid catalysis ? Explain its mechanism with a suitable example.
- (E) Write the structure of threo-2,3-dibromo butanoic acid and assign configurational descriptors (R/S) to the chiral centres in the molecule.
- (F) Assign configurational descriptors to the top and bottom faces of the following :



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



- (H) Illustrate the use of the following in organic synthesis with one example each.

- (i) PCC
- (ii) Chloranil
- (iii) Dess-Martin reagent