$(2\frac{1}{2} \text{ Hours})$

[Total Marks:60

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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 diagrams for benzene and cyclooctatetraene. Show the distribution of electrons in the MOs and comment on their aromaticity.
- (b) What is the structure of azulene $(C_{10}H_8)$? Explain its aromaticity and high dipole moment.
- (c) Answer the following:

(i) What are homoaromatic compounds? Give an example.

(ii) Comment on the aromaticity of [14] annulene.

(d) Draw the π MOs of a diene and a dienophile showing electron distribution. Label the FMOs and show their interaction in Diels-Alder reaction.

(B) Answer any one of the following:-

- (a) Draw the π MOs of ethene and butadiene by LCAO method. Explain the effect of conjugation on the UV spectra of ethene and butadiene.
- (b) Draw a π MO diagram to show the relative energies of the MOs of formaldehyde and ethene. Explain their reactivity with nucleophiles on the basis of their FMOs.

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

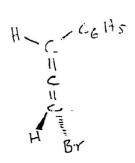
- (a) What is an E₁cB reaction? Give one example with mechanism.
- (b) Explain the use of the following techniques in proving the benzyne 4 mechanism of aromatic S_N.
 - (i) Product analysis
 - (ii) Detection and trapping of intermediates.
- (c) Explain the following:-

(i) Trifluoroacetic acid is a stronger acid than acetic acid

(ii) Salicylic acid is more acidic than p-hydroxybenzoic acid

(d) Arrange the following in increasing order of basicity and explain: 4 aniline, ethylamine, diphenylamine, diethylamine.

- (B) Answer any one of the following:
 - (a) What is the principle of microscopic reversibility? Explain its significance in the kinetic vs thermodynamic control of organic reactions with the help of a potential energy diagram.
 - (b) Answer the following:
 - (i) Give equations specifying reaction conditions to represent an organic reaction that can undergo thermodynamic and kinetic control (no mechanism).
 - (ii) Give a complete equation to represent the pyrolysis of acetates.
- 3. (A) Answer any two of the following:
 - (a) Explain the chirality of spiranes. Write the structures of a pair of enantiomeric spiranes with their configurational descriptors.
 - (b) Answer the following:
 - (i) Write the structure of a molecule with a pseudoasymmetric centre and assign a configurational descriptor to the pseudoasy nmetric centre.
 - (ii) What is the principal axis of symmetry in a molecule? Draw and label the principal axis of symmetry in naphthalene.
 - (c) Explain the addition and symmetry criteria for identification of enantiotopic and diastereotopic faces in a molecule with suitable examples.
 - (d) Explain enantiomerism in the following with suitable examples.
 - (i) Quarternary phosphonium compounds.
 - (ii) Silanes
 - (B) Answer any one of the following:-
 - (a) Answer the following:
 - (i) Assign the configurational descriptors to the following:



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- (ii) Write the structure of a molecule with a pair of diastereotopic ligands and assign stereochemical descriptors to these ligands.
- (b) Explain the principle of planar chirality with reference to ansa compounds. Write the structure of a chiral ansa compound with its stereochemical descriptor.
- 4. (A) Attempt any two of the following:-
 - (a) Predict the products in the following reactions:

(ii)
$$\frac{h_{3}c}{c_{*}H_{c}} \xrightarrow{DDQ} ?$$

$$\frac{DDQ}{c_{*}H_{c}} \xrightarrow{reflux}$$

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

(c) Complete the following reactions and name them:

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- (d) Write a complete equation to represent HIO₄ oxidation of butane 2.

 3-diol and explain the mechanism of the reaction.
- (B) Attempt any one of the following:-
 - (a) Complete the following reactions and give the mechanism of any one.

(b) Complete the following equations.

- 5. Answer any four of the following:-
 - (A) Explain the structure and aromaticity of ferrocene.
 - (B) Comment on the aromaticity of thiophene and pyridine.
 - (C) Elimination of HBr from compound A occurred 6.7 times faster than from compound B. Explain the type of kinetic isotope effect displayed and how the mechanism (E₁ or E₂) is proved.

$$CH_3CII_2CH_2Br$$
 $CH_3CD_2CH_2Br$ B

(D) What is general acid catalysis? Explain its mechanism with a suitable example.

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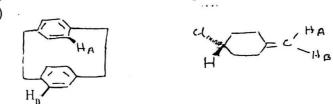
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- (E) Write the structure of erythro 2, 3-dichlorobutanal and assign 3 configurational descriptors [R/S] to the chiral centres in the molecule.
- (F) Identify the topic relationship between H_A and H_B in the following 3 and assign stereochemical descripter if required.



(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) Collin's reagent
 - (ii) K-selectride
 - (iii) Jones reagent.

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