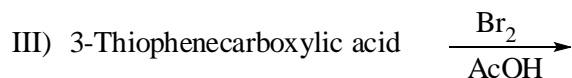
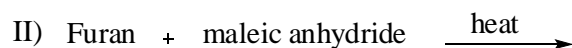
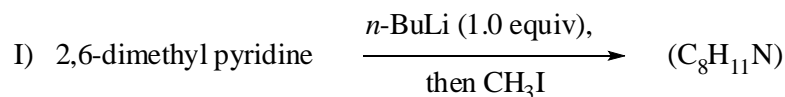
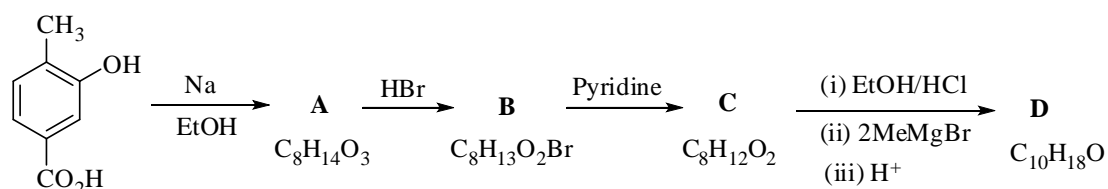
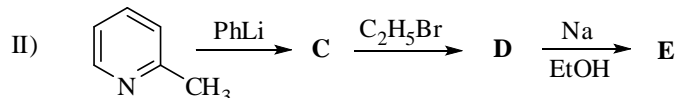
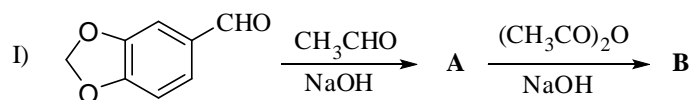


**B. Sc. Part-III (Honours) Examination, 2020****Subject: Chemistry****Paper: X****(New Syllabus)****Time: 2 Hours****Full Marks: 50***The figures in the margin indicate full marks.**Candidates are required to give their answers in their own words as far as practicable.***Group-A****1. Answer *any three* questions from the following:****3 × 5 = 15****(a)** Write down the structure of the major organic product formed in each of the following reactions. Include stereochemistry, if necessary and explain your answer.**(b)** Draw the structure of missing compounds **A** to **D** in the following transformations. Explain your way of thinking.**(c)** Draw a Fischer projection for the pyranose form of  $\beta$ -D-xylose. Show how periodate oxidation could distinguish between a methyl arabinofuranoside and a methyl xylopyranoside. How many ketotetroses are possible? Write Fischer projection formulas for each.**(d)** In terms of relative stability of intermediate, discuss the orientation of electrophilic substitution with furan and pyrrole. Why are these heterocycles more reactive than benzene towards electrophilic reactions?

(e) Identify compounds **A–E**.



2. Answer **any one** question from the following:

**1 × 10 = 10**

(a) Draw the structure of an achiral amino acid. Draw the structure of two amino acids with more than one chiral center.

Starting with diethyl  $\alpha$ -bromomalonate and potassium phthalimide and using any other necessary reagents, show how you might synthesize DL-leucine.

Discuss the activation of a terminal carboxylic acid with example.

(b) Using nitration of pyrrole as an example, predict whether electrophilic aromatic substitution occurs predominantly at carbon-2 or carbon-3.

Is maltose a reducing sugar? Does it mutarotate? Explain your reasoning.

When phenylhydrazine is reacted with 2-hexanone under conditions of the Fischer indole synthesis, a mixture of two isomeric indoles is formed. Give their structures and explain.

### Group-B

3. Answer **any three** questions from the following:

**3 × 5 = 15**

(a) The typical stretching frequency for a carbon-carbon double bond is  $1650\text{ cm}^{-1}$ . Estimate the stretching frequency of a carbon-carbon triple bond assuming that the relative bond force constants of triple and double bonds are in the ratio 3:2.

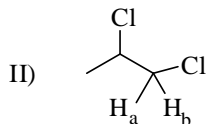
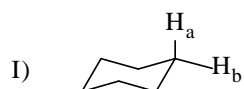
A compound with molecular formula  $\text{C}_7\text{H}_{15}\text{Cl}$  has two  $^1\text{H-NMR}$  absorptions at  $\delta\ 1.08$  and  $\delta\ 1.59$ , with relative integrals of 3:2, respectively. Give a structure that fits the data provided.

(b) How many  $\pi$  molecular orbitals are there for 1,3,5-hexatriene? Which of the MO's are bonding, antibonding, and frontier molecular orbitals?

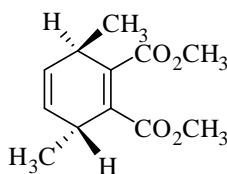
Taking proper example explain secondary orbital interaction in Diels-Alder reaction.

(c) Starting with cyclohexanone show how you could employ enamine in the synthesis of  $\text{CH}_3\text{COCH}_2\text{CH}_2\text{COOCH}_3$ .

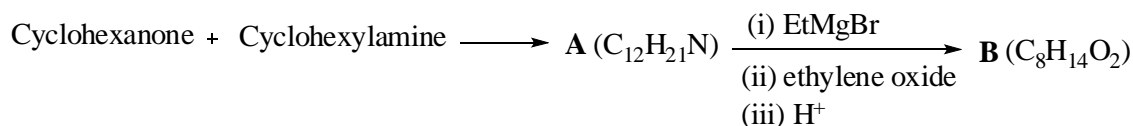
Specify whether the labeled protons in each of the following structures would be expected to have the same or different chemical shifts at room temperature. Justify your choice.



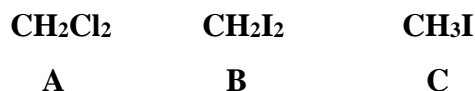
(d) Show the retrosynthetic path and then synthesize the following compound. You are advised to use Diels-Alder reaction.



Predict the product of the following Mannich reaction and outline reasonable mechanism that accounts for its formation.



(e) In the following set, the proton NMR spectra of the compounds shown consist of a single resonance. Arrange the compounds in order of increasing chemical shift, smallest first.



An unknown compound ( $\text{C}_3\text{H}_2\text{NCl}$ ) shows moderately strong IR absorptions around  $1650\text{ cm}^{-1}$  and  $2200\text{ cm}^{-1}$ . Its  $^1\text{H-NMR}$  spectrum consists of two doublets ( $J = 14\text{ Hz}$ ) at  $\delta 5.9$  and  $\delta 7.1$ . Propose a structure consistent with these data.

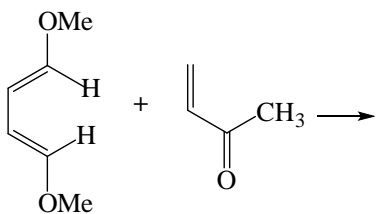
4. Answer *any one* question from the following:

**1 × 10 = 10**

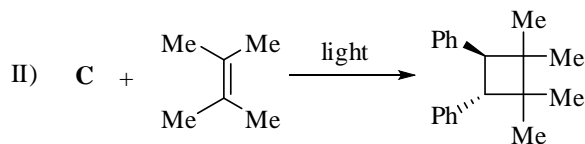
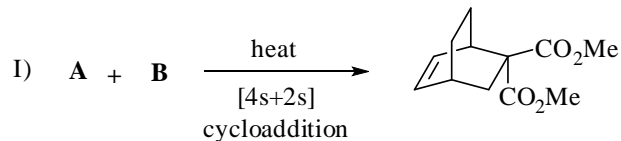
(a) Show the retrosynthetic analysis and a synthetic pathway for the preparation of 2-hexanone from ethyl acetoacetate.

Is Claisen rearrangement a sigmatropic reaction? Justify your choice by providing an example. Give the retrosynthetic pathways and then synthesize 2-bromobutane.

(b) Use *endo* rule to predict the product of the following reaction.



Provide stereochemistry of missing compounds **A** and **C** in the following transformations.



Which of the following is not one of the twelve principles of green chemistry?

- I) Using high temperatures to speed up reactions
- II) Minimizing toxic reagents used in a synthesis
- III) Maximization of atom economy
- IV) Minimizing the use of solvents

What will be the chemical shift (in Hz) of the  $\text{CH}_3$  protons of methylbromide ( $\delta$  2.68 ppm) in a spectrum taken at the following operating frequencies?

- I) 90 MHz
- II) 600 MHz

**B. Sc. Part-III (Honours) Examination, 2020**

**Subject: Chemistry**

**Paper: X**

**(Old Syllabus)**

**Time: 2 Hours**

**Full Marks: 50**

*The figures in the margin indicate full marks.*

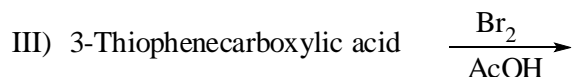
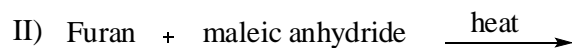
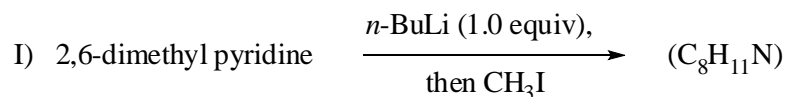
*Candidates are required to give their answers in their own words as far as practicable.*

**Group-A**

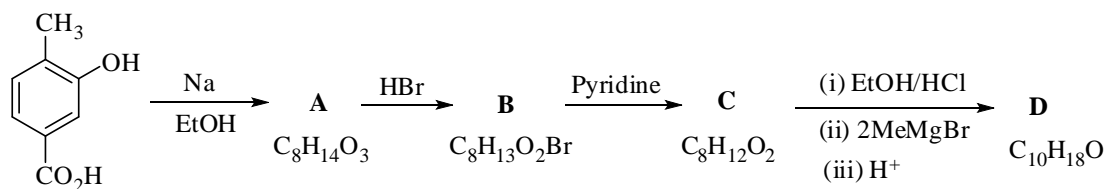
1. Answer *any three* questions from the following:

**3 × 5 = 15**

(a) Write down the structure of the major organic product formed in each of the following reactions. Include stereochemistry, if necessary and explain your answer.



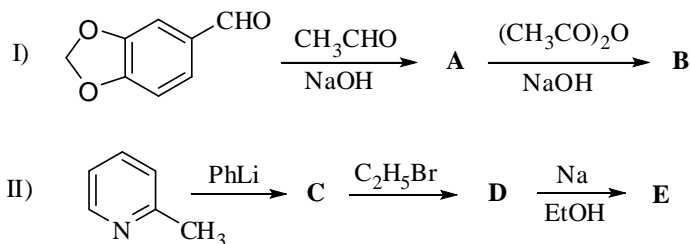
(b) Draw the structure of missing compounds **A** to **D** in the following transformations. Explain your way of thinking.



(c) Draw a Fischer projection for the pyranose form of  $\beta$ -D-xylose. Show how periodate oxidation could distinguish between a methyl arabinofuranoside and a methyl xylopyranoside. How many ketotetroses are possible? Write Fischer projection formulas for each.

(d) In terms of relative stability of intermediate, discuss the orientation of electrophilic substitution with furan and pyrrole. Why are these heterocycles more reactive than benzene towards electrophilic reactions?

(e) Identify compounds **A–E**.



2. Answer **any one** question from the following:

**1 × 10 = 10**

(a) Outline a Kiliani-Fischer synthesis of aldotetroses starting with D-erythrose (use Fischer projections). One epimer of the products formed can be oxidized with nitric acid to an optically active aldaric acid while similar oxidation of the other yields an optically inactive product. Draw the structure of the aldaric acid formed and comment on their optical activity?

How would you convert D-glucose to a mixture of methyl  $\alpha$ -D-glucopyranoside and methyl  $\beta$ -D-glucopyranoside? Draw the mechanism.

(b) Using nitration of pyrrole as an example, predict whether electrophilic aromatic substitution occurs predominantly at carbon-2 or carbon-3.

Is maltose a reducing sugar? Does it mutarotate? Explain your reasoning.

When phenylhydrazine is reacted with 2-hexanone under conditions of the Fischer indole synthesis, a mixture of two isomeric indoles is formed. Give their structures and explain.

### Group-B

3. Answer **any three** questions from the following:

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(a) The typical stretching frequency for a carbon-carbon double bond is  $1650\text{ cm}^{-1}$ . Estimate the stretching frequency of a carbon-carbon triple bond assuming that the relative bond force constants of triple and double bonds are in the ratio 3:2.

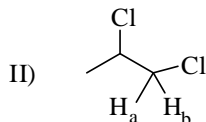
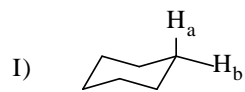
A compound with molecular formula  $\text{C}_7\text{H}_{15}\text{Cl}$  has two  $^1\text{H-NMR}$  absorptions at  $\delta$  1.08 and  $\delta$  1.59, with relative integrals of 3:2, respectively. Give a structure that fits the data provided.

(b) How many  $\pi$  molecular orbitals are there for 1,3,5-hexatriene? Which of the MO's are bonding, antibonding, and frontier molecular orbitals?

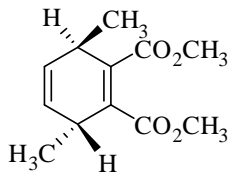
Taking proper example explain secondary orbital interaction in Diels-Alder reaction.

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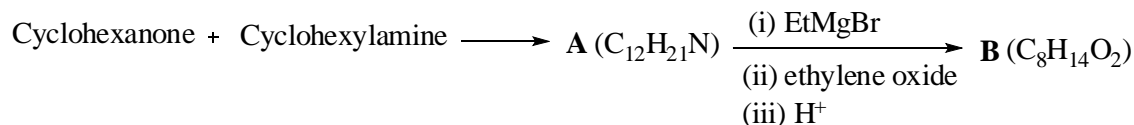
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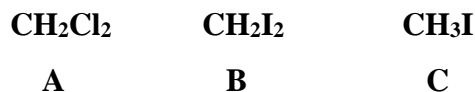
(d) Show the retrosynthetic path and then synthesize the following compound. You are advised to use Diels-Alder reaction.



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(e) In the following set, the proton NMR spectra of the compounds shown consist of a single resonance. Arrange the compounds in order of increasing chemical shift, smallest first.



An unknown compound ( $\text{C}_3\text{H}_2\text{NCl}$ ) shows moderately strong IR absorptions around  $1650\text{ cm}^{-1}$  and  $2200\text{ cm}^{-1}$ . Its  $^1\text{H-NMR}$  spectrum consists of two doublets ( $J = 14\text{ Hz}$ ) at  $\delta 5.9$  and  $\delta 7.1$ . Propose a structure consistent with these data.

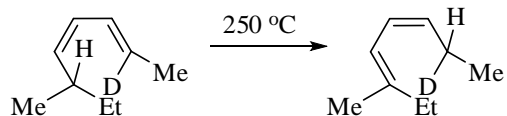
4. Answer **any one** question from the following: **1 × 10 = 10**

(a) Show the retrosynthetic analysis and a synthetic pathway for the preparation of 2-hexanone from ethyl acetoacetate.

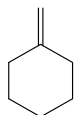
Is Claisen rearrangement a sigmatropic reaction? Justify your choice by providing an example. Give the retrosynthetic pathways and then synthesize 2-bromobutane.

(b) Convert diethyl malonate to 2-oxobutanoic acid .

Assign the values of i and j for the following [i,j] sigmatropic reaction.



Apply retrosynthetic analysis for the following compound and then synthesize it in one step.



Explain in detail how you would use the proton NMR spectra to distinguish between the following compounds.

