

M. Sc. CHEMISTRY EXAMINATION, 2023

(1st Semester, CBCS)

PAPER: II

[ORGANIC CHEMISTRY]

Time : Two Hours

Full Marks : 40

(20 marks for each Unit)

Use a separate answer script for each Unit.

UNIT – 1021

1. a) Draw the complete $^1\text{H-NMR}$ spectrum of 'acrylic acid', briefly explaining the relative chemical shifts of all the protons. Analyse the splitting pattern (multiplicities with approximate coupling constants) of all the proton signals with the help of tree diagrams. 4
- b) Predict the number and multiplicities of the signals in the proton-coupled $^{13}\text{C-NMR}$ spectrum of 'isopropyl benzoate'. 2
- c) Identify with appropriate justification the spin system (Pople notation) formed by the protons in 3, 5-dinitrobenzoic acid. What would be the change in multiplicities of the signals for the other protons in the spin system if H-4 is spin-decoupled? 2
- d) Write down the name and structure of a paramagnetic shift reagent. Explain its role in NMR spectroscopy. 2

[Turn over

[2]

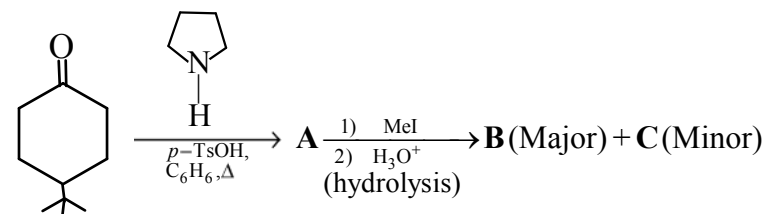
- e) At -115°C the methine proton of chlorocyclohexane resolves into two sets of signals. The one at δ 4.50 ppm appears as a broad singlet, while the other at 3.80 ppm as a well-resolved multiplet. Explain. 3
- f) Interpret the given peaks appearing in the EI-mass spectra of the following molecules: 1+1+1
- Anisole : m/z 93, 78.
 - 1-Heptene : m/z 56, 41.
 - N-Ethylacetamide : m/z 72, 30.
- g) "Mass spectrometry provides evidence for the isotopic abundance of bromine when studied with a brominated molecule." Explain the statement with the help of probable fragmentation pattern in the EI-mass spectrum of *p*-bromo benzophenone. 2
- h) Briefly explain chemical ionisation technique in mass spectrometry when isobutane is used as the reagent gas. 2

UNIT – 1022

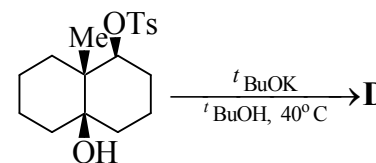
2. a) Comment on the chirality and optical activity of *cis*-decalin and compare its stability with respect to its diastereomer. $(1\frac{1}{2} + 1\frac{1}{2}) + 3$
- b) Discuss about the relative stability between *trans-t-trans* and *cis-t-trans*-perhydrophenanthrenes. 3

[3]

- c) Draw the conformers for one enantiomer of *cis*-2-methyl-5-isopropylcyclohexanone and logically comment on their relative stability. 2
- d) Identify **A**, **B** and **C** in the following sequence and account for the product distribution. $1\frac{1}{2} + 2$



- e) Suggest the product **D** in the following reaction with mechanism. 2



- f) (+)-*trans*-1-Decalone, on bromination, gives a monobrominated product **E**. **E** produces (+)-*trans*-1-decalone on reductive debromination. **E** shows strong negative Cotton Effect. Assign the configurational descriptors (*R/S*) to the ring junctions. $3\frac{1}{2}$