

Ex/SC/CHEM/PG/CORE/TH/II/2025

M. SC. CHEMISTRY EXAMINATION, 2025

(1st Semester)

CHEMISTRY

PAPER : PG/CORE/TH/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) Identify the spin system (Pople Notation) and splitting pattern with approximate chemical shift pattern with approximate chemical shift values for the following molecules (answer *any one*) : 3
(i) Vinyl acetate (ii) Furan-2-aldehyde
- (b) Briefly discuss two methods to convert a second order spectrum to a first order spectrum. 3
- (c) Integration of peaks for proton decoupled ¹³C NMR spectra is often misleading. Explain. 2
- (d) How will you distinguish 1, 4-dimethylcyclohexene and 4, 5-dimethylcyclohexene by EI-mass spectrometry? 2

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[Turn Over]

(2)

(e) Explain how you will obtain peaks at m/z 58 and 85 when 4, 5-dimethylhexane-2-one undergoes fragmentation in EI-mass spectrometer. 2

(f) Answer *any one* of the following questions :

(i) Predict the general appearance of the molecular ion peak from 1, 4-dichlorobutane, considering the chlorine and carbon isotopes only. 2

(ii) ^1H – NMR chemical shifts for 2-methylphenol changes with dilution, whereas ^1H – NMR chemical shifts of methyl salicylate remained unaltered upon dilution. Explain. 2

(g) Answer *any two* of the following questions :

(i) An organic compound with molecular formula $\text{C}_6\text{H}_{12}\text{O}$, shows the following spectral data :

^1H -NMR (CDCl_3 , 400 MHz) : δ 5.25 (1H, dd), 4.20 (1H, dd), 4.04 (1H, dd), 3.62 (2H, t), 1.61 (2H, pent), 1.44 (2H, sext), 0.82 (3H, t).

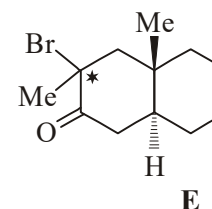
^{13}C -NMR (CDCl_3 , 100 MHz) : δ 12.1, 18.2, 36.1, 65.4, 91.4, 155.3.

Deduce the structure of the compound with justification. 3

(ii) Logically suggest an appropriate structure of the compound having the molecular formula $\text{C}_6\text{H}_{10}\text{Cl}_2\text{O}$ and showing the following spectral data : 3

(5)

(g) Two stereoisomers (**F** and **G**) are obtained by altering the configuration of the stereocentre (indicated by *) in the following molecule **E**. **F** shows strong positive Cotton Effect whereas **G** shows strong negative Cotton Effect. Indicate the preferred conformers of **F** and **G** applying Axial Haloketone Rule (No Octant projection is needed).



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(3)

$^1\text{H-NMR}$ (CDCl_3) : δ 9.8 (1H, t), 2.9 (2H, d),
1.8 (2H, t), 1.4 (2H, sext), 0.9 (3H, t).

$^{13}\text{C-NMR}$ (CDCl_3) : δ 202, 70, 58, 48, 18, 13.

- (iii) Deduce the structure of the organic compound with the following analytical and spectral data with proper justification. 3

Elemental analysis : C : 66.65, H : 6.71

ESI MS : m/z = 180

$^1\text{H-NMR}$ (400 MHz), CDCl_3) : 12.51 (br s),

6.85 (d, J = 7.1 Hz), 7.18 (d, J = 7.1 Hz),

3.98 (q, J = 8.6 Hz), 3.46 (s),

1.23 (t, J = 8.6 Hz).

$^{13}\text{C NMR}$ (100 MHz, CDCl_3) : 15.1, 40, 63.2, 115, 125.1, 130.4, 158.3, 179.1.

- (iv) 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 δ 3.80 ppm appears at a well-resolved multiplet. Explain. 3

UNIT—1022

3. (a) Compare the relative stability between *cis*-decalin and *trans*-decalin. Also comment on the chirality and optical activity of *cis*-decalin. 2+1+2

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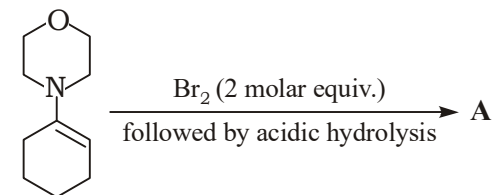
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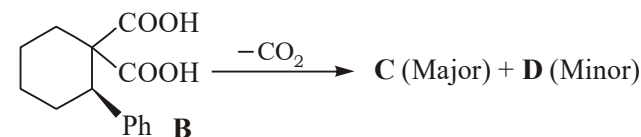
- (b) Discuss about the relative stability between *cis*-cisoid-*trans* and *cis*-*trans*-oid-*trans*-perhydrophenanthrenes. 3

- (c) For isopropylcyclohexane, [equatorial] : [axial] = 97 : 3 whereas for 2-isopropylcyclohexanone, [equatorial] : [axial] = 76 : 24 in their respective conformational equilibrium. Rationalise the change in the relative population of the conformers in the above-mentioned equilibria. 2

- (d) Logically predict the major product **A** of the following reaction. 2



- (e) Decarboxylation of the following compound **B** gives two compounds **C** and **D** respectively. Suggest the structures of **C** and **D** and rationalize their formation from mechanistic standpoint. 2



- (f) (–)-*trans*-10-Methyl-2-decalone shows negative Cotton Effect. Logically assign the configurational descriptors to the stereocentres. 3

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