M. Sc. Chemistry Examination, 2019

(1st Semester)

Organic Chemistry

Paper - II

Time : Two hours Full Marks : 50

(25 marks for each unit)

Use a separate answerscript for each unit.

UNIT - 1021

1. a) Explain briefly transverse relaxation process on the basis of flip-flop mechanism. 2

   b) Predict with justification the appearance of ^{1}H-NMR spectrum of an ultra pure sample of ethanol. Analyse the splitting pattern with the help of tree diagram.

   [Given : $\underline{J}_{CH_3, CH_2} = 7Hz$, $\underline{J}_{CH_2, OH} = 5Hz$] $2\frac{1}{2}$

   c) The proton-coupled ^{13}C-NMR spectrum of a neutral compound of molecular formula $C_{10}H_{12}O_2$ showed the following signals :

   δ 22 (q)

   68 (d)

   128 (d)

   129 (d)

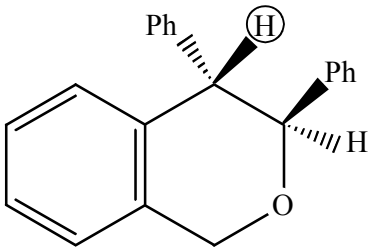
131 (s)

132 (d)

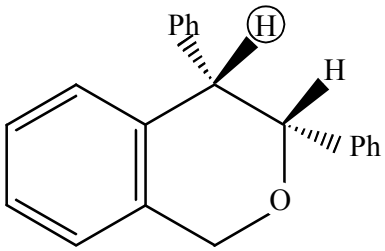
166 (s)

Logically deduce its structure. $2\frac{1}{2}$

d) The following two molecules **A** and **B** are irradiated with a radio frequency that is the resonance frequency of the encircled proton in **A** and **B**, respectively, while recording their respective proton NMR spectrum.



A



B

State what will happen in both the cases with proper explanation. 2

e) Identify the spin system (Pople notation) formed by aromatic protons in 4-nitroaniline. Give reason. 1

d) Write the structure of the products with justification focussing on the stereochemical aspects of the reaction of each of *cis*-and *trans*-6-ethyl-2-cyclohexenyl brosylate with piperidine. 3

j) ^{1}H-NMR spectrum of a compound having molecular formula $C_{10}H_{12}O_2$ shows the following signals :

δ 12·3 (1H, s)

7·2 - 7·3 (5H, m)

3·4 (1H, t)

2·1-2·2 (1H, m)

1·8-1·9 (1H, m)

0·9 (3H, t)

Logically suggest a structure for this compound. The EI mass spectrum of this compound shows two fragment ions at *m*/*z* 119 (62%) and 91 (100%). What are the feasible structures for these ions. 4

UNIT - 1022

2. a) Draw the conformation(s) of *cis*-*transoid*-cis-perhydrophenanthrene, and comment on the interaction energies, chirality and point group of the same (of the more stable conformer). 4

b) State 'Octant rule'. Assign with the help of this rule,the absolute configuration of (–)-*trans*-1-decalone, that shows positive Cotton effect. 4

c) i) How can *cis*-and *trans*-N-benzyl-2,6-dimethyl piperidines be distinguished by ^{1}H-NMR based on the nature of the peaks of their benylic protons ? Justify your answer. 2

ii) Draw the most stable conformation of *cis*-2-methyl-5-*tert*-butyl-1,3-dioxane, and account for your answer. 2

d) State 'Axial haloketone rule'. Applying this rule state which is the most stable conformation of 2-chloro-5-methylhexanone (**C**), that shows negative Cotton effect in isooctane. **C** is a pure crystalline chlorination product obtained after isolation and purification of a crude product of chlorination of (+)-3-methylcyclohexanone. 4

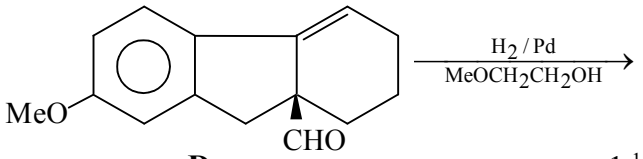
3. Answer ***any three*** of the following questions :

a) i) Draw the structure of the most stable conformer of 1-methyl-1-phenylcyclohexane and account for your answer. 2

ii) Draw the structure of *S-trans*-cyclooctene. 1

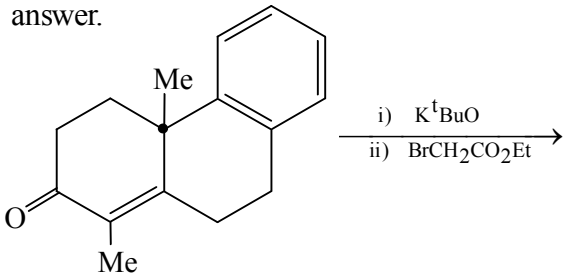
b) Predict the products mentioning expected major/minor, with justification, of the bromination reaction on trans 9-methyl-3-decalone. 3

c) i) What happens when catalytic hydrogenation is carried out on the following compound **D** ? Account for your answer focusing on the stereochemical outcome.



D $1\frac{1}{2}$

ii) Predict the product of the following reaction with proper stereochemical outcome and justify your answer.



$1\frac{1}{2}$

f) *cis*-and *trans*-4-*tert*-Butylcyclohexyl bromides show chemical shifts of 198 Hz and 160·5 Hz (at 60 MHz), respectively for α -H while bromocyclohexane shows a chemical shift of 191·5 Hz. Assuming that the presence of the *tert*-butyl group does not affect the chemical shifts, the equilibrium constant 'K' is found to be 4·8 (at the temperature of the experiment) corresponding to 83% of equatorial population. Justify the statement. 3

g) Interprete the given peaks appearing in the EI-mass spectra of the following molecules : $1\frac{1}{2}+1\frac{1}{2}+1\frac{1}{2}$

i) 2-Phenylethyl acetate : *m*/*z* 104, 91, 43.

ii) Ethyl 2-hydroxybenzoate : *m*/*z* 166, 120, 92.

iii) *N*-Ethylacetamide : *m*/*z* 87, 72, 30.

h) In the EI mass spectrum of *n*-butylbenzene, the peak appearing at *m*/*z* 92 (59%) is a pure carbon isotope peak for the peak appearing at *m*/*z* 91 (100%). State whether the statement is true or not. Justify your answer. $1\frac{1}{2}$

i) Briefly explain the basic differences between EI and CI mass spectrometry. 2