M.Sc. CHEMISTRY EXAMINATION, 2018

(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 why the detection of carbon signals is difficult compared to detection of proton signals in respective NMR experiment. 2

   (b) What kind of a curve is FID ? $^1/_2$

   (c) What is the role of FT in FT NMR ? $^1/_2$

   (d) Write down the name and structure of a paramagnetic shift reagent. Mention two uses of these reagents. 2

   (e) Identify the spin system (Pople notation) formed by the protons in 1,2,3-trinitrobenzene. What would be the change in multiplicities of the signals for H-4 and H-6 if H-5 is spin decoupled ? $1^1/_2$

   (f) Justify the following statements : $1^1/_2+1^1/_2$

   (i) The ^{1}H-NMR spectrum of N, N-dimethyl-formamide at 150°C shows only one signal for the two methyl groups whereas the same recorded at 25°C shows two signals.

(ii) One diastereomer of 1,3,5-trimethylcyclohexane shows three signals in its proton-decoupled ^{13}C-NMR spectrum.

(g) A compound having molecular formula $C_8H_{14}O_3$ has strong infrared absorption at 1757 and 1828 cm^{-1}. The proton-decoupled ^{13}C-NMR spectrum of this compound has three discrete signals. Its ^{1}H-NMR spectrum shows the following signals : δ 1.20 (d, J = 6.7Hz) and 2.70 (septet, J = 6.7Hz) with the integration ratio 6 : 1. Logically suggest a structure for this compound. The EI mass spectrum of this compound shows two abundant fragment ions, at *m/z* 71(100%) and 43 (88%). What are the feasible structures for these ions ? 4

(h) Identify with proper justification the protons of methyl acrylate showing the following signals in its ^{1}H-NMR spectrum.

δ 3.7 (3H, s)

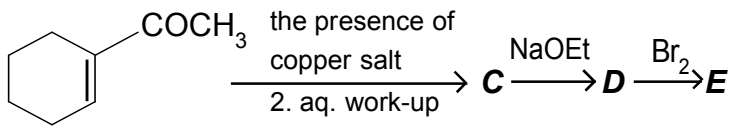
5.8 (1H, dd, J = 10.5, 1.4 Hz)

6.1 (1H, dd, J = 17.4, 10.5 Hz)

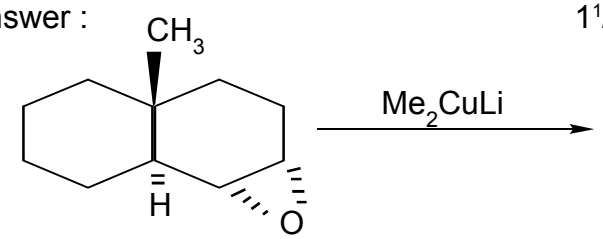
6.4 (1H, dd, J = 17.4, 1.4 Hz)

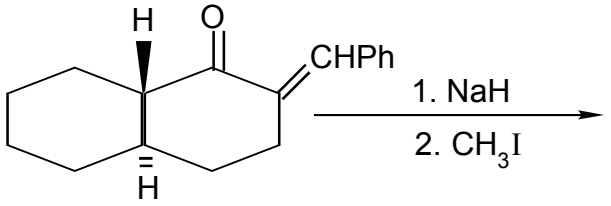
Analyse the splitting pattern of proton signals with the help of tree diagram and draw the complete spectrum. 4

(b) Complete the following sequence of reactions with justification : 3

(i) 

(c) Write the structure of the product(s) with proper stereochemical outcome with mention of the major/ minor product where applicable and account for your answer : $1\frac{1}{2} + 1\frac{1}{2}$

(i) 

(ii) 

(d) What is the basis of optical activity of a chiral compound ? 3

— X —

(i) Predict the general appearance of the molecular ion peaks for 1,3,5-trichlorobenzene in its EI mass spectrum, considering the chlorine and carbon isotopes only. Calculate also the relative abundances of all those peaks, when it is given that among all those peaks which correspond to molecular ions, the peak appearing at the lowest *m/z* value is the base peak for the molecule. 3

(j) The EI mass spectrum of toluene records two strong peaks at *m/z* 91 and 65 and a broad peak at *m/z* 46.4. Explain this observation. $1^1/_2$

(k) Interprete the given peaks appearing in the EI-mass spectra of the following molecules : $1^1/_2+1^1/_2$

(i) 1-Heptene : *m/z* 98(16%), 56(100%), 41(98%)

(ii) Maleic anhydride : *m/z* 98(20%), 54(100%), 26(98%).

UNIT - 1022

2. (a) State Octant rule. With the help of this rule deduce the conformation of (+) - *cis*-10-methyl-2-decalone that shows negative Cotton effect. 4

(b) Discuss on the conformation, interactions, interaction energies and relative stability of *trans-transoid-trans*- and *trans-transoid-cis*-perhydrophenanthrenes. 4

(c) What happens when each of *cis*-and *trans*-2-phenylcyclopentyl tosylate is separately reacted with K^tBuO in ^tBuOH ? What will happen if the said reaction of the *trans*-substrate is performed in the presence of an 18-crown-6 ? 4

(d) (i) Applying 'Axial haloketone rule' deduce the configuration of (–) – *trans*–1– decalone ***(A)*** based on the following experimental observations : 3

$$\boldsymbol{A} \xrightarrow{Br_2} \boldsymbol{B}$$

I : ***B*** on catalytic reduction gives pure *trans*-1-decalone.

II : ***B*** exhibits positive Cotton effect.

(ii) State any two limitations of the comparison method based on empirical/semiempirical rules, used for deduction of configuration/conformation/ position of functional group of a chiral molecule having cyclohexanone skeleton. 1

3. Answer any ***three*** of the following questions : 3x3

(a) 2-Bromobutane-3-d on reaction with base produces undeuterated *trans*-butene and deuterated *cis*-butene. What stereochemical and mechanistic implication does it reflect from the stated observation ? Discuss elaborately with Newmann conformations of the starting molecule. 3