

M. Sc. CHEMISTRY EXAMINATION, 2017

(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

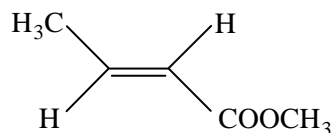
1. a) Explain briefly the following : 2+2
- i) Longitudinal relaxation process
 - ii) ^{13}C - Satellite peaks
- b) A slightly acidic compound of molecular formula $\text{C}_7\text{H}_6\text{O}_2$ gave a precipitate with 2, 4 - dinitrophenylhydrazine. Its proton-coupled ^{13}C NMR spectrum showed the following signals : $\delta 117(\text{d})$, $\delta 130(\text{s})$, $\delta 133(\text{d})$, $\delta 164(\text{s})$ and $\delta 191(\text{d})$. Logically deduce its structure. 2
- c) A compound having molecular formula $\text{C}_9\text{H}_{12}\text{O}$ has strong infrared absorption at 3300 cm^{-1} to 3400 cm^{-1} . The proton-decoupled ^{13}C NMR spectrum of this compound has six discrete signals. Its ^1H -NMR spectrum has three sets of lines : singlets at $\delta 1.1(6\text{H})$, $1.9(1\text{H})$ and

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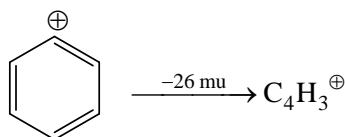
7.3(5H) ppm. Logically suggest a structure for this compound. 3

- d) Draw and explain complete $^1\text{H-NMR}$ spectrum of the following molecule :



Analyse the splitting pattern of proton signals with the help of tree diagram. 3

- e) Explain the following facts : 3+1
- The $^1\text{H-NMR}$ spectrum of chlorocyclohexane, recorded at -115°C , showed among other peaks two relatively down field signals : one, a broad singlet at δ 4.50 ppm and another, a well resolved multiplet at δ 3.80 ppm.
 - In CI-MS where isobutane is used as the reagent gas, spectra are typically acquired above m/z 60 or 70.
- f) Calculate the expected apparent mass of the metastable ion produced when the following fragmentation process takes place in the second field free region of a double focusing EI-mass spectrometer. 1

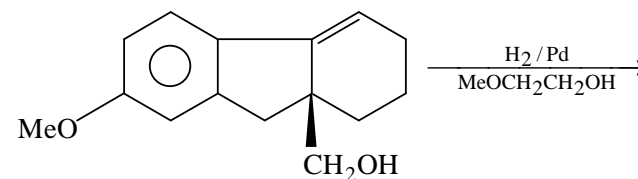


[5]

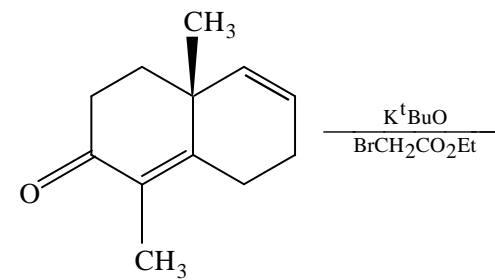
curve in octane solution and a bisignate curve in methanol solution. 3

- d) Give the structure of the product(s) with stereochemistry, and mention as major / minor, if applicable. 2

i)



ii)



- e) Draw the structure of *R-trans*-cyclooctene. 1

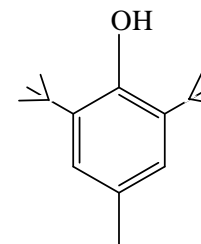
[4]

UNIT - 1022

2. Discuss on the stereochemical outcome of *any three* of the following reactions : 4×3
- Bromination of 2-keto- and 3-keto-steroids (only partial structure of the substrate and product involving rings A-B will do).
 - Reaction of 2 α -hydroxy-10 β -methyl- $\Delta^{1,9}$ -octalin separately with (i) TBHP, Mo(CO)₆ and (ii) mCPBA. Also comment on the major / minor / main product(s).
 - Reaction of *cis*- and *trans*-6-isopropyl-2-cyclohexenyl tosylate separately with piperidine.
 - Saponification of 2 α -acetoxy-9 α -hydroxy-10 β -methyl decaline vs. that of 2 β -acetoxy-9 α -hydroxy-10 β -methyl decaline. Comment on their relative rate of reaction also.
3. a) Discuss on the conformation, interactions, interaction energies and relative stability of *trans-transoid-trans*- and *trans-transoid-cis*-perhydroanthracenes. 4
- Describe 'Octant rule'. With the help of this rule determine the absolute configuration of (-)-trans-1-decalone, that shows positive cotton effect. 1 $\frac{1}{2}$ + 1 $\frac{1}{2}$
 - Account for the following observations : (-)-Menthone shows a positive CD curve in water but a negative CD

[3]

- g) Interpret the following statements : 1 $\frac{1}{2}$ + 1 $\frac{1}{2}$ + 2
- The EI mass spectrum of anisole shows peaks at m/z 108, 93 and 78.
 - The EI mass spectrum of ethyl crotonate shows peaks at m/z 114, 86 and 69.
 - The EI-mass spectrum of the following molecule gives peaks at m/z 221 (4 – 5%), 220 (24%), 206 (15%) and 205 (100%) :



- h) It is known that in a magnetic analyzer of a mass spectrometer, $\frac{m}{z} = \frac{B^2 r^2}{2V}$. Interpret the terms involved in the equation and explain its significance in the construction of a mass analyzer tube. 3

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