45

EASTERN UNIVERSITY, SRI LANKA
SECOND EXAMINATION IN SCIENCE (FIRST SEMESTER) – MAY 2001
CH203 - ORGANIC SPECTROSCOPY

Time allowed: 01 Hour.

Answer all the parts

1. a) A solution of 1.03 mg of benzonitrile (PhCN) in ethanol (100 cm^3) had an absorbance of 1.20 at 224 nm, when measured in a 2 cm cell. What is molar absorptivity (molar extinction coefficient) of this band?

   b) (i) The chemical shift of protons in benzene is 7.27 ppm. Would the ^1H signals for nitrobenzene appear at low (down) field or high (up) field from that of benzene? Explain your answer.

   (ii) Give the increasing order of the chemical shift (δ) values of protons in the methyl group of the following compounds. Give reason(s) for your answer.

   CH_3NH_2, CH_3F, CH_3OH

   c) (i) C==O stretching frequency in an ester is greater than that in an amide. Explain.

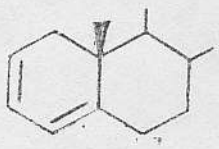
   (ii) The mass spectrum of an organic compound had two sets of peaks and each set having 2 peaks of equal intensity; one set occurs at m/e 200 and 198 and the other at 157 and 155. What inference could you make from this observation? (no details required)

   d) The chemical shift for a particular proton is 366 Hz in 60 MHz proton NMR. Express its absorption in terms of δ and τ.

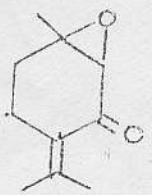
Contd...

2. a) (i) Using Woodward-Fieser-Scott rules, calculate the λ_{max} value of the UV absorption band of the following compounds.

I)



II)



(ii) The mass spectrum of 1-Phenylethanol showed fragmentations at 107, 79 77 and 51. Give the structures of these ions and indicate the possible pathways for their formations.

b) An organic compound A ($C_{11}H_{12}O_2$) showed absorptions at 3030, 2850, 1690, 1620, 1050 and 830 cm^{-1} in its IR spectrum. The ^1H NMR spectrum of A had signals at δ 7.80 (d, J= 16 Hz, 1H), 7.45 (d, J= 9Hz, 2H), 7.05 (d,J= 9Hz, 2H), 6.10 (d, J= 16Hz, 1H), 3.90 (s,3H) and 2.05 (s,3H). Interpret the given spectral data and deduce the structure of the compound A.

c) Briefly explain how you would distinguish between the members of each of the following pairs of compounds using the method indicated in the bracket.

(i) Orthohydroxybenzaldehyde and Parahydroxybenzaldehyde (IR)

(ii) 2,4-Dimethylpentan-3-one and 2,2-Dimethylpentan-3-one (MS)