EASTERN UNIVERSITY, SRI LANKA
SECOND EXAMINATION IN SCIENCE
EXTERNAL DEGREE (2004)
EXCH 202 SPECTROSCOPIC METHODS, REACTION MECHANISM AND AROMATICITY

Time: 02 hours

Answer four questions only

1. Answer both parts (a) and (b).

a. Three isomeric compounds **A**, **B** and **C** having the molecular formula $C_4H_8O_3$ gives the following ^1H NMR spectra. Deduce the plausible structures of these compounds.

Compound **A** (δ): 1.3 (3H, t, J=7Hz), 3.6 (2H, q, J=7Hz), 4.15 (2H, s) and 12.1 (1H,s)

Compound **B** (δ): 1.2 (3H, d, J=7Hz), 2.35 (2H, d, J=7Hz) and 4.15 (1H, sextet, J=7Hz). The spectrum runs in D_2O.

Compound **C** (δ): 3.5 (3H, s), 3.8 (3H, s) and 4.05 (2H,s).

b. Describe the following terms using suitable examples.

i) Chromophore (UV)
ii) Blue shift (UV)
iii) Bending Vibration (IR)

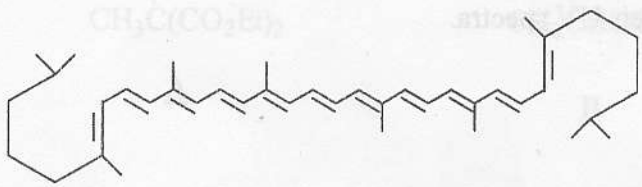
2. Answer all the parts (a), (b), (c) and (d).

a. i. The Fieser-Kuhn equation for calculating the λ_{max} values of polyenes in hexane solution is given below.

$$\lambda_{max} = 114 + 5M + n\,(48.0 - 1.7n) - 16.5R_{endo} - 10R_{exo}$$

Identify all the terms in the above equation.

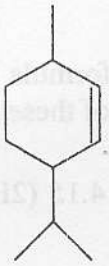
ii) Calculate the wavelength corresponds to maximum absorption of the compound.



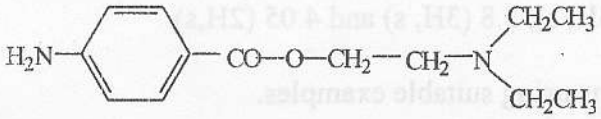
b. Briefly describe how you would distinguish between the members of each of the following pairs of compounds using the methods indicated within the brackets.

1. $CH_3(CH_2)_4CH_2OH$ and $CH_3CH_2\underset{\displaystyle OH}{\underset{|}{C}}HOH$ (IR)

2. $CH_3\overset{\displaystyle O}{\overset{\|}{C}}CH_3$ and CH_3CH_2CHO (IR)

3.  and  (UV)

c. The structure of the dental local anesthetic, procaine is shown below.



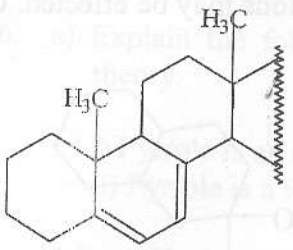
Draw the ^{1}H NMR spectrum of the above compound indicating the approximate chemical shift values of different protons and the multiplicities of the signals.

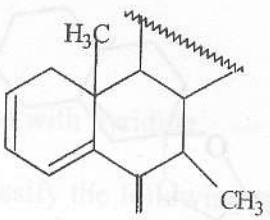
d. A compound **D**, of the molecular formula $C_7H_7NO_2$ reacts with both dil. acid and base. **D** is one of the components of folic acid and plays a vital role in the growth of bacteria. From the following IR spectral data, deduce the structure of the compound **D**.

(cm^{-1}): 3450, 3360, 3050, 3000-2500 (broad band), 1700, 1680, 1180 and 830.

3. Answer all the parts.

a. Using Woodward – Fieser - Scott rule to calculate the λ_{max} values of the following compounds in their UV spectra.

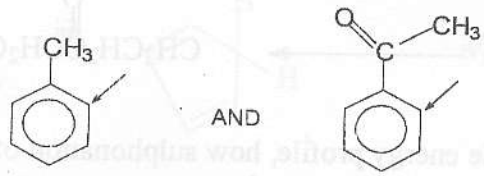
1. 

2. 

b. In each of the following pairs of compounds, predict which of the designated protons will have lower δ value in ^{1}H NMR spectra. Explain your choice.

(i) $CH_3—F$ AND $CH_3—Cl$

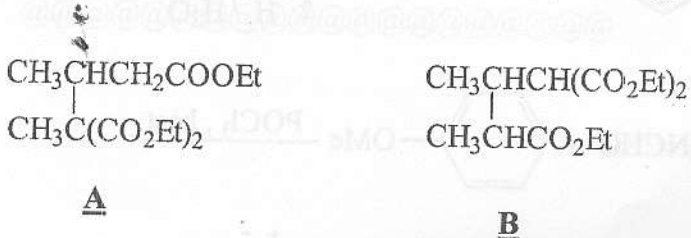
(ii) $CH_3—CH_2—Br$ AND $CH_3—CH_2—CH_2—Br$

(iii) 

c. One molar solution of cyclohexanol in CCl_4 shows IR absorption band at 3640 (weak) and 3320 (strong) cm^{-1}. But 0.03 molar solution shows only one absorption band at 3640cm^{-1}(strong). Explain.

d. The E_1 mass spectrum of methyl octanoate shows peaks at m/z values 158, 127, 87, 74 and 59. Give the structures of the ions responsible for these peaks.

4. a) When diethyl methylmalonate [$CH_3CH(COOEt)_2$] is added to ethyl crotonate ($CH_3CH=CHCOOEt$) in the presence of an equimolar amount of sodium ethoxide (NaOEt), the product **B** formed, instead of the expected product **A**. Explain.



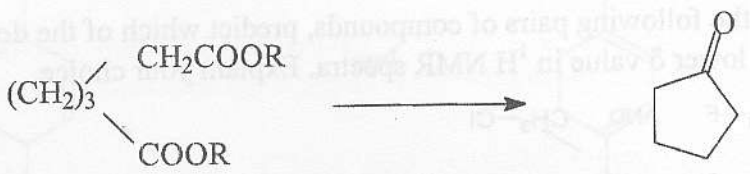
A **B**

b) Explain why the α-position of naphthalene is more reactive than its β-position.

c) By means of equations show how the following conversions may be effected. Give essential experimental conditions.

i)

ii)



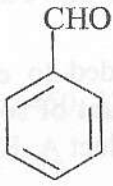
iii) $CH_3CH_2CN \longrightarrow CH_3CH_2\overset{O}{\overset{\|}{C}}CH_2CH_3$

5. a) Explain, with the help of a suitable energy profile, how sulphonation of naphthalene under different conditions can lead to different products.

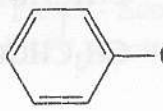
b) How would you show by chemical degradation that naphthalene contains two benzene nuclei?

c) For the following reactions, give the structure of the major product that would be formed in each case and suggest plausible mechanisms for the reactions involved in the formation of these major products.

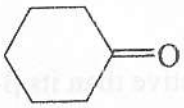
i)



+ $(CH_3CO)_2O$ $\xrightarrow[2.\ H^+/H_2O]{1.\ CH_3COONa}$

ii) Me_2NCHO +  $\xrightarrow{POCl_3,\ heat}$

iii)

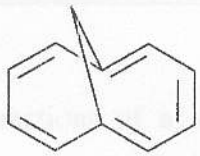


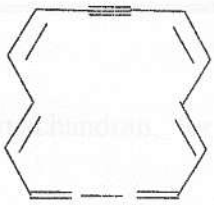
$\xrightarrow{Ph_3\overset{+}{P}\overset{-}{C}HCH_3}$

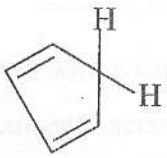
6. a) Explain the following properties of pyrrole based on the molecular orbital theory.

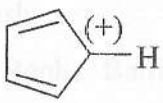
i) Pyrrole is an aromatic compound.
ii) Pyrrole is a weak base in comparison with pyridine.

b) State Huckel's rule for aromaticity. Classify the following species as aromatic, anti aromatic or non-aromatic. Give reasons for your classification.

i) 

ii) 

iii) 

iv) 

c) Giving reasons, arrange the following compounds in increasing/decreasing order of their aromatic stability.

Furan, Thiophen and pyrrole.

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