EASTERN UNIVERSITY, SRI LANKA
SECOND EXAMINATION IN SCIENCE 1998/99 RE-REPEAT
EXCH 202 MOLECULAR SPECTROSCOPY, AROMATICITY AND REACTION MECHANISM

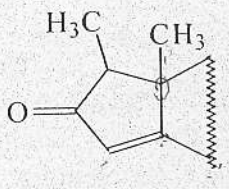
Time: 02 Hours

Answer FOUR questions only

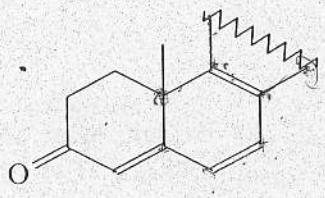
1) Answer **all** parts (a), (b) and (c).

a) Calculate the λ_{max} values of the UV absorption band of the following compounds

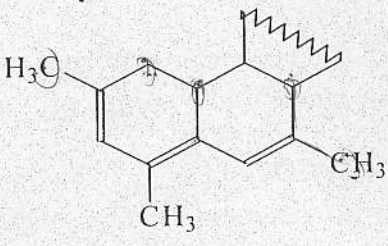
i)



ii)



iii)



b) i) Give the equation which relates the absorbance of a solution to its concentration and identify all the terms in it.

ii) The UV spectrum of a solution containing 20.5 mg of $CH_3OCH{=}CHC{\equiv}CH$ in 100 ml ethanol when measured in a 2 cm cell had a band at 235 nm with an absorbance 0.70. Calculate the molar absorptivity, ε, of $CH_3OCH{=}CHC{\equiv}CH$ at 235 nm.

c) The mass spectrum of $CH_3COCH(CH_3)CH_2CH_3$ showed fragmentations at m/e 100, 85, 72, 57 and 43. Give structures of these fragmented ions and indicate the possible pathways for their formation

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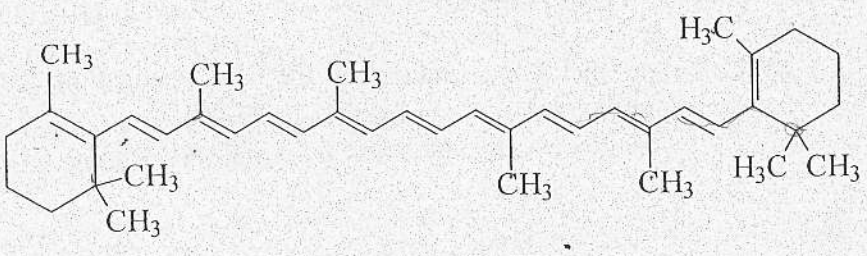
2) Answer **all** parts (a), (b) and (c).

a) i) The Fieser-Kuhn rule for polyene is given by

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

Identify all the terms in it.

ii. Calculate the λ_{max} value of β-carotene.



b) Explain why acetonitrile (CH_3CN) has resonance at δ 1.97 while methyl chloride (CH_3Cl) has resonance at δ 3.05, even though the electro negativity of cyano group is larger than that of the chlorine atom.

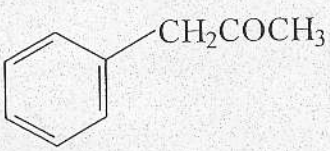
c) Give the increasing order of C=O stretching frequencies of the following compounds. Give reason(s) for your answer.

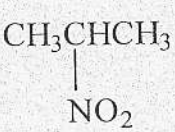
RCOOR′, $RCONH_2$, RCOCl

3) Answer **all** parts (a), (b) and (c).

a) An organic compound **A** ($C_8H_8O_2$) showed weak absorption at about 3000cm^{-1}, 2850 cm^{-1} and 2750 cm^{-1} and strong absorption at 1680 cm^{-1}, 1260 cm^{-1}, 1030cm^{-1} and 840 cm^{-1}. ^1H NMR spectrum of the compound **A** had signals at δ 10.0 (s, 1H), 7.5 (dd, 4H), 3.9 (s, 3H).
Interpret the given data and deduce the structure of the compound **A**.

b) Sketch the proton NMR spectrum including multiplet patterns expected for the following compounds with TMS as standard. Predict the approximate chemical shifts in your spectrum.

i) 

ii) 

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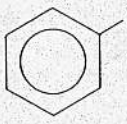
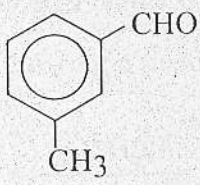
c) Explain why the position of the OH resonance of phenol varies with concentration in solution. But the hydroxy proton of *ortho*-hydroxyacetophenone does not show any great shift upon dilution.

4) Answer **all** parts (a), (b) and (c).

Write the mechanism for each of the following reactions. Indicate all the steps clearly.

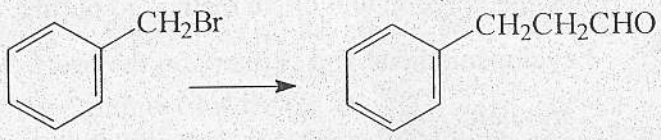
a)  + $CH_2(COOEt)_2$ $\xrightarrow[\text{ii) } H^+/H_2O,\ \text{Heat}]{\text{i) Pyridine}}$

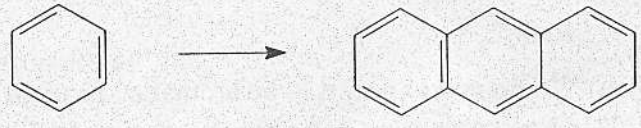
b) 2  $\xrightarrow[\text{EtOH/Heat}]{\text{NaCN/HCl}}$

c) $CH_3CHO + CH_3OH \xrightarrow{HCl(g)}$

5. Answer **all** parts (a), (b) and (c).

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

i) 

ii) 

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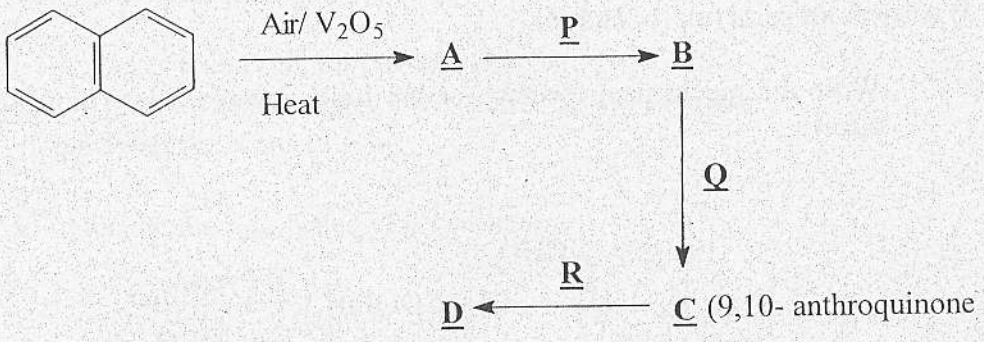
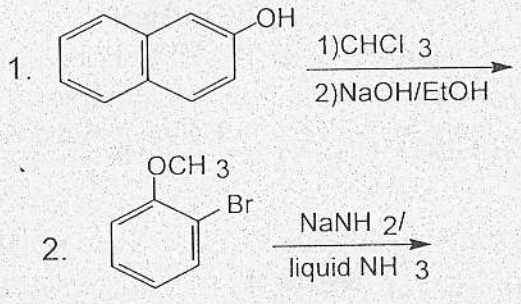
b) Give the structures of the compounds **A**, **B**, **C**, **D** and identify **P**, **Q**, and **R**.



c) Draw the structures of the products you would expect for each of the following reactions.



6. Answer **all** parts (a), (b) and (c).

a) State Huckel's rule.

b) i) Use the polygon and circle method to outline the π molecular orbitals of cyclopentadiene and explain, on the basis, why cyclopentadiene is not aromatic.

ii) What electron distribution would you expect for the cyclopentadienyl anion?

iii) Would you expect it to be aromatic? Explain your answer.

iv) Would you expect the cyclopentadienyl anion to be aromatic on the basis of Huckel's rule?

c) Why basicity of aliphatic amines is greater than that of pyridine.

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