EASTERN UNIVERSITY, SRI LANKA
SECOND EXAMINATION IN SCIENCE
EXTERNAL DEGREE
EXCH 202 SPECTROSCOPY, AROMATICITY AND REACTION MECHANISM
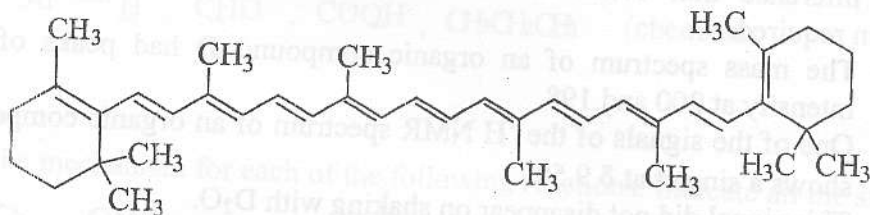### REPEAT 2002/2003 (2004)

Time: 03 Hours

ANSWER FOUR QUESTIONS ONLY

1.a. i. The Fieser-Kuhn rule for polyene is

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

Identify all the terms in it.

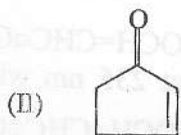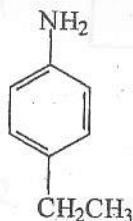ii. Calculate the longest wavelength λ_{max} value of β-carotene.

b. Write the definition of the following terms
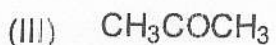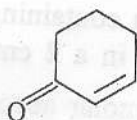   i. Stretching vibration
   ii. Auxochrome

c. Briefly explain how you would distinguish between the members of each of the following pairs of compounds using the methods indicated.
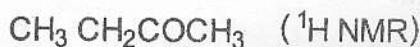

(I) AND (IR)

(II) AND (UV)

(III) CH_3COCH_3 AND $CH_3\,CH_2COCH_3$ (^{1}H NMR)
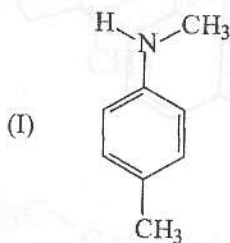
2. a. An organic compound $\underline{A}$ ($C_8H_8O_2$) shows absorption at 3 030, 2 900, 2 850, 1 620, 1050 and 830 cm^{-1} in its IR spectrum. Its ^1H NMR spectrum has signals at δ 3.90 (s, 3H), 7.05 (d, J=9Hz, 2H), 7.45 (d, J=9Hz, 2H) and 9.55 (s, 1H).

Interpret the given data and deduce the structure of the compound $\underline{A}$.

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) $CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_3$ (II)
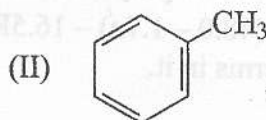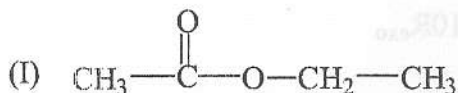
c. Give the inference that could be made from the following observation; no explanation required.

   i. The mass spectrum of an organic compound $\underline{D}$ had peaks of equal intensity at 200 and 198

   ii. One of the signals of the ^1H NMR spectrum of an organic compound $\underline{E}$ shows a singlet at δ 9.50
   This signal did not disappear on shaking with D_2O.

3. a. Using Woodward – Fieser – Scott rule, calculate the wavelength of maximum absorption λ_{max} in the UV spectrum of the following compounds.

(i)

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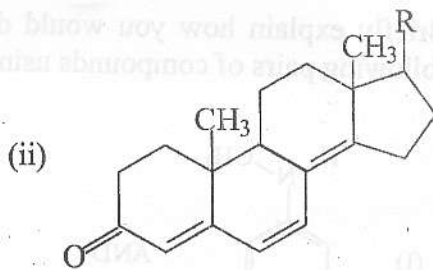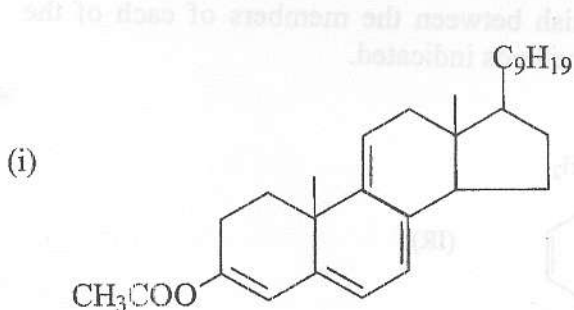
b. (i) Give the equation which relates the absorbance of a solution to its concentration and identify all the terms in it.

   (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. Explain the following

The compound (i) has lower λ_{max} of absorption than the compound (ii).
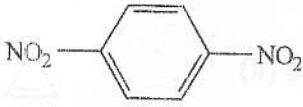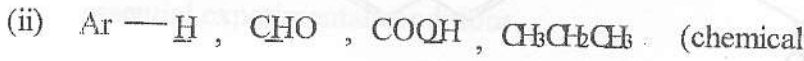

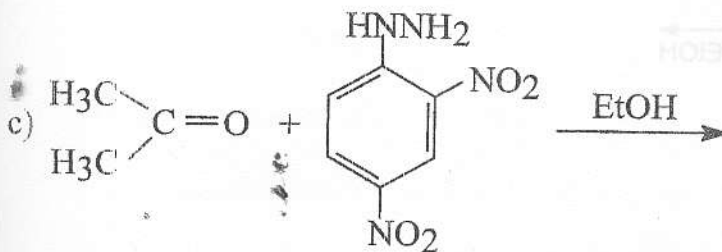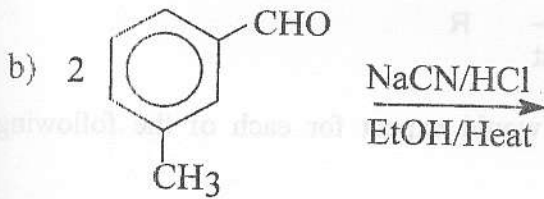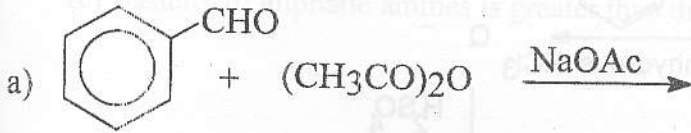(i)   (ii)

d. Arrange the compounds in each of the following groups in the order of increasing values, which are indicated within the brackets.

(i) $>C-H$, $>C-O$, $>C=O$, $Ar-H$ (Stretching

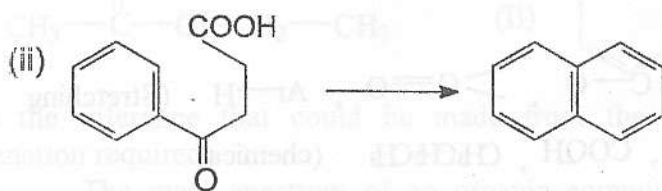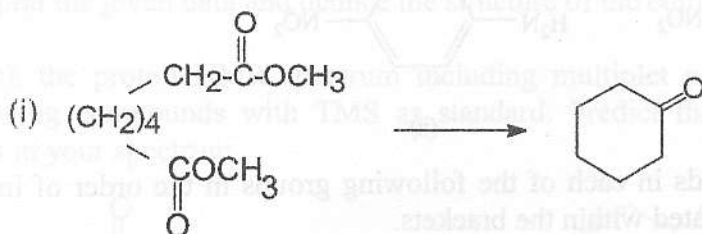(ii) $Ar-H$, CHO , $COOH$, $CH_3CH_2CH_3$ (chemical

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

a)

$+$ $(CH_3CO)_2O$ $\xrightarrow{NaOAc}$

b) 2

$\xrightarrow[EtOH/Heat]{NaCN/HCl}$

c)

$\xrightarrow{EtOH}$
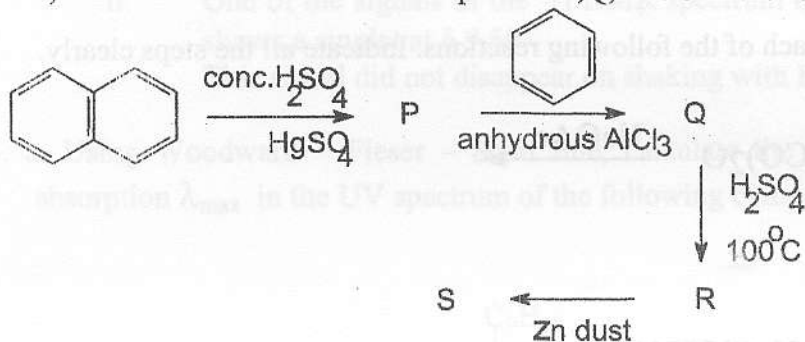
5. a) By means of equations show how the following conversions may be effected. Give essential experimental conditions.

(i)
$(CH_2)_4$ with $CH_2\text{-}C\text{-}OCH_3$ (O) and $COCH_3$ (O) groups $\longrightarrow$ cyclohexanone

(ii)
benzene ring with $CH_2\text{-}CH_2\text{-}COOH$ and $C=O$ group $\longrightarrow$ naphthalene derivative

b) Give the structures of the compounds P,Q,R & S in the following reaction sequence.

naphthalene $\xrightarrow[\text{HgSO}_4]{\text{conc.}H_2SO_4}$ P $\xrightarrow[\text{anhydrous AlCl}_3]{}$ Q

Q $\xrightarrow[100°C]{H_2SO_4}$ R

R $\xrightarrow{\text{Zn dust}}$ S

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

1. 2-naphthol (OH) $\xrightarrow[\text{2)NaOH/EtOH}]{\text{1)CHCl}_3}$

2.
benzene with OCH_3 and Br groups $\xrightarrow[\text{liquid NH}_3]{\text{NaNH}_2/}$

Contd....

6. (a) Classify the following compounds as aromatic, anti-aromatic or non-aromatic, based on Huckel's rule.
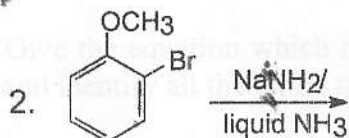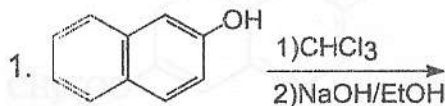
(i)
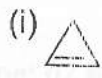
(ii) cyclooctatetraene

(iii) cycloheptatrienyl cation

(b) By means of equations show how the following conversion may be effected. Give essential experimental conditions.

 (+) Br⁻

(c) Basicity of aliphatic amines is greater than that of pyridine. Explain.

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