



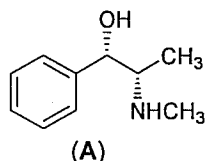
THE OPEN UNIVRVERSITY OF SRI LANKA
B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2012 / 2013
LEVEL 4 - FINAL EXAMINATION
CMU2221 / CME4221 - ORGANIC CHEMISTRY I
DURATION: 3 HOURS

Monday, 9th December 2013

9.30 a.m. - 12.30 p.m.

ANSWER ALL QUESTIONS

1. (a) The structure of (+)-pseudoephedrine (**A**) is given below.



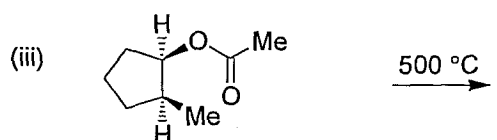
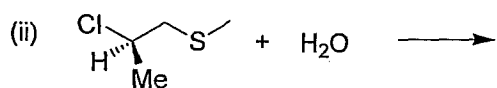
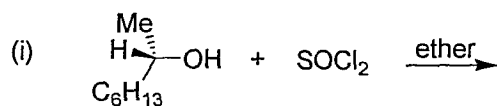
- (i) Label the stereocenters of **A** (as p, q, r, etc.) and determine the configurations of each of them as *R* or *S* showing the priorities of the groups attached to stereocenters according to Cahn-Ingold-Prelog rules.
- (ii) Draw the enantiomer of **A** and label it as **B**.
- (iii) $[\alpha]_D$ value of **A** is $+52^\circ$. What is the $[\alpha]_D$ value of **B**?
- (iv) (**C**) is a diastereoisomer of (+)-pseudoephedrine. Both **A** and **C** gave the same ketone on oxidation. Draw the structure of **C**.
- (v) What is the stereochemical relationship between **B** and **C**?
- (vi) $[\alpha]_D$ of a synthetic sample of (+)-pseudoephedrine was found to be $+41.6^\circ$. Calculate the enantiomeric excess (**ee**) and the percentage of (+)-pseudoephedrine in the synthetic sample.

(40 Marks)

- (b) (i) Give the mechanism of the solvolysis of 2-bromo-2-methylpropane in ethanol.
- (ii) Draw the completely labeled energy diagram for the above reaction.
- (iii) Consider the solvolysis reaction of 2-bromo-2-methylpropane in ethanol containing water. Explain giving reasons what happens to the rate of the reaction when the reaction is carried out with increasing amounts of water.

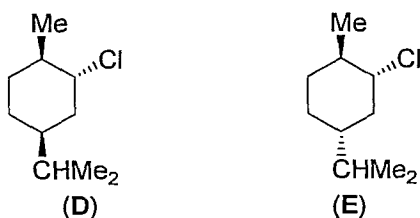
(30 Marks)

(c) Giving the mechanism predict the product of any **one (01)** of the following reactions.



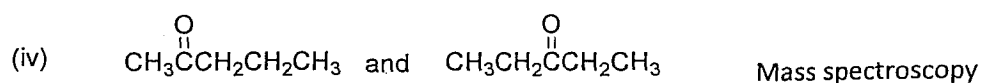
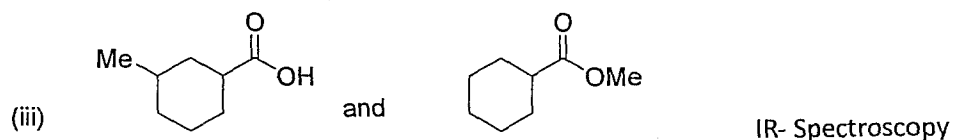
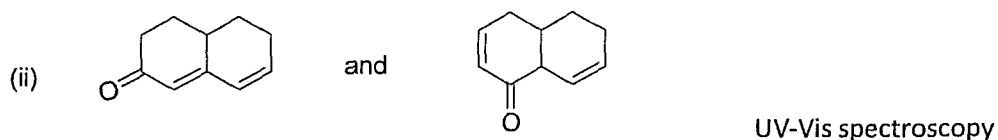
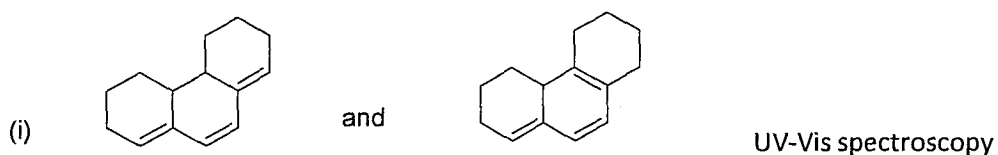
(16 Marks)

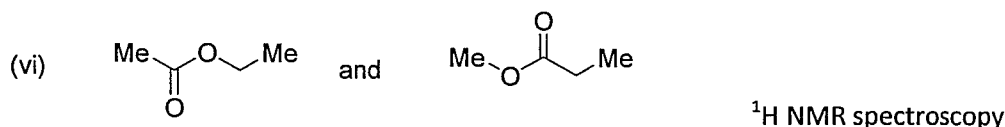
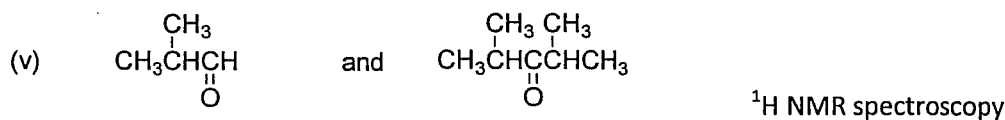
(d) Giving the mechanisms predict the product(s) of when following two compounds (**D**) and (**E**) are reacted with NaOEt in EtOH and comment on the relative rates of the reactions.



(14 Marks)

2. (a) Briefly giving reasons state how you would distinguish between the compounds in any **FOUR (04)** of the following pairs using the indicated spectroscopic method.





(20 Marks)

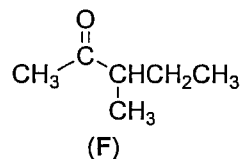
(b) (i) Write down the mathematical relationship (equation) between the stretching frequency, $\bar{\nu}$ and the force constant, (f) of a diatomic molecule.

(ii) Comment on the relative positions of stretching frequencies of C–O and C–H bonds.

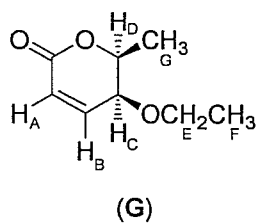
(15 Marks)

(c) Answer any **two (02)** of the following.

(i) Giving the fragmentation pathways predict the structures of major fragment ions and their m/z values of the following compound **F**.



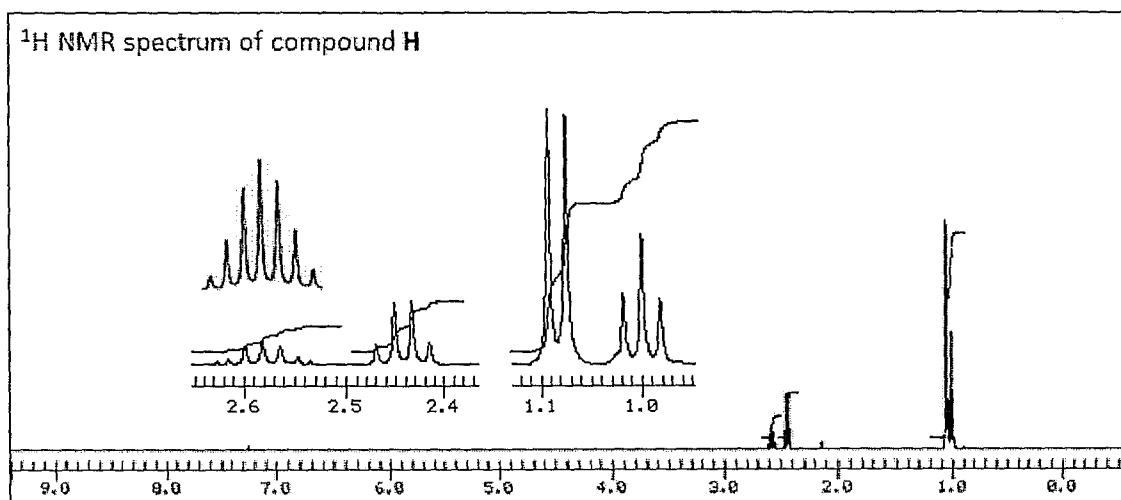
(ii) Sketch the ^1H NMR spectrum of the following compound **G** showing relative positions from TMS (*NOT necessary to give δ values*), multiplicities and numerical values of relative intensities. (*H atoms are labeled from A–G for your convenience*).



(iii) Considering the energy levels of molecular orbitals of C=C and C=O groups construct molecular orbital energy level diagram for an α,β -unsaturated ketone. Sketch the typical pattern of the UV spectrum of an α,β -unsaturated ketone indicating the transitions associated with each peak.

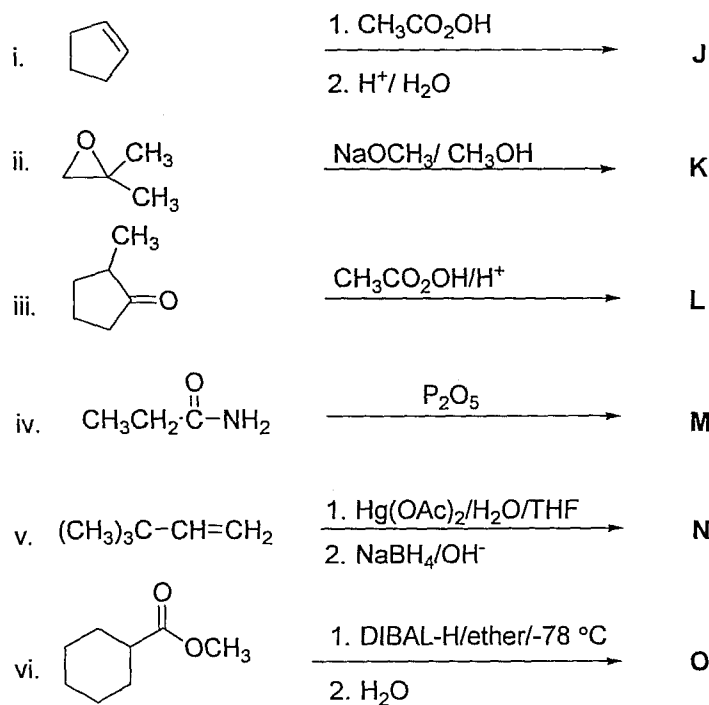
(30 Marks)

- (d) ^1H NMR spectrum of compound **H** ($\text{C}_6\text{H}_{12}\text{O}$) along with some useful expansions is given below. The IR spectrum of **H** showed a strong absorption at 1718 cm^{-1} among other peaks while no absorptions are observed above 2900 cm^{-1} . Deduce the structure of compound **H**.



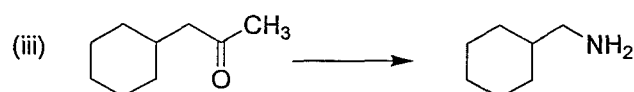
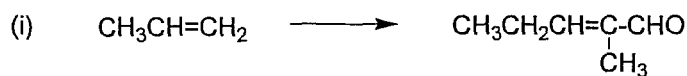
(35 Marks)

3. (a) Give the major products (**J–O**) of the following reactions.



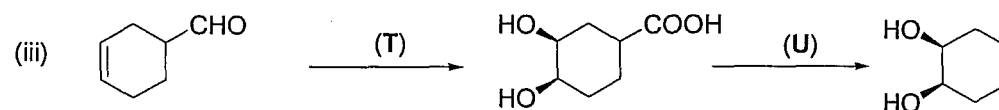
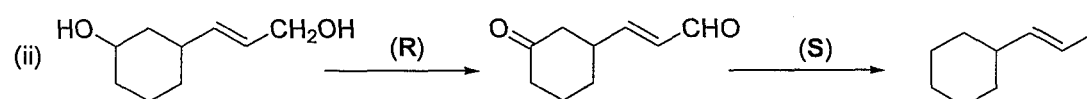
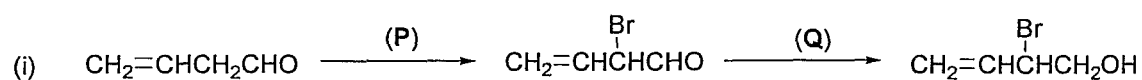
(30 marks)

(b) Giving necessary reagents and conditions show how any **two(02)** of the following transformations can be carried out.



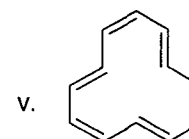
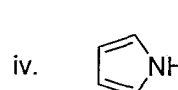
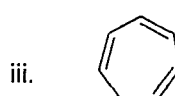
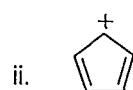
(40 marks)

(c) Give most suitable reagents (P–U) for the reaction sequences given below.



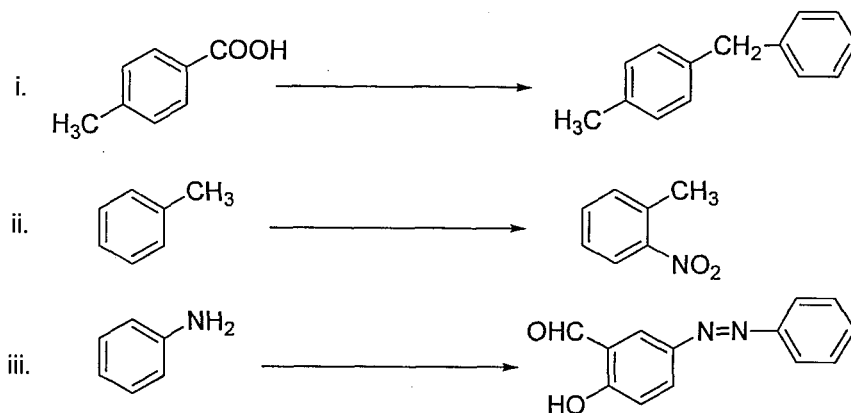
(30 marks)

4. (a) Categorize the following compounds as aromatic, non-aromatic or anti-aromatic giving reasons.



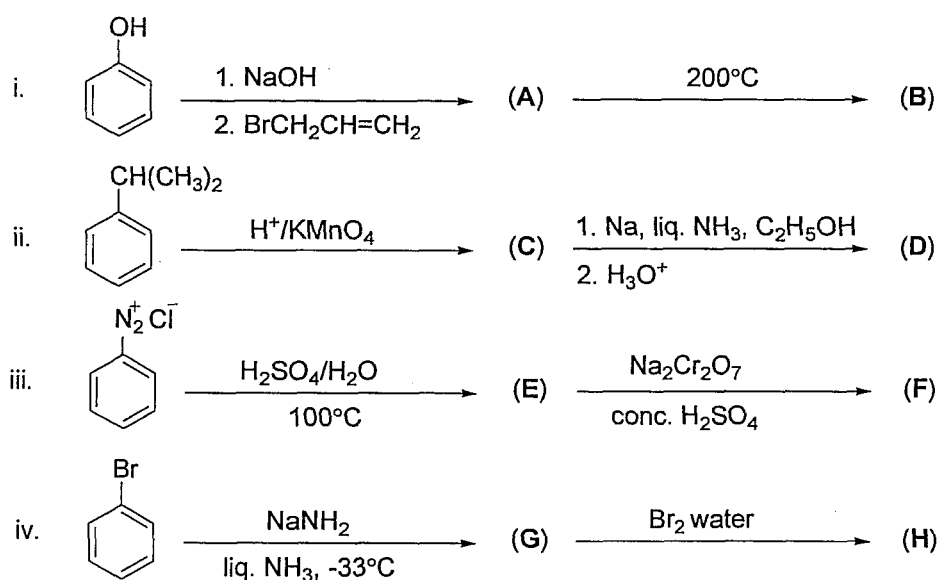
(20 marks)

(b) Giving necessary reagents and conditions show how any **two (02)** of the following transformations can be carried out.



(40 marks)

(c) Give the structures of the missing compounds in the following reactions.



(40 marks)

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