



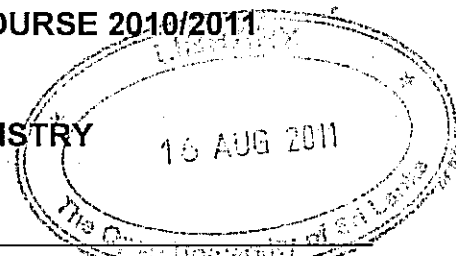
THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2010/2011

LEVEL 4 - FINAL EXAMINATION

CMU2221 / CME4221 - ORGANIC CHEMISTRY

DURATION: 3 HOURS

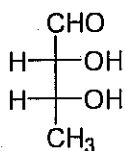


Thursday 30th June 2011

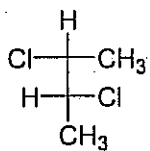
9.30 a.m. - 12.30 p.m.

ANSWER ALL QUESTIONS

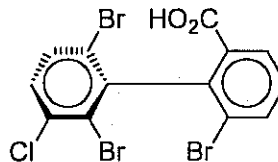
1. (a) State whether each of the following compounds (A) – (D) is chiral or achiral.



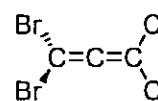
(A)



(B)



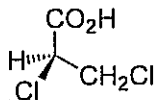
(C)



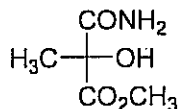
(D)

(08 marks)

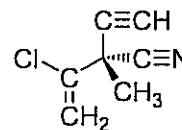
- (b) Showing the priority order of the groups, according to Cahn-Ingold-Prelog rules, designate the configuration of stereocenters of the following compounds, (E) – (G).



(E)



(F)



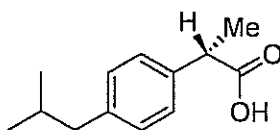
(G)

(12 marks)

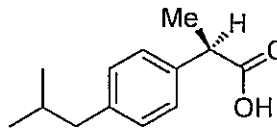
- (c) A synthetic sample of ibuprofen showed specific rotation, $[\alpha]_D = +24.6^\circ$.

$[\alpha]_D$ of (+)(*S*)-Ibuprofen is $+61.5^\circ$.

- Calculate the percent optical purity of (+)(*S*)-ibuprofen in the sample.
- Calculate the percentages of (*S*) and (*R*)-ibuprofen in the sample.
- How would you attempt to separate (*S*) and (*R*)-ibuprofen from the above synthetic sample using a chemical method?



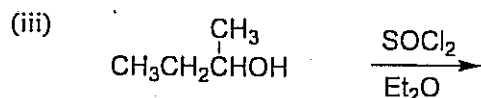
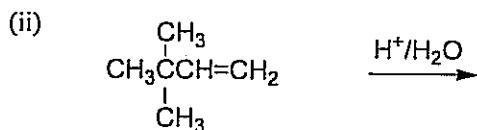
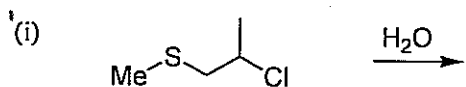
(+)(*S*)-ibuprofen



(-)(*R*)-ibuprofen

(20 marks)

(d) Predict the expected products of any TWO (02) of the following reactions. Give the mechanism for the formation of the predicted products.



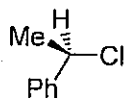
(20 marks)

(e) Indicating the mechanism predict the product formed, with its stereochemistry, when *cis*-2-butene is reacted with bromine.

(20 marks)

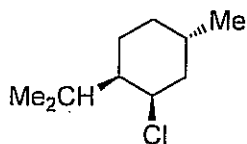
(f) Explain ONE (01) of the following observations.

- (i) Reaction of an optically pure 1-chloro-1-phenylethane with water results in 98% racemization (2% net inversion) while the reaction with NaOH in DMSO results in 100% inversion to give 1-phenylethanol.

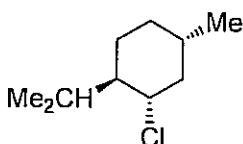


1-chloro-phenylethane

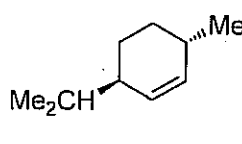
- (ii) Neomenthyl chloride when reacted with sodium ethoxide in ethanol **readily** produces 2-menthene and (25%) 3-menthene (75%), while menthyl chloride **slowly** but **exclusively** gives 2-menthene under the same conditions.



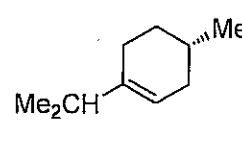
neomenthyl chloride



menthyl chloride



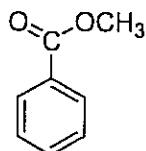
2-menthene



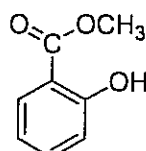
3-menthene

(20 marks)

2. (a) Explain why the carbonyl stretching frequency of methyl benzoate occurs at 1724 cm^{-1} while that of methyl salicylate occurs at 1680 cm^{-1} .



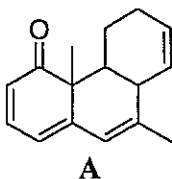
methylbenzoate



methyl salicylate

(15 marks)

- (b) Calculate the expected UV λ_{\max} of compound A using Woodward-Fieser rules for α,β -unsaturated ketones.



Basic value for α,β -unsaturated ketone = 215 nm

Increments;

Double bond extending conjugation +30 nm

Exocyclic double bond +05 nm

Alkyl group or ring residues at:

α - position +10 nm

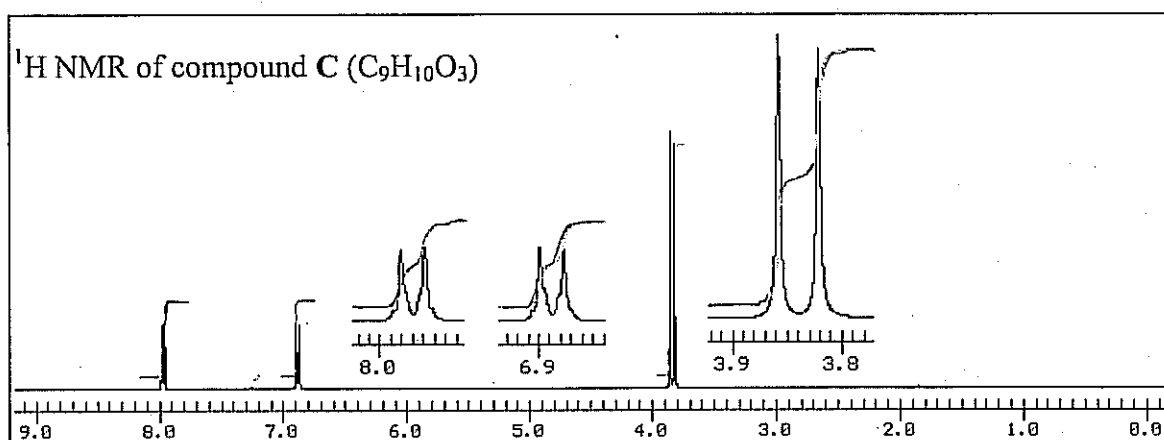
β - position +12 nm

γ or higher position +18 nm

Homoannular component +39 nm

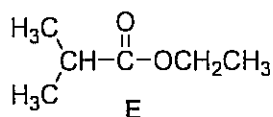
(10 marks)

- (c) The ^1H NMR spectrum of compound C, ($\text{C}_9\text{H}_{10}\text{O}_3$) and some useful expansions are given below. It showed an absorption band at 1725 cm^{-1} in its IR spectrum among other peaks while no peaks were observed above 2900 cm^{-1} . Deduce the structure of C.



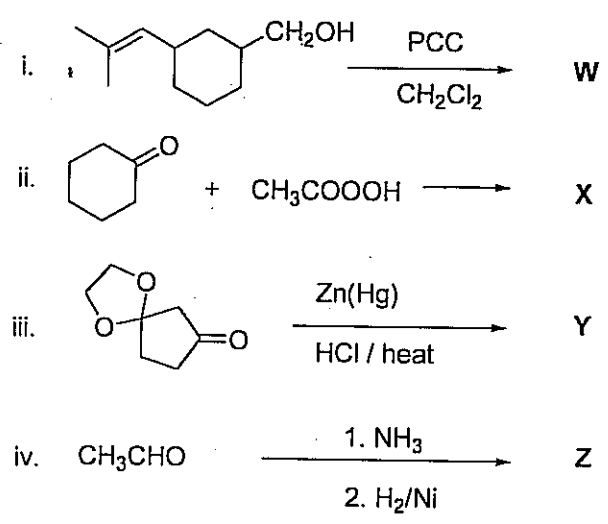
(40 marks)

- (d) (i) Predict the number of signals, area ratios and multiplicities of the signals in the ^1H -NMR spectrum of **E**.
- (ii) Sketch the ^1H -NMR spectrum of **E**, showing relative positions of peaks from TMS.
N.B. δ values of peaks are not expected
- (iii) Draw the structures of the fragments responsible for the peak at $m/z = 71$ and $m/z = 43$ in the mass spectrum of compound **E**.



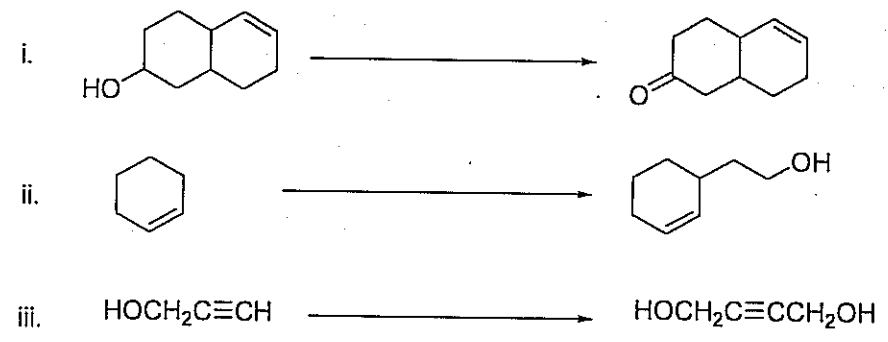
(35 marks)

3. (a) Give the structures of the products (W – Z) formed in the following reactions.



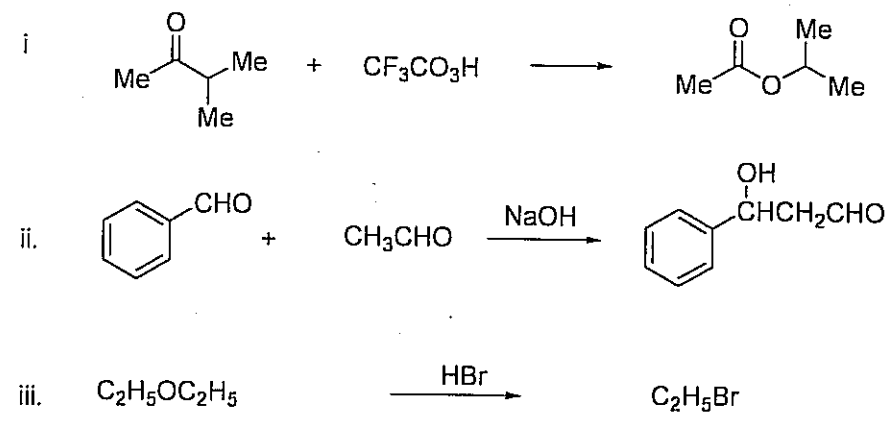
(20 marks)

(b) Giving necessary reagents and conditions show how you would carry out any **TWO (02)** of the following multi-step conversions.



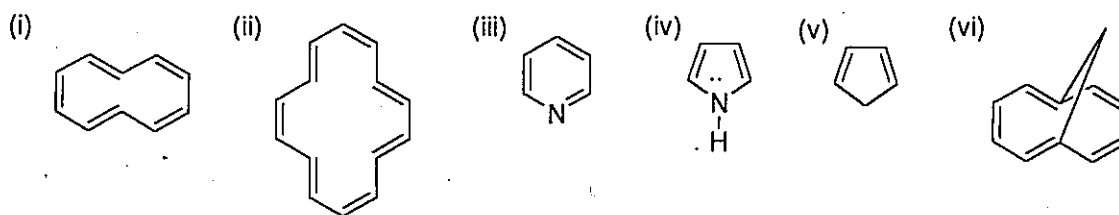
(40 marks)

(c) Provide mechanisms for any **TWO (02)** of the following conversions.



(40 marks)

4. (a) Predict which of the following compounds shows aromatic properties. Explain your answer!



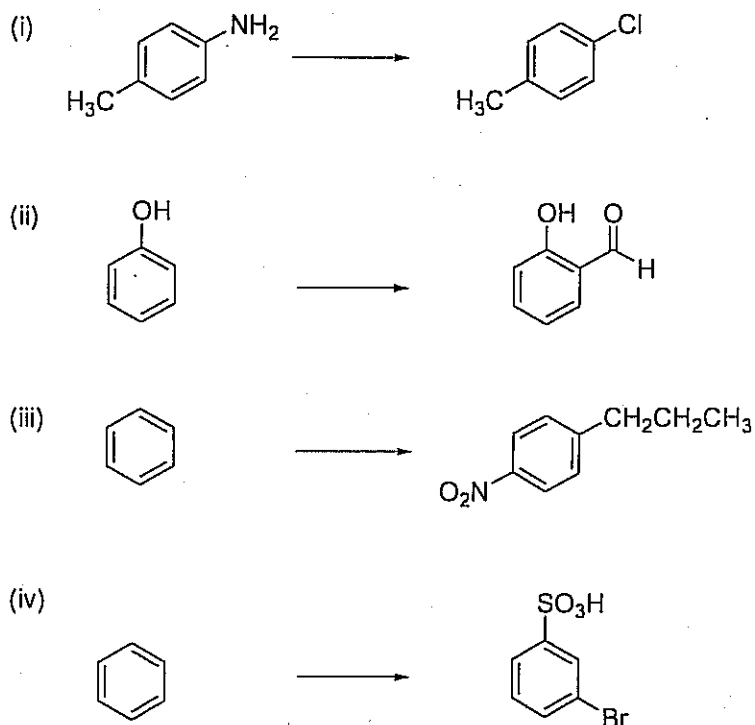
(30 marks)

- (b) Give an example of a nucleophilic substitution reaction of *p*-nitrochlorobenzene. Give the structures of the intermediate ions and explain why *p*-nitrochlorobenzene is more reactive than the *m*-isomer.

(25 Marks)

- (c) Giving necessary reagents and reaction conditions indicate how you would effect any **THREE (03)** of the following conversions.

N.B. Conversions may involve more than one step.



(45 Marks)

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