THE OPEN UNIVRVERSITY OF SRI LANKA

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

LEVEL 4 - FINAL EXAMINATION

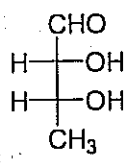
CMU2221 / CME4221 - ORGANIC CHEMISTRY

DURATION: 3 HOURS

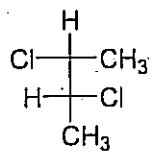
Thursday 30th June 2011 9.30 a.m. – 12.30 p.m.

ANSWER ALL QUESTIONS

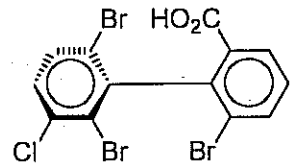
1. (a) State whether each of the following compounds (**A**) – (**D**) is chiral or achiral.



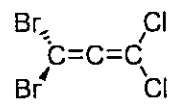
(A)



(B)



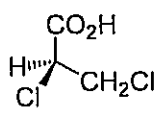
(C)



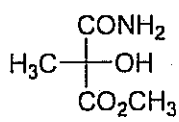
(D)

(08 marks)

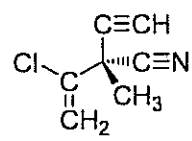
(b) Showing the priority order of the groups, according to Cahn-Ingold-Prelog rules, designate the configuration of stereocenters of the following compounds, (**E**) – (**G**).



(E)



(F)



(G)

(12 marks)

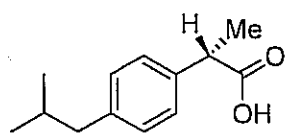
(c) A synthetic sample of ibuprofen showed specific rotation, $[\alpha]_D = +24.6°$.

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

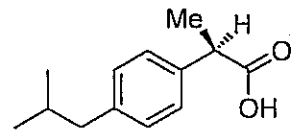
(i) Calculate the percent optical purity of (+)(*S*)-ibuprofen in the sample.

(ii) Calculate the percentages of (*S*) and (*R*)-ibuprofen in the sample.

(iii) How would you attempt to separate (*S*) and (*R*)-ibuprofen from the above synthetic sample using a chemical method?



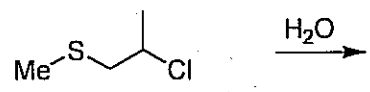
(+)(*S*)-ibuprofen

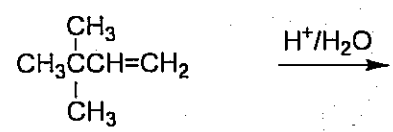


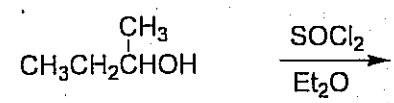
(-)(*R*)-ibuprofen

(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.

(i) 

(ii) 

(iii) 

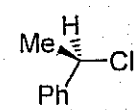
(20 marks)

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

(20 marks)

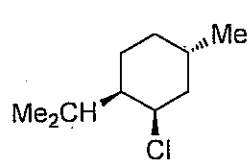
(f) Explain **ONE** (**01**) of the following observations.

(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-phenyethanol.

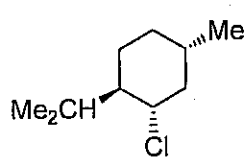


1-chloro-phenylethane

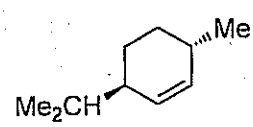
(ii) Neomenthyl chloride when reacted with sodium ethoxide in ethanol **readily** produces 2-menthene and (25%) 3-menthene (75%), while menthyl chloride **slowly** but **exclusively** gives 2-menthene under the same conditions.



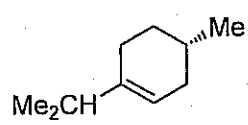
neomenthyl chloride



menthyl chloride



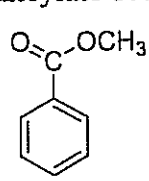
2-menthene



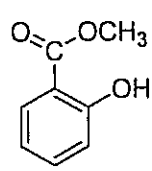
3-menthene

(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}.



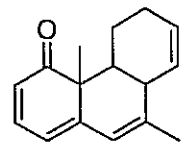
methylbenzoate



methy salicylate

(15 marks)

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

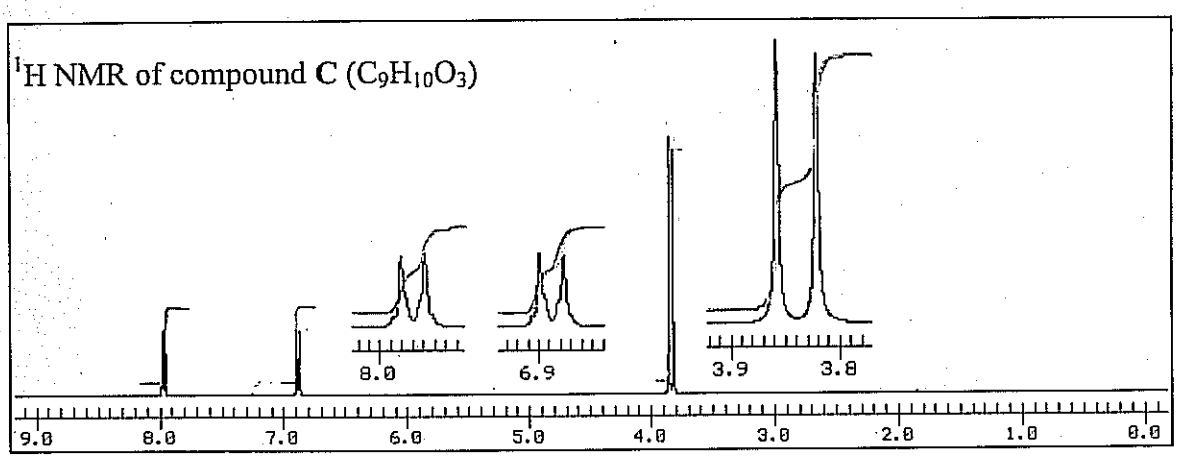


A

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 ^{1}H NMR spectrum of compound **C**, ($C_9H_{10}O_3$) 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**.



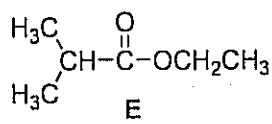
(40 marks)

(d) (i) Predict the number of signals, area ratios and multiplicities of the signals in the ^{1}H-NMR spectrum of **E**.

(ii) Sketch the ^{1}H-NMR spectrum of **E**, showing relative positions of peaks from TMS.

N.B. *δ values of peaks are not expected*

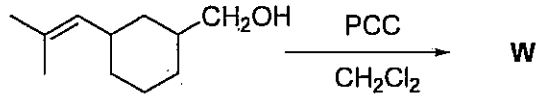
(iii) Draw the structures of the fragments responsible for the peak at m/z = 71 and m/z = 43 in the mass spectrum of compound **E**.

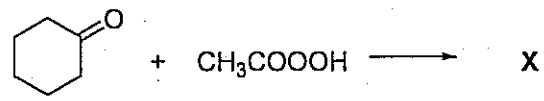


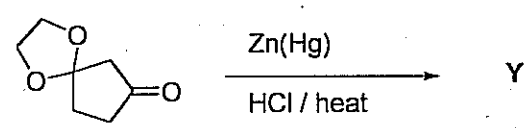
E

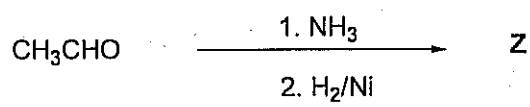
(35 marks)

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

i. 

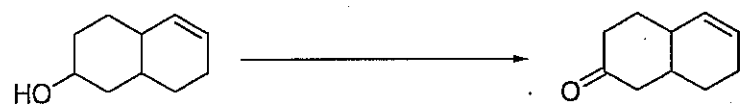
ii. 

iii. 

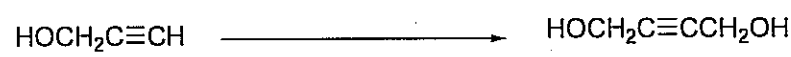
iv. 

(20 marks)

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

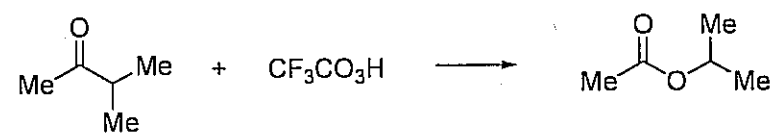
i. 

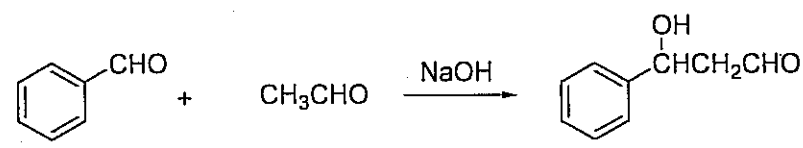
ii. 

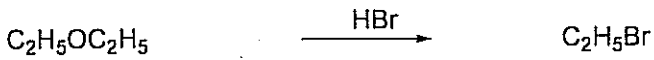
iii. 

(40 marks)

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

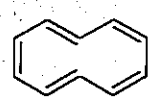
i 

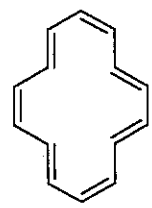
ii. 

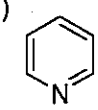
iii. 

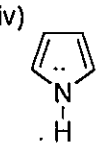
(40 marks)

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

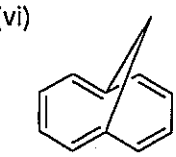
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

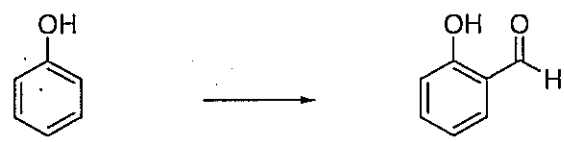
(30 marks)

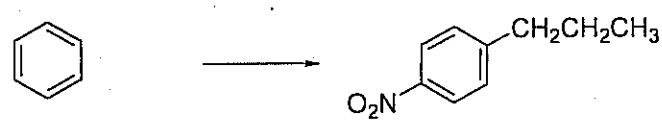
(b) Give an example of a nucleophilic substitution reaction of *p*-nitrochlorobenzene. Give the structures of the intermediate ions and explain why *p*-nitrochlorobenzene is more reactive than the *m*-isomer.

(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.*

(i) 

(ii) 

(iii) 

(iv) 

(45 Marks)