00390

THE OPEN UNIVRVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2014 / 2015

LEVEL 4 - FINAL EXAMINATION

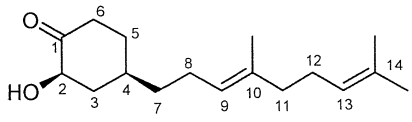
CMU2221 / CME4221 - ORGANIC CHEMISTRY I

DURATION: 3 HOURS

Wednesday 28th October 2015 9.30 a.m. - 12.30 p.m.

ANSWER ALL QUESTIONS

1. (a) (i) How many stereoisomers are possible for the following compound **A**?



(A)

(ii) Draw the structure of the enantiomer of **A**.

(iii) Draw the structure of a diastereoisomer of **A**.

(iv) Determine the configuration of the stereocenters of the compound **A** as R/S or E/Z. (*Carbon atoms are numbered for your convenience*).

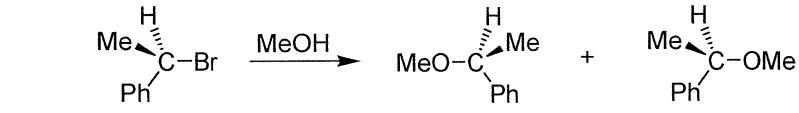
(v) Draw the structures of possible stereoisomeric products when compound **A** is reacted with H_2/Pd.

(32 Marks)

(b) $[\alpha]_D$ value of optically pure (+)-pseudoephedrine is +52°. $[\alpha]_D$ of a synthetically prepared sample of (+)-pseudoephedrine was found to be +40.6°. Calculate the enantiomeric excess (**ee**) and the percentage of (+)-pseudoephedrine in the synthetic sample.

(08 Marks)

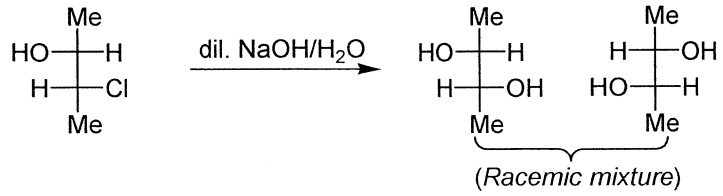
(c) Explain why, (*R*)-1-bromo-1-phenylethane undergoes solvolysis in methanol with partial racemization as given below.



(*R*)-1-bromo-1-phenylethane major product

(20 Marks)

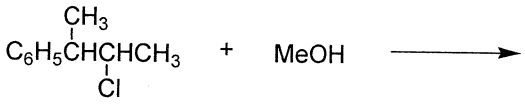
(d) Indicate the mechanism and explain the product formation of the following reaction.



(*Racemic mixture*)

(20 Marks)

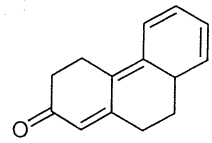
(e) Indicate the mechanism and predict the major product of the following reaction.



(20 Marks)

2. (a) Calculate the expected λ_{max} of the compound **B** using Woodward-Fieser rules for α, β-unsaturated ketone given below.

Base value for α,β-unsaturated ketone	=	215 nm
Increments for		
Double bond extending conjugation	=	+ 30 nm
Alkyl group or ring residue at α	=	+ 10 nm
β	=	+ 12 nm
γ and higher	=	+ 18 nm
Exocyclic double bond position	=	+ 05 nm
Homoannular diene component	=	+ 39 nm



(B)

(10 Marks)

(b) Answer any **ONE (01)** of the following.

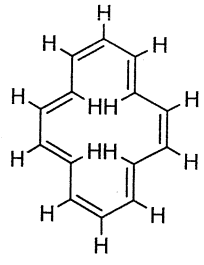
(i) Propose the structure of the compound **C** ($C_9H_{18}O_2$) which shows only two singlets at δ1.24 ppm and 1.40 ppm in its ^{1}H NMR spectrum. Assign the δ values to the proposed structure.

(ii) Propose the structure of the compound **D** ($C_7H_6O_3$) which shows a broad band between 3200 – 3600 cm^{-1} in the IR spectrum in CCl_4 which does not change on dilution. Briefly explain the answer.

(10 Marks)

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

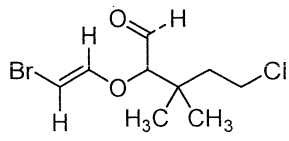
(i) Explain why [14]-annulene shows two singlets, at δ 7.6 (10H) and δ 0.0 (4H) in its ^{1}H NMR spectrum.



[14]-annulene

(ii) Write down the mathematical relationship (equation) between the stretching frequency, ($\bar{\nu}$) and the force constant, (f) of a diatomic molecule. Hence, deduce whether the C–O or C–H bond has the higher stretching frequency.

(iii) How many different types of H atoms are present in compound **F**? Label them using a, b, c, d, ….. etc. Sketch the ^{1}H NMR spectrum of the compound **F** showing relative positions from TMS (***NOT** necessary to give δ values*), multiplicities and numerical values of relative intensities.



(F)

(30 Marks)

(d) Compound **F** is a monohalogenated organic compound containing 4 C atoms. Mass spectrum, IR spectrum and the ^{1}H NMR spectrum of compound **F** are given below.

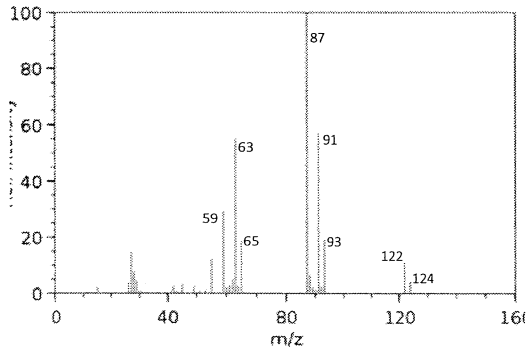
(i) Giving reasons identify the halogen present in **F**.

(ii) Giving reasons identify the possible functional group/s present in **F**.

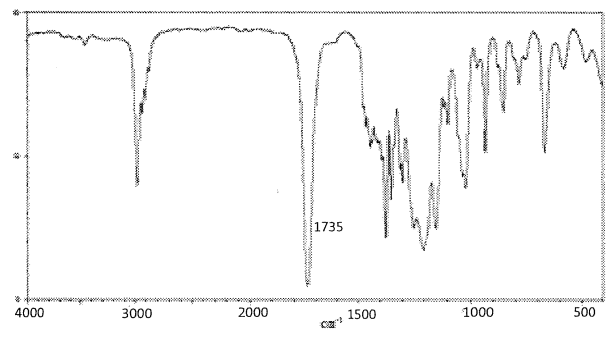
(iii) Elucidate the structure of **F** and assign the ^{1}H NMR signals to your proposed structure.

(iv) Give the structures of fragment ions at m/z 91/93, 87, 63/65 and 59 of the mass spectrum of **F**.

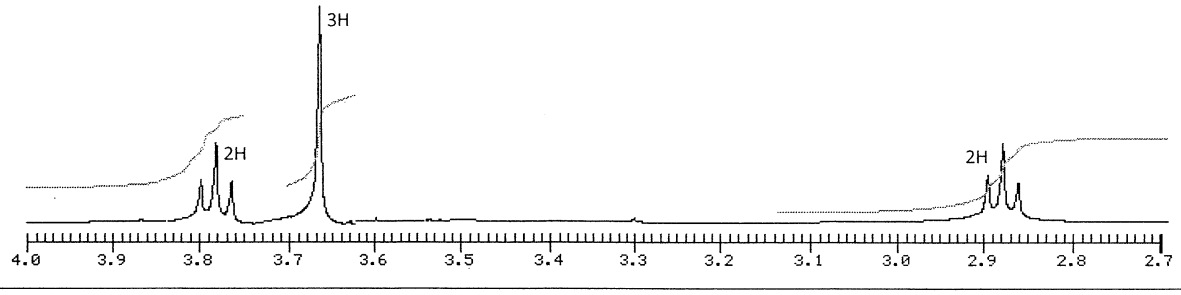
Mass spectrum of compound F



IR spectrum of compound F



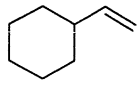
^{1}H NMR spectrum of compound F



(50 Marks)

3. (a) Give the structures of the major products (**G – L**) in the reaction sequences given below.

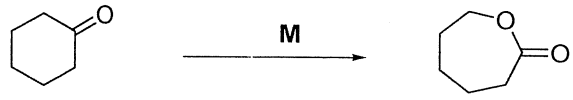
(i) C_2H_5COOH $\xrightarrow[2.\ NH_3]{1.\ SOCl_2}$ **G** $\xrightarrow[2.\ H_2O]{1.\ LiAlH_4/ether}$ **H**

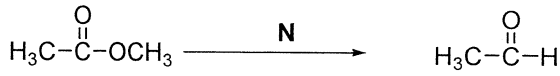
(ii)  $\xrightarrow[2.\ NaBH_4/OH^-]{1.\ Hg(OAc)_2/H_2O/THF}$ **I** $\xrightarrow[2.\ alc.\ KCN]{1.\ PBr_3/ether}$ **J**

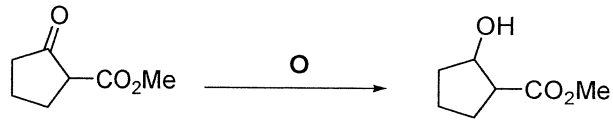
(iii) $HC{\equiv}C{-}CH_2OH$ $\xrightarrow[2.\ MeMgBr/\ dry\ ether]{1.\ \text{  }\ /\ H^+}$ **K** $\xrightarrow[2.\ H^+/H_2O]{1.\ HCHO}$ **L**

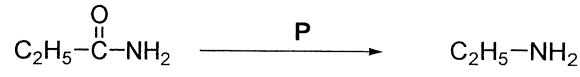
(30 Marks)

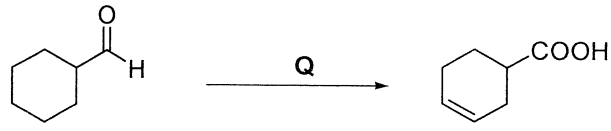
(b) Give suitable reagents and conditions (**M – R**) to effect the following reactions.

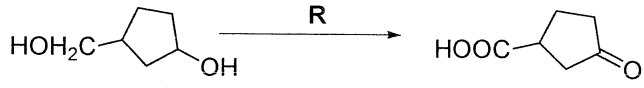
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

(30 Marks)

(c) Show how you would carry out any **TWO (02)** of the following transformations.

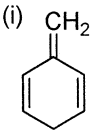
(i) 

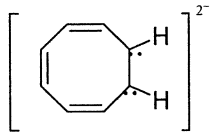
(ii) $(CH_3)_2CHBr \longrightarrow (CH_3)_2C{=}CH_2$

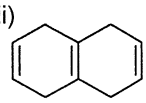
(iii) $CH_3\underset{\underset{OH}{|}}{C}HCH_3 \longrightarrow CH_3CH_2CH_2OH$

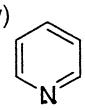
(40 Marks)

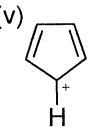
4. (a) Predict whether each of the following compound is aromatic, anti-aromatic or non-aromatic. Explain your answer.

(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi)

(30 Marks)

(b) (i) Considering the structures of the intermediates that are formed during the electrophilic substitution of phenoxide ion ($C_6H_5O^-$), explain why the reaction occurs at the *ortho* and *para* positions with activation of nucleus.

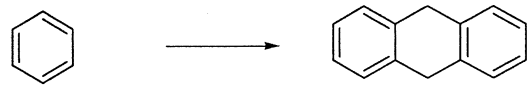
(ii) Explain which one of the following groups activates the aromatic nucleus more in electrophilic substitution.

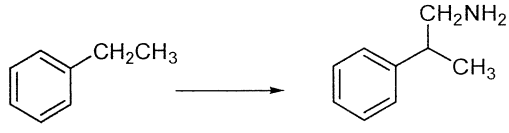
$-NH_2$ or $-NHCOCH_3$

(40 Marks)

(c) Giving necessary reagents and reaction conditions indicate how you would carry out any **TWO (02)** of the following conversions.
N.B. conversions may involve more than one step.

(i) 

(ii) 

(iii) 

(30 Marks)