THE OPEN UNIVRVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2015 / 2016

LEVEL 4 - FINAL EXAMINATION

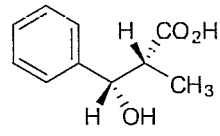
CMU2221 / CME4221 - ORGANIC CHEMISTRY I

DURATION: 3 HOURS

Monday, 16th January 2017 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 the diastereoisomer of **A**, which gives the same ketone as **A** on oxidation with PCC.

(iv) Determine the configuration of the stereocenters of the compound **A** as R/S. (*Label the stereocenters with numerals or letters*).

(v) Write down the steps you would take to separate a racemic mixture of **A** into optically pure isomers?

(40 Marks)

(b) (i) Give the mechanism of the solvolysis of 2-bromo-2-methylpropane in water.

(ii) Draw the completely labeled energy diagram for the above reaction.

(iii) It is observed that when this reaction is carried out in acetone-water mixture the rate of the solvolysis reaction is decreased. Explain this observation.

(25 Marks)

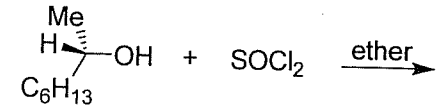
(c) (i) Giving reasons state which of the two anions, $C_2H_5O^-$ and $C_2H_5S^-$, shows higher nucleophilicity in ethanol *(No marks if reasoning is not given).*

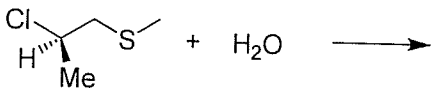
(ii) When 2-bromopropane is reacted with $C_2H_5S^-\ Na^+$ in ethanol two products are being formed. Give the structures of those two products.

(iii) Giving reasons, state which one is the major product of this reaction (*No marks if reasoning is not given).*

(25 Marks)

(d) Giving the mechanism predict the product (with its stereochemistry) of any **one (01)** of the following reactions.

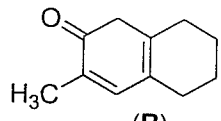
(i) 

(ii) 

(10 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

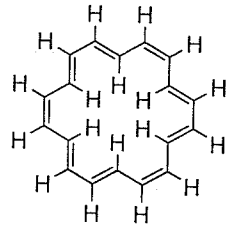


(B)

(10 Marks)

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

(i) Explain why [18]-annulene shows highly deshielded and highly shielded two singlets, at δ 8.2 (12H) and δ -1.8 (6H) in its ^{1}H NMR spectrum. *(Your answer should include reasons for the deshielding and shielding of these two peaks).*



[18]-annulene

(ii) Considering the energy levels of molecular orbitals of ethylene, explain why conjugation of double bonds leads to an increase of wavelength at which UV absorbs (UV λ_{max}).

(iii) Using mass spectroscopy, how would you identify the presence of Br and Cl in organic compounds?

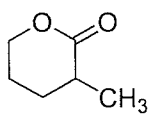
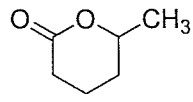
(20 Marks)

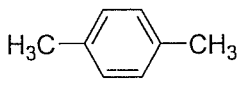
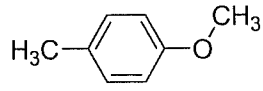
(c) Briefly giving reasons state how you would distinguish between the compounds in any **FOUR (04)** of the following pairs using the indicated spectroscopic method.

(i) $HOCH_2CH_2CH{=}CH_2$ and $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_3$ — IR spectroscopy

(ii) $CH_3CH_2C{\equiv}C{-}H$ and $CH_3C{\equiv}CCH_3$ — IR spectroscopy

(iii) $CH_3\overset{O}{\overset{\|}{C}}\underset{CH_3}{\underset{|}{C}}HCH_2CH_3$ and $CH_3\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2CH_3$ — Mass spectroscopy

(iv)  and  — ^{1}H NMR spectroscopy

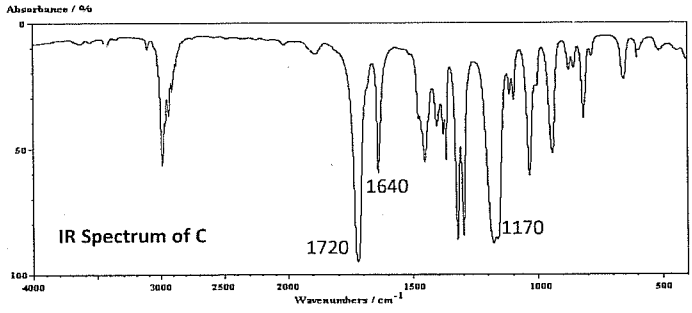
(v)  and  — ^{1}H NMR spectroscopy

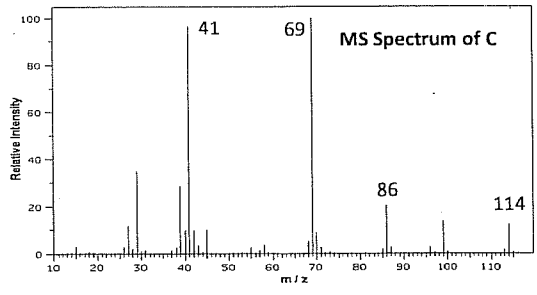
(20 Marks)

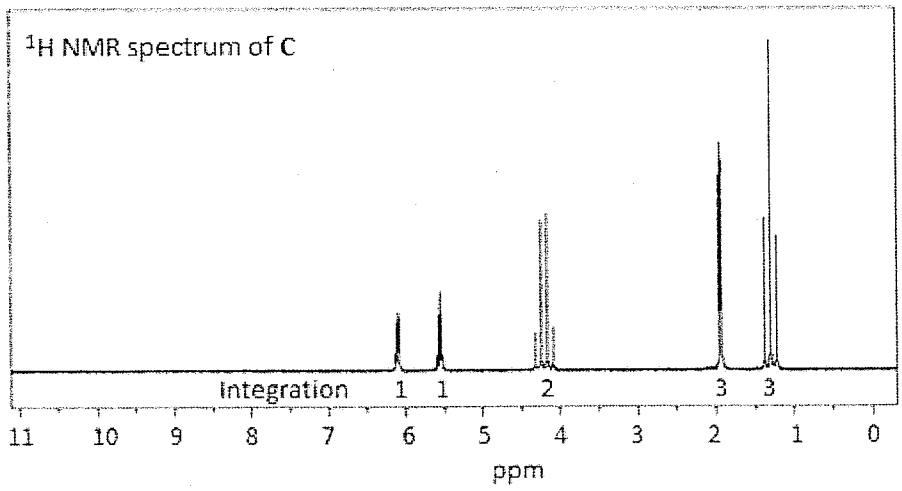
(d) Mass spectrum, IR spectrum and the ^{1}H NMR spectrum of compound **C** ($C_6H_{10}O_2$) are given below.

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

(ii) Give the structures of fragment ions at m/z 114, 86, 69 and 41 of the mass spectrum of **C**.







(50 Marks)

3. (a) Giving reasons explain any **TWO (02)** of the following statements.

(i) *p*- Nitroaniline is more basic than aniline.

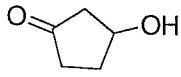
(ii) Reaction undergone by benzaldehyde in the presence of conc. KOH is different to what is shown by acetaldehyde under the same conditions.

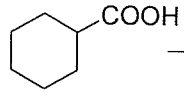
(iii) pK_a of chloroacetic acid is lower than that of acetic acid.

(20 marks)

(b) Give the structures of the major products (**D–H**) of the following reactions.

(i) $CH_3-CH(Br)CH_2Br \xrightarrow{NaNH_2}$ **D**

(ii)  $\xrightarrow{CrO_3/H^+}$ **E**

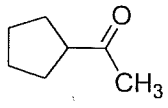
(iii)  $\xrightarrow[\text{ether}]{CH_2N_2}$ **F**

(iv) $CH_3CH_2-C(=O)-Cl \xrightarrow{CH_3NH_2}$ **G**

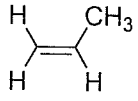
(v) $CH_3-C(=O)-OCH_3 \xrightarrow[2.\ H_2O]{1.\text{DIBAL-H, hexane,-78°C}}$ **H**

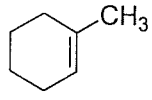
(25 marks)

(c) Give structures of the intermediates and the products of any **THREE (03)** of the reaction schemes given below.

(i)  $\xrightarrow{CH_3Li}$ **I** $\xrightarrow{H^+/H_2O}$ **J**

(ii)  $\xrightarrow[CH_2Cl_2]{PhCO_2OH}$ **K** $\xrightarrow{H^+/H_2O}$ **L**

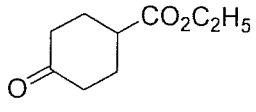
(iii)  $\xrightarrow[H_2O/THF]{Hg(OAc)_2}$ **M** $\xrightarrow[OH^-]{NaBH_4}$ **N**

(iv)  $\xrightarrow{THF/BF_3}$ **O** $\xrightarrow[25°C]{H_2O_2/NaOH}$ **P**

(30 marks)

(d) Giving suitable reagents and conditions show how any **ONE (01)** of the following conversions can be carried out.

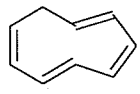
(i) $HO-CH_2C\equiv CH \longrightarrow HO-CH_2C\equiv C-CH_2OH$

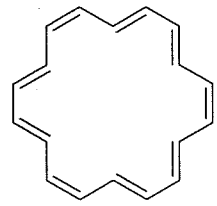
(ii) 

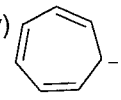
(25 marks)

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

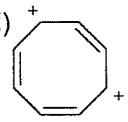
(i) 

(ii) 

(iii) 

(iv) 

(v) 

(vi) 

(30 marks)

(b) (i) Write the resonance structures of the intermediate that is formed in the nitration of anisole, ($C_6H_5OCH_3$) at the *ortho-* position. Account for the observed equal rates of nitration of $C_6H_5OCH_3$ and $C_6D_5OCH_3$.

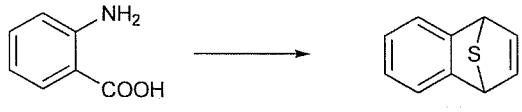
(ii) Compare the activation effects of the following *ortho-/para*-directing groups in electrophilic aromatic substitution and explain your answer.

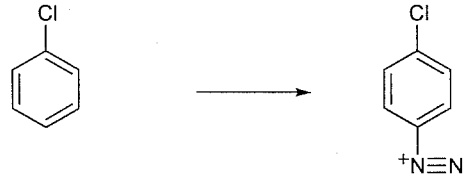
$-OH$, $-O^-$ and $-OCOCH_3$

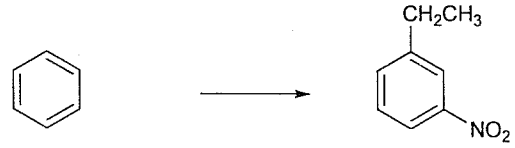
(40 marks)

(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)