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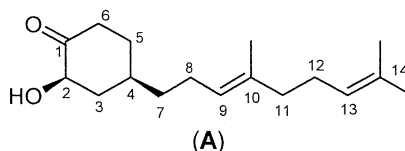
B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2014 / 2015

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.
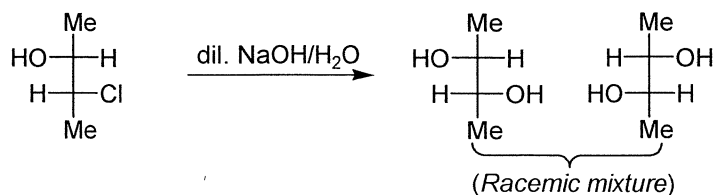
(08 Marks)

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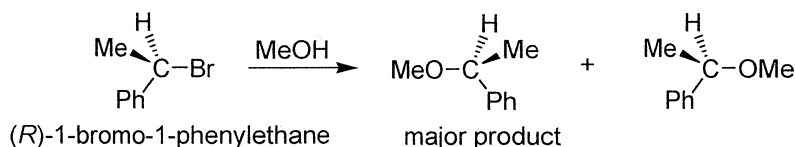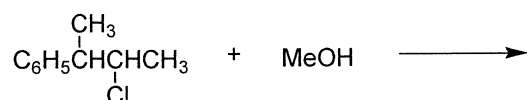

(20 Marks)

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

(20 Marks)

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

$$CH_3$$

$$C_6H_5CHCHCH_3 \quad + \quad MeOH \quad \longrightarrow$$

$$Cl$$

(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)
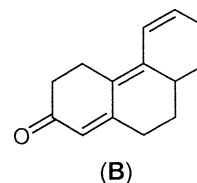
(10 Marks)

(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 $\delta 1.24$ ppm and 1.40 ppm in its ^1H 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 ^1H NMR spectrum.
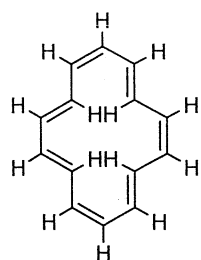
[14]-annulene

(ii)   Write down the mathematical relationship (equation) between the stretching frequency, $(\bar{v})$ 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)
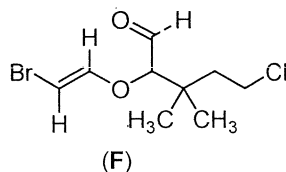
(30 Marks)

(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
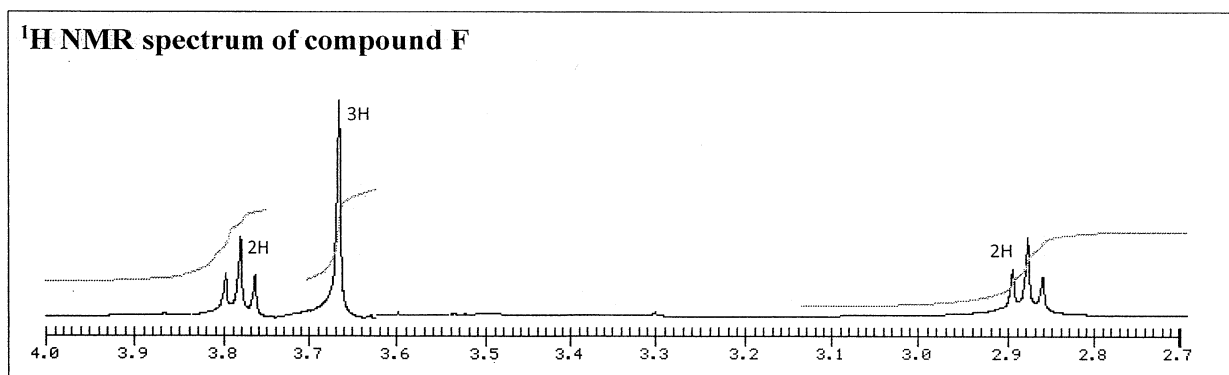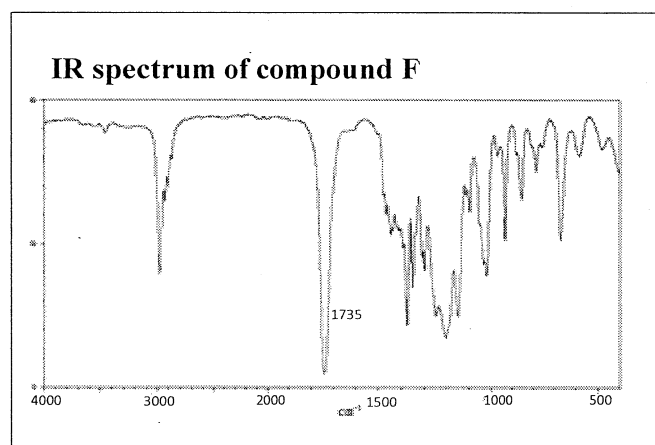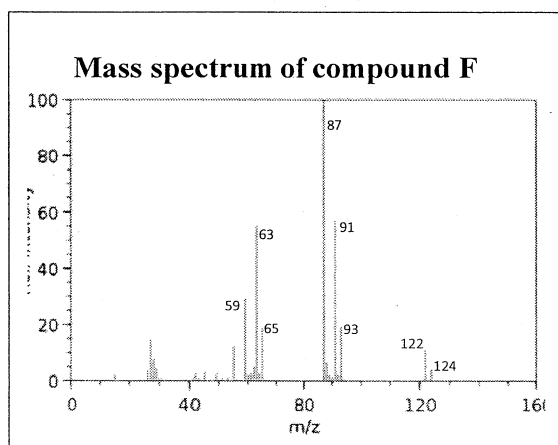
3. (a) Give the structures of the major products (**G – L**) in the reaction sequences given below.
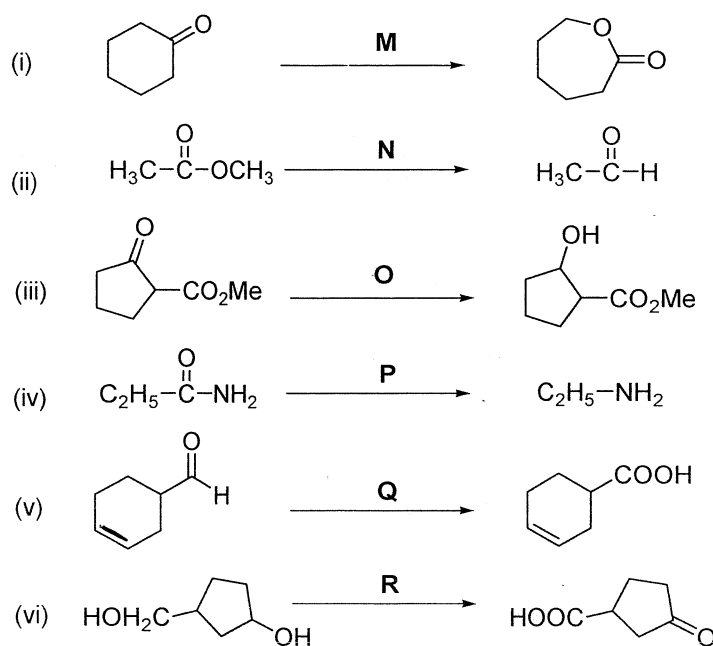
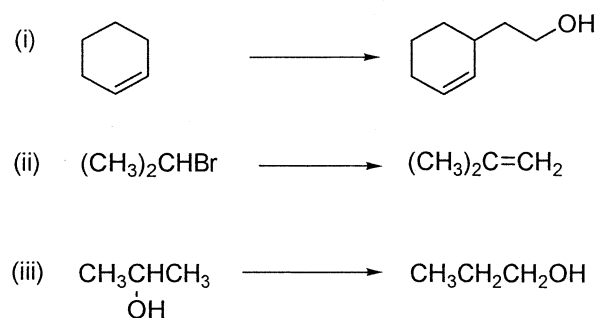(i) C_2H_5COOH $\xrightarrow[\text{2. NH}_3]{\text{1. SOCl}_2}$ **G** $\xrightarrow[\text{2. H}_2\text{O}]{\text{1. LiAlH}_4/\text{ether}}$ **H**

(ii)

 $\xrightarrow[\text{2. NaBH}_4/\text{OH}^-]{\text{1. Hg(OAc)}_2/\text{H}_2\text{O/THF}}$ **I** $\xrightarrow[\text{2. alc. KCN}]{\text{1. PBr}_3/\text{ether}}$ **J**

(iii) $HC \equiv C-CH_2OH$ $\xrightarrow[\text{2. MeMgBr/ dry ether}]{\text{1. } \text{(dihydropyran)} / H^+}$ **K** $\xrightarrow[\text{2. H}^+/\text{H}_2\text{O}]{\text{1. HCHO}}$ **L**
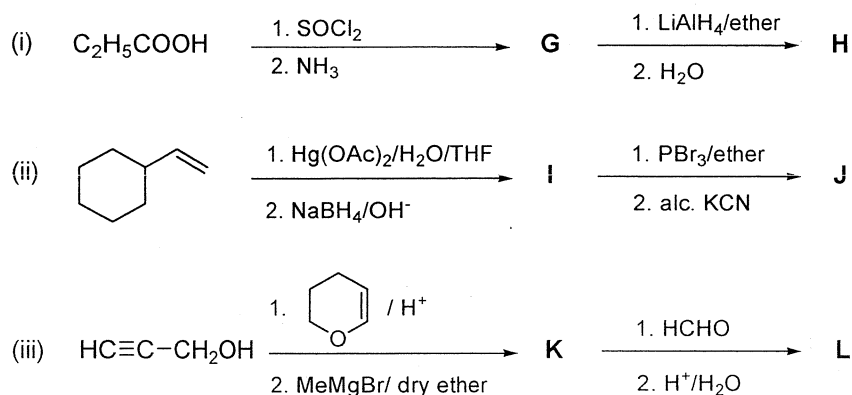
(30 Marks)

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

(i) $\xrightarrow{\text{M}}$

(ii) $H_3C-\overset{O}{\underset{||}{C}}-OCH_3$ $\xrightarrow{\text{N}}$ $H_3C-\overset{O}{\underset{||}{C}}-H$

(iii) $\xrightarrow{\text{O}}$

(iv) $C_2H_5-\overset{O}{\underset{||}{C}}-NH_2$ $\xrightarrow{\text{P}}$ $C_2H_5-NH_2$

(v) $\xrightarrow{\text{Q}}$

(vi) $HOH_2C-$$-OH$ $\xrightarrow{\text{R}}$ $HOOC-$$=O$

(30 Marks)

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

(i) $\longrightarrow$

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

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

(40 Marks)

4

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

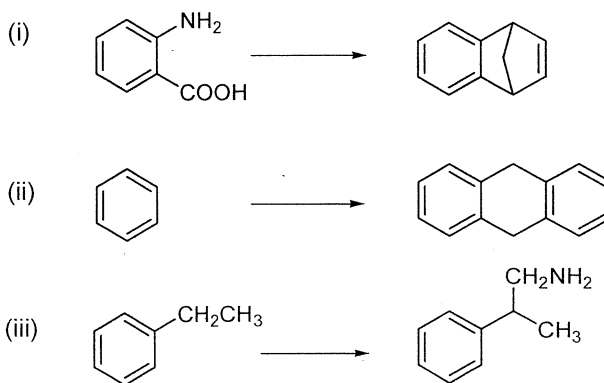(i) CH_2 (ii)   (iii)   (iv)   (v)   (vi)
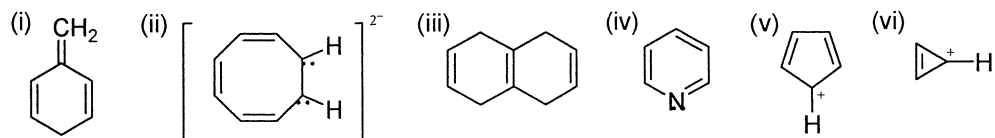
(30 Marks)

(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)