



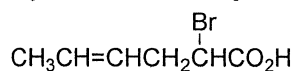
THE OPEN UNIVRVERSTY OF SRI LANKA  
 B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2013 / 2014  
 LEVEL 4 - FINAL EXAMINATION  
 CMU2221 / CME4221 - ORGANIC CHEMISTRY I  
 DURATION: 3 HOURS

Monday 24<sup>th</sup> November 2014

9.30 a.m. - 12.30 p.m.

ANSWER ALL QUESTIONS

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

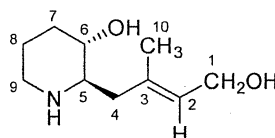


(A)

- (ii) Draw the stereoisomers of A using Fischer projection formulae to show the stereochemistry at the chiral carbon atom. (Label the structures you drew.)  
 (iii) Identify a pair of enantiomers  
 (iv) Identify a pair of diastereoisomers.

(21 Marks)

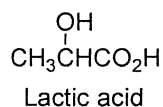
- (b) Determine the configuration of the stereocenters of the compound B. (*Carbon atoms are numbered for your convenience*).



(B)

(09 Marks)

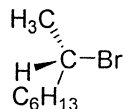
- (c) How would you attempt to separate a racemic mixture of lactic acid into optically pure (+) and (-) lactic acids?



(10 Marks)

(d) Consider the hydrolysis of 2-bromooctane.

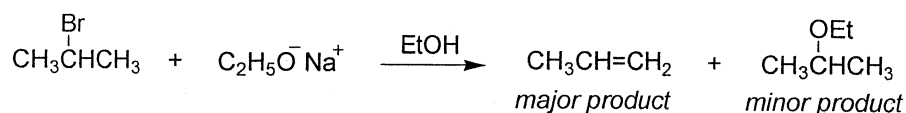
- (i) Explain why optically pure 2-bromooctane loses its optical purity in the presence of water.
- (ii) Give the structure of product with its stereochemistry when (*S*)-2-bromooctane is reacted with aq. NaOH. Explain your answer.



(*S*)-2-bromooctane

(20 Marks)

- (e) (i) Consider the two anions,  $C_2H_5O^-$  and  $C_2H_5S^-$  in ethanol. Giving reasons state which anion show higher nucleophilicity.
- (ii) The following reaction occurs when 2-bromopropane is reacted with  $C_2H_5O^- Na^+$  in ethanol.

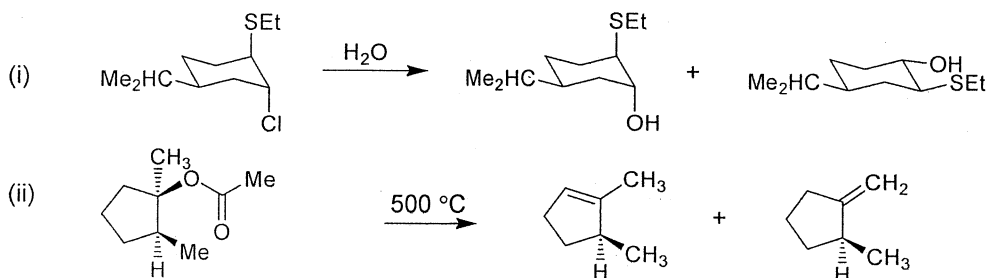


Give the structures of the products when 2-bromopropane is reacted with  $C_2H_5S^- Na^+$  in ethanol.

Giving reasons, state which one is the major product of this reaction.

(20 Marks)

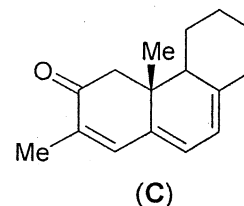
(f) Giving the mechanism account for the product formation of the following reactions.



(20 Marks)

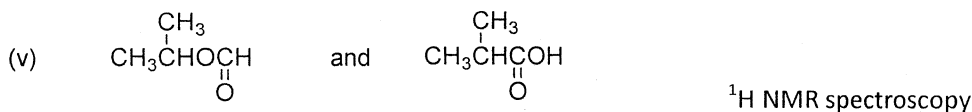
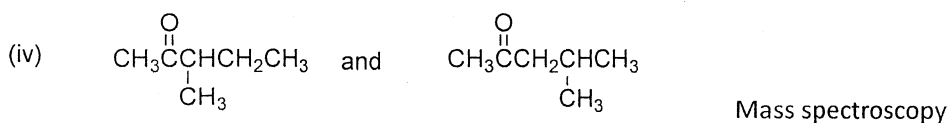
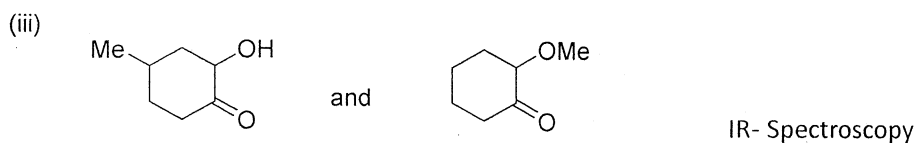
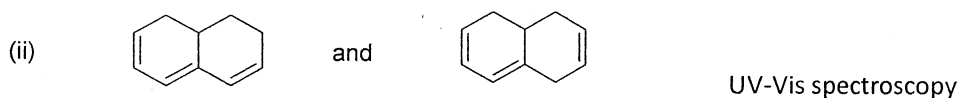
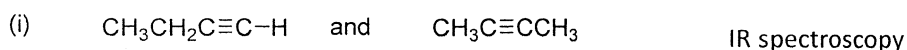
2. (a) Calculate the expected  $\lambda_{\text{max}}$  of the compound **C** using Woodward-Fieser rules for  $\alpha, \beta$ -unsaturated ketones given below.

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



(10 Marks)

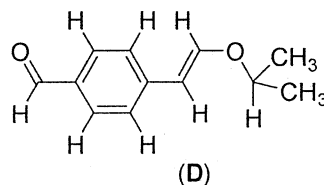
(b) Briefly giving reasons state how you would distinguish between the compounds in **any FOUR (04)** of the following pairs using the indicated spectroscopic method.



(20 Marks)

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

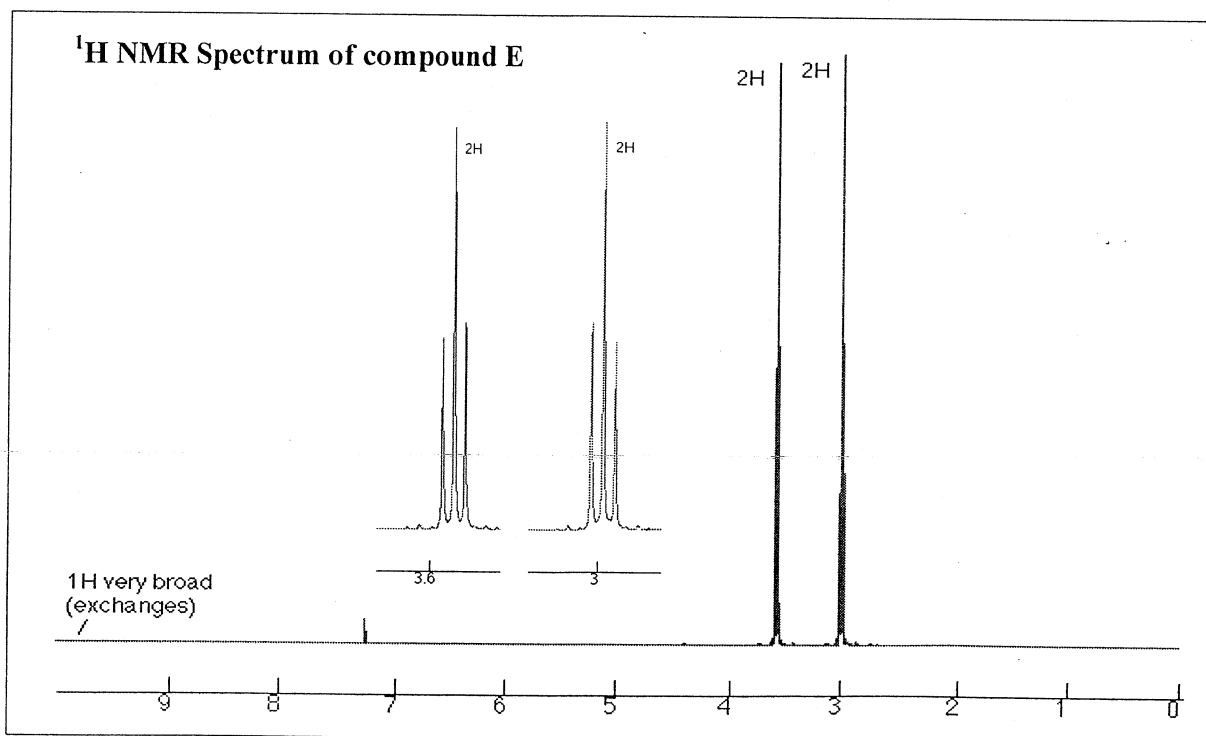
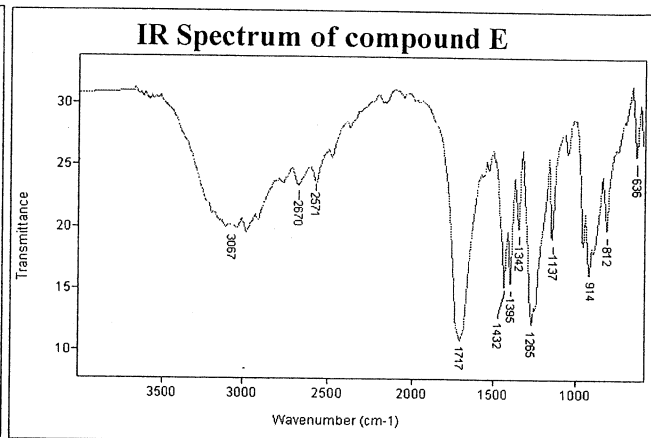
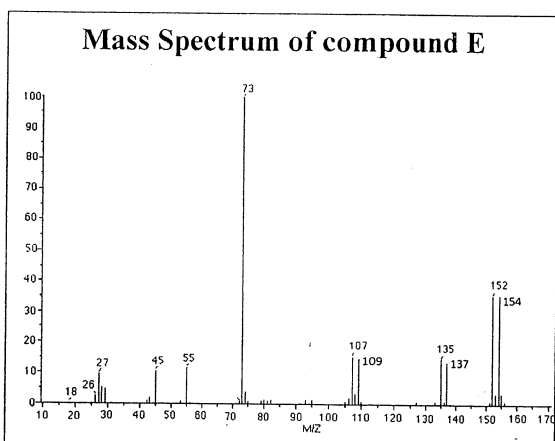
- (i) Explain why benzene shows a down field singlet (around  $\delta$  7.0 ppm) in its  $^1\text{H}$  NMR spectrum compared to aliphatic hydrocarbons.
- (ii) How many different types of H atoms are present in compound **D**? Label them using a, b, c, d, ..... etc. Sketch the  $^1\text{H}$  NMR spectrum of the compound **D** showing relative positions from TMS (*NOT necessary to give  $\delta$  values*), multiplicities and numerical values of relative intensities.



- (iii) Considering the energy levels of molecular orbitals of ethylene ( $\text{CH}_2=\text{CH}_2$ ) and 1,3-butadiene ( $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ ) explain why ethylene absorbs UV at a lower wavelength ( $\lambda_{\text{max}} = 175$  nm) compared to butadiene ( $\lambda_{\text{max}} = 217$  nm).

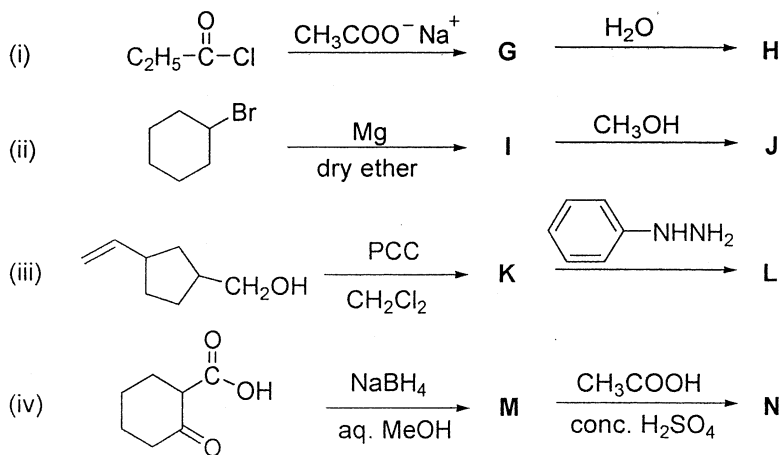
(20 Marks)

- (d) Compound **E** is a monohalogenated organic compound. Mass spectrum, IR spectrum and the  $^1\text{H}$  NMR spectrum of compound **E** are given below (see page 4).
- Giving reasons identify the halogen present in **E**.
  - Giving reasons identify the possible functional group/s present in **E**.
  - Elucidate the structure of **E** and assign the  $^1\text{H}$  NMR signals to your proposed structure.
  - Showing the possible fragmentation pathways, give the structures of fragment ions at  $m/z$  135/137, 107/109 and 73 of the mass spectrum of **E**.



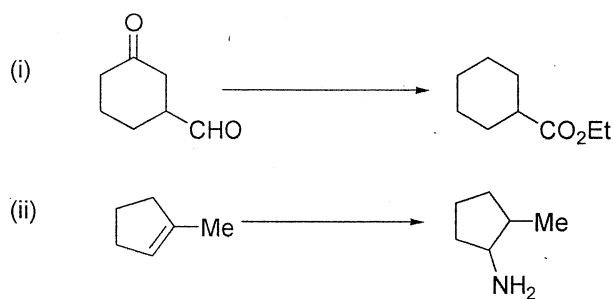
(50 Marks)

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



(40 Marks)

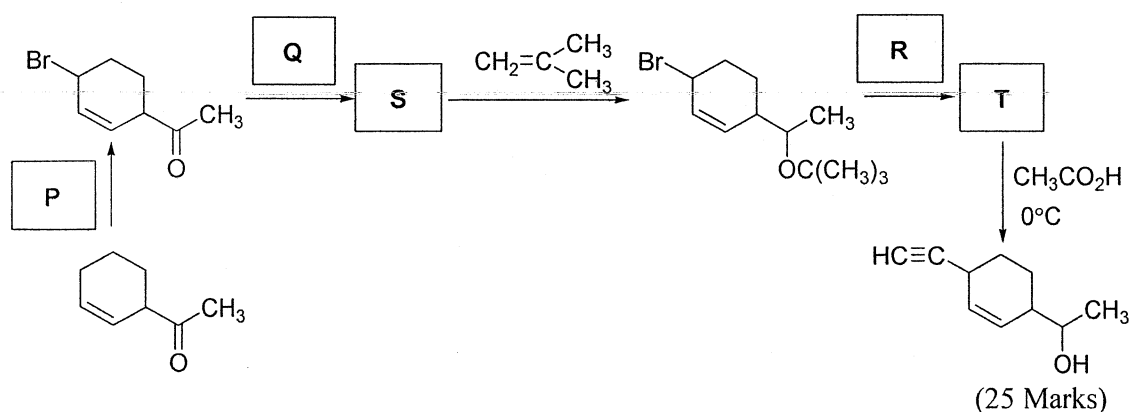
- (b) Using **only** any of the reagents/conditions given in the list below, show how any **ONE (01)** of the following multistep transformations can be carried out.

**Reagents/conditions:**

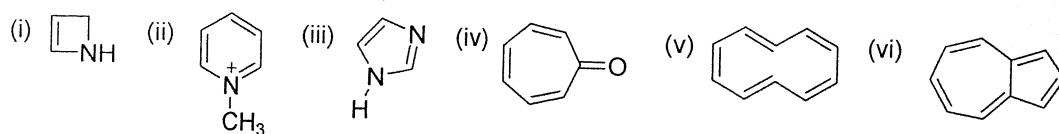
$\text{H}_2/\text{Ni}$   
 $\text{CrO}_3/\text{H}^+$   
 $\text{EtOH}/\text{H}^+$   
 $\text{PCC}/\text{CH}_2\text{Cl}_2$   
 $\text{H}_2\text{O}_2/\text{NaOH}/25^\circ\text{C}$   
 $\text{HS-CH}_2\text{-CH}_2\text{-SH}/\text{H}^+$   
 $\text{NH}_3$   
 $\text{MeONa}$   
 $\text{Dil. Na}_2\text{CO}_3$   
 $\text{BH}_3/\text{THF}$

(35 Marks)

- (c) Complete the following reaction scheme giving the missing reagents P, Q and R and intermediate products S and T.



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



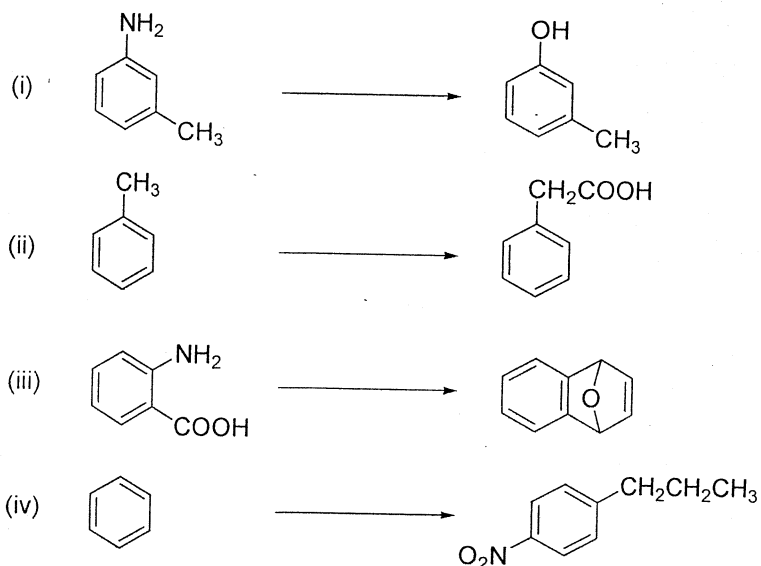
(30 Marks)

- (b) Considering the structures of the intermediate  $\sigma$ -complexes, explain why aniline undergoes electrophilic substitution readily at the *ortho* and *para* positions.

(25 Marks)

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

*N.B. conversions may involve more than one step.*



(45 Marks)

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