



00114

THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2011 / 2012

LEVEL 4 - FINAL EXAMINATION

CMU2221 / CME4221 - ORGANIC CHEMISTRY I

DURATION: 3 HOURS

Monday, 26<sup>th</sup> November 2012

9.30 a.m. - 12.30 p.m.

ANSWER ALL QUESTIONS

1. (a) Consider the compound 2,3,4-trihydroxybutanal.
- Show how you calculate the number of stereoisomers possible for this compound.
  - Draw the Fischer projection formulae of stereoisomers and label them as A, B, C, ... etc.
  - Name a pair of enantiomers.
  - Name a pair of diastereomers.

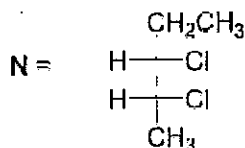
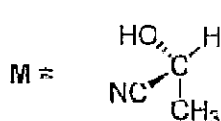
(20 Marks)

- (b) i. Draw the structures of the compounds K and L showing their stereochemistry.

K = (E)-2-bromo-3-methyl-2-butene

L = 1(Z),3(E)-1-bromo-4-chloro-1,3-heptadiene

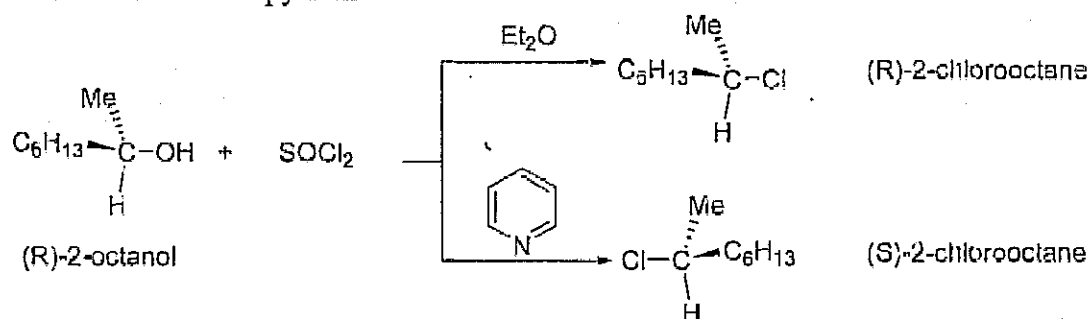
- ii. Give the R/S configurations of the stereocentres of compounds M and N, labeling the groups according to Cahn-Ingold-Prelog priority rules.



(20 Marks)

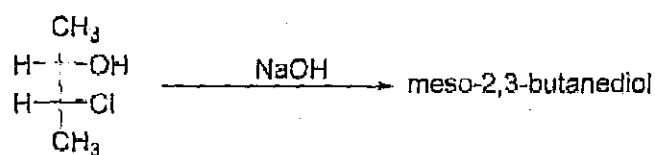
- (c) Explain any one (01) of the following observations.

- Relative rate of solvolysis of *tert*-butyl chloride is 1200 times faster in H<sub>2</sub>O than in ethanol.
- The following reaction takes place in diethyl ether with retention of configuration while with inversion in pyridine.



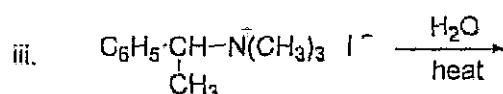
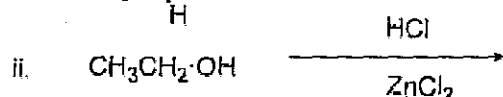
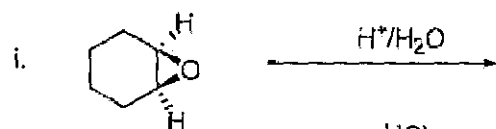
(20 Marks)

- (d) Explain the formation of the given products in the following reaction giving appropriate mechanism.



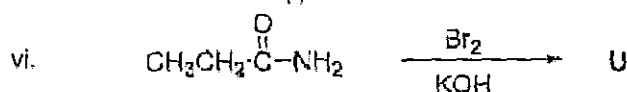
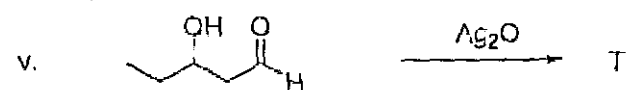
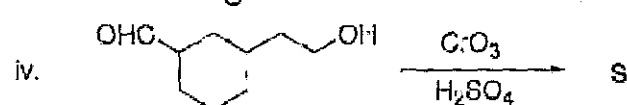
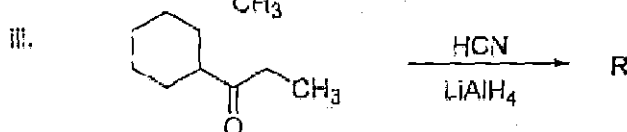
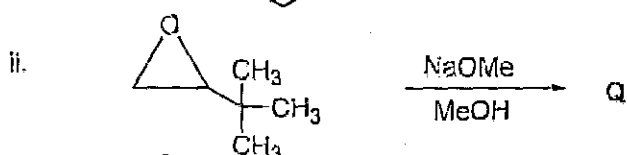
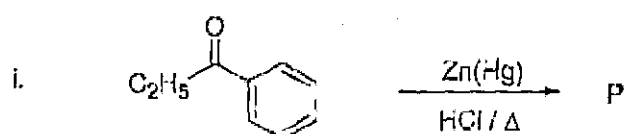
(20 Marks)

- (e) Predict the products of any two (02) of following giving mechanisms.



(20 Marks)

2. (a) Give the structures of the products (P – U) of the following reactions.



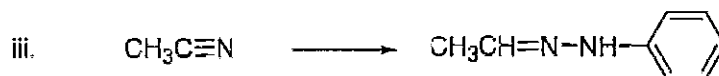
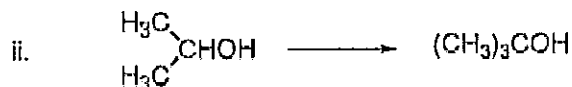
(30 Marks)

- (b) Give explanations for any three (03) of the following with appropriate structural representations.

- Addition of  $\text{H}_2\text{O}$  to chloral ( $\text{Cl}_3\text{C-CHO}$ ) to give hydrate takes place more easily than to acetaldehyde ( $\text{CH}_3\text{CHO}$ ).
- $\text{p}K_a$  of 2-chloropropanoic acid is lower than that of 3-chloropropanoic acid.
- p*-methoxyaniline is more basic than *p*-chloroaniline.
- 2,4-pentadione exists in the enol form to an extent of about 76%.

(30 Marks)

(c) Show how any **two (02)** of the following multistep transformations can be effected.

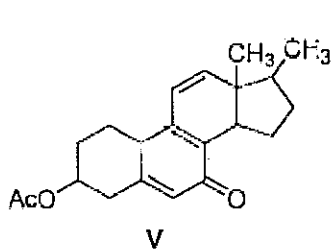


(40 Marks)

13. (a) A phenolic ester  $C_8H_8O_3$  showed a broad IR band at  $3300\text{ cm}^{-1}$  in  $CCl_4$ . Dilution shifted the band to  $3600\text{ cm}^{-1}$  and was observed as a sharp band. Deduce the structure of the compound and explain your answer.

(15 Marks)

(b) Calculate the expected  $\lambda_{\text{max}}$  of the following compound **V** using Woodward-Fieser rules for  $\alpha, \beta$ -unsaturated ketones.

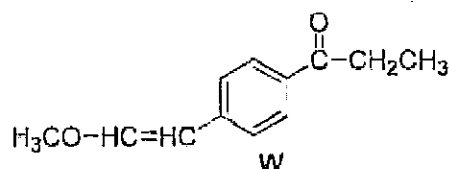
 <p style="text-align: center;"><b>V</b></p>	Basic value for $\alpha, \beta$ -unsaturated ketone	= 215 nm
	Increments for,	
	Double bond extending conjugation	= +30 nm
	Alkyl group or ring residue at $\alpha$	= +10 nm
	$\beta$	= +12 nm
	$\gamma$ or higher	= +18 nm
	Exocyclic double bond	= +05 nm
Homoannular diene component	= +39 nm	

(10 Marks)

(c) i. Predict the number of signals, area ratios and multiplicities of the signals in the  $^1\text{H-NMR}$  spectrum of **W**.

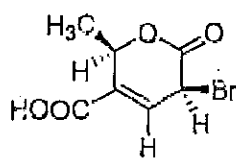
ii. Sketch the  $^1\text{H-NMR}$  spectrum of **W**, showing relative positions of peaks from TMS.

*N.B.*  $\delta$  values of peaks are not expected.



(30 Marks)

(d) Sketch the  $^1\text{H-NMR}$  spectrum of **X** showing the relative distance from TMS, relative areas and multiplicities of the signals. (Assign the signals to the H atoms in **X** by labeling them as a, b, c etc.)



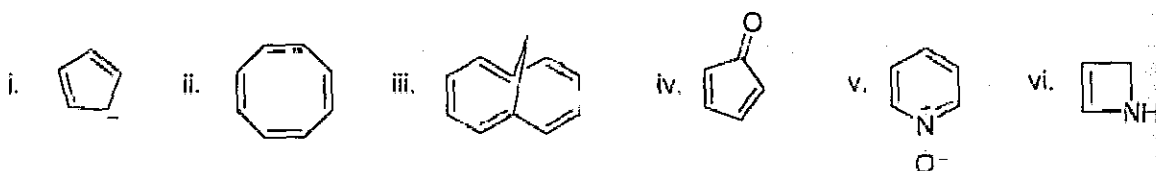
X

(30 Marks)

- (e) Draw the fragmentation of octan-2-one,  $\text{CH}_3(\text{CH}_2)_5\text{COCH}_3$  which give rise to the peaks at  $m/z = 85$  and  $m/z = 58$  in mass spectrum.

(15 Marks)

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



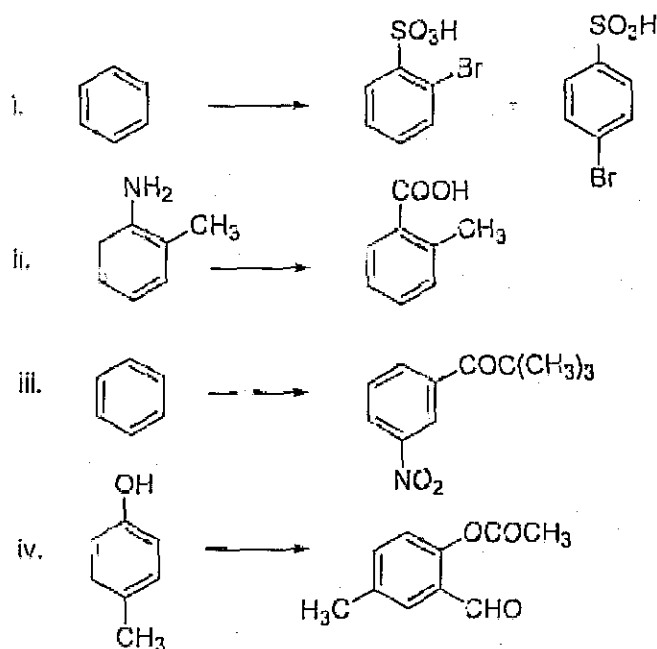
(30 Marks)

- (b) Chlorobenzene, 3-chloronitrobenzene and 4-chloronitrobenzene are separately treated with methylamine in ethanol solution. A product is readily obtained in one case. Give the structure of the product obtained and outline a mechanism for the reaction. Explain why the other two compounds do not react.

(25 Marks)

- (c) Giving necessary reagents and reaction conditions indicate how you would affect any three (03) of the following conversions.

N.B. Conversions may involve more than one step.



(45 Marks)