



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, 26th November 2012

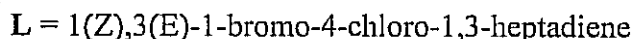
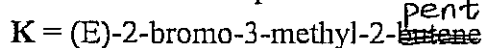
9.30 a.m. - 12.30 p.m.

ANSWER ALL QUESTIONS

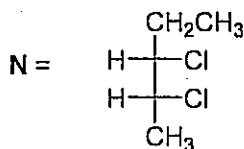
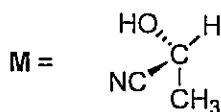
1. (a) Consider the compound 2,3,4-trihydroxybutanal.
- Show how you calculate the number of stereoisomers possible for this compound.
 - Draw the Fischer projection formulae of stereoisomers and label them as A, B, C, ... etc.
 - Name a pair of enantiomers.
 - Name a pair of diastereomers.

(20 Marks)

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



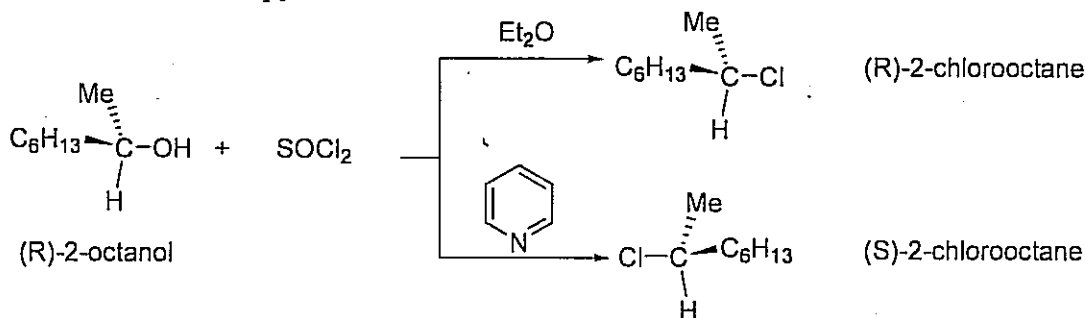
- ii. Give the R/S configurations of the stereocentres of compounds M and N, labeling the groups according to Cahn-Ingold-Prelog priority rules.



(20 Marks)

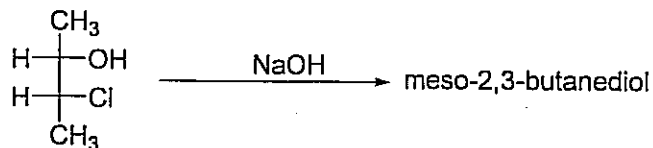
- (c) Explain any one (01) of the following observations.

- Relative rate of solvolysis of *tert*-butyl chloride is 1200 times faster in H₂O than in ethanol.
- The following reaction takes place in diethyl ether with retention of configuration while with inversion in pyridine.



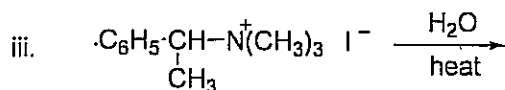
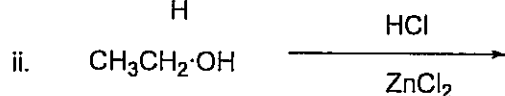
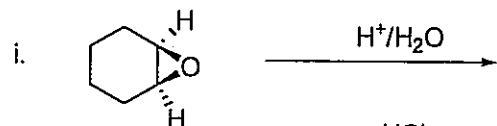
(20 Marks)

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



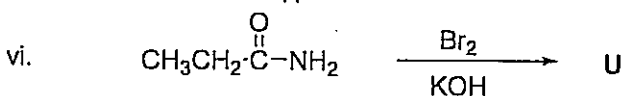
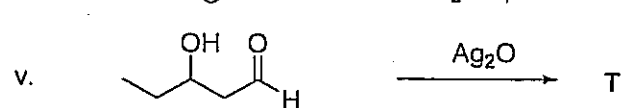
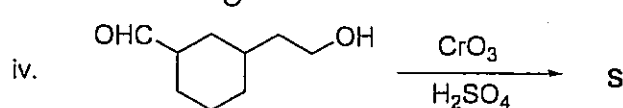
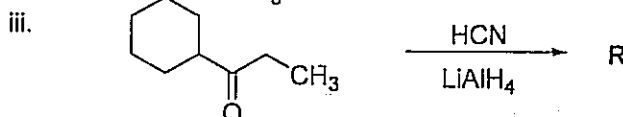
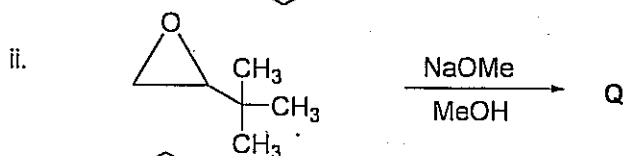
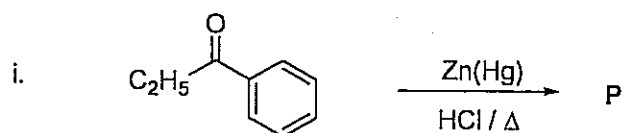
(20 Marks)

- (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.



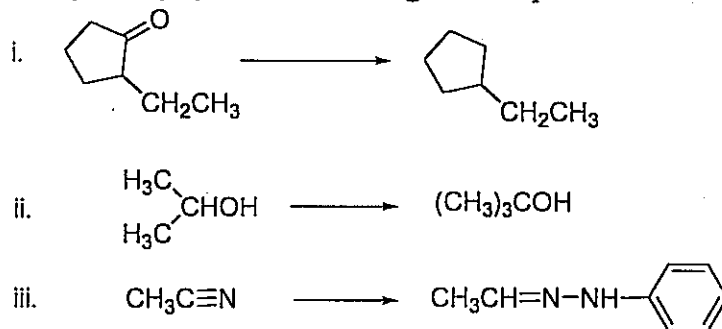
(30 Marks)

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

- Addition of H_2O to chloral ($\text{Cl}_3\text{C-CHO}$) to give hydrate takes place more easily than to acetaldehyde (CH_3CHO).
- pK_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.

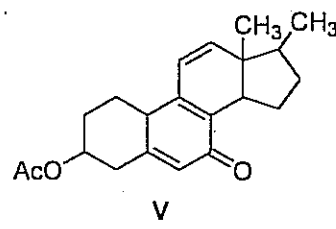


(40 Marks)

3. (a) A phenolic ester $C_8H_8O_3$, showed a broad IR band at 3300 cm^{-1} in CCl_4 . Dilution shifted the band to 3600 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 λ_{max} of the following compound **V** using Woodward-Fieser rules for α, β -unsaturated ketones.

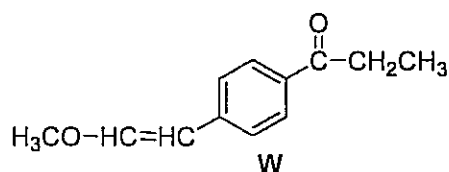
 <p style="text-align: center;">V</p>	Basic value for α, β -unsaturated ketone	= 215 nm
	Increments for, Double bond extending conjugation	= +30 nm
	Alkyl group or ring residue at α	= +10 nm
	β	= +12 nm
	γ or higher	= +18 nm
	Exocyclic double bond	= +05 nm
	Homoannular diene component	= +39 nm

(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**.

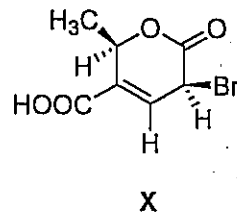
ii. Sketch the $^1\text{H-NMR}$ spectrum of **W**, showing relative positions of peaks from TMS.

N.B. δ 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.)

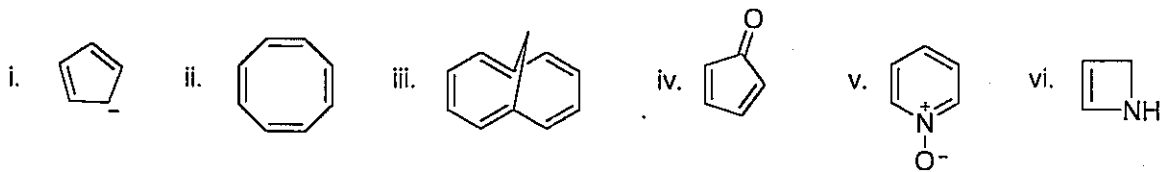


(30 Marks)

- (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.



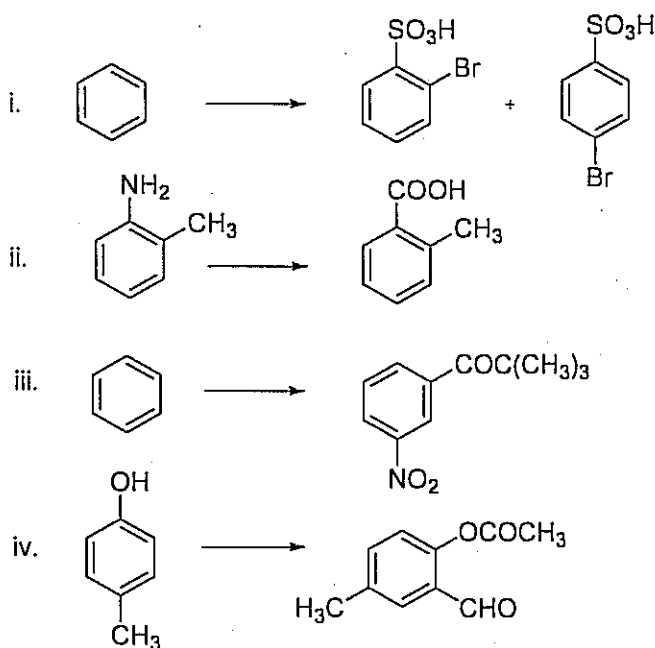
(30 Marks)

- (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)