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THE OPEN UNIVRVERSITY OF SRI LANKA

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

LEVEL 4 - FINAL EXAMINATION

CHU 2221 / CHE 4221 - ORGANIC CHEMISTRY I

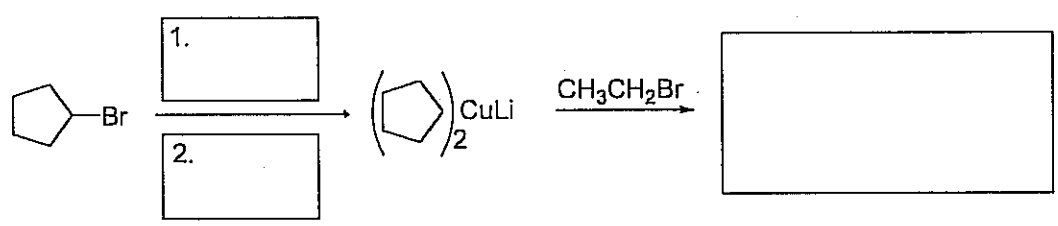
DURATION: 3 HOURS

Monday, 26th November 2012 — 9.30 a.m. - 12.30 p.m.

THIS PAPER CONSISTS OF TWO PARTS, PART A AND PART B

PART A: ANSWER ALL QUESTIONS (01 HOUR)
Write your answers in the spaces provided.

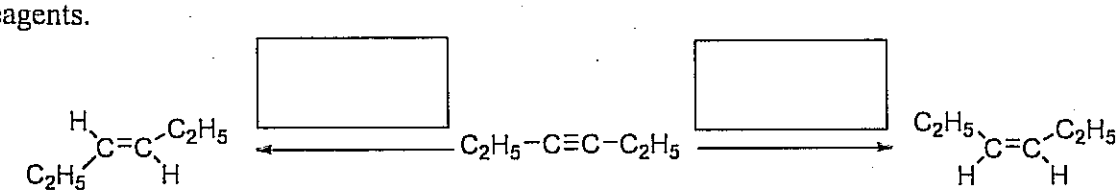
1. Give the missing reagents and products of the following reaction scheme.



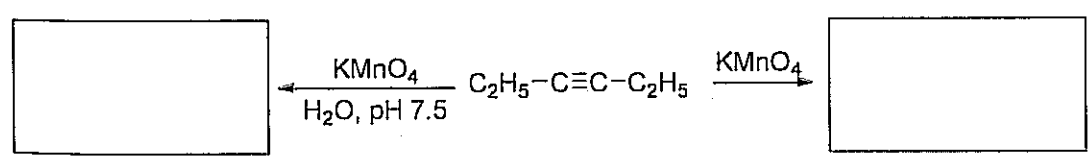
(07 Marks)

2. Complete the following reactions giving structures of the products or appropriate reagents.

(i).



(ii).



(10 Marks)

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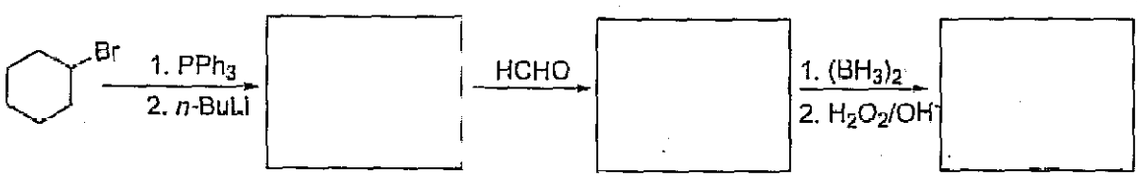
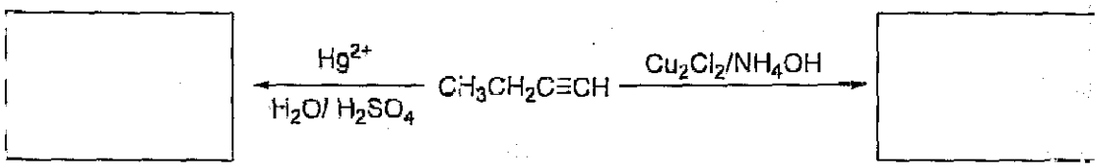
3. Give the structures of the products of each step of the following reaction scheme.



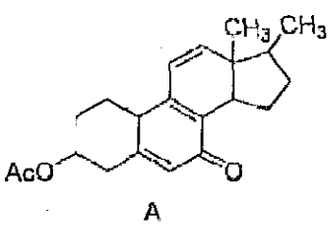
(09 Marks)

4. Give the structures of the products of the following reactions.



(06 Marks)

5. Calculate the expected λ_{max} of the following compound **A**, using Woodward-Fieser rules for α, β-unsaturated ketones.

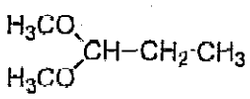


A

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	
	λ_{max}	

(08 Marks)

6. Sketch the ^{1}H-NMR spectrum of B showing the relative distance from TMS, relative areas and multiplicities of signals.



B

(08 Marks)

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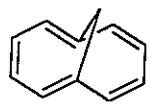
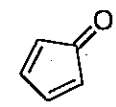
7. Predict which of the following compounds will be expected to show aromatic properties. Explain your answer.





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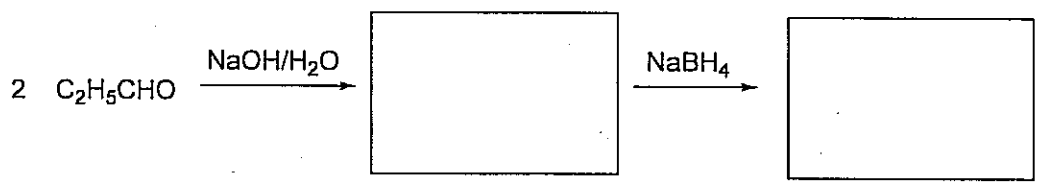
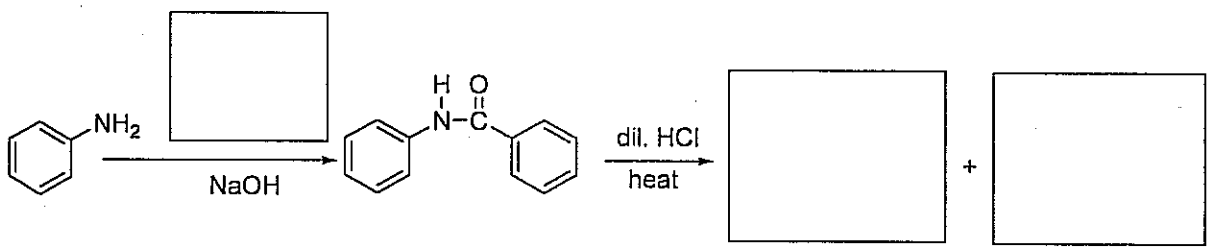
(10 Marks)

8. Give the structures of the products of the following reaction sequence.



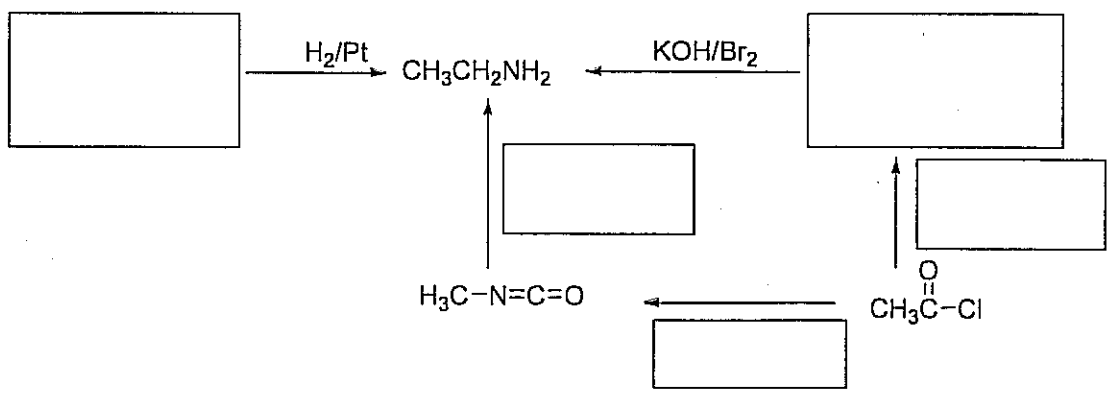
(08 Marks)

9. Complete the following reaction sequence by giving the missing reagents and products.



(06 Marks)

10. Give suitable starting materials/products and reagents for the following reaction schemes.



(12 Marks)

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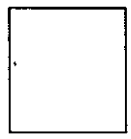
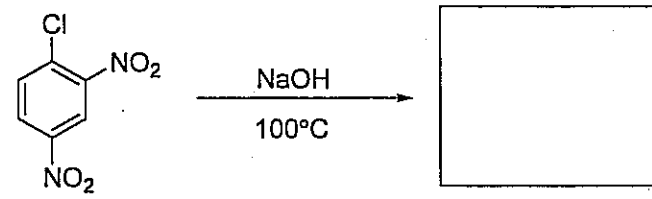
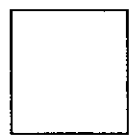
11. Identify the major product in the following reaction.

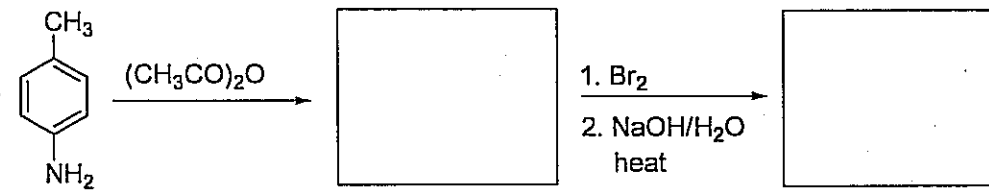




(08 Marks)

12. Complete the reaction scheme given below.





(08 Marks)

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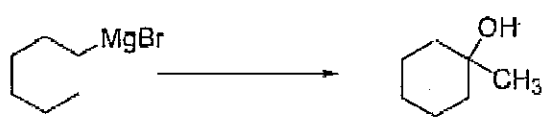
PART B: ANSWER ANY FOUR (04) QUESTIONS. (02 HOURS)

13. An aliphatic compound, **A** ($C_6H_{13}Br$), on treatment with alcoholic KOH yielded compound **B** (C_6H_{12}). Upon ozonolysis in the presence of Zn, **B** gave **C** (C_2H_4O) and **D** (C_4H_8O). Both **C** and **D** answered the iodoform test. When treated with HBr, **B** yielded **E**, which is isomeric with **A**.
    (a) Deduce the structures of **A, B, C, D** and **E.**
    (b) Suggest a chemical test to distinguish between **C** and **D.**
    (c) Give the structures of the products formed when ozonolysis is done in the absence of Zn.

(50 Marks)

14. (a) Giving necessary reagents and conditions show how you would carry out any **two (02)** of the following transformations.

i. $CH_3CH_2CH_2OH \longrightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_3$

ii. 

iii. $CH_2\underset{\displaystyle Cl}{\underset{|}{C}}H-\underset{\displaystyle Cl}{\underset{|}{C}}H_2 \longrightarrow CH_3C{\equiv}C-COOH$

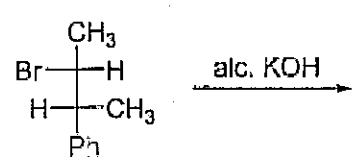
(24 Marks)

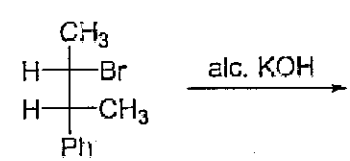
(b) Giving appropriate mechanisms, predict the product/s of the following hydrolysis reaction.

$$H_3C-S-\underset{\displaystyle CH_3}{\underset{|}{C}}H-CH_2-Cl \xrightarrow{H_2O}$$

(10 Marks)

(c) Giving appropriate mechanisms, predict the products of the following elimination reactions.

i. 

ii. 

(16 Marks)

15. (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.

(10 Marks)

(b) Draw the structures of the fragments responsible for the peaks at m/z = 85 and m/z = 58 in the mass spectrum of octan-2-one. [$CH_3(CH_2)_5COCH_3$]

(10 Marks)

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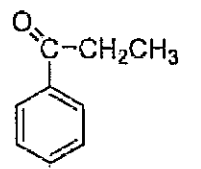
(c) i. Predict the number of signals, area ratios and multiplicities of the signals in the ^{1}H NMR spectrum of **E.**

ii. Sketch the 1H-NMR spectrum of **E**, showing relative positions of peaks from TM *N.B. δ values of peaks are not expected.*



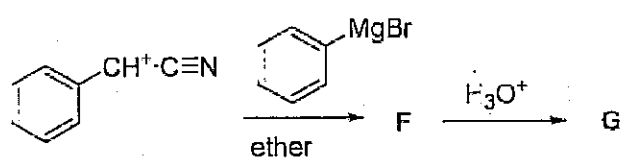
E

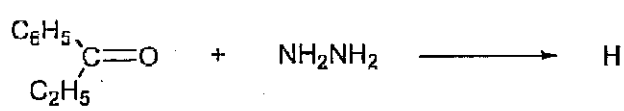
(30 M

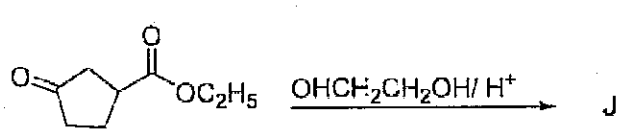
16. (a) Cyclopentadienyl anion is aromatic. Explain this statement using an energy level diagram.

(10 Ma

(b) Give the structures of the products from **F** to **J** in the following reactions.

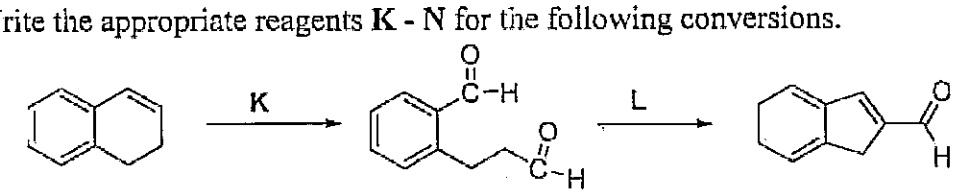
i. 

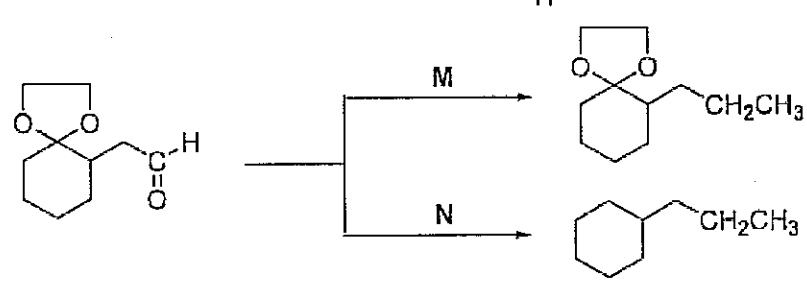
ii. 

iii. 

(20 Ma

(c) Write the appropriate reagents **K - N** for the following conversions.

i. 

ii. 

(20 M

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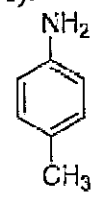
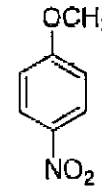
17. (a) Outline a method to separate the mixture of *p*-toluidine and *p*-nitroanisole (both compounds are solids).



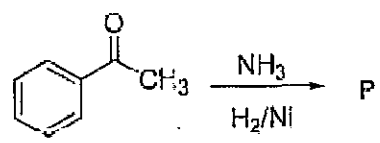
p-toluidine

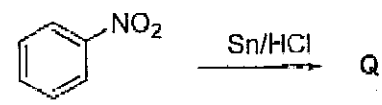


p-nitroanisole

(15 Marks)

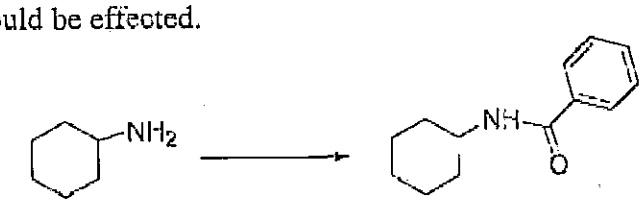
(b) Predict the products **P** – **Q** that you expect from the following reactions.

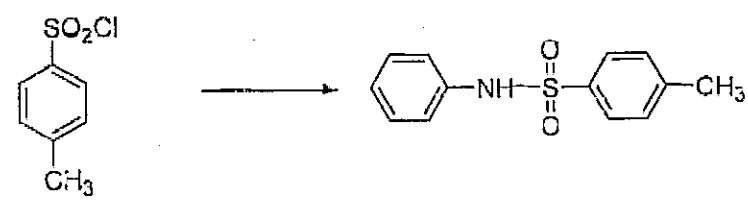
i. 

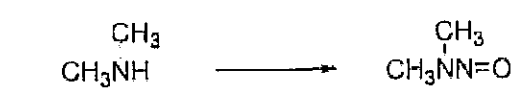
ii. 

(10 Marks)

(c) Giving necessary reagents and conditions show how the following transformations would be effected.

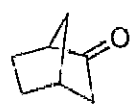
i. 

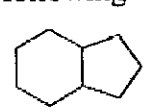
ii. 

iii. 

(15 Marks)

(d) Give IUPAC names of the following compounds.

i. 

ii. 

(10 Marks)

18. (a) Write resonance structures for the σ complex formed when anisole, $C_6H_5OCH_3$ undergoes nitration at *ortho* position. Account for the observed equal rates of nitration of $C_6H_5OCH_3$ and $C_6D_5OCH_3$.

(20 Marks)

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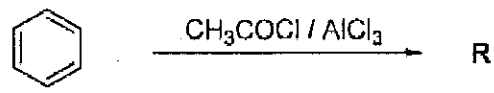
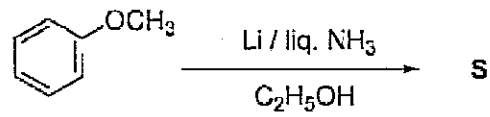
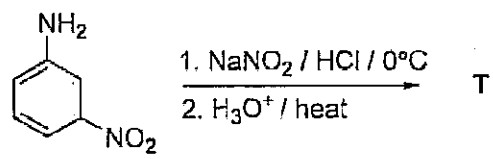
(b) Give the major products **R – T** of the following reactions.

i. 

ii. 

iii. 

(30 Marks)