00094

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THE OPEN UNIVRVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME STAND ALONE COURSE 2010/2011

LEVEL 4 - FINAL EXAMINATION

CHU 2221 / CHE 4221 - ORGANIC CHEMISTRY

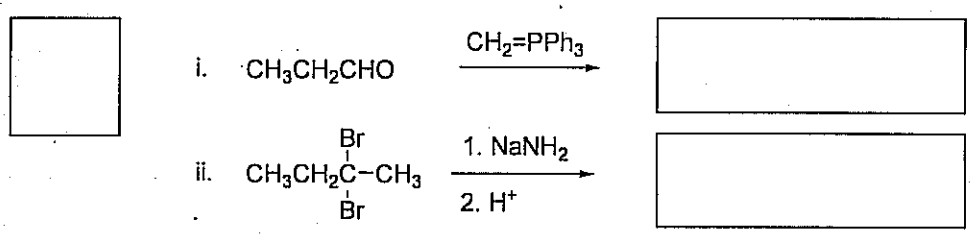
DURATION: 3 HOURS

Thursday 30th June 2011 — 9.30 a.m. – 12.30 p.m.

THIS PAPER CONSISTS TWO PARTS, PART A AND PART B

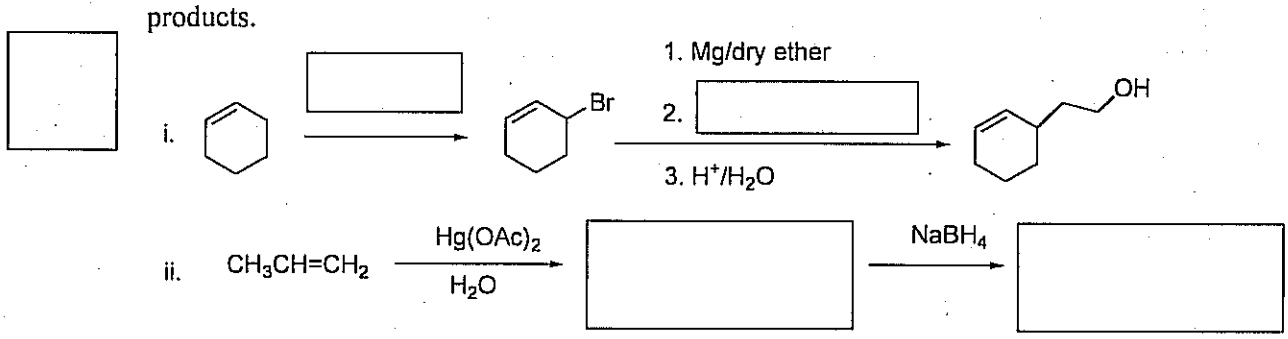
PART A: ANSWER ALL QUESTIONS (01 HOUR)
Write your answers in the spaces provided at each question.

1. Give the structure of the product of the following reactions.



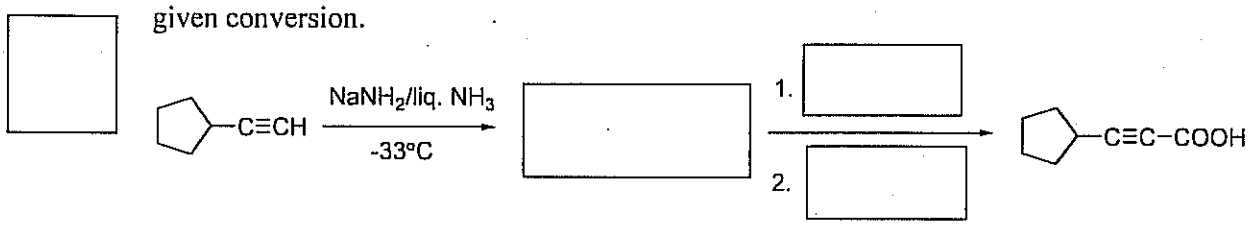
(08 marks)

2. Complete the following reaction schemes giving appropriate reagents, intermediates and products.



(10 Marks)

3. Give the structure of the missing product and the set of suitable reagents to carry out the given conversion.



(06 marks)

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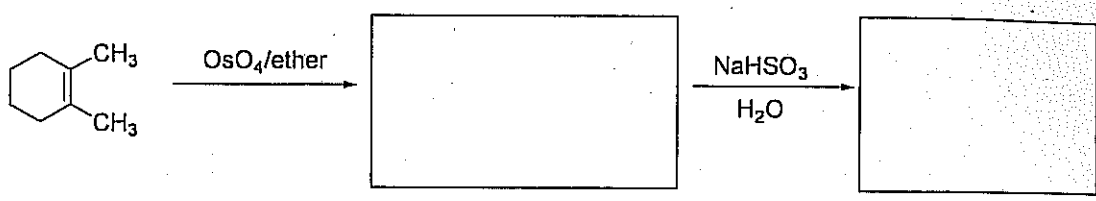
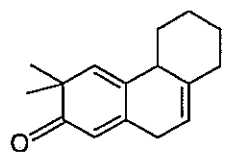
4. Give the possible structures of the products in the following reaction scheme.



(08 Marks)

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

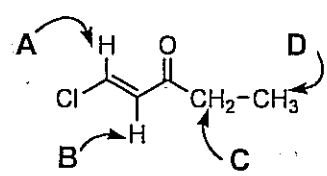


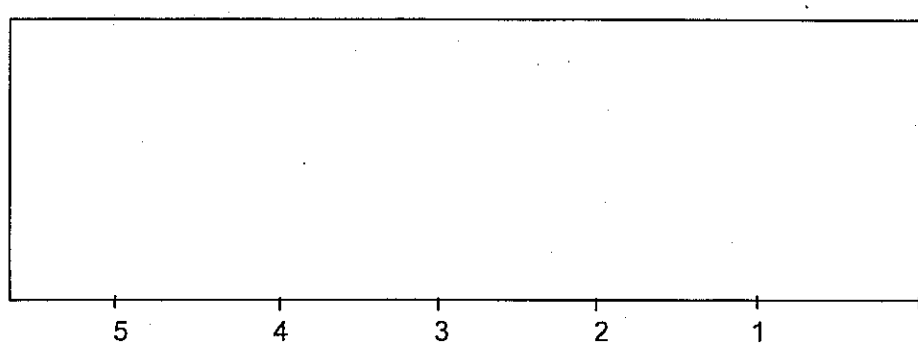
A

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
Calculated λ_{max}		

(08 marks)

6. In the ^{1}H NMR spectrum of the compound shown below, the approximate δ values of the protons labelled **A**, **B**, **C**, and **D** are 5, 4, 2, and 1 ppm, respectively. Sketch the ^{1}H NMR spectrum of this compound in the box provided, **clearly showing the splitting patterns of the 4 signals.**





(08 marks)

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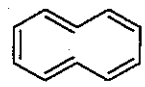
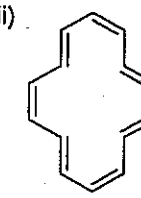
7. Which of the following species will be expected to be aromatic? Account for your answer.

(i) 

(ii) 

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(10 marks)

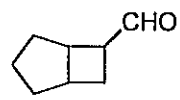
8. Give the structures of the products of the following reaction sequence.

$CH_3CH_2COCH_3$ $\xrightarrow{HCN}$ [ ] $\xrightarrow[heat]{HCl/H_2O}$ [ ]

(06 Marks)

9. Give the IUPAC names of the following compounds.

[ ]

i. 

.....

ii. 
.....

(08 marks)

10. Draw a possible structure for the amine that gives a precipitate (which is insoluble in acidic medium) with benzene sulphonyl chloride in the presence of excess aqueous KOH (Hinsberg test).

[ ]

(10 marks)

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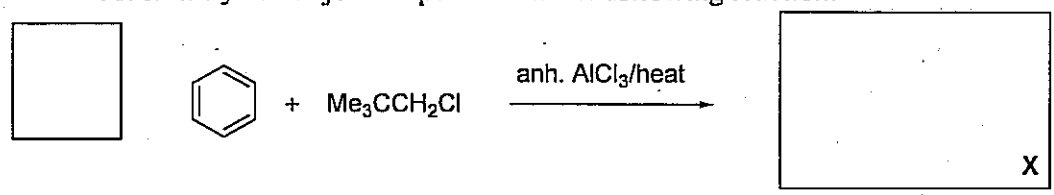
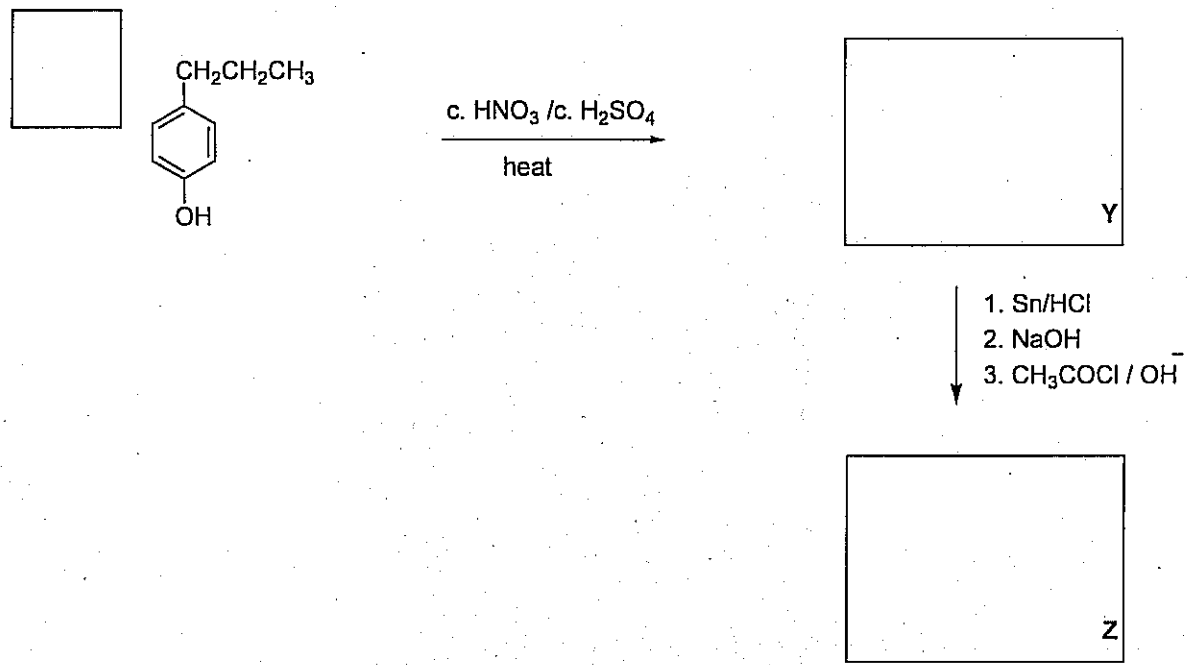
11. Identify the major compound **X** in the following reaction.



Major compound

(08 marks)

12. Predict the products **Y** and **Z** in the reaction scheme given below.



(08 marks)

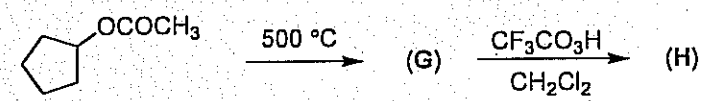
PART B: ANSWER ANY FOUR (04) QUESTIONS (02 HOURS)

13. (a) A neutral compound **B** ($C_7H_{12}O$) gave an orange precipitate with Brady's reagent but with Tollen's reagent no silver mirror was obtained. **B** when reacted with $NaBH_4$ in methanol gave **C** ($C_7H_{14}O$) which on treatment with conc. H_2SO_4 at 160 °C gave **D** (C_7H_{12}). When Br_2 water is added to **D** the colour of Br_2 disappeared. Ozonolysis of **D** in the presence of Zn/H_2O gave **E** ($C_7H_{12}O_2$). **E** when reacted with CrO_3/HOAc gave **F** ($C_7H_{12}O_3$). **F** gave yellow precipitate when reacted with NaOH / I_2. The filtrate on acidification gave hexane-1,6-dioic acid.

Explaining all the above reactions and observations deduce the structures of **B, C, D, E** and **F**.

(40 Marks)

(b) Give the structures of compounds **G** and **H** in the following reaction scheme.



(10 Marks)

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

(i)

(ii)

(iii) $CH_3CH_2CH_2OH \longrightarrow CH_3\underset{\displaystyle OH}{\underset{|}{C}}HCH_2OCH_3$

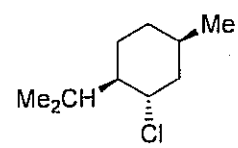
(20 Marks)

(b) Giving appropriate mechanisms, predict the structure of the major product of the following reactions.

$Me_3\underset{\displaystyle OH}{\underset{|}{C}}HMe \xrightarrow{H^+/H_2O}$

(10 Marks)

(c) Draw the two chair conformations of the following compound **K** and label them as **K1** and **K2**. Which conformation is more stable?



(K)

Compound **K** was treated with alcoholic KOH. Giving explanations, answer the following.

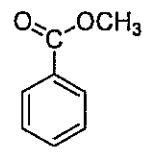
(i) Which conformation is reacts readily with alcoholic KOH?

(ii) Give the mechanism of the above reaction.

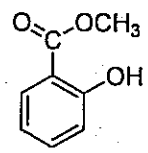
(iii) What is/are the product(s) of this reaction?

(20 Marks)

15. (a) Explain why the carbonyl stretching frequency of methyl benzoate occurs at 1724 cm^{-1} while that of methyl salicylate occurs at 1680 cm^{-1}.



methylbenzoate



methy salicylate

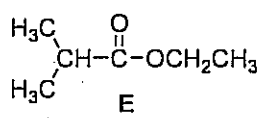
(10 marks)

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

(ii) Sketch the ^{1}H-NMR spectrum of **E**, showing relative positions of peaks from TMS.

N.B. *δ values of peaks are not expected*

(iii) Draw the structures of the fragments responsible for the peak at m/z = 71 and m/z = 43 in the mass spectrum of compound **E**.



E

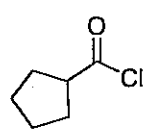
(30 marks)

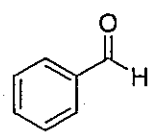
(c) The ^{1}H NMR spectrum of the diol **C**, $C_6H_{14}O_2$ has two signals at δ1.70 (singlet, 12H) and δ5.20 (broad singlet, 2H, disappears with D_2O). Identify C and assign its ^{1}H NMR signals.

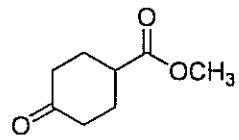
(10 marks)

16. (a) Give the structures of **J** – **M** of the following reactions.

i. $(CH_3)_2CH(CH_2)_3OH \xrightarrow[CH_2Cl_2,\ 25°C]{PCC}$ **J**

ii.  $\xrightarrow[diethylether,\ -78°C]{(CH_3)_2CuLi}$ **K**

iii.  $+ H_2NNH_2 \xrightarrow{heat}$ **L**

iv.  $\xrightarrow[2.\ H_3O^+]{1.\ LiAlH_4/ether}$ **M**

(20 marks)

(b) Consider the reaction between acetyl chloride and NH_3 to form the corresponding amide.

i. Write the mechanism of the above reaction.

ii. Explain why an excess of NH_3 should be used in this reaction.

(20 marks)

(c) Arrange the following three acids in the order of increasing acidity giving reasons.

CH_3COOH $ClCH_2COOH$ $ClCH_2CH_2COOH$

(10 marks)

17. (a) Explain the following statements.

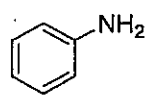
i. Cyclopropane readily undergoes ring opening reactions.

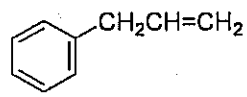
ii. Trimethylamine $[(CH_3)_3N]$ has a very low boiling point when compared with that of propylamine $[CH_3CH_2CH_2NH_2]$ with equal molecular weight.

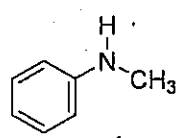
(20 marks)

(b) Give the major product of the following reactions.

i. $C_2H_5\text{-}\overset{\overset{O}{\|}}{C}\text{-}NH_2 \xrightarrow{Br_2/KOH}$

ii.  $\xrightarrow[CH_3COO^-Na^+]{(CH_3CO)_2O}$

iii.  $\xrightarrow[Zn/Cu]{CH_2I_2/ether}$

iv.  $\xrightarrow{NaNO_2/HCl}$

(20 marks)

(c) Write the mechanism for the following reaction.

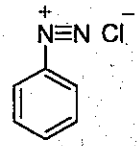
$$CH_3CH_2\underset{\underset{NH_2}{|}}{C}HCH_3 \xrightarrow[2.\ Ag_2O]{1.\ \text{excess } CH_3I} CH_3CH_2CH{=}CH_2$$

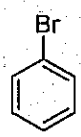
(10 marks)

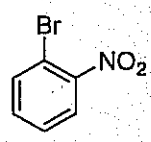
18. (a) Considering the resonance structures of the intermediate ion that could be formed in the electrophilic substitution of phenoxide ion, $C_6H_5O^-$, explain why the reaction occurs mainly at the *ortho* and *para* positions with activation of nucleus.

(20 Marks)

(b) Give the major products of the following reactions.

(i)  $\xrightarrow{C_6H_5OH}$ P

(ii)  $\xrightarrow[NH_3,-33°C]{NaNH_2}$ Q

(iii)  $\xrightarrow[130°C]{NaOH}$ R

(30 Marks)