00144

THE OPEN UNIVRVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2017 / 2018

LEVEL 4 - FINAL EXAMINATION

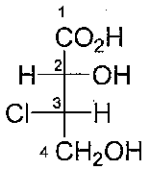
CMU2221 / CME4221 - ORGANIC CHEMISTRY I

DURATION: 3 HOURS

Saturday 06th April 2019 9.30 a.m. - 12.30 p.m.

ANSWER ALL QUESTIONS

1. (a) Consider the compound (**A**) drawn below as a Fischer projection formula. (*Carbon atoms are numbered for your convenience*).



A

(i) Determine the configurations of chiral centers as *R* or *S* showing the priorities of the groups attached to them according to Cahn-Ingold-Prelog rules.
Note: *If priorities of the groups are* ***not clearly shown*** *marks will not be awarded*

(ii) How many stereoisomers are possible for **A**?

(iii) Draw the Fischer projection formula of the enantiomer of **A** and label it as **B**.

(iv) Draw the Fischer projection formula of a diastereoisomer of **A** and label it as **C**.

(v) What is the stereochemical relationship between **B** and **C**?

(40 Marks)

(b) Explain the following observations.
2-chloro-2-methyl propane undergoes hydrolysis in water while 1-chlorobutane does not undergo hydrolysis under the same conditions. With the addition of NaOH into the reaction medium, 1-chlorobutane undergoes hydrolysis and the rate of hydrolysis is found to be dependent on the concentration of NaOH.

(30 Marks)

(c) Giving the mechanisms predict the product(s) of (**D**) when reacted with NaOEt in EtOH.

(**D**)

(10 Marks)

(c)

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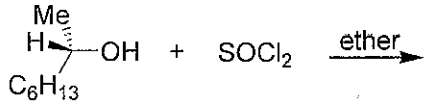
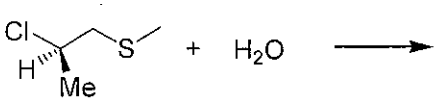
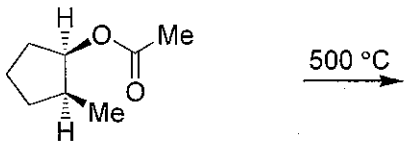
(d) Giving the mechanism predict the product of any **TWO (02)** of the following reactions.

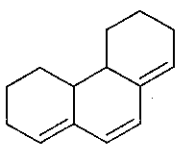
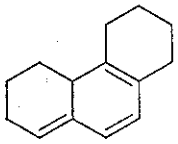
(i) 

(ii) 

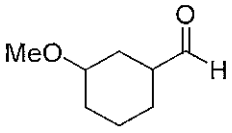
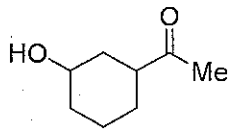
(iii) 

(20 Marks)

2. (a) State how you would distinguish between the compounds in **any FOUR (04)** of the following pairs using the indicated spectroscopic method. Briefly state the reasons for your answers.

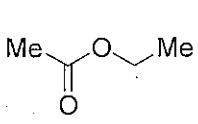
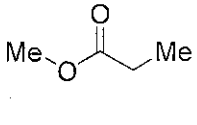
(i)  and  UV-Vis spectroscopy

(ii) $CH_3CH_2C{\equiv}CH$ and $CH_3C{\equiv}CCH_3$ IR spectroscopy

(iii)  and  IR Spectroscopy

(iv) $CH_2{=}C(CH_3)CH_2CH_2Br$ and $CH_3CH(CH_2CH_3)CH_2CH_2CH_2Cl$ Mass spectroscopy

(v) $CH_3C(Cl)(CH_3)CH_3$ and $CH_3CH(CH_3)CH_2Cl$ ^{1}H NMR spectroscopy

(vi)  and  ^{1}H NMR spectroscopy

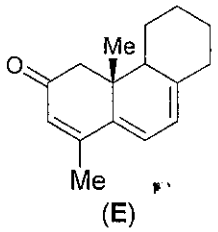
(20 Marks)

(b) Explain why in the IR spectroscopy $\nu_{C-H} > \nu_{C-O}$.

(15 Marks)

(c) Calculate the expected λ_{max} of the compound **E** using Woodward-Fieser rules for α, β-unsaturated ketones given below.

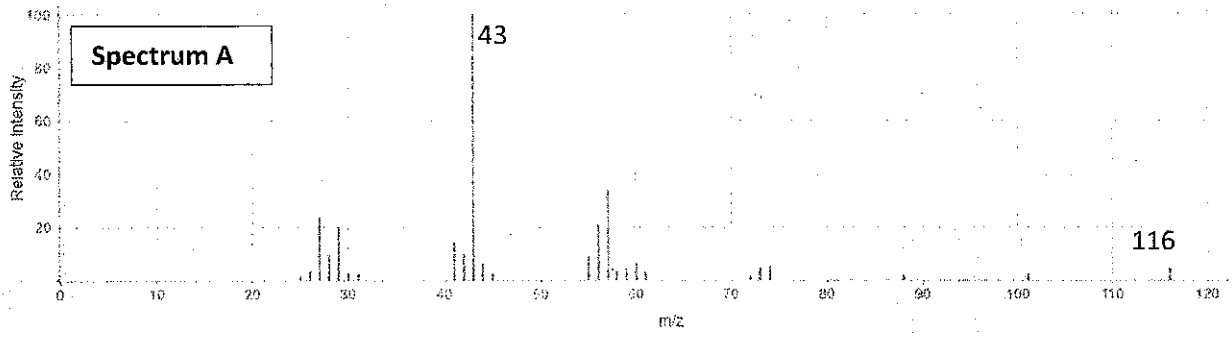
Base value for α,β-unsaturated ketone	=	215 nm
Increments for		
Double bond extending conjugation	=	+ 30 nm
Alkyl group or ring residue at α	=	+ 10 nm
β	=	+ 12 nm
γ and higher	=	+ 18 nm
Exocyclic double bond position	=	+ 05 nm
Homoannular diene component	=	+ 39 nm

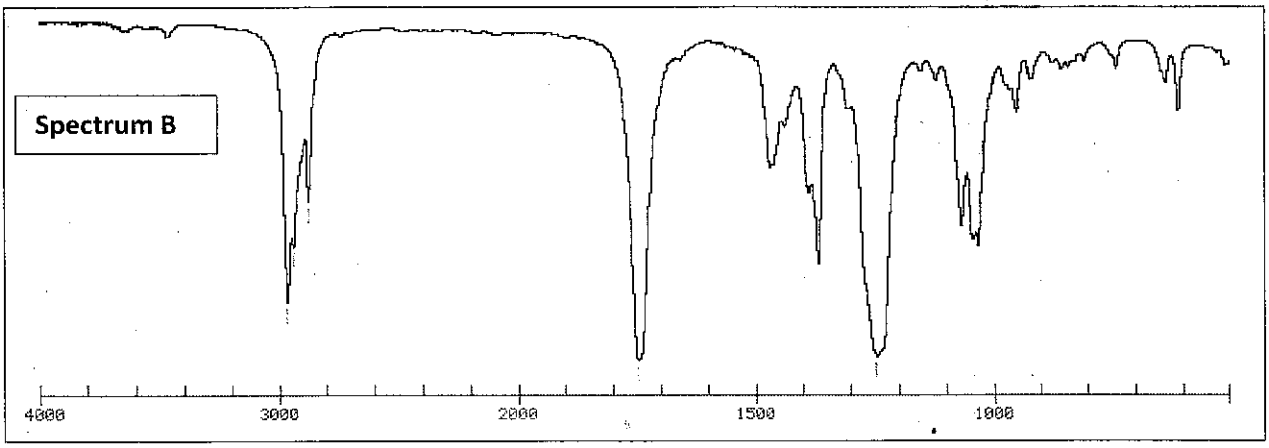


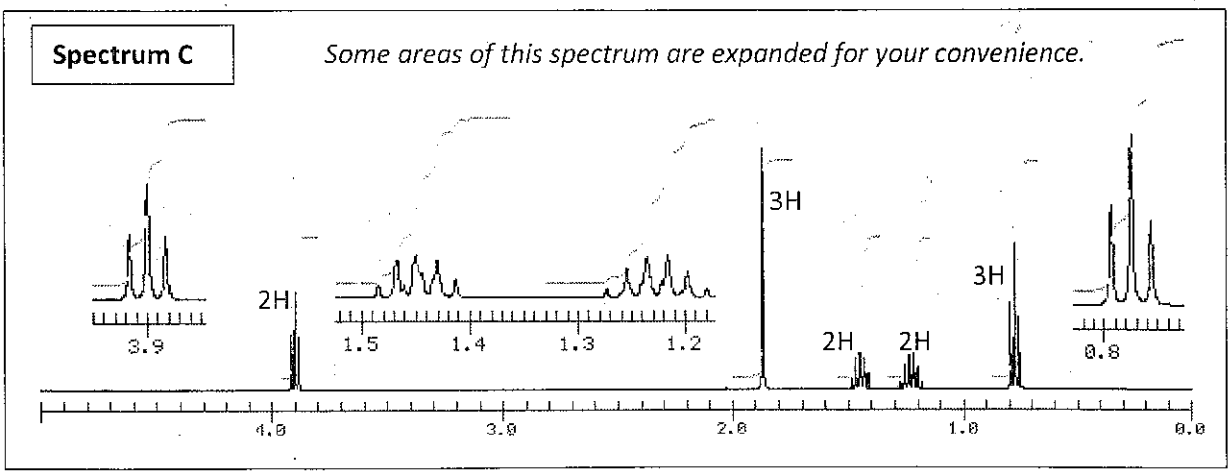
(E)

(15 Marks)

(d) Given below are some spectra of compound **F** ($C_6H_{12}O_2$).



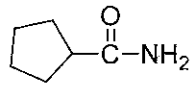


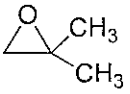


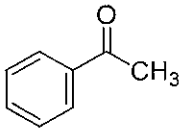
(i) State the name of the spectrum given by A, B and C.
(ii) State what information could be obtained from **spectrum B** and **spectrum C**.
(iii) What is/are the functional group/s present in the compound **F**?
(iv) How many different types of H atoms are there in this molecule?
(v) Deduce the structure of **F** and assign the signals in **spectrum C**.
(vi) Give the possible structure of the fragment ion at *m/e* 43.

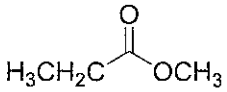
(50 Marks)

3. (a) Give the structures of the major products (**J–O**) of the following reactions.

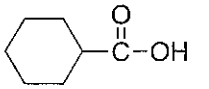
(i)  $\xrightarrow{P_2O_5}$ **G**

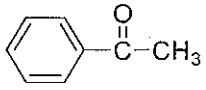
(ii)  $\xrightarrow{NaOCH_3/\ CH_3OH}$ **H**

(iii)  $\xrightarrow[\text{conc. HCl}]{Zn(Hg)}$ **I**

(iv)  $\xrightarrow[2.\ H_2O]{1.\ \text{DIBAL-H/ether/-78 °C}}$ **J**

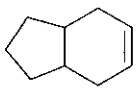
(v) $(CH_3)_3C{-}CH{=}CH_2$ $\xrightarrow[2.\ NaBH_4/OH^-]{1.\ Hg(OAc)_2/H_2O/THF}$ **K**

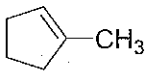
(vi)  $\xrightarrow{PCl_5}$ **L**

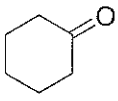
(vii)  $\xrightarrow[Cl_2\ (excess)]{CH_3CO_2H}$ **M**

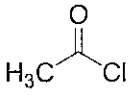
(35 marks)

(b) Give the structures of the intermediates and the major products (**N**– **U**) of the following reaction schemes.

(i)  $\xrightarrow[CH_2Cl_2]{C_6H_5CO_2OH}$ **N** $\xrightarrow{H^+/\ H_2O}$ **O**

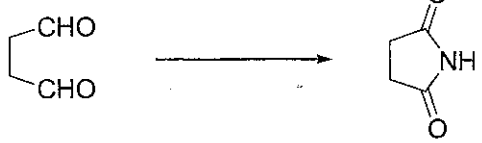
(ii)  $\xrightarrow{THF/BF_3}$ **P** $\xrightarrow[25\ °C]{H_2O_2/\ NaOH}$ **Q**

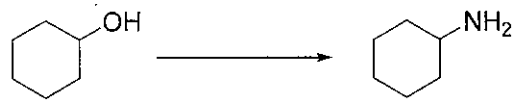
(iii)  $\xrightarrow{HCN}$ **R** $\xrightarrow{H^+/\ H_2O}$ **S**

(iv)  $\xrightarrow{NH_3}$ **T** $\xrightarrow[KOH]{Br_2}$ **U**

(40 marks)

(c) Giving necessary reagents and conditions show how any **ONE (01)** of the following transformations can be carried out.

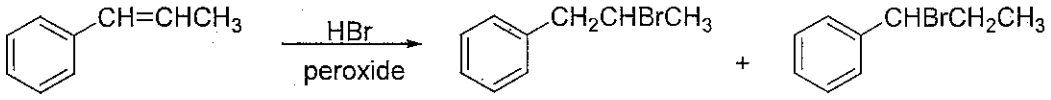
(i) 

(ii) 

(25 marks)

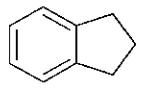
4. (a) Answer only **ONE (01)** part, either part (i) or part (ii).
In the reactions given below, out of the two products shown only one is formed.
Giving reasons show which product is formed

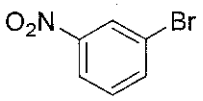
(i) $CH_2=CH-CH=CH_2 \xrightarrow[40\ °C]{HBr} CH_3-CH=CHCH_2Br + CH_3\cdot CHBrCH=CH_2$

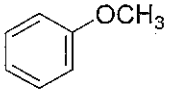
(ii) 

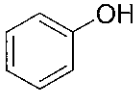
(30 marks)

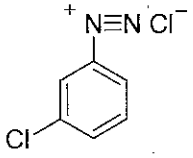
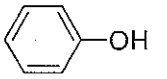
(b) Give the structures of the major products (**A–H**) in the following reactions..

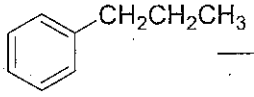
(i)  $\xrightarrow[heat]{KMnO_4/OH}$ **A**

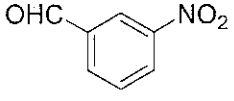
(ii)  $\xrightarrow[liq.\ NH_3,\ -33\ °C]{NaNH_2}$ **B**

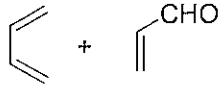
(iii)  $\xrightarrow[liq.\ NH_3,\ C_2H_5OH]{Li}$ **C**

(iv)  $\xrightarrow[2.\ H^+/H_2O]{1.CHCl_3,\ NaOH,\ heat}$ **D**

(v)  $\xrightarrow[dil.\ NaOH,\ 0°C]{}$  **E**

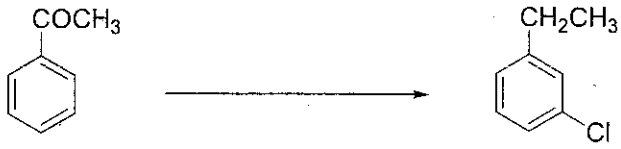
(vi)  $\xrightarrow[CCl_4,\ heat]{NBS}$ **F**

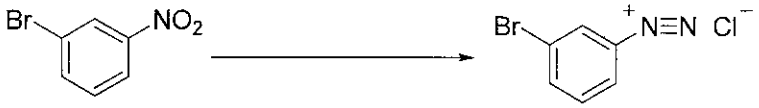
(vii)  $\xrightarrow[anhyd.\ AlCl_3]{CH_3Cl}$ **G**

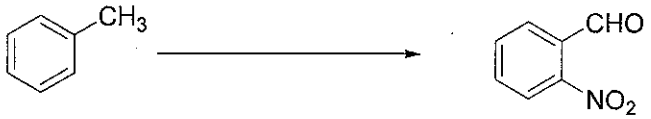
(viii)  $\xrightarrow{30\ °C}$ **H**

(40 marks)

(c) Giving necessary reagents and conditions show how any **TWO (02)** of the transformations can be carried out.

(i) 

(ii) 

(iii) 

(40 marks)