THE OPEN UNIVERSITY OF SRI LANKA

B. Sc. DEGREE PROGRAMME / STAND ALONE COURSE 2016 / 2017

LEVEL 5 - FINAL EXAMINATION

CMU3120 / CME5120 - ORGANIC CHEMISTRY

DURATION: 02 HOURS

Friday, 11th August 2017 1.30 – 3.30 p.m.

Answer ALL FOUR (04) questions.

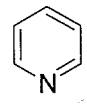
1. Answer any **FOUR (04)** parts from (a) – (e).

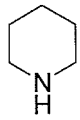
   (a) Explain why pyridine is less basic than piperidine.

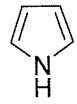
   (b) Arrange pyrrole, pyridine and benzene in the order of their increasing reactivity towards electrophilic reagents. Explain your answer in terms of the structures of the corresponding intermediates.

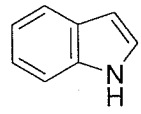
   (c) Explain why electrophilic substitution in indole occurs mainly at C-3 position rather than at C-2 position.

   (d) Give an example for a nucleophilic substitution reaction in six-membered aromatic heterocyclic compound. Draw the resonance structures of the intermediate ion and indicate the most stable contributing structure,

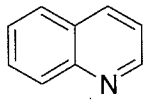

pyridine

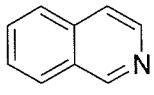

piperidine


pyrrole


indole

   (e) Give the structures of major products **A**, **B** and **C** of the following reactions.

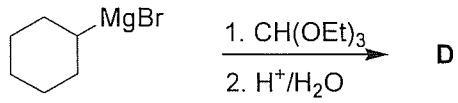
   (i)  $\xrightarrow{HNO_3/Ac_2O}$ **A**

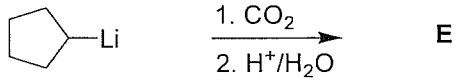
   (ii)  $\xrightarrow[2.\ H_2O]{1.\ NaNH_2}$ **B**

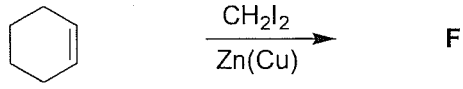
   (iii)  $\xrightarrow{Ac_2O\ /SnCl_4}$ **C**

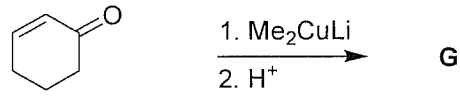
(25 x 4 = 100 Marks)

2. (a) Give the structures of the products **D** – **G** of the following reactions.

(i) 

(ii) 

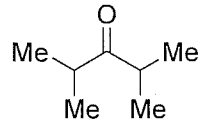
(iii) 

(iv) 

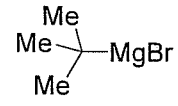
(40 Marks)

(b) Reaction between di-*iso*propyl ketone and *tert*-butylmagnesium bromide followed by acidification does not yield the desired alcohol. Instead, two side reactions take place.

Give the mechanism and the product(s) of **one** of the side reactions.



di-*iso*propylketone

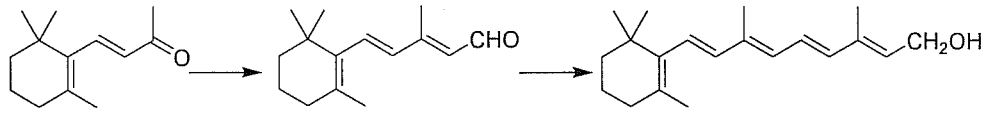


tert-butylmagenesium bromide

(20 Marks)

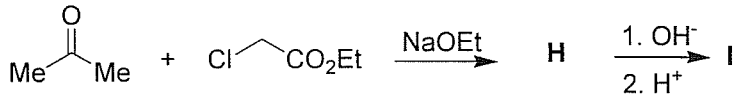
(c) Answer any **ONE** (**01**) of the following parts.

(i) Giving necessary reagents and conditions and using Reformatzky reaction as one of the carbon-carbon bond formation reaction show how you would carry out the following synthesis of Vitamin A from β-ionone.



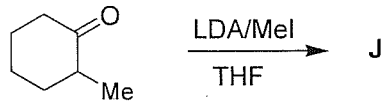
β-ionone Vitamin A

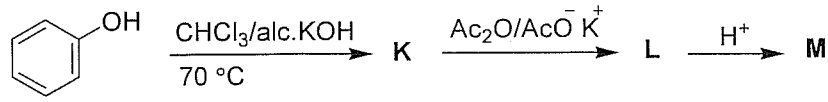
(ii) Give the structures of the products **H** and **I** and the mechanism of the following reaction.

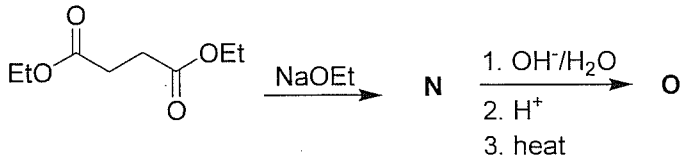


(40 Marks)

3. (a) Give the structures of the compounds **J** – **O** of the following reaction schemes.

(i) 

(ii) 

(iii) 

(30 Marks)

(b) Answer either **PART I** or **PART II**.

PART I

Benzaldehyde when treated with NaCN in ethanol gives >80% benzoin.

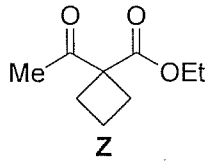
(i) Give the mechanism of the formation of benzoin from the above reaction.

(ii) Give reasons as to why benzoin condensation takes place in aromatic aldehydes in contrast to aliphatic aldehydes.

benzoin

PART II

Acetoacetic ester when treated with 1,3-dibromobutane in the presence of NaOEt, the following four membered alicyclic compound **Z** is not formed.



Z

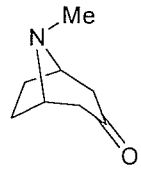
(i) Give the product of this reaction and the mechanism of its formation.

(ii) Explain why the expected four membered alicyclic compound **Z** is not formed.

(30 Marks)

(c) (i) Briefly describe Mannich reaction giving an appropriate example and its mechanism.

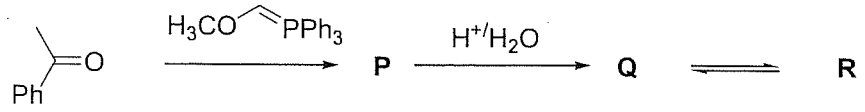
(ii) Show how tropinone is synthesized using Robinson's synthesis which illustrates the use of Mannich reaction in organic synthesis.

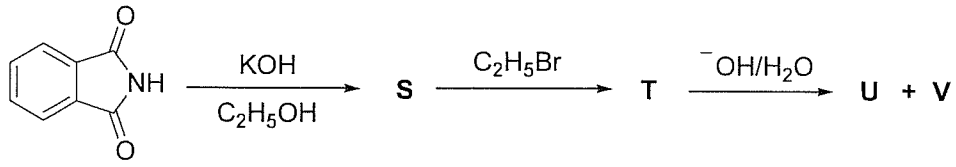


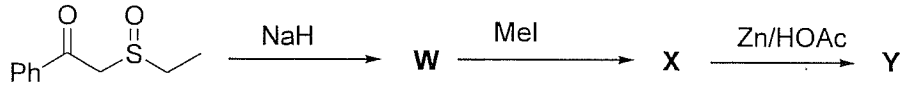
tropinone

(40 Marks)

4. (a) Give the products and intermediates (**P – Y**) in the following reaction schemes.

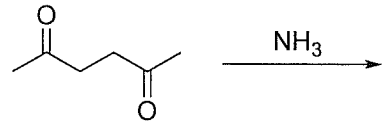
i. 

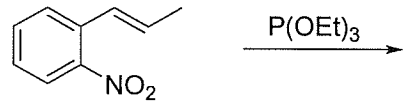
ii. 

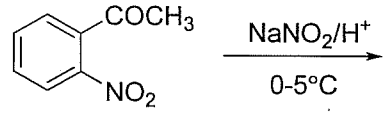
iii. 

(30 Marks)

(b) Giving mechanisms identify the major products of any **TWO (02)** of the following reactions.

i. 

ii. 

iii. 

(30 Marks)

(c) Indicate the synthetic route leading to any **ONE (01)** of the following.

(i) $(CH_3)_3C\text{-}NH_2$ employing Ritter reaction using $(CH_3)_3C\text{-}OH$ as one of the starting materials.

(ii) $CH_3CH(NH_2)COOH$ employing Strecker synthesis using CH_3CHO as one of the starting materials.

(40 Marks)