UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2007/2008

June 2008

KOT 323 – Organic Chemistry III
[Kimia Organik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **SIXTEEN** printed pages before you begin the examination.

Instructions:

Answer **FIVE** (5) questions only.

Answer each question on a new page.

You may answer either in Bahasa Malaysia or in English.

If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

...2/-

1. (a) The following questions are about keto-enol tautomerism.

(i) What is keto-enol tautomerism? Show an example.

(ii) Generally the keto tautomer is much more stable in normal ketone. However, in β-diketone, the enol form is relatively more stable. Why?

(iii) Show both how a base or an acid can catalyse the keto-enol interconversion.

(iv) The iodoform test is a good example of keto-enol interconversion affecting a reaction to completion. Show the mechanism of this reaction.

(10 marks)

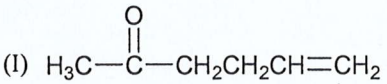
(b) LDA or lithium diisopropylamide is a very strong base that can be used to abstract an α-hydrogen.

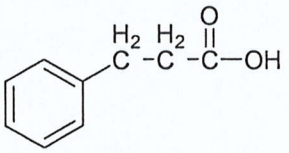
(i) Write the structure of LDA.

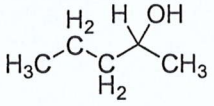
(ii) How is LDA normally prepared?

(iii) What are the products that can be obtained when cyclopentanone is first reacted with LDA followed by an excess of methyl iodide?

(iv) How can the following compounds be prepared from acetone + LDA?

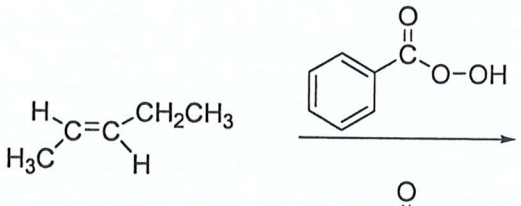
(I) 

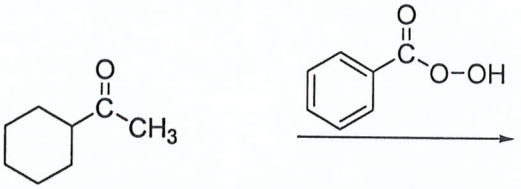
(II) 

(III) 

(10 marks)

2. (a) Give the product(s) of the following reactions;

(i) 

(ii) 

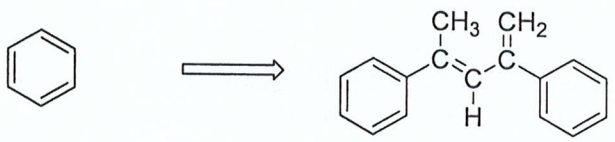
(iii) 

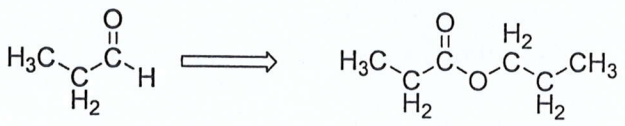
(iv) 

(8 marks)

(b) Show how the following transformations can be realized in the shortest steps possible;

(i) $CH_3CH_2Br \Longrightarrow CH_3CH_2CH_2OH$

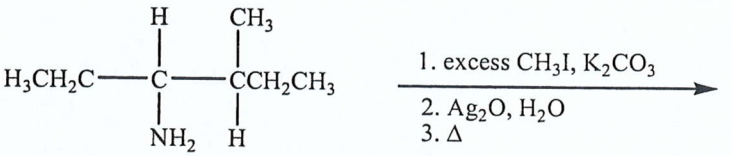
(ii) 

(iii) 

(12 marks)

3. (a) Give the major product of the following reactions:

(i)



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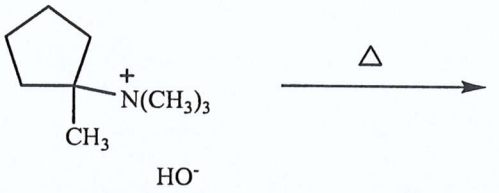
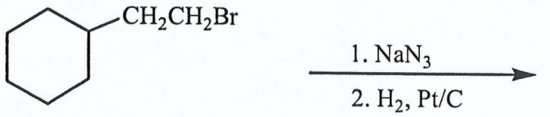


(iii)



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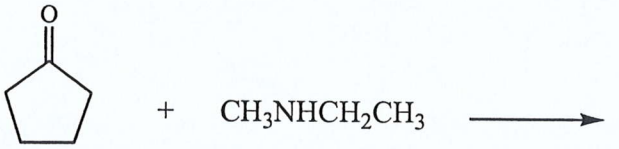
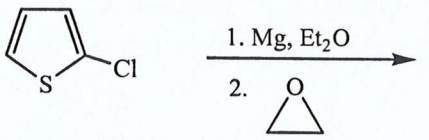


(v)



(10 marks)

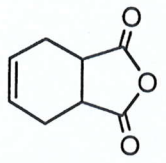
(b) (i) Using the resonance contributors theory, explain the orientation of the electrophilic substitution of furan.

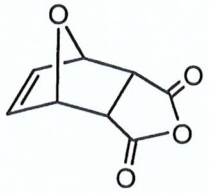
(ii) Compare the relative reactivity of furan and pyrrole towards the electrophilic substitution reaction. Explain briefly.

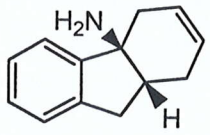
(iii) Compare the basicity of pyrrole with pyrrolidine. Explain your answer.

(10 marks)

4. (a) Give the diene and dienophile needed to synthesise each of the following compounds:

(i) 

(ii) 

(iii) 

(6 marks)

(b) Using the frontier orbital analysis (HOMO-LUMO), explain why the Diels-Alder reaction occurs relatively at ease.

(4 marks)

(c) 

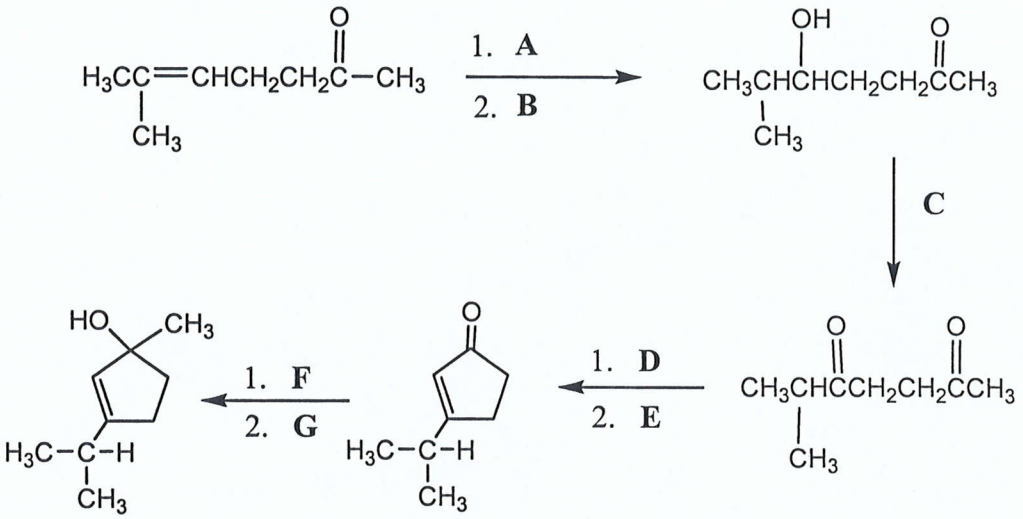
(i) What is the name of the pericyclic reaction?

(ii) Give the structure of **A** and **B**.

(iii) Using the Woodwad-Hoffmann rules, explain your answer.

(10 marks)

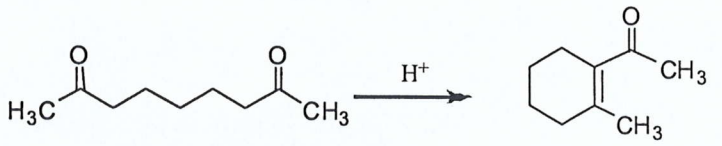
5. (a) Give the reagents of **A** to **G** in the reactions below.



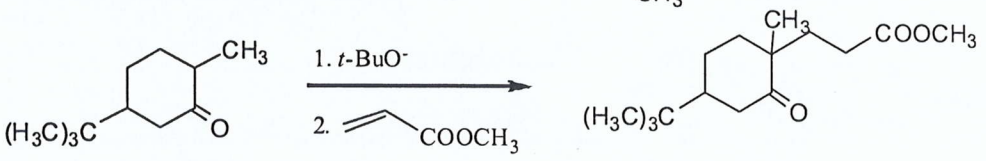
(8 marks)

(b) Give the mechanism of the formation of each compound from the given starting material.

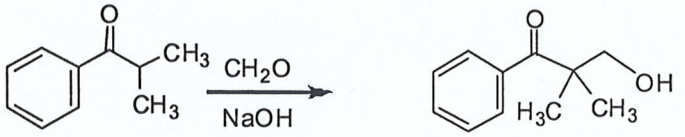
(i)



(ii)



(iii)



(12 marks)

1. (a) Soalan berikut adalah mengenai tautomerisme keto-enol.

(i) Apakah tautomerisme keto-enol? Tunjukkan suatu contoh.

(ii) Secara umumnya tautomer keto adalah jauh lebih stabil bagi keton lazim. Walau bagaimanapun, bagi β-diketone, bentuk enol adalah agak lebih stabil secara relatif. Kenapa?

(iii) Tunjukkan bagaimana kedua-dua suatu bes atau suatu asid boleh memangkinkan saling pertukaran bentuk keto-enol ini.

(iv) Ujian iodoform adalah suatu contoh yang baik menunjukkan saling pertukaran bentuk keto-enol yang menyebabkan sesuatu tindak balas berlaku dengan sempurna. Tunjukkan mekanisme tindak balas ini.

(10 markah)

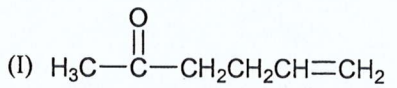
(b) LDA atau litium diisopropilamida adalah suatu bes yang amat kuat yang boleh digunakan untuk mengabstrak suatu α-hidrogen.

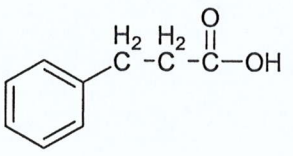
(i) Tuliskan struktur LDA.

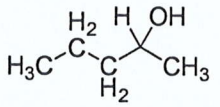
(ii) Bagaimana LDA lazimnya disediakan?

(iii) Apakah hasil yang boleh didapati apabila siklopentanon pada mulanya ditindak balaskan dengan LDA kemudian diikuti dengan metil iodida berlebihan?

(iv) Bagaimana sebatian berikut boleh disediakan dari aseton + LDA?

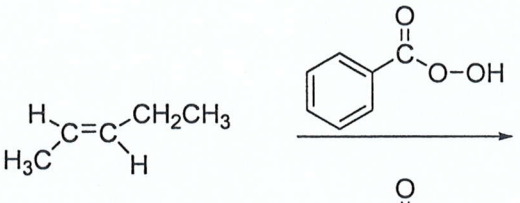
(I) 

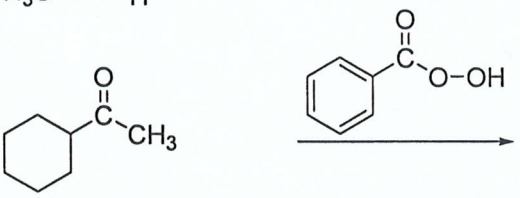
(II) 

(III) 

(10 markah)

2. (a) Berikan hasil tindak balas berikut;

(i) 

(ii) 

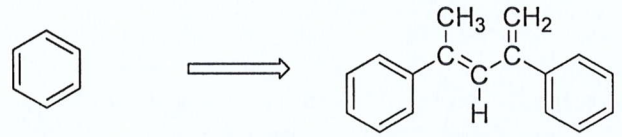
(iii) 

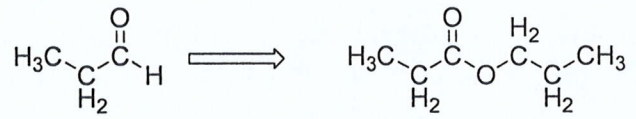
(iv) 

(8 markah)

(b) Tunjukkan bagaimana transformasi berikut boleh dilakukan di dalam beberapa langkah terpendek yang mungkin;

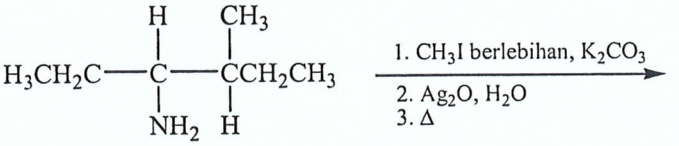
(i) $CH_3CH_2Br \Longrightarrow CH_3CH_2CH_2OH$

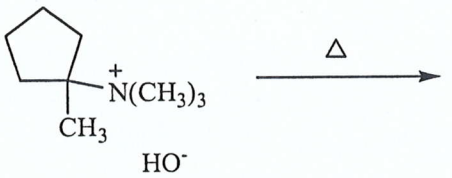
(ii) 

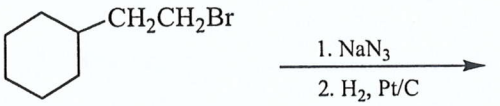
(iii) 

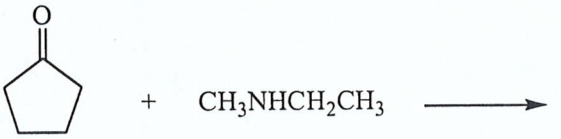
(12 markah)

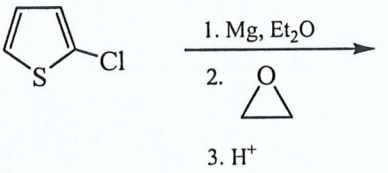
3. (a) Berikan hasil major bagi setiap tindak balas berikut:

(i) 

ii) 

(iii) 

(iv) 

(v) 

(10 markah)

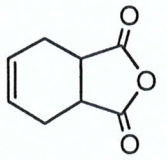
(b) (i) Dengan menggunakan teori penyumbang resonans, jelaskan orientasi tindak balas penukargantian elektrofilik bagi furan.

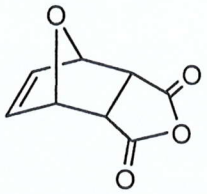
(ii) Bandingkan kereaktifan relatif bagi furan dan pirola terhadap tindak balas penukargantian elektrofilik. Jelaskan dengan ringkas.

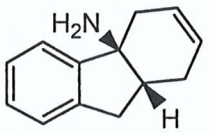
(iii) Bandingkan kebesan pirola dan pirolidina. Jelaskan jawapan anda.

(10 markah)

4. (a) Berikan diena dan dienofil yang diperlukan untuk mensintesis setiap yang berikut:

(i) 

(ii) 

(iii) 

(6 markah)

(b) Dengan menggunakan analisis orbital perbatasan (HOMO-LUMO), jelaskan mengapa tindak balas Diels-Alder berlaku dengan mudah.

(4 markah)

(c) 

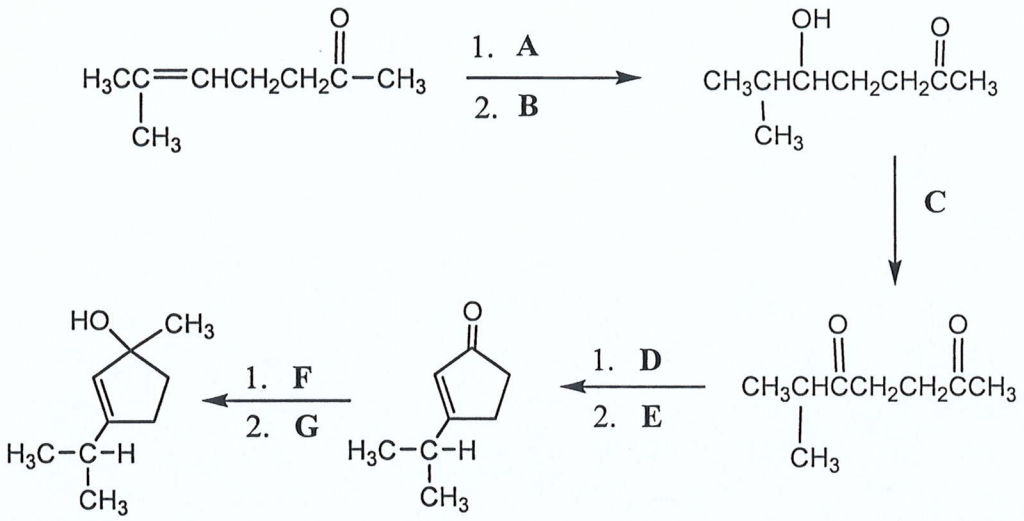
(i) Apakah nama tindak balas perisiklik ini?

(ii) Berikan struktur **A** dan **B**.

(iii) Dengan menggunakan peraturan Woodward-Hoffmann, jelaskan jawapan anda.

(10 markah)

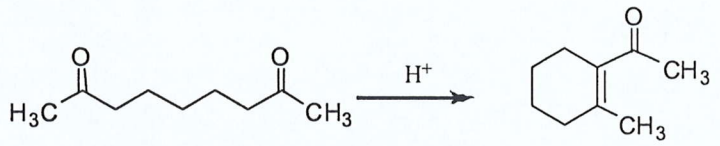
5. (a) Berikan reagen **A** ke **G** dalam tindak balas di bawah.



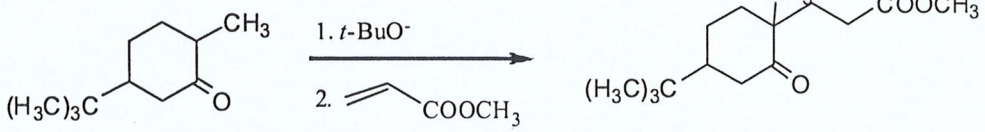
(8 markah)

(b) Berikan mekanisme bagi pembentukan setiap sebatian berikut daripada bahan permulaan yang diberikan.

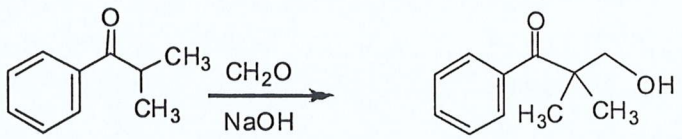
(i)



(ii)



(iii)



(12 markah)