
UNIVERSITI SAINS MALAYSIA

Second Semester Examination
Academic Session 2007/2008

April 2008

KOT 323 – Organic Chemistry III
[Kimia Organik III]

Duration : 3 hours
[Masa : 3 jam]

Please check that this examination paper consists of **EIGHTEEN** 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.

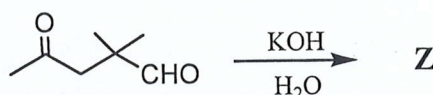
...2/-

- 2 -

1. (a) (i) What is the product of a mixed Claisen condensation between methyl benzoate and cyclohexanone?
- (ii) What is the difference in the mechanisms of Claisen condensation and aldol addition?

(5 marks)

- (b) Treatment of the keto-aldehyde shown below with KOH gives a compound **Z** with molecular formula $C_7H_{10}O$.



- (i) Draw the structure of **Z**.
- (ii) Show the mechanism of the reaction.

(5 marks)

- (c) Compound **A** with molecular formula $C_6H_{12}O$ is optically active and tested positive with the iodoform test. **A** reacts with CH_3MgBr to produce compound **B** which undergoes dehydration to give compound **C** as the major product. Treatment of **C** with ozone followed by addition of Zn and H_2O will produce compounds **D** and **E**. Compound **D** reacts with $LiAlH_4$ to produce an optically active compound **F**. Compound **E** reacts with pyrrolidine to produce **G**. Draw the structures of **A**, **B**, **C**, **D**, **E**, **F** and **G**.

(10 marks)

2. (a) In terms of relative stability of the intermediate, discuss the orientation of electrophilic substitution with furan, pyrrole and thiophene. Use the general structure below to draw the resonance contributors:



(4 marks)

...3/-

- 3 -

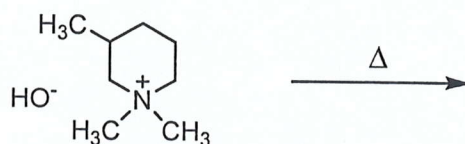
(b) Give the mononitration product for each of the following compounds.

(i) 3-nitropyrrole

(ii) 3-methoxythiophene

(4 marks)

(c) (i) What is the major product of the following reaction?



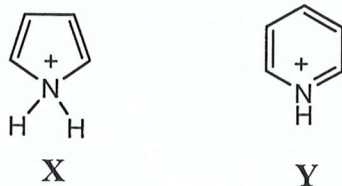
(ii) Using structure 2c(i) and 2-bromobutane as examples, explain why the E2 reaction of alkyl halide occurs via Zaitsev elimination while that of quaternary ammonium ion occurs via Hofmann elimination.

(8 marks)

(d) Explain the following observations:

(i) Pyridine does not undergo Friedel-Crafts reaction.

(ii) X is more acidic than Y.



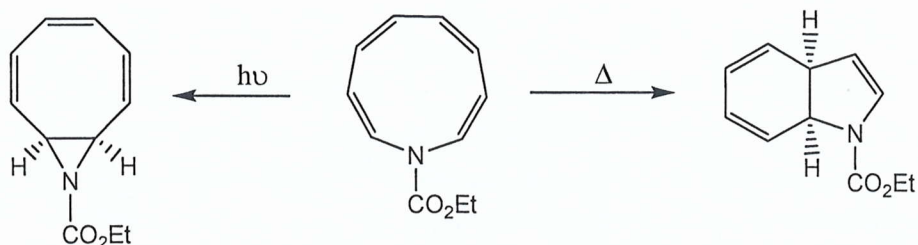
(4 marks)

...4/-

- 5 -

(c) For the reaction below:

- (i) Explain its different behaviour, including the stereochemistry, under thermal or photochemical condition.
- (ii) Give the mechanism for each transformation.

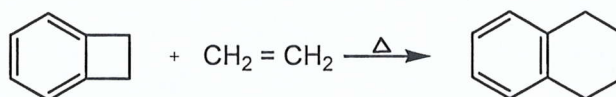


(10 marks)

4. (a) The thermal ring closure of (2*E*, 4*Z*, 6*Z*, 8*Z*)-decatetraene and (2*E*, 4*Z*, 6*Z*, 8*E*)-decatetraene follows the Woodward-Hoffmann rules. Predict the structure of the dimethylcyclooctatriene produced by each of these.

(6 marks)

- (b) (i) Propose a mechanism for the reaction below.
- (ii) What would be the reaction product if *cis*-2-butene were used instead of ethene?

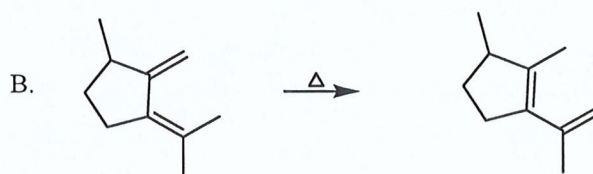
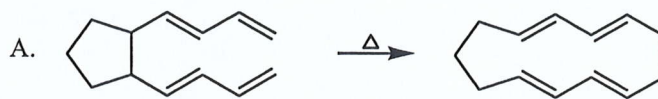


(7 marks)

...6/-

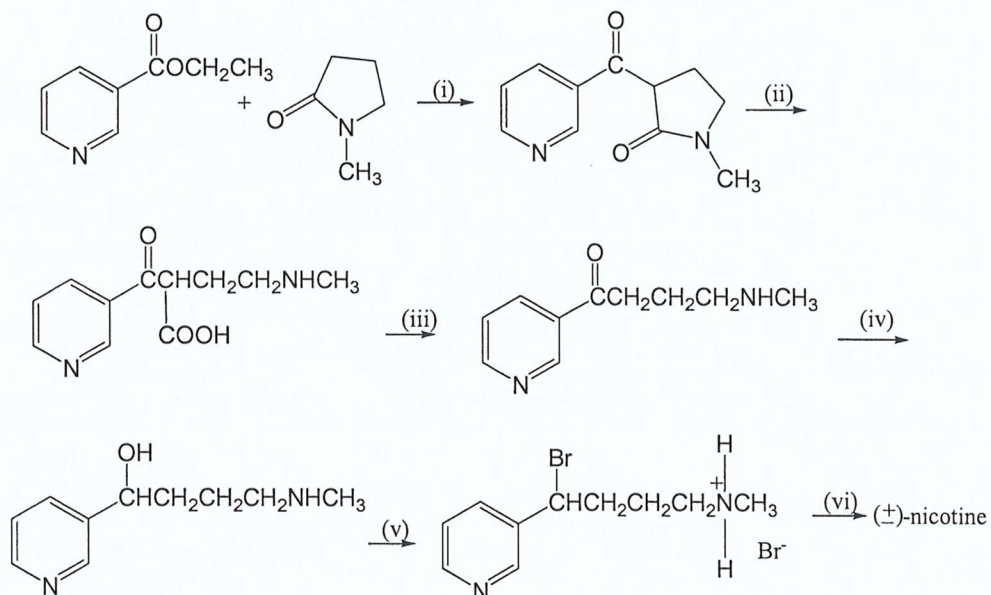
- 6 -

- (c) (i) Name the kind of sigmatropic rearrangement that occurs in each of the following reactions.
- (ii) Using arrows, show the electron rearrangement that takes place in each of the reactions.



(7 marks)

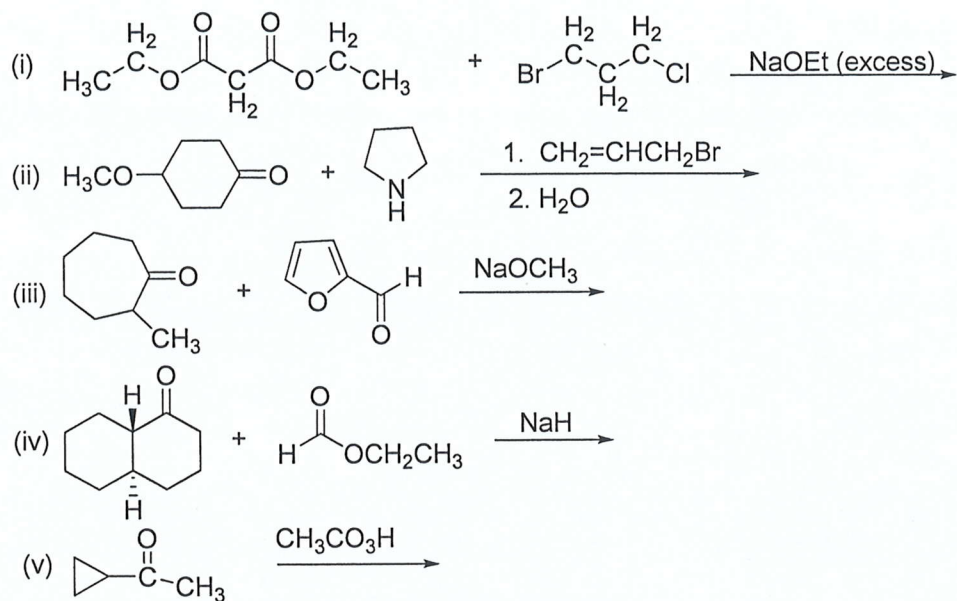
5. (a) Nicotine has been synthesized by the following route. Suggest reagents that could be used for each.



(10 marks)

...7/-

6. (a) Give the main product/s of the following reactions:

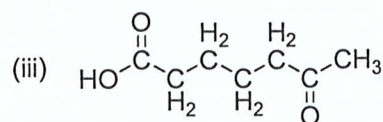
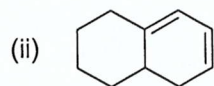
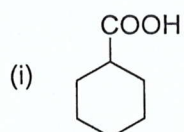


(15 marks)

(b) Condensation of benzaldehyde with diethyl malonate in the presence of sodium ethoxide is an example of the Knoevenagel condensation. Using the two compounds as examples, show the mechanism of the Knoevenagel condensation.

(5 marks)

7. (a) Show how the following compounds can be synthesized from cyclohexanone.



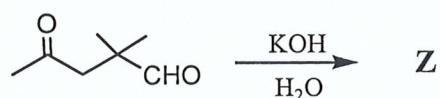
(12 marks)

...9/-

1. (a) (i) Apakah hasil kondensasi Claisen campuran antara metil benzoat dan sikloheksanon?
- (ii) Apakah perbezaan dalam mekanisme kondensasi Claisen dan penambahan aldol?

(5 markah)

- (b) Pengolahan keto-aldehid yang ditunjukkan di bawah dengan KOH memberikan sebatian **Z** dengan formula molekul $C_7H_{10}O$.



- (i) Lukis struktur **Z**.
- (ii) Tunjukkan mekanisme tindak balas tersebut.

(5 markah)

- (c) Sebatian **A** dengan formula molekul $C_6H_{12}O$ adalah aktif optik dan diuji positif terhadap ujian iodoform. **A** bertindakbalas dengan CH_3MgBr menghasilkan sebatian **B** yang kemudiannya mengalami proses pendehidratan menghasilkan sebatian **C** sebagai hasil utama. Pengolahan **C** dengan ozon diikuti penambahan Zn dan H_2O menghasilkan sebatian **D** dan **E**. Sebatian **D** bertindakbalas dengan $LiAlH_4$ menghasilkan sebatian aktif optik **F**. Sebatian **E** bertindakbalas dengan pirolidina menghasilkan **G**. Lukis struktur **A**, **B**, **C**, **D**, **E**, **F** dan **G**.

(10 markah)

2. (a) Dengan mengambil kira kestabilan relatif bagi perantaraan, bincangkan orientasi penukargantian elektrofilik bagi furan, pirola dan tiofena, Gunakan struktur am di bawah untuk melukis penyumbang resonans.



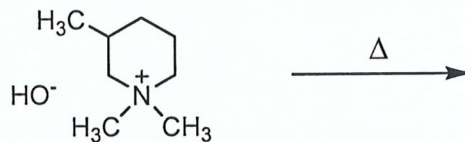
(4 markah)

- (b) Berikan hasil pemononitratan bagi setiap sebatian berikut.

- (i) 3-nitropirola
(ii) 3-metoksitiofena

(4 markah)

- (c) (i) Apakah hasil utama bagi tindak balas di bawah?

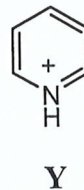
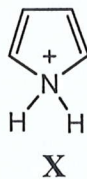


- (ii) Dengan menggunakan struktur soalan 2c(i) dan 2-bromobutana sebagai contoh, jelaskan mengapa tindak balas E2 bagi alkil halida berlaku melalui penyingkiran Zaitsev, manakala bagi ion ammonium kuartener berlaku melalui penyingkiran Hofmann.

(8 markah)

- (d) Jelaskan yang berikut:

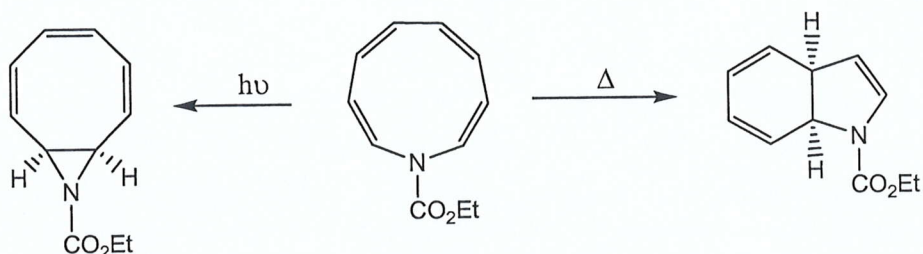
- (i) Piridina tidak melalui tindak balas Friedel-Crafts.
(ii) X lebih berasid berbanding Y.



(4 markah)

(c) Bagi tindak balas di bawah:

- (i) Jelaskan perilaku yang berbeza, termasuk stereokimia, di bawah keadaan terma atau fotokimia.
- (ii) Berikan mekanisme bagi setiap transformasi.

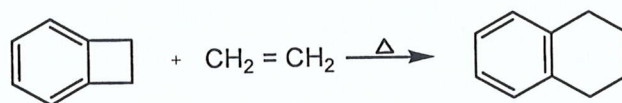


(10 markah)

4. (a) Penutupan gelang terma bagi $(2E, 4Z, 6Z, 8Z)$ -dekatetraena and $(2E, 4Z, 6Z, 8E)$ -dekatetraena mengikut peraturan Woodward-Hoffmann. Ramalkan struktur dimetilsiklooktatriena yang terhasil daripada setiap sebatian tersebut.

(6 markah)

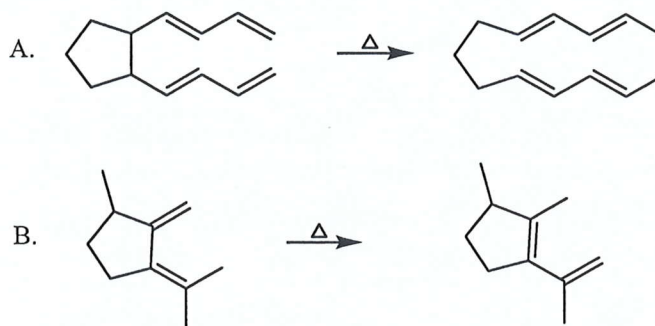
- (b) (i) Cadangkan suatu mekanisme bagi tindak balas yang berikut.
- (ii) Apakah hasil tindak balas yang dijangkakan jika *cis*-2-butena digunakan sebagai ganti etena?



(7 markah)

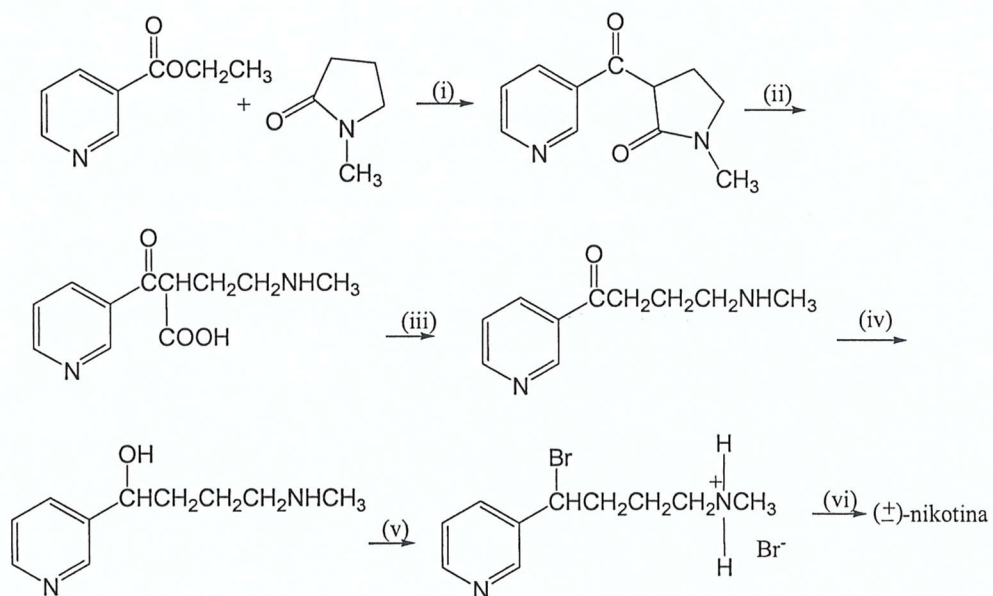
- 15 -

- (c) (i) Namakan jenis penyusunan semula sigmatropik yang berlaku dalam setiap tindak balas yang berikut.
- (ii) Gunakan anak panah untuk menunjukkan penyusunan semula elektron yang berlaku di dalam setiap tindak balas.



(7 markah)

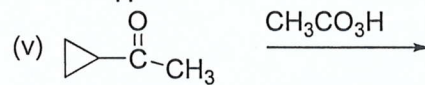
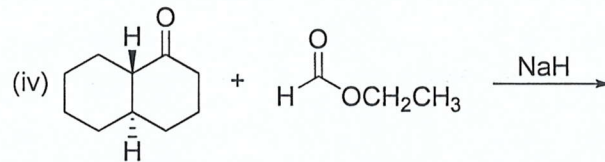
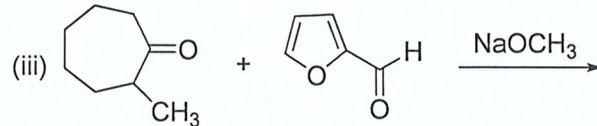
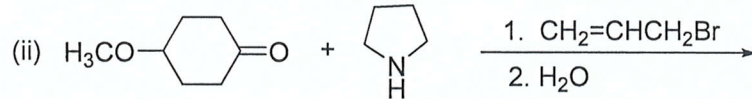
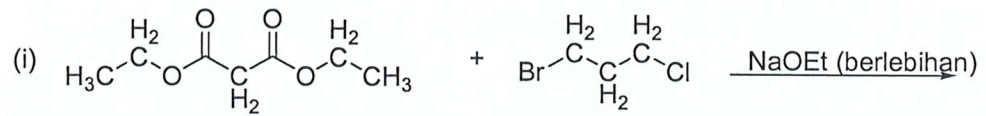
5. (a) Nikotina telah disintesis dengan laluan berikut. Cadangkan reagen yang boleh digunakan dalam setiap langkah.



(10 markah)

...16/-

6. (a) Berikan hasil (-hasil) utama dalam tindak balas berikut;

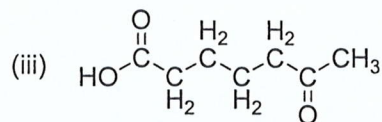
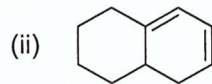
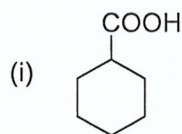


(15 markah)

- (b) Kondensasi benzaldehid dengan dietil malonat dalam kehadiran natrium etoksida adalah suatu contoh kondensasi Knoevenagel. Dengan menggunakan dua sebatian di atas sebagai contoh, tunjukkan mekanisma kondensasi Knoevenagel ini.

(5 markah)

7. (a) Tunjukkan bagaimana sebatian berikut boleh disintesis daripada sikloheksanon.



(12 markah)

...18/-