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UNIVERSITI SAINS MALAYSIA

Second Semester Examination  
2010/2011 Academic Session

April/May 2011

**KOT 323 – Organic Chemistry III**  
*[Kimia Organik III]*

Duration : 3 hours  
*[Masa : 3 jam]*

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Please check that this examination paper consists of TWENTY ONE pages of printed material before you begin the examination.

**Instructions:**

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

You may answer the questions 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.

In the event of any discrepancies, the English version shall be used.

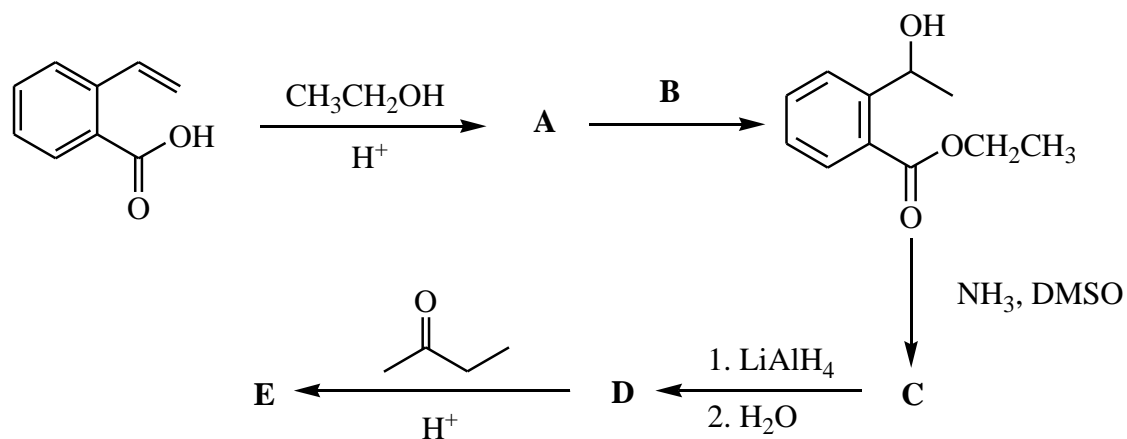
-2-

Answer any **FIVE** questions.

1. (a) Fischer esterification takes place by an acid-catalyzed mechanism, all attempts at base-catalyzed condition (using  $\text{RO}^-$ , for example) seem to fail. Explain why Fischer esterification cannot be catalyzed by base.

(4 marks)

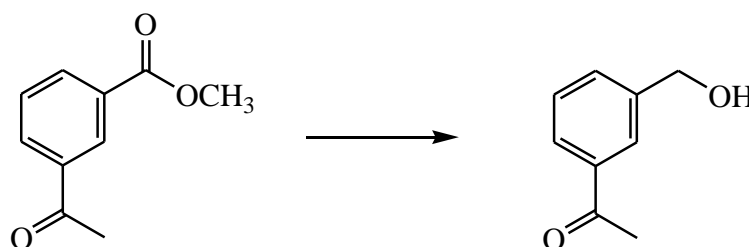
- (b) Give the products and reagents **A** to **E** for the following reactions:



(6 marks)

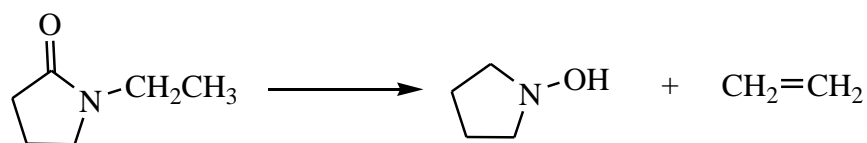
- (c) Propose the synthetic method for each of the following conversions. No mechanism is needed.

(i)



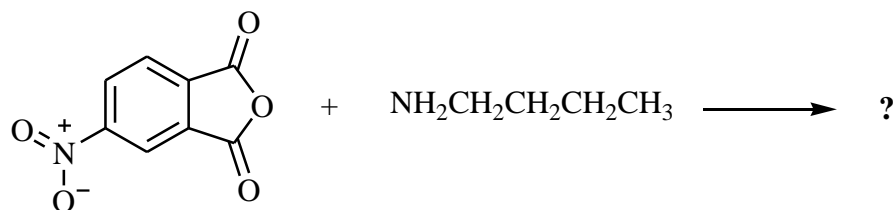
-3-

(ii)



(10 marks)

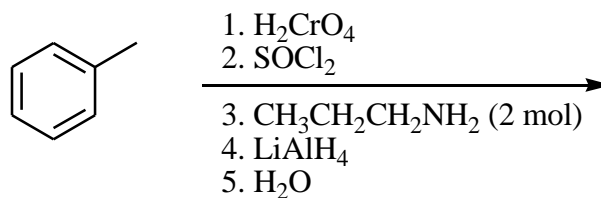
2. (a) What will be the major product of the reaction of 4-nitrophthalic anhydride and *n*-butylamine? Explain.



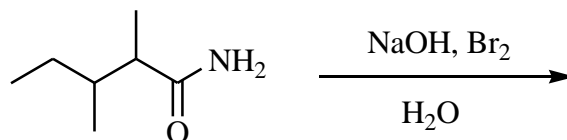
(6 marks)

- (b) Give the product of each of the following reactions:

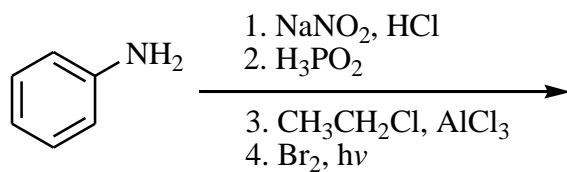
(i)



(ii)

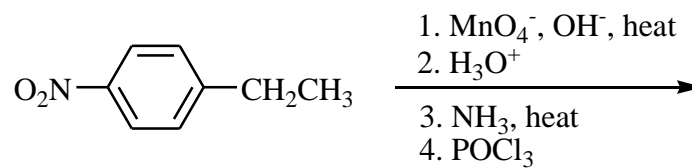


(iii)

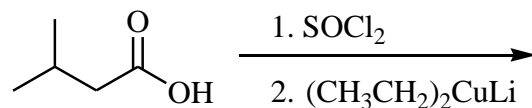


-4-

(iv)

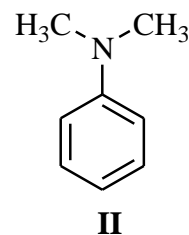
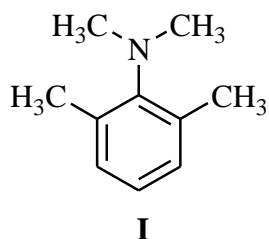


(v)



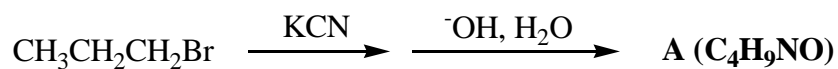
(10 marks)

- (c) Explain why *N,N*,2,6-tetramethylaniline, **I** is a much stronger base than *N,N*-dimethylaniline, **II**.



(4 marks)

3. (a) The reaction below will give compound **A**.

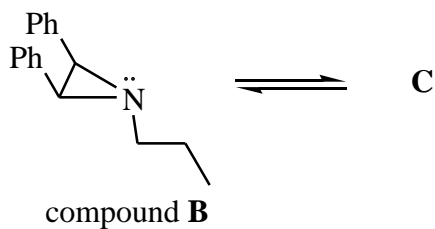


- (i) What is compound **A**?  
 (ii) Give the mechanism for the above reaction to get compound **A**.

(7 marks)

-5-

- (b) Acyclic amines undergo nitrogen inversion rapidly. In contrast, NMR experiments show that compound **B** below undergoes inversion to **C** only at elevated temperatures.

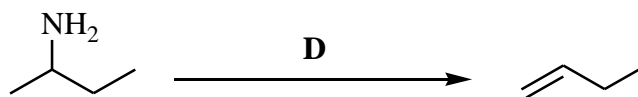


- (i) Write a structural formula for the inverted product, **C**.  
 (ii) Why compound **B** cannot undergo inversion rapidly at room temperature?

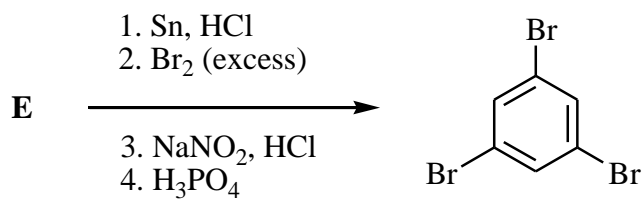
(4 marks)

- (c) Give the reagents, starting material or product of the following reactions:

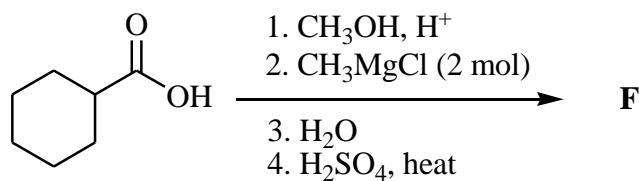
(i)



(ii)



(iii)

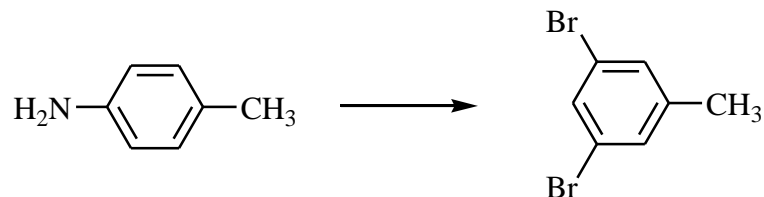


(9 marks)

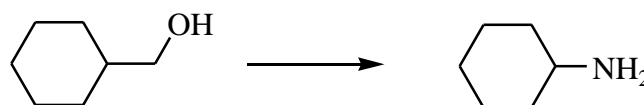
-6-

4. (a) Propose the synthetic method for each of the following conversions. No mechanism is needed.

(i)

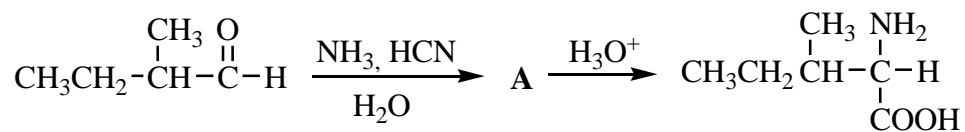


(ii)



(10 marks)

- (b) Isoleucine was prepared using a Strecker synthesis.

**Isoleucine**

Draw the structure of compound **A** and provide a mechanism for each step in the synthesis.

(4 marks)

- (c) Define what is meant by isoelectric point (pI) and give an example.

(2 marks)

-7-

- (d) (i) Draw vertical lines through the peptide bonds in the decapeptide below that will be cleaved by cyanogen bromide.

Try-Ser-Ala-Met-Ser-Pro-Met-Gly-Gly-Asp

- (ii) After treatment with peroxyformic acid, the peptide hormone vasopressin is partially hydrolyzed. The following fragments are recovered. Propose a structure for vasopressin.

Phe-Gln-Asn

Pro-Arg-Gly-NH<sub>2</sub>

Cys-Tyr-Phe

Asn-Cys-Pro-Arg

Tyr-Phe-Gln-Asn

(4 marks)

5. (a) Give the structures for compounds **A** through **G** in the reactions below:

(i)

(ii)

(iii)

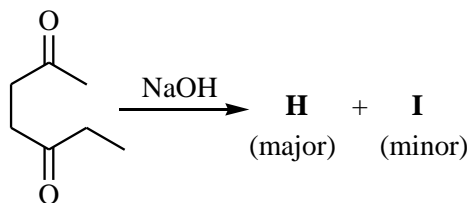
(iv)

(10 marks)

...8/-

-8-

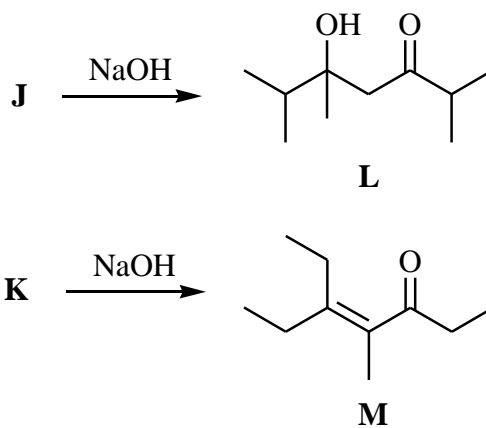
- (b) Intramolecular aldol cyclization of 2,5-heptanedione with dilute sodium hydroxide yields two **enone** products, **H** and **I** in the ratio of 9:1. The major product **H** has two singlet absorptions in its  $^1\text{H}$  NMR spectrum at  $\delta$  1.65 and 1.90 ppm. There are no absorptions in the range of 5-10 ppm.



- (i) Give the structures of compounds **H** and **I**.  
 (ii) Provide a mechanism for the formation of **H** and **I**.

(6 marks)

- (c) Compounds **L** and **M** are prepared by aldol reaction from starting materials, **J** and **K**, respectively. Draw the structures for the starting materials.



(4 marks)



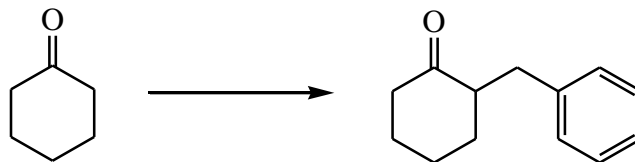
6. (a) Robinson annulation of cyclohexanone and methyl vinyl ketone (MVK) is shown below.

Write the mechanism of the reactions involved, giving the structures of **A** and all the intermediates.

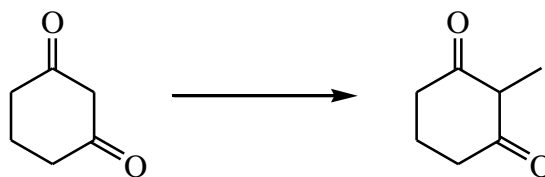
(7 marks)

- (b) Give the synthetic method for each of the following conversions. No mechanism is needed.

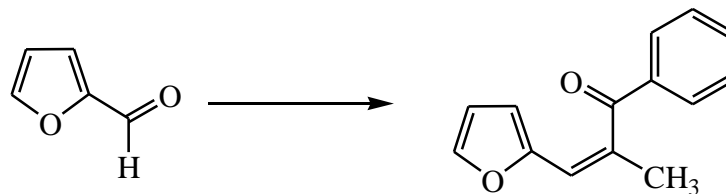
(i)



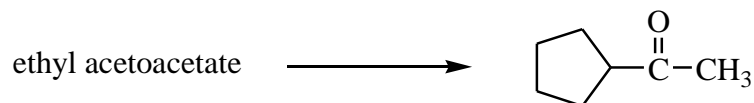
(ii)



(iii)



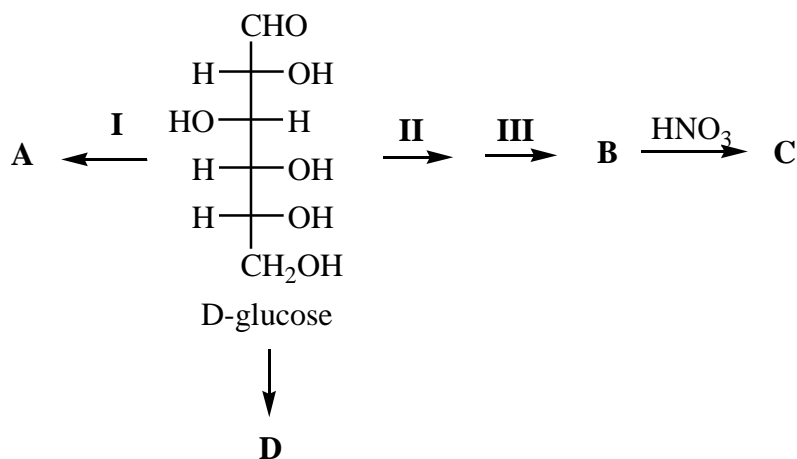
(iv)



(10 marks)

-10-

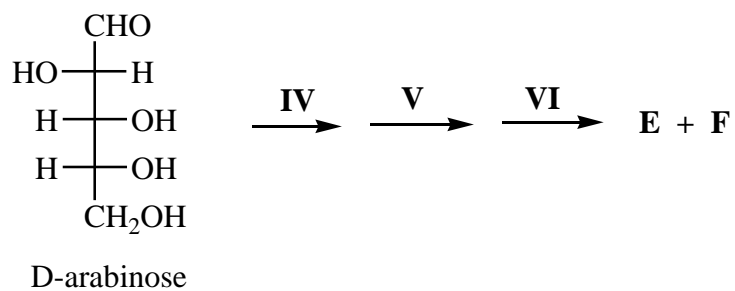
- (c) Treatment of ketone **B** with  $\text{Br}_2/\text{NaOH}$ , followed by acidification gives bromoform and pivalic acid,  $(\text{CH}_3)_3\text{C}-\text{COOH}$ . What is the structure of **B**?  
(3 marks)
7. (a) Define the following terms by giving an example for each.  
(i) Epimer  
(ii) Anomer  
(5 marks)
- (b) D-glucose produced an alditol **A** upon reduction. When D-glucose was subjected to Ruff degradation, compound **B** was generated which then yielded an aldaric acid **C** upon oxidation with nitric acid. D-glucose reacts with two moles of phenylhydrazine to yield an osazone **D**. Use these data to provide structures of compounds **A**, **B**, **C** and **D** and also reagent(s) **I**, **II** and **III**.



(9 marks)

-11-

- (c) D-arabinose undergoes the Kiliani-Fischer synthesis.



- (i) Provide the structures of compounds **E** and **F**.
- (ii) Provide the reagents involved in this synthesis.
- (iii) What is the relationship between **E** and **F**?

(6 marks)

## TERJEMAHAN

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### Arahan:

Jawab **LIMA** (5) soalan.

Anda dibenarkan menjawab soalan ini sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

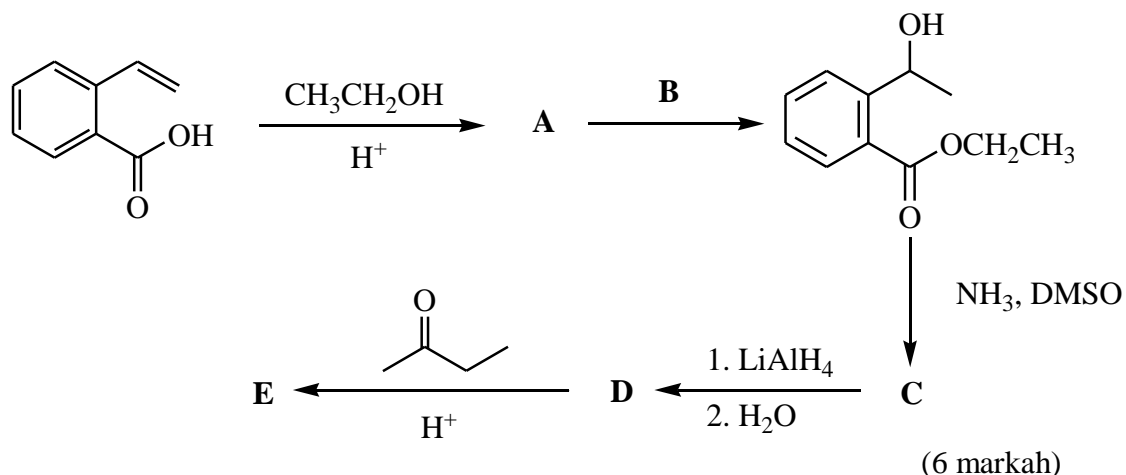
Sekiranya terdapat sebarang percanggahan pada soalan peperiksaan, versi Bahasa Inggeris hendaklah diguna pakai.

Jawab hanya **LIMA** soalan.

1. (a) Pengesteran Fischer berlaku melalui mekanisme bermangkin asid, semua percubaan dalam keadaan bermangkin bes (contohnya,  $\text{RO}^-$ ) didapati gagal. Terangkan kenapa pengesteran Fischer tidak boleh dimangkin oleh bes.

(4 markah)

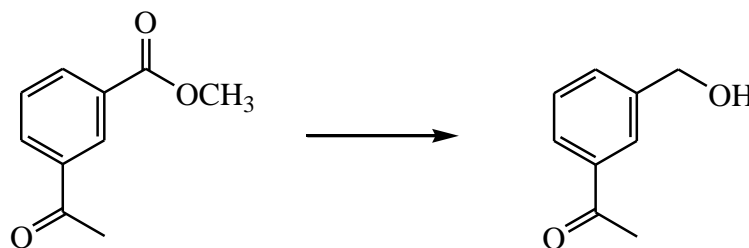
- (b) Berikan hasil dan reagen **A** hingga **E** bagi tindak balas berikut:



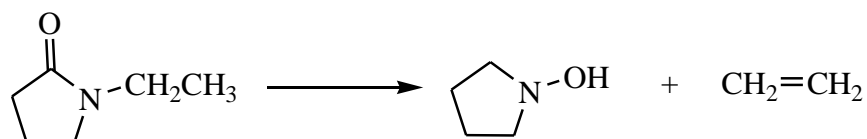
(6 markah)

- (c) Cadangkan suatu cara sintesis bagi setiap penukaran berikut. Mekanisme tidak diperlukan.

(i)



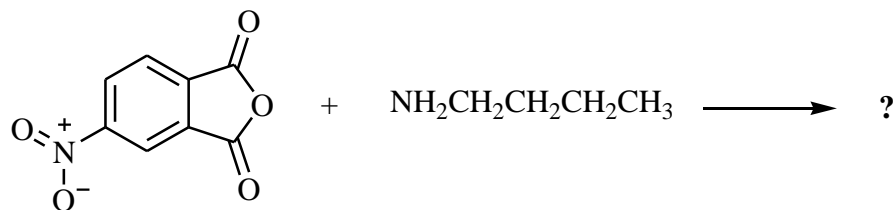
(ii)



(10 markah)

-14-

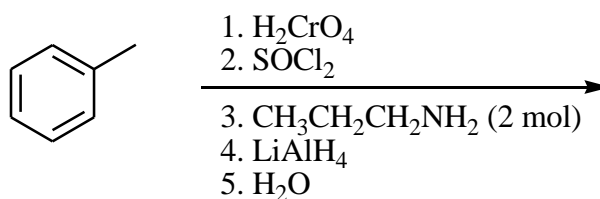
2. (a) Apakah hasil utama bagi tindak balas antara 4-nitroftalik anhidrida dengan *n*-butilamina? Jelaskan.



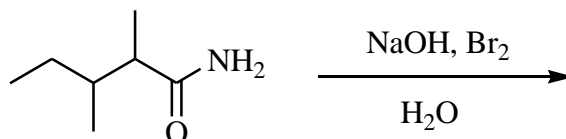
(6 markah)

- (b) Berikan hasil bagi setiap tindak balas berikut:

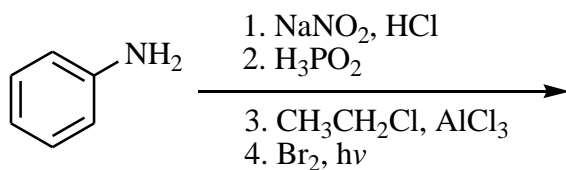
(i)



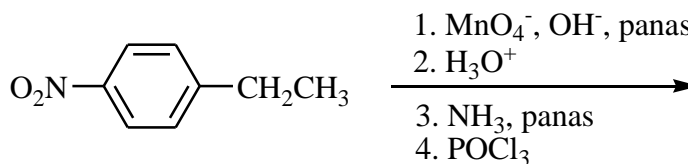
(ii)



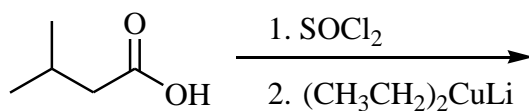
(iii)



(iv)



(v)

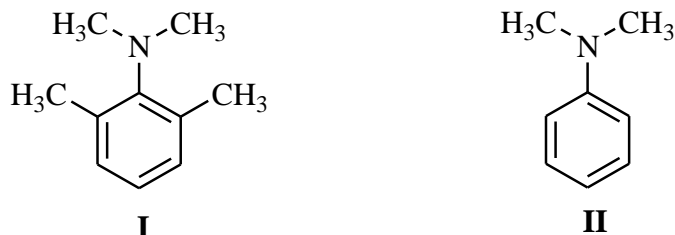


(10 markah)

...15/-

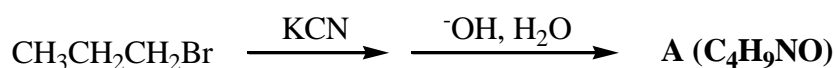
-15-

- (c) Terangkan kenapa *N,N,2,6*-tetrametilnilina, **I** merupakan bes yang lebih kuat daripada *N,N*-dimetilnilina, **II**.



(4 markah)

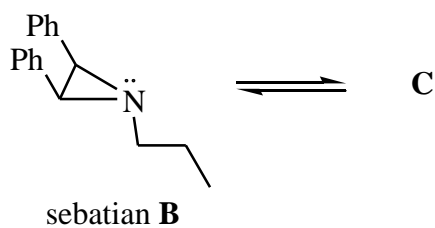
3. (a) Tindak balas berikut akan memberi sebatian **A**.



- (i) Apakah sebatian **A**?  
 (ii) Berikan mekanisme bagi tindak balas di atas untuk mendapatkan sebatian **A**.

(7 markah)

- (b) Amina asiklik mengalami songsangan nitrogen dengan cepat. Sebaliknya, eksperimen NMR menunjukkan sebatian **B** di bawah mengalami songsangan kepada **C** hanya pada suhu ternakik.



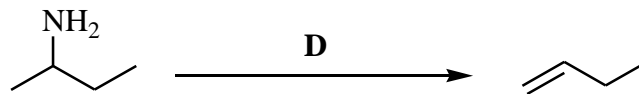
- (i) Tuliskan formula struktur bagi hasil songsangan, **C**.  
 (ii) Mengapakah sebatian **B** tidak mengalami songsangan dengan cepat pada suhu bilik?

(4 markah)

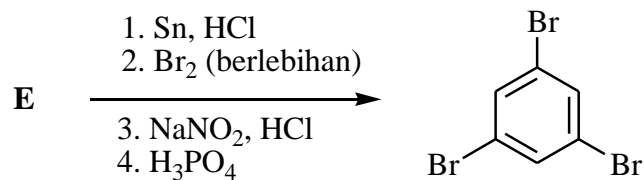
-16-

(c) Berikan reagen, bahan permulaan atau hasil bagi tindak balas berikut:

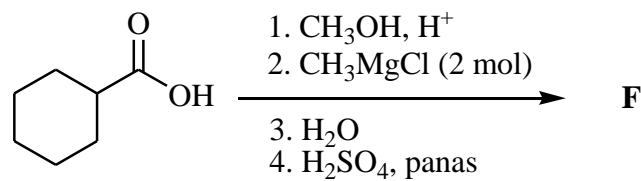
(i)



(ii)



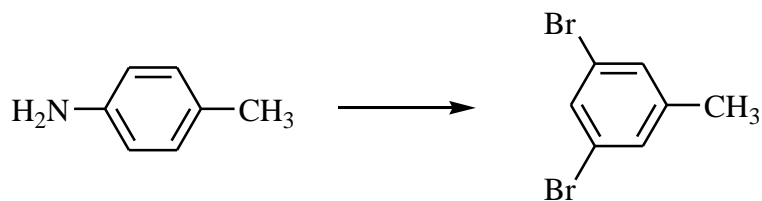
(iii)



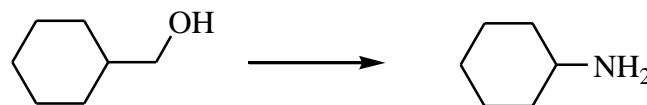
(9 markah)

4. (a) Cadangkan suatu cara sintesis bagi setiap penukaran berikut. Mekanisme tidak diperlukan.

(i)



(ii)



(10 markah)





-18-

5. (a) Berikan struktur bagi sebatian **A** hingga **G** dalam tindak balas di bawah.

(i)

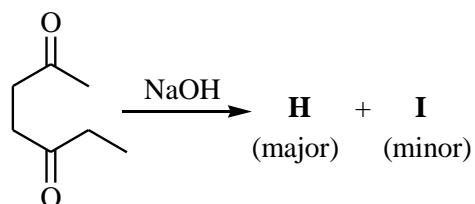
(ii)

(iii)

(iv)

(10 markah)

(b) Pensiklikan intramolekul aldol bagi 2,5-heptanadion dengan natrium hidroksida cair memberikan dua hasil **enon**, **H** dan **I** dalam nisbah 9:1. Hasil utama **H** menunjukkan dua isyarat singlet dalam spektrum  $^1\text{H}$  NMR pada  $\delta$  1.65 dan 1.90 ppm. Tiada isyarat diperhatikan dalam julat 5-10 ppm.



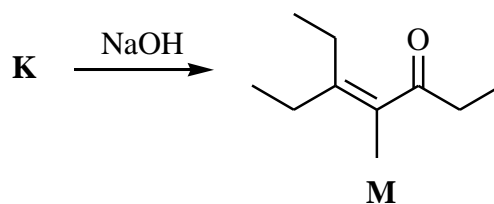
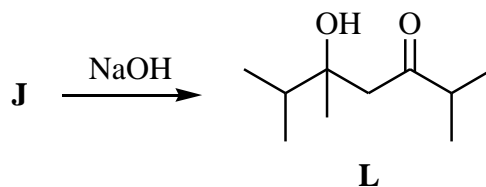
(i) Berikan struktur bagi sebatian **H** dan **I**.

(ii) Tunjukkan mekanisme bagi pembentukan **H** dan **I**.

(6 markah)

-19-

- (c) Sebatian **L** dan **M** telah disediakan dengan tindak balas aldol bermula daripada bahan permulaan, **J** dan **K**, masing-masing. Lukiskan struktur bagi semua bahan permulaan.



(4 markah)

6. (a) Anulasi Robinson bagi sikloheksanon dan metil vinil keton (MVK) ditunjukkan seperti di bawah.

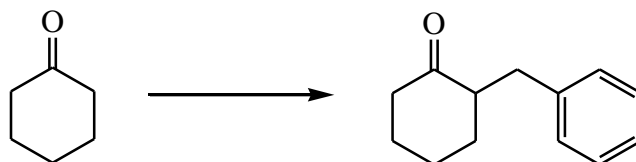
Tuliskan mekanisme bagi tindak balas yang terlibat, dengan memberikan struktur **A** dan kesemua bahan perantara.

(7 markah)

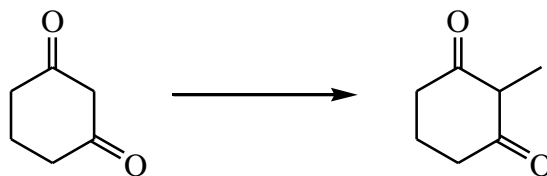
-20-

(b) Berikan suatu cara sintesis bagi setiap penukaran berikut. Mekanisme tidak diperlukan.

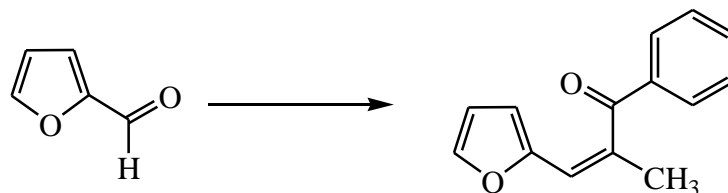
(i)



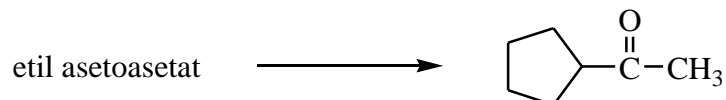
(ii)



(iii)



(iv)



(10 markah)

(c) Tindak balas keton **B** dengan Br<sub>2</sub>/NaOH, diikuti oleh pengasidan memberikan bromoform dan asid pivalik, (CH<sub>3</sub>)<sub>3</sub>C-COOH. Apakah struktur bagi **B**?

(3 markah)

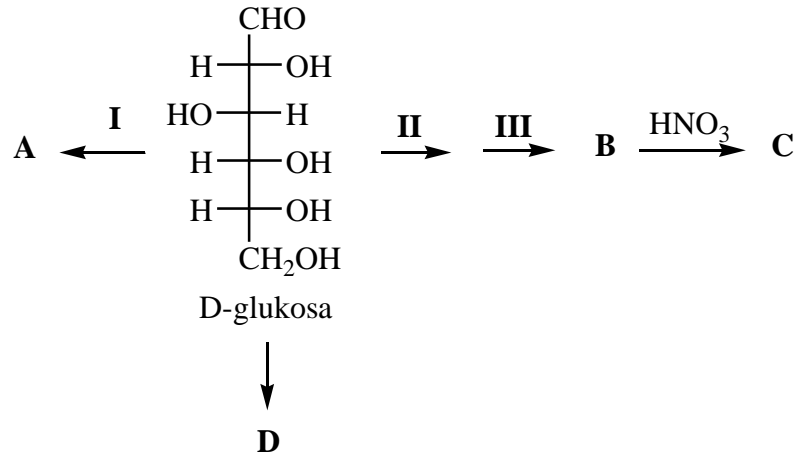
7. (a) Takrifkan istilah berikut dengan memberi satu contoh untuk setiap istilah.

(i) Epimer

(ii) Anomer

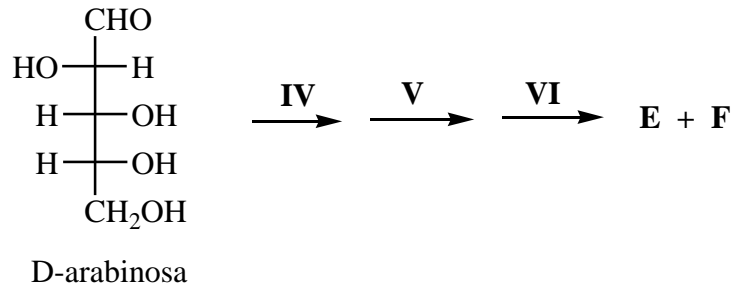
(5 markah)

- (b) Penurunan D-glukosa menghasilkan suatu alditol **A**. Apabila D-glukosa mengalami degradasi Ruff, sebatian **B** dihasilkan, yang mana kemudiannya menghasilkan suatu asid aldarik **C** apabila dioksidakan dengan asid nitrik. D-glukosa bertindak balas dengan dua mol fenilhidrazin bagi menghasilkan suatu osazon **D**. Gunakan kesemua data bagi menghasilkan struktur sebatian **A**, **B**, **C** dan **D**, dan juga reagen **I**, **II** dan **III**.



(9 markah)

- (c) D-arabinosa mengalami sintesis Kiliani-Fischer.



- Berikan struktur sebatian **E** dan **F**.
- Berikan reagen yang terlibat dalam sintesis ini.
- Apakah hubungan antara **E** dengan **F**?

(6 markah)