INDEX NO:- ----------

UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

November 2008

KOT 121 – Organic Chemistry I
[Kimia Organik I]

Duration: 3 hours
[Masa : 3 jam]

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

Instructions:

PART A (40 marks), comprising 40 multiple-choice questions (MCQ), **has to be answered within the first hour of the examination on the OMR forms provided. The completed OMR forms will be collected one hour after the commencement of the examination.**

PART B (60 marks) consists of essay-type questions. Answer any **THREE ONLY**, beginning the answer to each question on a new page.

You may answer the question either in Bahasa Malaysia or in English.

Ensure that your OMR form is complete [with your index number, course code, answers to the questions]. Use only a 2B pencil on your OMR form.

Submit the answer scripts and question paper to the invigilator before you leave the examination hall at the end of the examination.

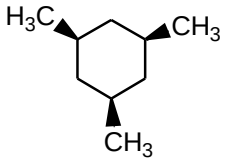
…2/-

PART B (60 MARKS)

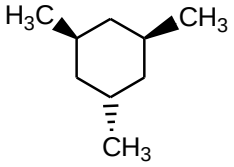
Answer THREE questions.
Only the first THREE questions answered in the answer book will be marked.
You must start each question on a new page.

This section contains FOUR questions.

1. (a) (i) Draw the most stable chair conformations of **I** and **II**.



I



II

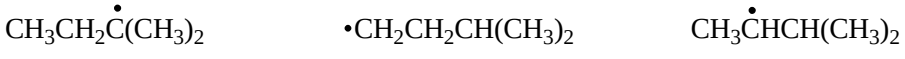
(ii) Which of the chair conformations in 1(a)(i) would you expect to be more stable? Explain your answer.

(6 marks)

(b) Consider the one-step conversion of **A** to **B**. Given that the reaction is endothermic by 5 kcal/mol and that the energy difference between **B** and the transition state for the process is 15 kcal/mol, sketch a reaction-energy diagram for this reaction.

(4 marks)

(c) (i) Rank the free radicals (**C** - **E**) shown below in order of <u>decreasing</u> stability.



C **D** **E**

(ii) The relative reactivity of the 1° : 2° : 3° hydrogens of $(CH_3)_3CCH_2CH_3$ in free radical chlorination is 1 : 3.8 : 5.0. Provide the structures of the possible monochlorinated products and estimate the percentage of each product.

(10 marks)

2. (a) List the following compounds in order of increasing reactivity in an S_N1 reaction.

CH_3Br, $CH_3CH_2CH_2I$, $(CH_3)_3CI$, $CH_3CHBrCH_3$, CH_3CHICH_3

(3 marks)

(b) (i) Give the major product of the reaction of 2-bromo-3-methylbutane with sodium hydroxide.

(ii) Show the mechanism of the reaction.

(4 marks)

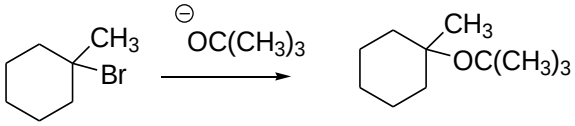
(c) Which base, ammonia (NH_3) or triethylamine [$(CH_3CH_2)_3N$], would be a better choice for use in converting 1-chlorohexane to hex-1-ene? Explain briefly.

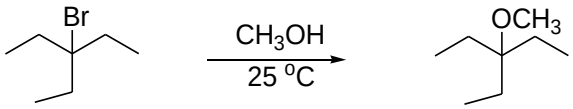
(3 marks)

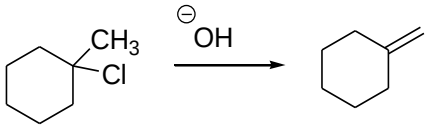
(d) The heat of hydrogenation of cyclobutene is higher than that of cyclopentene. Explain briefly.

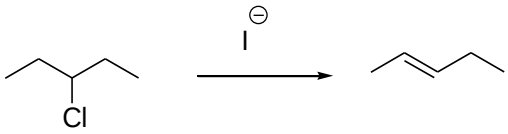
(2 marks)

(e) Explain why the following reactions do not afford the major products that are given. In each of the reactions, draw the structure of the major product actually formed.

(i) 

(ii) 

(iii) 

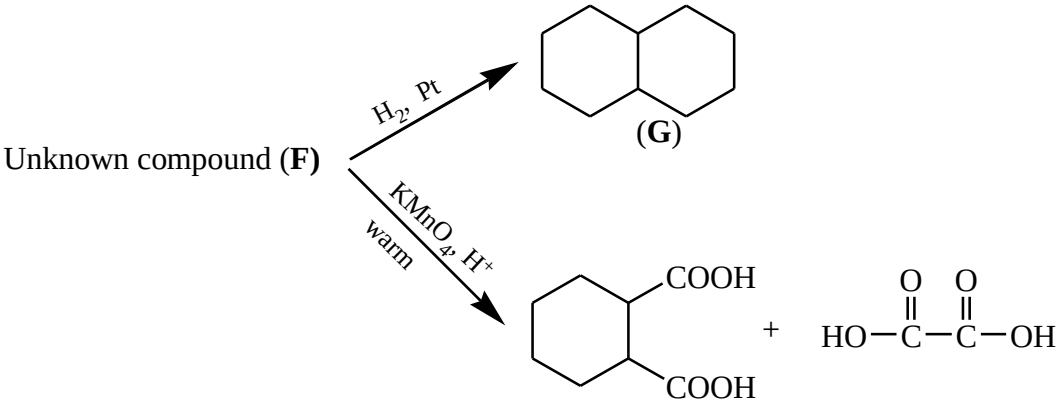
(iv) 

(8 marks)

3. (a) When (*Z*)-3-methyl-3-hexene undergoes hydroboration-oxidation, two isomeric products are formed. Give their structures, and label each asymmetric carbon atom as (*R*) or (*S*). What is the relationship between these isomers?

(6 marks)

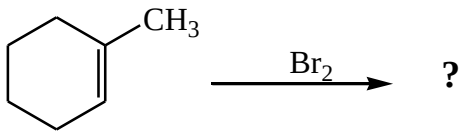
(b) An unknown compound (**F**) undergoes catalytic reduction to give decalin (**G**). When treated with warm, acidified potassium permanganate, the compound cleaves according to the following reaction. Propose the structure of the unknown compound (**F**).



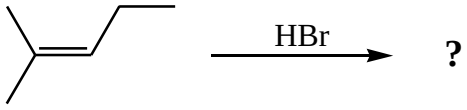
(4 marks)

(c) Complete each of the following reactions and show the step-by-step mechanism involved.

(i)



(ii)



(10 marks)

4. (a) Four isomeric dimethylcyclopropanes are drawn below:

(i) How are the compounds in each pair related (enantiomers, diastereomers, constitutional isomers): **A** and **B**; **A** and **C**; **B** and **C**; **C** and **D**?

(ii) Label each compound as chiral or achiral.

(iii) Which compounds, alone, would be optically active?

(iv) Which compounds have a plane of symmetry?

(v) How do the boiling points of the compounds in each pair compare: **A** and **B**; **B** and **C**; **C** and **D**?

(vi) Which of the compounds are *meso* compounds?

(vii) Would an equal mixture of compounds **C** and **D** be optically active?

(viii) Would an equal mixture of compounds **B** and **C** be optically active?

A **B** **C** **D**

(14 marks)

(b) Pure monosodium glutamate (MSG) exhibits a specific rotation of + 24^{o}.

(i) Calculate the *ee* of a solution where $[\alpha] = +10^{o}$.

(ii) If the *ee* of a solution of MSG is 80 %, what is $[\alpha]$ of this solution?

(6 marks)

TERJEMAHAN

Arahan:

BAHAGIAN A (40 markah) mengandungi 40 soalan multipilihan (MCQ), **perlu dijawab dalam masa satu jam pertama di dalam borang jawapan OMR yang disediakan. Borang OMR akan dikutip satu jam selepas peperiksaan bermula.**

BAHAGIAN B (60 Markah) mengandungi soalan bertulis. Jawab TIGA soalan sahaja. Jawab tiap-tiap soalan di muka surat yang baru.

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

Pastikan borang OMR diisi dengan lengkap [nombor angka giliran, kod kursus, jawapan]. Gunakan hanya pensil 2B bagi borang OMR anda.

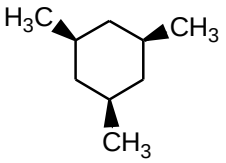
Sila serahkan buku jawapan dan kertas soalan ini kepada Pengawas sebelum anda keluar dari dewan peperiksaan.

<u>BAHAGIAN B</u> (60 MARKAH)

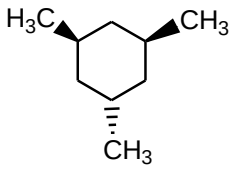
Jawab sebarang TIGA soalan.
Hanya TIGA jawapan yang pertama akan diperiksa.
<u>Jawab tiap-tiap soalan pada muka surat yang baru.</u>

Bahagian ini mengandungi EMPAT soalan.

1. (a) (i) Lukis konformasi kerusi yang paling stabil dalam **I** dan **II**.



I



II

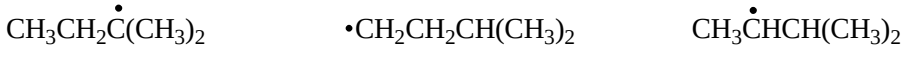
(ii) Manakah antara konformasi kerusi dalam 1(a)(i) yang anda jangkakan adalah lebih stabil? Jelaskan jawapan anda.

(6 markah)

(b) Pertimbangkan penukaran **A** kepada **B** melalui satu langkah. Tindak balas tersebut adalah endotermik sebanyak 5 kcal/mol dan perbezaan tenaga antara **B** dan keadaan peralihan untuk proses tersebut ialah 15 kcal/mol. Lakarkan rajah tindak balas-tenaga untuk tindak balas ini.

(4 markah)

(c) (i) Susun radikal bebas (**C** - **E**) di bawah dalam urutan kestabilan yang menurun.



C **D** **E**

(ii) Kereaktifan relatif hidrogen 1° : 2° : 3° $(CH_3)_3CCH_2CH_3$ dalam pengklorinan radikal bebas ialah 1 : 3.8 : 5.0. Berikan semua struktur yang mungkin bagi hasil pengklorinan mono tersebut dan anggarkan peratusan setiap hasil tersebut.

(10 markah)

2. (a) Senaraikan sebatian berikut dalam susunan kereaktifan yang meningkat dalam tindak balas S_N1 .

CH_3Br, $CH_3CH_2CH_2I$, $(CH_3)_3CI$, $CH_3CHBrCH_3$, CH_3CHICH_3

(3 markah)

(b) (i) Berikan hasil major tindak balas 2-bromo-3-metilbutana dengan natrium hidroksida.

(ii) Tunjukkan mekanisme tindak balas berikut.

(4 markah)

(c) Bes manakah, ammonia (NH_3) atau trietilamina $[(CH_3CH_2)_3N]$, merupakan pilihan terbaik digunakan dalam menukar 1-kloroheksana kepada heks-1-ena? Jelaskan dengan ringkas.

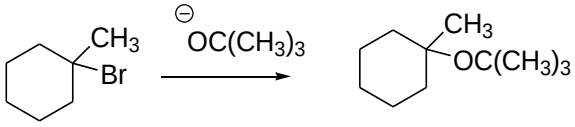
(3 markah)

(d) Haba penghidrogenan relatif bagi siklobutena adalah lebih tinggi daripada siklopentena. Jelaskan dengan ringkas.

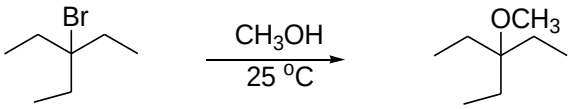
(2 markah)

(e) Jelaskan mengapa tindak balas berikut tidak membentuk hasil major yang diberikan. Lukis struktur hasil major yang sepatutnya terbentuk.

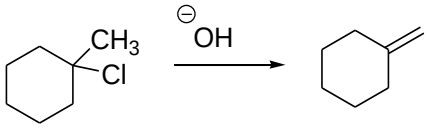
(i)



(ii)



(iii)



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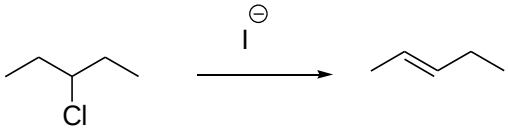
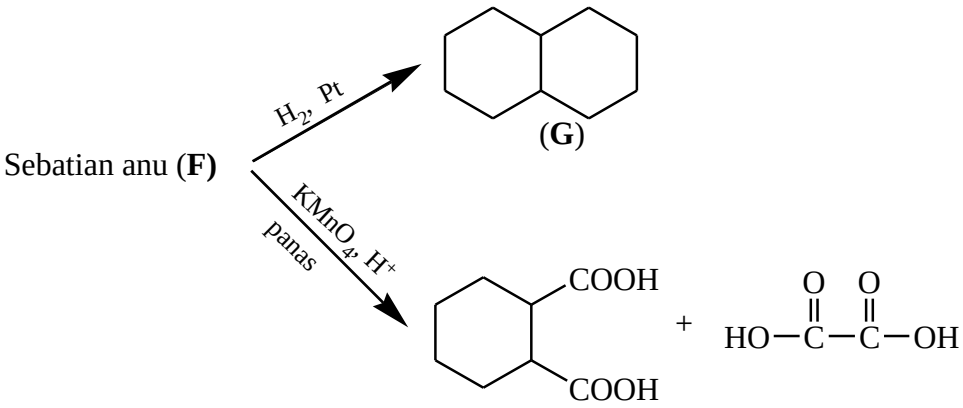


(8 markah)

3. (a) Apabila (*Z*)-3-metil-3-heksena melalui tindak balas penghidroboratan-pengoksidaan, dua isomer dihasilkan. Berikan struktur, dan labelkan setiap karbon atom asimetri sebagai (*R*) atau (*S*). Apakah kaitan antara isomer berikut?

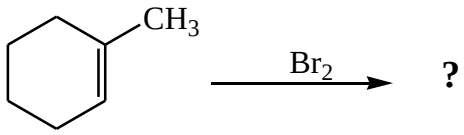
(6 Markah)

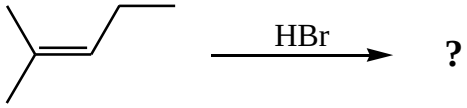
(b) Sebatian anu (**F**) melalui penurunan mangkin memberikan dekalin (**G**). Apabila ditindak balas dengan kalium permanganat berasid panas, pemecahan sebatian berlaku berdasarkan tindak balas berikut. Berikan struktur sebatian anu (**F**).



(4 markah)

(c) Lengkapkan tindak balas berikut dan tunjukkan setiap langkah mekanisme yang terlibat.

(i) 

(ii) 

4. (a) Empat isomer bagi dimetilsiklopropana dilukis di bawah:

(i) Apakah hubungan antara setiap pasangan berikut (enantiomer, diastereomer, isomer juzuk): **A** dan **B**; **A** dan **C**; **B** dan **C**; **C** dan **D**?

(ii) Tandakan setiap sebatian sebagai kiral atau akiral.

(iii) Jika berasingan, sebatian manakah adalah aktif optik?

(iv) Sebatian yang manakah mempunyai suatu satah simetri?

(v) Di dalam setiap pasangan, bagaimana takat didih suatu sebatian berbanding dengan pasangannya: **A** dan **B**; **B** dan **C**; **C** dan **D**?

(vi) Sebatian yang manakah *meso*?

(vii) Adakah suatu campuran **C** dan **D** dalam jumlah yang sama aktif optik atau tidak?

(viii) Adakah suatu campuran **B** dan **C** dalam jumlah yang sama aktif optik atau tidak?

A **B** **C** **D**

(14 markah)

(b) Mononatrium glutamat (MSG) tulen menunjukkan putaran spesifik + 24^{o}.

(i) Hitunglah *ee* bagi suatu larutan yang [α] ialah + 10^{o}.

(ii) Jika *ee* suatu larutan MSG ialah 80 %, apakah [α] bagi larutan ini?

(6 markah)