
UNIVERSITI SAINS MALAYSIA

First Semester Examination
2011/2012 Academic Session

January 2011

KOT 222 – Organic Chemistry II
[Kimia Organik II]

Duration : 3 hours
[Masa : 3 jam]

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

Instructions:

Answer any **FIVE** (5) questions. If a candidate answers more than five questions only the first five questions in the answer sheet will be graded.

Answer each question on a new page.

You may answer either in Bahasa Malaysia or in English.

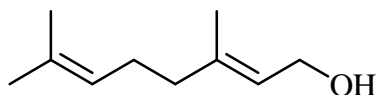
In the event of any discrepancies, the English version shall be used.

Appendix: Spectroscopy Tables.

-2-

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

1. (a) Geraniol is a monoterpene and an alcohol. It has a rose-like odour and is used in perfumes. The structure for geraniol is shown below.

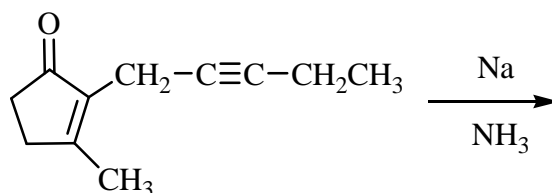


- (i) Why only one of the C=C of the geraniol is epoxidised with the Sharpless reagent?
- (ii) Draw the product of this Sharpless reaction using (+)-DET.

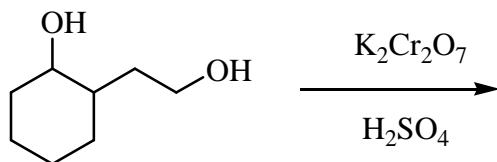
(4 marks)

- (b) Give the product(s) of each of the reactions below:

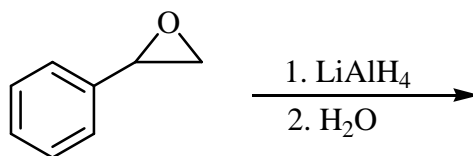
(i)



(ii)



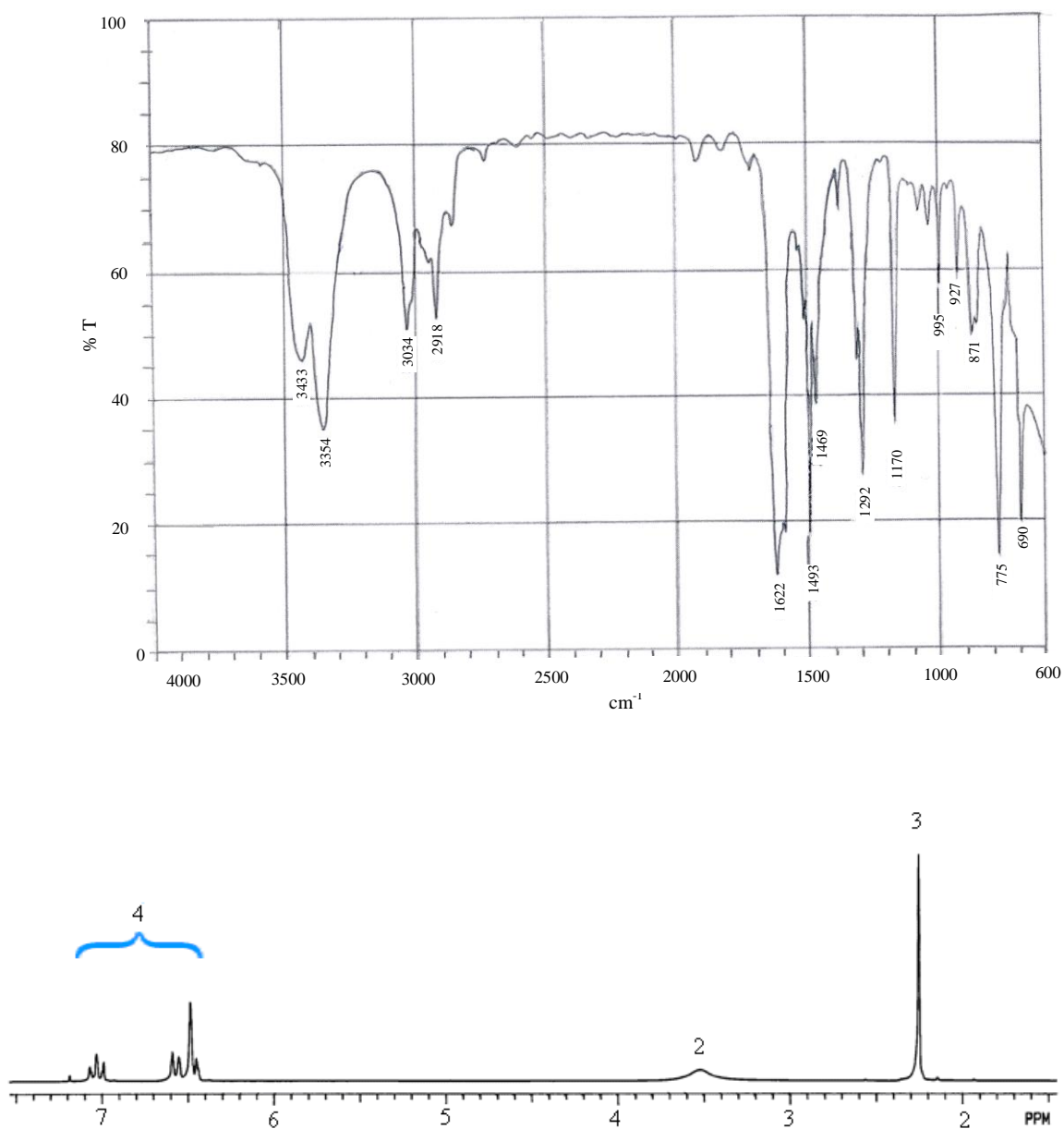
(iii)



(6 marks)

-3-

- (c) A new compound was isolated. Mass spectrometry provided a molecular formula of C_7H_9N . The IR and 1H NMR spectra are as shown below. Explain how you derive a structure for this compound from the given spectra.



(5 marks)

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-4-

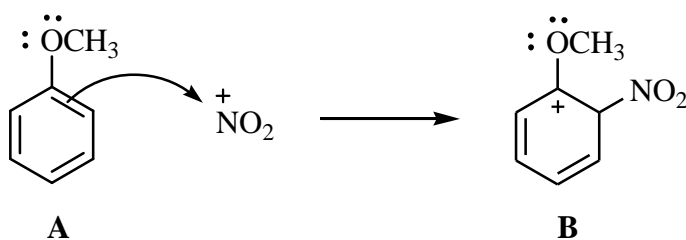
(d) Draw the expected ^1H NMR spectrum for each of the following compounds. Clearly show the position of the chemical shifts, the integration and the splitting pattern (*s*, *d*, *t*, etc.) for all the signals.

(i) 3-Bromo-3-methylbutanoic acid

(ii) 4-Bromo-1-ethylbenzene

(5 marks)

2. (a) Nitration of anisole (**A**) gives the resonance contributor (**B**). Draw the rest of the resonance contributors and show the most stable resonance contributor. Explain your choice.

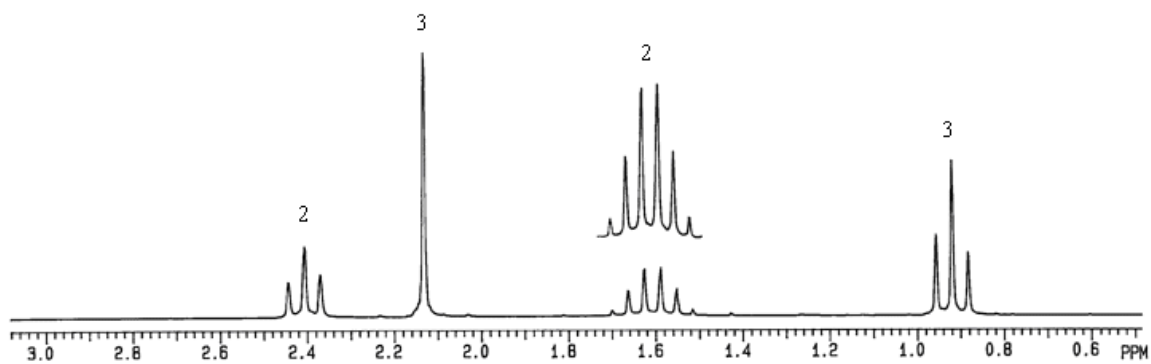
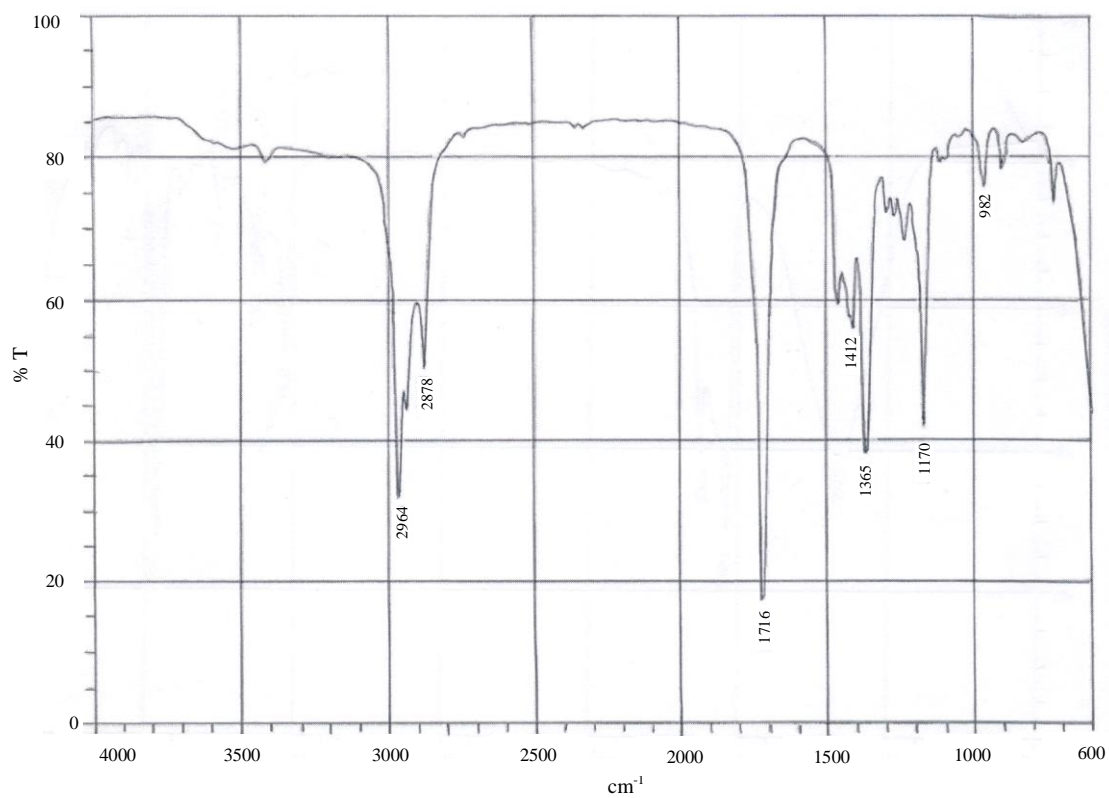


(5 marks)

-5-

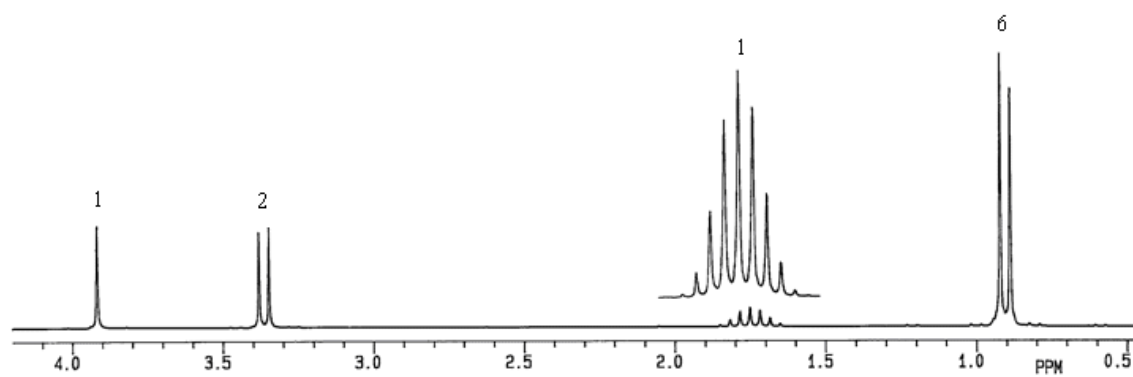
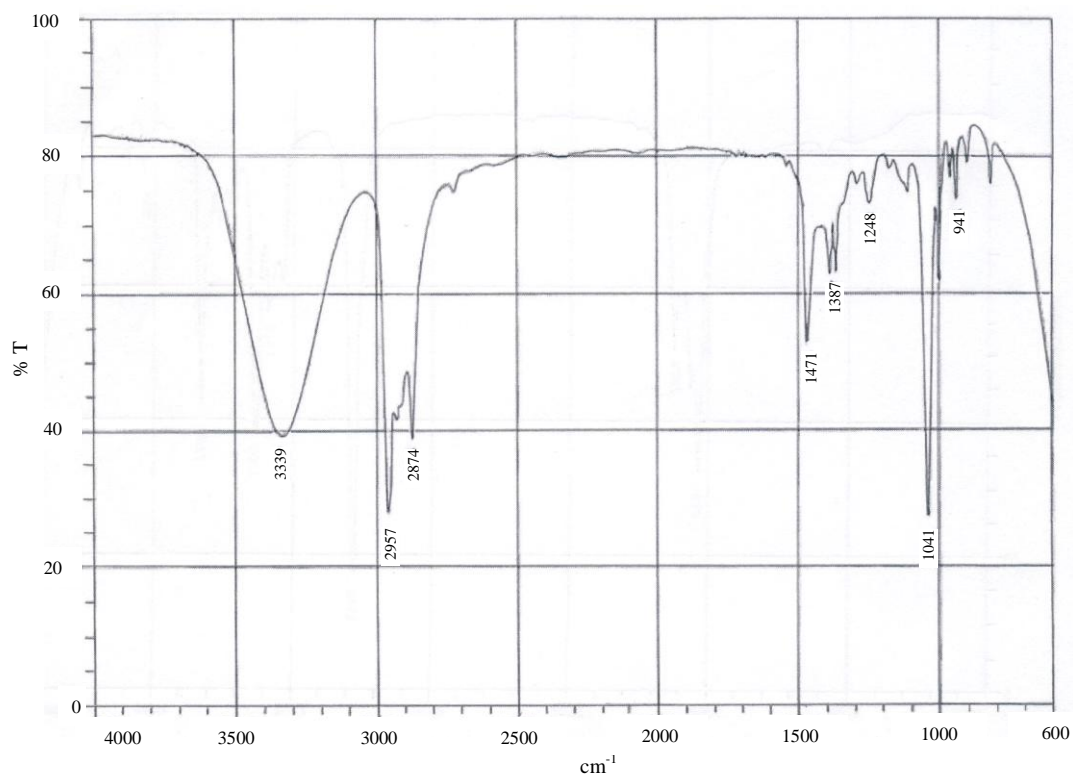
(b) In each question below you are given the molecular formula, IR and ^1H NMR spectra. Determine the structure and the name of the compound.

(i) $\text{C}_5\text{H}_{10}\text{O}$



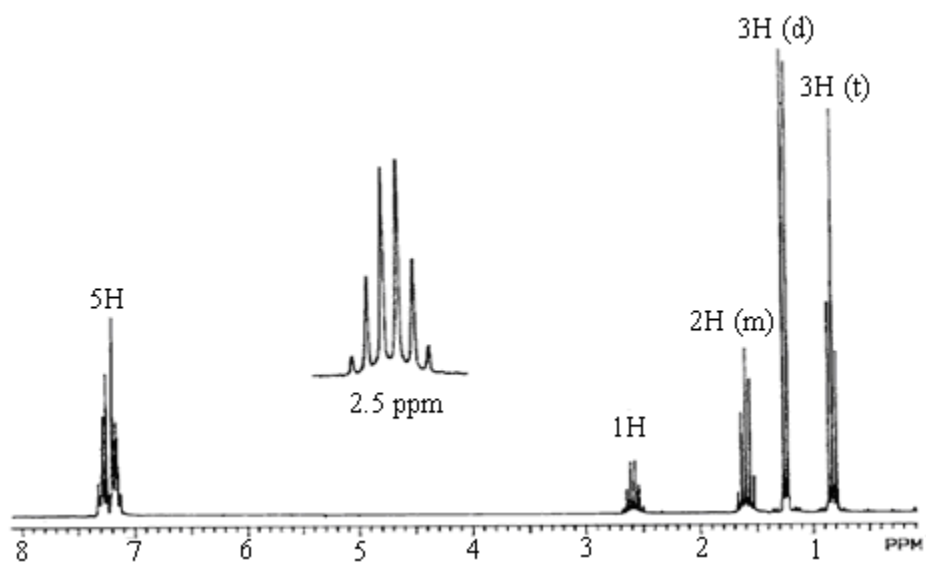
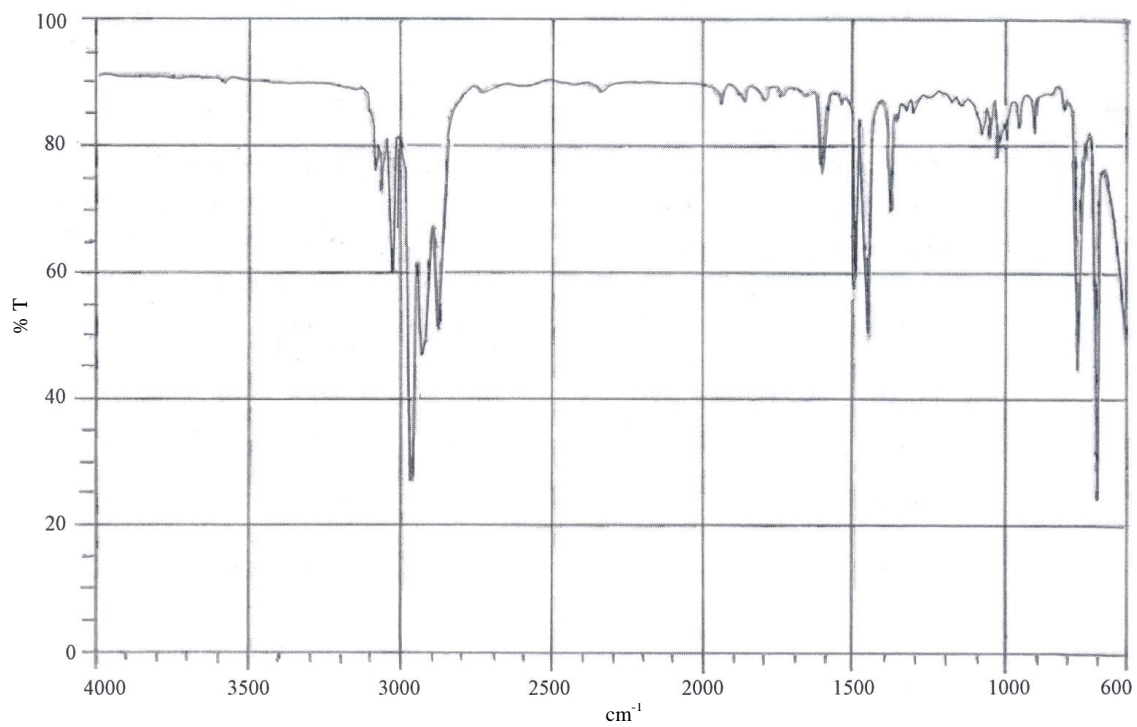
...6/-

-6-

(ii) $C_4H_{10}O$ 

...7/-

-7-

(iii) $C_{10}H_{14}$ 

(15 marks)

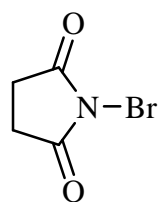
...8/-

-8-

3. (a) The free-radical chlorination of (*S*)-(+)-1-chloro-2-methylbutane gives a total of six fractions of formula $C_5H_{10}Cl_2$ separable by careful fractional distillation. Four fractions are optically active, and two fractions are optically inactive. Draw structural formulas for the compounds making up each fraction. Account for the optical activity or inactivity in each case.

(14 marks)

- (b) Show the reaction mechanism for the halogenation of 1-butene using *N*-bromosuccinimide (NBS) in the presence of light.



NBS

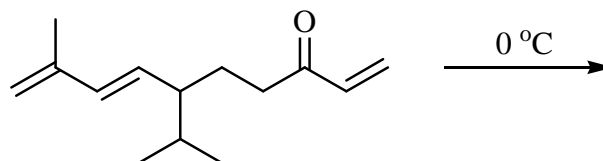
(4 marks)

- (c) Show how one of the products from the reaction in question 3 (b) can be converted to a stable diene.

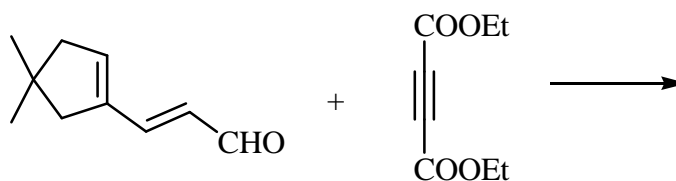
(2 marks)

4. (a) Give the product(s) of each of the reactions below:

(i)



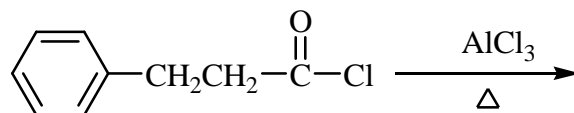
(ii)



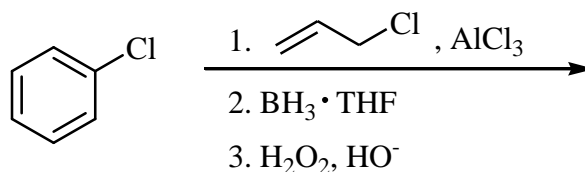
...9/-

-9-

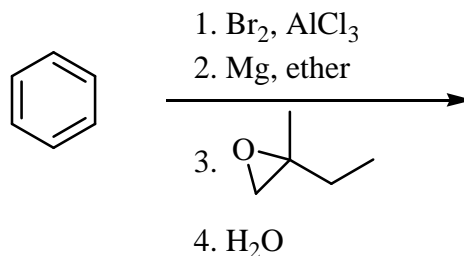
(iii)



(iv)



(v)



(10 marks)

- (b) Reaction of 1 equivalent of HCl with 1,3-pentadiene gives both the 1,2 and 1,4 adducts. At low temperature, 1,2 adduct is the major product. However, at high temperature, 1,4 adduct is the major product. Explain this finding using the energy diagram.

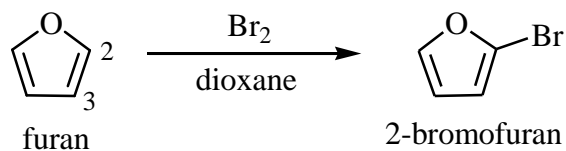
(5 marks)

- (c) The mass spectrum of chloroethane shows two molecular ion peaks at m/z values of 64 and 66. The peak at m/z 64 is approximately three times as intense as that at m/z 66.

- (i) Explain this observation.
- (ii) Show how the fragmentation of the molecular ion of chloroethane gives rise to a peak at the m/z value of 29.

(5 marks)

5. (a) Furan undergoes electrophilic aromatic substitution more readily than benzene. For example, furan reacts with bromine without the need of Lewis acid catalyst to give 2-bromofuran.

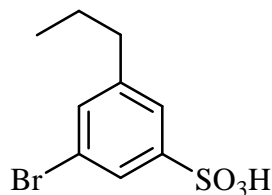


Propose the mechanisms for the bromination of furan at the 2-position and at the 3-position. Explain why furan undergoes bromination primarily at the 2-position.

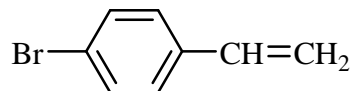
(10 marks)

- (b) Propose a synthesis for each of the following compounds starting with benzene and any other reagents. No mechanism is required.

(i)



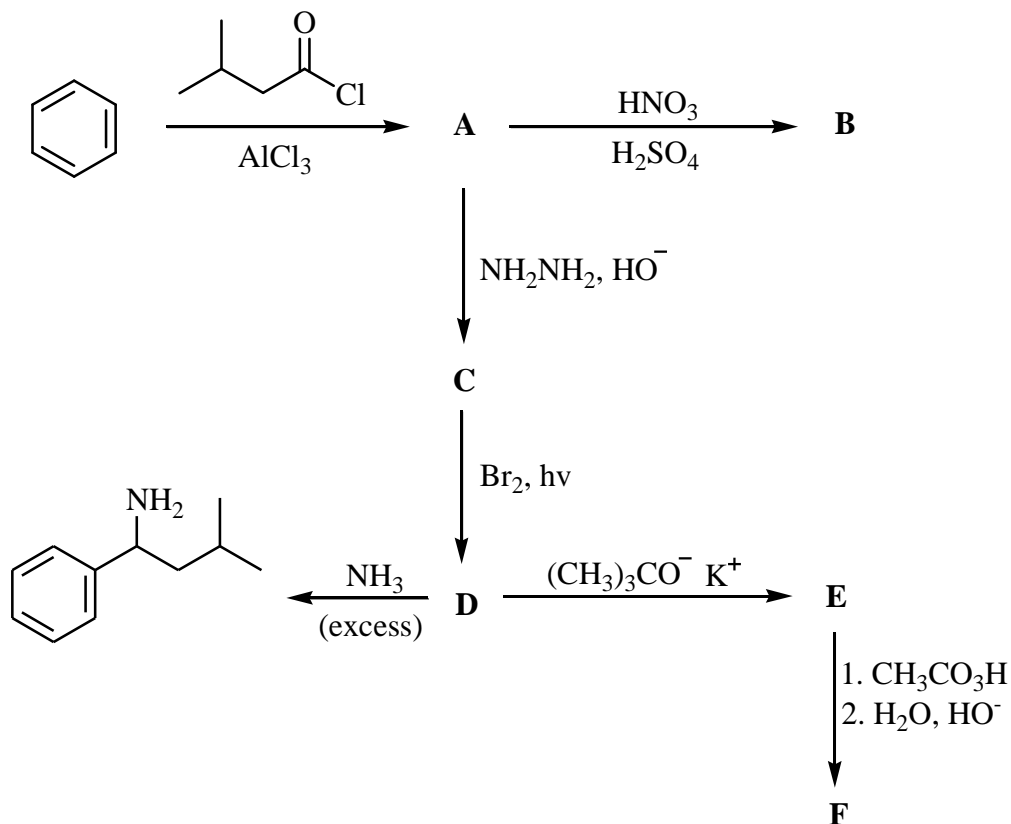
(ii)



(10 marks)

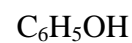
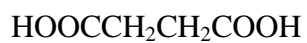
-11-

6. (a) Give the structures of compounds **A** through **F** in the following series of reactions.



(6 marks)

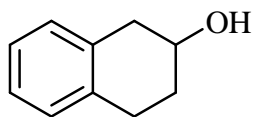
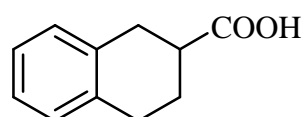
- (b) Rank the following compounds in order of increasing acidity. Justify your answer.



(4 marks)

-12-

- (c) Show the steps required to separate compound **G** and compound **H** using an extraction procedure.

**G****H**

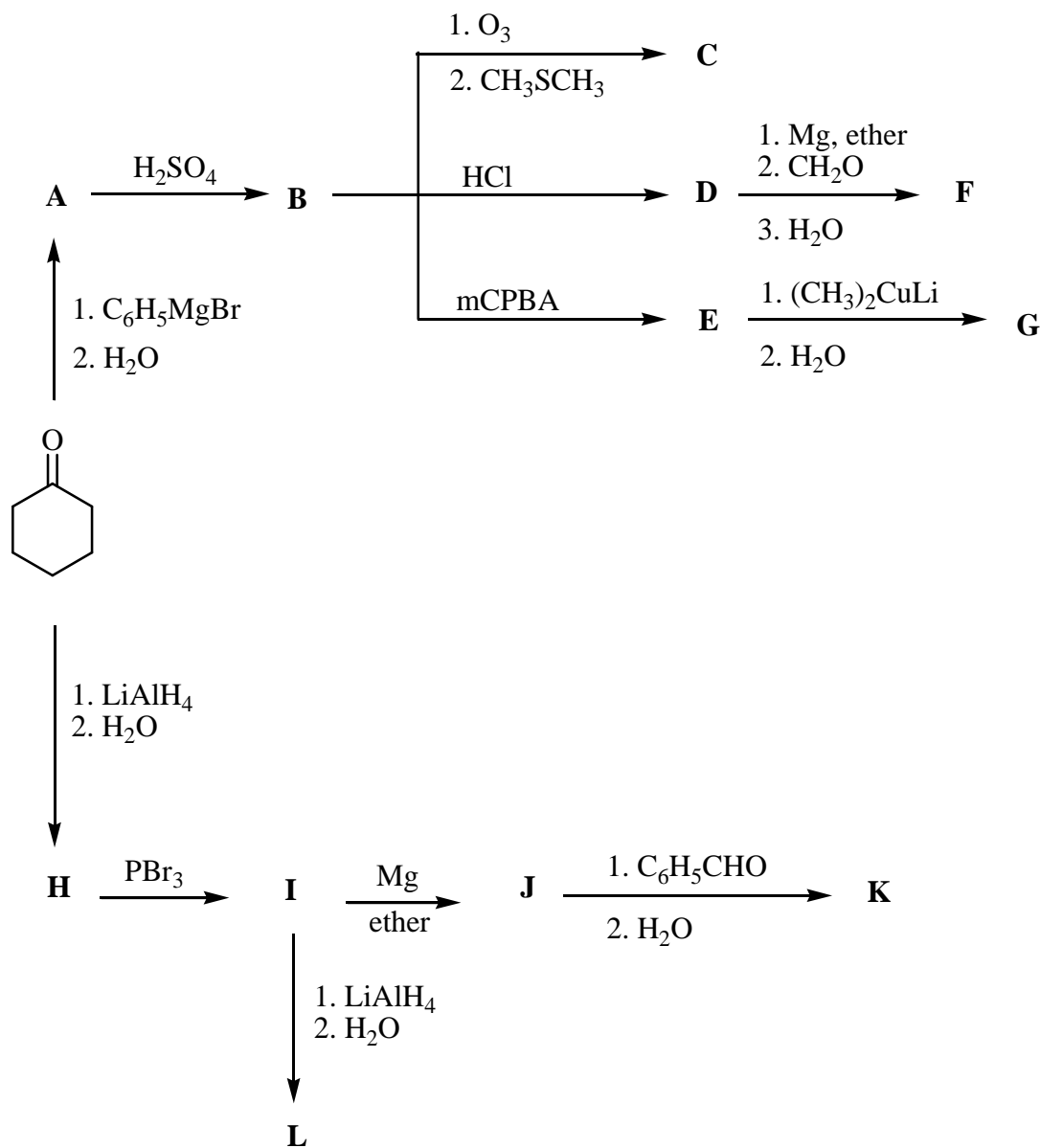
(5 marks)

- (d) Identify the reagents **I - N** in the reaction sequence below:

(5 marks)

-13-

7. Identify the compounds **A** - **L** in the following reaction scheme. Compounds **F**, **G** and **K** are isomers of molecular formula $C_{13}H_{18}O$. How could 1H NMR spectroscopy distinguish these three compounds from each other?



(20 marks)

TERJEMAHAN

Arahan:

Jawab **LIMA** soalan sahaja. Jika calon menjawab lebih daripada lima soalan hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

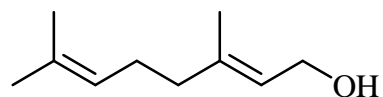
Jawab setiap soalan pada muka surat yang baru.

Anda boleh menjawab sama ada dalam Bahasa Malaysia atau Bahasa Inggeris.

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

Jawab **LIMA** (5) soalan.

1. (a) Geraniol ialah sejenis monoterpenoid dan juga alkohol. Ia mempunyai bau seperti ros dan digunakan dalam minyak wangi. Struktur bagi geraniol ditunjukkan di bawah.

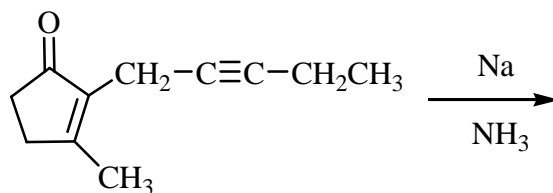


- (i) Kenapa hanya satu daripada C=C bagi geraniol diepksidakan oleh reagen Sharpless?
- (ii) Lukiskan hasil bagi tindak balas Sharpless ini menggunakan (+)-DET.

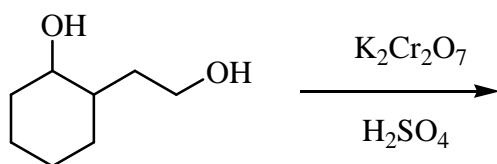
(4 markah)

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

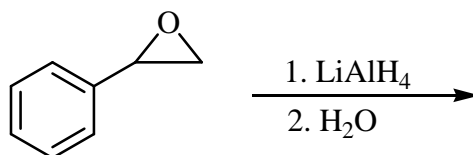
(i)



(ii)



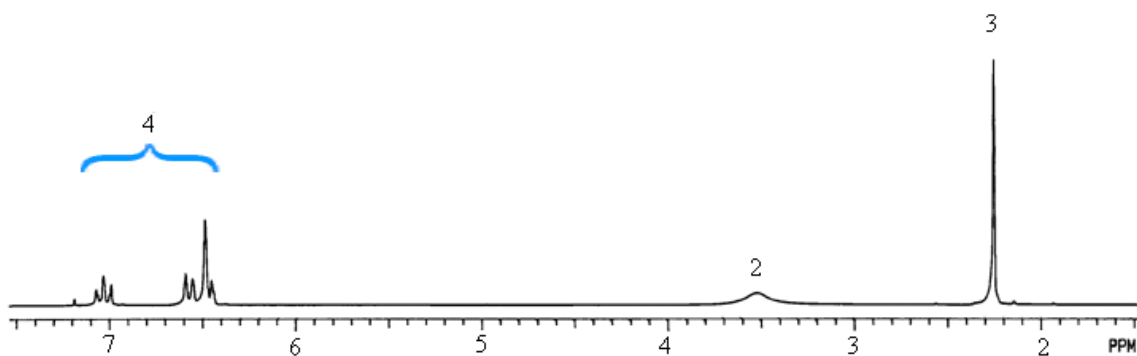
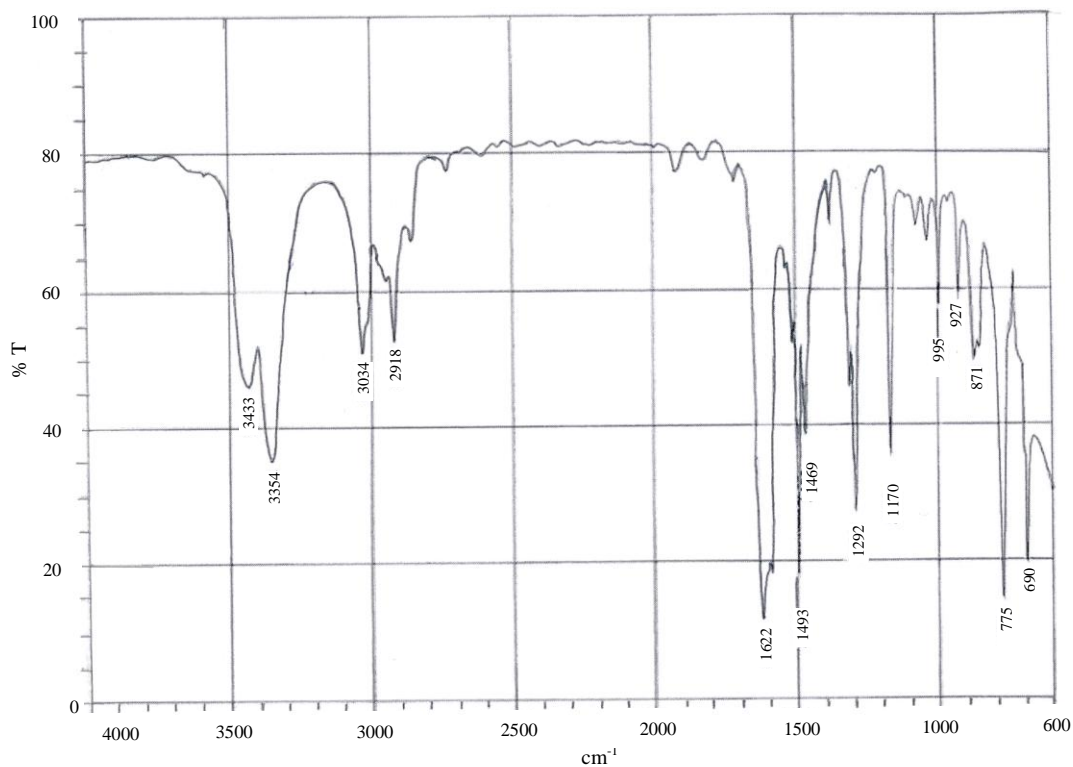
(iii)



(6 markah)

-16-

- (c) Suatu sebatian baru telah dipencilkan. Spektrometri jisim memberikan formula molekulnya sebagai C_7H_9N . Spektrum IR and 1H NMR adalah seperti yang ditunjukkan di bawah. Jelaskan bagaimana anda terbitkan struktur bagi sebatian ini daripada spektrum yang diberikan.

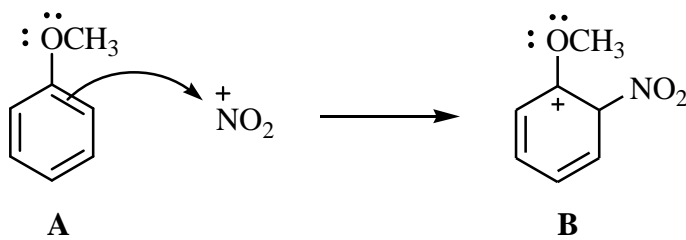


(5 markah)

...17/-

-17-

- (d) Lukiskan spektrum ^1H NMR yang dijangkakan bagi setiap sebatian berikut. Tunjukkan secara jelas kedudukan anjakan kimia, integrasi dan corak pemecahan (*s*, *d*, *t* dan sebagainya) bagi semua isyarat.
- (i) Asid 3-bromo-3-metilbutanoik
- (ii) 4-Bromo-1-etilbenzena
- (5 markah)
2. (a) Penitratan anisol (**A**) memberi penyumbang resonans (**B**). Lukiskan penyumbang resonans yang selebihnya dan tunjukkan penyumbang resonans yang paling stabil. Terangkan pilihan anda.

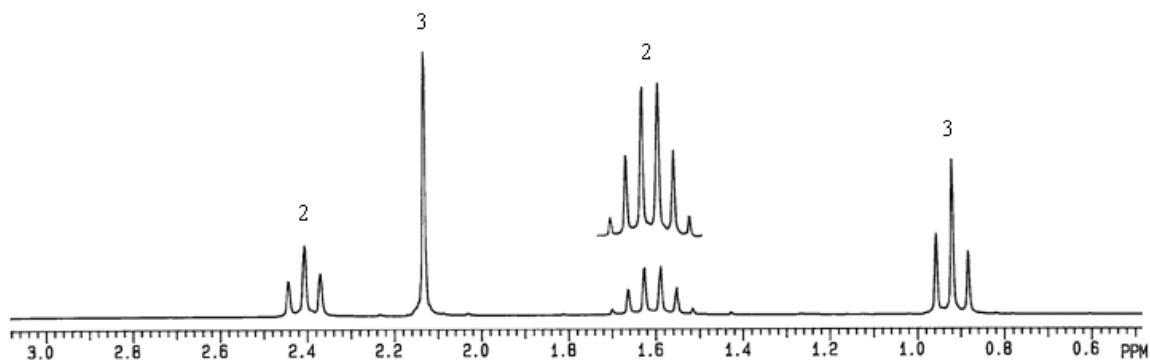
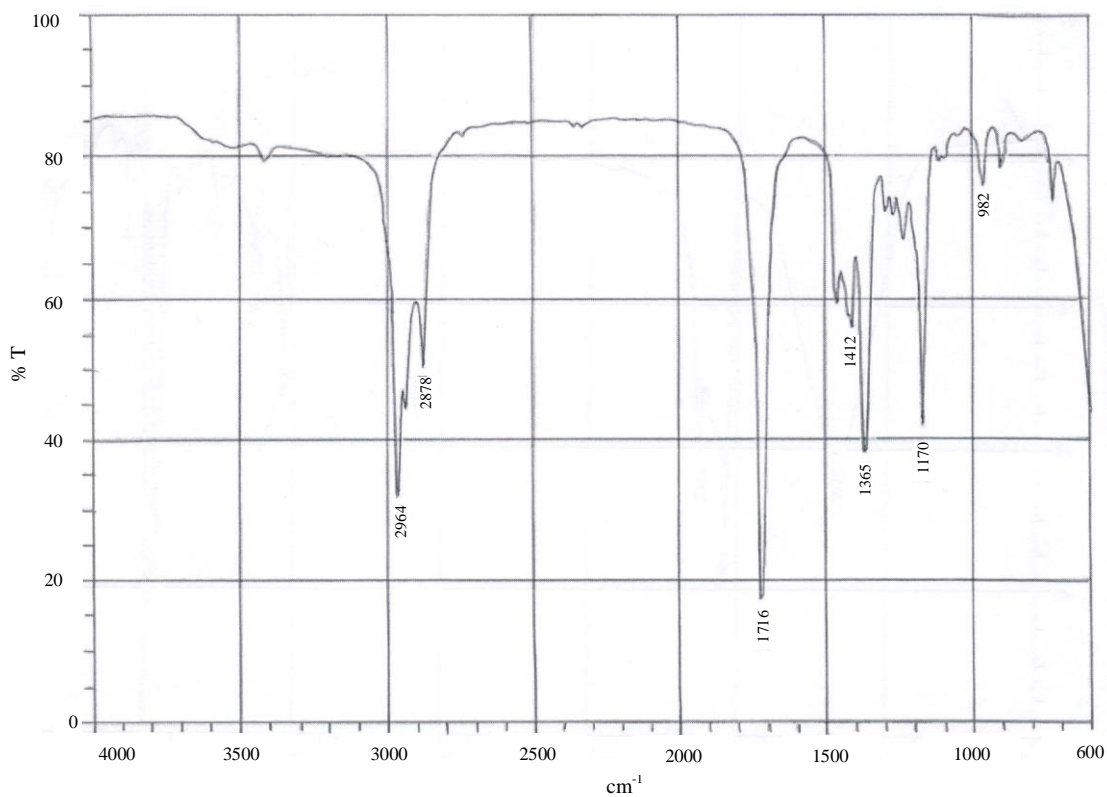


(5 markah)

-18-

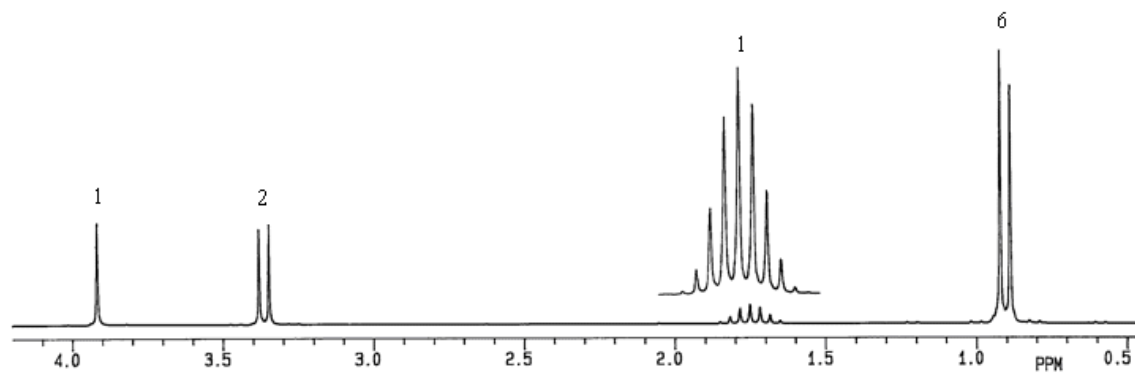
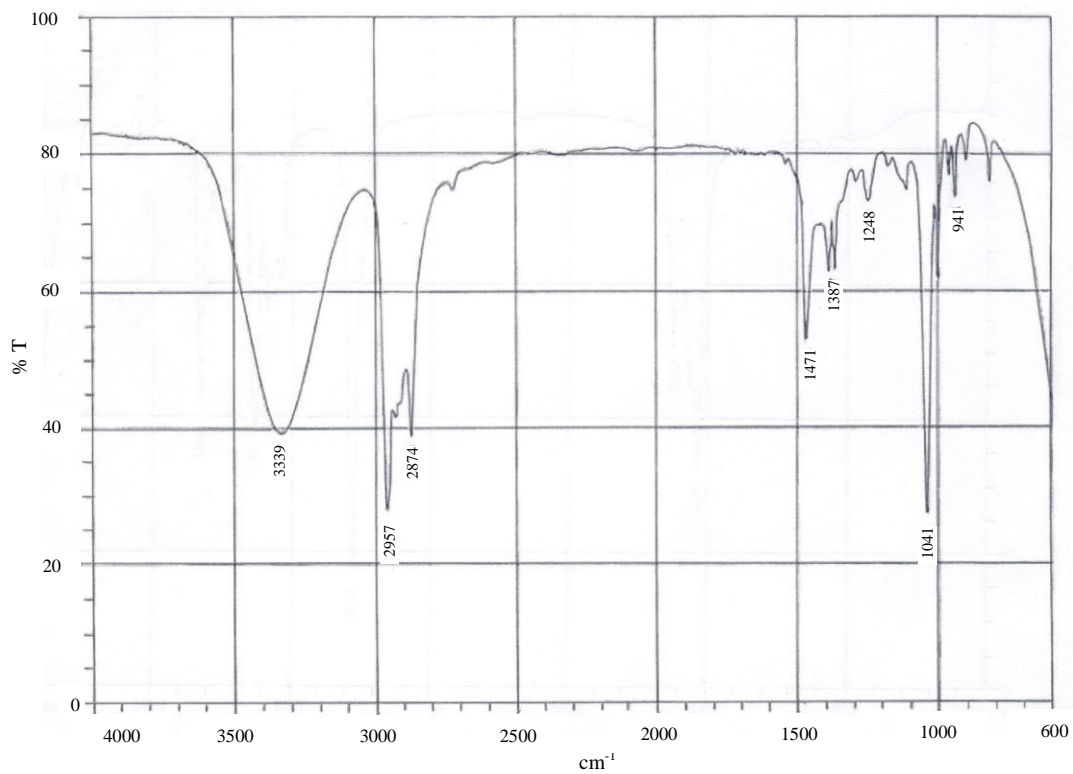
(b) Bagi setiap soalan berikut, anda diberikan formula molekul, spektrum IR dan ^1H NMR. Tentukan struktur dan nama bagi setiap sebatian.

(i) $\text{C}_5\text{H}_{10}\text{O}$



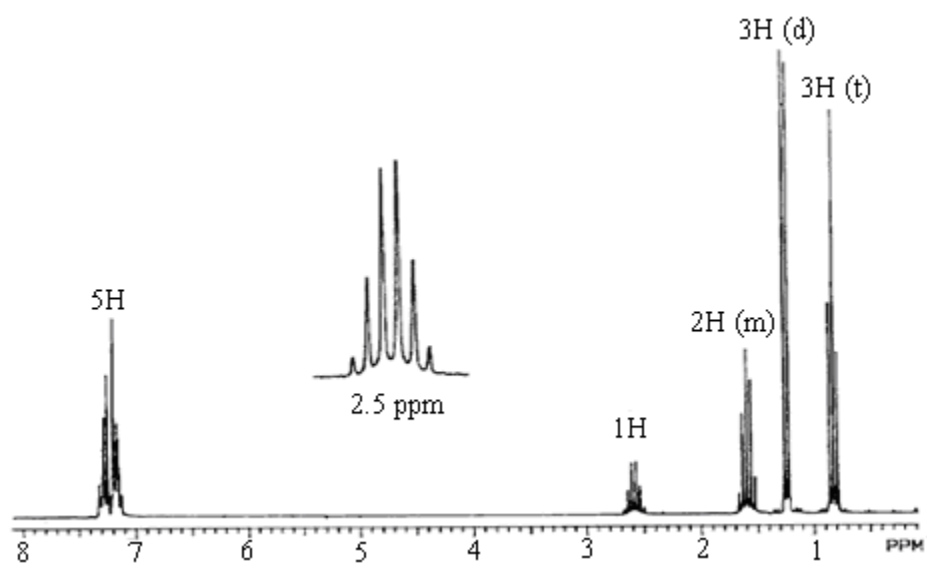
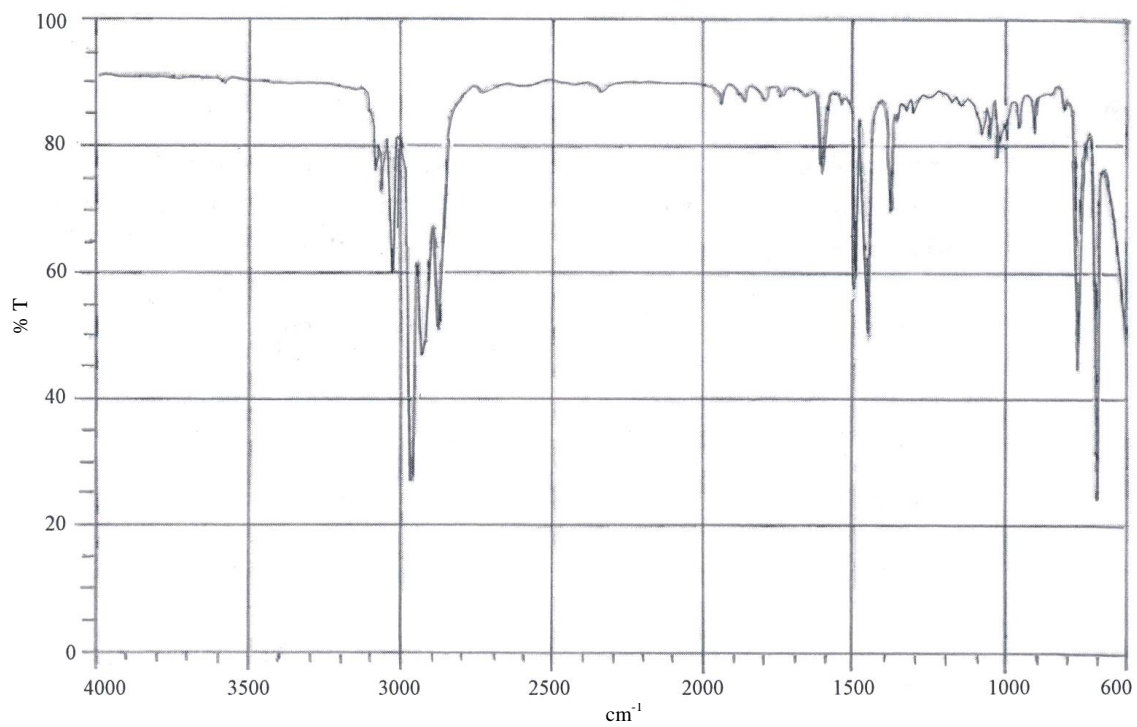
...19/-

-19-

(ii) $C_4H_{10}O$ 

...20/-

-20-

(iii) $C_{10}H_{14}$ 

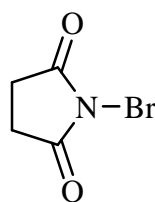
(15 markah)

...21/-

-21-

3. (a) Pengklorinan radikal bebas terhadap (*S*)-(+)-1-kloro-2-metilbutana menghasilkan sejumlah enam pecahan yang berformula $C_5H_{10}Cl_2$ yang dapat dipisahkan dengan penyulingan berperingkat yang teliti. Empat pecahan adalah aktif optik dan dua pecahan tidak aktif optik. Lukiskan formula struktur bagi sebatian yang membentuk setiap pecahan. Jelaskan keaktifan optik atau ketidakaktifan optik dalam setiap kes. (14 markah)

- (b) Tunjukkan mekanisme tindak balas bagi penghalogenan 1-butena dengan menggunakan *N*-bromosuksinimida (NBS) dengan kehadiran cahaya.



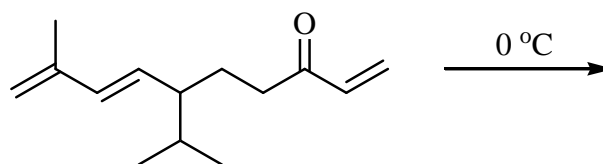
NBS

(4 markah)

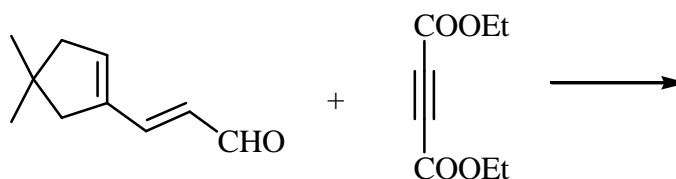
- (c) Tunjukkan bagaimana salah satu hasil daripada tindak balas dalam soalan 3 (b) boleh ditukarkan kepada suatu diena yang stabil. (2 markah)

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

(i)

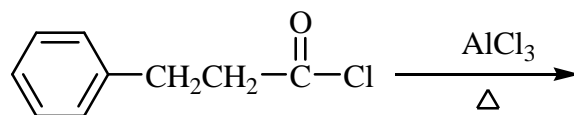


(ii)

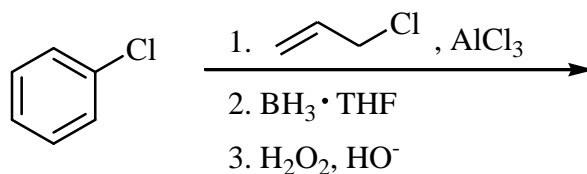


-22-

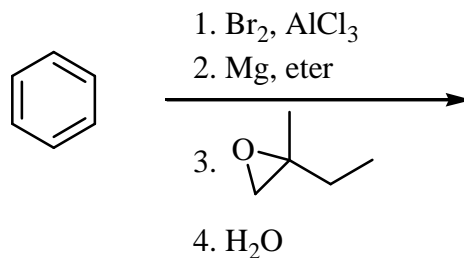
(iii)



(iv)



(v)



(10 markah)

- (b) Tindak balas satu ekuivalen HCl dengan 1,3-pentadiena memberikan kedua-dua aduk 1,2 dan 1,4. Pada suhu rendah, aduk 1,2 adalah hasil utama tetapi pada suhu tinggi, aduk 1,4 adalah hasil utama. Terangkan penemuan ini dengan menggunakan gambar rajah tenaga.

(5 markah)

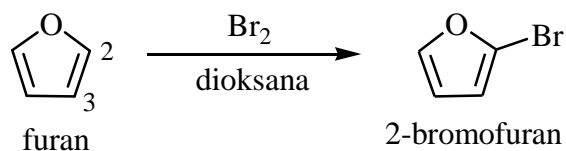
- (c) Spektrum jisim bagi kloroetana menunjukkan dua puncak ion molekul pada m/z 64 dan 66. Puncak pada m/z 64 adalah lebih kurang tiga kali lebih tinggi daripada m/z 66.

(i) Jelaskan pemerhatian ini.

(ii) Tunjukkan bagaimana fragmentasi ion molekul bagi kloroetana menghasilkan satu puncak pada m/z 29.

(5 markah)

5. (a) Furan lebih bersedia melalui penukaran elektrofilik aromatik berbanding dengan benzena. Sebagai contoh, furan bertindak balas dengan bromin tanpa memerlukan pemangkin asid Lewis untuk memberikan 2-bromofuran.

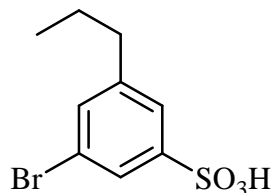


Cadangkan mekanisme bagi pembrominan furan pada posisi 2 dan 3. Terangkan mengapa furan melalui pembrominan terutamanya pada posisi 2.

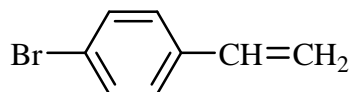
(10 markah)

- (b) Cadangkan suatu sintesis bagi setiap sebatian berikut bermula dengan benzena dan sebarang reagen. Mekanisme tidak diperlukan.

(i)



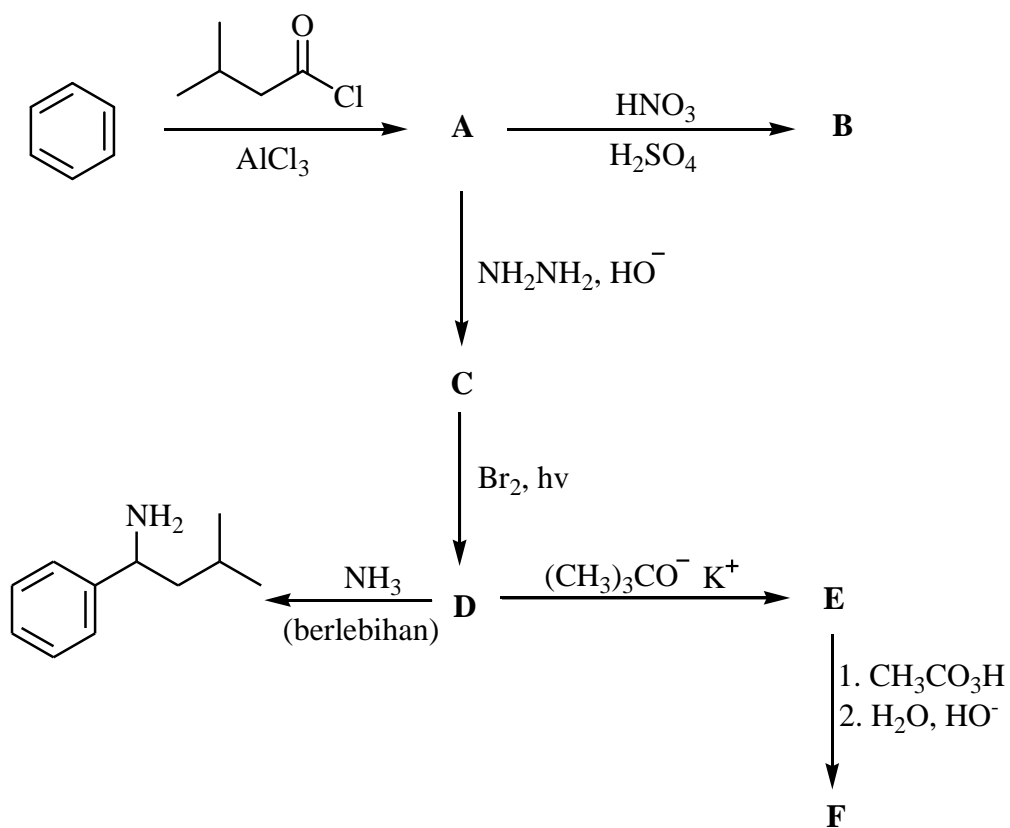
(ii)



(10 markah)

-24-

6. (a) Berikan struktur bagi sebatian **A** hingga **F** dalam siri tindak balas berikut.



(6 markah)

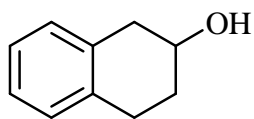
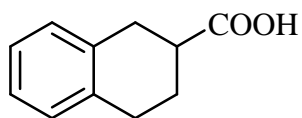
- (b) Susunkan sebatian yang berikut mengikut tertib keasidan yang meningkat. Jelaskan jawapan anda.



(4 markah)

-25-

- (c) Tunjukkan semua langkah yang diperlukan untuk memisahkan sebatian **G** daripada sebatian **H** dengan menggunakan prosedur pengekstrakan.

**G****H**

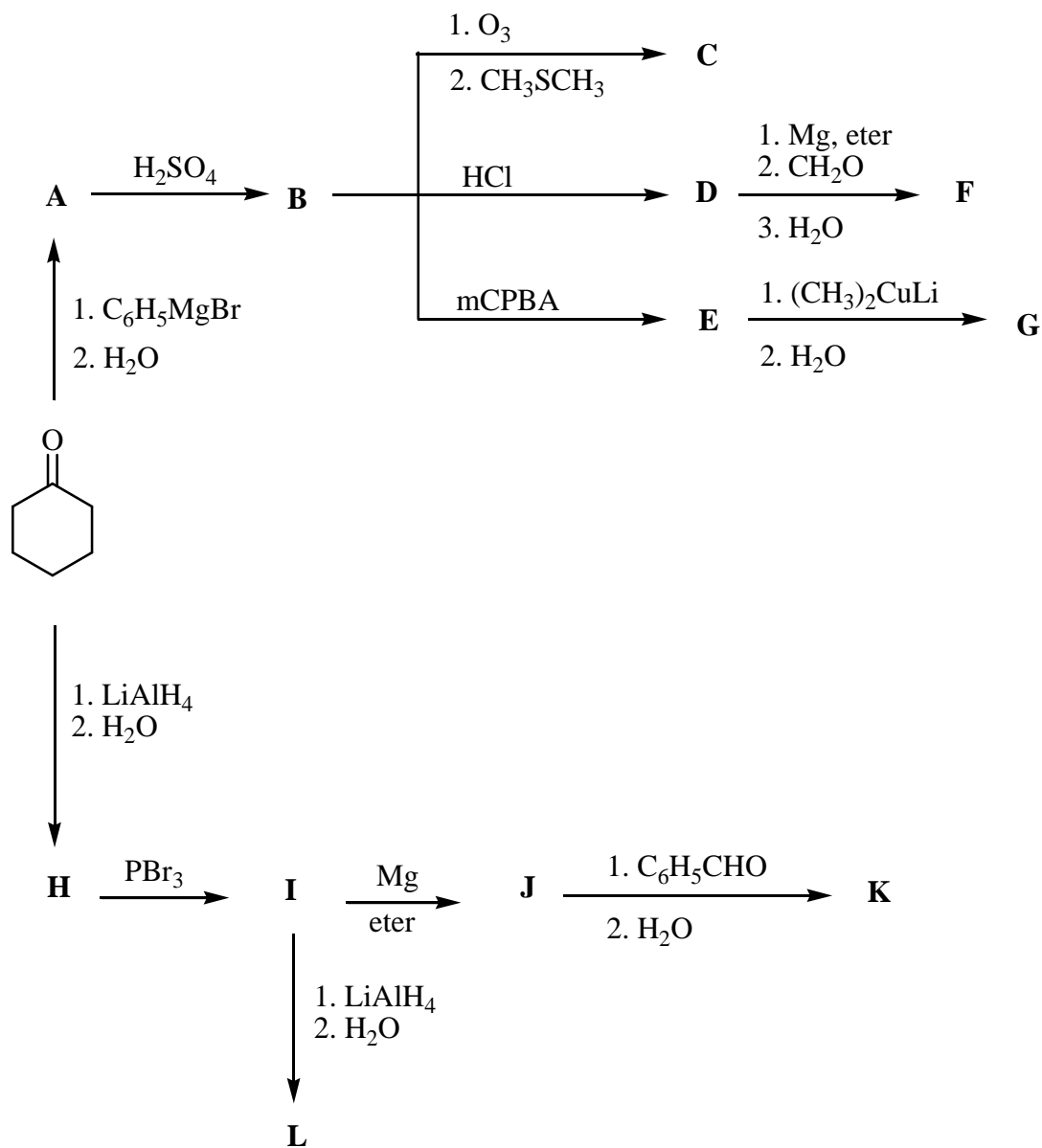
(5 markah)

- (d) Kenalpastikan reagen **I – N** dalam urutan tindak balas berikut:

(5 markah)

-26-

7. Kenalpastikan sebatian **A** - **L** dalam skema tindak balas berikut. Sebatian **F**, **G** dan **K** adalah isomer yang berformula molekul $C_{13}H_{18}O$. Bagaimanakah spektroskopi 1H NMR dapat membezakan ketiga-tiga sebatian tersebut?



(20 markah)

-oooOooo-

...27/-

Spectroscopy Tables

¹ H NMR	
	<u>δ (ppm)</u>
RCH ₃	0.9
R ₂ CH ₂	1.3
R ₃ CH	1.5
C=C-H	4.6 – 5.9
C≡C-H	2.0 – 3.0
Ar-H	6.0 – 8.5
Ar-C-H	2.2 – 3.0
C=C-CH ₃	1.7
H-C-F	4.0 – 4.5
H-C-Cl	3.0 – 4.0
H-C-Br	2.5 – 4.0
H-C-I	2.0 – 4.0
H-C-OH	3.4 – 4.0
H-C-OR	3.3 – 4.0
H-C-O-CO-R	3.7 – 4.1
H-C-COOR	2.0 – 2.2
H-C-COOH	2.0 – 2.6
H-C-C=O	2.0 – 2.7
R-CHO	9.0 – 10.0
R-OH	1.0 – 5.5
Ar-OH	4.0 – 12.0
C=C-OH	15 - 17
R-COOH	10.5 – 12.0
R-NH ₂	1.0 – 5.0

Atomic Weight	
H	1.0
C	12.0
N	14.0
O	16.0
F	19.0
Cl	35.45
Br	79.9
I	126.9
Si	28.0
P	31.0
S	32.0

¹³ C NMR	
	<u>δ (ppm)</u>
C-I	0 – 40
C-Br	25 – 65
C-Cl	35 – 80
-CH ₃	8 – 30
-CH ₂ -	15 – 55
-CH-	20 – 60
≡C	65 – 85
=C	100 – 150
C-O	40 – 80
C=O	170 – 210
C(Ar)	110 – 160
C-N	30 – 65
C=N	110 – 125

IR	
	<u>cm⁻¹</u>
=C-H	3020 – 3080
=C-H	675 – 1000
C=C	1640 – 1680
≡C-H	3300
≡C-H	600 – 700
C≡C	2100 – 2260
Ar-H	3000 – 3100
Ar-H	675 – 870
C=C	1500 – 1600
O-H	3610 – 3640
O-H	3200 – 3600 (broad)
C-O	1080 – 1300
C=O	1690 – 1760 (s)
O-H (acid)	2500 – 3000 (broad)
C-O	1080 – 1300
C=O	1690 – 1760
N-H	3300 – 3600
C-N	1180 – 1360
-NO ₂	{ 1515 – 1560
	{ 1345 – 1385