
UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang
Sidang Akademik 2009/2010

June 2010

KOT 222 – Organic Chemistry II
[Kimia Organik II]

Duration : 3 hours
[Masa : 3 jam]

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

Instructions:

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

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

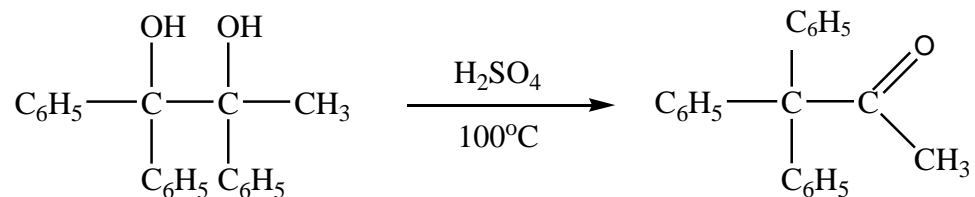
If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

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

Appendix: Spectroscopy Table.

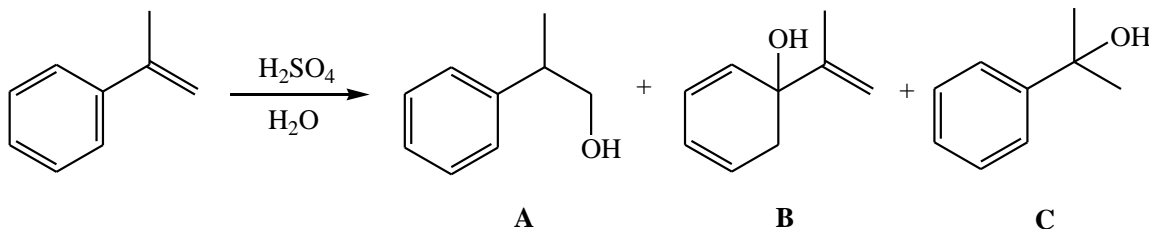
-2-

1. (a) Provide a detailed, stepwise mechanism for the pinacol rearrangement of 1,1,2-triphenyl-1,2-propanediol.



(6 marks)

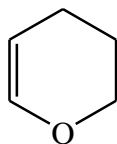
- (b) Consider this reaction:



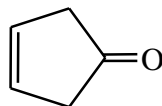
- (i) Choose the major product and give explanation for your choice.
 (ii) Provide a complete mechanism for the formation of the major product.

(8 marks)

- (c) Which structure best fits the following FTIR spectrum? Briefly explain why the other two structures are excluded.



Dihydropyran



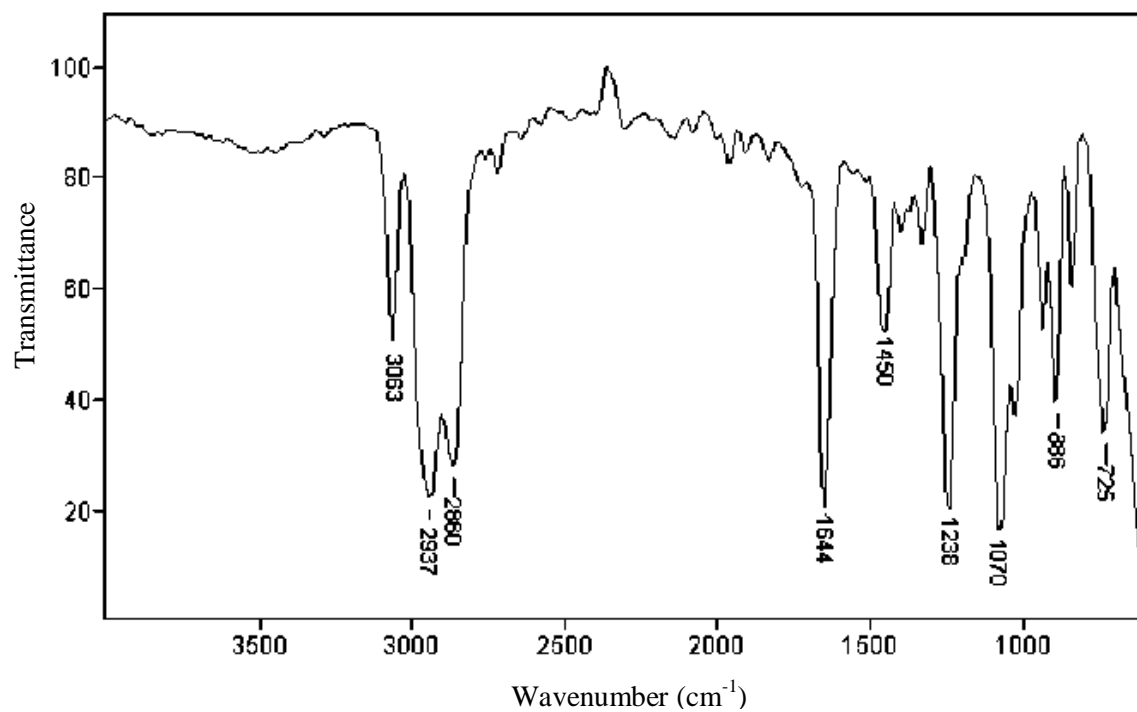
Cyclopent-3-en-1-one



1-Methoxy-2-butyne

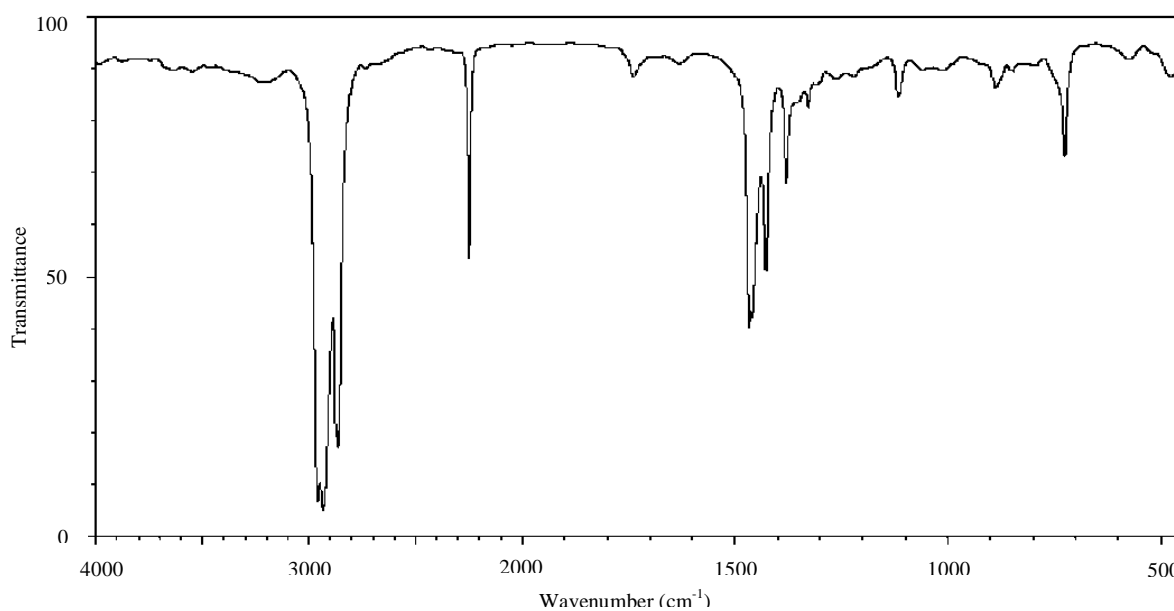
...3/-

-3-



(6 marks)

2. The mass spectrum of compound **A** shows the molecular ion peak at m/z 111. Using the data below, propose the structure for compound **A**.

FTIR:

...4/-

-4-

 ^1H NMR (ppm):

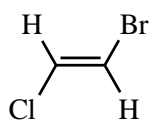
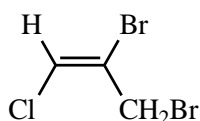
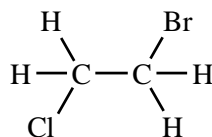
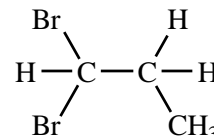
1.5 (triplet, integral = 1), 1.3 (sextet, integral = 1), 1.1 (singlet, integral = 3), 0.9 (triplet, integral = 1.5)

 ^{13}C NMR (DEPT):

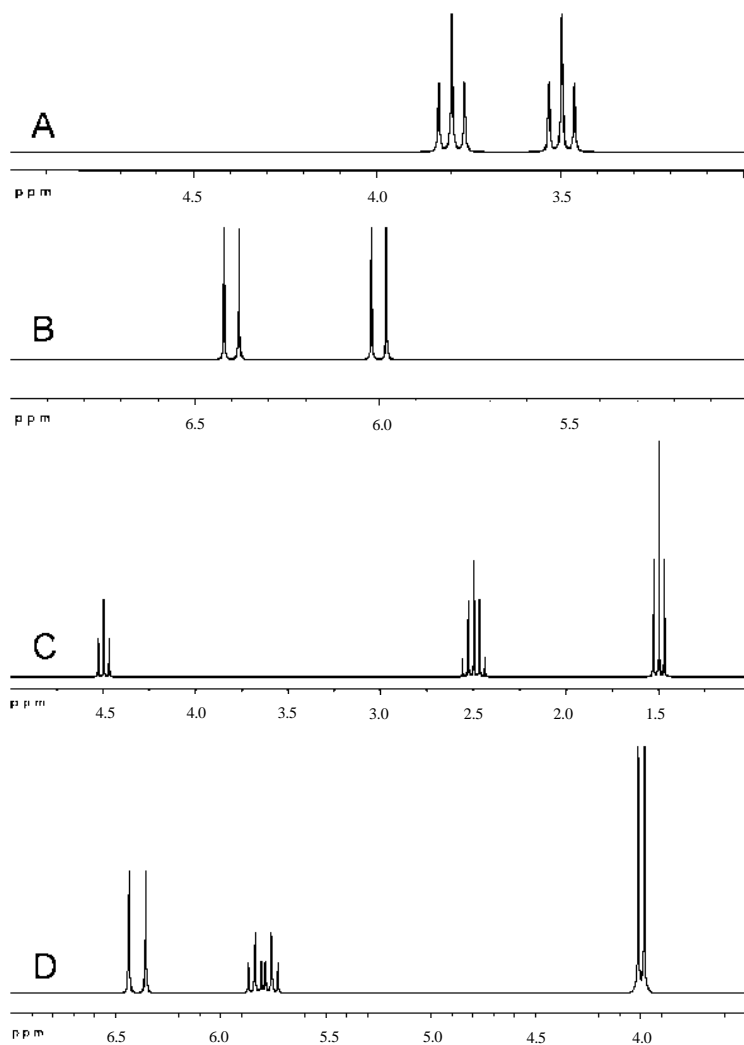
125.1 (singlet), 46.5 (triplet), 35.0 (singlet), 25.8 (quartet), 22.7 (triplet), 13.8 (quartet). The two singlets are of roughly equal height. The 25.8 ppm quartet is significantly taller than the 13.8 ppm quartet.

(20 marks)

3. (a) Match each of the four structures **1-4** shown below with its corresponding proton NMR spectra **A, B, C** or **D** and explain your reasoning. Include in your answer a brief explanation for the observed resonance multiplicities within each spectrum.

**1****2****3****4**

-5-



(12 marks)

- (b) The following compounds give similar but distinctive mass spectra. Both compounds give prominent peaks at m/z 116, 73, 57 and 43, but one compound gives a distinctive strong peak at m/z 87 and the other compound gives a strong peak at m/z 101.

-6-

Determine which compound gives the peak at m/z 87 and which one gives the peak at m/z 101. Propose fragmentations leading to the formation of both ions.

(6 marks)

- (c) In the FTIR spectra, explain why the carbonyl (C=O) stretching frequency for acetone is higher than the carbonyl (C=O) stretching frequency for acetophenone.

(2 marks)

4. (a) Provide products. If no reaction occurs, explain why.

(i)

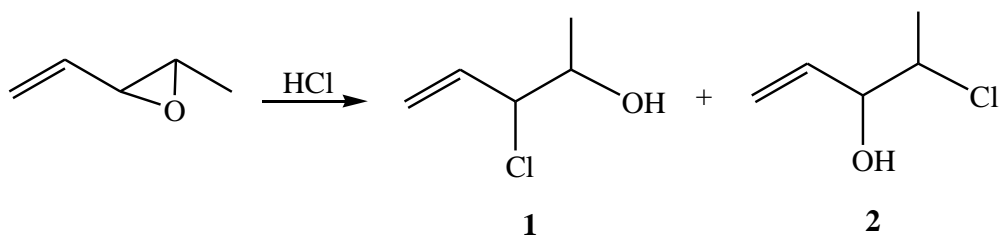
(ii)

(4 marks)

- (b) (i) Give the mechanisms for the formation of compounds **1** and **2** in the reaction below.

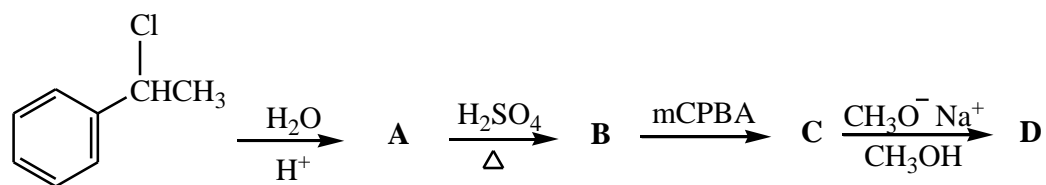
-7-

(ii) Identify the major product and explain your selection.



(8 marks)

(c) Give structures for compounds **A** through **D** in the conversions below:



(8 marks)

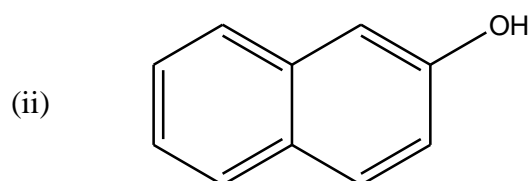
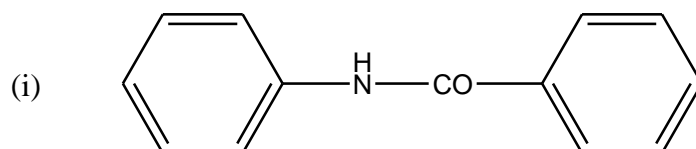
5. (a) Are the following substituents *ortho-para* - directors or *meta* - directors? Explain briefly.

- (i) SO_3H
- (ii) CH_2OH
- (iii) COOH
- (iv) CF_3
- (v) NO

(5 marks)

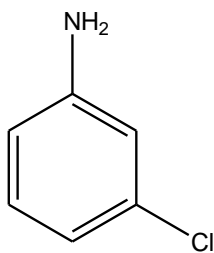
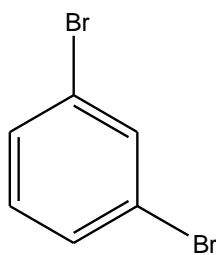
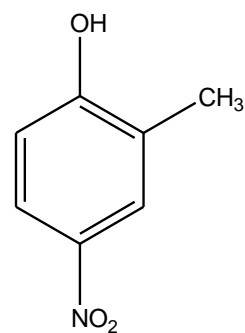
-8-

- (b) Give the major products obtained from the reaction of the following compounds with $\text{Br}_2/\text{FeBr}_3$.



(3 marks)

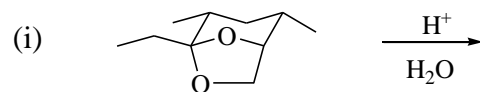
- (c) Show how each of the compounds **1** – **3** can be synthesized from benzene.

**1****2****3**

(12 marks)

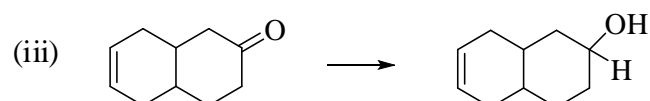
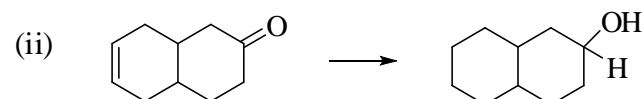
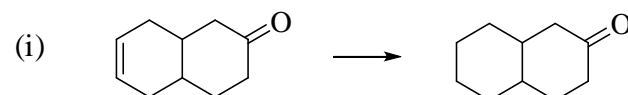
-9-

6. (a) Give the products of each of the following reactions:



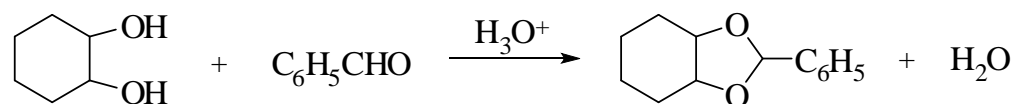
(6 marks)

(b) Show how you would accomplish the following syntheses efficiently and in good yield. You may use any necessary reagents.



(6 marks)

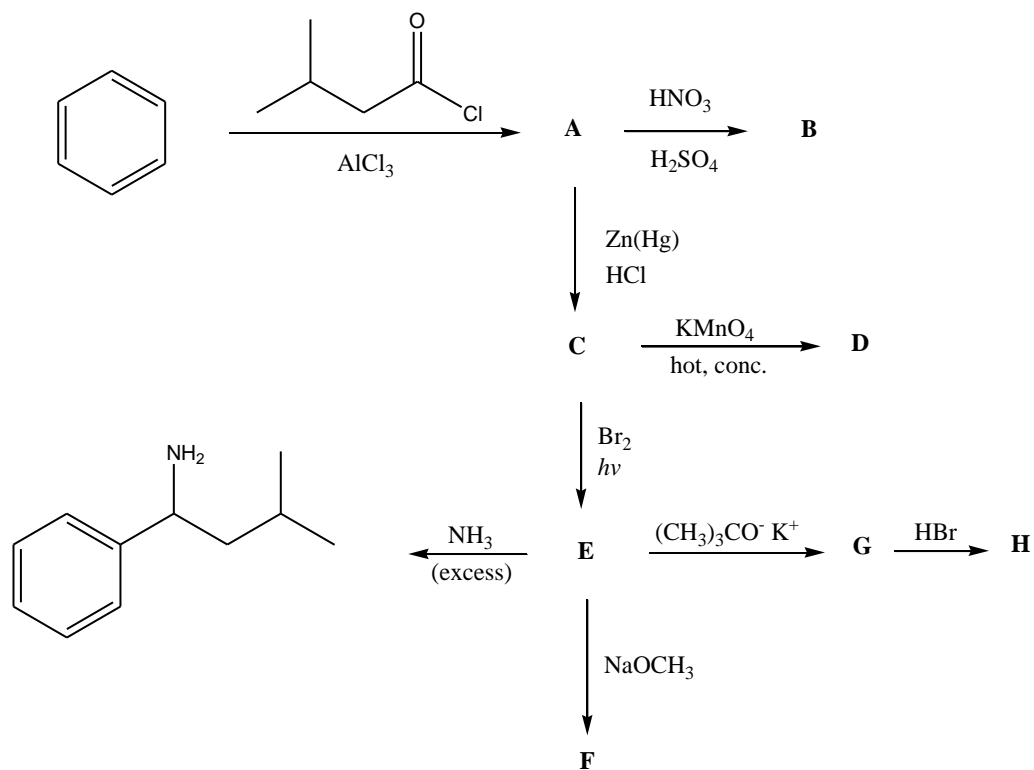
(c) Write a stepwise mechanism for the following reaction:



(8 marks)

-10-

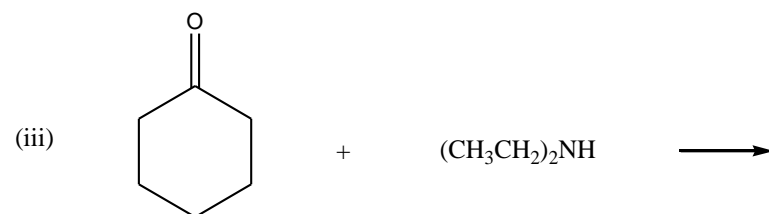
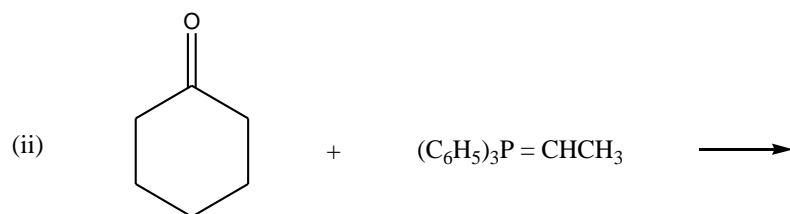
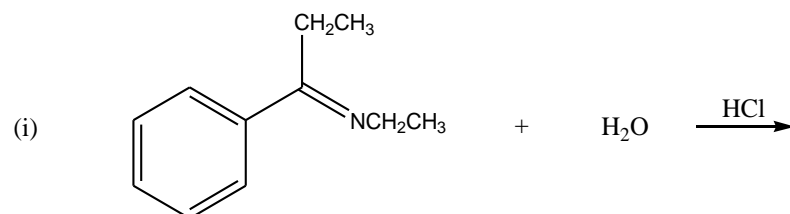
7. (a) Give the structures of compounds **A** through **H** in the following series of reactions:



(14 marks)

-11-

(b) Give the products of each of the following reactions:



(6 marks)

TERJEMAHAN

Arahan:

Jawab **LIMA** (5) soalan.

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

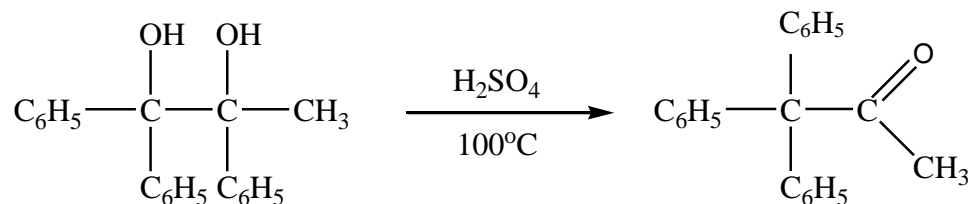
Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

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

Lampiran: Jadual Spektroskopi.

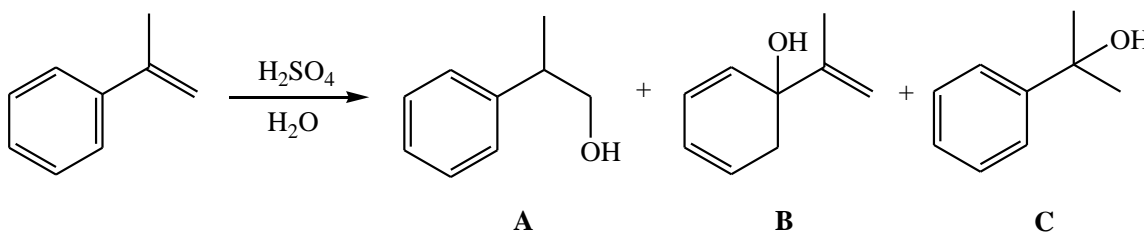
-13-

1. (a) Berikan mekanisme seselangkah yang terperinci bagi penyusunan semula pinakol untuk 1,1,2-trifenil-1,2-propanadiol.



(6 markah)

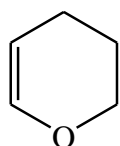
- (b) Pertimbangkan tindak balas ini:



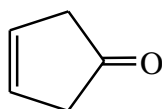
- (i) Pilihlah hasil utama dan jelaskan pilihan anda.
(ii) Berikan mekanisme yang lengkap bagi pembentukan hasil utama.

(8 markah)

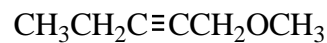
- (c) Struktur manakah yang paling sesuai bagi spektrum FTIR berikut? Terangkan secara ringkas mengapa dua struktur yang lain dikecualikan.



Dihidropiran

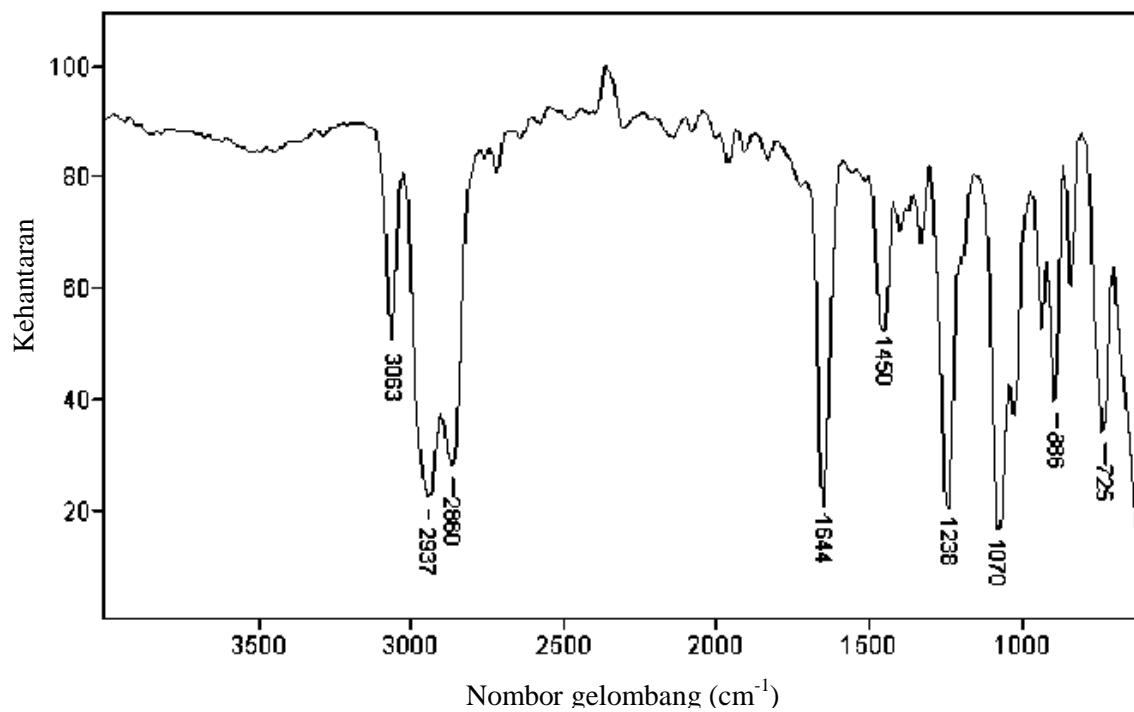


Siklopent-3-en-1-on



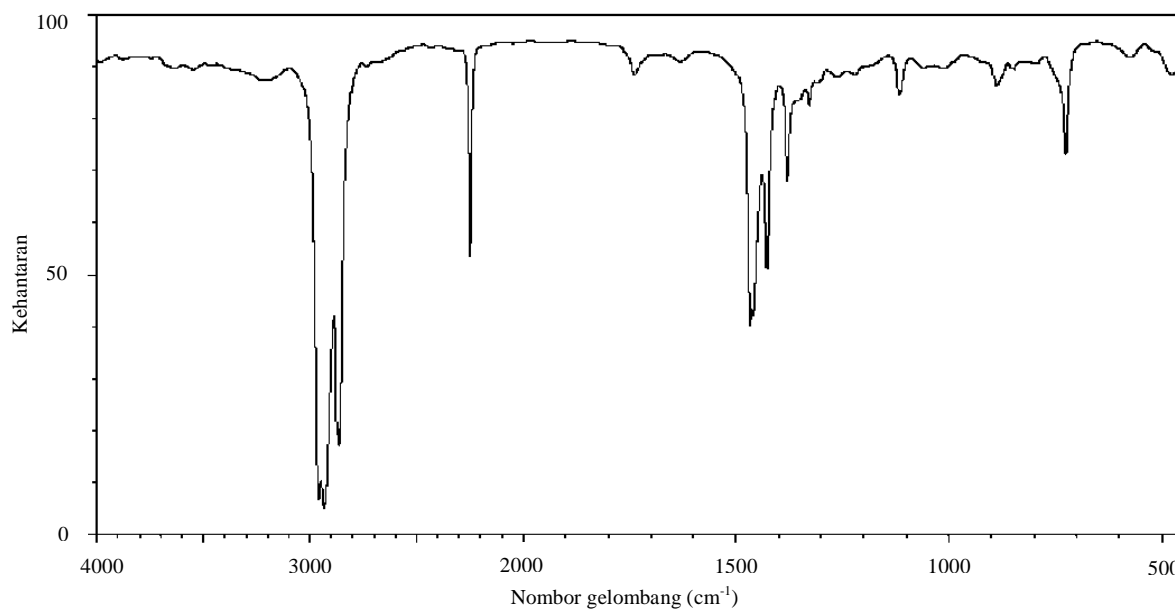
1-Metoksi-2-butuna

-14-



(6 markah)

2. Spektrum jisim bagi sebatian **A** menunjukkan puncak ion molekul pada m/z 111. Dengan menggunakan data di bawah, cadangkan struktur bagi sebatian **A**.

FTIR:

...15/-

-15-

 ^1H NMR (ppm):

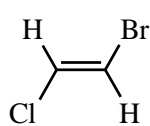
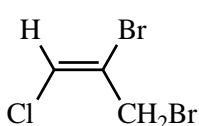
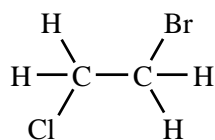
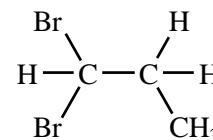
1.5 (triplet, integral = 1), 1.3 (seksitet, integral = 1), 1.1 (singlet, integral = 3), 0.9 (triplet, integral = 1.5)

 ^{13}C NMR (DEPT):

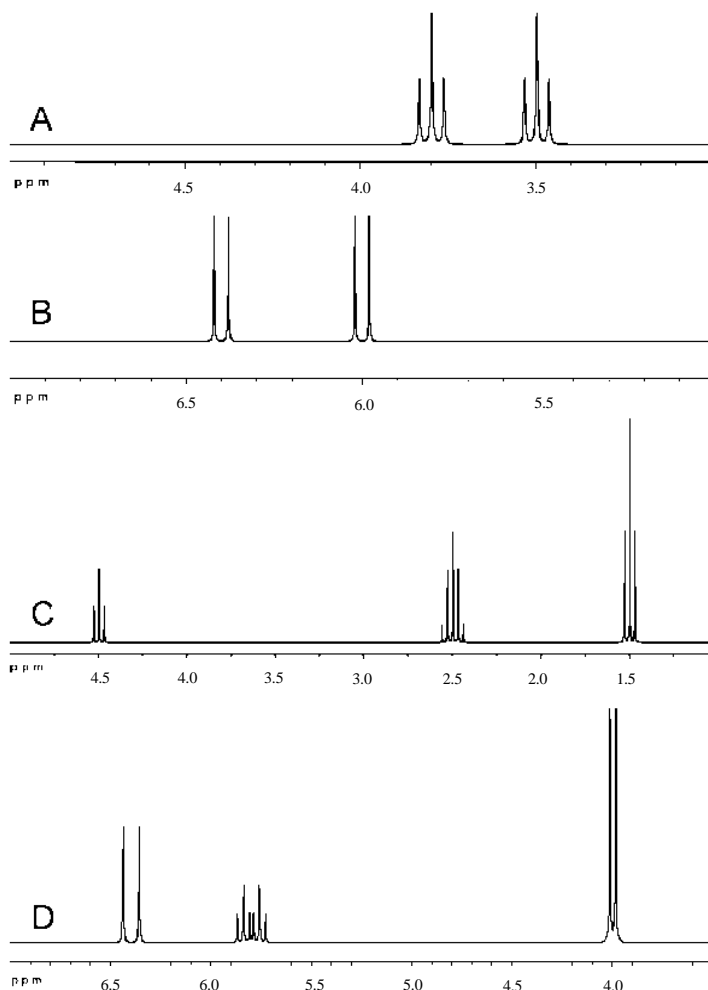
125.1 (singlet), 46.5 (triplet), 35.0 (singlet), 25.8 (kuartet), 22.7 (triplet), 13.8 (kuartet).
Kedua-dua singlet mempunyai ketinggian yang lebih kurang sama. Kuartet 25.8 ppm ternyata lebih tinggi daripada kuartet 13.8 ppm.

(20 markah)

3. (a) Padankan setiap struktur **1-4** yang ditunjukkan di bawah dengan spektrum NMR **A, B, C** dan **D** masing-masing dan jelaskan alasan anda. Dalam huraian anda, jelaskan dengan ringkas kemultipelan resonans yang diperhatikan dalam setiap spektrum.

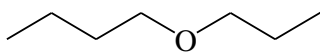
**1****2****3****4**

-16-

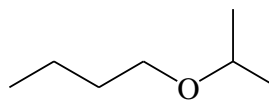


(12 markah)

- (b) Sebatian di bawah memberi spektrum jisim hampir sama. Kedua-dua sebatian memberi puncak utama pada m/z 116, 73, 57 dan 43. Tetapi, satu sebatian memberi puncak khusus yang jelas pada m/z 87 dan sebatian yang lain memberi puncak yang jelas pada m/z 101.



butil propil eter



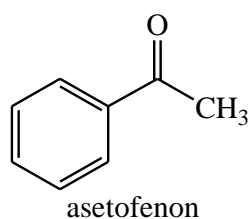
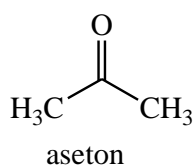
butil isopropil eter

-17-

Tentukan sebatian yang manakah yang memberikan puncak pada m/z 87 dan 101 masing-masing. Cadangkan fragmentasi bagi pembentukan kedua-dua ion tersebut.

(6 markah)

- (c) Dalam spektrum FTIR, jelaskan mengapa frekuensi peregangan karbonil (C=O) bagi aseton adalah lebih tinggi daripada frekuensi peregangan karbonil (C=O) bagi asetofenon.



(2 markah)

4. (a) Berikan hasil. Sekiranya tiada tindak balas, jelaskan mengapa.

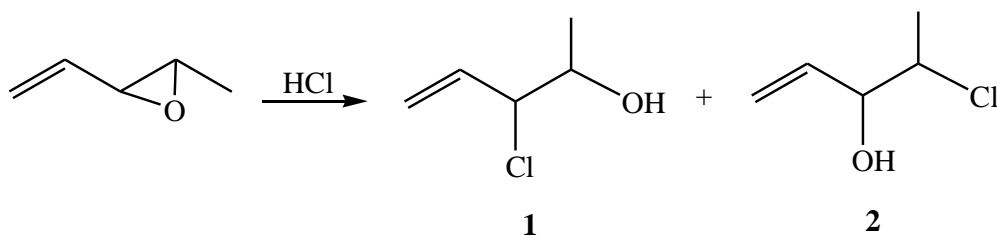
(i)

(ii)

(4 markah)

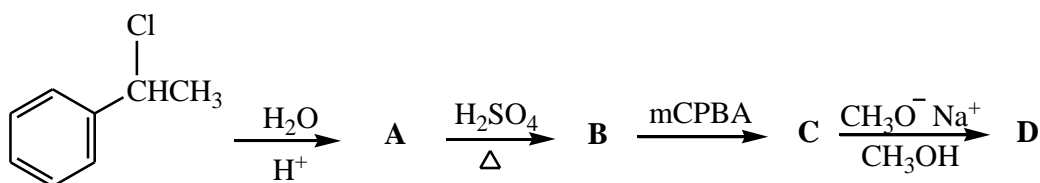
-18-

- (b) (i) Berikan mekanisme bagi pembentukan sebatian **1** dan **2** dalam tindak balas di bawah.
- (ii) Kenalpastikan hasil utama dan jelaskan pilihan anda.



(8 markah)

- (c) Berikan struktur bagi sebatian A hingga D dalam penukaran di bawah:

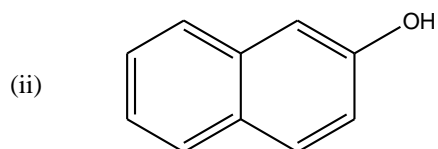
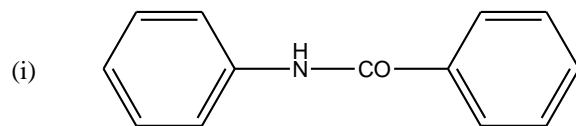


(8 markah)

5. (a) Adakah penukarganti berikut pengarah orto-para atau pengarah meta? Jelaskan secara ringkas.
- (i) SO_3H
 - (ii) CH_2OH
 - (iii) COOH
 - (iv) CF_3
 - (v) NO

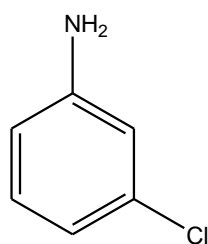
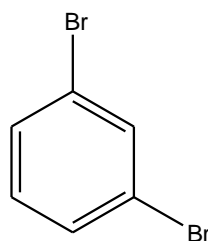
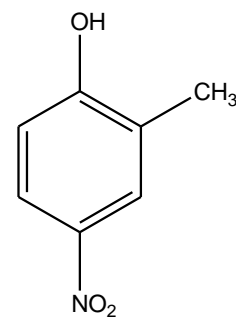
(5 markah)

- (b) Berikan hasil utama yang diperoleh daripada tindak balas bagi setiap sebatian berikut dengan $\text{Br}_2/\text{FeBr}_3$.



(3 markah)

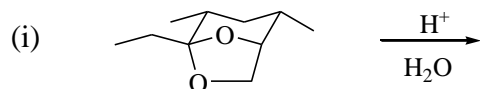
- (c) Tunjukkan cara sintesis bagi setiap sebatian **1** - **3** daripada benzena.

**1****2****3**

(12 markah)

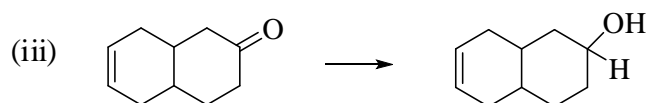
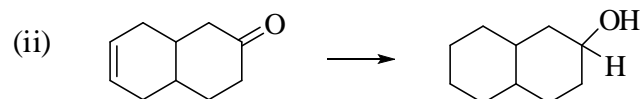
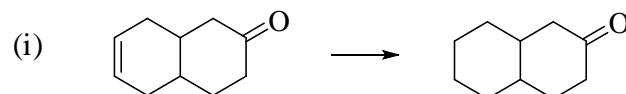
-20-

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



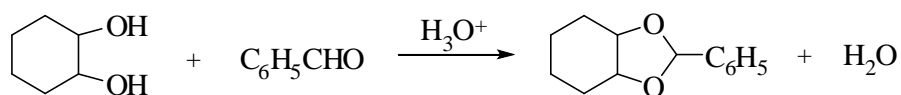
(6 markah)

(b) Tunjukkan bagaimana anda dapat mencapai setiap sintesis berikut secara berkesan dan memberikan peratusan hasil yang tinggi. Anda boleh menggunakan sebarang reagen yang diperlukan.



(6 markah)

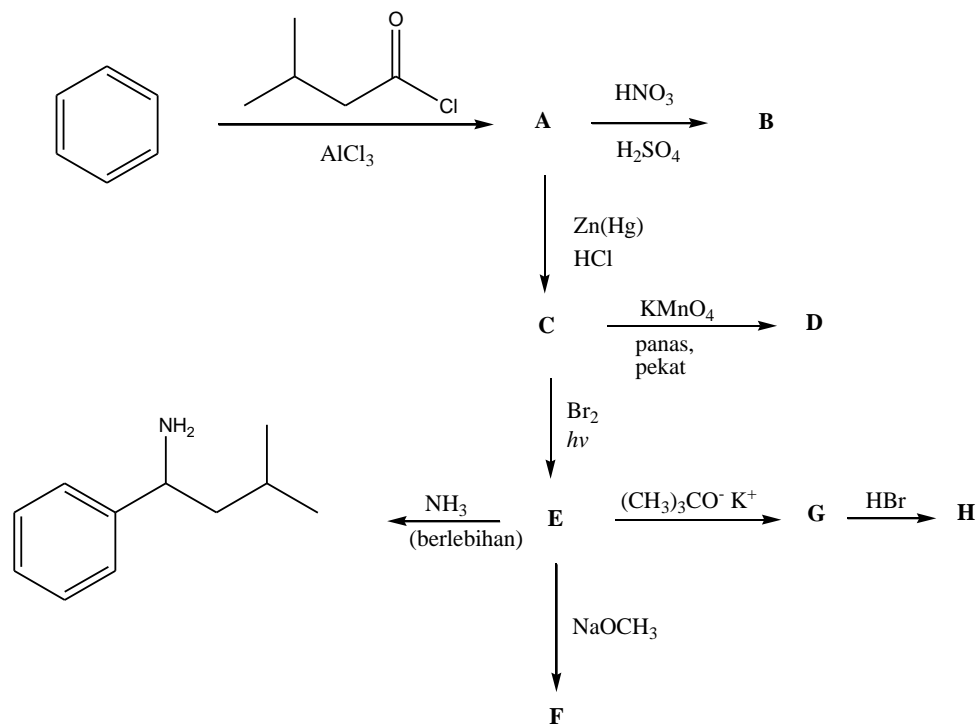
(c) Tuliskan suatu mekanisme seselangkah bagi tindak balas berikut:



(8 markah)

-21-

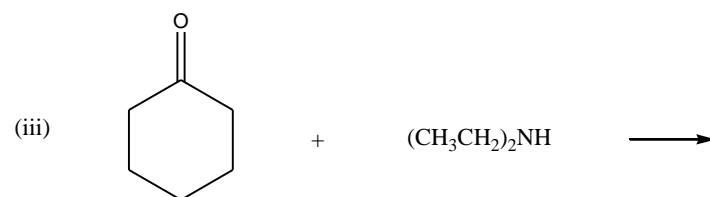
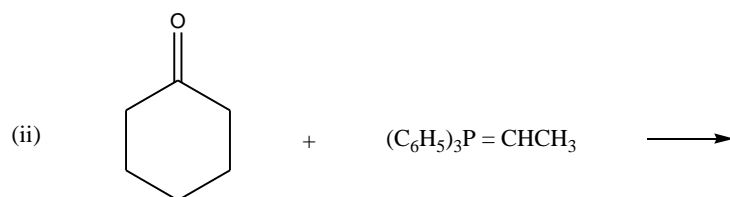
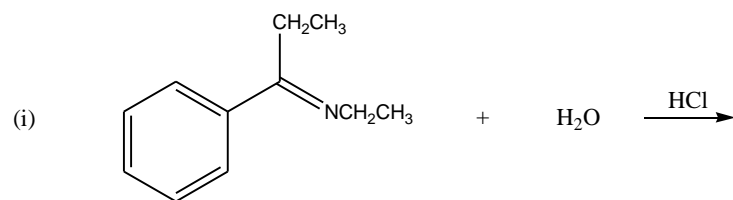
7. (a) Berikan struktur bagi sebatian **A** hingga **H** dalam siri tindak balas berikut:



(14 markah)

-22-

(b) Berikan hasil bagi setiap tindak balas berikut:



(6 markah)

Spectroscopy Tables

<u>¹H NMR</u>		<u>Infrared Absorption</u>	<u>¹³C NMR</u>		
	δ (ppm)		cm^{-1}	δ (ppm)	
RCH ₃	0.9	= C - H	3020 - 3080	C - I	0 - 40
R ₂ CH ₂	1.3	= C - H	675-1000	C - Br	25 - 65
R ₃ CH	1.5	C = C	1640-1680	C - Cl	35 - 80
C=C-H	4.6-5.9	\equiv C - H	3300	- CH ₃	8 - 30
C \equiv C-H	2.0-3.0	\equiv C - H	600-700	- CH ₂ -	15 - 55
Ar-H	6.0-8.5	C \equiv C	2100-2260	- CH -	20 - 60
Ar - C - H	2.2-3.0	Ar - H	3000-3100	\equiv C	65 - 85
C=C-CH ₃	1.7	Ar - H	675-870	= C	100 - 150
H - C - F	4.0-4.5	C = C	1500-1600	C - O	40 - 80
H - C - Cl	3.0 - 4.0	O - H	3610 - 3640	C = O	170 - 210
H - C - Br	2.5-4.0	O - H	3200	C (Ar)	110 - 160
H - C - I	2.0-4.0	3600(broad)		C - N	30 - 65
H-C-OH	3.4 -4.0	C - O	1080-1300	C = N	110 - 125
H - C - OR	3.3-4.0	C = O	1690 - 1760 (s)		
RCOO - C - H	3.7-4.1	O - H (acid)	2500- 3000	<u>Atomic weight</u>	
		(broad)		H = 1.0	
H - C - COOR	2.0	C - O	1080-1300	C = 12.0	
-2.2		C = O	1690-1760	N = 14.0	
H - C - COOH	2.0	N - H	3300 - 3600	O = 16.0	
-2.6		C - N	1180-1360	F = 19.0	
H-C-C=O	2.0-2.7	- NO ₂	1515-1560	Cl = 35.45	
R - CHO	9.0-10.0		1345-1385	Br = 79.9	
R-OH	1.0-5.5			I = 126.9	
Ar-OH	4.0-12.0			Si = 28.0	
C=C-OH	15-17			P = 31.0	
RCOOH	10.5 -			S = 32.0	
12.0					
RNH ₂	1.0 - 5.0				