
UNIVERSITI SAINS MALAYSIA

First Semester Examination
Academic Session 2008/2009

November 2008

KOT 222 – Organic Chemistry II
[Kimia Organik II]

Duration : 3 hours
[Masa : 3 jam]

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

Instructions:

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

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

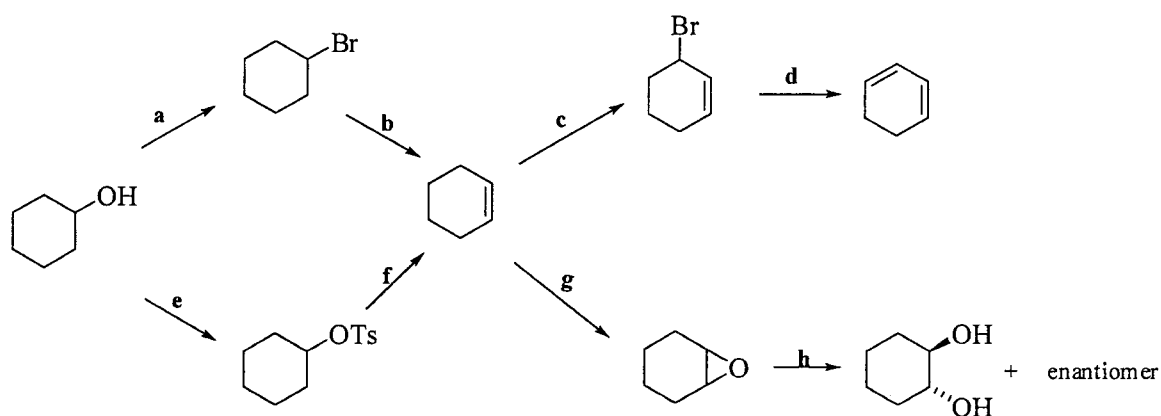
If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

Appendix: Spectroscopic Table.

...2/-

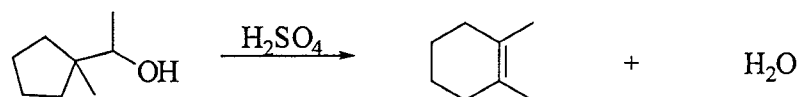
Answer any **FIVE** questions.

1. (a) Identify the reagents (**a-h**) needed to carry out each reaction.



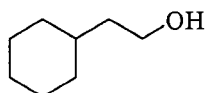
(12 marks)

- (b) Draw a stepwise, detailed mechanism for the following reaction, accounting for the formation of the products.



(4 marks)

- (c) Show how you would synthesize the following compound, using as starting materials cyclohexanol and any alcohol containing four or fewer carbon atoms, and any necessary solvents and inorganic reagents.



(4 marks)

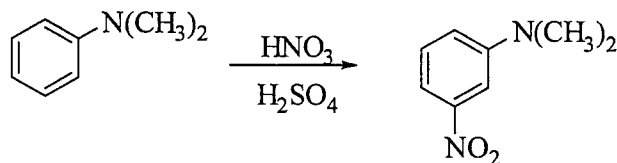
2. (a) Explain in detail, using resonance structures, why a COOCH_3 group is a *meta* director that deactivates a benzene ring toward electrophilic aromatic substitution.

(5 marks)

...3/-

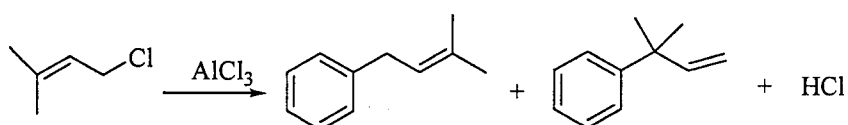
- 3 -

- (b) Explain why the *meta* product is formed in the following reaction despite the fact that $-\text{N}(\text{CH}_3)_2$ is usually an *ortho*, *para* director.



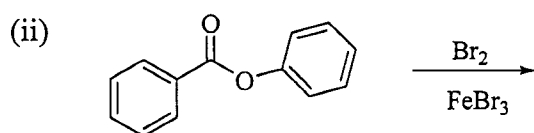
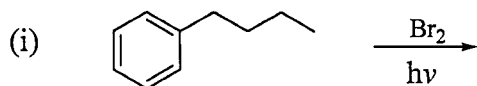
(5 marks)

- (c) Draw a stepwise mechanism for the following reaction:



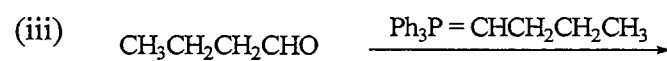
(5 marks)

- (d) Draw the products of each reaction.



(5 marks)

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

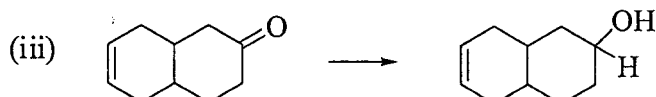
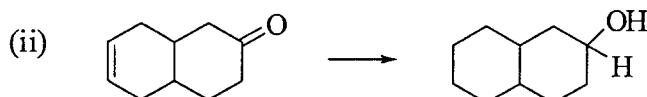
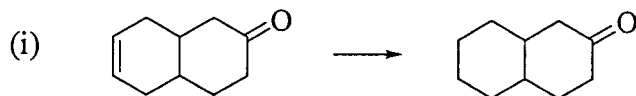


(6 marks)

...4/-

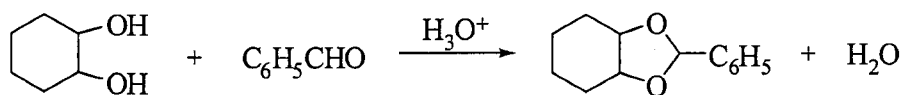
- 4 -

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



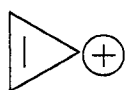
(6 marks)

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



(8 marks)

4. (a) Use the inscribed polygon method to show why cyclopropenyl cation (1) is aromatic while cyclobutadiene (2) is not aromatic.



(1)



(2)

(5 marks)

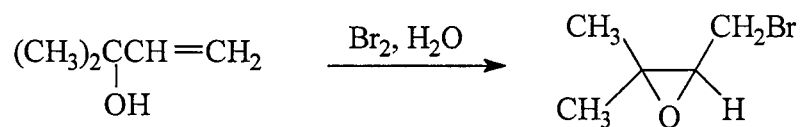
- (b) Show how you would synthesize 3-nitro-4-bromobenzoic acid using toluene as the starting material.

(5 marks)

...5/-

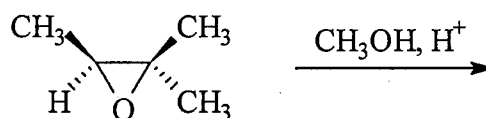
- 5 -

- (c) Suggest in detail a reasonable mechanism for the reaction shown below.



(6 marks)

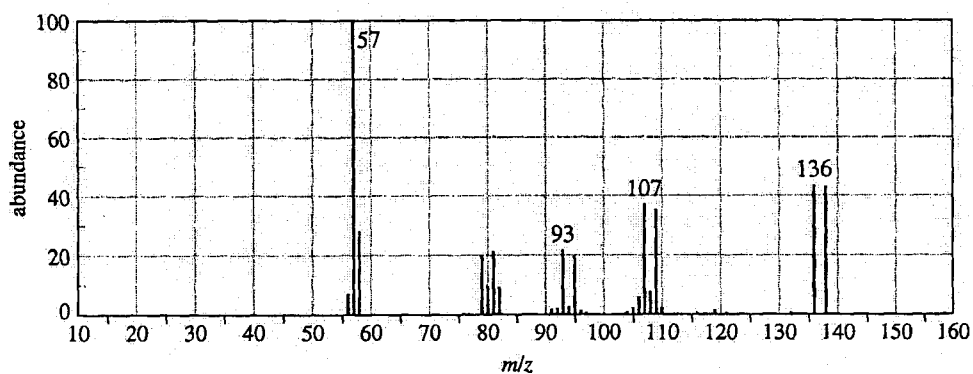
- (d) Provide the major product of the reaction below.



(4 marks)

5. (a) Using only given mass spectrometric data:

- (i) Predict what the compound is and state your reasons.
 (ii) Suggest the structures for the fragments at 136, 107, and 93. Explain why the base peak is at m/z 57.

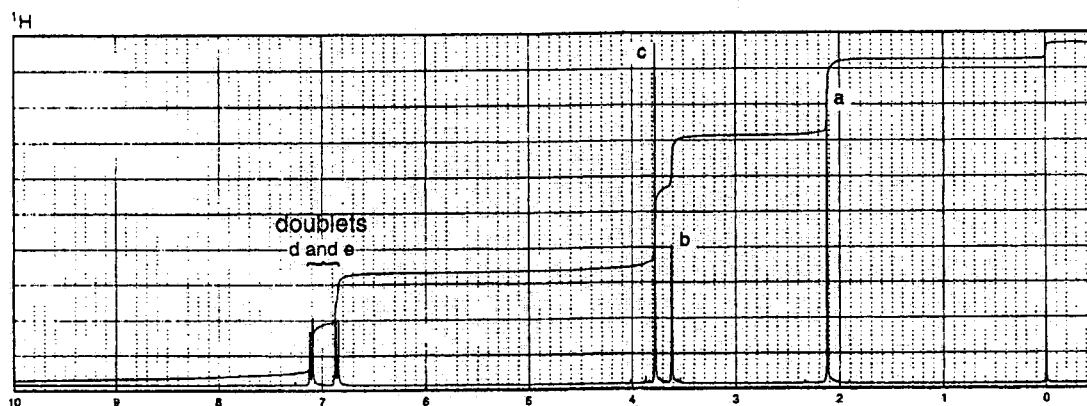
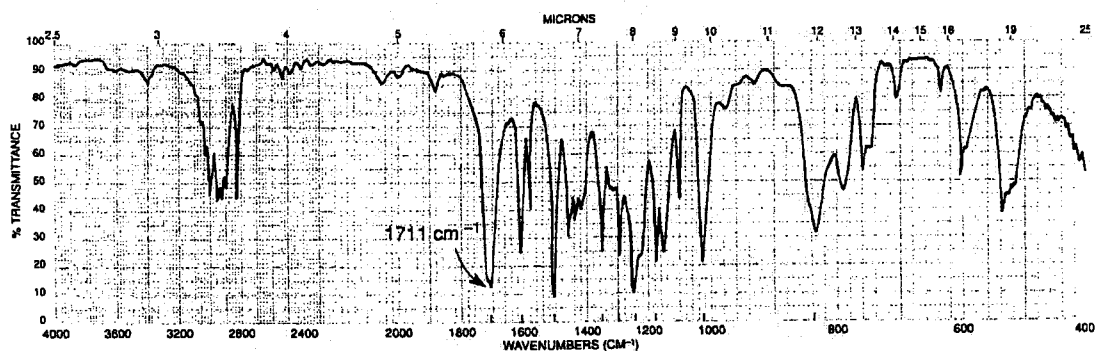


(8 marks)

...6/-

- 6 -

- (b) Compound "X" has a formula $C_{10}H_{12}O_2$. The IR, 1H NMR and ^{13}C NMR (decoupling) with DEPT-135, DEPT-90 spectral data are given below. Deduce the structure of "X" using the information given.



^{13}C Carbon	DEPT-135	DEPT-90
29 ppm	Positive	No peak
50 ppm	Negative	No peak
55 ppm	Positive	No peak
114 ppm	Positive	Positive
126 ppm	No peak	No peak
130 ppm	Positive	Positive
159 ppm	No peak	No peak
207 ppm	No peak	No peak

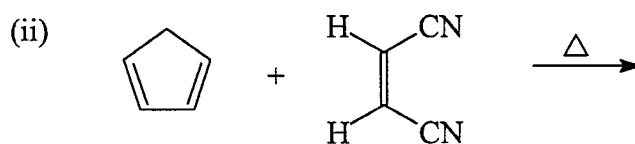
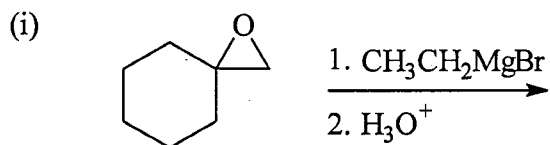
(12 marks)

...7/-

- 7 -

6. (a) Show the best method for preparing 4-propoxytoluene via the Williamson ether synthesis. (4 marks)
- (b) Draw the lowest and the highest energy π molecular orbitals of 1,3-butadiene. (4 marks)
- (c) How could IR spectroscopy be used to distinguish between the following pairs of compounds.
- (i) $\text{HOCH}_2\text{CH}_2\text{CHO}$ and $\text{CH}_3\text{CH}_2\text{COOH}$
- (ii) $\text{CH}_3\text{CH}_2\text{C}\equiv\text{CH}$ and $\text{CH}_3\text{C}\equiv\text{CCH}_3$
- (6 marks)

- (d) Provide the major organic product in each of the reactions below.

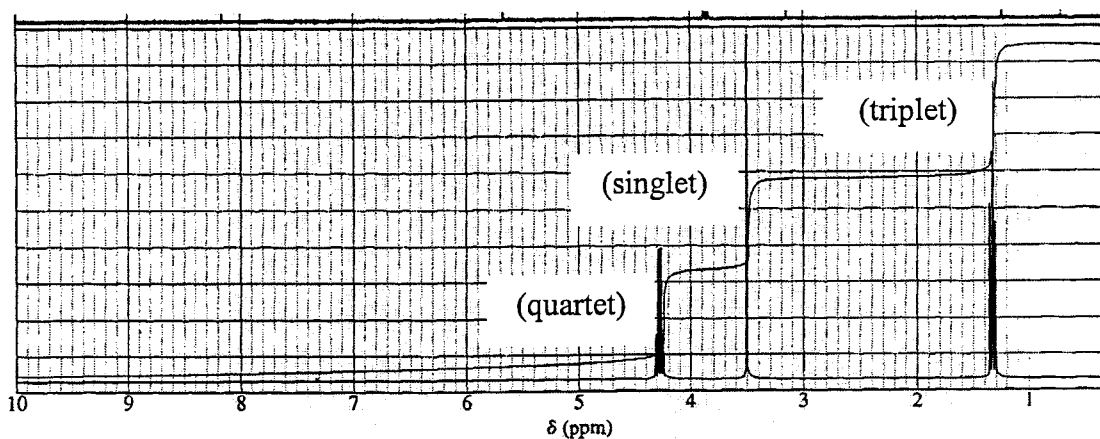
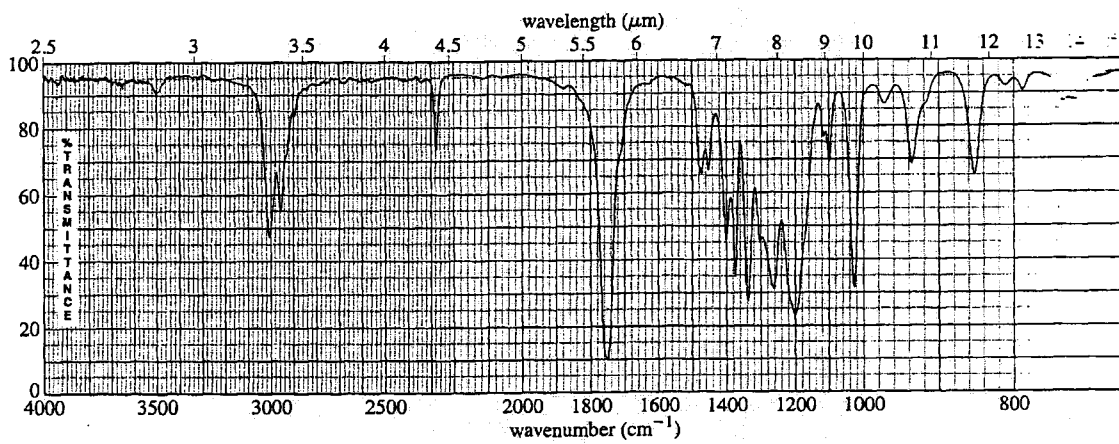


(6 marks)

...8/-

- 8 -

7. An unknown compound gives a mass spectrum with a weak molecular ion at m/z 113 and a base peak ion at m/z 68. Its HNMR and IR spectra are shown below. The ^{13}C NMR (decoupling) signals are found at the following chemical shifts: 163, 117, 63, 25 and 14 ppm.
- Determine the structure and show how it is consistent with the observed data.
 - Propose a favorable fragmentation to explain the prominent MS peak at m/z 68.



(20 marks)

...9/-

TERJEMAHAN

Arahan:

Jawab LIMA (5) soalan.

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

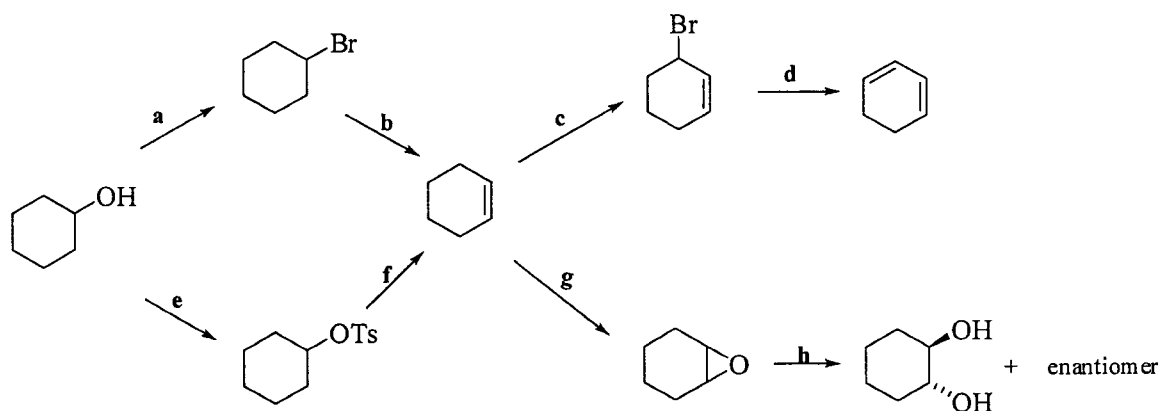
Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.

Lampiran: Jadual Spektroskopi.

...10/-

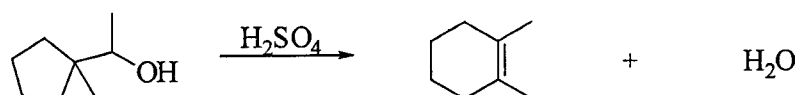
Jawab LIMA soalan.

1. (a) Kenalpasti reagen (a-h) yang diperlukan untuk melakukan setiap tindak balas.



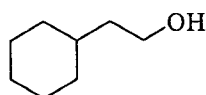
(12 markah)

- (b) Tulis suatu mekanisme terperinci, langkah demi langkah, bagi tindak balas berikut untuk menjelaskan pembentukan hasil.



(4 markah)

- (c) Tunjukkan bagaimana anda dapat mensintesis sebatian berikut bermula dengan menggunakan sikloheksanol dan sebarang alkohol yang mempunyai empat atau kurang daripada empat atom karbon. Anda boleh menggunakan sebarang pelarut dan reagen tak organik.



(4 markah)

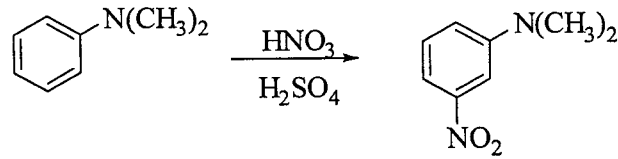
2. (a) Mengapa kumpulan COOCH_3 merupakan suatu pengaruh *meta* yang mendeaktifkan gelang benzena terhadap tindak balas penukargantian elektrofilik aromatik? Jelaskan secara terperinci dengan menggunakan struktur-struktur resonans..

(5 markah)

...11/-

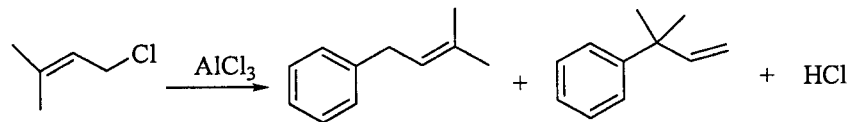
- 11 -

- (b) Jelaskan mengapa hasil *meta* terbentuk di dalam tindak balas berikut sungguh pun $-N(CH_3)_2$ ialah suatu pengarah *orto, para*.



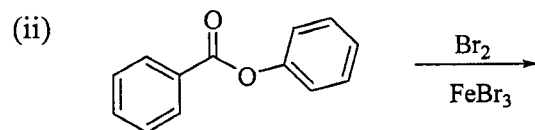
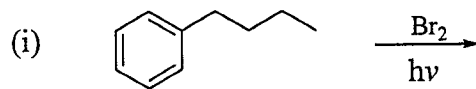
(5 markah)

- (c) Tulis suatu mekanisme, langkah demi langkah, bagi tindak balas berikut:



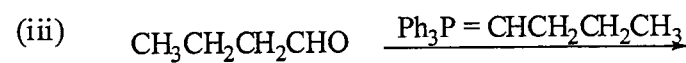
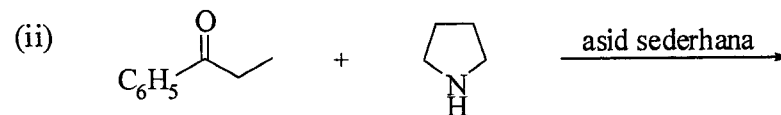
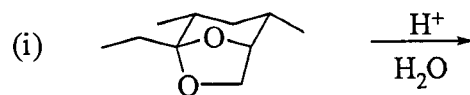
(5 markah)

- (d) Beri hasil kepada setiap tindak balas berikut:



(5 markah)

3. (a) Beri hasil kepada setiap tindak balas berikut:

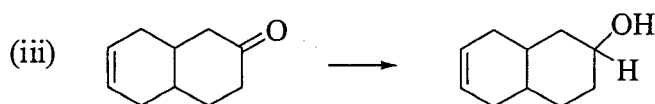
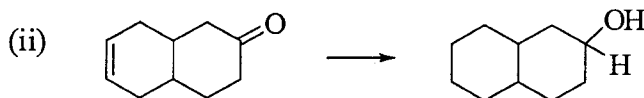
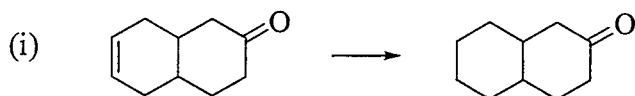


(6 markah)

...12/-

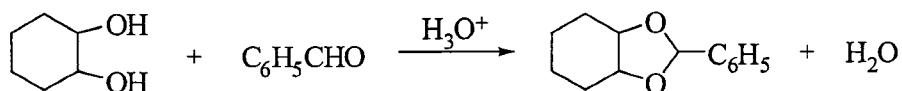
- 12 -

- (b) Tunjukkan bagaimana anda dapat mencapai setiap sintesis berikut dengan efisien dan peratusan hasil yang tinggi? Anda boleh menggunakan sebarang reagen yang diperlukan.



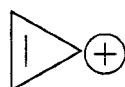
(6 markah)

- (c) Tulis suatu mekanisme, langkah demi langkah, bagi tindak balas berikut:



(8 markah)

4. (a) Gunakan peraturan poligon untuk menunjukkan kenapa kation siklopropenil (1) adalah aromatik manakala siklobutadiena (2) tidak.



(1)



(2)

(5 markah)

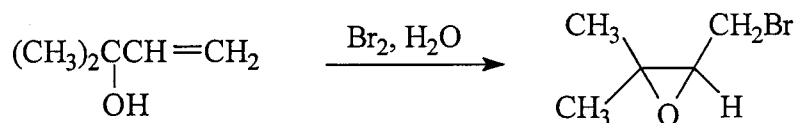
- (b) Tunjukkan bagaimana anda dapat mensintesiskan asid 3-nitro-4-bromobenzoik daripada toluena sebagai bahan pemulaan.

(5 markah)

...13/-

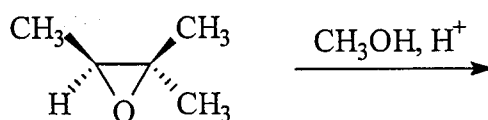
- 13 -

- (c) Cadangkan dengan terperinci mekanisme yang sesuai bagi tindak balas berikut.



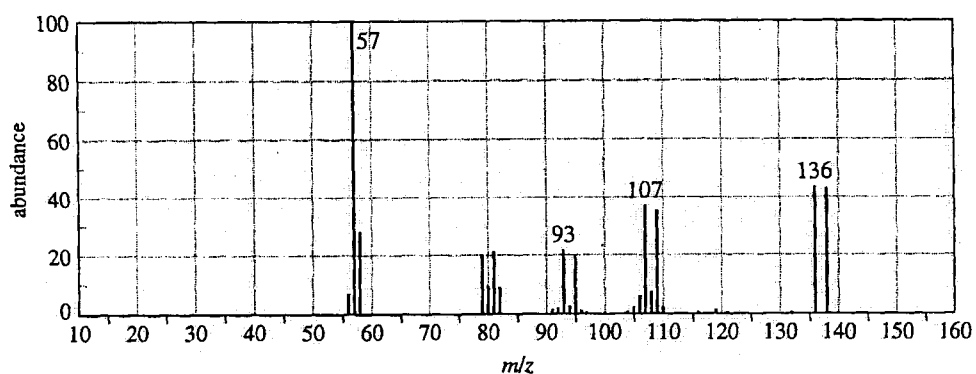
(6 markah)

- (d) Berikan hasil utama bagi tindak balas berikut.



(4 markah)

5. (a) Dengan menggunakan data spektrometri jisim;
- Ramalkan sebatian tersebut dan berikan alasan anda.
 - Cadangkan struktur bagi pecahan-pecahan pada 136, 107 dan 93. Bincangkan mengapakah puncak asas adalah pada m/z 57.

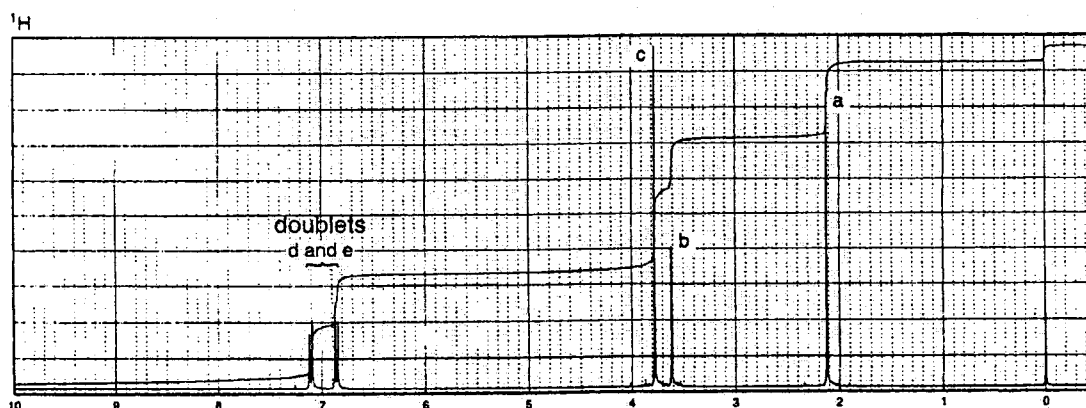
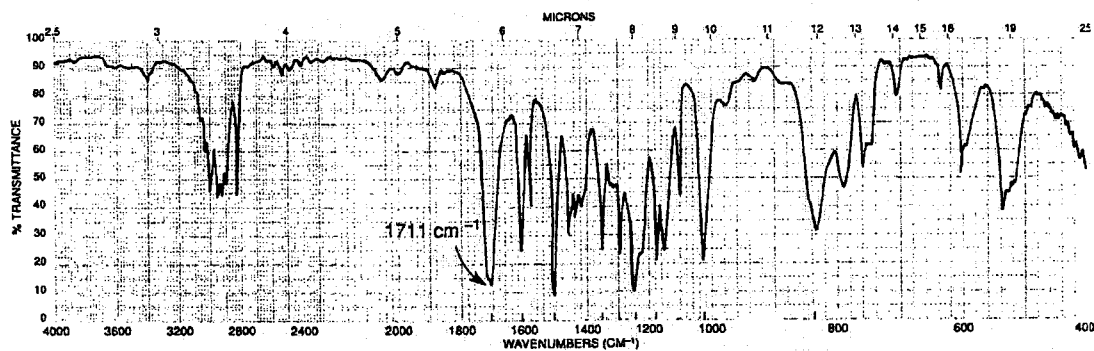


(8 markah)

...14/-

- 14 -

- (b) Sebatian "X" mempunyai formula $C_{10}H_{12}O_2$. Data spektrum IR, 1H NMR, ^{13}C NMR (penyahgandingan), DEPT-135 dan DEPT-90 diberikan. Deduksikan struktur "X" dengan menggunakan maklumat yang diberi.



^{13}C	DEPT-135	DEPT-90
29 ppm	Positif	Tiada
50 ppm	Negatif	Tiada
55 ppm	Positif	Tiada
114 ppm	Positif	Positif
126 ppm	Tiada	Tiada
130 ppm	Positif	Positif
159 ppm	Tiada	Tiada
207 ppm	Tiada	Tiada

(12 markah)

...15/-

6. (a) Tunjukkan keadah yang terbaik untuk menyediakan 4-propoksitoluena daripada sintesis eter Williamson.

(4 markah)

- (b) Lukis tenaga molekul orbital π yang terendah dan tertinggi bagi sebatian 1,3-butadiena.

(4 markah)

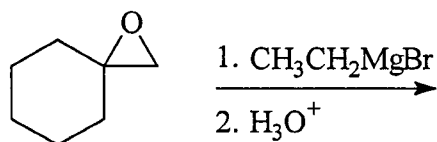
- (c) Bagaimana spektroskopi IR dapat membezakan pasangan sebatian berikut.



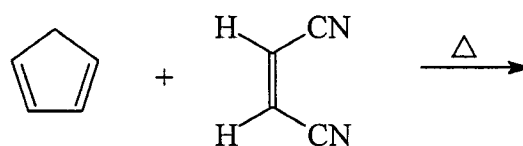
(6 markah)

- (d) Berikan hasil utama bagi setiap tindak balas berikut.

(i)



(ii)



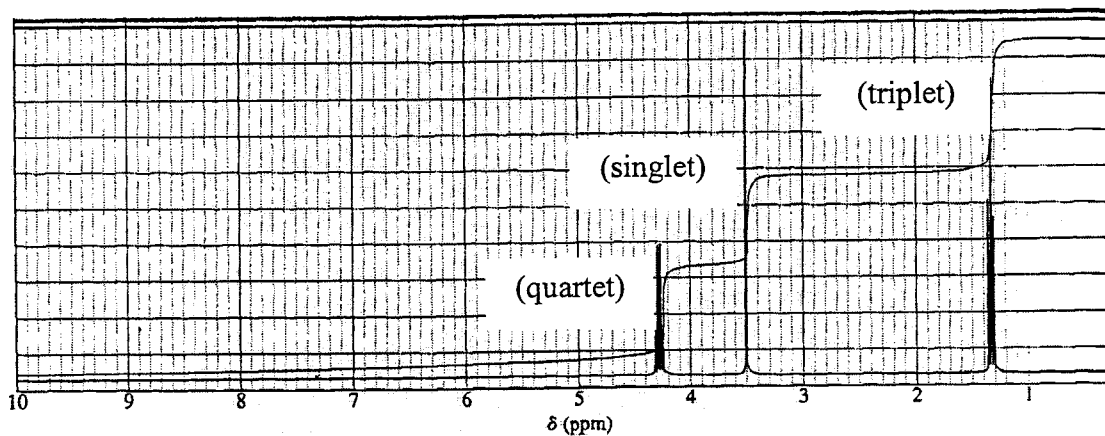
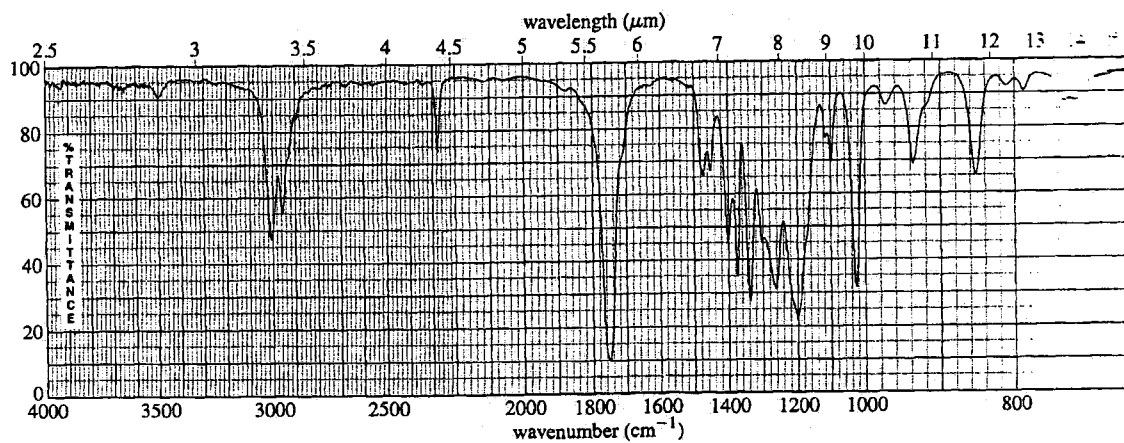
(6 markah)

...16/-

- 16 -

7. Sebatian yang tidak diketahui memberikan spektrum jisim dengan ion molekul lemah pada m/z 113 dan puncak utama pada m/z 68. Spektrum HNMR dan IR bagi sebatian ini ditunjukkan. Isyarat ^{13}C NMR (penyahgandingan) diperhatikan pada anjakan kimia berikut: 163, 117, 63, 25 dan 14 ppm.

- (i) Tentukan struktur sebatian ini dan tunjukkan bagaimana ketepatan struktur ini dengan pemerhatian daripada data yang diberikan.
- (ii) Cadangkan pemecahan ion utama yang akan berlaku untuk menerangkan puncak MS yang nyata pada m/z 68.



(20 markah)

...17/-

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

-oooOooo-