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UNIVERSITI SAINS MALAYSIA

Peperiksaan Kursus Semasa Cuti Panjang  
Sidang Akademik 2007/2008

June 2008

**KOT 222 – Organic Chemistry II**  
**[Kimia Organik II]**

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

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

**Instructions:**

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

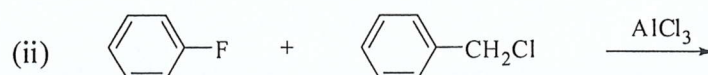
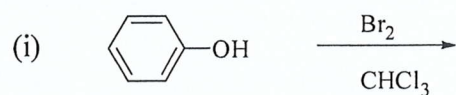
You may answer the question either in Bahasa Malaysia or in English.

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

**Appendix:** Spectroscopy Table.

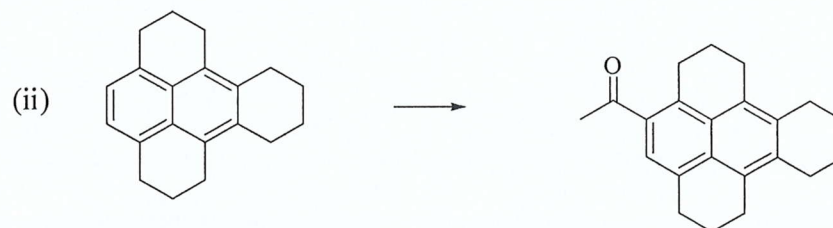
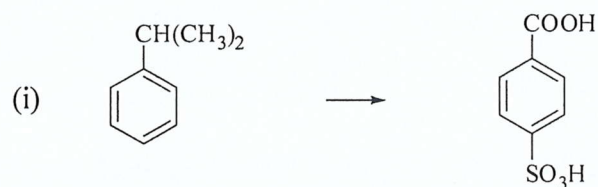
Answer any FIVE questions.

1. (a) Predict the major product of each of the following reactions. Only monosubstitution is involved in each case.



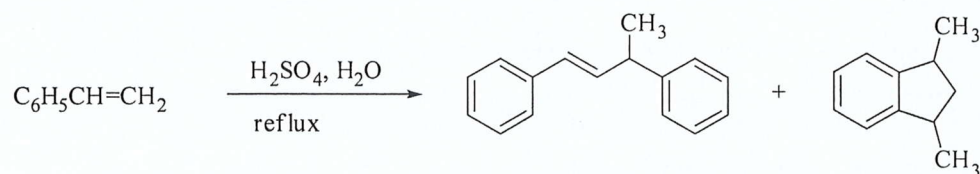
(8 marks)

- (b) Suggest a sequence of reactions for carrying out each of the following synthetic transformations.



(8 marks)

- (c) When styrene is refluxed with aqueous sulphuric acid, two major products are formed. Suggest a reasonable mechanism for the formation of each of these products.

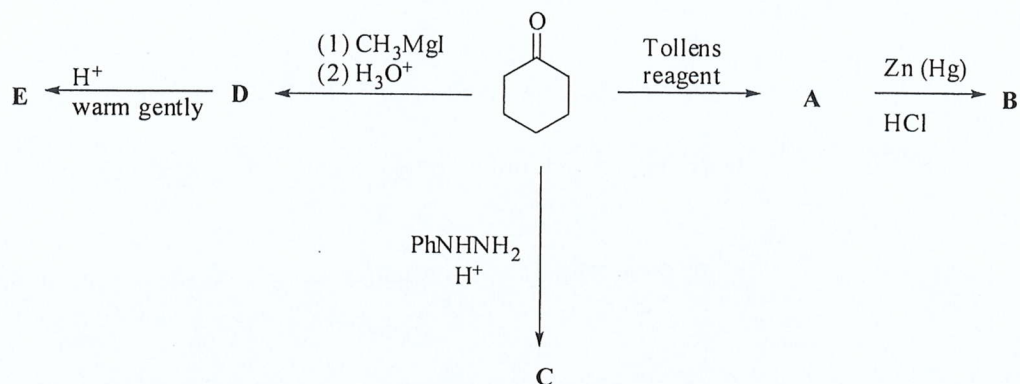


(4 marks)

...3/-

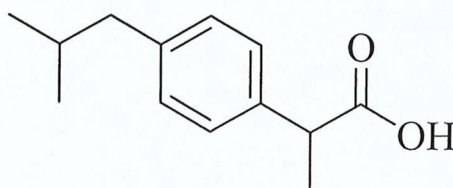
- 5 -

4. (a) Give structures for compounds A through E below.



(10 marks)

- (b) Ibuprofen is an anti-inflammatory drug which comes from the real name isobutyl-propionic phenolic acid whose structure is shown below. Label all the hydrogen atoms in the structures and write their chemical shifts as accurate as possible. Draw the  $^1\text{H}$ -nmr spectrum of this compound showing the actual splitting patterns.



ibuprofen

(10 marks)

5. Answer the following questions in one or two sentences only.
- (a) What type of electronic transition gives rise to the R-band in a UV-vis spectrum?
  - (b) Name one out-of-plane bending vibration in IR spectroscopy.
  - (c) Why is the O-H stretching band for a carboxylic acid very broad in the IR spectrum?
  - (d) Why is the absorption band frequency for a C=C stretch in the benzene ring lower than that in an alkene?
  - (e) What is the fundamental difference of mass-spectrometry from the other types of spectroscopies?
  - (f) How would you determine the presence of an OH peak in a  $^1\text{H}$ -nmr spectrum?
  - (g) What is the correct name for "benzyl cation" ( $\text{C}_7\text{H}_7^+$ ) formed during mass-spectral acquisition of toluene?
  - (h) What is COSY spectrum?
  - (i) What is LUMO?
  - (j) What does GCMS stand for?
- (20 marks)
6. (a) A  $\text{C}_9\text{H}_{12}\text{O}$  compound has strong infrared absorption at 3300 to 3400  $\text{cm}^{-1}$ . The  $^{13}\text{C}$ -nmr spectrum of this compound has six discrete signals. Its  $^1\text{H}$ -nmr spectrum has three sets of lines: singlets at  $\delta$ 1.1 (6H), 1.9 (1H) and 7.3 (5H) ppm. Suggest a structure for this compound.

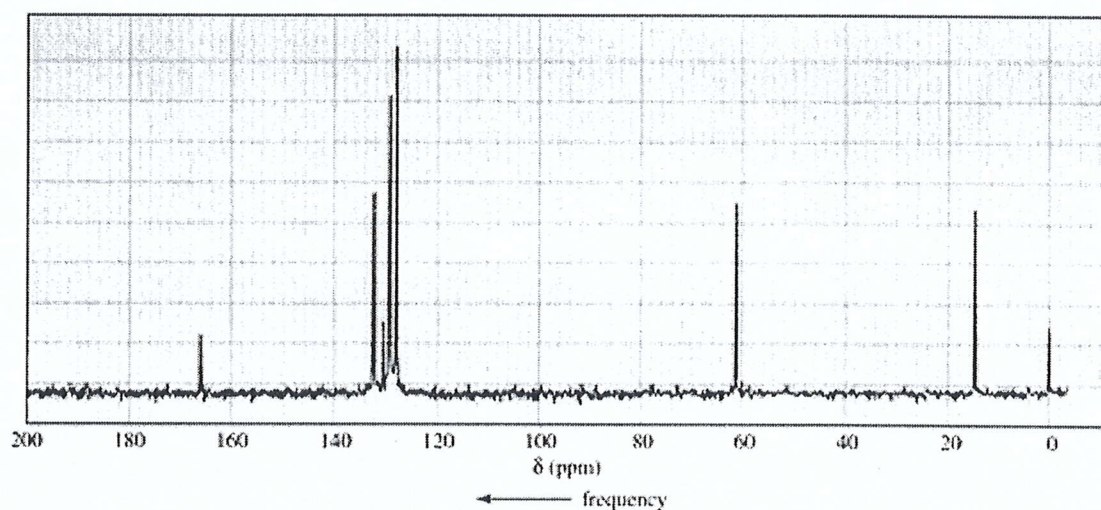
(5 marks)



- 7 -

- (b) The  $^{13}\text{C}$ -nmr spectrum below is for either ethyl benzoate or phenyl propanoate. Draw the structures for both compounds and identify which one the spectrum belongs to.

(5 marks)



- (c) A compound used as a moth repellent has three molecular ion peaks at  $m/z=146$  (100%), 148 (65%) and 150 (10%) amu in its mass spectrum. A pair of smaller peaks are seen at  $m/z=111$  (34%) and 113 (11%). The infrared spectrum shows sharp absorption just above  $3000\text{ cm}^{-1}$  region, and also at  $1480\text{ cm}^{-1}$ . The  $^1\text{H}$ -nmr shows a single sharp signal at  $\delta = 7.2$  ppm, and the  $^{13}\text{C}$ -nmr has two signals ( $\delta = 133$  and  $130$  ppm). Suggest a structure for this compound.

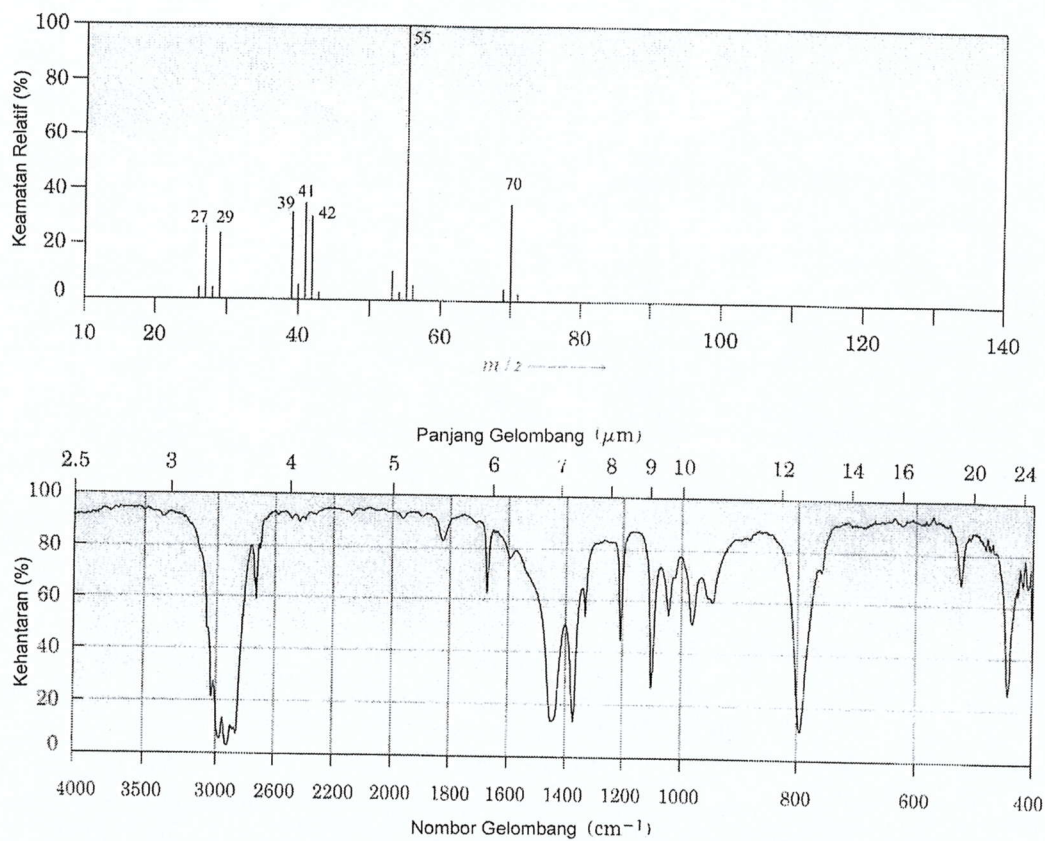
(5 marks)

...8/-

- 8 -

- (d) The mass-spectrum and IR spectrum below are for a hydrocarbon. Determine the structure of this hydrocarbon.

(5 marks)

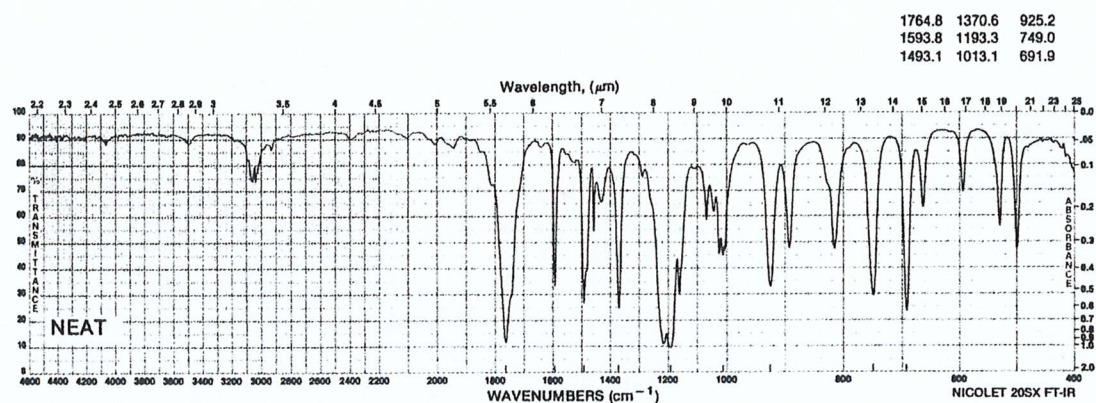


...9/-

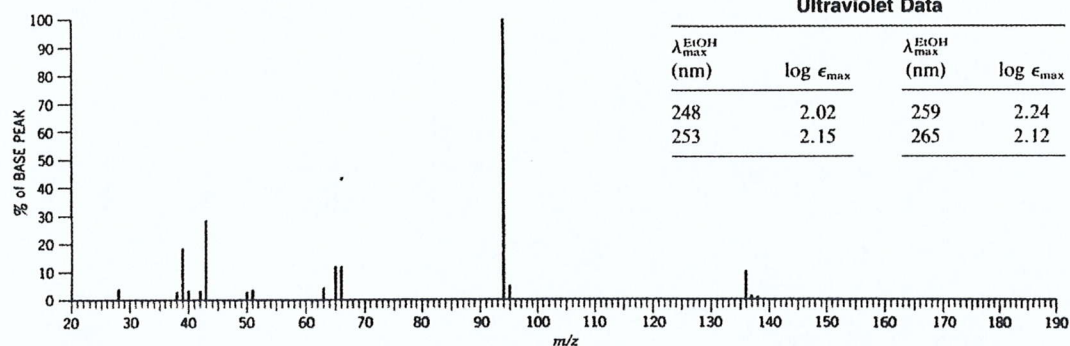
7. Determine the structure of compound X based on the following spectral data. Show clearly how the structure is derived.

(20 marks)

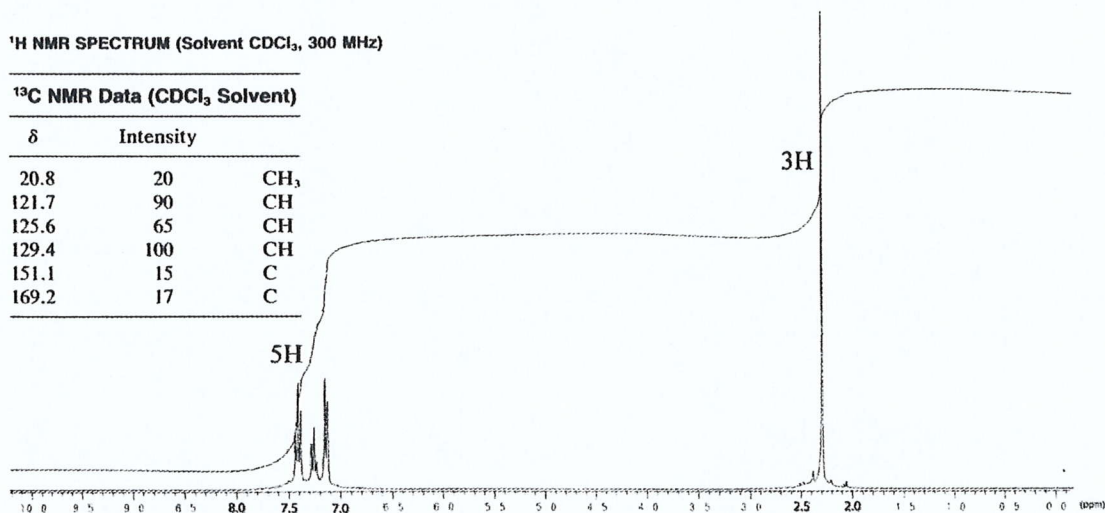
## INFRARED SPECTRUM



## MASS SPECTRAL DATA (Relative Intensities)

 $^1\text{H}$  NMR SPECTRUM (Solvent  $\text{CDCl}_3$ , 300 MHz) $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  Solvent)

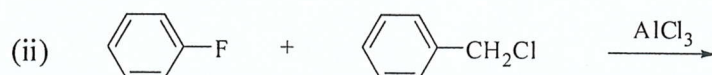
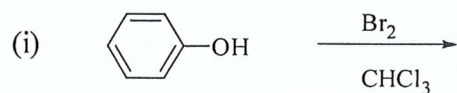
$\delta$	Intensity	
20.8	20	$\text{CH}_3$
121.7	90	$\text{CH}$
125.6	65	$\text{CH}$
129.4	100	$\text{CH}$
151.1	15	$\text{C}$
169.2	17	$\text{C}$



...10/-

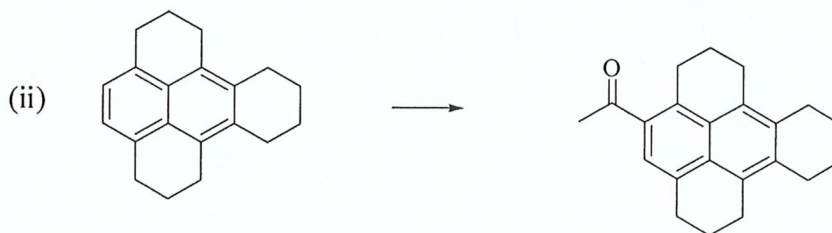
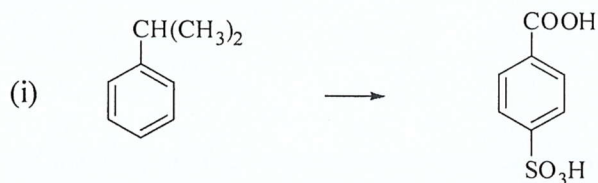
Jawab LIMA soalan.

- 1.. (a) Ramalkan hasil utama daripada setiap tindak balas berikut. Hanya penukargantian mono sahaja yang terlibat di dalam setiap kes.



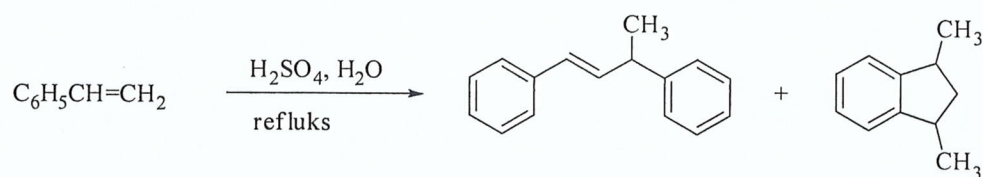
(8 markah)

- (b) Cadangkan suatu urutan tindak balas untuk melakukan setiap transformasi sintesis yang berikut:



(8 markah)

- (c) Apabila stirena direflukskan dengan asid sulfurik akueus, dua hasil utama terbentuk. Cadangkan suatu mekanisme yang munasabah bagi pembentukan setiap hasil tersebut.

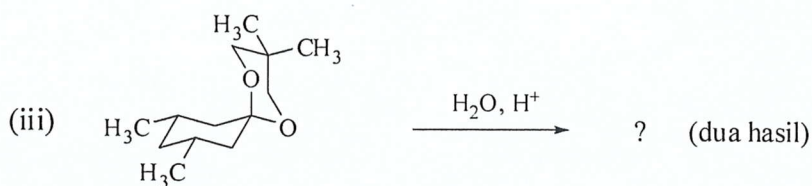
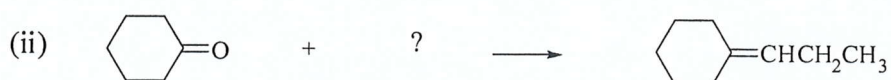


(4 markah)

...12/-

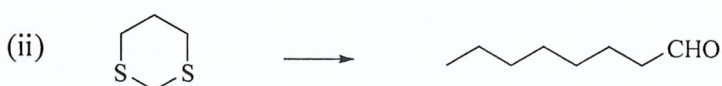
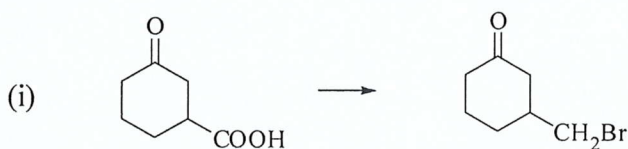


2. (a) Bagi setiap tindak balas berikut, tulis struktur bahan tindak balas, reagen atau hasil di tempat yang bertanda (?).



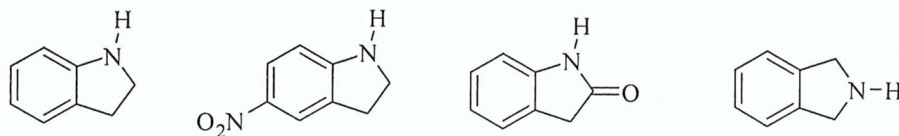
(8 markah)

- (b) Cadangkan suatu skema tindak balas untuk melakukan setiap transformasi berikut dengan menggunakan bahan pemulaan yang ditunjukkan.



(12 markah)

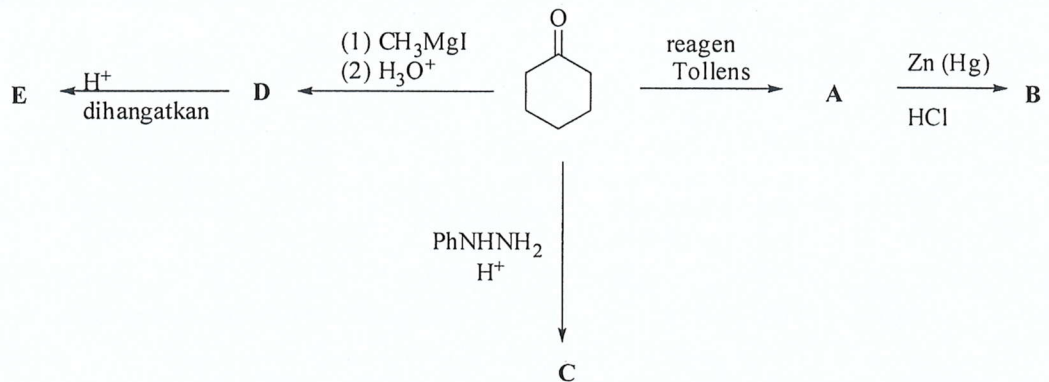
3. (a) Kenalpasti bes yang paling kuat dan bes yang paling lemah di antara yang berikut:



(3 markah)

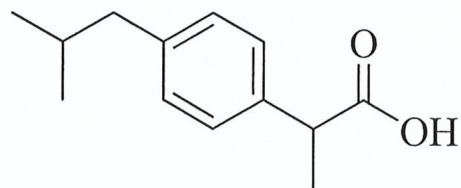
...13/-

4. (a). Beri struktur kepada sebatian A hingga E di bawah:



(10 markah)

- (b) Ibuprofen adalah suatu ubat “anti-inflammatory” yang terbit dari nama asal asid isobutyl-propionik fenolik di mana strukturnya ditunjukkan di bawah. Labelkan semua atom hydrogen di dalam struktur tersebut dan tuliskan anjakan kimia masing-masing setepat yang mungkin. Lukiskan spektrum  $^1\text{H}$ -nmr bagi sebatian ini dengan menunjukkan corak pecahan signal sebenar.



ibuprofen

(10 markah)

5. Jawab soalan berikut dalam satu atau dua ayat sahaja.
- (a) Apakah jenis peralihan elektron yang memberikan jalur-R di dalam spektrum UV-nampak?
  - (b) Namakan salah satu getaran pembengkokan luar satah di dalam spektroskopi IR.
  - (c) Mengapakah jalur regangan O-H untuk suatu asid karboksilik sangat lebar di dalam spektrum IR?
  - (d) Mengapakah frekuensi jalur penyerapan bagi suatu regangan C=C di dalam gelang benzena lebih rendah dari yang terbit dari suatu alkena?
  - (e) Apakah perbezaan asas spektrometri jisim dari jenis spektroskopi lain?
  - (f) Bagaimana anda boleh menentukan kehadiran suatu puncak OH di dalam spektrum  $^1\text{H-nmr}$ ?
  - (g) Apakah nama sebenar bagi “kation benzil” ( $\text{C}_7\text{H}_7^+$ ) yang terbentuk semasa pengambilan spektrum jisim bagi toluena?
  - (h) Apakah spektrum COSY?
  - (i) Apakah LUMO?
  - (j) Apakah nama bagi singkatan GCMS?
6. (a) Suatu sebatian  $\text{C}_9\text{H}_{12}\text{O}$  memberikan penyerapan inframerah yang kuat pada 3300 to 3400  $\text{cm}^{-1}$ . Spektrum  $^{13}\text{C-nmr}$  sebatian ini mempunyai enam signal jelas. Spektrum  $^1\text{H-nmr}$  sebatian ini pula mengandungi tiga set puncak ia itu, singlet pada  $\delta 1.1$  (6H), 1.9 (1H) dan 7.3 (5H) ppm. Cadangkan suatu struktur bagi sebagian ini.

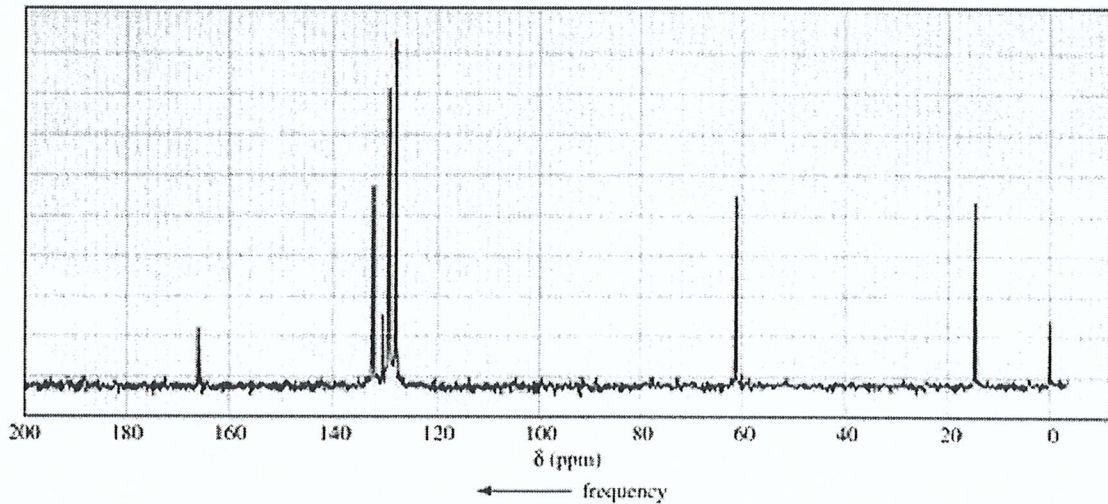
(20 markah)

(5 markah)

- 16 -

- (b) Spektrum  $^{13}\text{C}$ -nmr di bawah adalah untuk sama ada etil benzoat atau fenil propanoat. Lukis kedua-dua struktur sebatian ini dan kenal pasti spektrum sebatian manakah ini.

(5 markah)



- (c) Suatu sebatian yang digunakan sebagai penghalang rama-rama mempunyai tiga puncak ion molekul pada  $m/z=146$  (100%), 148 (65%) dan 150 (10%) amu di dalam spektrum jisimnya. Sepasang puncak kecil kelihatan pada  $m/z=111$  (34%) dan 113 (11%). Spektrum inframerah sebatian ini menunjukkan penyerapan tajam pada daerah sedikit di atas  $3000\text{ cm}^{-1}$  dan juga pada  $1480\text{ cm}^{-1}$ . Spektrum  $^1\text{H}$ -nmr pula menunjukkan suatu signal tunggal yang tajam pada  $\delta = 7.2\text{ ppm}$ , dan spektrum  $^{13}\text{C}$ -nmr mempunyai dua signal ( $\delta = 133$  dan  $130\text{ ppm}$ ). Cadangkan suatu struktur bagi sebatian ini.

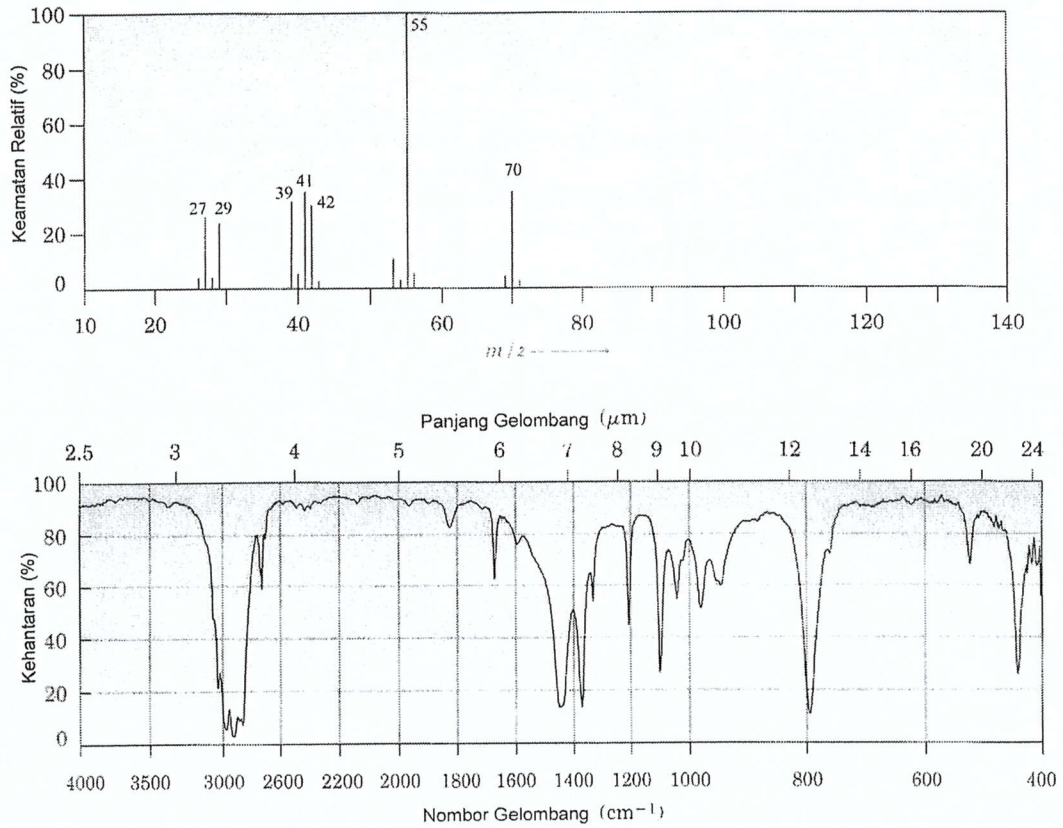
(5 markah)



- 17 -

- (d) Spektrum jisim dan spektrum IR di bawah adalah untuk suatu hidrokarbon. Tentukan struktur hidrokarbon ini.

(5 markah)

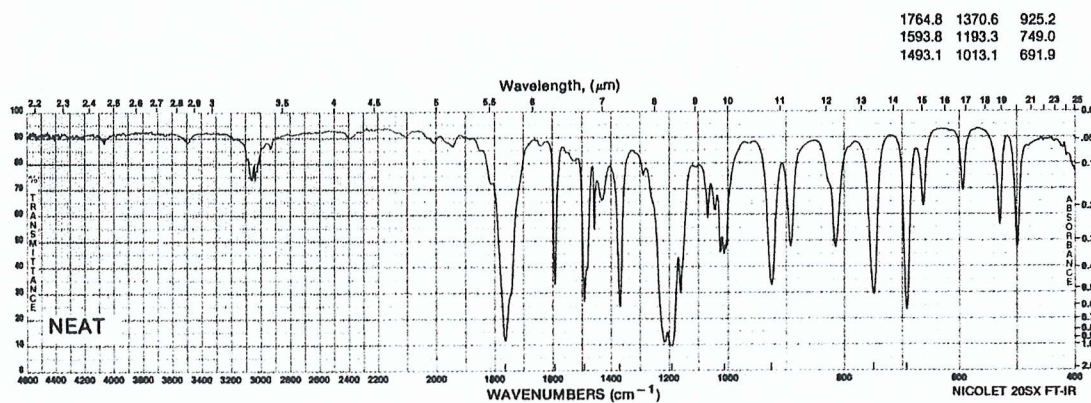


...18/-

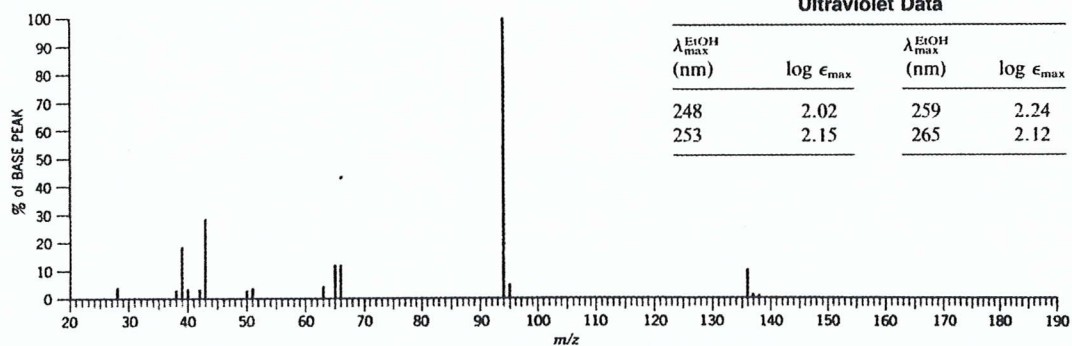
7. Tentukan struktur sebatian X berdasarkan data spektrum berikut. Tunjukkan dengan jelas bagaimana struktur ini ditentukan.

(20 markah)

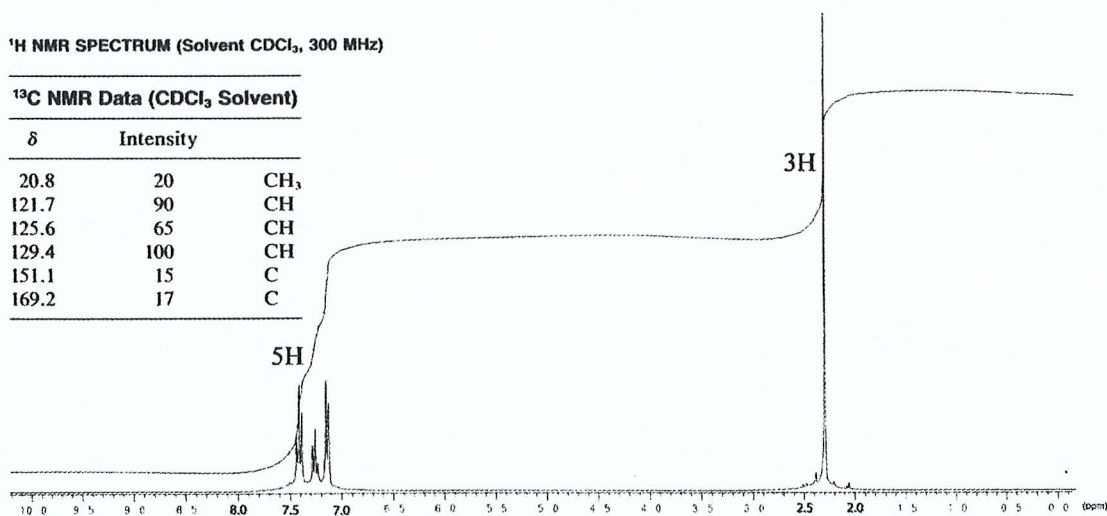
## INFRARED SPECTRUM



## MASS SPECTRAL DATA (Relative Intensities)

 $^1\text{H}$  NMR SPECTRUM (Solvent  $\text{CDCl}_3$ , 300 MHz) $^{13}\text{C}$  NMR Data ( $\text{CDCl}_3$  Solvent)

$\delta$	Intensity	
20.8	20	$\text{CH}_3$
121.7	90	CH
125.6	65	CH
129.4	100	CH
151.1	15	C
169.2	17	C



Spectroscopy Tables

<u><sup>1</sup>H NMR</u>		<u>Infrared Absorption</u>	<u><sup>13</sup>C NMR</u>
	$\delta$ (ppm)	$\text{cm}^{-1}$	$\delta$ (ppm)
RCH <sub>3</sub>	0.9	= C - H	C - I
R <sub>2</sub> CH <sub>2</sub>	1.3	= C - H	C - Br
R <sub>3</sub> CH	1.5	C = C	C - Cl
C=C-H	4.6-5.9	$\equiv$ C - H	- CH <sub>3</sub>
C $\equiv$ C-H	2.0-3.0	$\equiv$ C - H	- CH <sub>2</sub> -
Ar-H	6.0-8.5	C $\equiv$ C	- CH -
Ar - C - H	2.2 -3.0	Ar - H	$\equiv$ C
C=C-CH <sub>3</sub>	1.7	Ar - H	= C
H - C - F	4.0-4.5	C = C	C - O
H-C-Cl	3.0 - 4.0	O - H	C = O
H - C - Br	2.5-4.0	O - H	C (Ar)
H - C - I	2.0-4.0	3600(broad)	C - N
H-C-OH	3.4 -4.0	C - O	C = N
H - C - OR	3.3-4.0	C = O	
RCOO - C - H	3.7-4.1	O - H (acid)	<u>Atomic weight</u>
H - C - COOR	2.0	(broad)	H = 1.0
-2.2		C - O	C = 12.0
H - C - COOH	2.0	C = O	N = 14.0
-2.6		N - H	O = 16.0
H-C-C=O	2.0-2.7	C - N	F = 19.0
R - CHO	9.0-10.0	- NO <sub>2</sub>	Cl = 35.45
R-OH	1.0-5.5		Br = 79.9
Ar-OH	4.0-12.0		I = 126.9
C=C-OH	15-17		Si = 28.0
RCOOH	10.5 -		P = 31.0
12.0			S = 32.0
RNH <sub>2</sub>	1.0 - 5.0		