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UNIVERSITI SAINS MALAYSIA

First Semester Examination  
2010/2011 Academic Session

November 2010

**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 THIRTY 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.

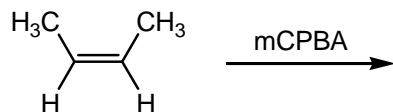
If a candidate answers more than five questions, only the answers to the first five questions in the answer sheet will be graded.

**Appendix:** Spectroscopy Tables.

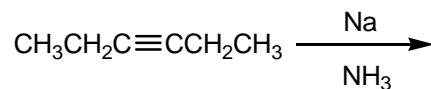
-2-

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

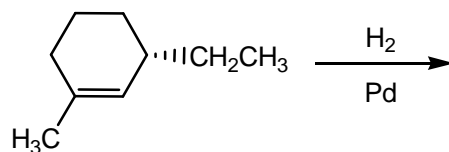
(i)



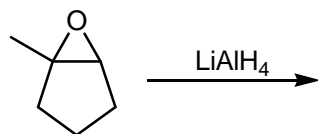
(ii)



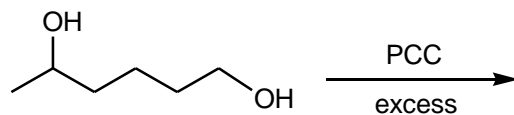
(iii)



(iv)



(v)

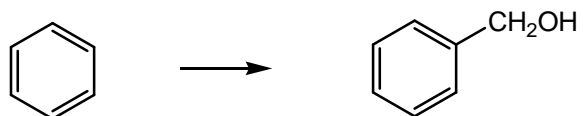


(10 marks)

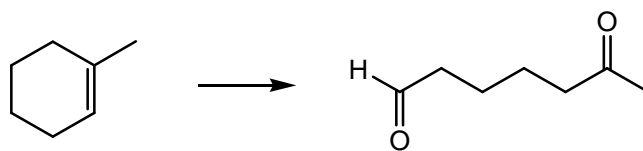
-3-

(b) Show how each of the following compounds could be prepared using the indicated starting material. No mechanism is required.

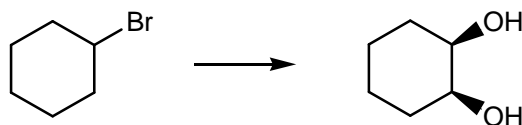
(i)



(ii)



(iii)

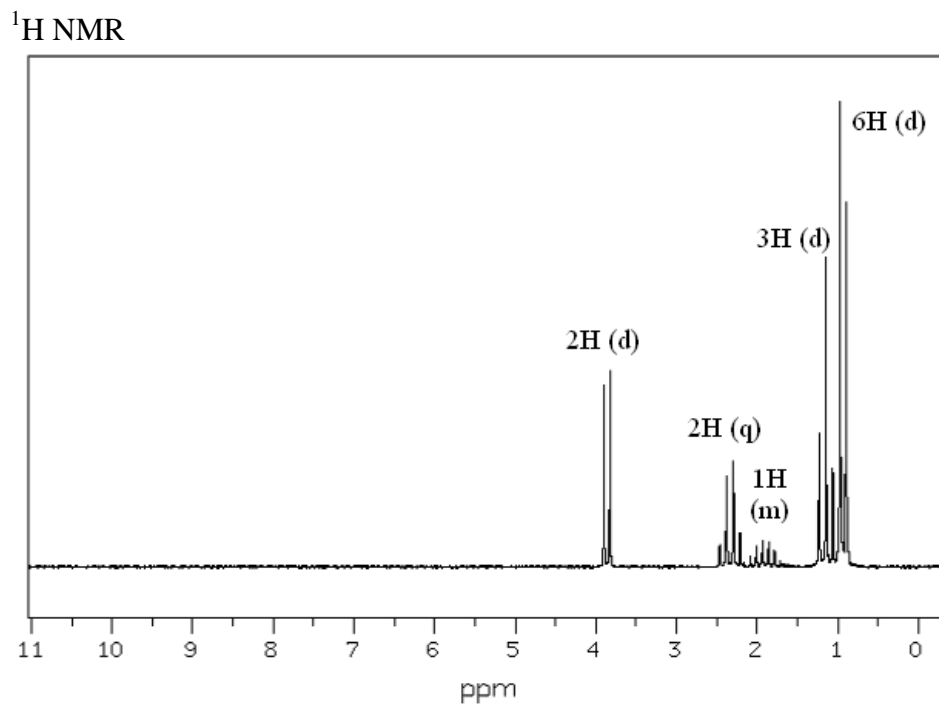
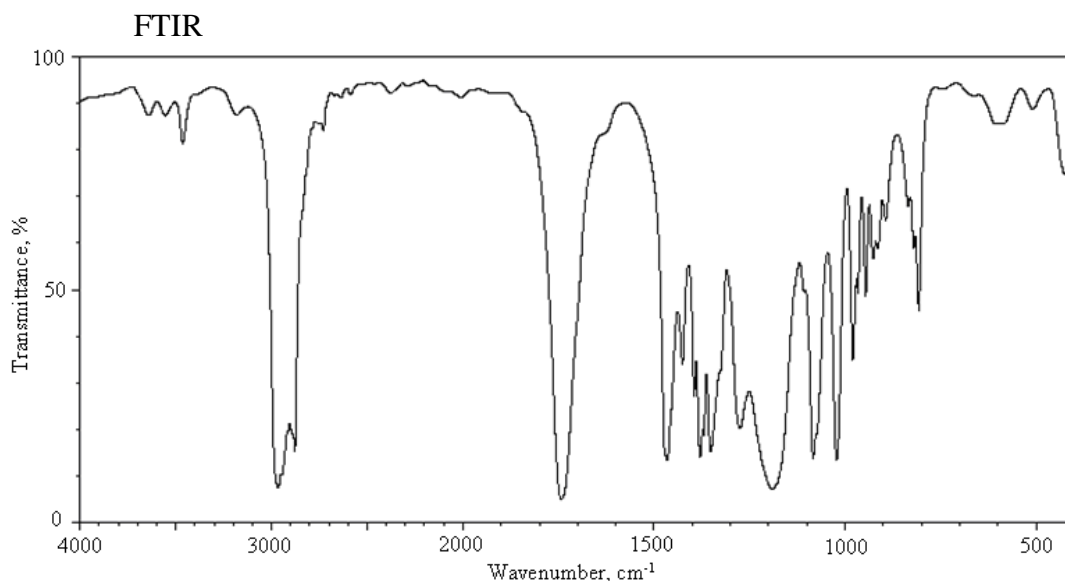


(10 marks)

-4-

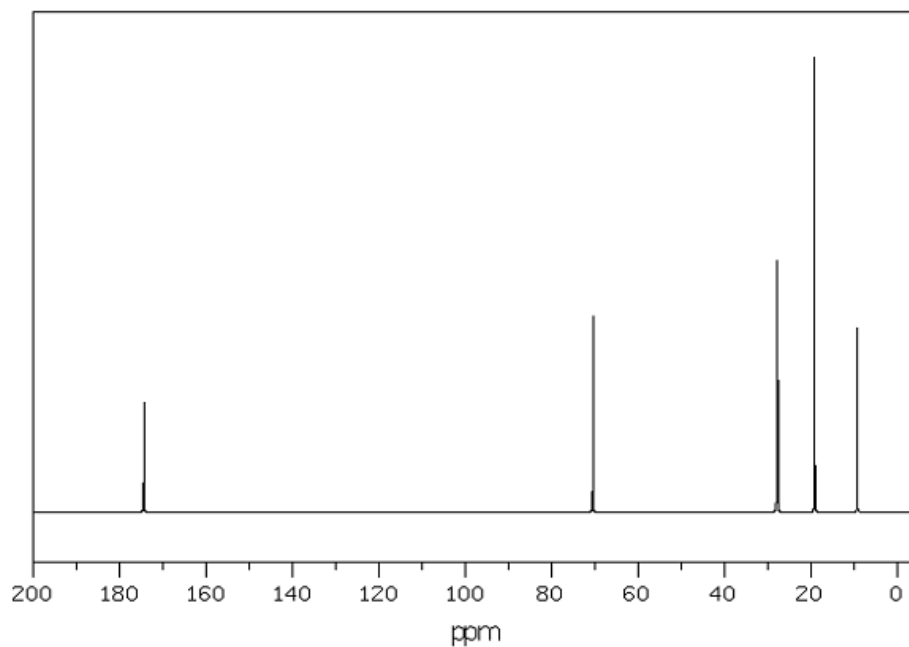
2. (a) Compound **A** has a molecular formula of  $C_7H_{14}O_2$ . The spectral information (FTIR,  $^1H$  NMR and  $^{13}C$  NMR) are provided below. Give the structure for compound **A** and the spectral interpretation that led to your answer.

(15 marks)



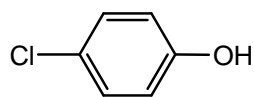
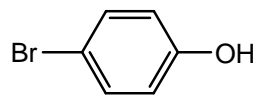
...5/-

-5-

 $^{13}\text{C}$  NMR

- (b) For the pair of compounds below, **A** and **B**, choose the most appropriate spectroscopic technique (MS, FTIR,  $^1\text{H}$  NMR or  $^{13}\text{C}$  NMR) that will allow you to distinguish between the two compounds. Precisely describe the difference that you expect to see in the spectra of the two compounds.

[ $^{79}\text{Br} = 78.92$ ,  $^{81}\text{Br} = 80.92$ ,  $^{35}\text{Cl} = 34.97$ ,  $^{37}\text{Cl} = 36.96$ ]

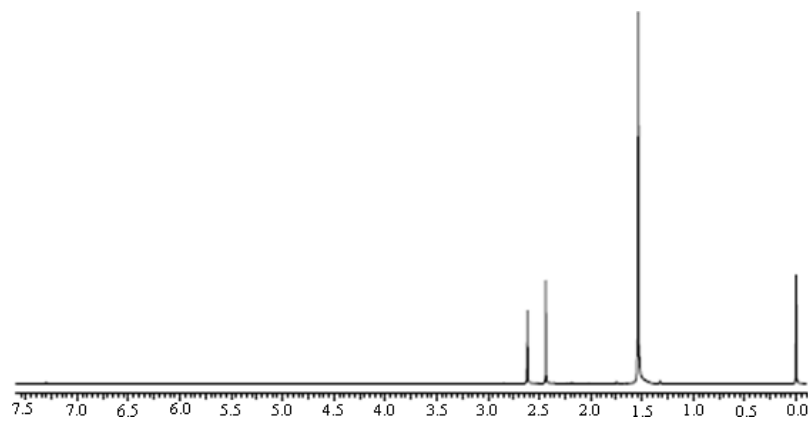
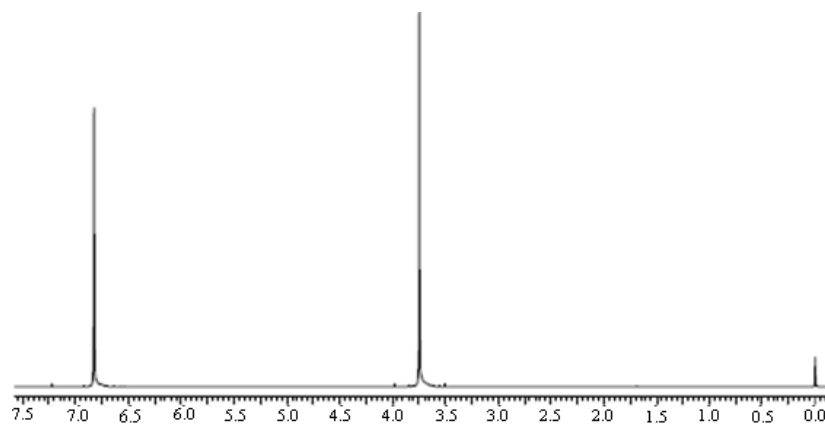
**A****B**

(5 marks)

...6/-

-6-

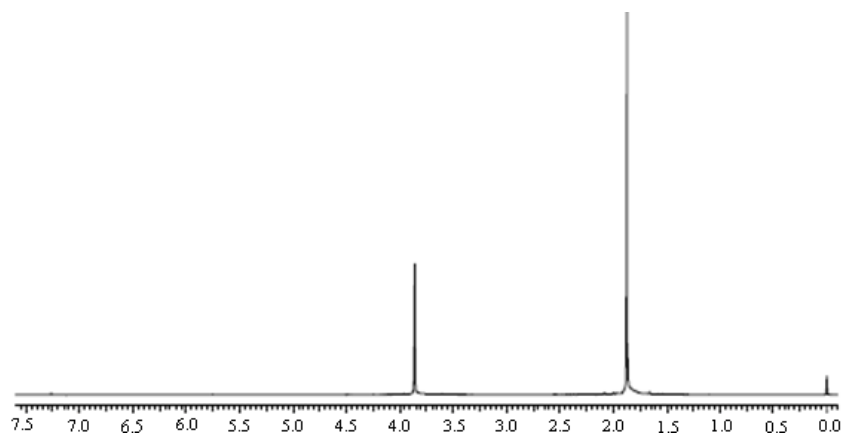
3. (a) Match each of the following spectra, **A-D**, to one of the compounds listed below. Explain your choice. (12 marks)

**1****2****3****4****5****6****7****A****B**

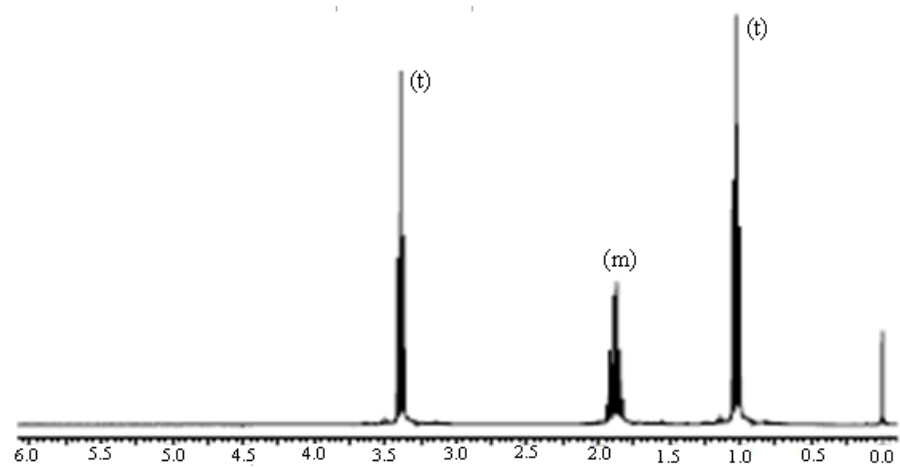
...7/-

-7-

C



D

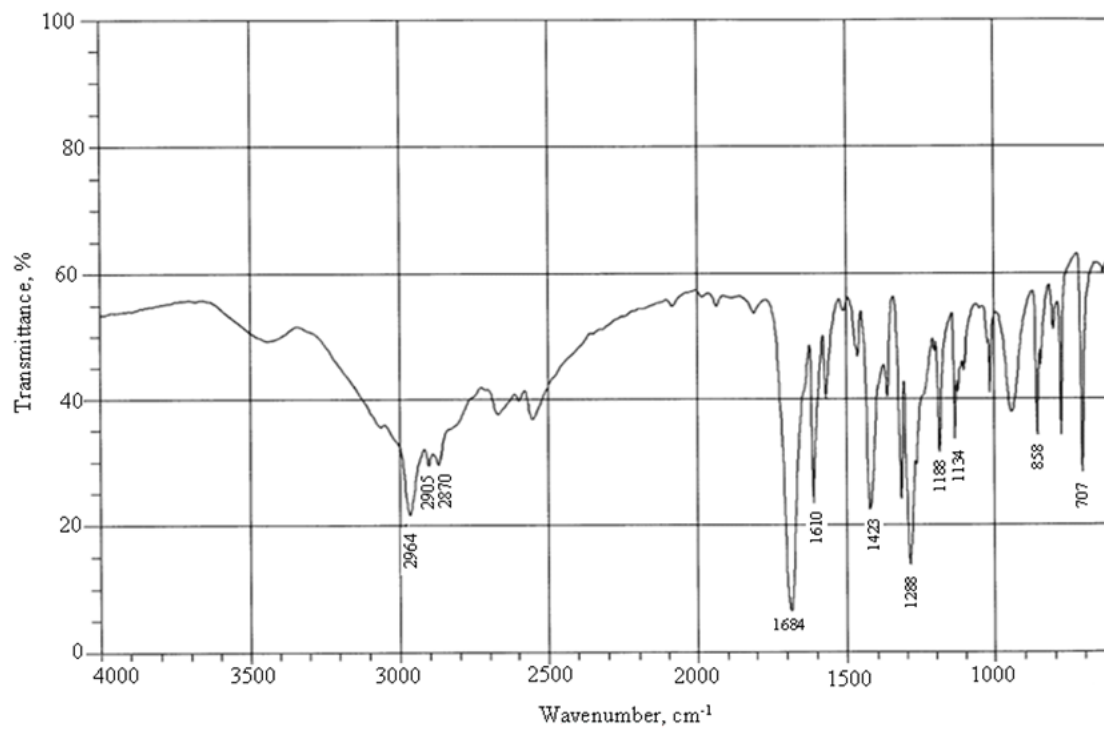
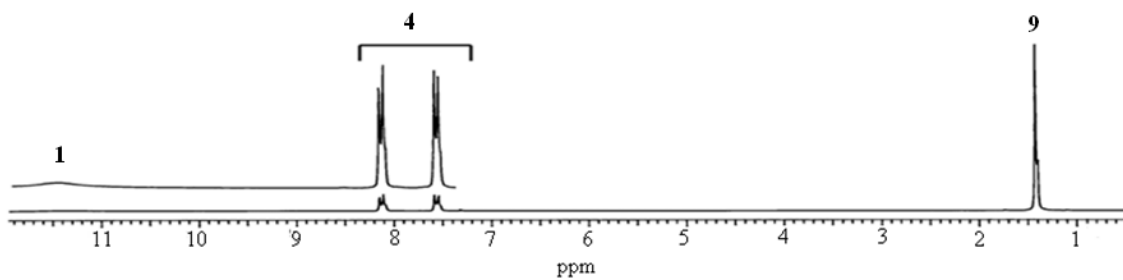


-8-

- (b) Suggest a structure for  $C_{11}H_{14}O_2$ , which is consistent with the FTIR and  $^1H$  NMR spectra shown below.

(8 marks)

FTIR

 $^1H$  NMR

...9/-



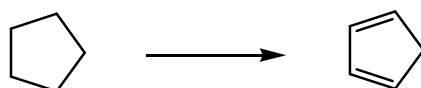
-9-

4. (a) When 2-methyl-1,3-butadiene undergoes 1,4 addition of hydrogen chloride, the major product that is formed is 1-chloro-3-methyl-2-butene. Little or no 1-chloro-2-methyl-2-butene is formed. Explain this fact by writing the mechanism of the reaction.

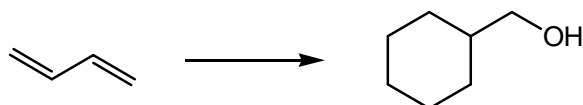
(4 marks)

- (b) Show the synthetic steps for each of the following transformations. No mechanism is required.

(i)

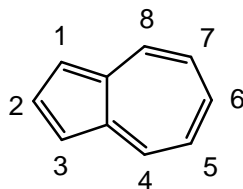


(ii)



(8 marks)

- (c) The structure of azulene is as shown below:

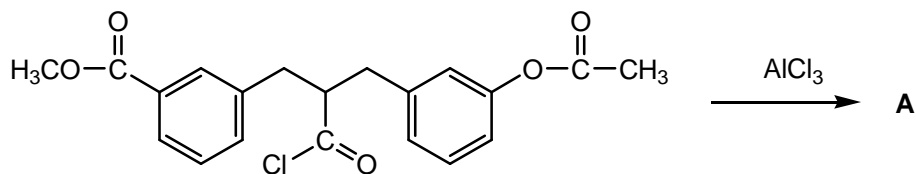


- (i) Explain why azulene is an aromatic compound.  
 (ii) Explain why azulene is readily attacked by electrophiles at position 1 compared to position 2.

(8 marks)

-10-

5. (a) The following reaction is an intramolecular Friedel-Crafts acylation. Predict the product, **A**, and write the mechanism of the reaction.

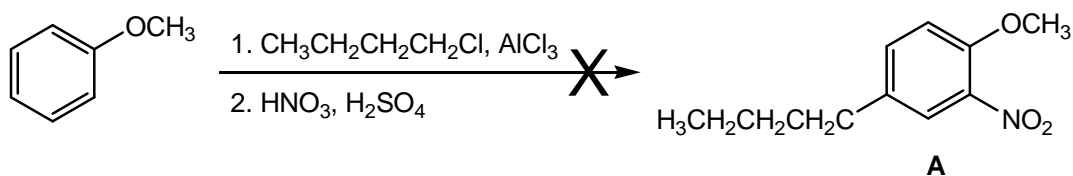


(6 marks)

- (b) Explain in detail using resonance structures why a phenyl group ( $C_6H_5-$ ) is an *ortho*, *para* director that activates a benzene ring towards electrophilic attack.

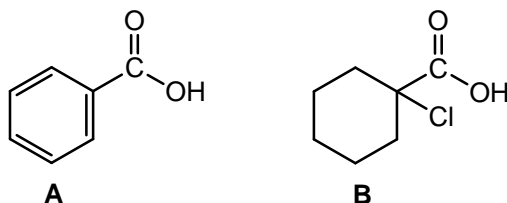
(4 marks)

- (c) Explain why the following reaction will not form the given product **A**. Suggest a synthesis of **A** starting from phenol ( $C_6H_5OH$ ).



(6 marks)

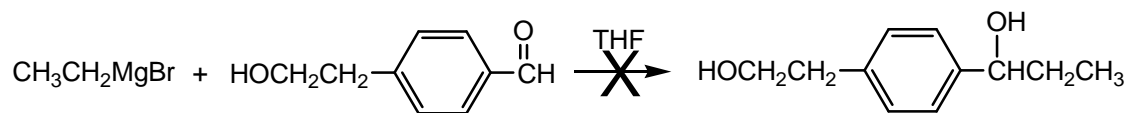
- (d) Compare the acidity of the two compounds below. Justify your answer.



(4 marks)

-11-

6. (a) An attempt to add  $\text{CH}_3\text{CH}_2\text{MgBr}$  to the following aldehyde fail. Why? What can you do to get the desired product from the reaction? Show the synthetic steps.



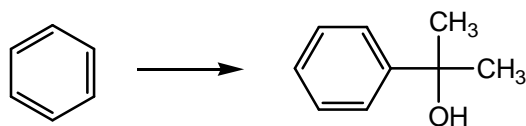
(8 marks)

- (b) Explain why aldehydes are more reactive towards nucleophilic addition reactions than ketones.

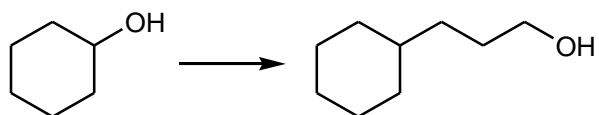
(4 marks)

- (c) Show the synthetic steps which could be used for the following transformations. No mechanism is required.

(i)



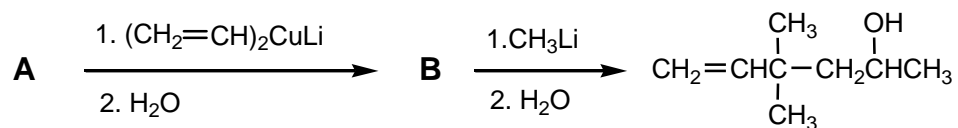
(ii)



(8 marks)

-12-

7. (a) Identify compounds **A** and **B**.



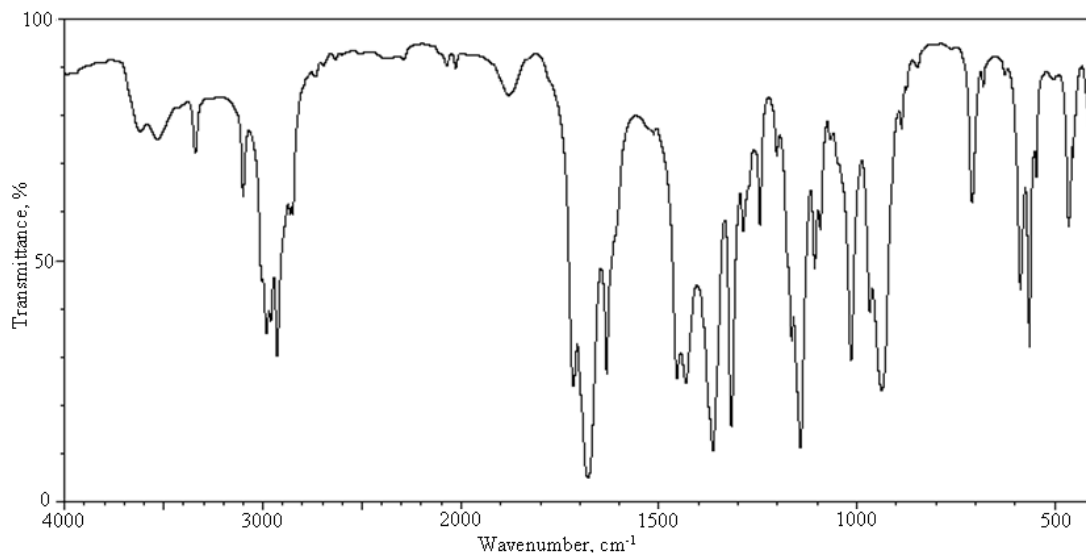
(5 marks)

- (b) Match each of the following FTIR spectra, **A-E**, to one of the compounds listed below. Give your reasoning for each match.

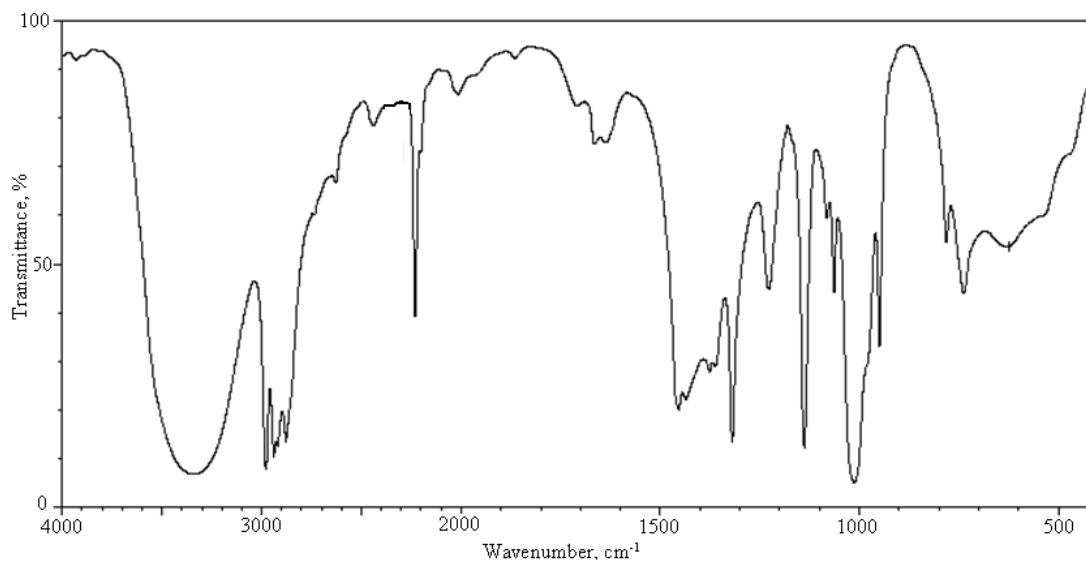
(15 marks)

**1****2****3****4****5****6****7****8**

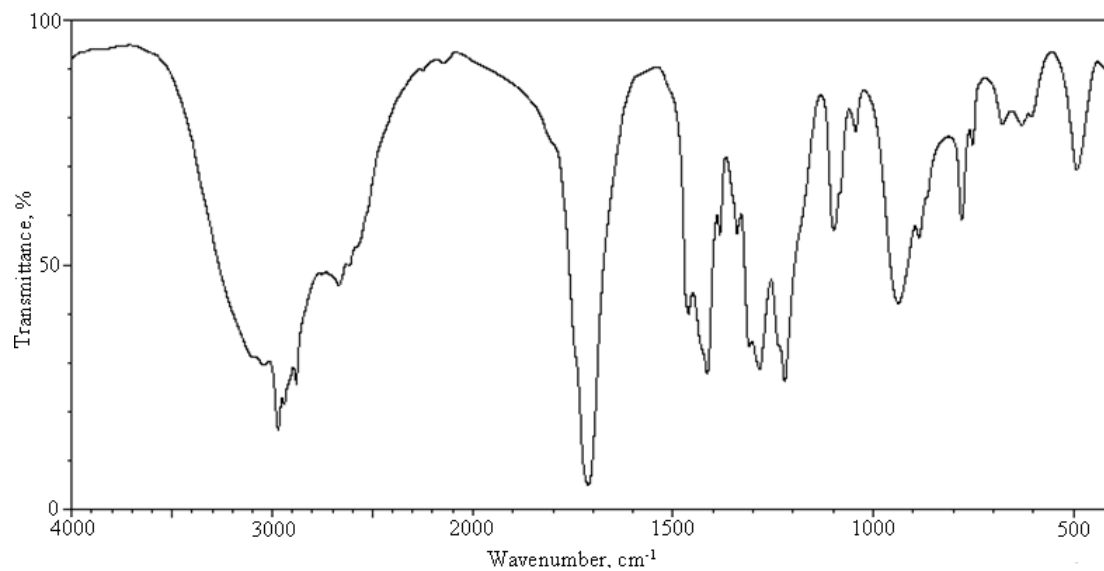
**Spectrum A**



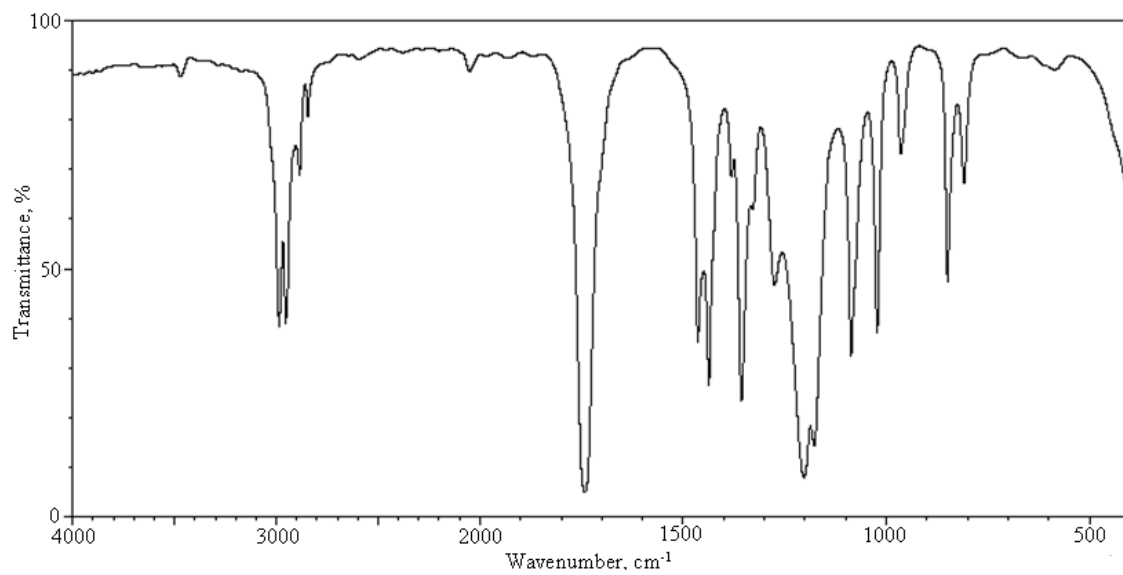
**Spectrum B**



**Spectrum C**

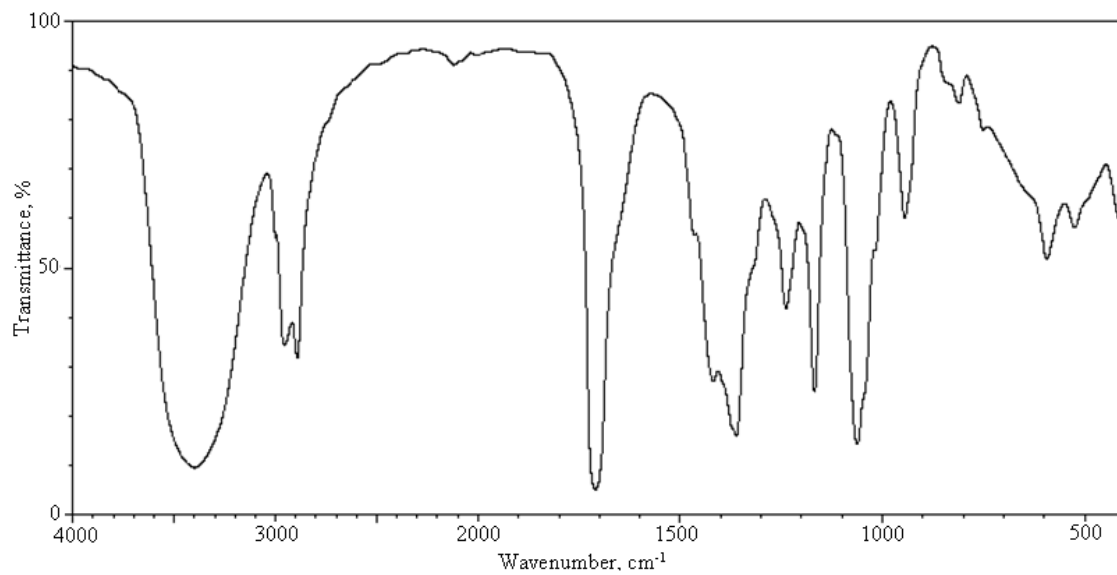


**Spectrum D**



-15-

**Spectrum E**



**TERJEMAHAN**

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**Arahan:**

Jawab **LIMA** (5) soalan.

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

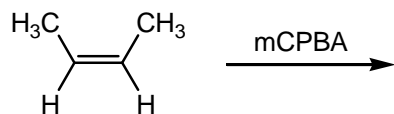
Jika calon menjawab lebih daripada lima soalan, hanya lima soalan pertama mengikut susunan dalam skrip jawapan akan diberi markah.



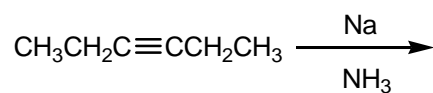
-17-

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

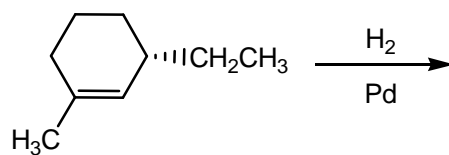
(i)



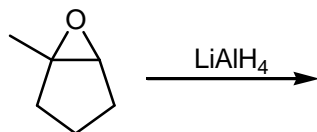
(ii)



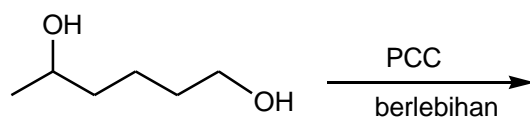
(iii)



(iv)



(v)

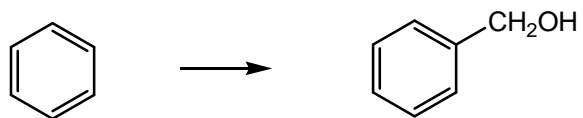


(10 markah)

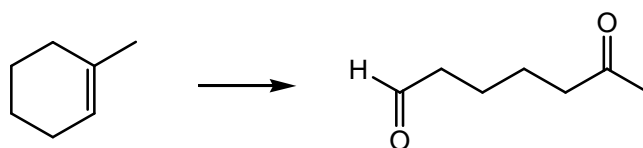
-18-

(b) Tunjukkan bagaimana setiap sebatian berikut dapat disediakan daripada bahan permulaan yang diberikan. Mekanisme tidak diperlukan.

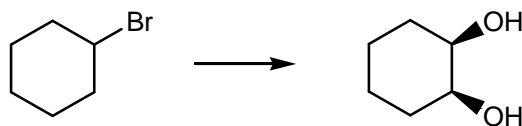
(i)



(ii)



(iii)

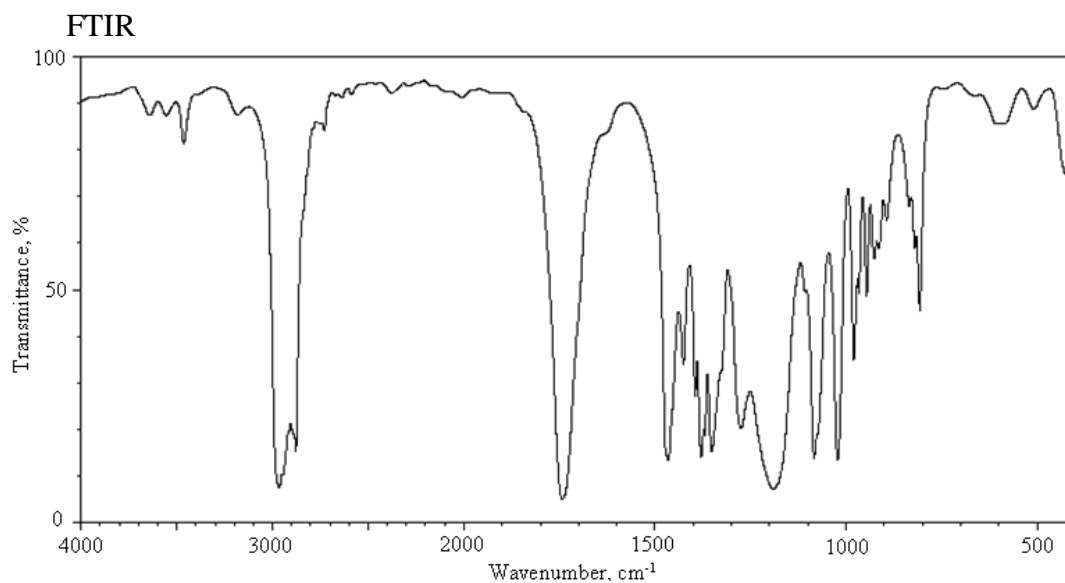
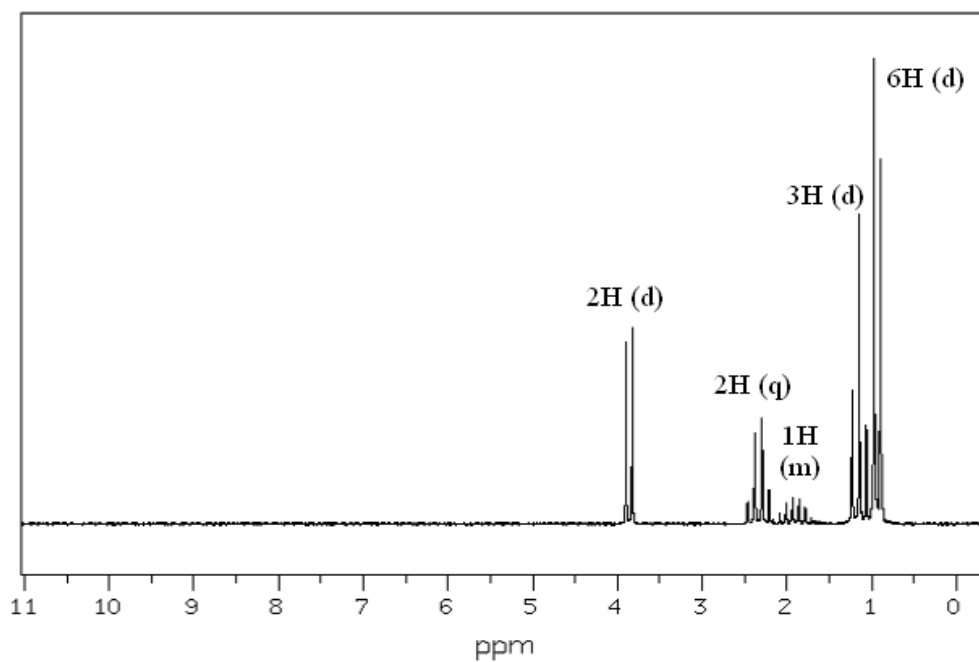


(10 markah)

-19-

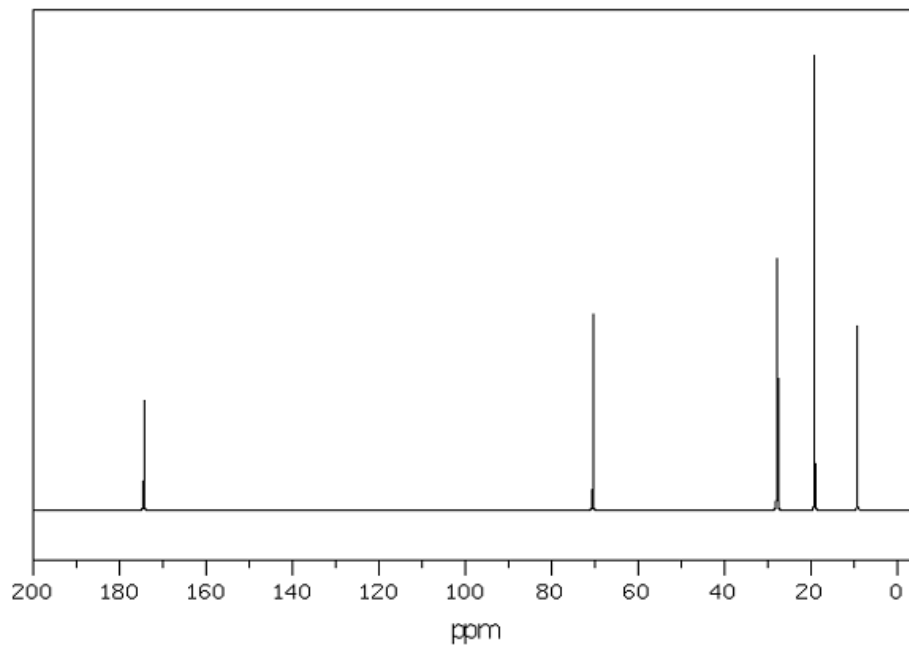
2. (a) Sebatian **A** mempunyai formula molekul  $C_7H_{14}O_2$ . Maklumat spektrum (FTIR,  $^1H$  NMR dan  $^{13}C$  NMR) disediakan di bawah. Berikan struktur sebatian **A** dan interpretasi spektrum yang merumuskan jawapan anda.

(15 markah)

 $^1H$  NMR

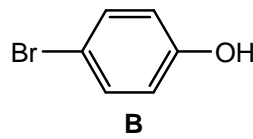
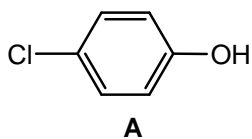
...20/-

-20-

 $^{13}\text{C}$  NMR

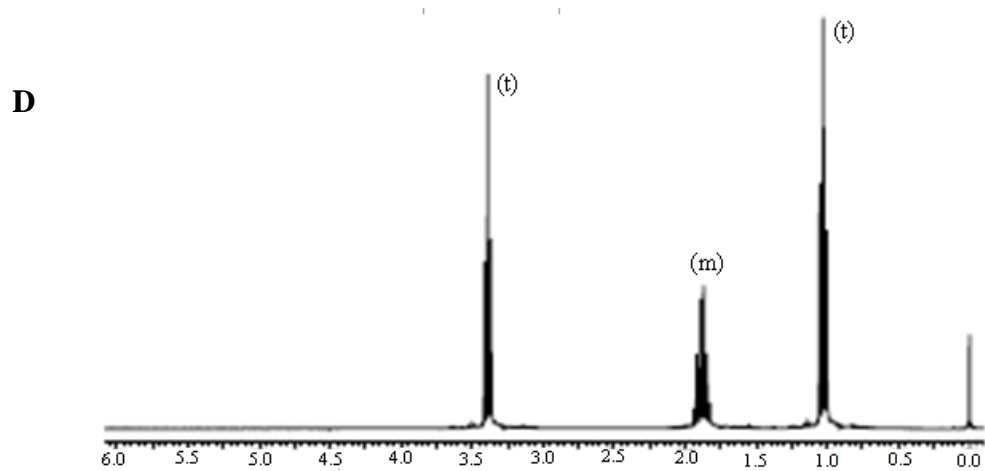
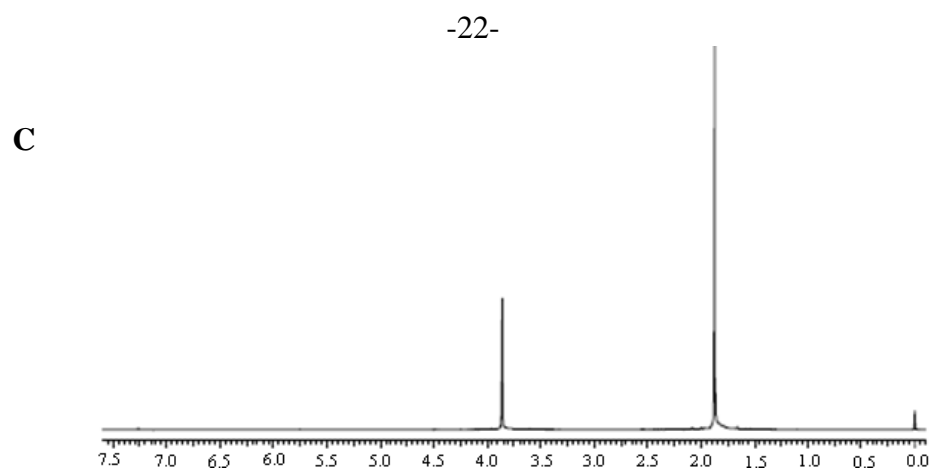
- (b) Bagi sepasang sebatian di bawah, **A** dan **B**, pilih teknik spektroskopi yang paling sesuai (MS, FTIR,  $^1\text{H}$  NMR atau  $^{13}\text{C}$  NMR) bagi membezakan antara dua sebatian tersebut. Jelaskan secara tepat perbezaan dalam spektrum yang anda jangka bagi kedua-dua sebatian tersebut.

[ $^{79}\text{Br} = 78.92$ ,  $^{81}\text{Br} = 80.92$ ,  $^{35}\text{Cl} = 34.97$ ,  $^{37}\text{Cl} = 36.96$ ].



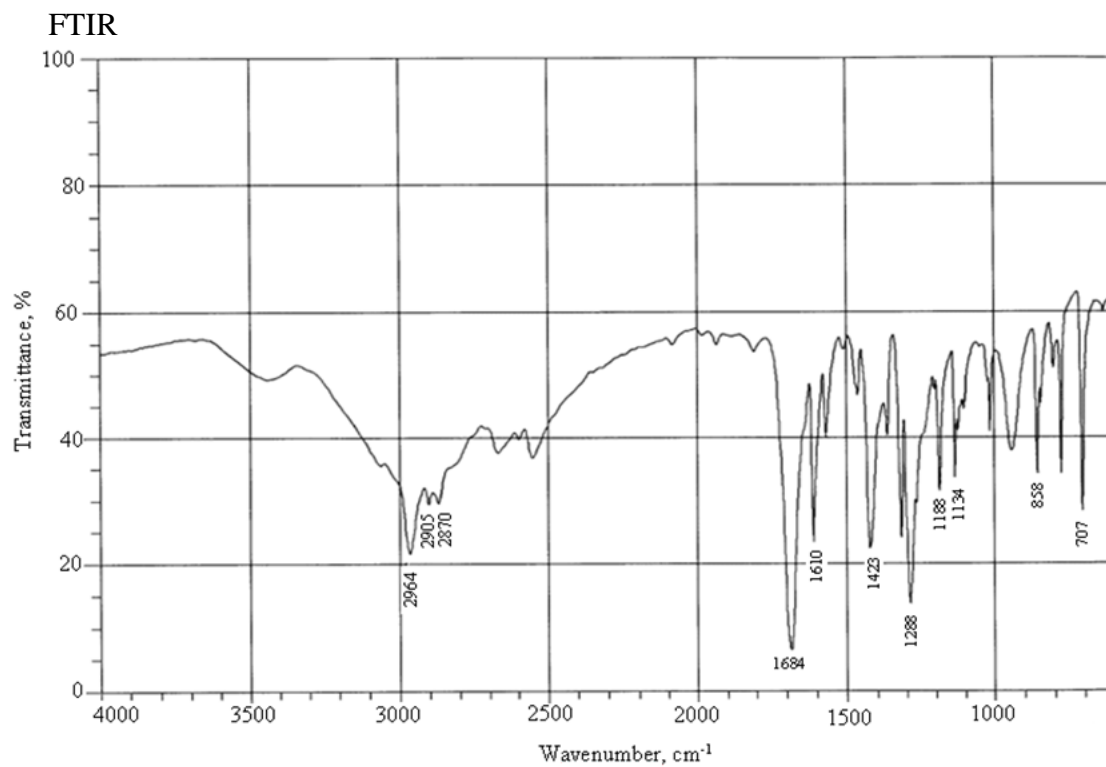
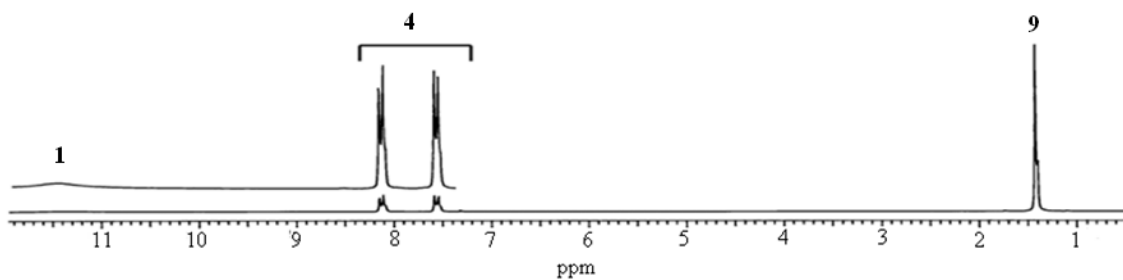
(5 markah)





-23-

- (b) Cadangkan satu struktur bagi  $C_{11}H_{14}O_2$  yang selaras dengan spektrum FTIR dan  $^1H$  NMR yang ditunjukkan di bawah. (8 markah)

 $^1H$  NMR

...24/-

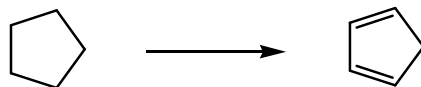
-24-

4. (a) Apabila 2-metil-1,3-butadiena mengalami penambahan hidrogen klorida secara 1,4, hasil utama yang terbentuk ialah 1-kloro-3-metil-2-butena. Tiada atau sedikit 1-kloro-2-metil-2-butena sahaja yang terbentuk. Jelaskan fakta ini dengan menuliskan mekanisme bagi tindak balas tersebut.

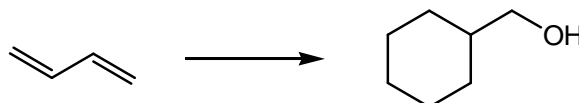
(4 markah)

- (b) Tunjukkan langkah sintesis bagi setiap transformasi berikut. Mekanisme tidak diperlukan.

(i)

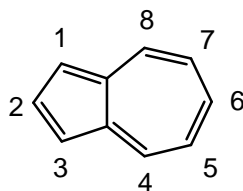


(ii)



(8 markah)

- (c) Struktur azulena ditunjukkan seperti di bawah:



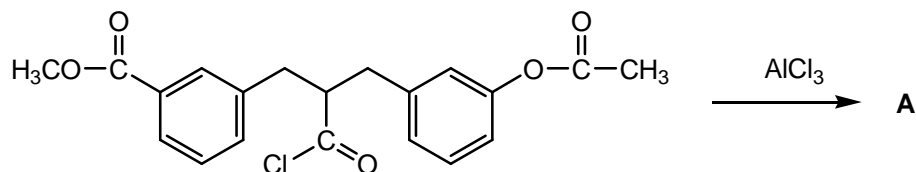
- (i) Terangkan mengapa azulena ialah suatu sebatian aromatik.  
 (ii) Terangkan mengapa azulena lebih cenderung diserang oleh elektrofil pada posisi 1 berbanding dengan posisi 2.

(8 markah)



-25-

5. (a) Tindak balas berikut merupakan suatu pengasilan Friedel-Crafts intramolekul. Ramalkan hasil **A** dan tuliskan mekanisme bagi tindak balas ini.

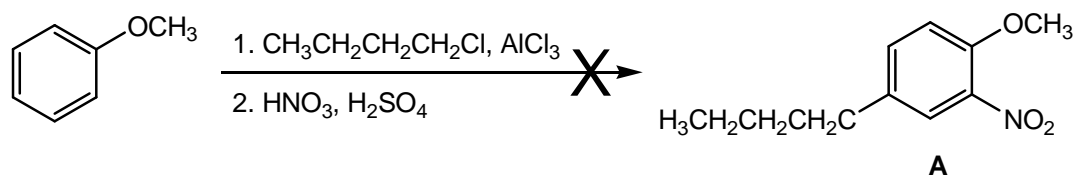


(6 markah)

- (b) Jelaskan secara terperinci dengan menggunakan struktur resonans, mengapa kumpulan fenil ( $\text{C}_6\text{H}_5-$ ) merupakan suatu pengarah *orto*, *para* yang mengaktifkan gelang benzena terhadap serangan elektrofilik.

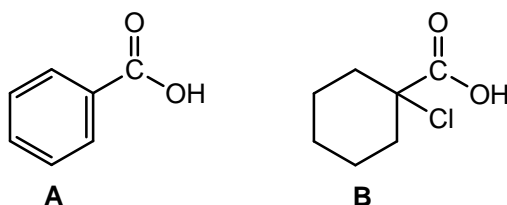
(4 markah)

- (c) Jelaskan mengapa tindak balas berikut tidak membentuk hasil **A** seperti yang ditunjukkan. Cadangkan suatu sintesis bagi **A** bermula dengan fenol ( $\text{C}_6\text{H}_5\text{OH}$ ).



(6 markah)

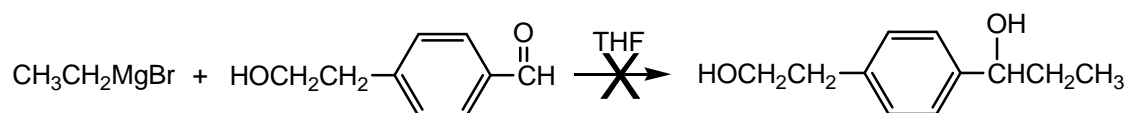
- (d) Bandingkan keasidan bagi dua sebatian berikut. Terangkan jawapan anda.



(4 markah)

-26-

6. (a) Suatu percubaan untuk menambahkan  $\text{CH}_3\text{CH}_2\text{MgBr}$  kepada aldehid berikut gagal. Kenapa? Apakah yang anda boleh lakukan untuk mendapatkan hasil yang diinginkan daripada tindak balas tersebut? Tunjukkan langkah sintesis.



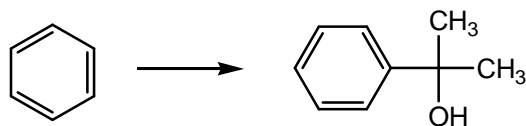
(8 markah)

- (b) Terangkan mengapa aldehid adalah lebih reaktif terhadap tindak balas penambahan nukleofilik berbanding dengan keton.

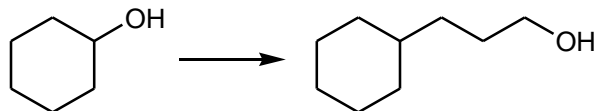
(4 markah)

- (c) Tunjukkan langkah sintesis yang boleh digunakan bagi transformasi berikut. Mekanisme tidak diperlukan.

(i)



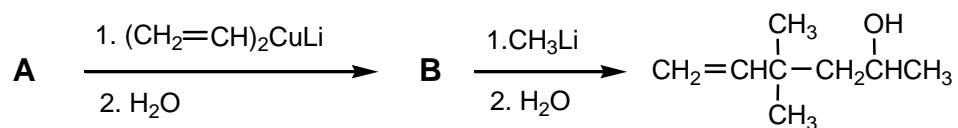
(ii)



(8 markah)

-27-

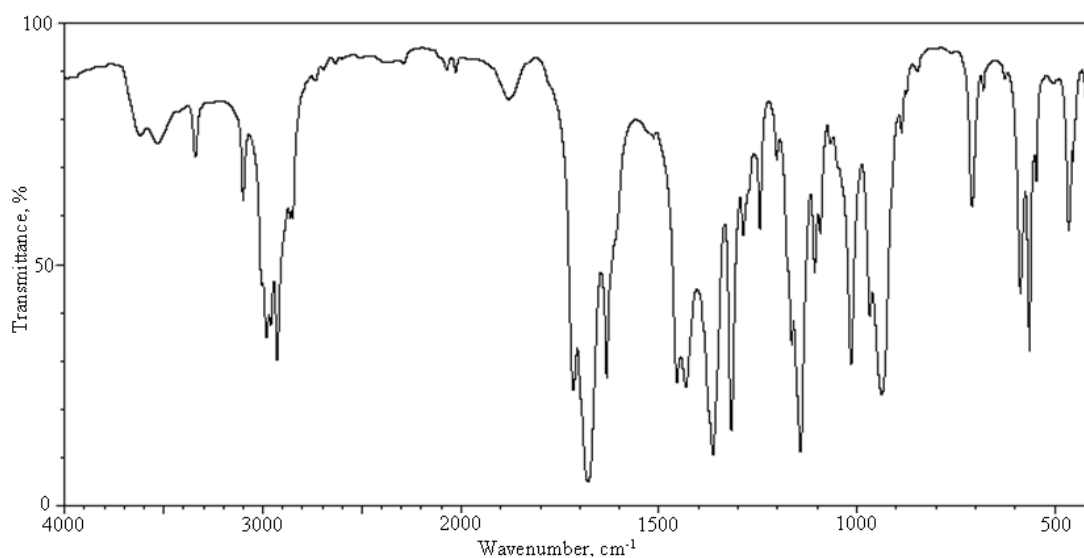
7. (a) Kenalpastikan sebatian **A** dan **B**.



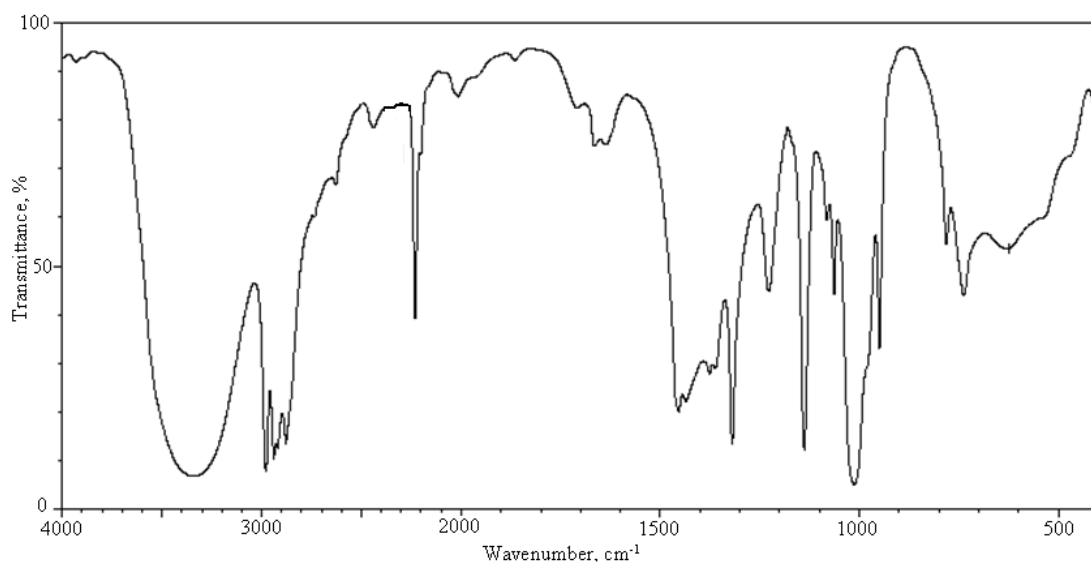
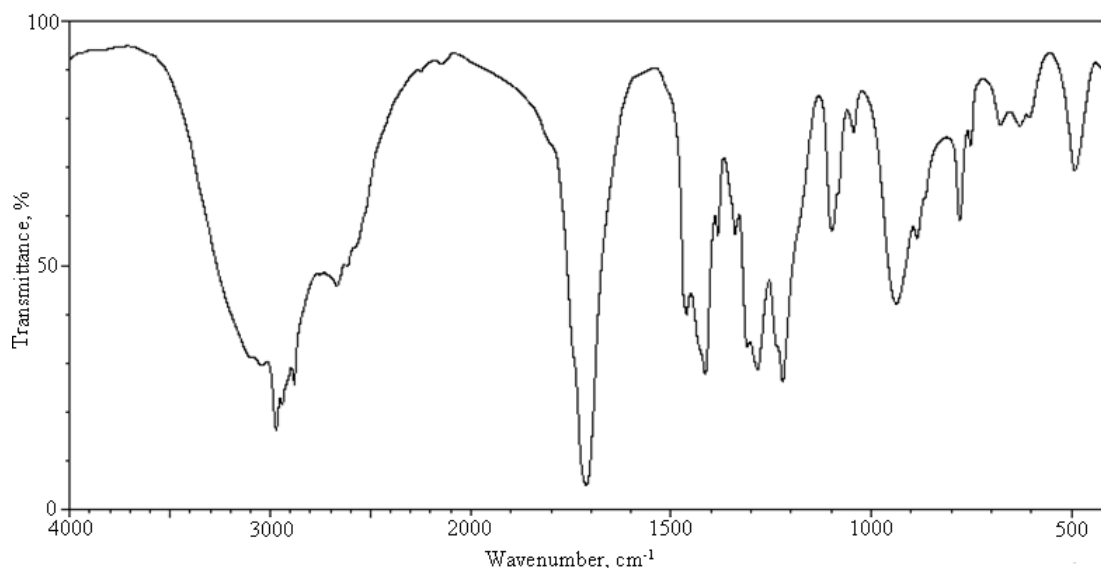
(5 markah)

- (b) Padankan spektrum FTIR yang berikut, **A-E**, dengan satu daripada sebatian yang disenaraikan. Berikan penjelasan bagi setiap padanan.

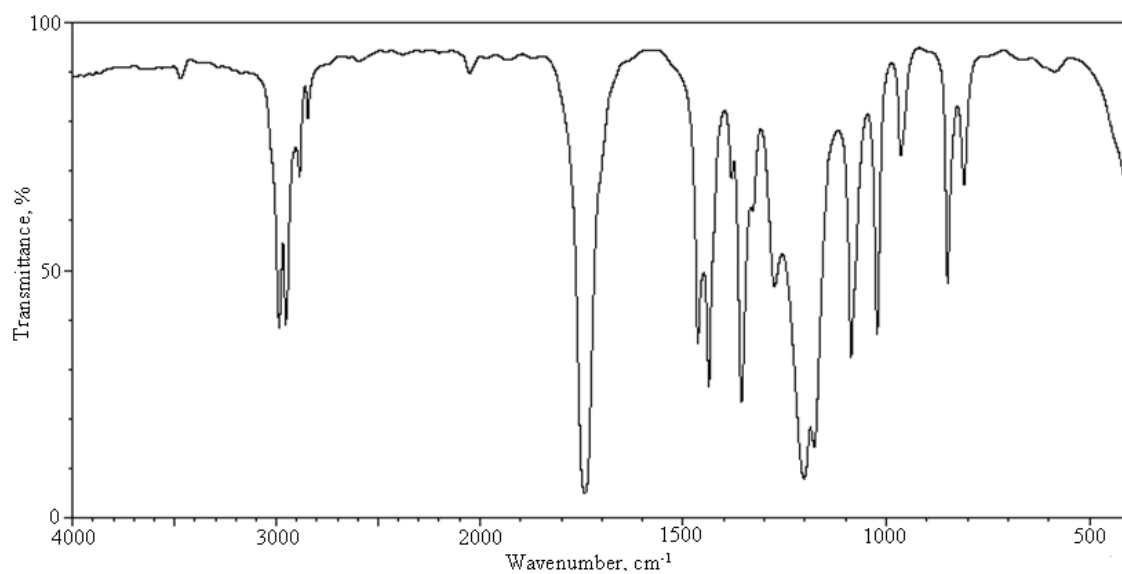
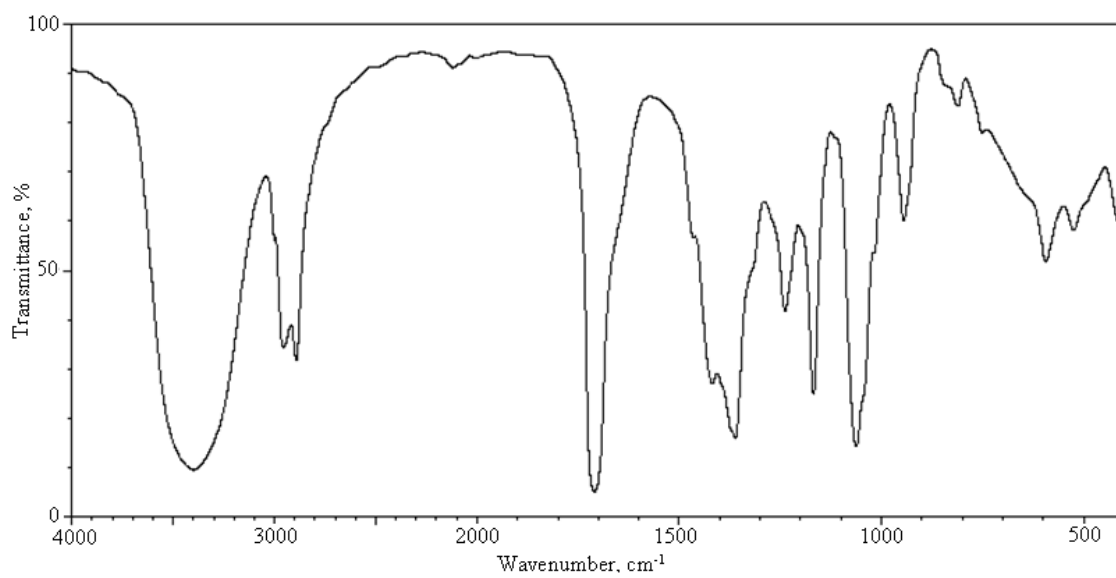
(15 markah)

**1****2****3****4****5****6****7****8****Spektrum A**

-28-

**Spektrum B****Spektrum C**

-29-

**Spektrum D****Spektrum E**

...30/-

## Spectroscopy Tables

<sup>1</sup> H NMR	
	<u>δ (ppm)</u>
RCH <sub>3</sub>	0.9
R <sub>2</sub> CH <sub>2</sub>	1.3
R <sub>3</sub> 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 <sub>3</sub>	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 <sub>2</sub>	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

<sup>13</sup> C NMR	
	<u>δ (ppm)</u>
C-I	0 – 40
C-Br	25 – 65
C-Cl	35 – 80
-CH <sub>3</sub>	8 – 30
-CH <sub>2</sub> -	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<sup>-1</sup></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 <sub>2</sub>	{ 1515 – 1560
	{ 1345 – 1385