BINDURA UNIVERSITY OF SCIENCE EDUCATION

CHEMISTRY DEPARTMENT

JUN 2022

CH203: ORGANIC CHEMISTRY II

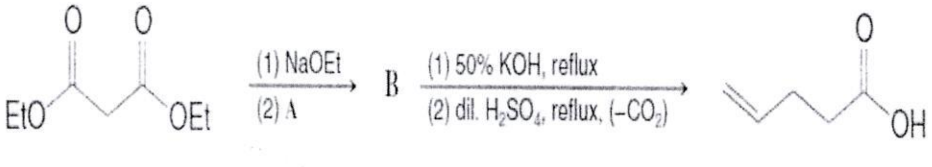
2 HOURS

ANSWER QUESTION ONE AND FOUR OTHERS, TWO FROM EACH OF THE SECTIONS A AND B. EACH QUESTION CARRIES 20 MARKS

……………………………………………………………………………………………

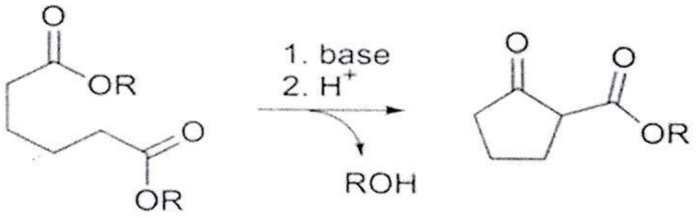
1 (a) Define the following terms as used in organic chemistry.
  (i) Organometallic compound **[2 marks]**
  (ii) Radical cation **[2 marks]**
  (ii) Alpha carbon **[2 marks]**

(b) Provide structures for compounds **A** and **B** in the following synthesis.



[1; 2 marks]

(c) Propose a mechanism for the Dieckmann condensation below.



[8 marks]

(d) How many different kinds of H atoms does $CH_3CH_2CH_2CH_2CH_3$ contain? **[3 marks]**

SECTION A: ANSWER ANY TWO QUESTIONS

2 (a) With the aid of examples discuss the following synthesis;
  (i) Claisen condensation **[5 marks]**
  (ii) Michael reaction **[5 marks]**

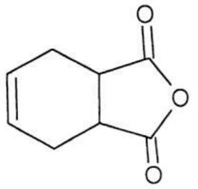
(iii) Self Aldol Reaction **[5 marks]**

(b) Describe the ideal properties of a commercial organic product.

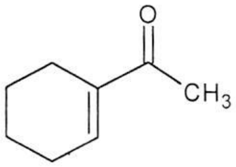
[5 marks]

3 (a) Predict the starting materials required to prepare each of the compounds below by Diels alder reactions.

(i)

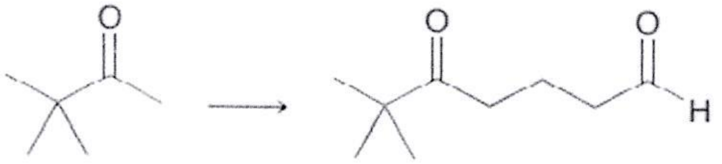


(ii)



[8 marks]

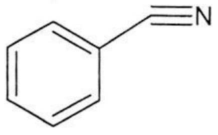
(b) Using any reagents of your choice, show how you might accomplish the following transformation.



[10 marks]

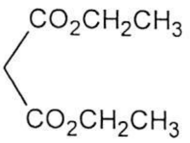
(c) Predict the products of the synthesis below;

(i)



$\xrightarrow[\text{2. } H_3O^+]{\text{1. } CH_3CH_2MgBr\text{, ether}}$

(ii)



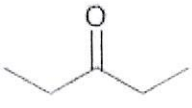
$\xrightarrow[\text{2. } CH_3CH_2OH]{\text{1. } NaOC_2H_5}$

[2 marks]

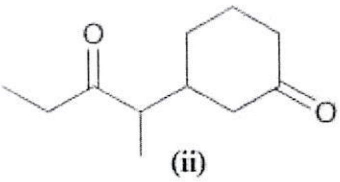
4 (a) Using reaction outlines describe the differences between crossed Aldol condensation and Robinson annulation.

[12 marks]

(b) Draw and label all of the acidic hydrogen atoms in the molecules below,



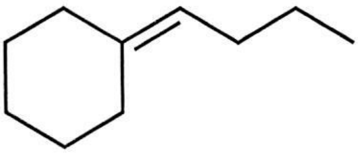
(i)



(ii)

[2 marks]

(c) Apply a detailed retro-synthetic analysis to synthesize the compound below.



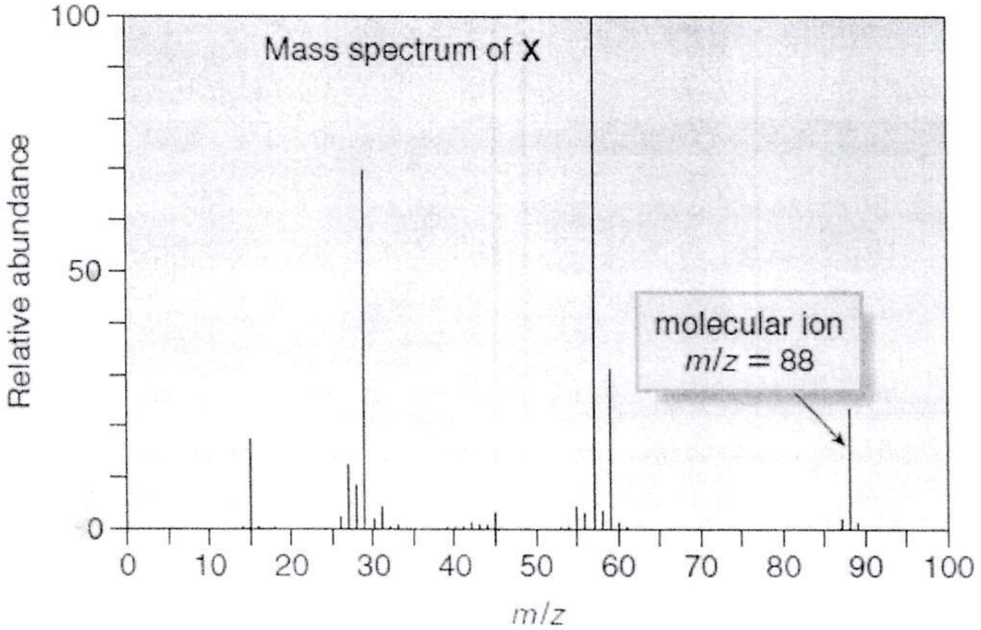
[6 marks]

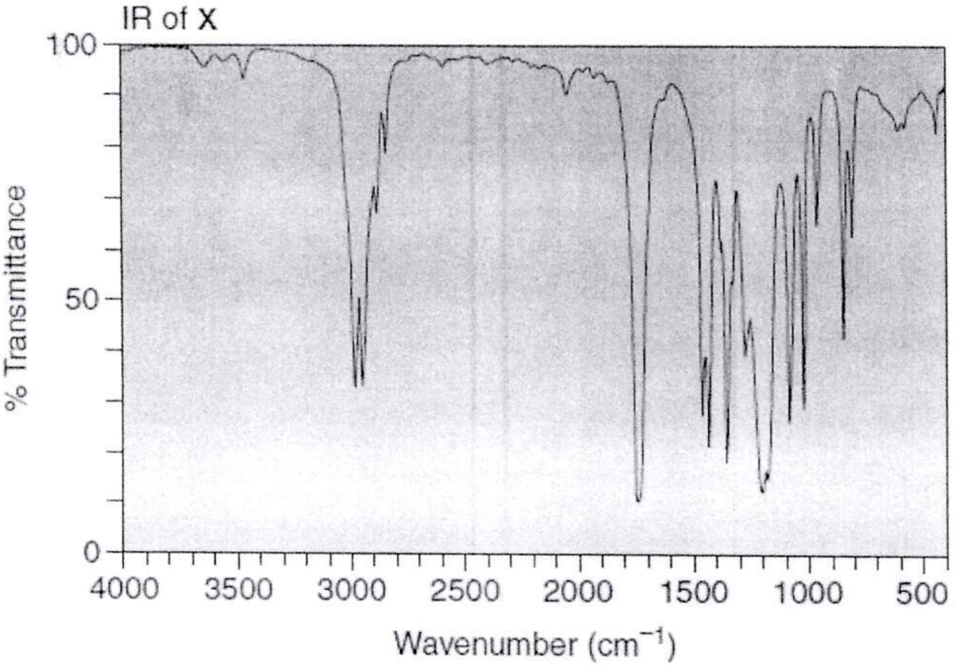
SECTION B: ANSWER ANY <u>TWO</u> QUESTIONS

5 (a) Propose possible molecular formulas for a compound with a molecular ion at $m/z = 86$. **[10 marks]**

(b) How can two isomers having molecular formula C_2H_6O be distinguished by IR spectroscopy? **[10 marks]**

6 (a) Interpret the mass and IR spectrum of X shown below; **[10 marks]**

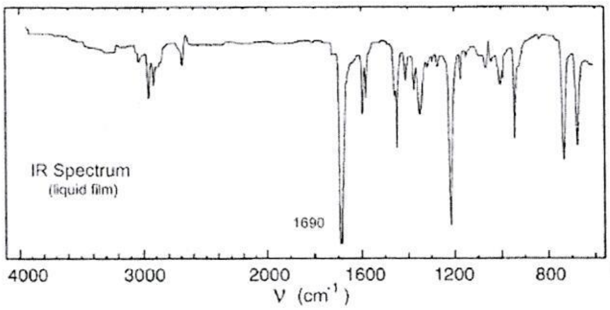


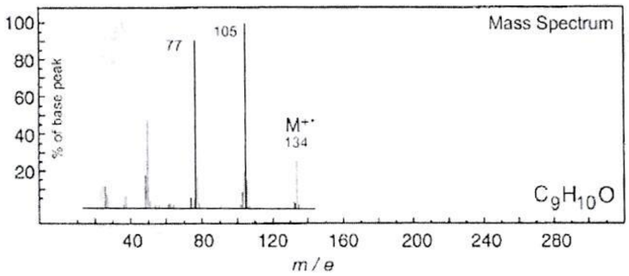


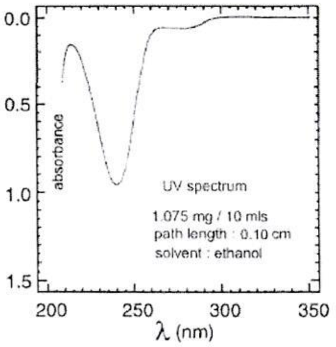
(b) Calculate the HDI for a compound with molecular formula $C_4H_8ClNO_2$, and identify the structural information provided by the HDI. **[10 marks]**

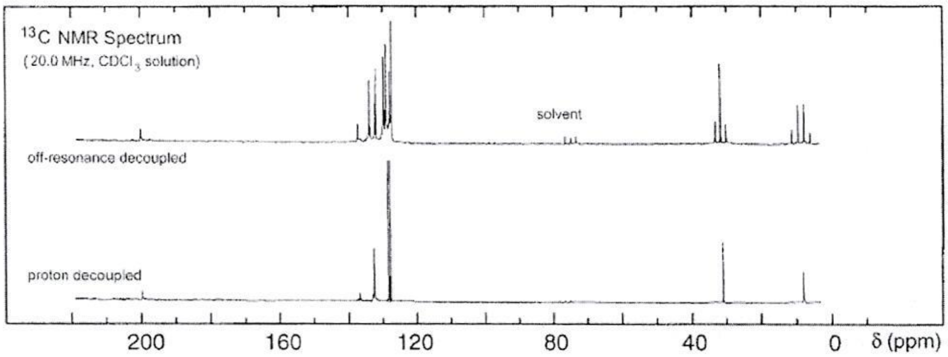
7 Using the IR, MS, NMR and UV data identify unknown B (figures attached). Clearly show steps leading to the structure. **[20 marks]**

Unknown B


IR Spectrum
(liquid film)
1690
4000
3000
2000
1600
1200
800
ν (cm⁻¹)


Mass Spectrum
% of base peak
100
80
60
40
20
77
105
M⁺˙
134
C9H10O
40
80
120
160
200
240
280
m / e


0.0
0.5
1.0
1.5
absorbance
UV spectrum
1.075 mg / 10 mls
path length : 0.10 cm
solvent : ethanol
200
250
300
350
λ (nm)


13C NMR Spectrum
(20.0 MHz, CDCl3 solution)
solvent
off-resonance decoupled
proton decoupled
200
160
120
80
40
0
δ (ppm)

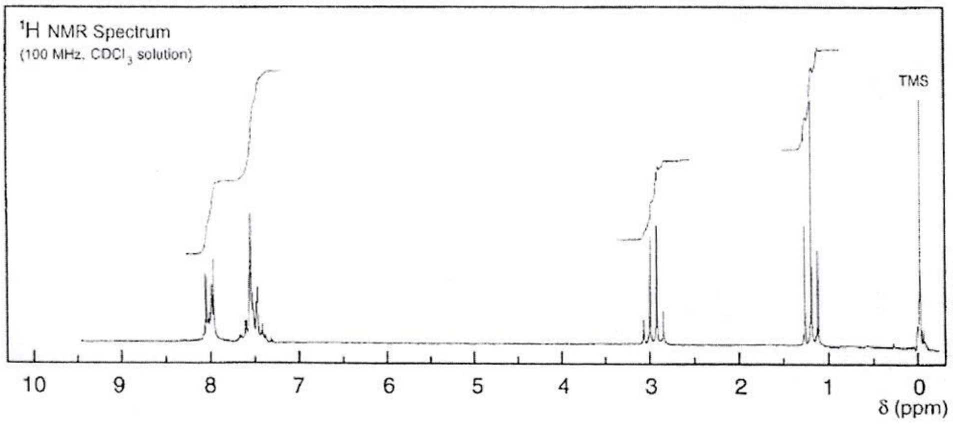

1H NMR Spectrum
(100 MHz, CDCl3 solution)
TMS
10
9
8
7
6
5
4
3
2
1
0
δ (ppm)

Table 13.2 Important Absorption Bands in the Infrared Spectral Region

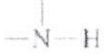
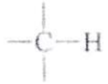
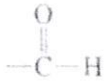
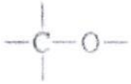
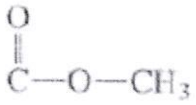
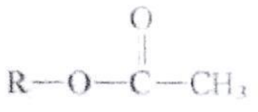
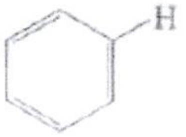
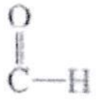
Position (cm^{-1})	Group	Comments
3550–3200	$-O-H$	Strong intensity, very broad band
3400–3250	 $-\overset{\vert}{N}-H$	Weaker intensity and less broad than O—H; NH_2 shows two bands, NH shows one
3300	$\equiv C-H$	Sharp. C is sp hybridized
3100–3000	 $=\overset{\vert}{C}-H$	C is sp^2 hybridized
3000–2850	 $-\underset{\vert}{\overset{\vert}{C}}-H$	C is sp^3 hybridized; 3000 cm^{-1} is a convenient dividing line between this type of C—H bond and the preceding type
2830–2700	 $-\overset{O}{\overset{\Vert}{C}}-H$	Two bands
2260–2200	$-C\equiv N$	Medium intensity
2150–2100	$-C\equiv C-$	Weak intensity
1820–1650	 $-\overset{O}{\overset{\Vert}{C}}-$	Strong intensity, exact position depends on substituents; see Table 13.1
1660–1640	 $C=C$	Often weak intensity
1600–1450		Four bands of variable intensity
1550 and 1380	$-NO_2$	Two strong intensity bands
1300–1000	 $-\underset{\vert}{\overset{\vert}{C}}-O-$	Strong intensity
900–675		Strong intensity

Table 14.1 Approximate Chemical Shifts of Hydrogens in ^{1}H-NMR Spectra

Type of Hydrogen	Chemical Shift (δ)	Type of Hydrogen	Chemical Shift (δ)
$-C-CH_3$	0.9	$Cl-CH_3$	3.0
$C{=}C-CH_3$	1.6	$O-CH_3$	3.3
$C{\equiv}C-H$	1.8	 $\overset{O}{\overset{\|}{C}}-O-CH_3$	3.7
$N-H$	1–3	O_2N-CH_3	4.1
$O-H$	2–5	$F-CH_3$	4.2
 $R-O-\overset{O}{\overset{\|}{C}}-CH_3$	2.0	 $C{=}C{-}H$	5.5–6.5
 $\overset{O}{\overset{\|}{C}}-CH_3$	2.2		7–8
$N-CH_3$	2.2	 $\overset{O}{\overset{\|}{C}}-H$	10
$I-CH_3$	2.2	 $\overset{O}{\overset{\|}{C}}-O-H$	12
$N{\equiv}C-CH_3$	2.2		
$Ph-CH_3$	2.3		
$Br-CH_3$	2.7		

Note that these positions are only approximate. Furthermore, most of these positions are given for CH_3 groups.
CH_2 groups appear farther downfield by about 0.3 ppm and CH groups by about 0.7 ppm.

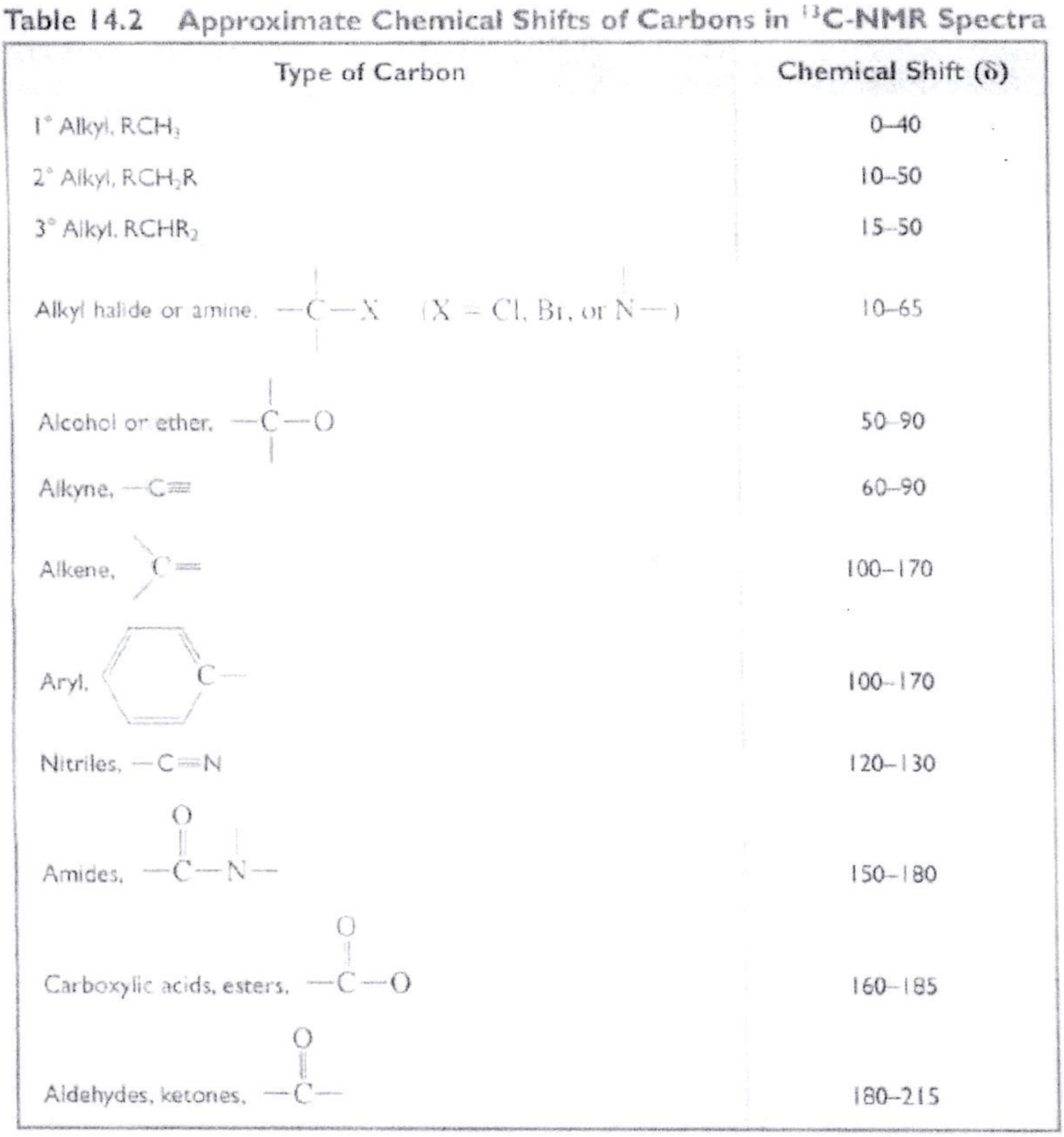


Table 14.2 Approximate Chemical Shifts of Carbons in ^{13}C-NMR Spectra

Type of Carbon	Chemical Shift (δ)
1° Alkyl, RCH$_3$	0–40
2° Alkyl, RCH$_2$R	10–50
3° Alkyl, RCHR$_2$	15–50
Alkyl halide or amine, $-\overset{\vert}{\underset{\vert}{C}}-X$ (X = Cl, Br, or $\overset{\vert}{N}-$)	10–65
Alcohol or ether, $-\overset{\vert}{\underset{\vert}{C}}-O$	50–90
Alkyne, $-C\equiv$	60–90
Alkene, $>C=$	100–170
Aryl,	100–170
Nitriles, $-C\equiv N$	120–130
Amides, $-\overset{O}{\overset{\Vert}{C}}-\overset{\vert}{N}-$	150–180
Carboxylic acids, esters, $-\overset{O}{\overset{\Vert}{C}}-O$	160–185
Aldehydes, ketones, $-\overset{O}{\overset{\Vert}{C}}-$	180–215

End of exam