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# KIBABII UNIVERSITY

UNIVERSITY EXAMINATIONS  
2017/2018 ACADEMIC YEAR  
FOURTH YEAR FIRST SEMESTER  
SUPPLEMENTARY EXAMINATIONS  
FOR THE DEGREE OF BACHELOR OF SCIENCE

**COURSE CODE: SCH 430**

**COURSE TITLE: ORGANIC SPECTROSCOPY**

DURATION: 2 HOURS

**DATE: 03/10/2018**

**TIME: 3:00-5:00PM**

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## INSTRUCTIONS TO CANDIDATES

- Answer **QUESTION ONE** (Compulsory) and any other two (2) Questions.
- Indicate **answered questions** on the front cover.
- Start every question on a new page and make sure question's number is written on each page.

This paper consists of 3 printed pages. Please Turn Over



KIBU observes ZERO tolerance to examination cheating

### Question 1

- a) Briefly explain the difference between the following; [4mks]
- Ultraviolet spectroscopy (UV) and Infrared Spectroscopy (IR)
  - Nuclear Magnetic Resonance (NMR) and Mass spectrometry (MS)
- b). Caffeine molecules absorb infrared radiation at  $1656\text{ cm}^{-1}$ . Calculate the following:
- wavelength of this radiation; [2mks]
  - frequency of this radiation; [2mks]
  - Energy change associated with this absorption. [1mk]
- c) State Beer- Lamberts law. [2mks]
- d) How does the percent transmittance of a solution vary with;
- increasing concentration?
  - increasing path length?
- e) A solution of thickness 2 cm transmits 40% incident light. Calculate the concentration of the solution, given that  $\epsilon = 6000\text{ dm}^3/\text{mol}/\text{cm}$ . [3mks]
- f) Predict whether UV-VIS spectroscopy can be used to distinguish between the following isomers. Estimate  $\lambda_{\text{max}}$  (there may be more than one) for each.
- $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_3$  and  $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}_3$  [3mks]
  - $\text{CH}_3-\text{CO}-\text{O}-\text{CH}_2-\text{CH}_3$  and  $\text{CH}_3-\text{CH}_2-\text{CO}-\text{O}-\text{CH}_3$  [3mks]
- g) How will you distinguish between  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions? Apply the effect of solvation to illustrate this. [4mks]
- h) Lycopene is responsible for the red colour of tomatoes. Explain. [4mks]

### Question 2

- Distinguish between absorption Spectroscopy and emission Spectroscopy. [2mks]
- Explain two types of molecular vibrations in IR: [2mks]
- How will you estimate ring strain using IR and UV-Visible spectra. [4mks]
- What would be the effect of an increase in temperature on the infrared spectrum of a hydrogen-bonded compound? [2mks]
- State FOUR factors affecting position of C=O absorption bands in IR [4mks]
- Predict the structure of the compound (commercial sample) with the following spectral characteristics and justify your answer. [6mks]  
MF:  $\text{C}_4\text{H}_{10}\text{O}$ ;  
IR: 3450 (broad), 2980, 1450, 1200,  $1050\text{cm}^{-1}$   
 $^1\text{H}$ NMR: 1.5 (3H, t), 2.8 (2H, dq), 3.4 (1H, m), 4.5 (1H, s), 2.1 (3H, d).  
 $^{13}\text{C}$  NMR: 22.6, 68.7, 32.0, 9.9 ppm.  
DEPT 45: 4 signals, DEPT 90 : 1 signal, DEPT 135: 3 +ve and 1 -ve signals.

### Question 3



a) Using examples, explain the following terms;

i. Chromophore

[2mks]

ii. Auxochrome

[2mks]

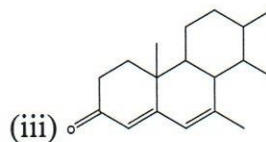
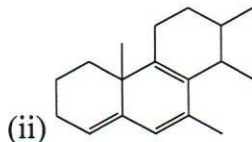
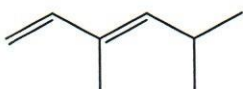
iii. Bathochromic shift

[2mks]

iv. Hypsochromic shift

[2mks]

b) Using Woodward-Fieser's rule, calculate wavelengths of maximum UV absorption for following compounds: 9mks



c) State three applications of UV spectroscopy.

[3mks]

#### Question 4

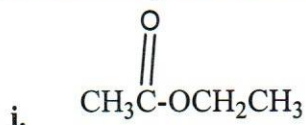
a) State four factors affecting chemical shifts in proton nmr spectra.

[4mks]

b) Proton n.m.r. spectra are usually recorded using a solution of a substance to which tetramethylsilane (TMS) has been added. Give FOUR reasons why TMS is a suitable standard.

[4mks]

c) Sketch the proton nmr spectrum showing the splitting patterns of each of the following;



[3mks]



[3mks]



[3mks]

d) State three factors increasing the sensitivity in  $^{13}\text{C}$ -NMR spectroscopy.

[3mks]

#### Question 5

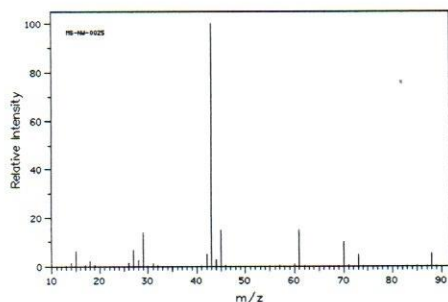
a) Outline four processes involved in basic principles of Mass spectrometry.

[4mks]

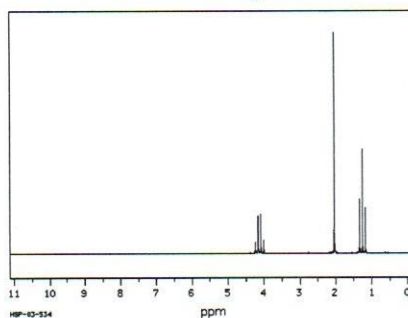
b) Use the following spectra to analyse and deduce the structure of A:

[16mks]

Mass spectrum:



Proton nmr spectrum:



Infra-red spectrum: sharp absorption at  $1715\text{ cm}^{-1}$ , no broad absorptions between  $1500$  and  $3500\text{ cm}^{-1}$

## Woodward-Fieser Rules for Dienes

Parent	Homoannular $\lambda=253$ nm	Heteroannular $\lambda=214$ nm =217 (acyclic)
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Increments for:

Double bond extending conjugation	+30	
Alkyl substituent or ring residue		+5
Exocyclic double bond		+5
Polar groupings:		
-OC(O)CH <sub>3</sub>		+0
-OR		+6
-Cl, -Br		+5
-NR <sub>2</sub>		+60
-SR		+30

## Woodward-Fieser Rule for Enones

Enone & Dienone	Base values ( $\lambda_{\max}$ )
Acyclic $\alpha,\beta$ -unsaturated ketones	215 nm
6-membered cyclic $\alpha,\beta$ -unsaturated ketones	215 nm
5-membered cyclic $\alpha,\beta$ -unsaturated ketones	202 nm
$\alpha,\beta$ -unsaturated aldehydes	210 nm
$\alpha,\beta$ -unsaturated carboxylic acid & esters	195 nm

Increments for:

Double bond extending conjugation (DEC):	+30
Exocyclic double bond:	+5
Homodiene component:	+39

# Woodward-Fieser Rule for Enones

## Increments for:

Alkyl group/ring residue:	$\alpha$	+10
	$\beta$	+12
	$\gamma$ & higher	+18
Polar groups: -OH:	$\alpha$	+35
	$\beta$	+30
	$\delta$	+50
-OAc:	$\alpha, \beta, \gamma$	+6
-OMe:	$\alpha$	+35
	$\beta$	+30
	$\gamma$	+17
	$\delta$	+31
-SAlk:	$\beta$	+85
-Cl:	$\alpha$	+15
	$\beta$	+12
-Br:	$\alpha$	+25
	$\beta$	+30
-NR <sub>2</sub> :	$\beta$	+95

## Characteristic Infrared Absorption Frequencies

Bonding		Frequency (cm <sup>-1</sup> )	Intensity*	Type of Vibration (stretching unless noted)	
C—H	alkane	2850–3000	w–m		
	—CH <sub>3</sub>	1375 and 1450	w–m	out-of-plane bending	
	—CH <sub>2</sub> —	1450	m	out-of-plane bending	
	alkene		3000–3100	w–m	
			650–1000	s	out-of-plane bending
	alkyne	3300	s		
	aromatic		3000–3100	s	
			690–900	s	out-of-plane bending
	aldehyde		2700–2800	w	
			2800–2900	w	
C—C	alkane	(not interpretatively useful)			
C=C	alkene	1600–1680	w–m		
	aromatic	1450 and 1600	w–m		
C≡C	alkyne	2100–2250	w–m		
C—O	alcohol, ether, ester, carboxylic acid, anhydride	1050–1250	s		
C=O	amide	1630–1680	s		
	carboxylic acid	1700–1750	s		
	ketone	1705–1780	s		
	aldehyde	1705–1740	s		
	ester	1735–1800	s		
	anhydride	1760 and 1810	s		
O—H	acid chloride	1800	s		
	alcohol, phenol				
	free	3600–3650	m		
	hydrogen bonded	3200–3500	m		
	carboxylic acid	2400–3400	m		
N—H	amine and amide	3100–3500	m–s		
C≡N	nitrile	2200–2250	m		

\* s = strong, m = medium, w = weak



### Characteristic <sup>1</sup>H-NMR Chemical Shifts

Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*	Type of Hydrogen (R = alkyl, Ar = aryl)	Chemical Shift (δ)*
(CH <sub>3</sub> ) <sub>4</sub> Si	0 (by definition)		3.7-3.9
RC(H) <sub>3</sub>	0.8-1.0		4.1-4.7
RC(H) <sub>2</sub> R	1.2-1.4	RC(H) <sub>2</sub> I	3.1-3.3
R <sub>3</sub> C(H)	1.4-1.7	RC(H) <sub>2</sub> Br	3.4-3.6
R <sub>2</sub> C=CR(H)R <sub>2</sub>	1.6-2.6	RC(H) <sub>2</sub> Cl	3.6-3.8
RC≡CH	2.0-3.0	RC(H) <sub>2</sub> F	4.4-4.5
ArC(H) <sub>3</sub>	2.2-2.5	ArO(H)	4.5-4.7
ArC(H) <sub>2</sub> R	2.3-2.8	R <sub>2</sub> C=C(H) <sub>2</sub>	4.6-5.0
RO(H)	0.5-6.0	R <sub>2</sub> C=C(H)R	5.0-5.7
RC(H) <sub>2</sub> OH	3.4-4.0	Ar(H)	6.5-8.5
RC(H) <sub>2</sub> OR	3.3-4.0		9.5-10.1
R <sub>2</sub> N(H)	0.5-5.0		10-13
	2.1-2.3		
	2.2-2.6		

\* Values are approximate. Other atoms within the molecule may cause the signal to appear outside these ranges.

### Characteristic <sup>13</sup>C-NMR Chemical Shifts

Type of Carbon	Chemical Shift (δ)	Type of Carbon	Chemical Shift (δ)
RC(H) <sub>3</sub>	0-40		110-160
RC(H) <sub>2</sub> R	15-55		160-180
R <sub>3</sub> C(H)	20-60		165-180
RC(H) <sub>2</sub> I	0-40		175-185
RC(H) <sub>2</sub> Br	25-65		180-210
RC(H) <sub>2</sub> Cl	35-80		
R <sub>3</sub> C(OH)	40-80		
R <sub>3</sub> C(OR)	40-80		
RC≡CR	65-85		
R <sub>2</sub> C=CR <sub>2</sub>	100-150		