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University Examinations 2023/2024

FOURTH YEAR SECOND SEMESTER EXAMINATION FOR THE DEGREE OF BACHELOR OF EDUCATION SCIENCE AND BACHELOR OF SCIENCE IN CHEMISTRY

SCH 3452: ORGANIC SPECTROSCOPY

DATE: APRIL 2024 **TIME: 2 HOURS**

INSTRUCTIONS: *Answer question* ***one*** *and any other* ***two*** *questions*

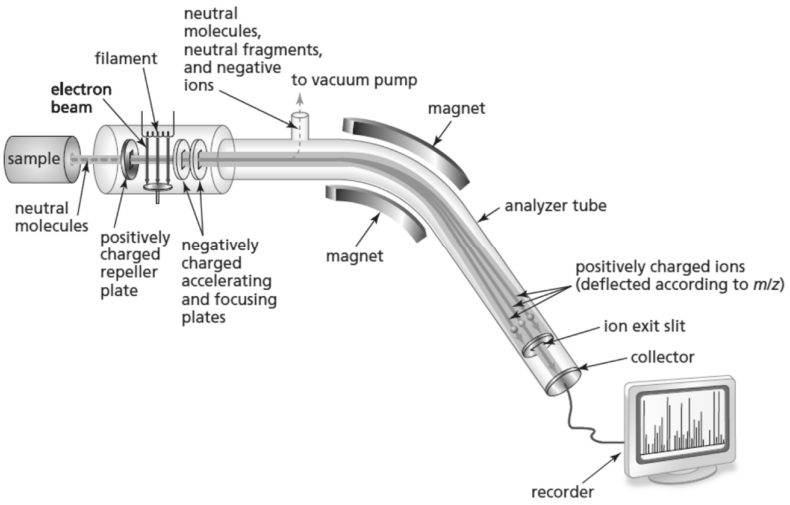
QUESTION ONE (30 MARKS)

a) Explain why these isotopes are the ones commonly analyzed by NMR in organic molecules: ^{1}H, ^{13}C, ^{15}N, ^{19}F, and ^{31}P (2 marks)

b) The following diagrams is a sketch of an instrument used in identification of organic compounds.

i) Name the instrument (1 mark)

ii) Briefly explain the working principle of the instrument (4 marks)



c) Explain the difference between alpha cleavage and McLafferty rearrangement in ketones (6 marks)

d) Explain the following terms as used in spectroscopy (8 marks)

i) Stretching vibration

ii) Absorption bands

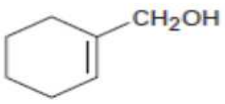
iii) Functional group region in IR

iv) Multiplet in nmr

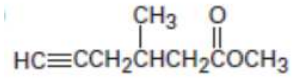
d) The ^1H NMR peak of $CHCl_3$ was recorded on a spectrometer operating at 200 MHz providing the value of 1454 Hz. Convert 1454 Hz into δ units (4 marks)

e) Where might the following compounds have IR absorptions? (5 marks)

i)



ii)



QUESTION TWO (20 MARKS)

a) Explain the following terms (6 marks)

(i) Chemical shift

(ii) Signal integration in nmr

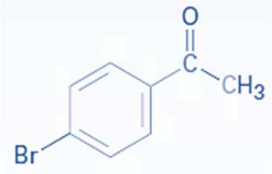
(iii) Spin-spin coupling

b)

(i) Mention the number of peaks in the 1H NMR spectrum of 1,4-dimethyl-benzene (para-xylene or p-xylene) (2 marks)

(ii) Mention the ratio of peak areas possible on integration of the spectrum (2 marks)

c) Predict the ^{13}C chemical shifts for *para*-bromoacetophenone carbons and sketch the 13C nmr spectrum for the molecule (10 marks)



QUESTION THREE (20 MARKS)

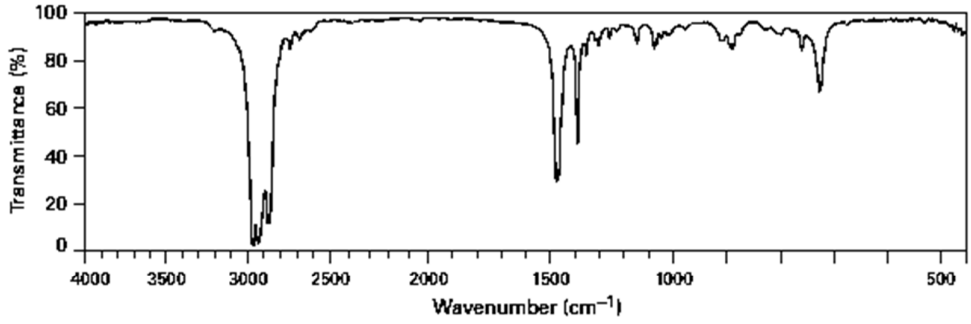
a) The amount of UV light absorbed is expressed as the sample's molar absorptivity (Ɛ), define the equation (4 marks)

b) Explain what happens when a molecule absorbs UV radiation (4 marks)

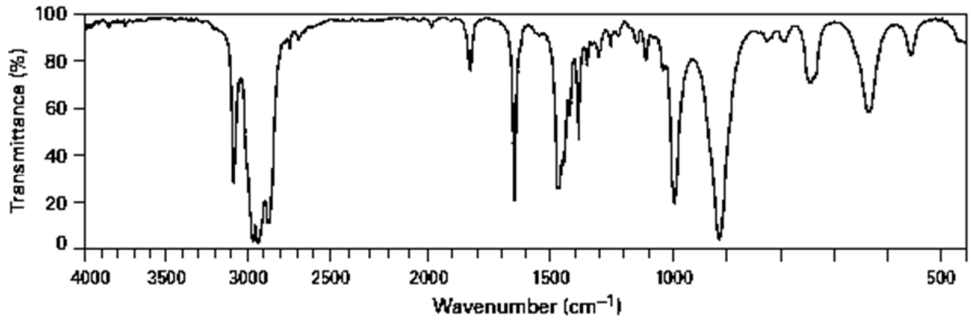
c) Methyl 2,2-dimethylpropanoate $(CH_3)_3CCO_2CH_3$ has two peaks in its 1H NMR spectrum. What are their approximate chemical shifts? (4 marks)

d) Look at the IR spectra of 1-hexene, and 1-hexyne and hexane in the Figure below. Identify and explain which spectrum belongs to which compound. (8 marks)

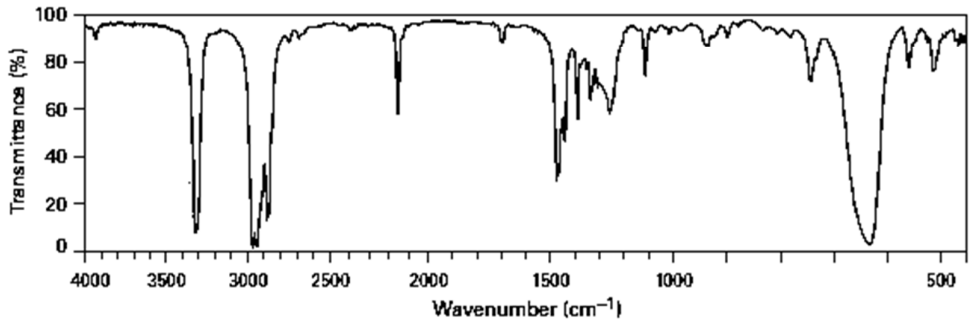
(i)


Transmittance (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

(ii)

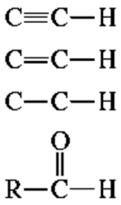

Transmittance (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

(iii)

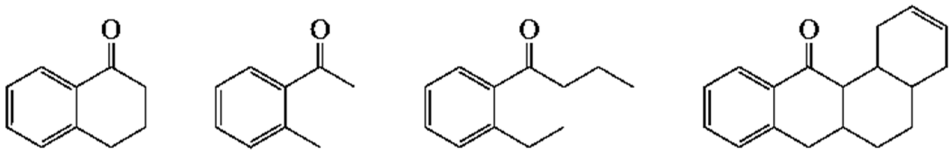

Transmittance (%)
100
80
60
40
20
0
4000
3500
3000
2500
2000
1500
1000
500
Wavenumber (cm⁻¹)

QUESTION FOUR (20 MARKS)

a) Give the wavenumber where the following C-H stretching would occur in IR spectrum (4 marks)



b) Draw the following compounds and highlight the conjugation pattern on them (4 marks)

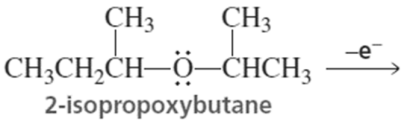


c) Fragmentation of 2-isopropoxybutane results into a molecular ion mainly in two ways:

(i) A C−O bond is cleaved heterolytically, with the electrons going to the more electronegative oxygen atom. Show the mechanism for this process. (3 marks)

(ii) A C−C bond is cleaved homolytically at an α-carbon because this leads to a relatively stable cation since all its atoms have complete octets. (An α-carbon is the carbon bonded to the oxygen.) Show the mechanism for this process. (3 marks)

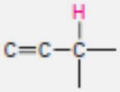
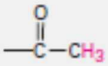
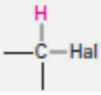
(iii) Sketch the mass spectrum expected (6 marks)

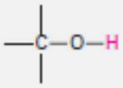
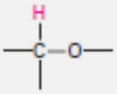
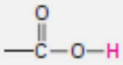


USEFUL DATA FOR REFERENCE

Functional Group	Absorption (cm^{-1})	Intensity
Alkane		
C–H	2850–2960	Medium
Alkene		
=C–H	3020–3100	Medium
C=C	1640–1680	Medium
Alkyne		
≡C–H	3300	Strong
C≡C	2100–2260	Medium
Alkyl halide		
C–Cl	600–800	Strong
C–Br	500–600	Strong
Alcohol		
O–H	3400–3650	Strong, broad
C–O	1050–1150	Strong
Arene		
C–H	3030	Weak
Aromatic ring	1660–2000	Weak
	1450–1600	Medium

Functional Group	Absorption (cm^{-1})	Intensity
Amine		
N–H	3300–3500	Medium
C–N	1030–1230	Medium
Carbonyl compound		
C=O	1670–1780	Strong
Aldehyde	1730	Strong
Ketone	1715	Strong
Ester	1735	Strong
Amide	1690	Strong
Carboxylic acid	1710	Strong
Carboxylic acid		
O–H	2500–3100	Strong, broad
Nitrile		
C≡N	2210–2260	Medium
Nitro		
NO_2	1540	Strong

Type of hydrogen		Chemical shift (δ)
Reference	$Si(CH_3)_4$	0
Alkyl (primary)	$-CH_3$	0.7–1.3
Alkyl (secondary)	$-CH_2-$	1.2–1.6
Alkyl (tertiary)		1.4–1.8
Allylic		1.6–2.2
Methyl ketone		2.0–2.4
Aromatic methyl	$Ar-CH_3$	2.4–2.7
Alkynyl	$-C\equiv C-H$	2.5–3.0
Alkyl halide		2.5–4.0

Type of hydrogen		Chemical shift (δ)
Alcohol		2.5–5.0
Alcohol, ether		3.3–4.5
Vinylic		4.5–6.5
Aryl	Ar–H	6.5–8.0
Aldehyde		9.7–10.0
Carboxylic acid		11.0–12.0