4

Massachusetts Institute of Technology

Organic Chemistry 5.13

September 13, 2006
Prof. Timothy F. Jamison

Notes for Lecture #4

Organic Structure Determination: Infrared Spectroscopy (IR) and MS Fragmentation Patterns

Molecules of the Day

Isoamyl acetate – *banana*
Benzaldehyde – *almonds*
(R)–Limonene – *lemon, lime*
1,4-Diaminobutane – *a.k.a. putrescine*

Imagine that four unlabelled vials, each containing one of our four "Molecules of the Day", had somehow become mixed up. How could IR spectroscopy (instead of your sense of smell) be employed to identify the contents of each vial?

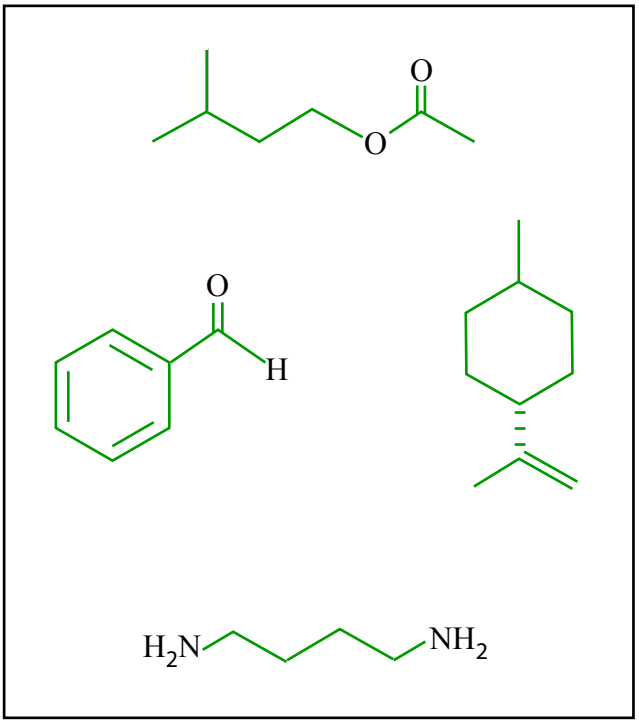


Figure by MIT OCW.

Three-Stage Strategy for Organic Structure Determination

- Determine the **molecular formula** using **elemental analysis** and **mass spectrometry**.
- Identify the **functional groups** using **infrared spectroscopy** (IR) and **nuclear magnetic resonance spectroscopy** (NMR).
- Elucidate the **connectivity** using **^{1}H NMR** ("proton NMR") and **^{13}C NMR** ("carbon NMR") spectroscopy.

Absorption Spectroscopy

Type of Radiation	Energy (kcal/mol)	Frequency	Wavelength	Molecular Interaction
—	—	—	—	Translation
Microwave	0.001 - 1	1 - 400 cm^{-1}		Molecular Rotations *Rotation of the molecular as a whole about its center of mass*
Infrared	1.1 - 11	400 - 4,000 cm^{-1}		Molecular Vibrations *Stretching and binding of bonds*
Visible	50 - 75		400 - 600 nm	Electronic Excitation *Promotion of electrons to higher energy levels*
Ultraviolet	75 - 150		200 - 400 nm	

Infrared Absorption Spectroscopy

4000 cm^{-1}	2000 cm^{-1}	1500 cm^{-1}	400 cm^{-1}
X - H Region	SP Region	X = Y Region	Fingerprint Region
2500 - 4000 cm^{-1}	2000 - 2500 cm^{-1}	1500 2000 cm^{-1}	400 - 1500 cm^{-1}
C-H N-H O-H Stretching	C=C C=N Stretching	C=C C=O C=N Stretching	Single Rond Stretching Bond Bending Polyatomic Vibrations

Figure by MIT OCW.

Infrared Spectra: Tables of Reference

X-H Region

Phenols and Alcohols	ROH	3700-3500 sharp or 3200-3600 broad(H-bonded)
Acids	RCO_2H	2800-3600 very broad
Amides and Amines	RCONHR	
	R_2NH	3300-3500
C-H bonds	C≡C-H	3100-3300
	C=C-H	3000-3200
	C-C-H	2850-3000
	RCHO	2700-2800

sp Region

Acetylenes	C≡C	2100
Nitriles	C≡N	2200
Ketenes	C=C=O	2150
Allenes	C=C=C	1950

Double Bond Region

Alkenes	C=C	1600-1670 weak unless conjugated
Imines	C=N	1600-1700
Nitro	$-NO_2$	1350-1550(two bands)

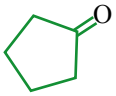
Carbonyl Groups

Note: subtract ca. 30 cm^{-1} for conjugation (e.g. with a double bond or aromatic ring)

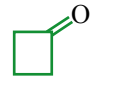
Ketones $R_2C=O$ 1710 (subtract ca. 30 cm^{-1} for conjugation)

Anhydrides	
RC(O)OCOR	1740-1780, 1800-1840 (two bands)
Acid Chlorides	
RCOCl	1790-1815
Esters	
RCO_2R	1725-1755
Acids	
RCO_2H	1700-1725
Amides	
$RCONR_2$	1630-1700
Urethanes	
R_2NCO_2R	1700
Aldehydes	
RCHO	1720-1740

6-membered and larger cyclic ketones 1710



1740



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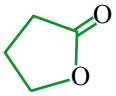

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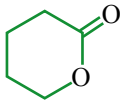

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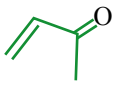

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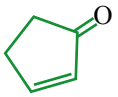

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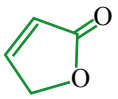

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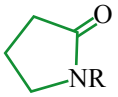
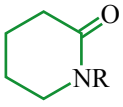


1690-1740



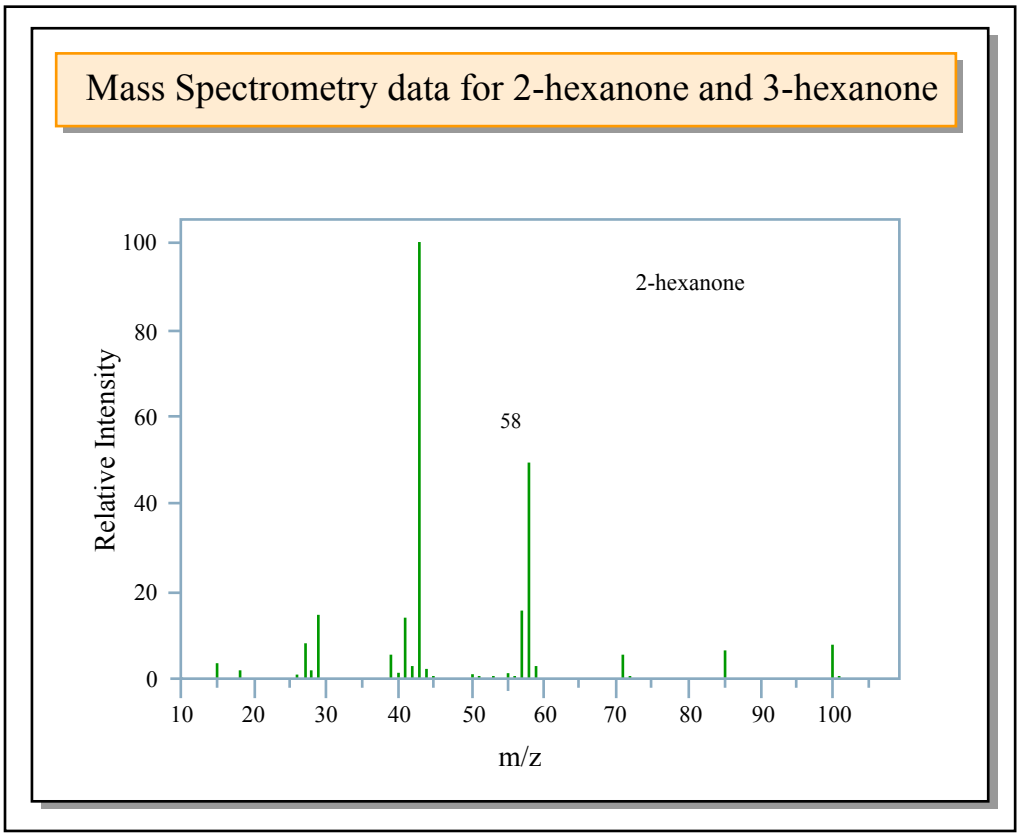
1650

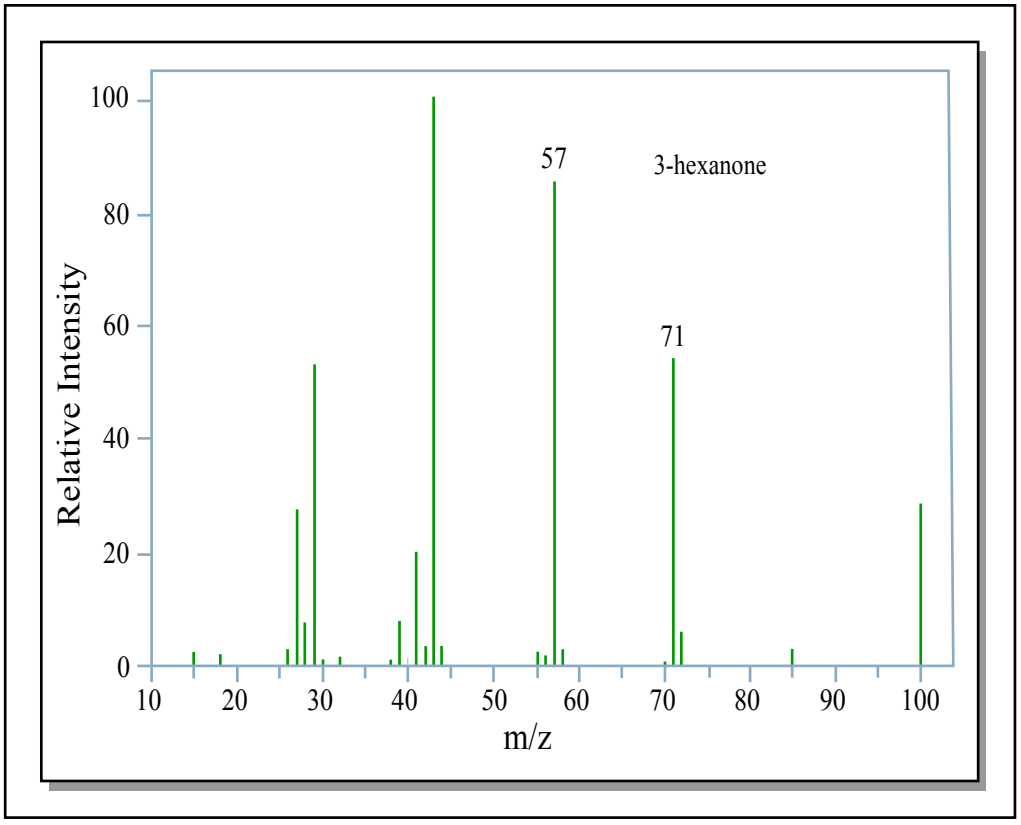
Figure by MIT OCW.

Infrared Spectra of 2-hexanone and 3-hexanone

Images of Infrared Spectra of 2-hexanone and 3-hexanone removed due to copyright restrictions.
Please see: http://www.aist.go.jp/RIODB/SDBS/cgi-bin/direct_frame_top.cgi?lang=eng

Mass Spectrometry data for 2-hexanone and 3-hexanone





Figures by MIT OCW.