CHEM 222 section 01 May change slightly before class.

LECTURE #09 Tues., Oct.02, 2007

Lecture topics & readings

Today's class

- Mass spectrometry (sections 12.1-12. 5)

Before next class

- read section on MS in Bruice

Next class

- start NMR (Ch.13)

(1) **Helpful website for spectroscopy topics: Michigan State University**
http://www.cem.msu.edu/~reusch/VirtualText/Spectrpy/spectro.htm#contnt

Our toolbox of characterization techniques

- Set of complementary techniques: separate expts; data used together
- Each reveals characteristic features of molecular structure
  - *e.g.*, functional groups, types of hydrogens, molecular mass

	UV/Vis	IR	NMR	MS
Underlying phenomenon	electronic excitation	vibrational excitation	nuclear spin excitation	molecular fragmentation
Signal observed	λ of light absorbed (in nm)	ν of IR absorbed (in cm^{-1})	^1H chemical shift, δ *cf* TMS (in ppm)	Mass/charge ratio of fragments (m/z)
Reveals	**Functional groups**	**Functional groups**	**Types of Hs** (⇨build up chains)	**Mass of molecule** and…
…specifically	▪ π-bonds ▪ conjugation	▪ O-H, N-H ▪ C=O ▪ C=C, C≡C ▪ *etc…*	▪ proximity to EWGs (via δ) ▪ # Hs on adj. C (via multiplicity)	▪ Halogens ▪ CH_3, Ph,…
Intensity of signal	▪ $A = \varepsilon lc$ ▪ ε_λ depends on molecule AND solvent	▪ s,m,w ▪ br *vs* sh ▪ not quantitative	Integration reveals # of Hs of each type	Useful in advanced applications (not for us)

Organic structure determination: Strategy

Questions guiding our experiments & data analysis:

EA:	Which elements are present? What is the empirical formula? Chem 205…
Mass spec:	What is the molecular size & formula?
UV/Vis:	Is a π system present? & Is it conjugated?
IR:	What functional groups are present?
NMR:	What is the carbon-hydrogen framework?

Note: we didn't cover these from simplest → most complex
…in an attempt to match the order of your usage in labs

Organic structure determination: the natural 1st step

Things you learn from molecular formulae

Degree of unsaturation:

 # elements of unsaturation = total # of π-bonds + rings
$= \frac{1}{2}(2C + 2 - H)$

For compounds containing heteroatoms:

- count halogens as H: they use up 1 bond to *C*
- ignore oxygens: can add O to chain without changing # C/H
- count N as half a *C*: midchain $-CH_2-$ units *vs.* -NH- units…

Given: data on spearmint oil

- EA ⇨ empirical formula = $C_{10}H_{14}O$
- MS ⇨ molecular mass ≈ 150 g/mol
- IR ⇨ intense absorption 1690 cm^{-1}

What can we say so far about its structure?

Organic structure determination: the natural 1st step

Things you learn from molecular formulae

Degree of unsaturation:

 # elements of unsaturation = total # of π-bonds + rings
= ½ (2C + 2 – H)

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What can we say so far about its structure?

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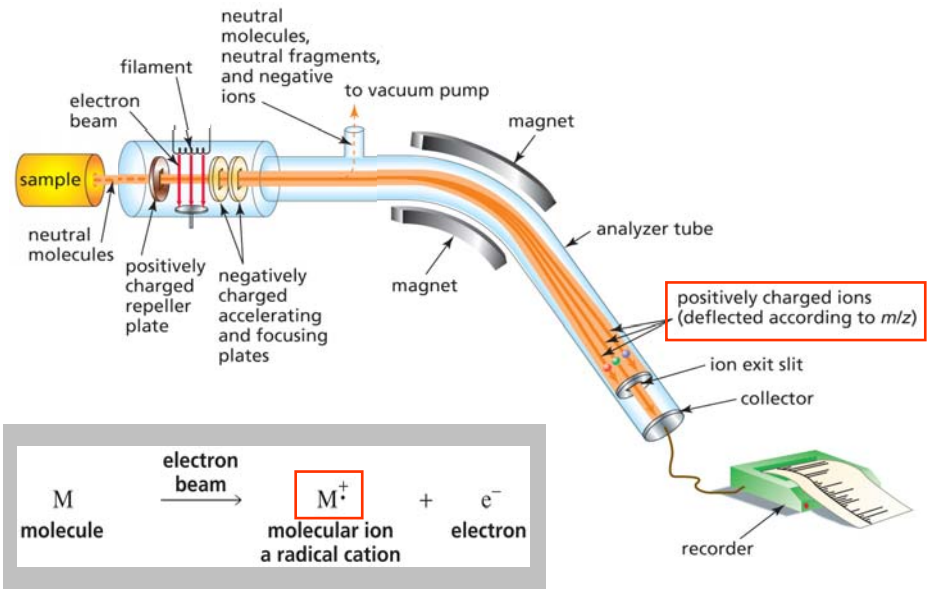
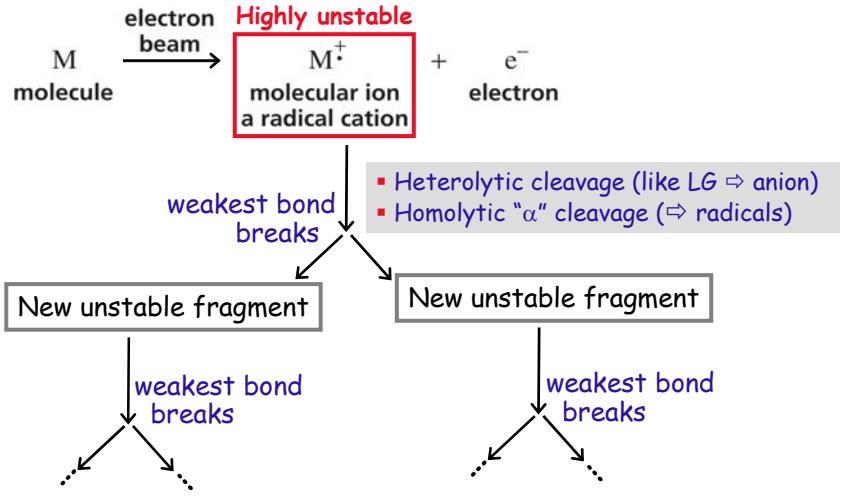
12.1 Mass spectrometry = MS, or *mass spec*

Bruice Fig.12.1

A schematic mass spectrometer:



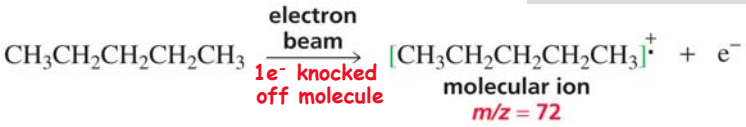
Molecular fragmentation: the basic idea

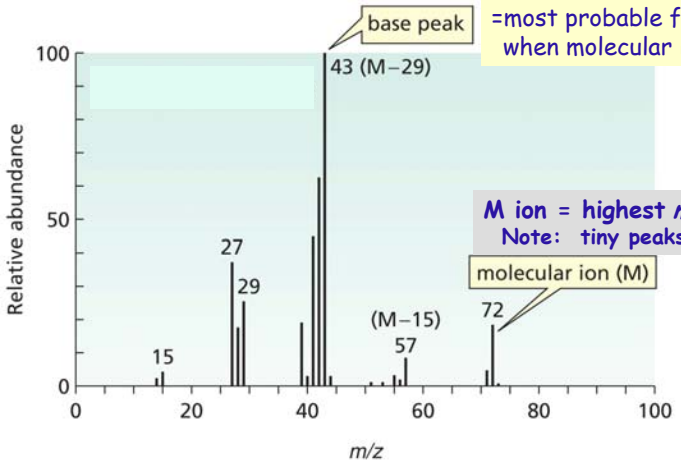


▪ Detector only senses fragments carrying + charge (= one per pair!)
  • more unstable fragment ⇨ less reaches detector ⇨ smaller peak

Mass spectrum of n-pentane

Key piece of data: "M ion"
molecular ion ⇨ reveals MM !

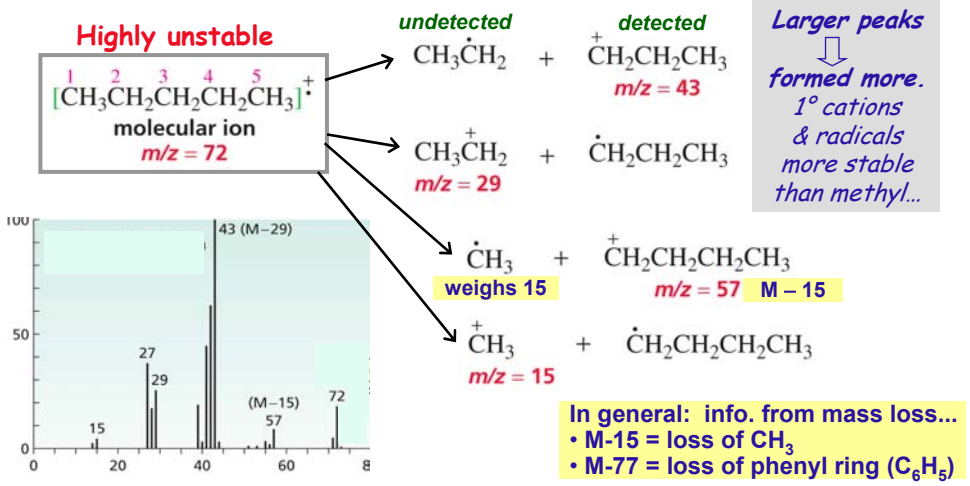




Bruice Fig.12.2

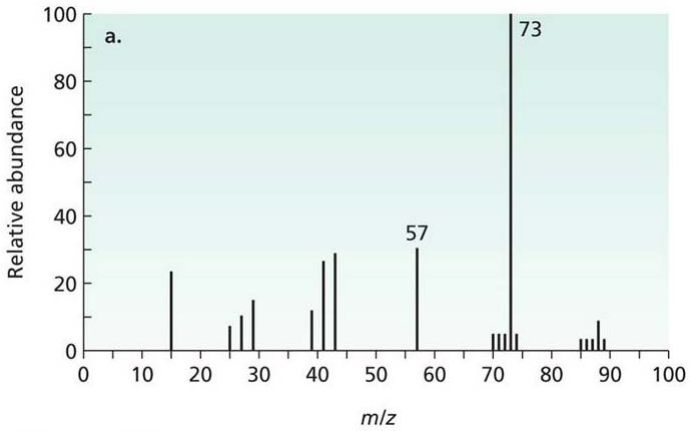
Fragmentation patterns of alkane radical cations

- Molecular ion: a C-C bond somewhere has only 1 e-…
- Fragmentation: C-C bond breaks ⇨ 1 radical & 1 carbocation
  - More stable products form faster (easier ‡ to form…) ⇨ larger peaks
  - Recall carbocation & radical stabilities: 3° > 2° > 1°…



Which compound is this spectrum from? Bruice Ex.10

1-methoxybutane 2-methoxybutane 2-methoxy-2-methylpropane



12.3 Isotope patterns reveal: type & # of atom(s)

For elements with 2 common isotopes: Cl, Br & sometimes C, N

- NOT: H, F, I ~1 isotope
- NOT: S 4 isotopes

carbon	^{12}C 98.89%	^{13}C 1.11%	
nitrogen	^{14}N 99.64%	^{15}N 0.36%	
chlorine	^{35}Cl 75.77%		^{37}Cl 24.23%
bromine	^{79}Br 50.69%		^{81}Br 49.31%
	Most molecules M	M+1	M+2

Table 12.2

Look at:
relative intensity of M+1 (M+2) *vs.* M ion

Works if no Ns present

 # C atoms = $\dfrac{\text{relative int. of M+1}}{0.011 \times (\text{relative int. of M})}$ ← *Int. if 1 C per molecule…*

Most useful for identifying presence of Cl, Br:

- if M+2 : M = 1:3 ⇨ molecule contains 1 Cl
- if M+2 : M = 1:1 ⇨ molecule contains 1 Br

Remember: halogens…
- no key IR signature
- no strong UV band

- So far: have seen low resolution spectra…

12.4 High resolution MS ⇨ exact mass ⇨ formula…

Compounds with a low-resolution M-ion peak at m/z = 122					
Exact mass	122.1096	122.0845	122.0732	122.0368	122.0579
Molecular formula	C_9H_{14}	$C_7H_{10}N_2$	$C_8H_{10}O$	$C_7H_6O_2$	$C_4H_{10}O_4$

Table 12.3

Isotope	Mass
^{1}H	1.007825 amu
^{12}C	12.00000 amu
^{14}N	14.0031 amu
^{16}O	15.9949 amu
^{32}S	31.9721 amu
^{35}Cl	34.9689 amu
^{79}Br	78.9183 amu

- Computer programs available to researchers can determine molecular formula from exact molecular mass (M ion peak)

- In this course: you will be told "MS revealed that the molecular formula = …"

12.5 Fragmentation patterns of functional groups

General trends:

- e^- ejected from lone pair if present, otherwise from a bond…
- Molecular ion (a radical cation) is VERY unstable
- Weakest bond will break, leaving another unstable species…

For alkyl halides, ethers, alcohols…

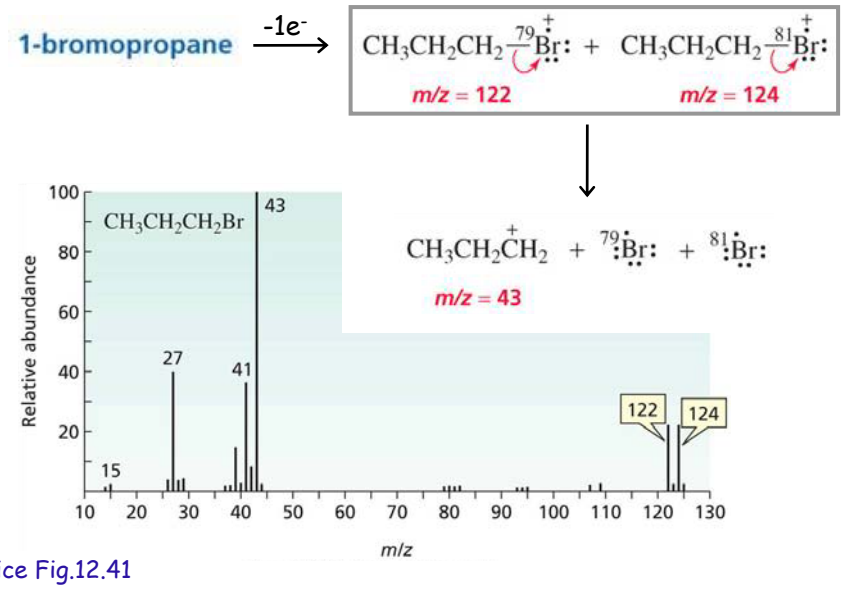
- C-X bonds break heterolytically **(X = more electronegative: O, halide)**
- C-E bonds break homolytically **(E = similar electronegativity)**
- Bonds most likely to break are:
  a) weakest bonds
  b) leading to most stable C+

When we interpret mass spectra, look for:

- Molecular ion ⇨ MM of compound
- Isotope patterns ⇨ presence of halogens, number of carbons (if no N)

Halides:

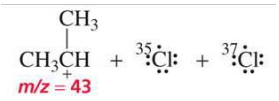
- heterolytic C-X cleavage occurs *(like LG leaving…)*



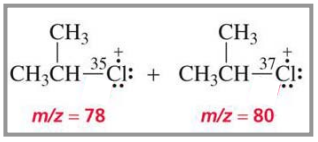
Bruice Fig.12.41

Chlorides: also see C-C cleavage

- Bond strengths: C-C ≈ C-Cl >> C-Br

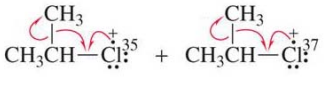


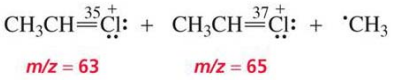
heterolytic C-X cleavage

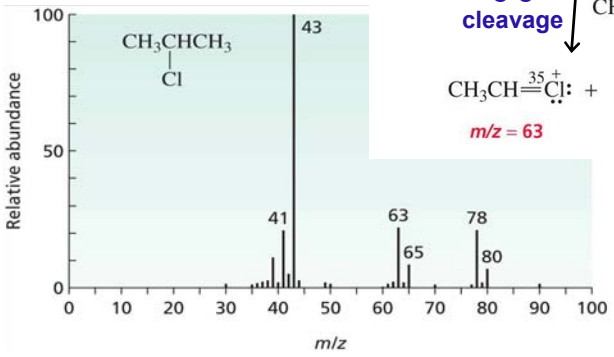


3 : 1

homolytic C-C cleavage



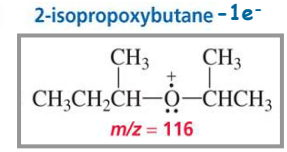




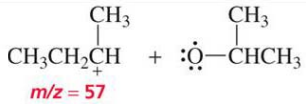
Bruice Fig.12.5

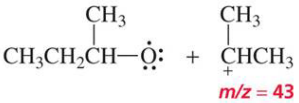
Ethers: similar to halides

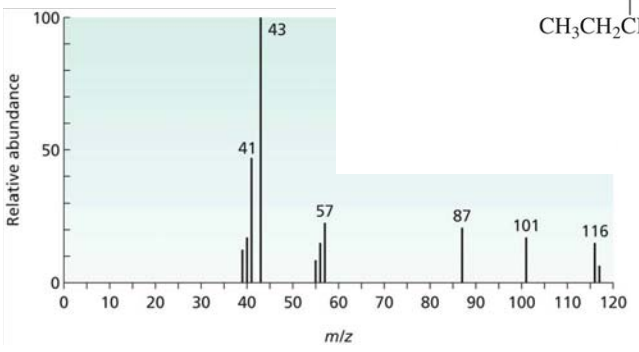
- C–O heterolytic cleavage *OR* C–C homolytic cleavage



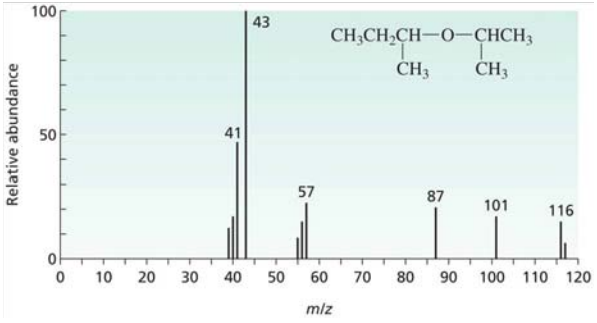
heterolytic C–O cleavage



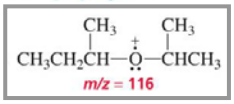




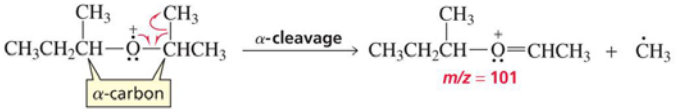
Bruice Fig.12.6



2-isopropoxybutane – 1e⁻



Molecular ion's C-C homolytic cleavage options:

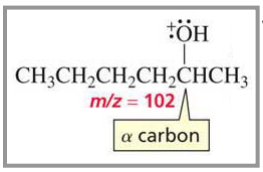


(17)

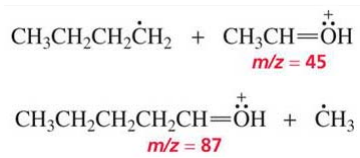
Alcohols: M ion so unstable, can be hard to see the peak…

- C–C homolytic cleavage (α-cleavage) dominates

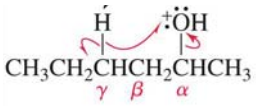
2-hexanol – 1e⁻



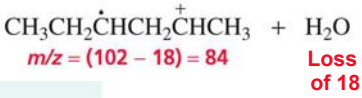
FAST
α-cleavage

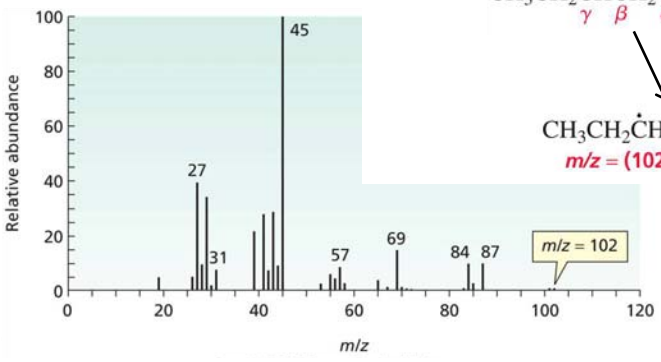


OR…



a double
α γ -cleavage

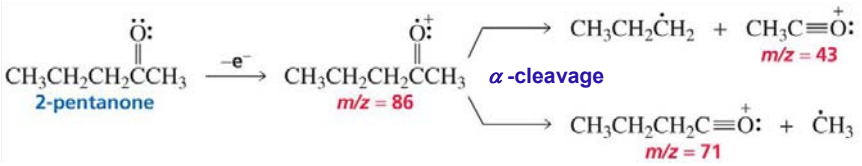




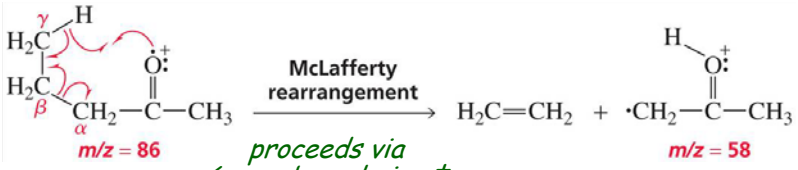
Bruice Fig.12.8

Ketones: M ion relatively stable ⇨ large M peak…

- *C–C* homolytic cleavage adjacent to *C=O*



- Also see: McLafferty rearrangement -- if γ Hs are present

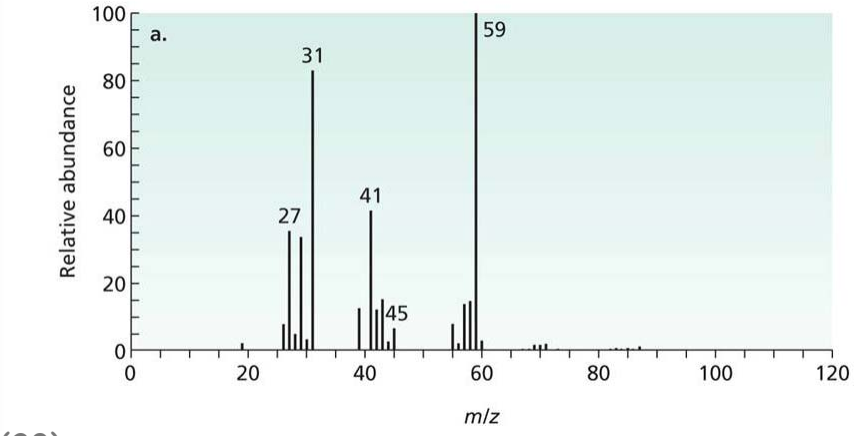


proceeds via 6-membered-ring ‡

(19)

Which compound is this spectrum from? Bruice Ex.15

Two products are obtained from the reaction of (Z)-2-pentene with water and a trace of H_2SO_4. The mass spectrum of ONE of the two products is shown below. Which compound is it?



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