

Figure Number: 12.02
Bruce
Organic Chemistry 5e

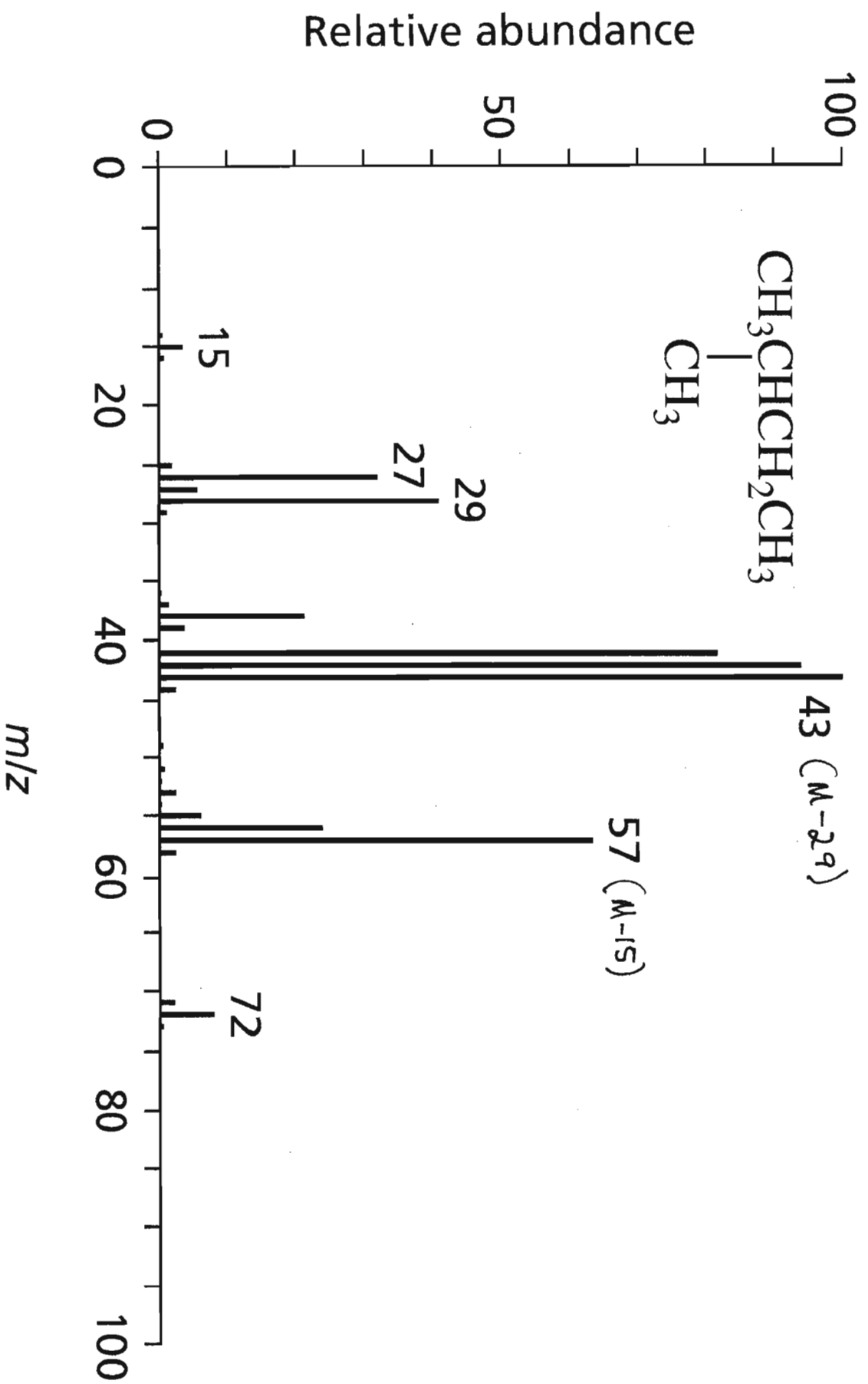


Figure Number: 12.03
Bruice
Organic Chemistry 5e



Isotopes + Mass Spec.

 $^{12}\text{C} = 12.000 \text{ amu}$ $^1\text{H} = 1.007825 \text{ amu}$ 

pentane

72.0939 amu

low res: 72

high-res. mass spec. can measure mol. mass
to 4 decimal places.

low res - molecular ion @ 122 amu

high res.

 C_9H_{14} 122.1096 $\text{C}_7\text{H}_{10}\text{N}_2$ 122.0845 $\text{C}_8\text{H}_{10}\text{O}$ 122.0732

etc.

$M+1$ peak - due to natural presence of ^{13}C
98.89% of carbons are ^{12}C
1.11% of carbons are ^{13}C

can be used to calculate # of C's

$$\# \text{C's} = \frac{\text{rel. intensity of } M+1}{(0.011 \times \text{rel. intensity of } M)}$$

$$\text{For our sample spectrum} = \frac{0.52}{(0.011 \times 18.56)} =$$

Other useful isotopes:

Cl: $M+2$ peak that is $1/3$ height of M

Br: $M+2$ peak \sim same height as M .

Table 12.2 The Natural Abundance of Isotopes Commonly Found in Organic Compounds

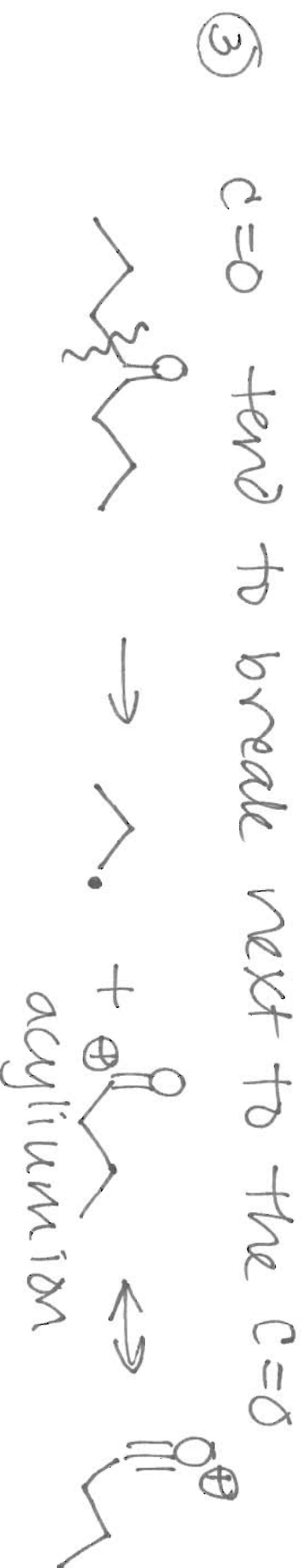
Element	Natural abundance		
Carbon	^{12}C 98.89%	^{13}C 1.11%	
Hydrogen	^1H 99.99%	^2H 0.01%	
Nitrogen	^{14}N 99.64%	^{15}N 0.36%	
Oxygen	^{16}O 99.76%	^{17}O 0.04%	^{18}O 0.20%
Sulfur	^{32}S 95.0%	^{33}S 0.76%	^{34}S 4.22%
			^{36}S 0.02%
Fluorine	^{19}F 100%		
Chlorine	^{35}Cl 75.77%		^{37}Cl 24.23%
Bromine	^{79}Br 50.69%		^{81}Br 49.31%
Iodine	^{127}I 100%		

Fragmentation:

- ① loss of CH_3 or CH_2CH_3 v. common
(-15) (-29)

Think about the stability of the resulting new fragment (recall cation stability).

- ② breaking a C-tertiary bond
(they tend to be weaker than C-C bonds)
anything that isn't C or H.

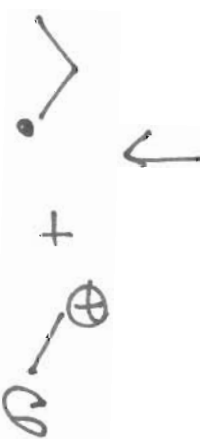


Alkyl halides, alcohols, ethers:

- heterolytic cleavage
(betw. atoms of diff. χ)



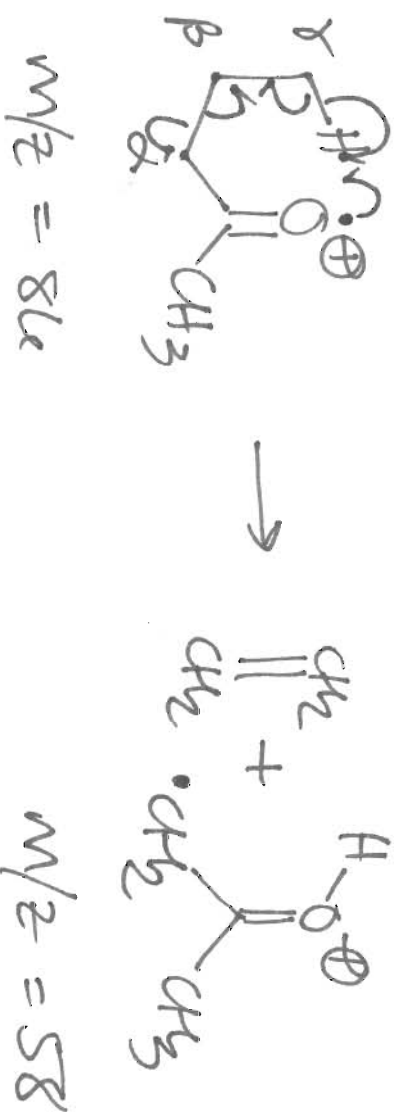
- homolytic cleavage
(betw. atoms of similar χ)



McLafferty Rearrangement - C=O compounds
w/ γ H's

* the carbon bearing the functional group
is the α carbon.

$\alpha, \beta, \gamma, \delta, \epsilon, \dots$



- movement of an e^- pair
- ↘ movement of a single e^-

Summary:

- only \oplus charged fragments are detected
- base peak, molecular ion peak
- purpose of $M+1$, $M+2$ (isotope effects)
- low res vs high res
- concept of fragmentation
- McLafferty rearr.
- $M-15$ lose CH_3
- $M-29$ lose CH_2CH_3