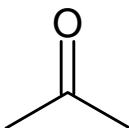


# Chapter 5. Mass spectrometry

ionization and fragmentation



- which fragmentations?

mass and frequency,  $m/z$  and count rate

Reading:

Pavia

Chapter 8

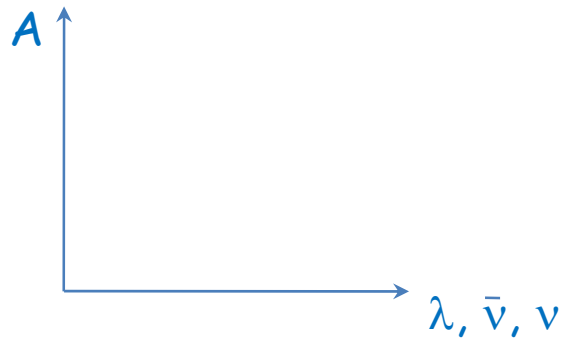
Don't need 8.3 B-D, 8.4 B-D

Use the text to clarify what's covered on the slides.

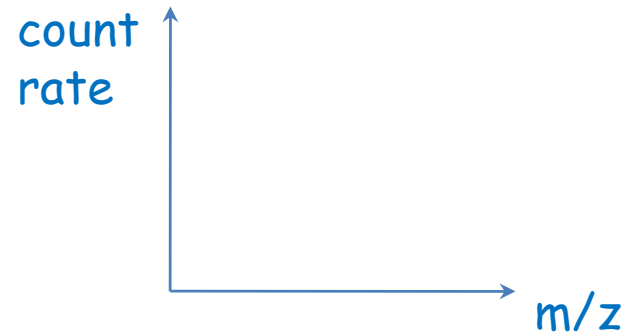
# 1. General

- not a spectroscopic technique (no absorption of radiation)

spectroscopy



spectrometry



count rate: usually in %

: "relative abundance"

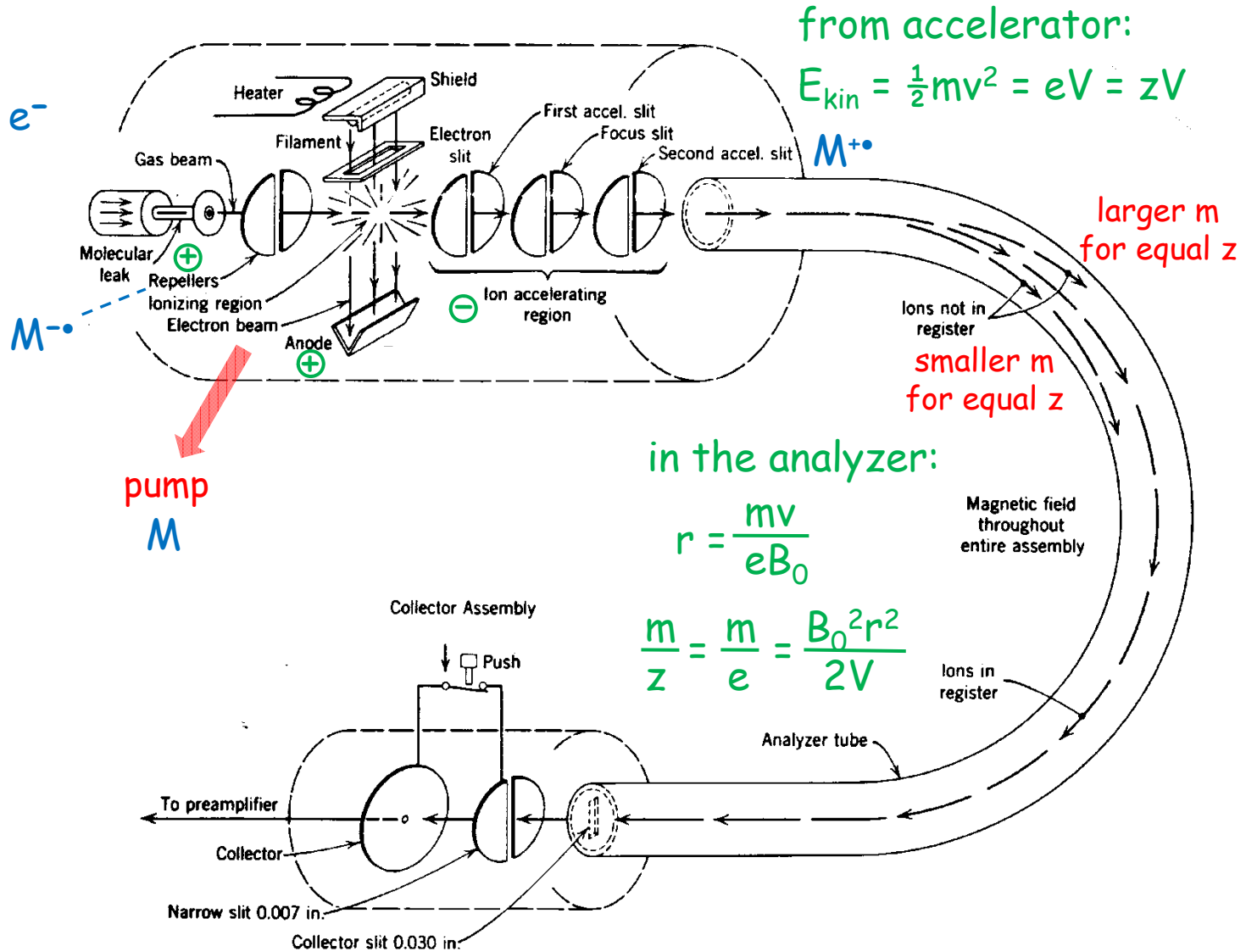
m/z: mass-to-charge ratio, here  $z = 1$

and: sample is often destroyed through fragmentation

# 2. Spectrometer

- simplest version: electron ionization, magnetic sector mass analyzer

desired event:



### 3. Mass spectrum

- from electron ionization (EI)



-  $M^{+\bullet}$ : radical cation (or cation radical)

: often incorrectly called "molecular ion,  $M^+$ "

: often the last peak in the spectrum, largest  $m/z$ : gives molar mass

- most abundant fragment (relative 100%): "base peak"

- other peak intensities given as % of base peak

- fragment "ions"

- "isotope peaks"

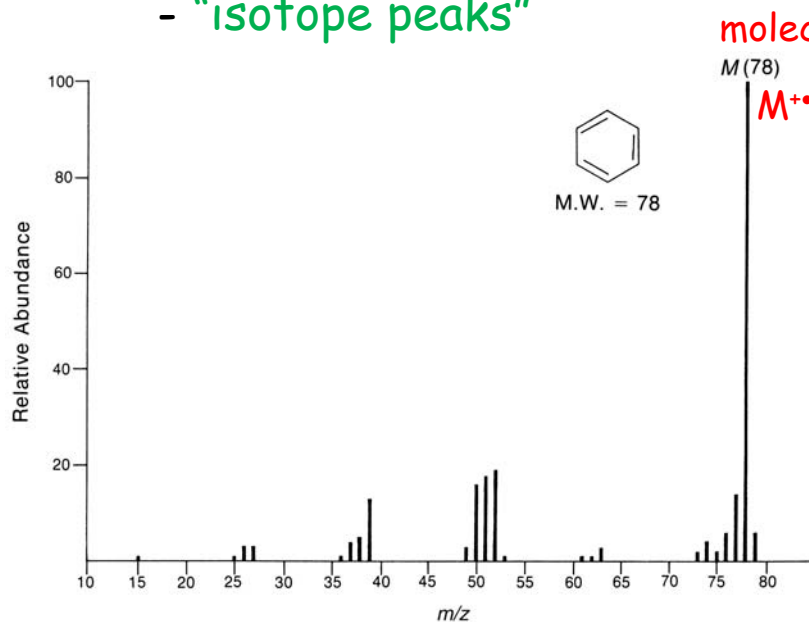


Figure 8.38

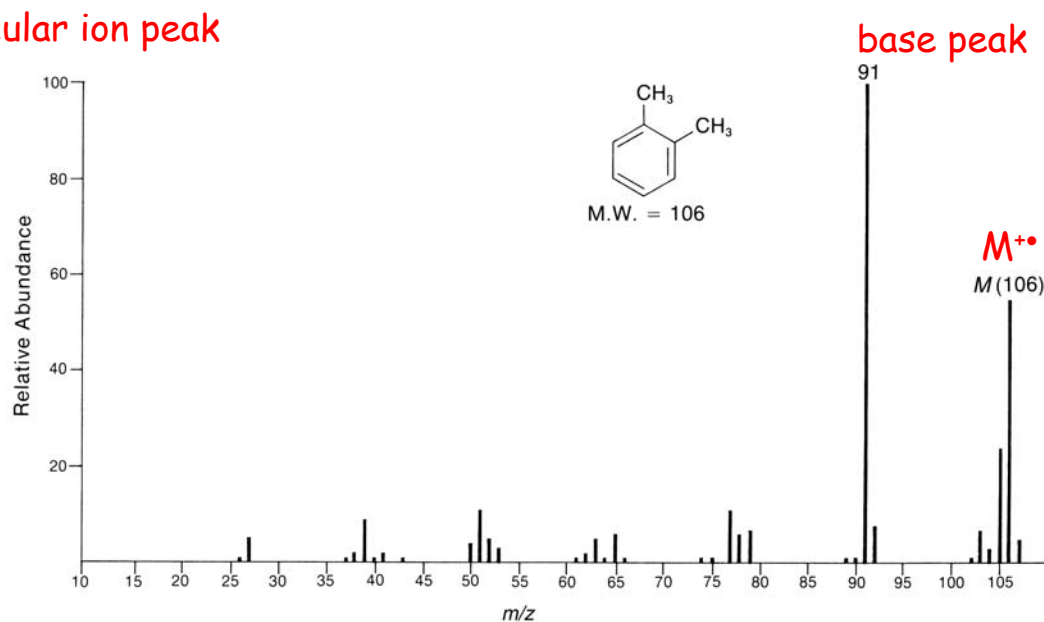


Figure 8.40

# 4. Molecular ion, $M^{+\bullet}$

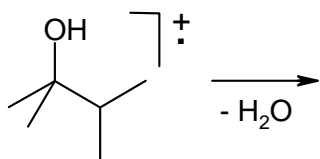
## Difficulties:

-  $M^{+\bullet}$  is not always the last peak in the mass spectrum

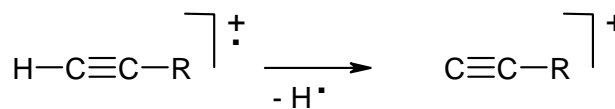
- last  $m/z$  can be

a) smaller than the molar mass

:  $M^{+\bullet}$  is too unstable, fragments before it reaches the detector



detected:  $M^{+\bullet} - 18$



detected:  $M^{+\bullet} - 1$

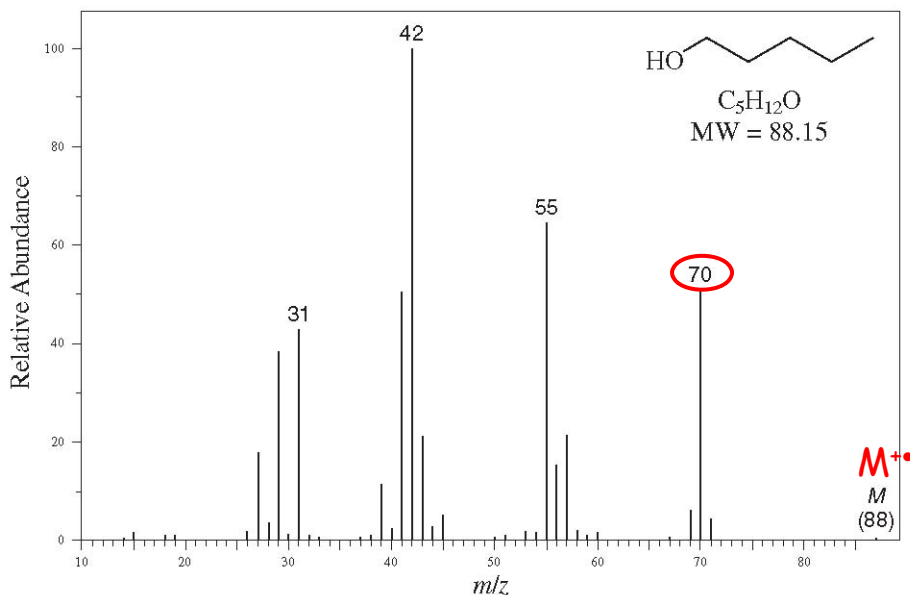


Figure 8.48

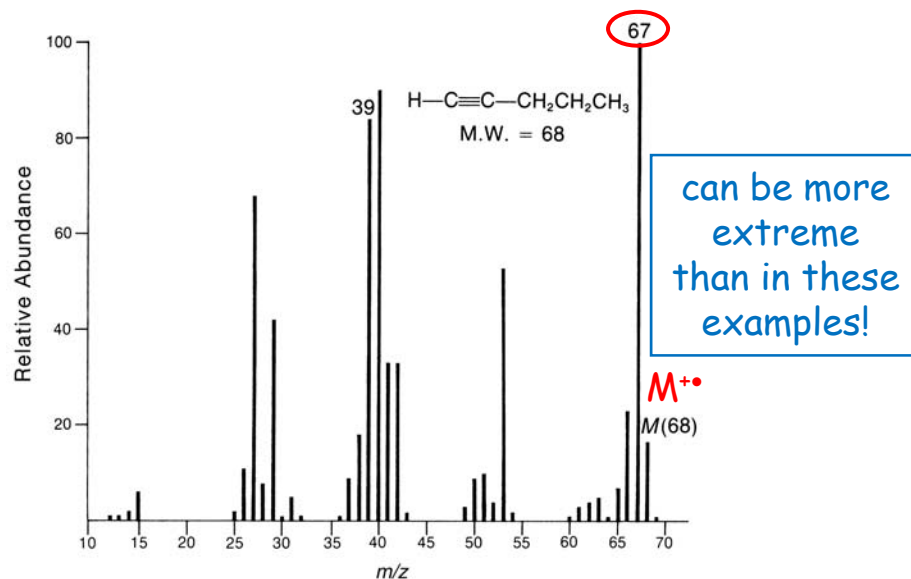


Figure 8.36

## 4. Molecular ion, $M^{+\bullet}$ , continued

### Difficulties:

- $M^{+\bullet}$  is not always the last peak in the mass spectrum
- last  $m/z$  can be

b1) greater than the molar mass, first case

: isotopes of higher mass are present in  $M^{+\bullet}$

$^{12}\text{C}$        $^{13}\text{C}$   
99%      1%

$^{35}\text{Cl}$        $^{37}\text{Cl}$   
76%      24%

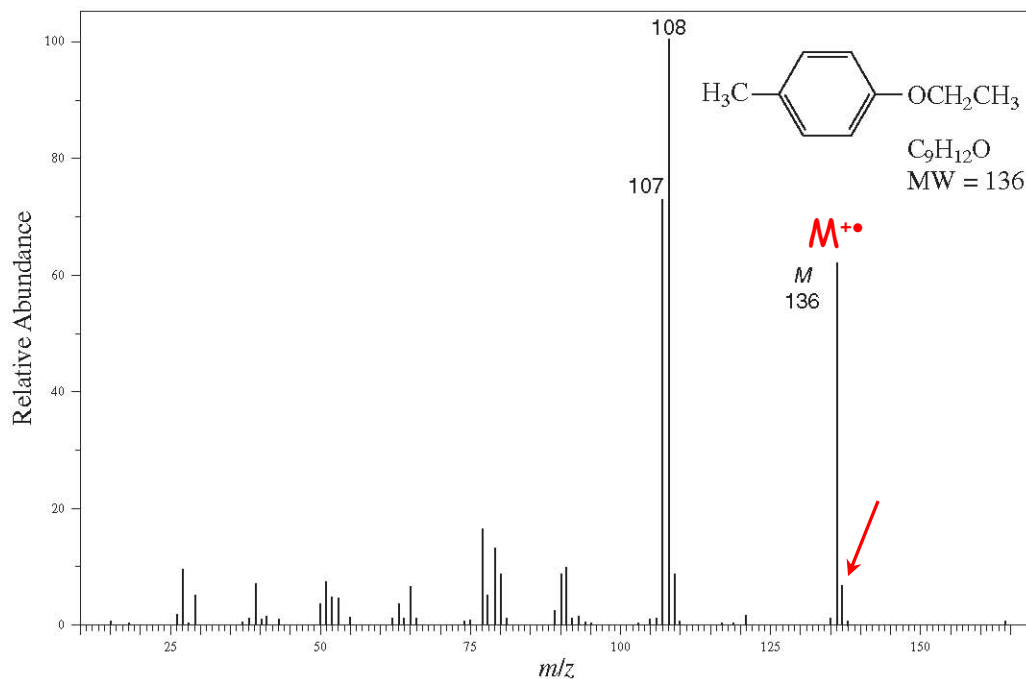


Figure 8.57

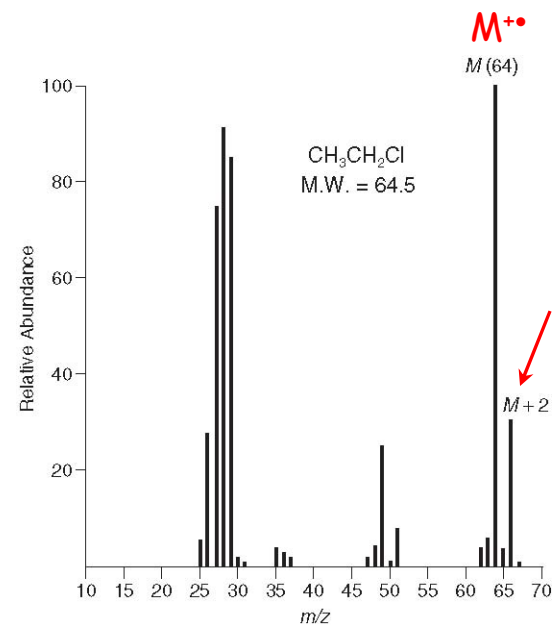


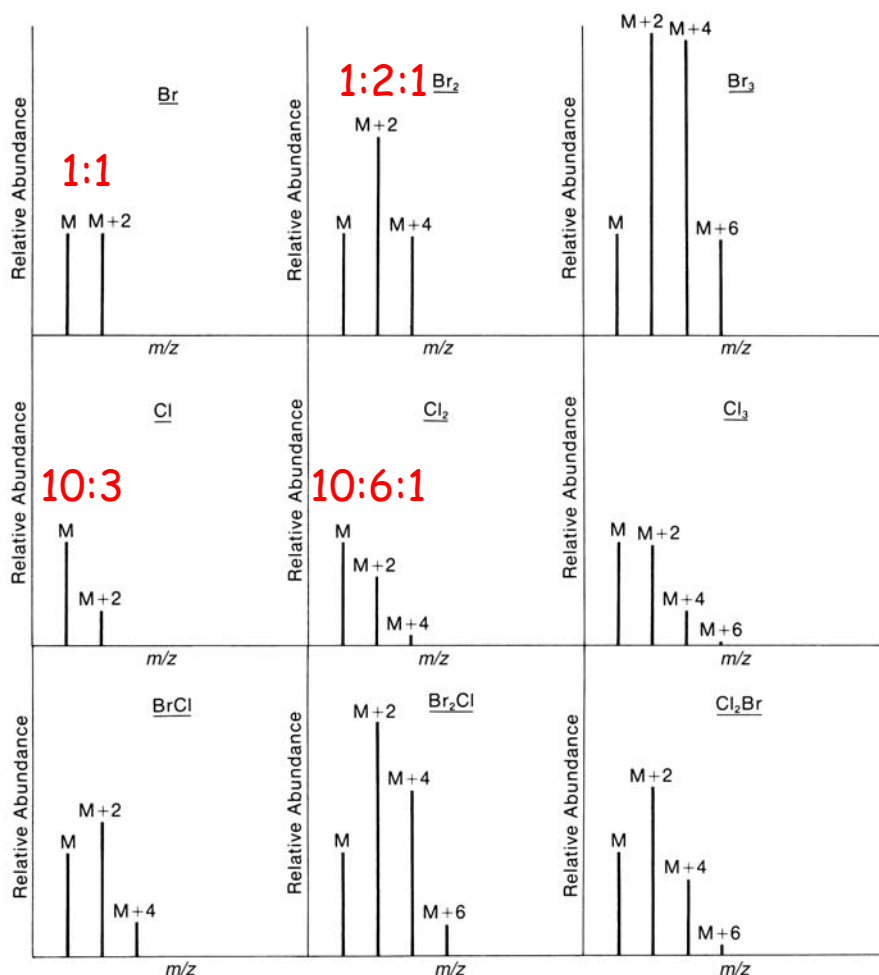
Figure 8.82

# 4. Molecular ion, $M^+$ , continued

- isotope peak patterns for Cl- and Br-containing ions

Figure 8.18

Table 8.8



Br

1:1 is 100 to 98 Figure 8.80

Br<sub>2</sub>

1:2:1 is 51 to 100 to 49  
or 100 to 195 to 95

Cl

10:3 is 100 to 33

Cl<sub>2</sub>

10:6:1 is 100 to 65 to 11

## 4. Molecular ion, $M^{+\bullet}$ , continued

### Difficulties:

- $M^{+\bullet}$  is not always the last peak in the mass spectrum
- last  $m/z$  can be

b2) greater than the molar mass, second case

: M collects a proton:  $M^+ + 1$

: sometimes for amines, hydrazines, azo compounds; carbonyls

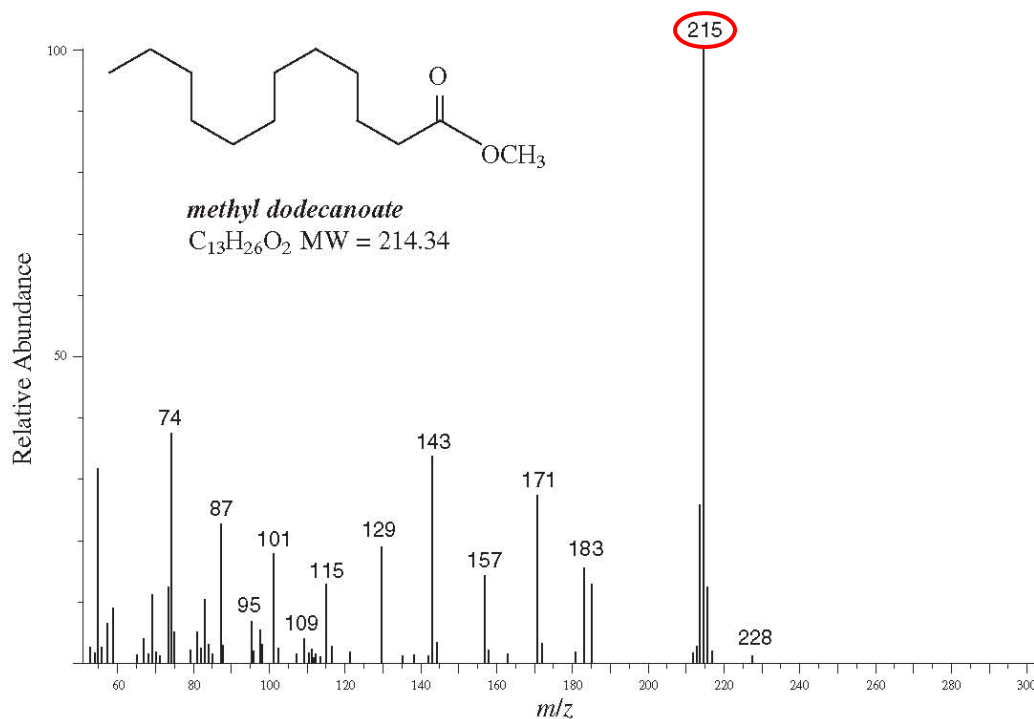


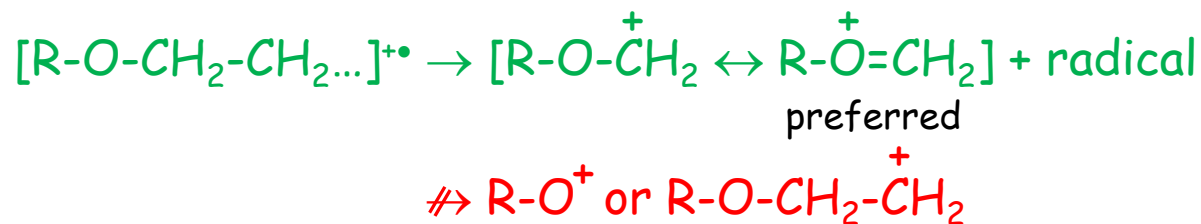
Figure 8.14



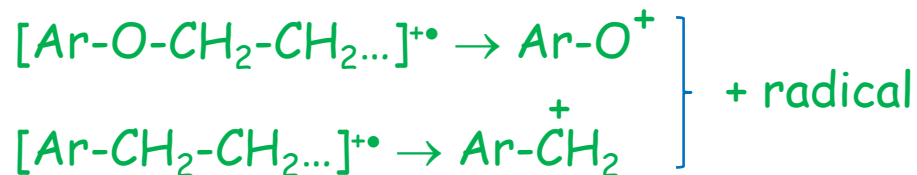
## 5. Fragmentation considerations

### a) Energy

- weak bonds break more readily
- fragmentations that lead to stabilized species are preferred
  - electron octet
  - resonance
  - charge on the most likely atom



but



resonance  
stabilization

## 5. Fragmentation considerations continued

b) Ions with an odd or even number of electrons

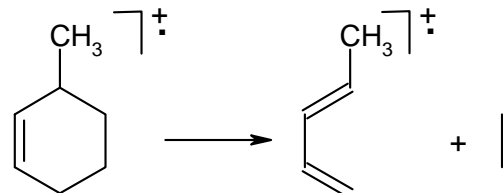
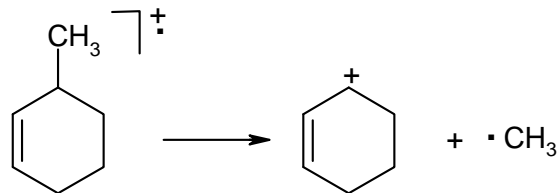
### I. Odd electron ions ( $OE^{\bullet+}$ )

- possess an unpaired electron, such as  $M^{\bullet+}$
- eliminate radicals  $R^{\bullet}$  or neutral, closed-shell species  $N$

(often small, stable molecules:



$OE^{\bullet+}$



### II. Even electron ions ( $EE^+$ )

- possess all paired electrons, such as  $M^+$
- eliminate neutral, closed-shell species  $N$



+ and • balance!

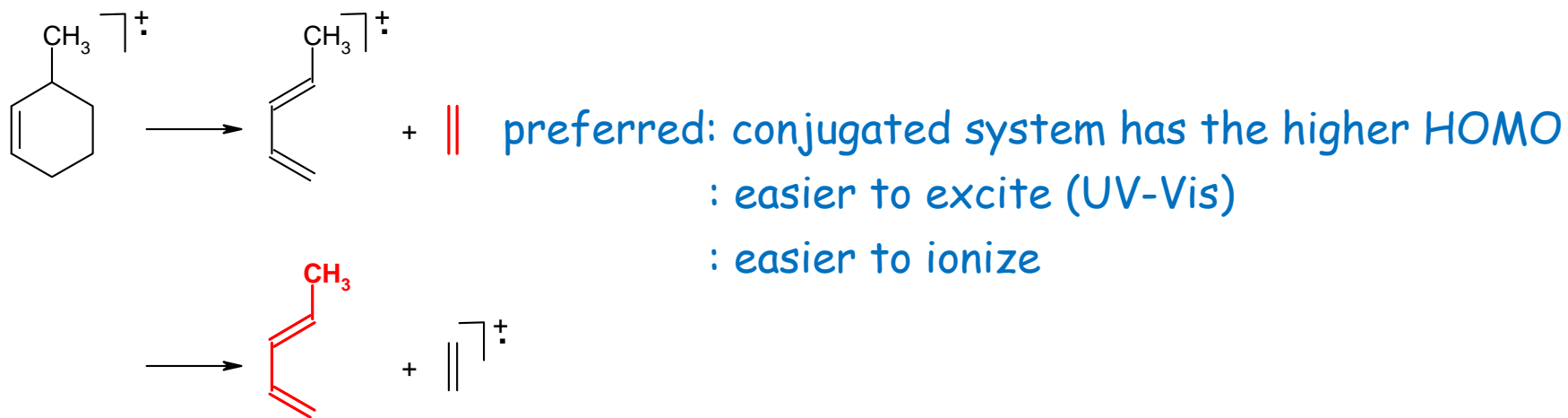
## 5. Fragmentation considerations continued

c) Ionization energy, IE

- follows from



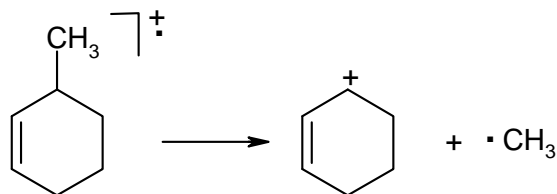
- fragment with the smallest IE carries the charge (Stevenson's rule)



## 5. Fragmentation considerations continued

Important to remember:

- ionization is the first event: fragmentations start from  $M^{+\bullet}$ , not from  $M$
- $+$  and  $\bullet$  balance
- H atom balance: it might be good to draw all H not to forget any
- mass balance
- $R^\bullet$  and N are not detected, do not give signals:  
⇒ masses for  $R^\bullet$  and N are listed differently:



(96)

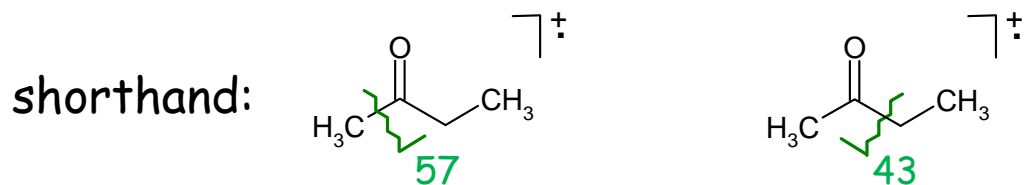
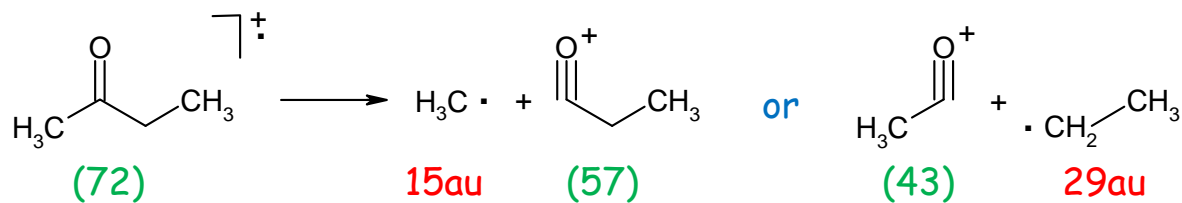
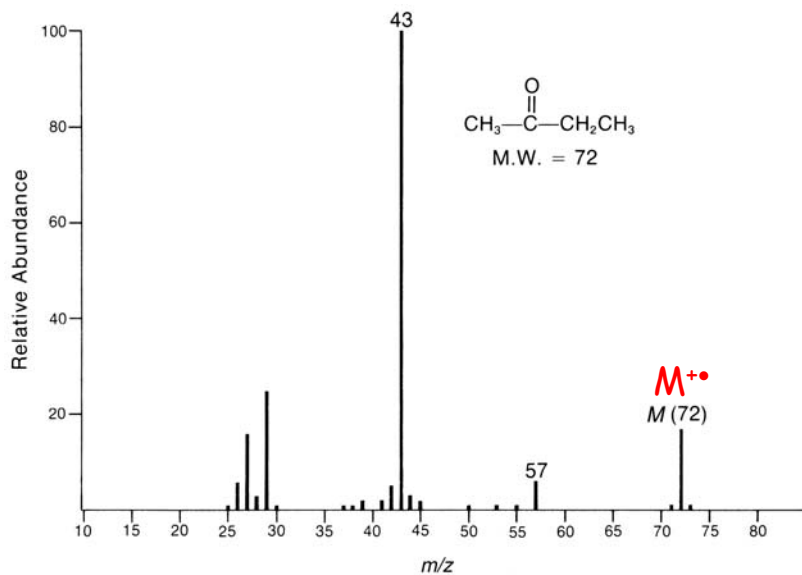
(81)

15au

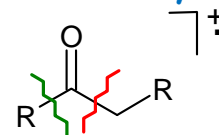
indicating that for this particular one-molecule fragmentation there is no signal at  $m/z$  15

# 6. Fragmentations

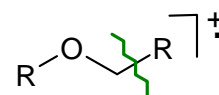
## a) $\alpha$ -cleavage



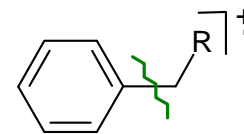
- for carbonyls



- for R-X-R, X = O, N, S



(- for phenyl)

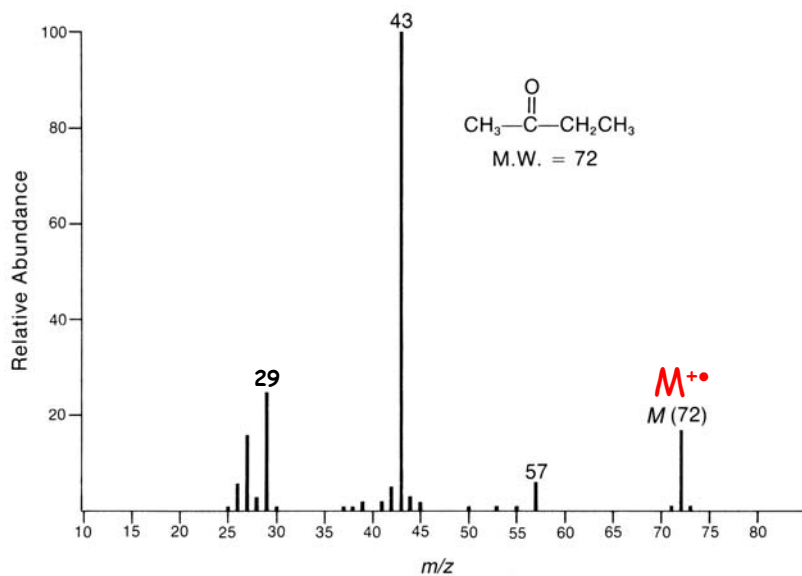


Which is more likely?

Figure 8.60

# 6. Fragmentations

## a) $\alpha$ -cleavage continued



## decarbonylation

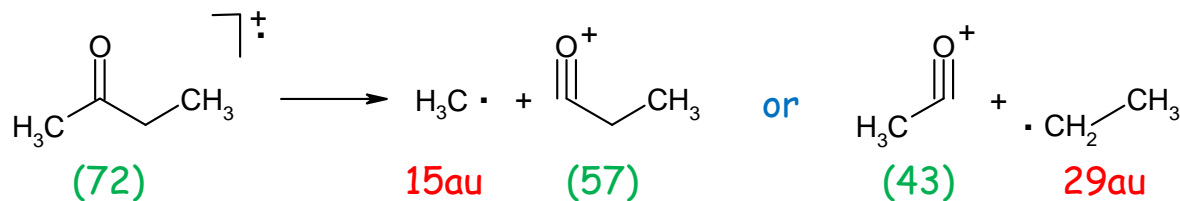
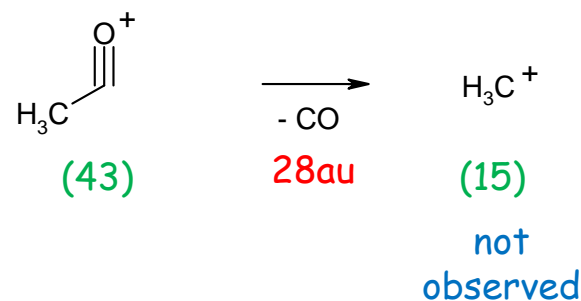
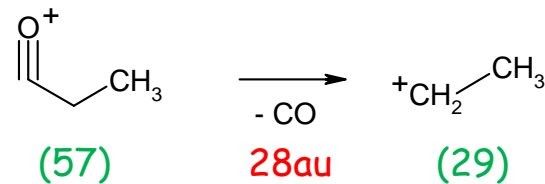


Figure 8.60

# 6. Fragmentations continued

b) benzyl and allyl cleavage - for aromatic compounds  
 - for unsaturated compounds

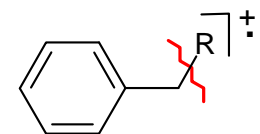


Figure 8.44

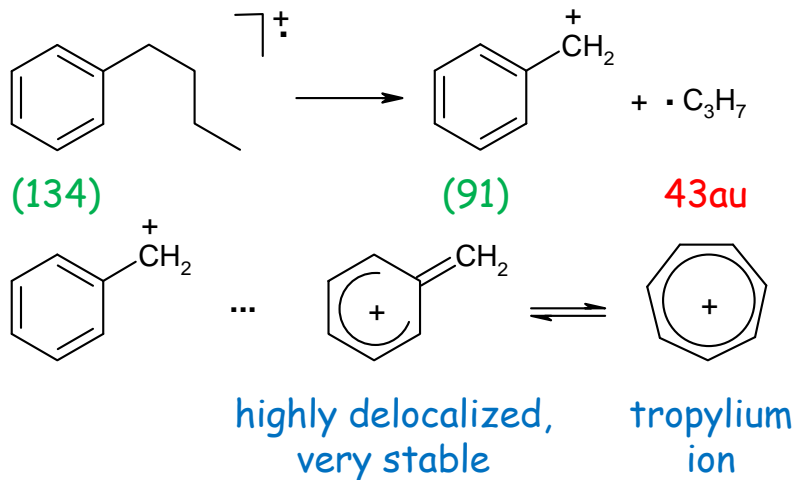
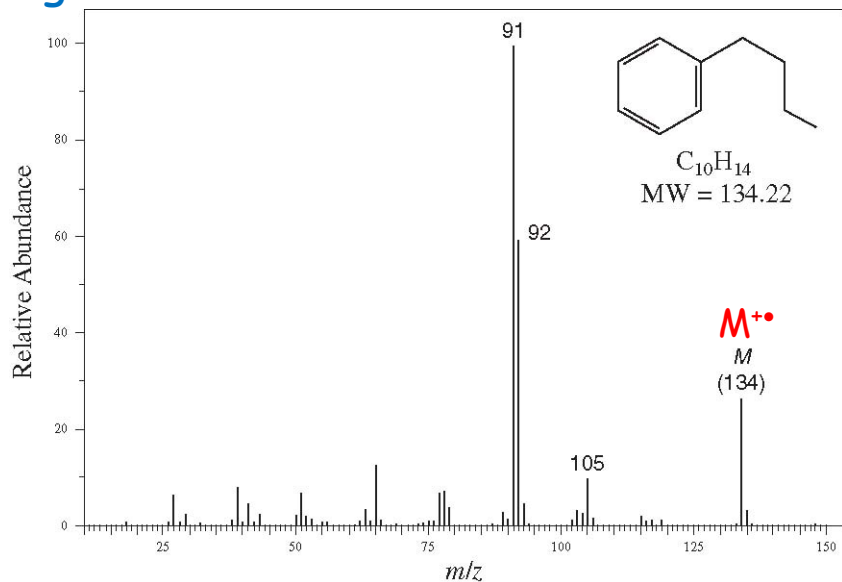
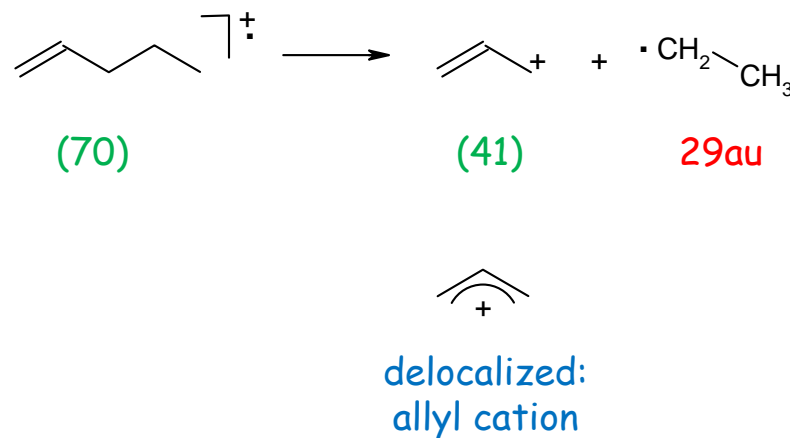
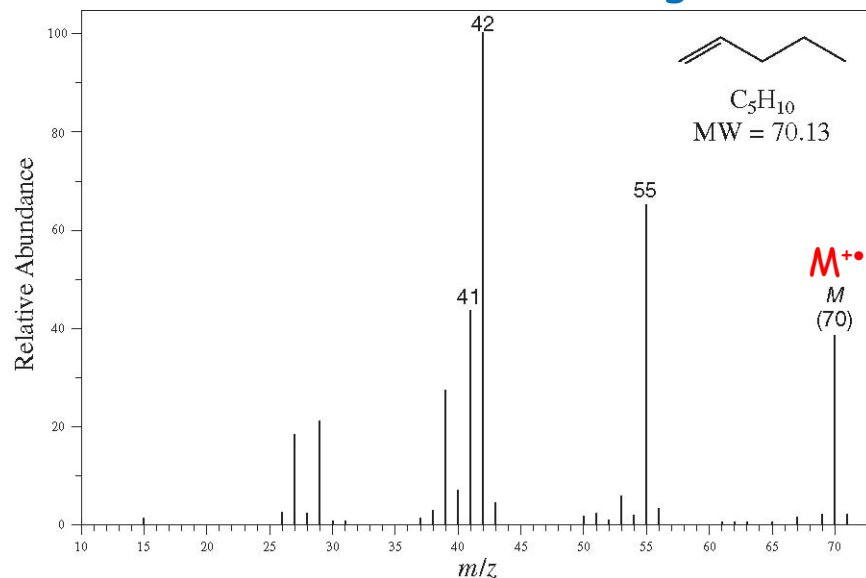


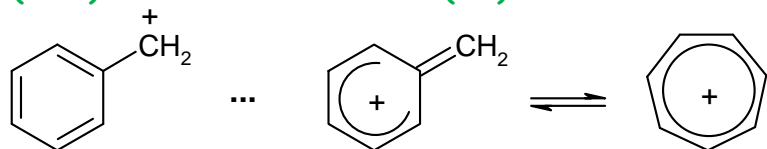
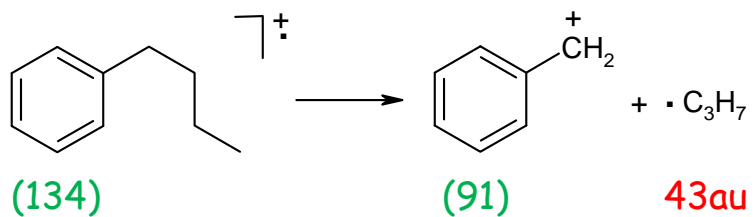
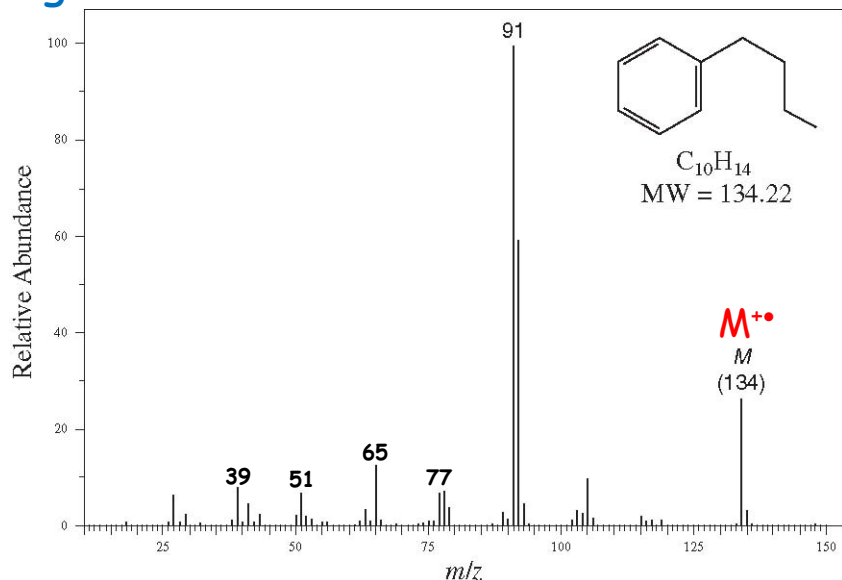
Figure 8.31



# 6. Fragmentations continued

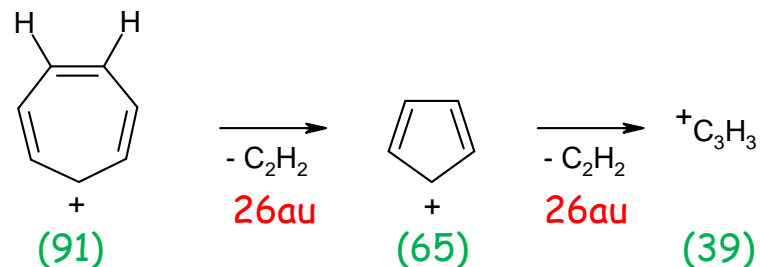
## b) benzyl cleavage continued

Figure 8.44

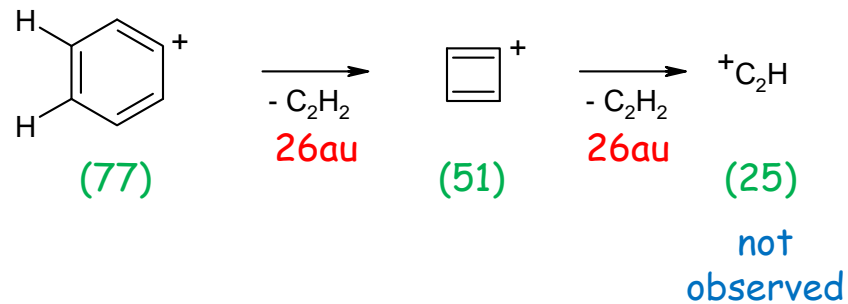


highly delocalized, very stable  $\rightleftharpoons$  tropylium ion

### tropylium fragmentation



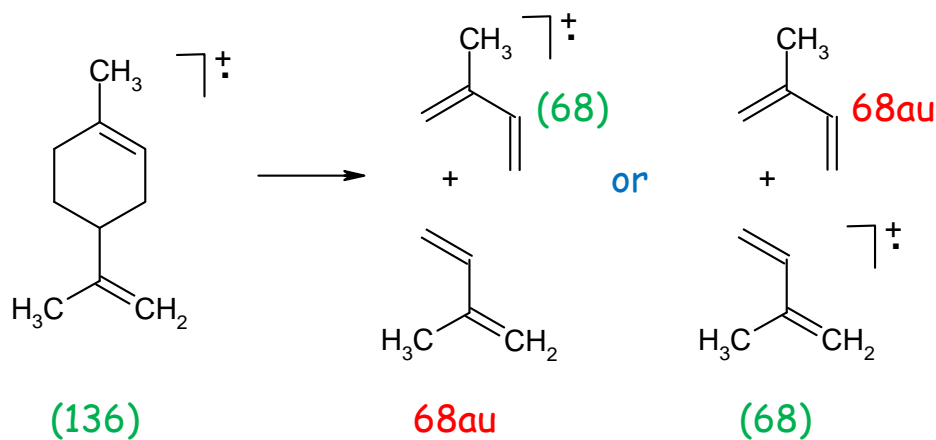
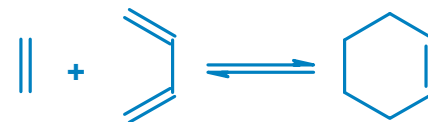
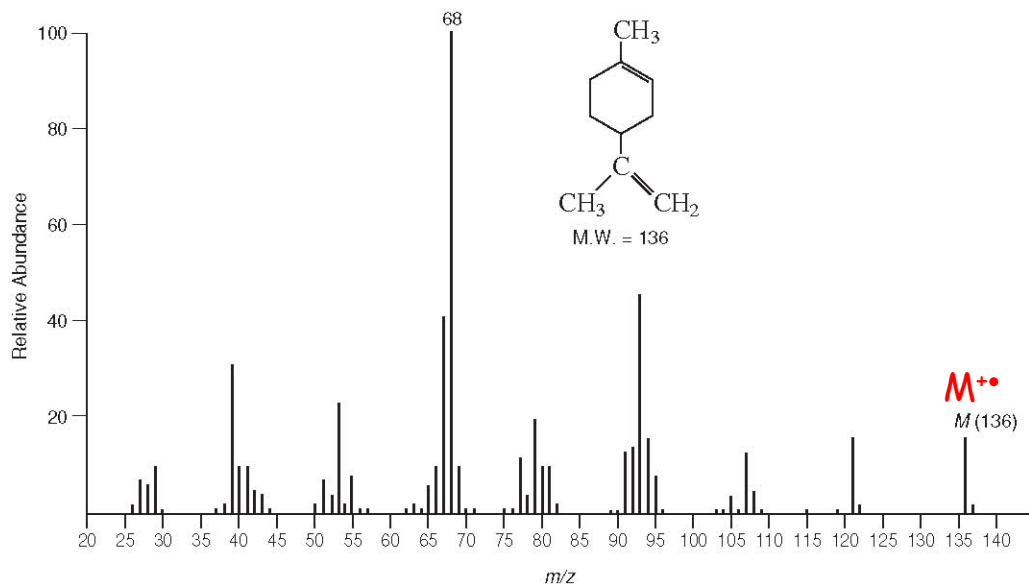
### phenyl fragmentation





# 6. Fragmentations continued

c) retro-Diels-Alder cleavage - for 6-membered rings with double bonds

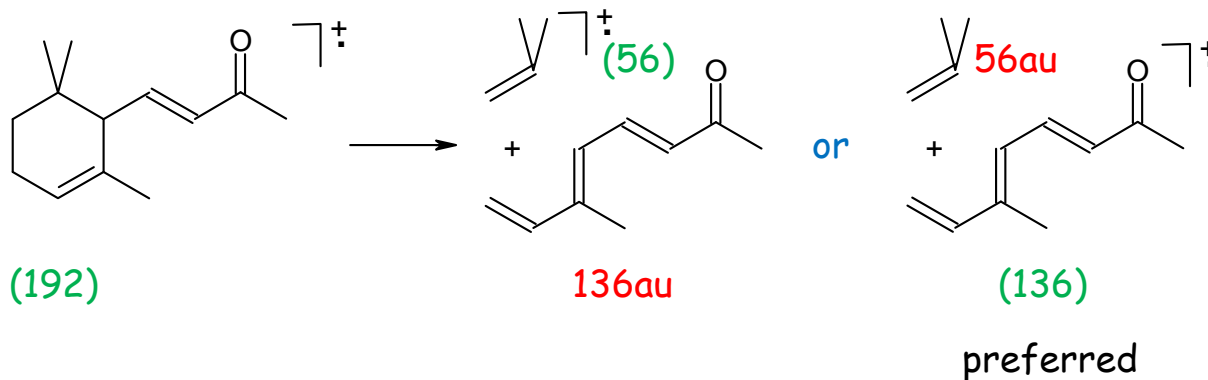
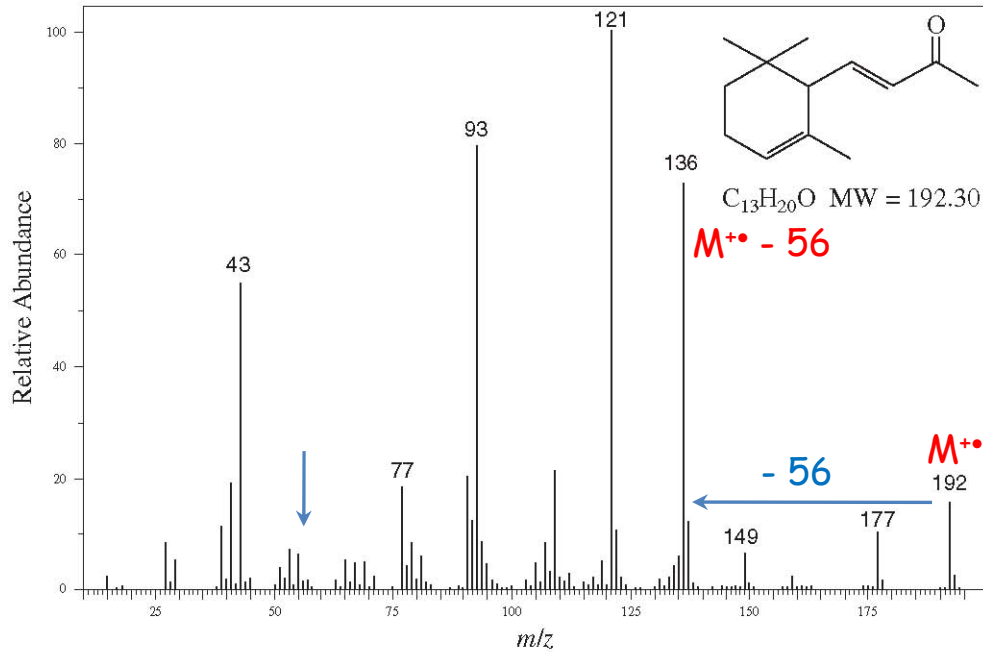


"or" is irrelevant: paths are identical ( $C_5H_8$ )

Figure 8.34

# 6. Fragmentations continued

## c) retro-Diels-Alder cleavage continued

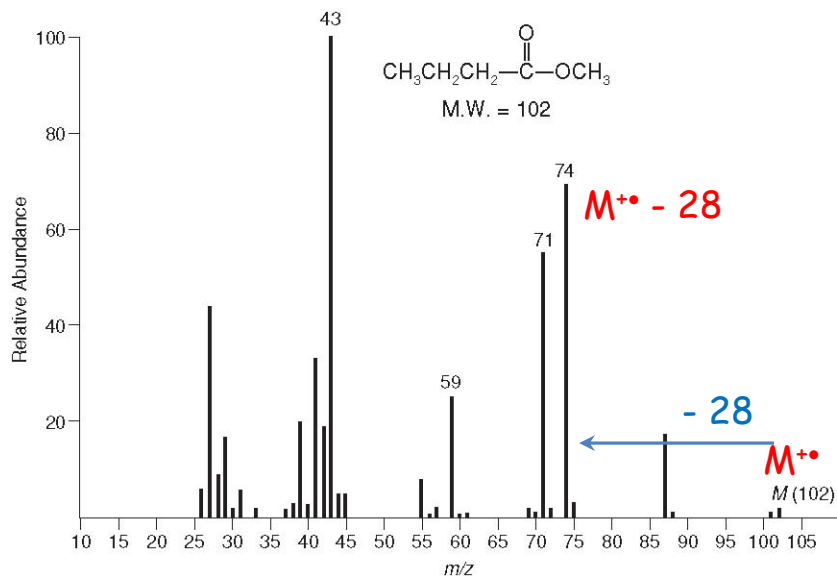


"or" is relevant!

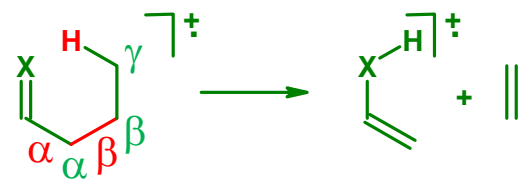
Figure 8.35

# 6. Fragmentations continued

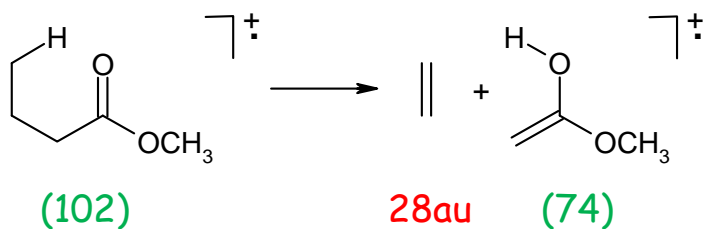
d) McLafferty rearrangement - for longer chains with double bonds (C=O  
C=C  
C=N)



$\beta$ -cleavage +  $\gamma$ -H shift



if C=C is part of an aromatic ring,  
the aromaticity is destroyed!



or...

## 6. Fragmentations continued

e) onium rearrangement - for compounds with  $X = O, N, P, S$  and charge on  $X$

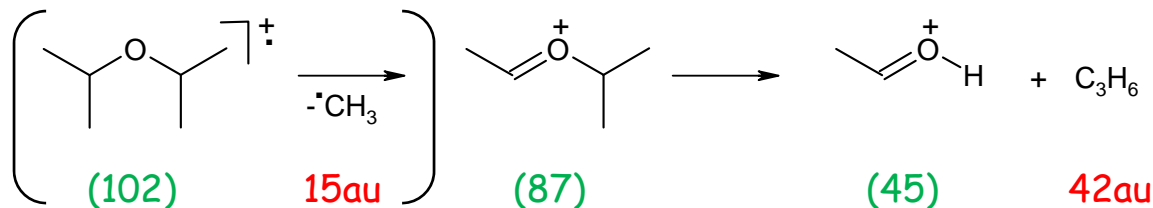
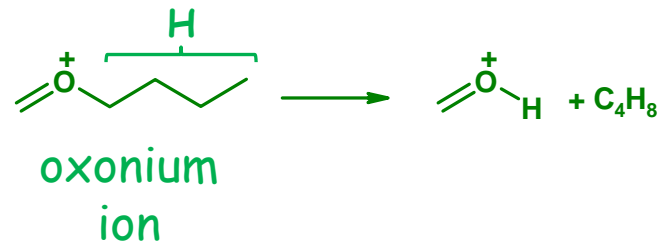
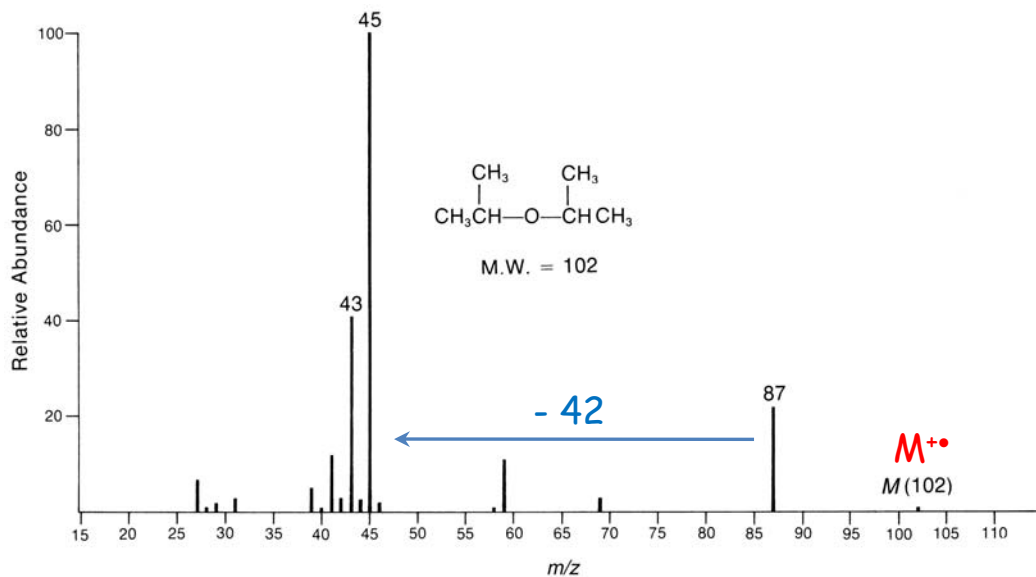


Figure 8.65