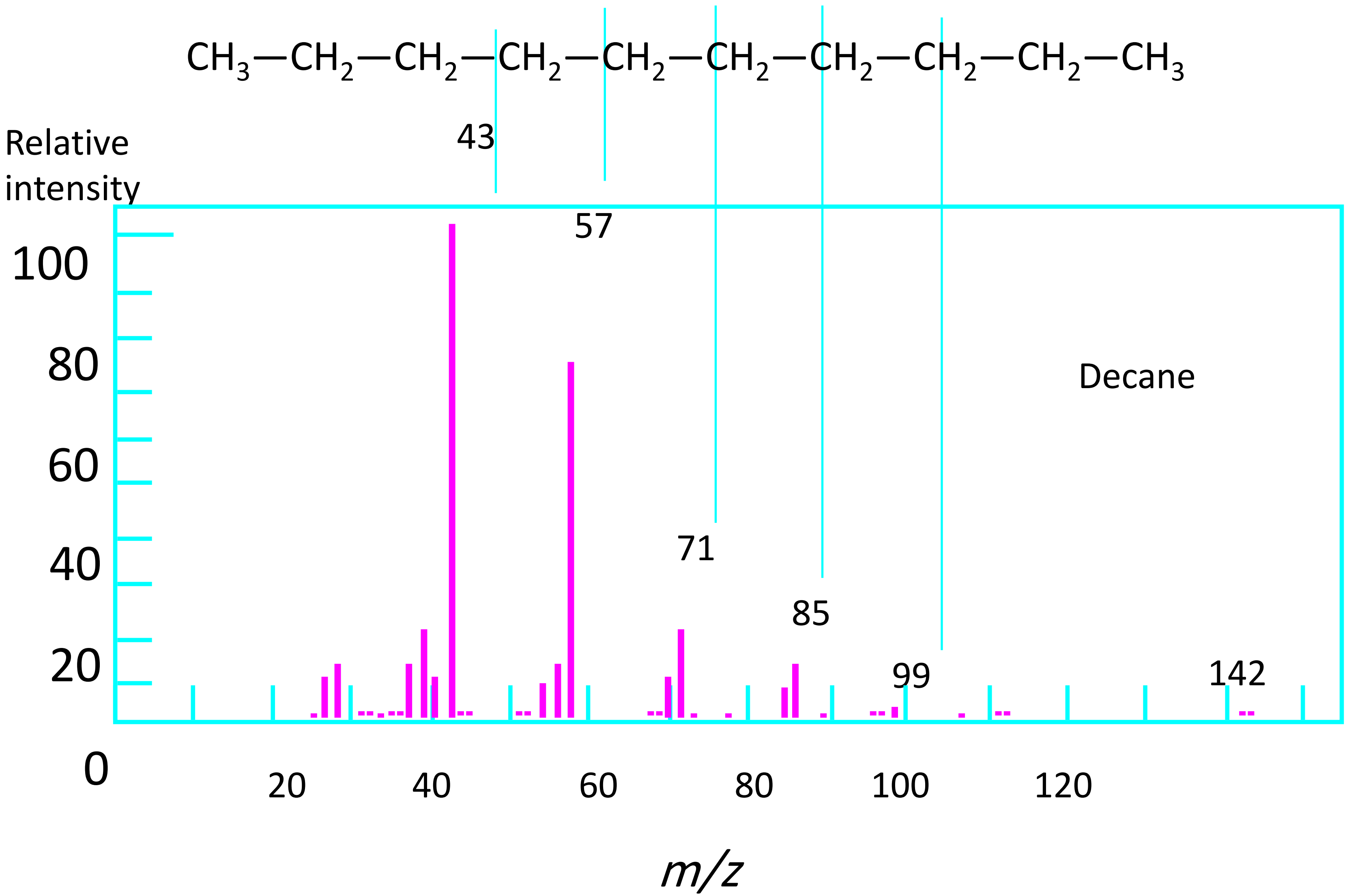
Mass Spectrometry
Lecture 8

Fragmentation Patterns

- Alkanes
  - Fragmentation often splits off simple alkyl groups:
    - Loss of methyl $M^+ - 15$
    - Loss of ethyl $M^+ - 29$
    - Loss of propyl $M^+ - 43$
    - Loss of butyl $M^+ - 57$
  - Branched alkanes tend to fragment forming the most stable carbocations.

Saturated hydrocarbons: *Alkanes*



2. Branched Alkanes

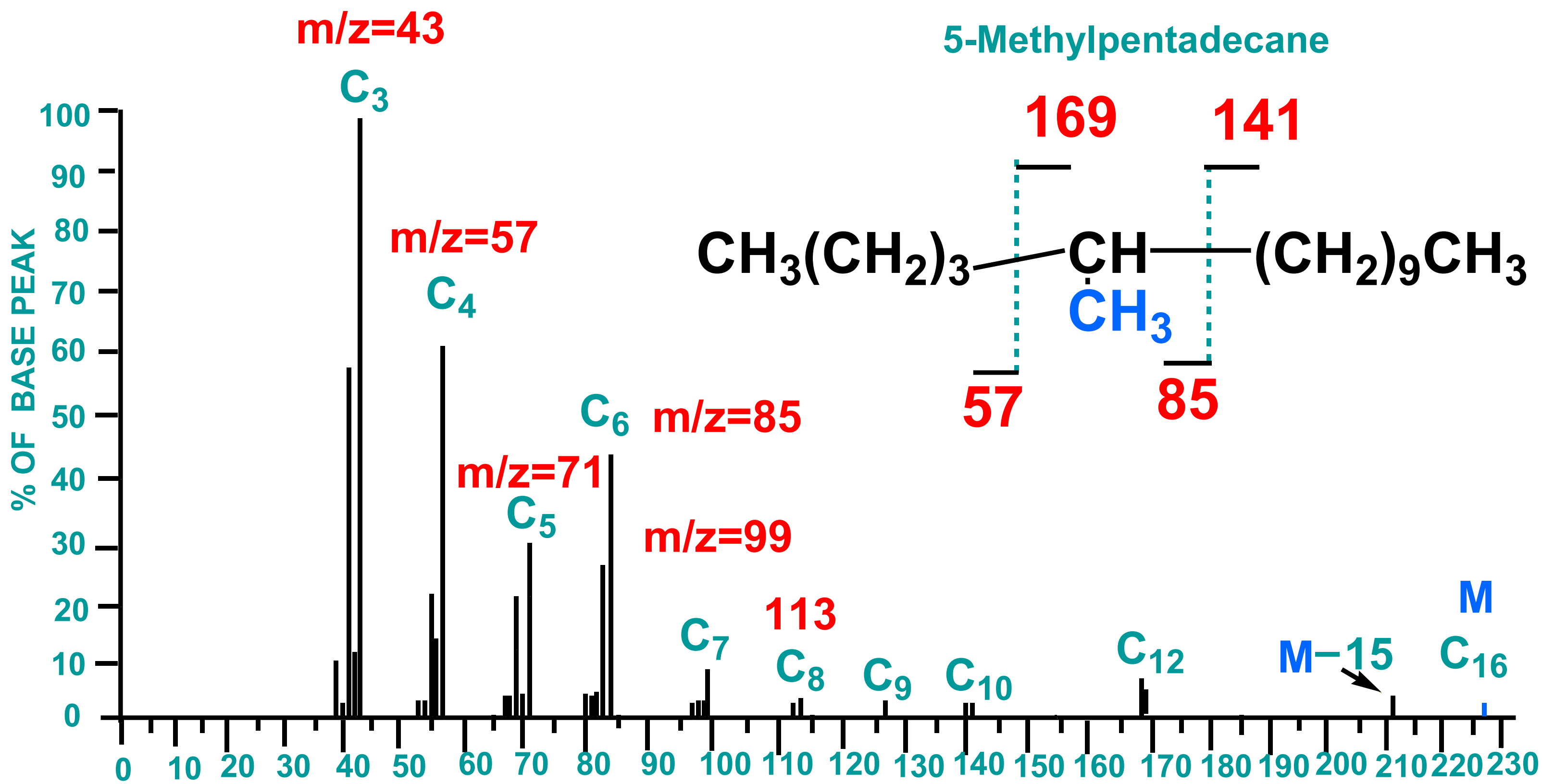


Figure 2 Mass spectrum of 5-methylpentadecane.

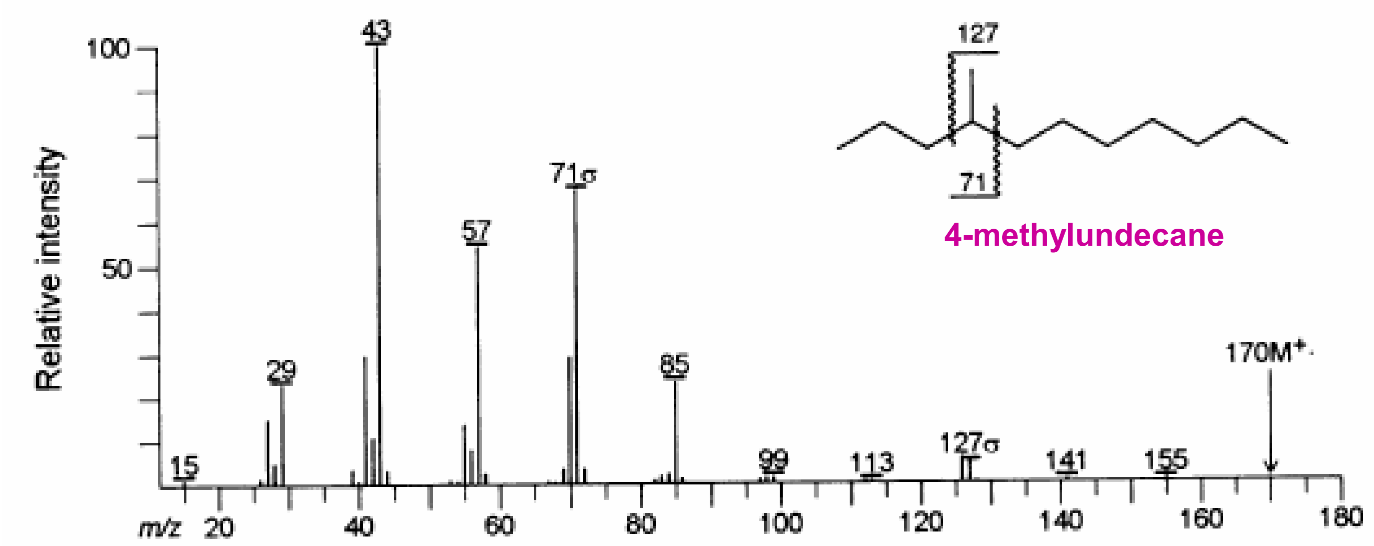


Figure 3 Mass spectrum of 4-methylundecane.

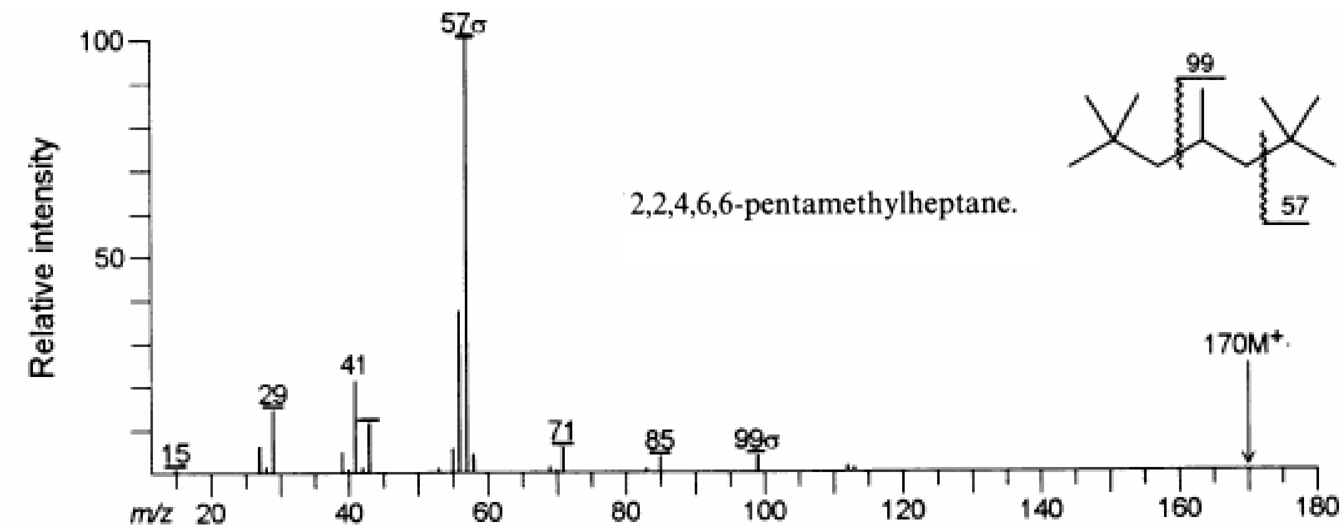


Figure 4 Mass spectrum of 2,2,4,6,6-pentamethylheptane.

3. Cycloalkanes

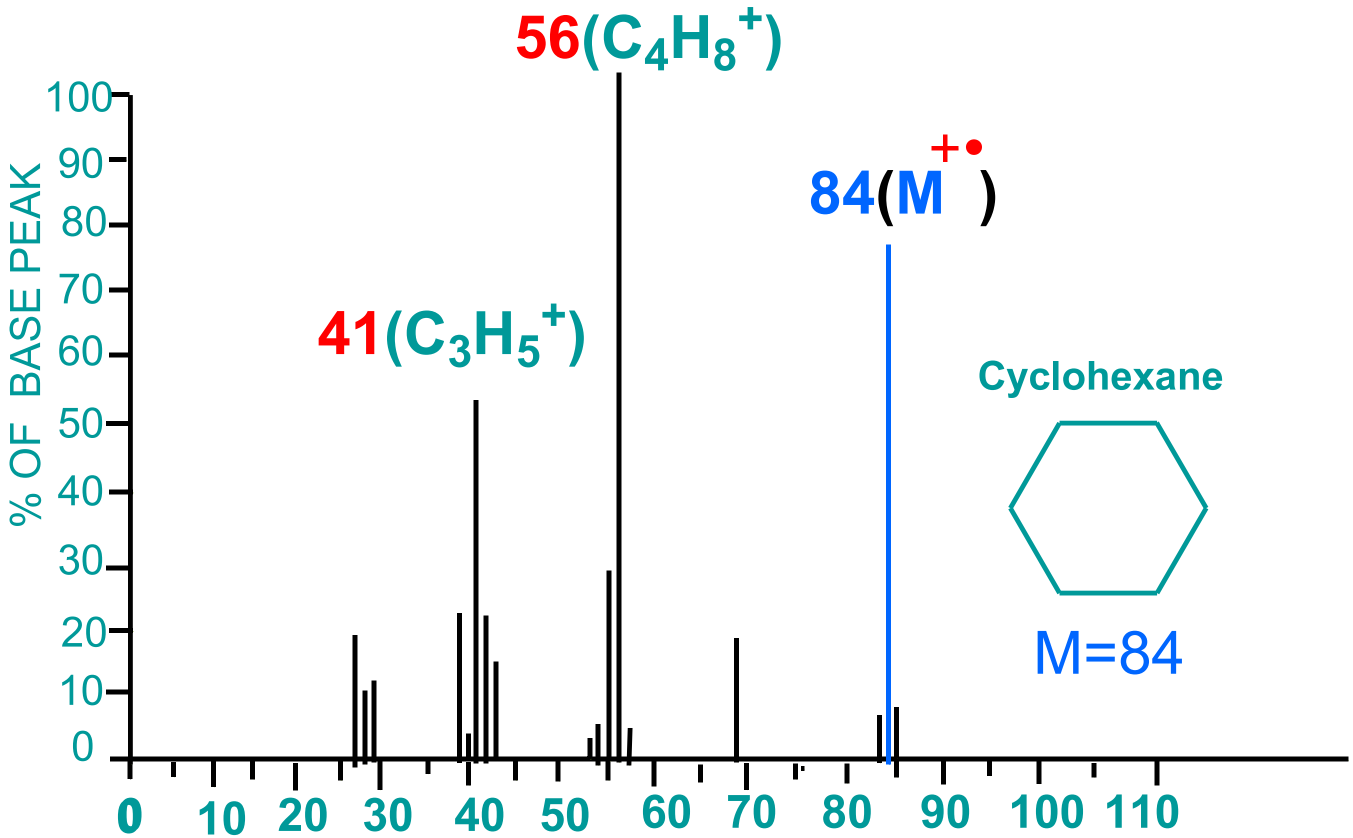


Figure 5 Mass spectrum of cyclohexane.

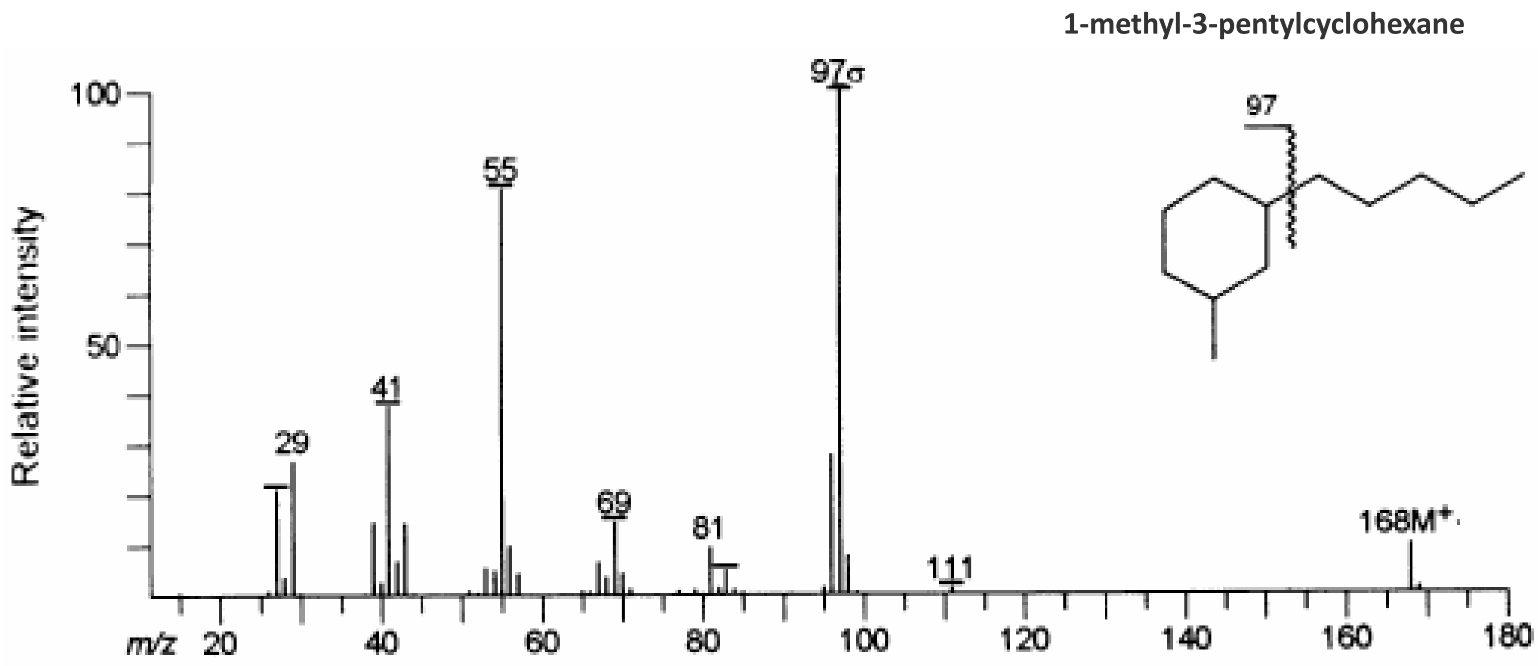
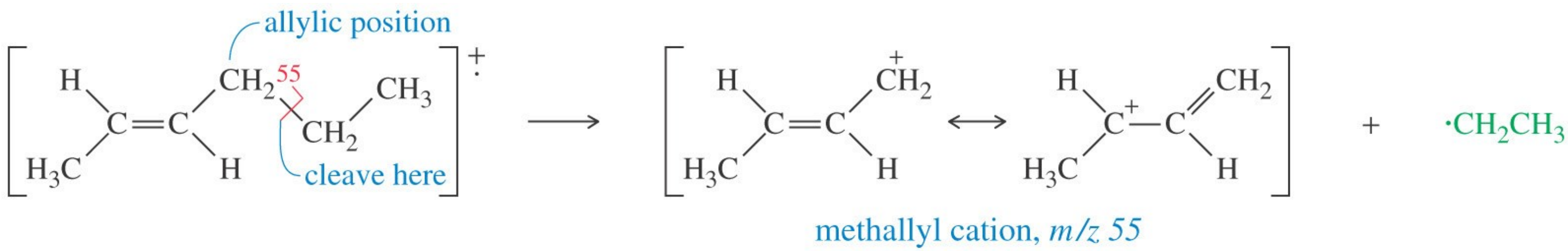
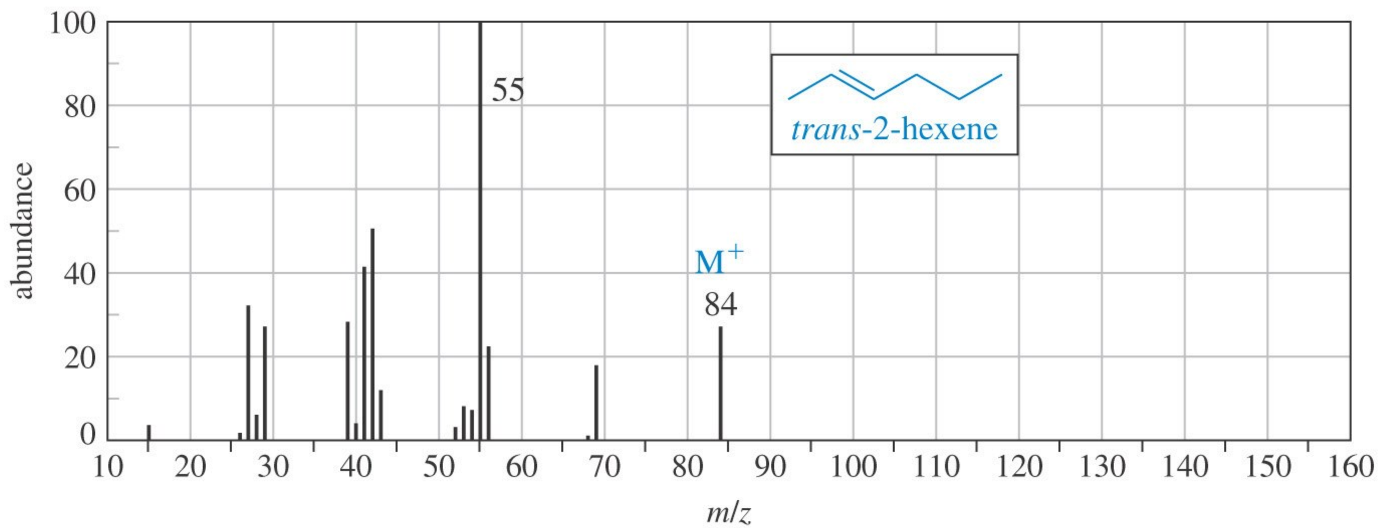


Figure 6 Mass spectrum of 1-methyl-3-pentylcyclohexane.

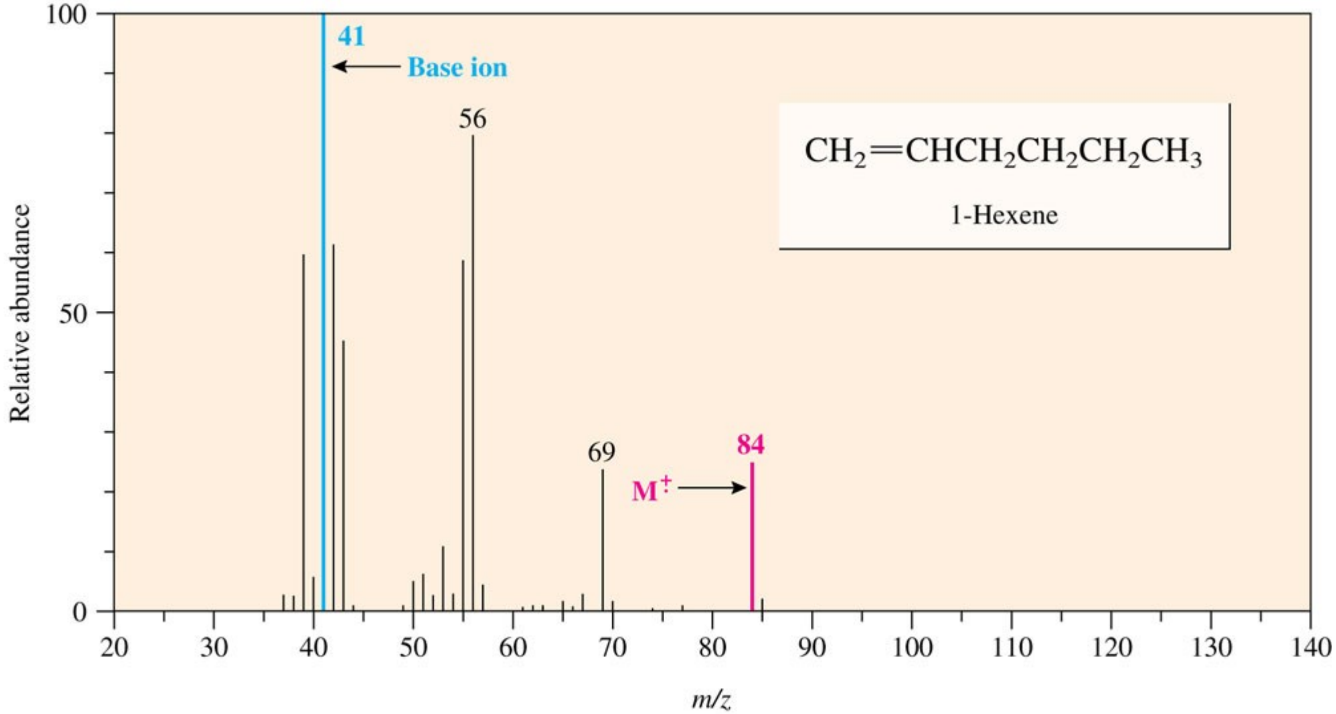
Fragmentation Patterns

- Alkenes:
  - Fragmentation typically forms resonance stabilized allylic carbocations



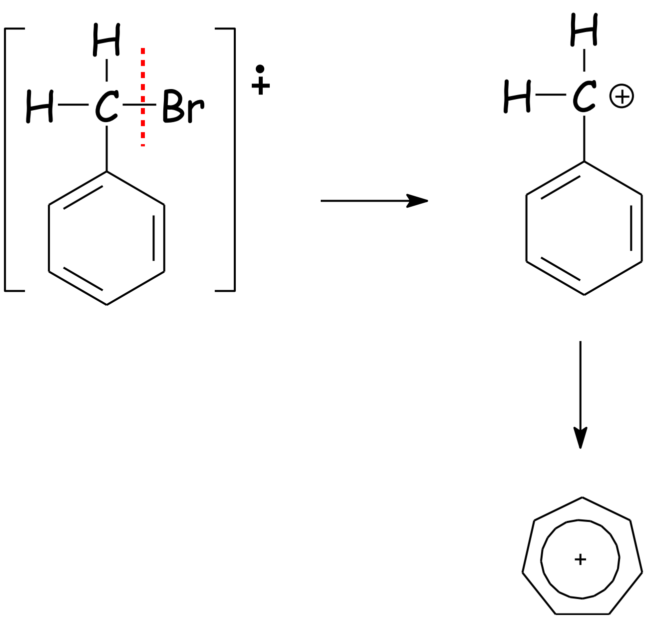


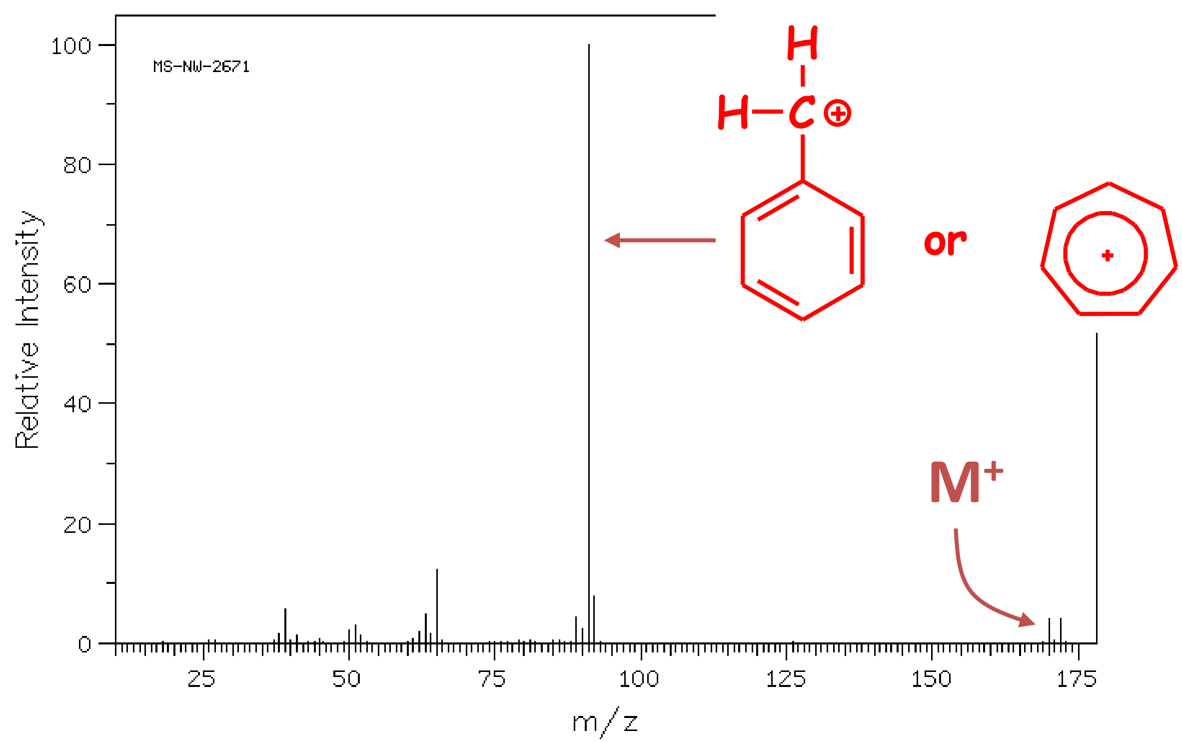
Fragmentation



Fragmentation Patterns

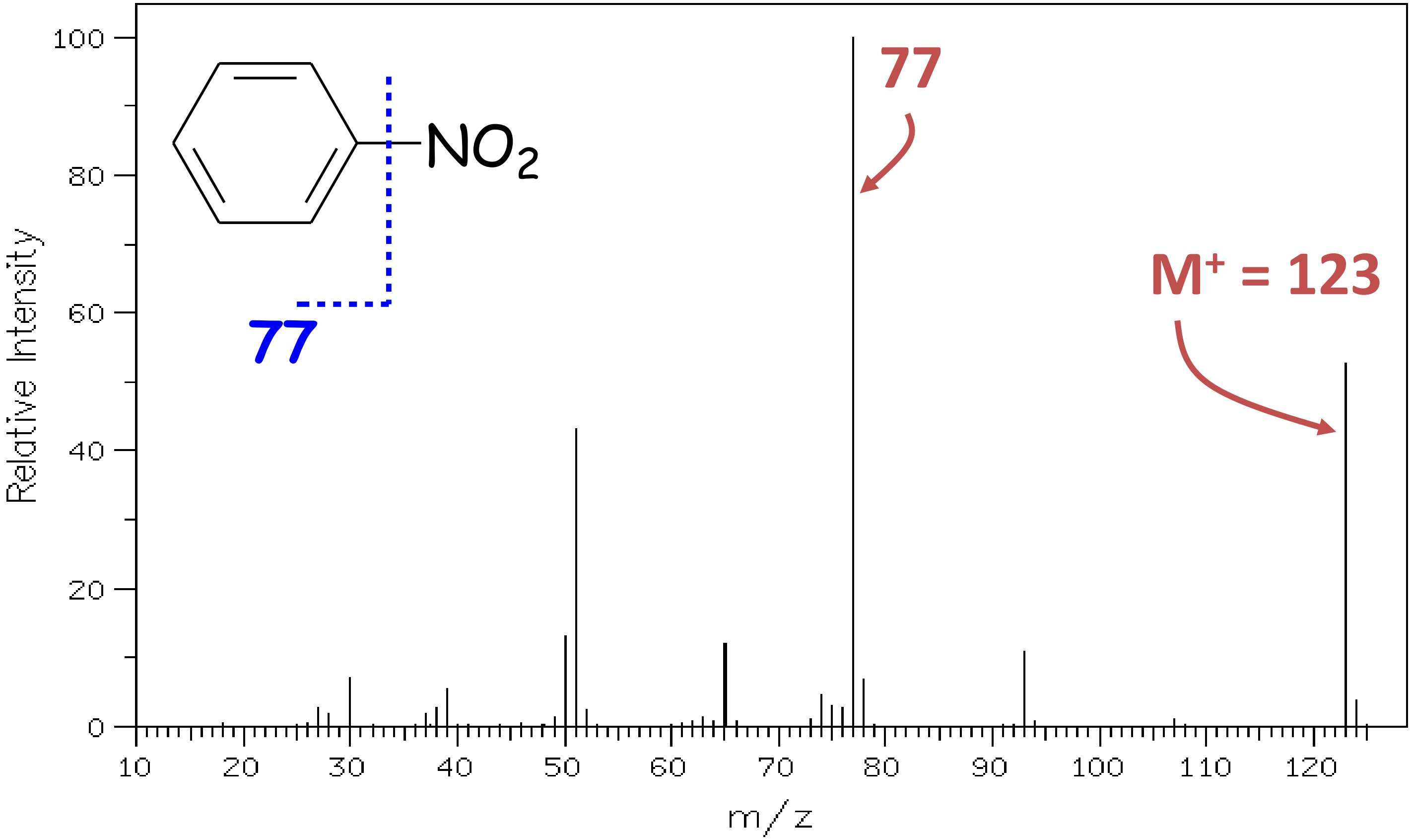
- Aromatics:
  - Fragment at the benzylic carbon, forming a resonance stabilized benzylic carbocation (which rearranges to the tropylium ion)





Fragmentation Patterns

Aromatics may also have a peak at m/z = 77 for the benzene ring.



Aromatic hydrocarbons

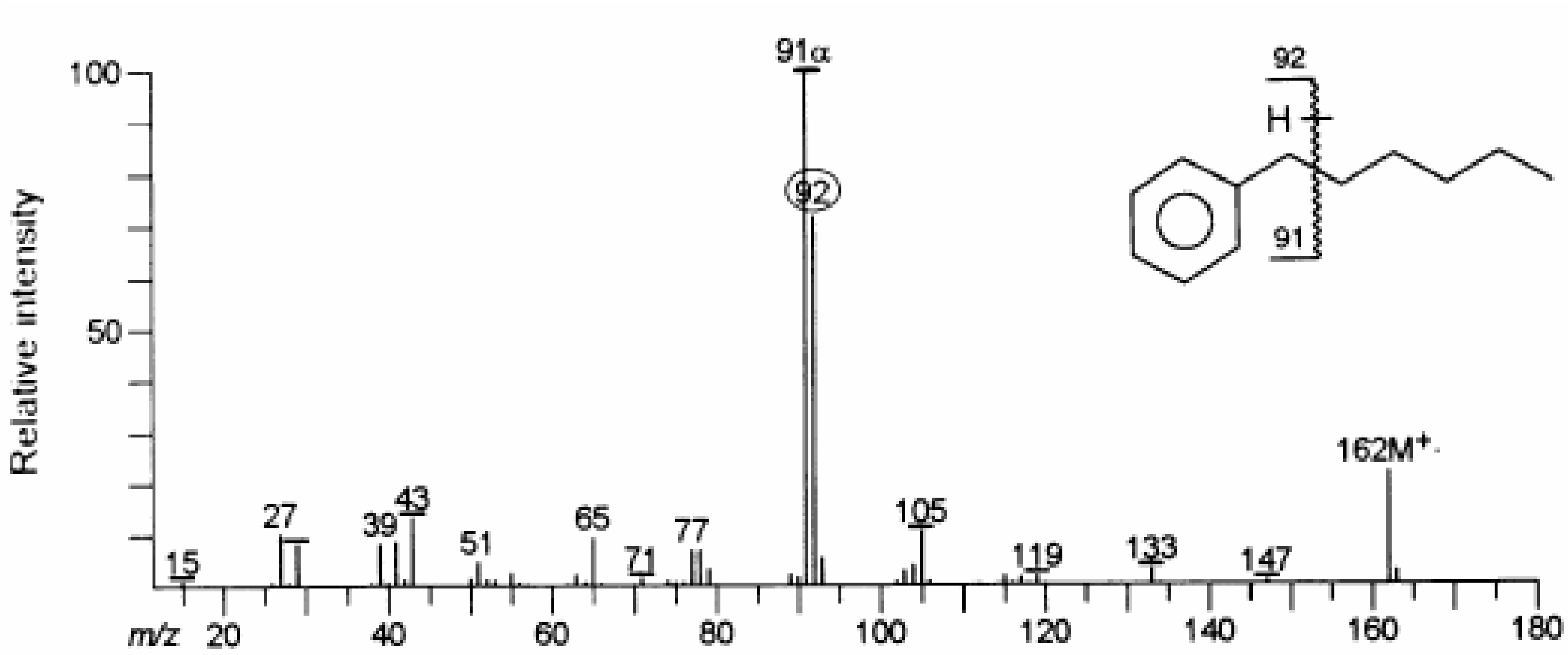


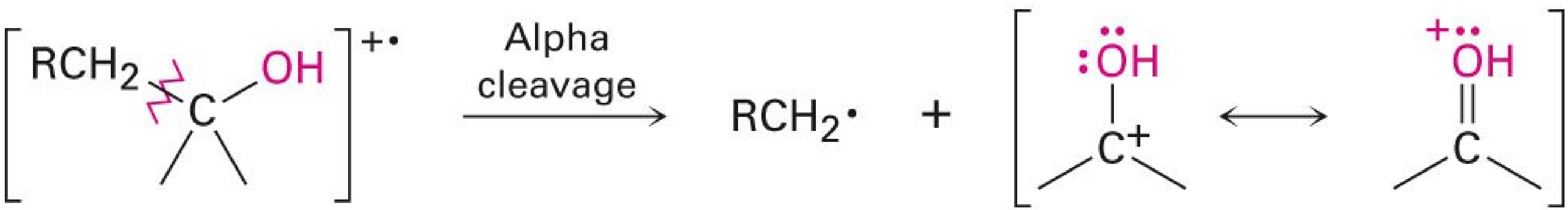
Figure 7 Mass spectrum of 1-phenylhexane

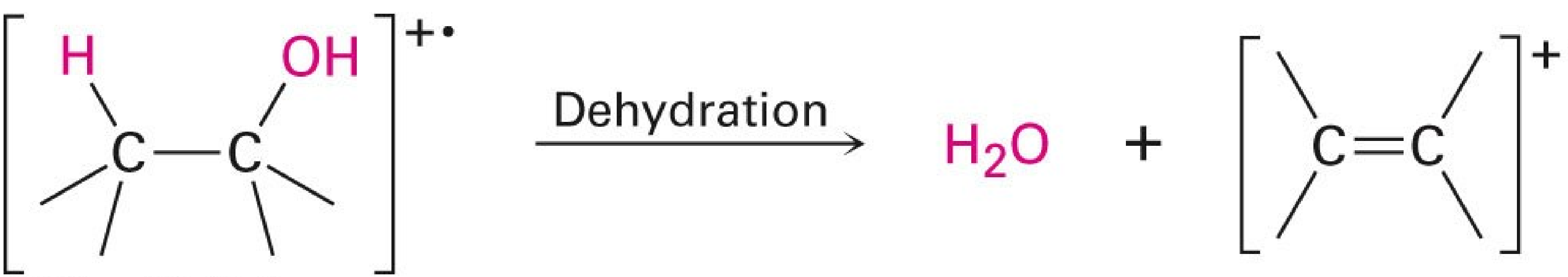
Alcohols, Phenol and Ether

1. Alcohol

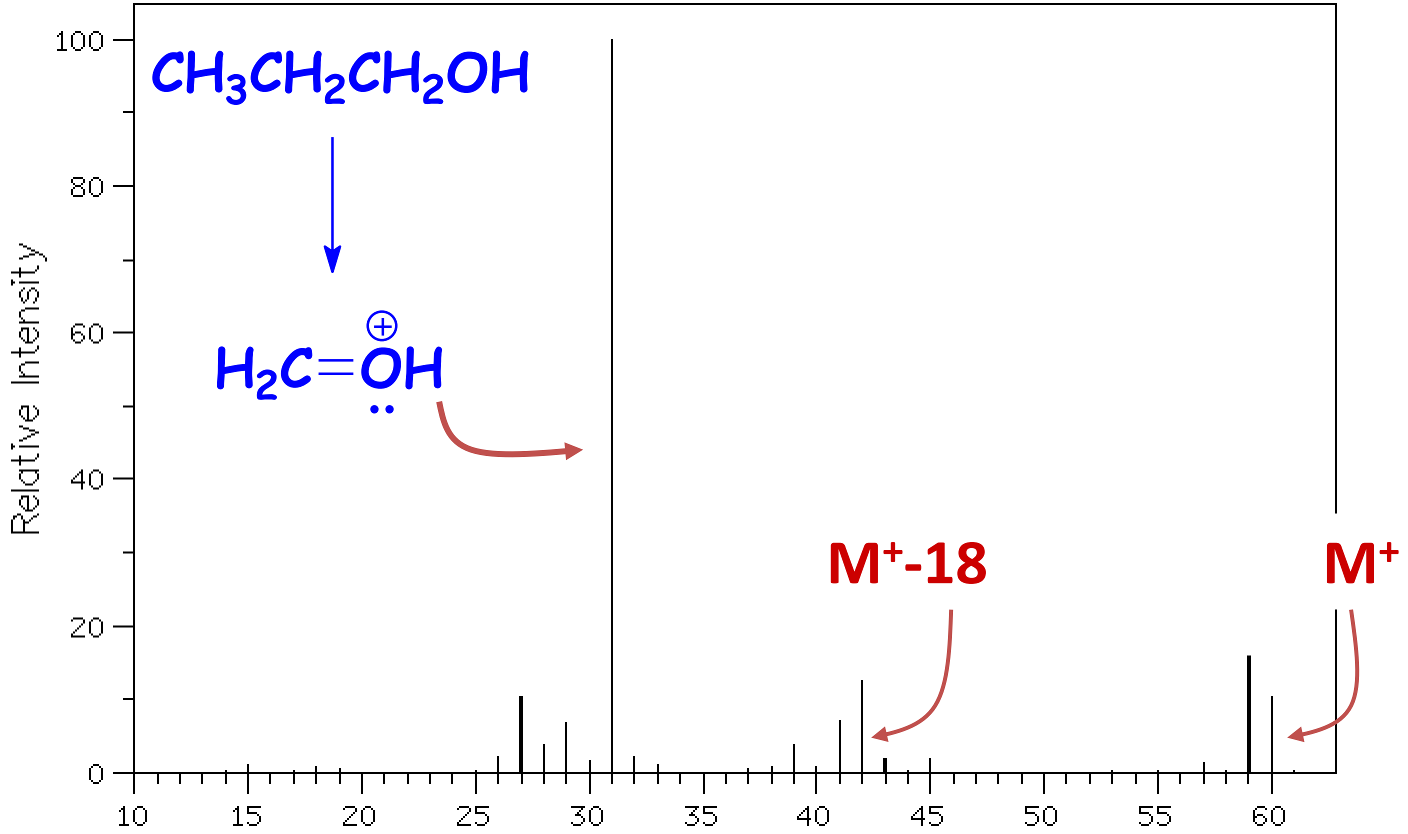
Alcohols:

- Alcohols undergo α-cleavage (at the bond next to the C-OH) as well as loss of H-OH to give C=C (M-18 common)





- MS for 1-propanol



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Fragmentation Patterns

3-Ethers

– α-cleavage forming oxonium ion

$$[R \vert CH_2 - O - R']^{+\cdot} \longrightarrow H_2C = \ddot{O}^{+} - R'$$

– Loss of alkyl group forming oxonium ion

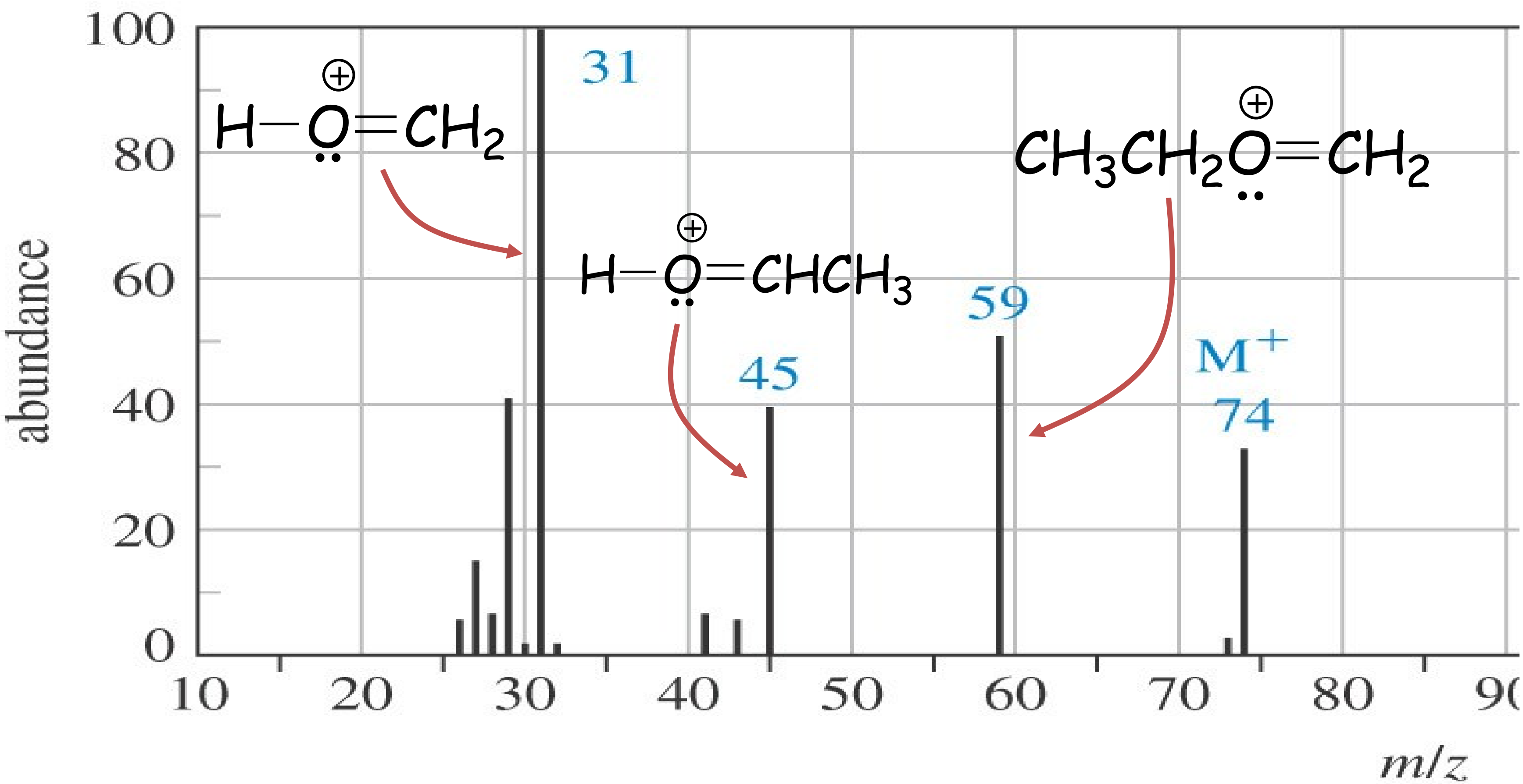
$$[R - CH_2 - O \vert R']^{+\cdot} \xrightarrow{\sim H} R - CH = \ddot{O}^{+} - H$$

– Loss of alkyl group forming a carbocation

$$[R - CH_2 - O \vert R']^{+\cdot} \longrightarrow \underset{\text{not observed}}{R - CH_2 - O\cdot} \quad + \quad \underset{\text{alkyl cation}}{{}^{+}R'}$$

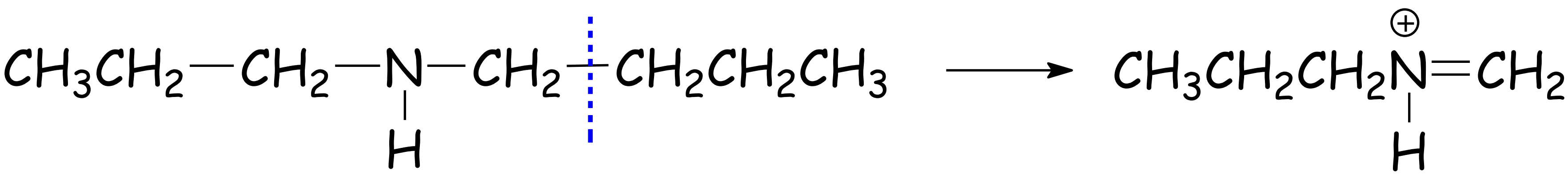
Fragmentation Patterns

MS of diethylether ($CH_3CH_2OCH_2CH_3$)



Fragmentation Patterns

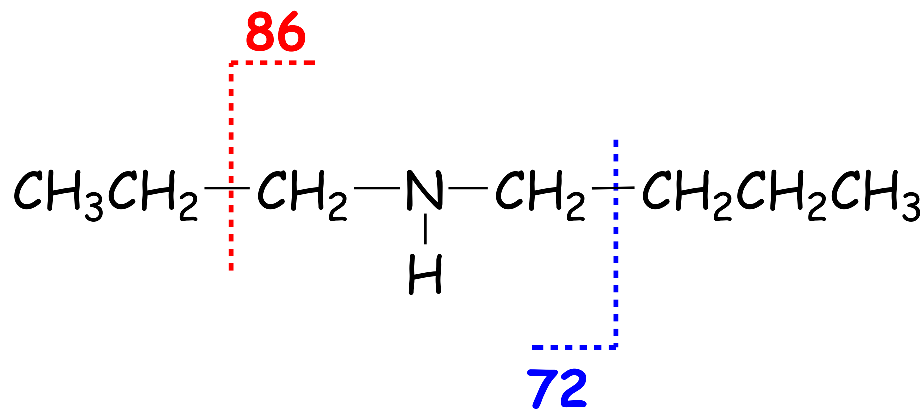
- Amines
  - Odd M^+ (assuming an odd number of nitrogens are present)
  - α-cleavage dominates forming an iminium ion

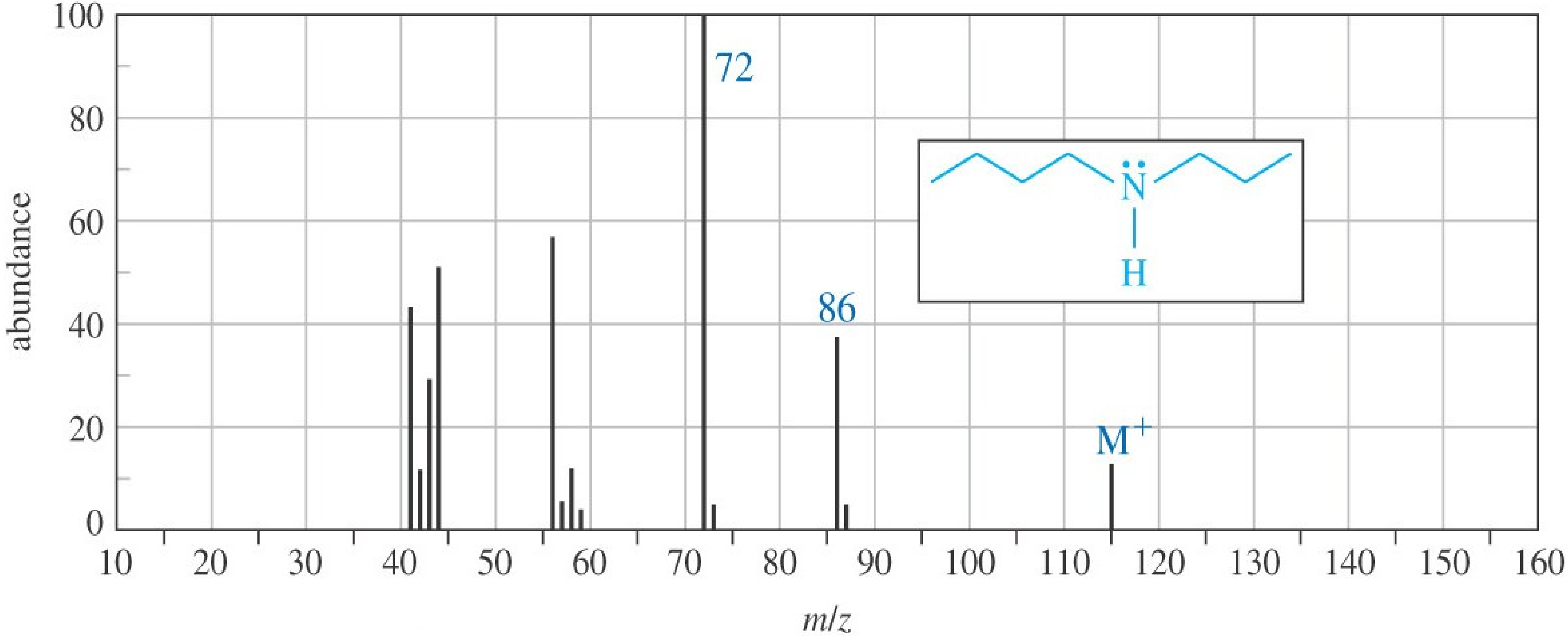


m/z =72

iminium ion

Fragmentation Patterns





Fragmentation Patterns

- Aldehydes (RCHO)
  - Fragmentation may form acylium ion

$$RC\equiv\overset{\oplus}{O}:$$

  - Common fragments:

$$RC\equiv\overset{\oplus}{O}:$$

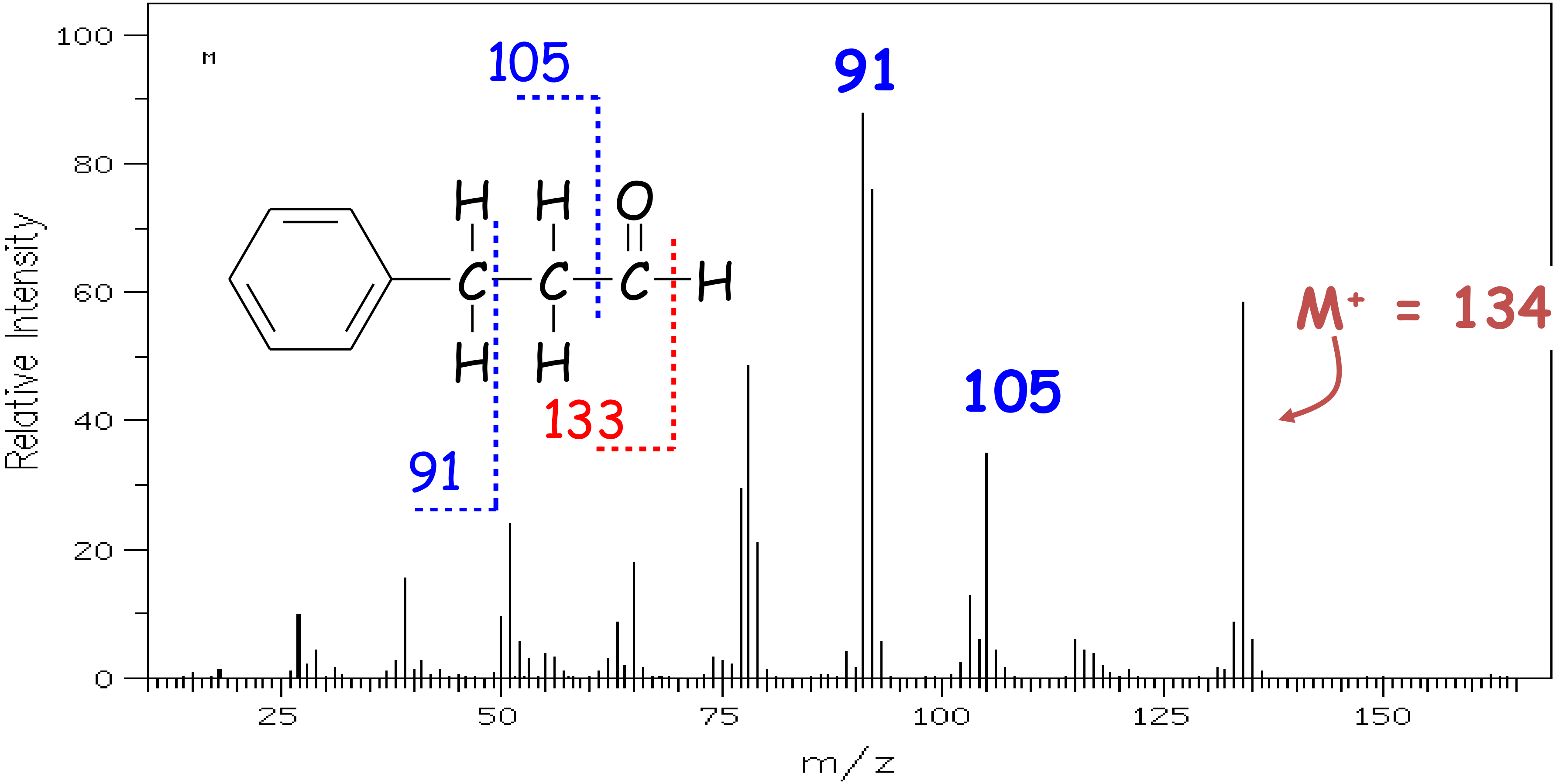
    - M^{+} - 1 for

$$R^{\oplus}\ (\text{i.e. } RCHO - CHO)$$

    - M^{+} - 29 for

Fragmentation Patterns

- MS for hydrocinnamaldehyde



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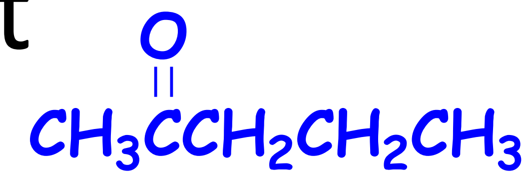
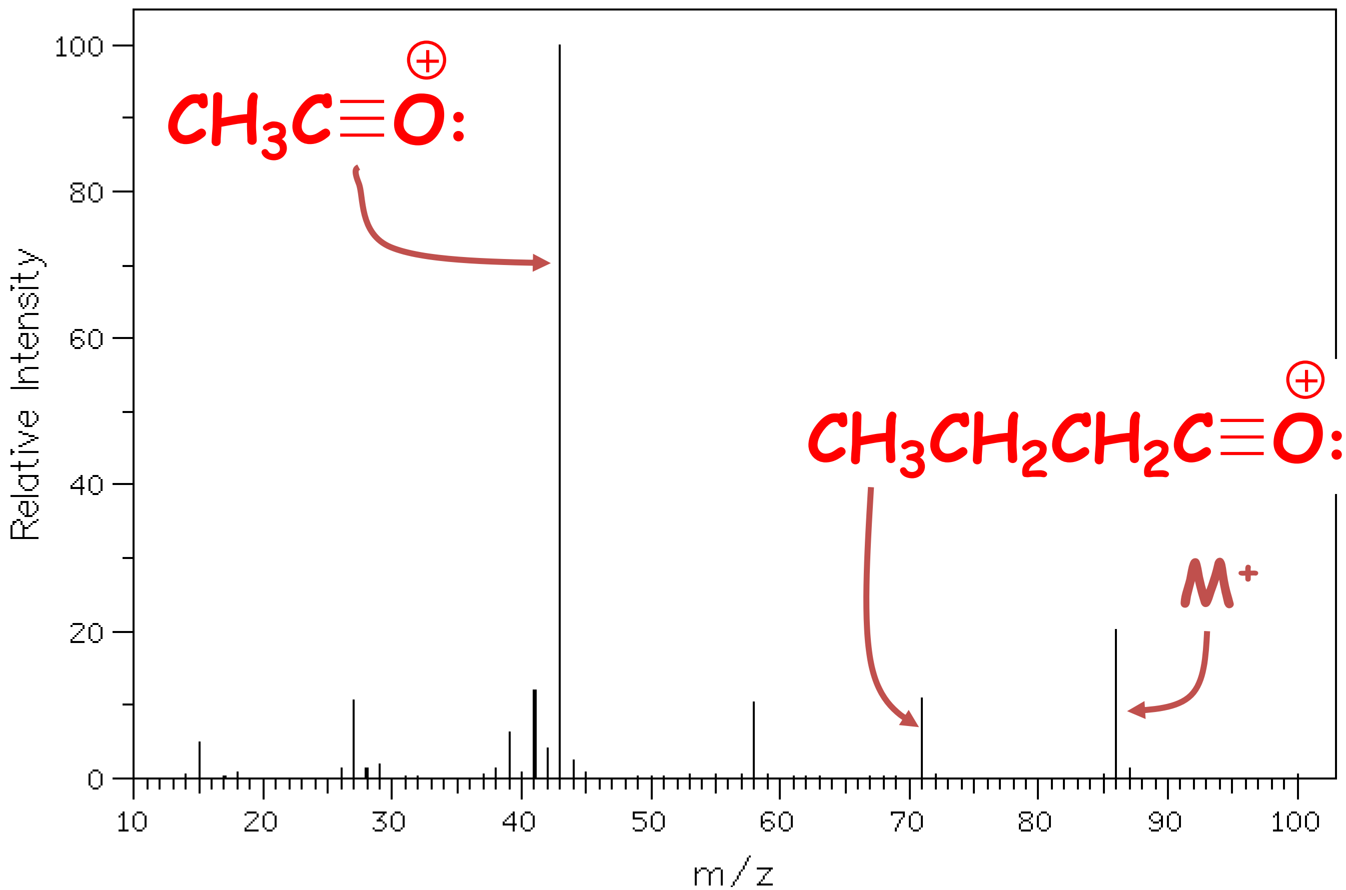
Fragmentation Patterns

- Ketones $\quad R\overset{\overset{\displaystyle O}{\|}}{C}R'$
  - Fragmentation leads to formation of acylium ion:
    - Loss of R forming $\quad R'C\equiv\overset{\oplus}{O}:$
    - Loss of R’ forming $\quad RC\equiv\overset{\oplus}{O}:$

Fragmentation Patt



- MS for 2-pentanone



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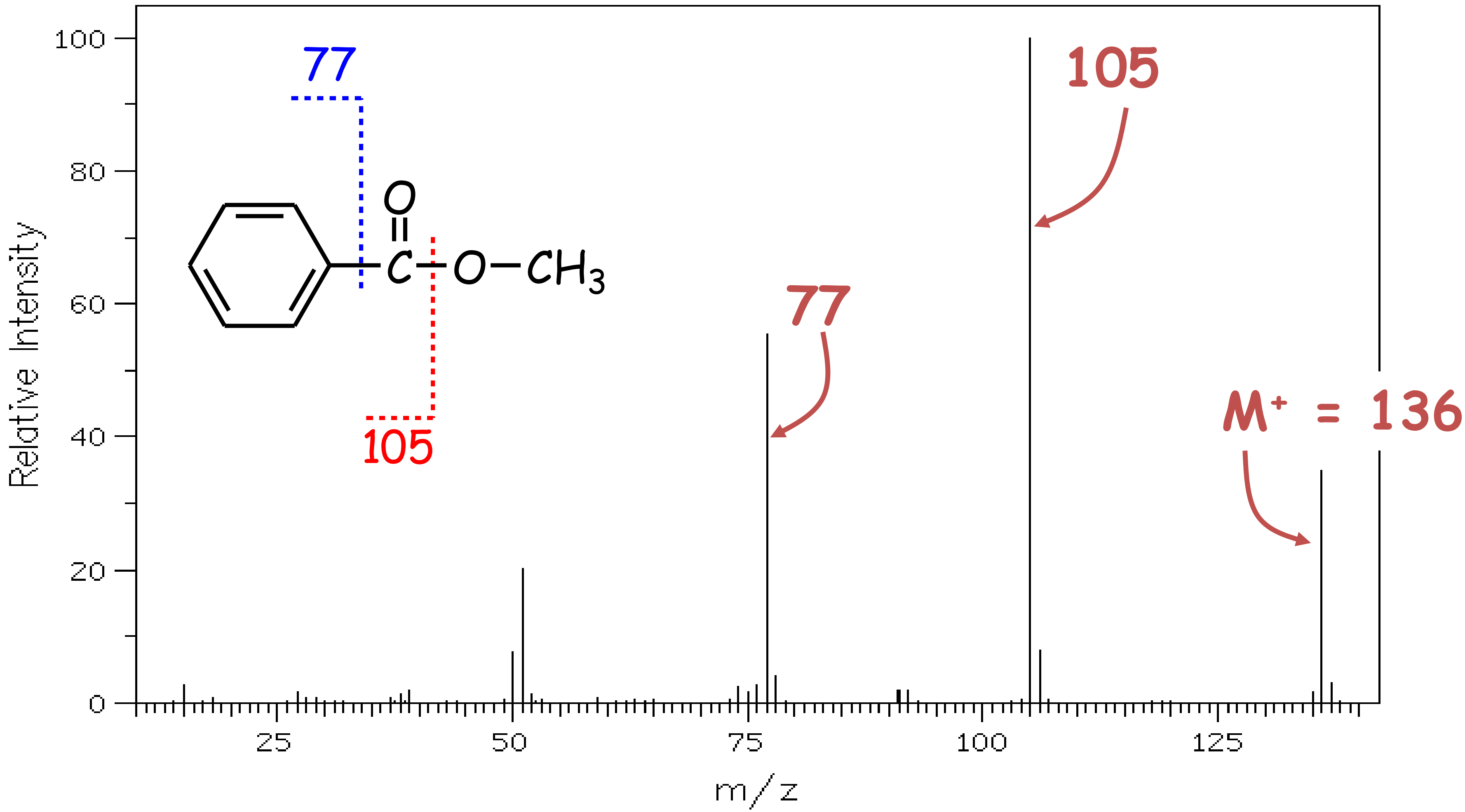
Fragmentation Patterns

- Esters (RCO_2R')
  - Common fragmentation patterns include:
    - Loss of OR'
      - peak at M^+ - OR'
    - Loss of R'
      - peak at M^+ - R'

Frgamentation Patterns



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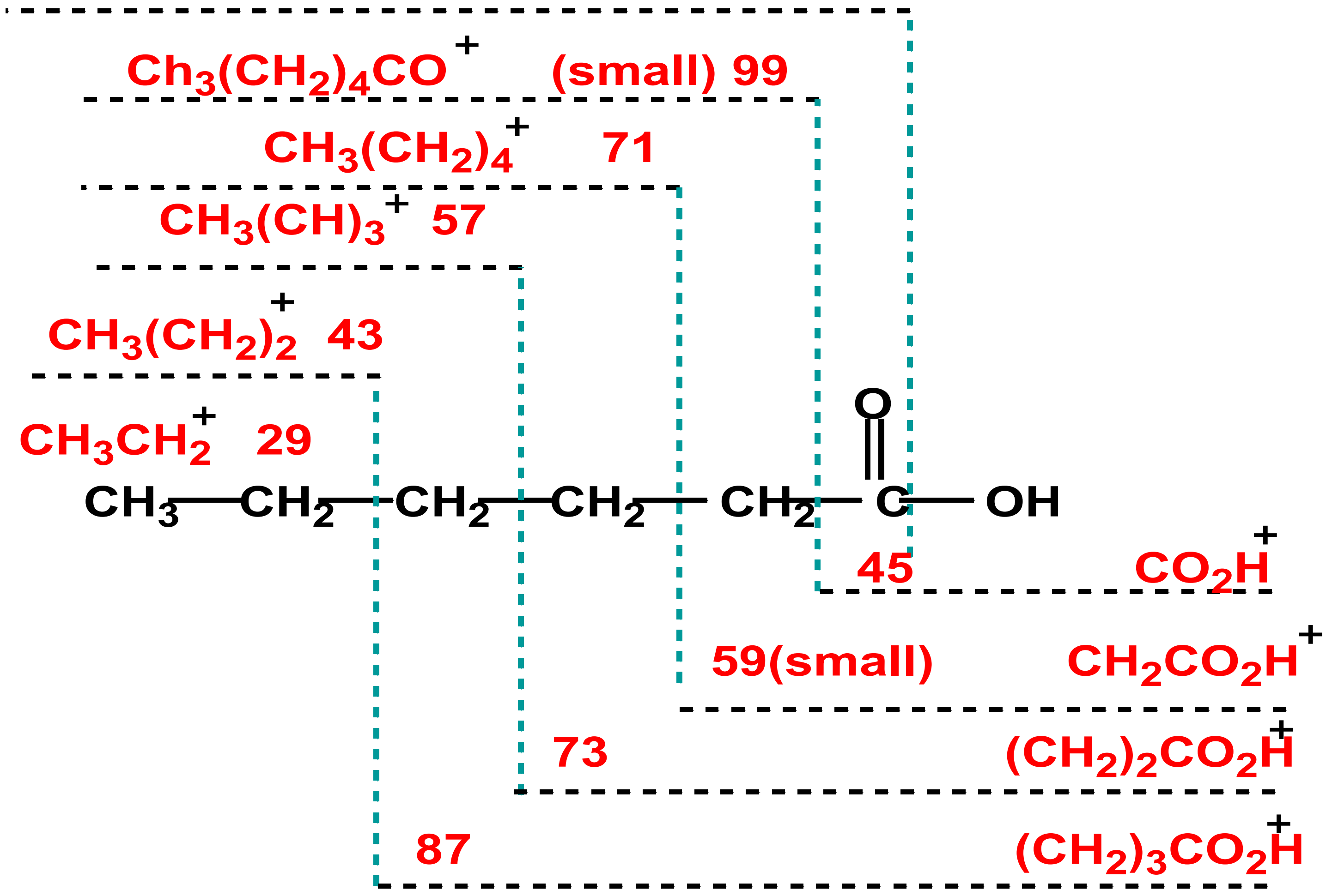
Carboxylic acid



Rule of Thirteen

- The "Rule of Thirteen" can be used to identify possible molecular formulas for an unknown hydrocarbon, C_nH_m.
  - Step 1: $n = M^+/13$ (integer only, use remainder in step 2)
  - Step 2: $m = n$ + remainder from step 1

Rule of Thirteen

- Example: The formula for a hydrocarbon with M^+ =106 can be found:
  - Step 1: n = 106/13 = 8 (R 0.15X 13 = 2)
  - Step 2: m = 8 + 2 = 10
  - Formula: C_8H_{10}

Rule of Thirteen

- If a heteroatom is present,
  - Subtract the mass of each heteroatom from the MW
  - Calculate the formula for the corresponding hydrocarbon
  - Add the heteroatoms to the formula

Rule of Thirteen

Example: A compound with a molecular ion peak at m/z = 102 has a strong peak at 1739 cm^{-1} in its IR spectrum. Determine its molecular formula.

Rule of Thirteen

- If a heteroatom is present,
  - Subtract the mass of each heteroatom from the MW
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Rule of Thirteen

Example: A compound with a molecular ion peak at m/z = 102 has a strong peak at 1739 cm^{-1} in its IR spectrum. Determine its molecular formula.

Step 1: Due to the compound has a strong peak at 1739 cm-1 in its IR spectrum therefore it contain ester group (COO-), so it Contain 2heteroatom O.
102-32 =70 MW of corresponding hydrocarbon.

Step 2: 70/13 = 5.384
n = 5 (R= 0.38 4X 13= 5)

Step 3: m 5+5 =10

Step 4: Chemical formula = CnHm + heteroatom
$C_5H_{10}O_2$

$CH_3CH_2CH_2COOCH_3$