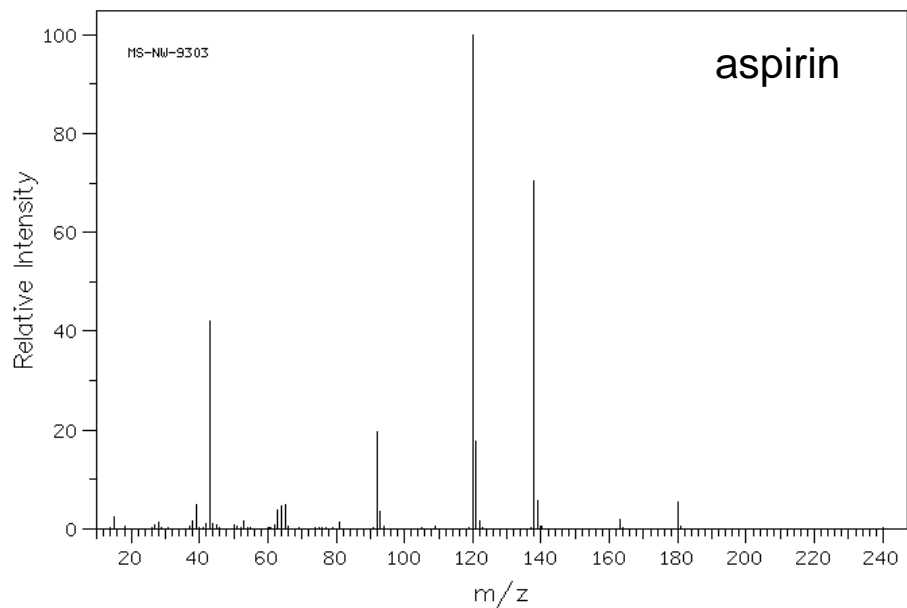
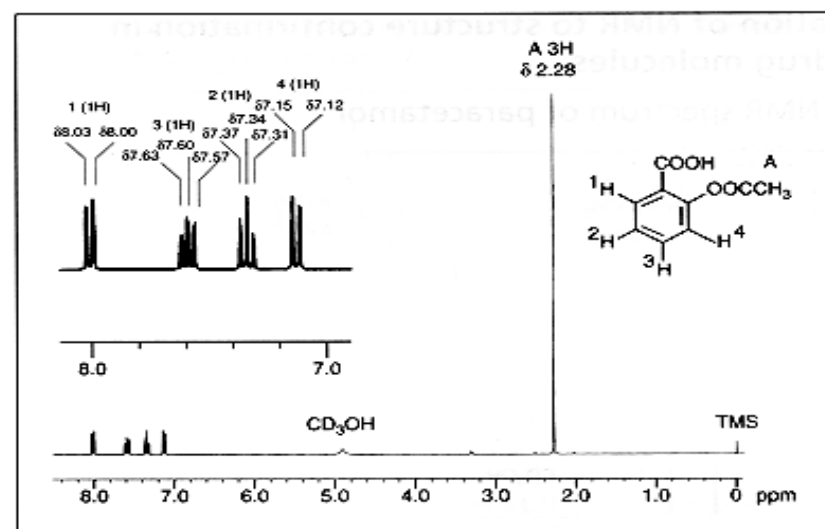


# *Mass Spectrometry Interpretation*

# MS vs NMR



**EI-MS**



**NMR**

# MS vs. NMR

- MS peaks are narrower than NMR peaks
- MS is much more ( $10^4$  x) more sensitive than NMR (**among most sensitive tools**)
- MS allows one to analyze much larger molecules (>50 kD) than NMR
- MS samples are more difficult to prepare
- MS is not particularly quantitative
- MS instruments cost a little less than NMR

# Appearance of the Spectrum

- molecular ion
  - highest mass ion except for isotope peaks
  - molecular weight
- Nitrogen Rule (even-odd rule)
  - compounds with 0 or even numbers of N atoms have even molecular weights and fragments of odd mass
  - compounds with an odd number of N atoms have odd molecular weights

# *Interpretation of Mass Spectra*

- ❖ Select a candidate peak for the molecular ion ( $M^+$ )
- ❖ Examine spectrum for peak clusters of characteristic isotopic patterns
- ❖ Test ( $M^+$ ) peak candidate by searching for other peaks correspond to reasonable losses
- ❖ Look for characteristic low-mass fragment ions
- ❖ Compare spectrum to reference spectra

# Exact Masses

Element	Symbol	Exact mass
hydrogen	${}_1\text{H}^1$	1.00783
carbon	${}_6\text{C}^{12}$	12.00000
nitrogen	${}_7\text{N}^{14}$	14.0031
oxygen	${}_8\text{O}^{16}$	15.9949

# Molecular Weight Determination

Compounds with nominal mass 28.

Exact mass

	exact mass
CO	27.9949
N <sub>2</sub>	28.0062
C <sub>2</sub> H <sub>4</sub>	28.0312

# Natural Isotopic Abundance Ratios

Element		M+		M+1		M+2
hydrogen	${}^1_1\text{H}^1$	100	${}^2_1\text{H}^2$	0.016		
carbon	${}^{12}_6\text{C}^{12}$	100	${}^{13}_6\text{C}^{13}$	1.08		
nitrogen	${}^{14}_7\text{N}^{14}$	100	${}^{14}_7\text{N}^{14}$	0.38		
oxygen	${}^{16}_8\text{O}^{16}$	100	${}^{17}_8\text{O}^{17}$	0.04	${}^{18}_8\text{O}^{18}$	0.20
sulfur	${}^{32}_{16}\text{S}^{32}$	100	${}^{32}_{16}\text{S}^{32}$	0.78	${}^{32}_{16}\text{S}^{32}$	4.40
chlorine	${}^{35}_{17}\text{Cl}^{35}$	100			${}^{37}_{17}\text{Cl}^{37}$	32.5
bromine	${}^{79}_{35}\text{Br}^{79}$	100			${}^{81}_{35}\text{Br}^{81}$	98.0



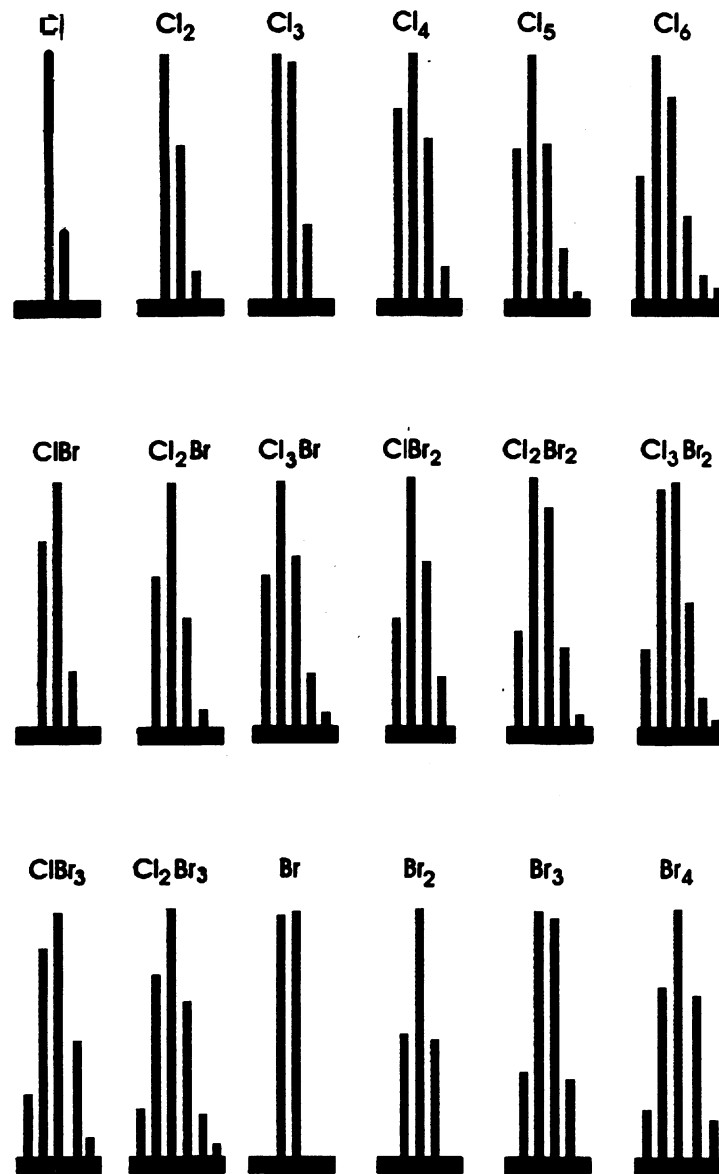
# Molecular Weight Determination

Compounds with nominal mass 28.

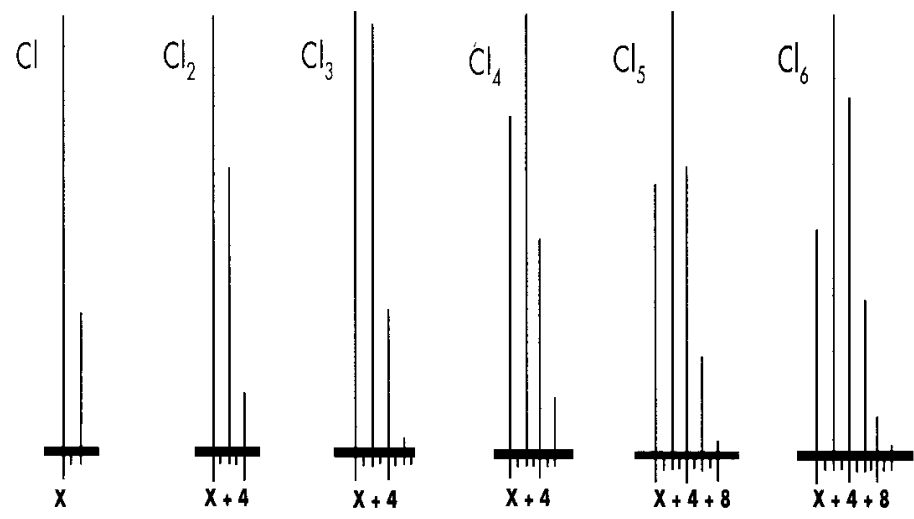
## Isotope Clusters

	M	M+1	M+2
CO	100%	1.12	0.2
N <sub>2</sub>	100%	0.76	0.00
C <sub>2</sub> H <sub>4</sub>	100%	2.23	0.01

# Halogen Isotope Clusters

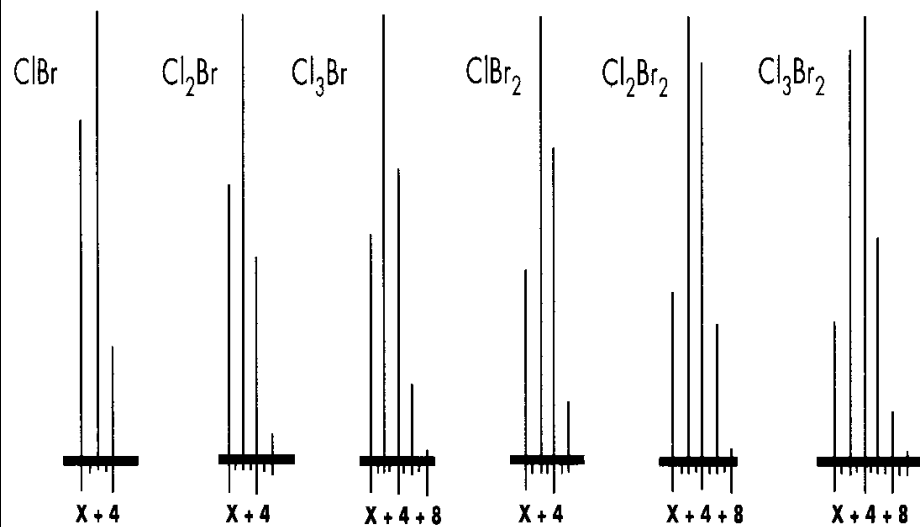


**GRAPHICAL REPRESENTATION OF RELATIVE ISOTOPE PEAK INTENSITIES FOR ANY GIVEN ION CONTAINING THE INDICATED NUMBER OF CHLORINE AND/OR BROMINE ATOMS**

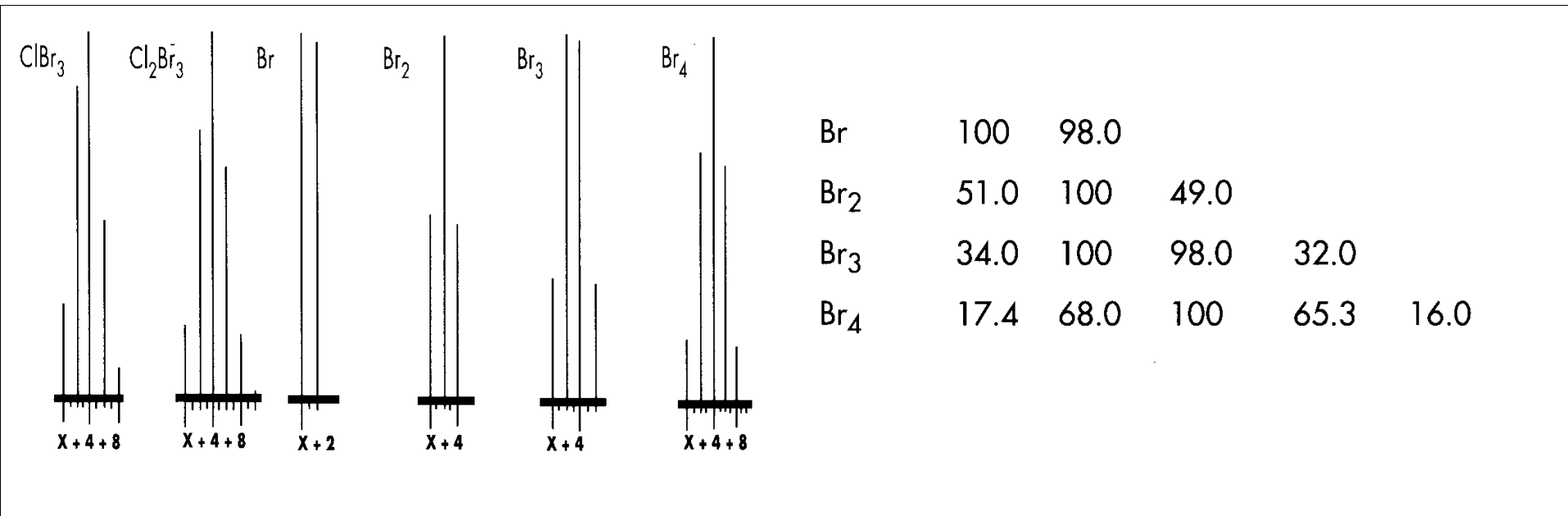


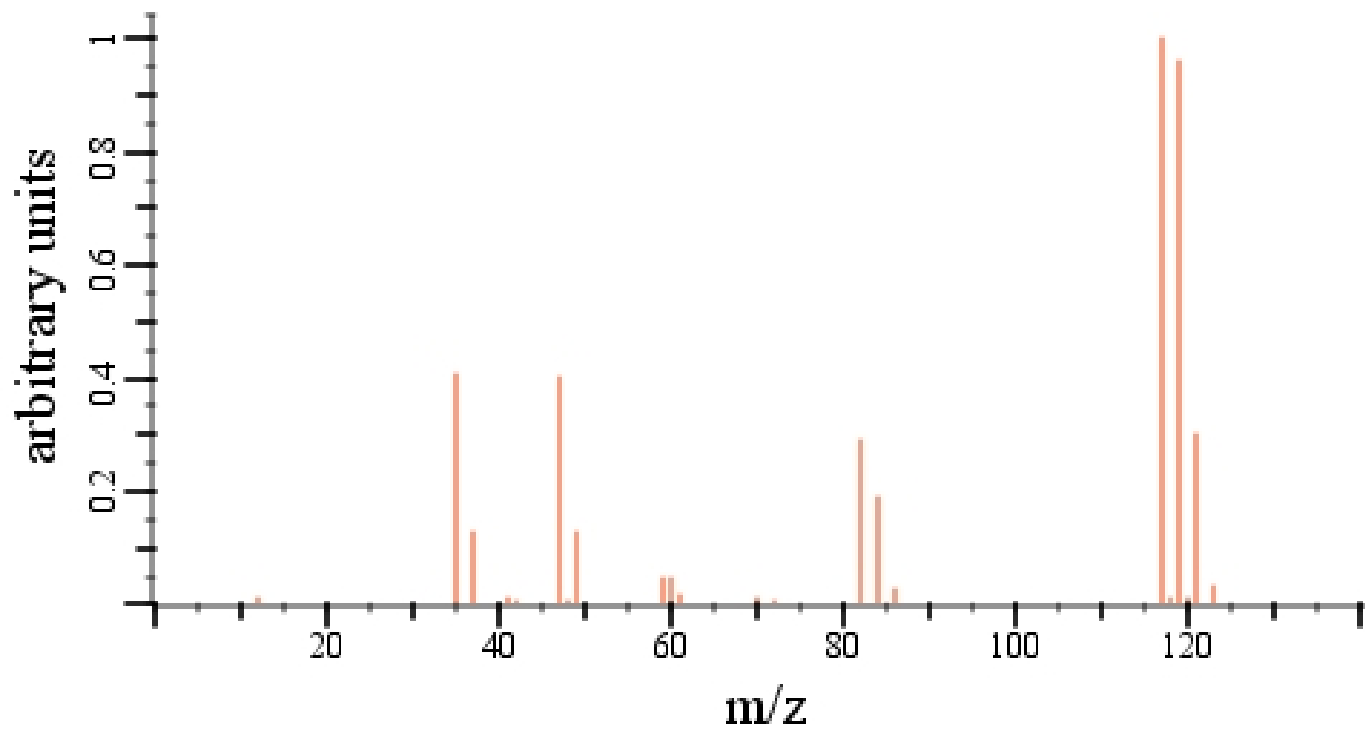
**CHLORINE-BROMINE ISOTOPE ABUNDANCE RATIOS**

Cl-Br	X	X+2	X+4	X+6	X+8	X+10
Cl	100	32.5				
Cl <sub>2</sub>	100	65.0	10.6			
Cl <sub>3</sub>	100	97.5	31.7	3.4		
Cl <sub>4</sub>	76.9	100	48.7	10.5	0.9	
Cl <sub>5</sub>	61.5	100	65.0	21.1	3.4	0.2
Cl <sub>6</sub>	51.2	100	81.2	35.2	8.5	1.1

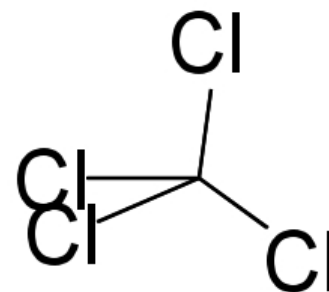


ClBr	76.6	100	24.4			
Cl <sub>2</sub> Br	61.4	100	45.6	6.6		
Cl <sub>3</sub> Br	51.2	100	65.0	17.6	1.7	
ClBr <sub>2</sub>	43.8	100	69.9	13.7		
Cl <sub>2</sub> Br <sub>2</sub>	38.3	100	89.7	31.9	3.9	
Cl <sub>3</sub> Br <sub>2</sub>	31.3	92.0	100	49.9	11.6	1.0
ClBr <sub>3</sub>	26.1	85.1	100	48.9	8.0	
Cl <sub>2</sub> Br <sub>3</sub>	20.4	73.3	100	63.8	18.7	2.0





Position	Intensity
135	0%
133	0%
124	0%
123	3%
122	0%
121	30%
120	1%
119	96%
118	1%
117	100%
116	0%



## SOME COMMON AND REASONABLE LOSSES FROM THE MOLECULAR ION

M - 1	loss of hydrogen radical	M- $\cdot\text{H}$
M - 15	loss of methyl radical	M- $\cdot\text{CH}_3$
M - 29	loss of ethyl radical	M- $\cdot\text{CH}_2\text{CH}_3$
M - 31	loss of methoxyl radical	M- $\cdot\text{OCH}_3$
M - 43	loss of propyl radical	M- $\cdot\text{CH}_2\text{CH}_2\text{CH}_3$
M - 45	loss of ethoxyl radical	M- $\cdot\text{OCH}_2\text{CH}_3$
M - 57	loss of butyl radical	M- $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$
M - 2	loss of hydrogen	M- $\text{H}_2$
M - 18	loss of water	M- $\text{H}_2\text{O}$
M - 28	loss of CO or ethylene	M- CO or M - $\text{CH}_2\text{H}_4$
M - 32	loss of methanol	M- $\text{CH}_3\text{OH}$
M - 44	loss of $\text{CO}_2$	M- $\text{CO}_2$
M - 60	loss of acetic acid	M- $\text{CH}_3\text{CO}_2\text{H}$
M - 90	loss of silanol: $\text{HO-Si}(\text{CH}_3)_3$	M- $\text{HO-Si}(\text{CH}_3)_3$

# Fragmentação

- Governada pela estabilidade do íon produzido
- consideração
  - regra do octeto
  - deslocalização por ressonância
  - polarizabilidade e hiperconjugação
  - eletronegatividade
- Regra de Stevenson:  
Para quebra de uma ligações simples, o fragmento com o potencial de ionização mais baixo fica com a carga  
(em outras palavras, forma-se o íon mais estável)



# Regras Gerais de Fragmentação

Quebra de Uma Ligação (Quebras- $\alpha$ )

Quebra de Duas Ligações

- Eliminação de H-X
- retro Diels-Alder
- Rearranjo de McLafferty

# FRAGMENTATION PATTERNS

## ALKANES

The mass spectra of simple hydrocarbons have peaks at  $m/z$  values corresponding to the ions produced by breaking C-C bonds. Peaks can occur at ...

$m/z$	15	29	43	57	71	85	etc.
	$\text{CH}_3^+$	$\text{C}_2\text{H}_5^+$	$\text{C}_3\text{H}_7^+$	$\text{C}_4\text{H}_9^+$	$\text{C}_5\text{H}_{11}^+$	$\text{C}_6\text{H}_{13}^+$	

- the stability of the carbocation formed affects its abundance
- the more stable the cation the higher the peak
- the more alkyl groups attached to the carbocation the more stable it is

**most stable** tertiary  $3^\circ$  > secondary  $2^\circ$  > primary  $1^\circ$  **least stable**

alkyl groups are electron releasing and stabilise the cation

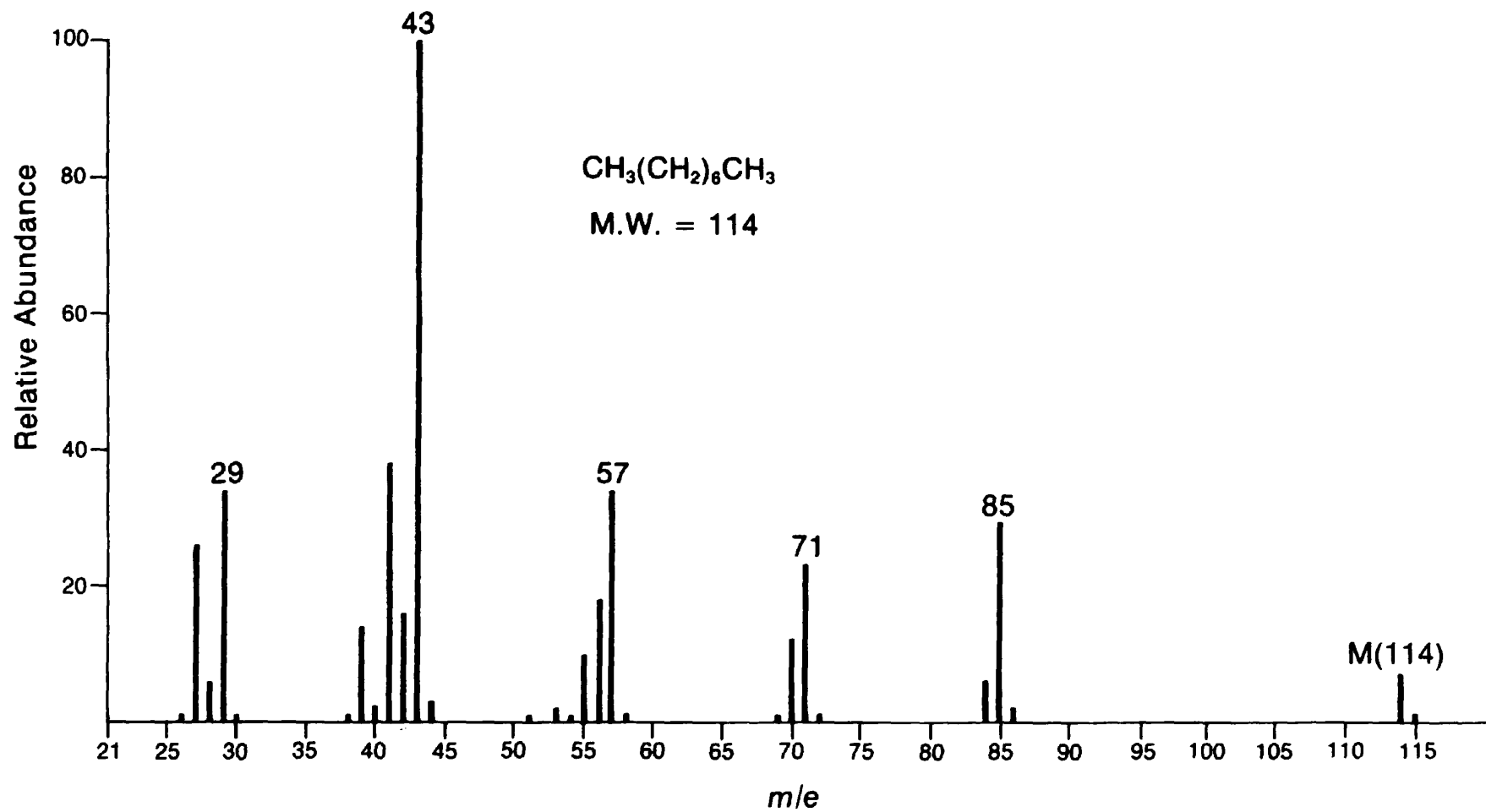
# Alkane Fragmentation

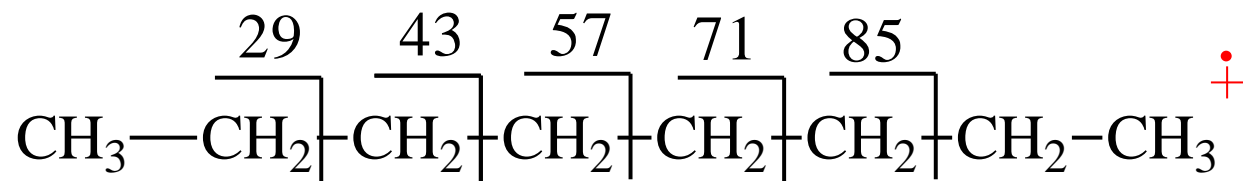
- Long chains give homologous series of  $m/z = 14$  units
- Long chains rarely lose methyl radical
- Straight chain alkanes give primary carbocation
- branched alkanes have small or absent  $M^+$
- enhanced fragmentation at branch points

## Cycloalkanes

- loss of side chain
- loss of ethylene fragments

# octane



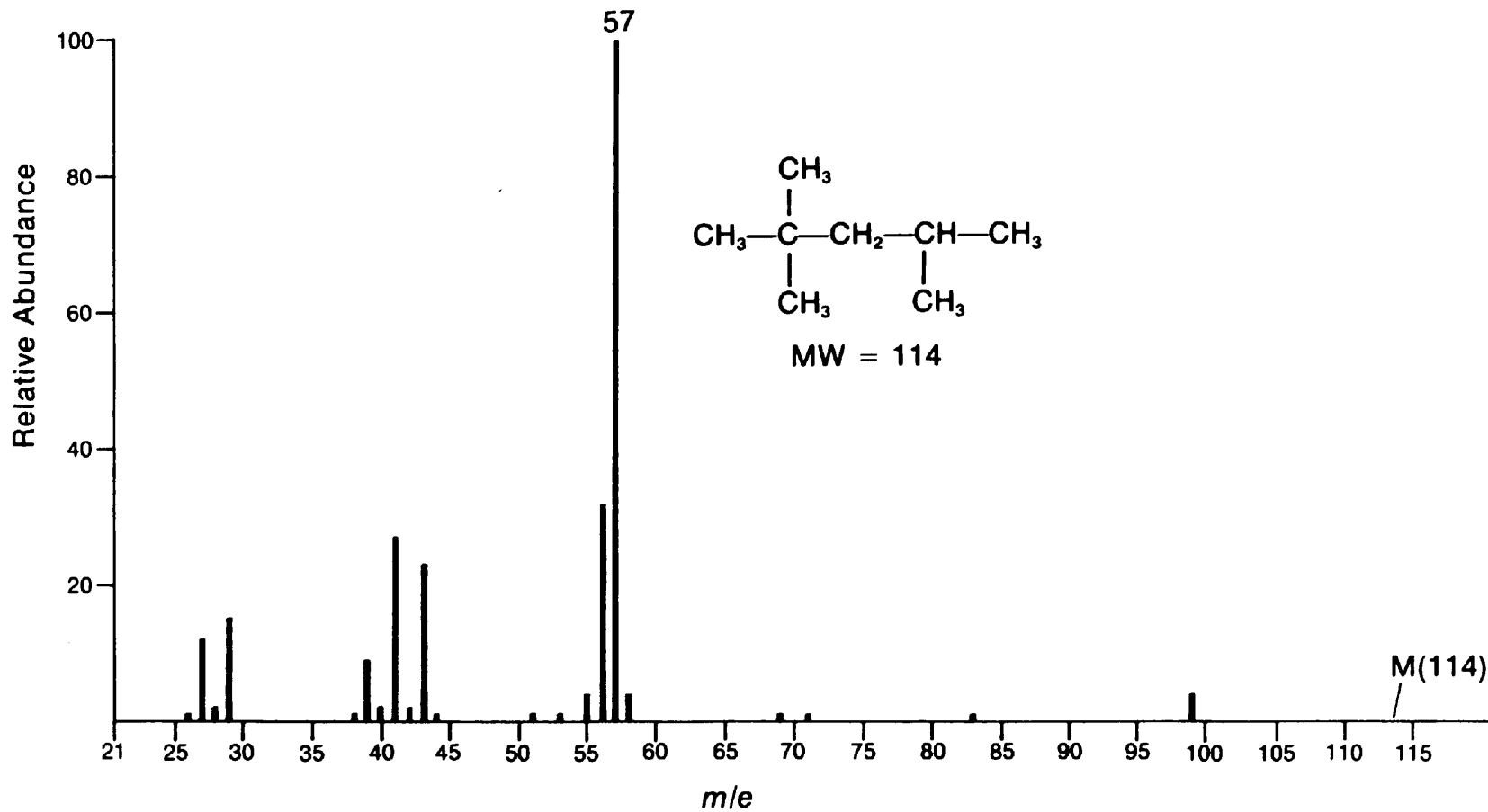


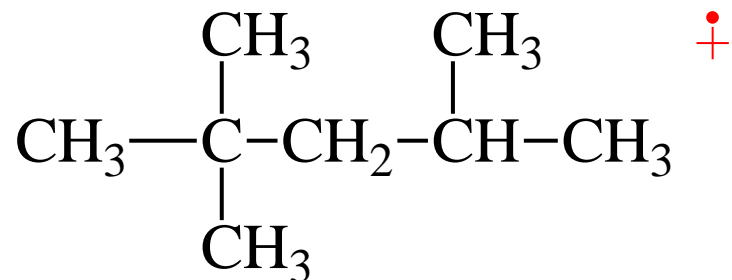
$$m/z = 114$$

linear alkane pattern

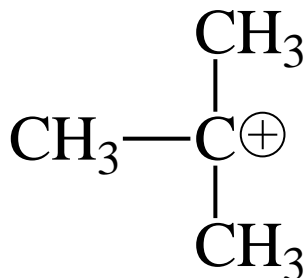
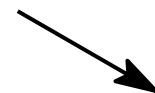
sequential peaks 14 mass units apart

# isooctane

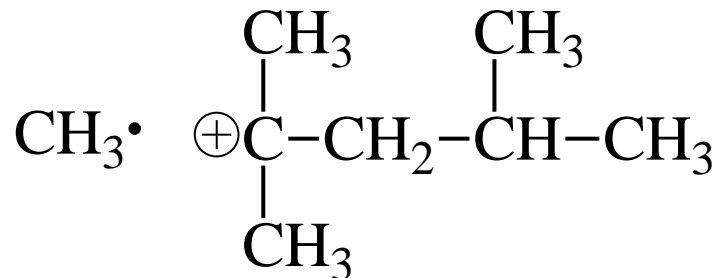
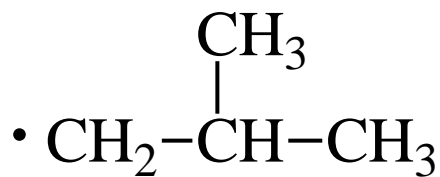




$m/z = 114$



$m/z = 57$



$m/z = 99$

branched alkane - formation of most stable carbocation

# Alkene Fragmentation

- Fairly prominent  $M^+$
- fragment ions of  $C_nH_{2n}^+$  and  $C_nH_{2n-1}^+$
- terminal alkenes lose allyl cation if possible

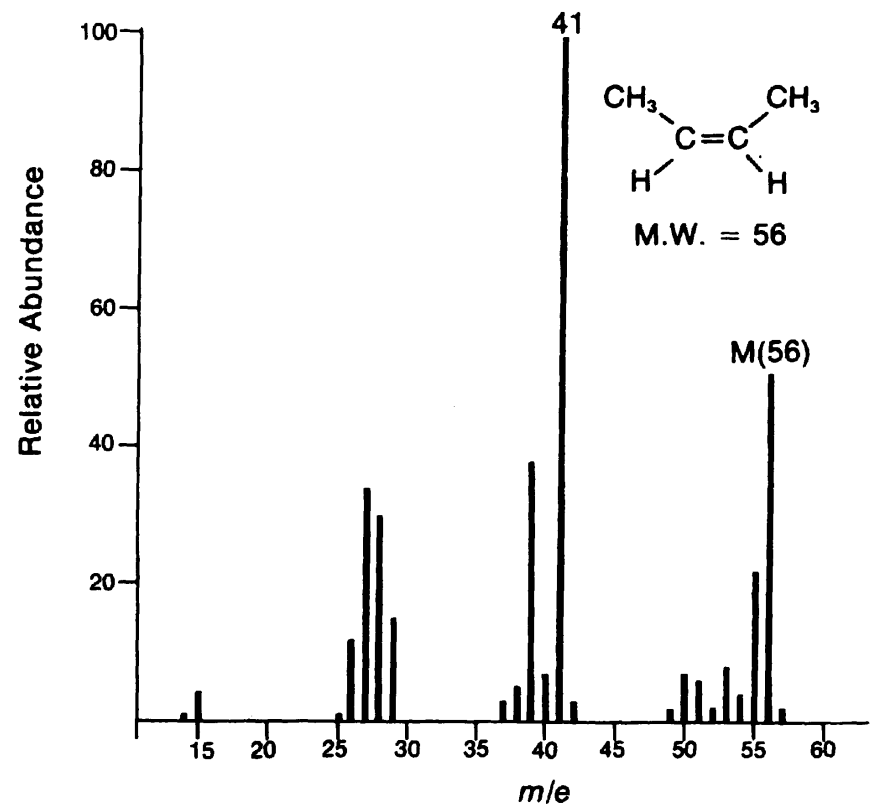
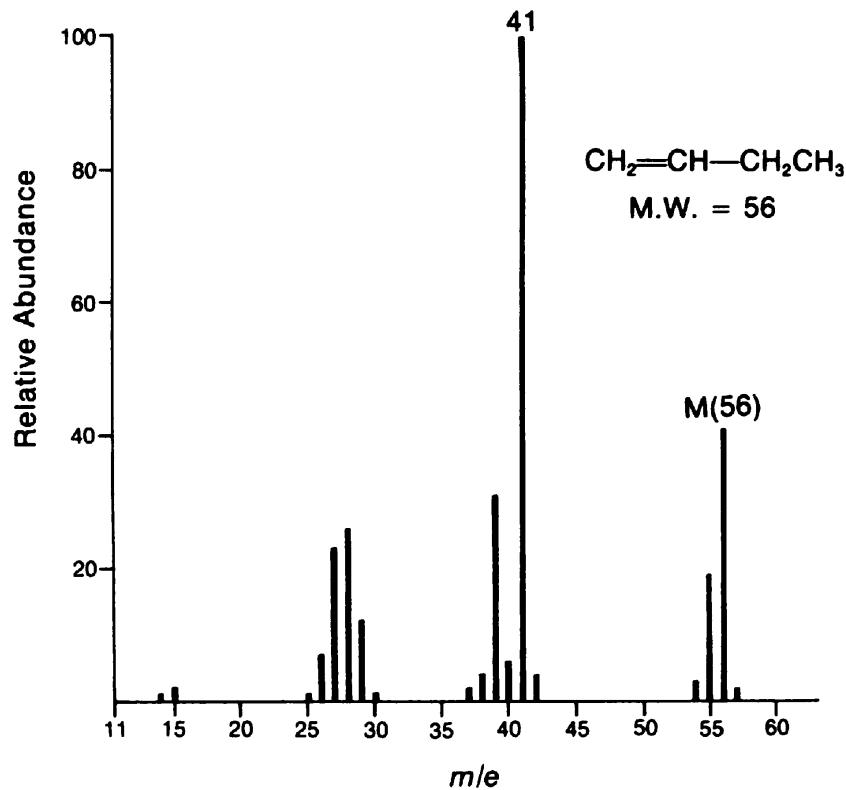
## Cycloalkenes

- prominent molecular ion
- retro Diels-Alder cleavage



# 1-butene & 2-butene

mass spectra are identical - not a good method for alkene isomers



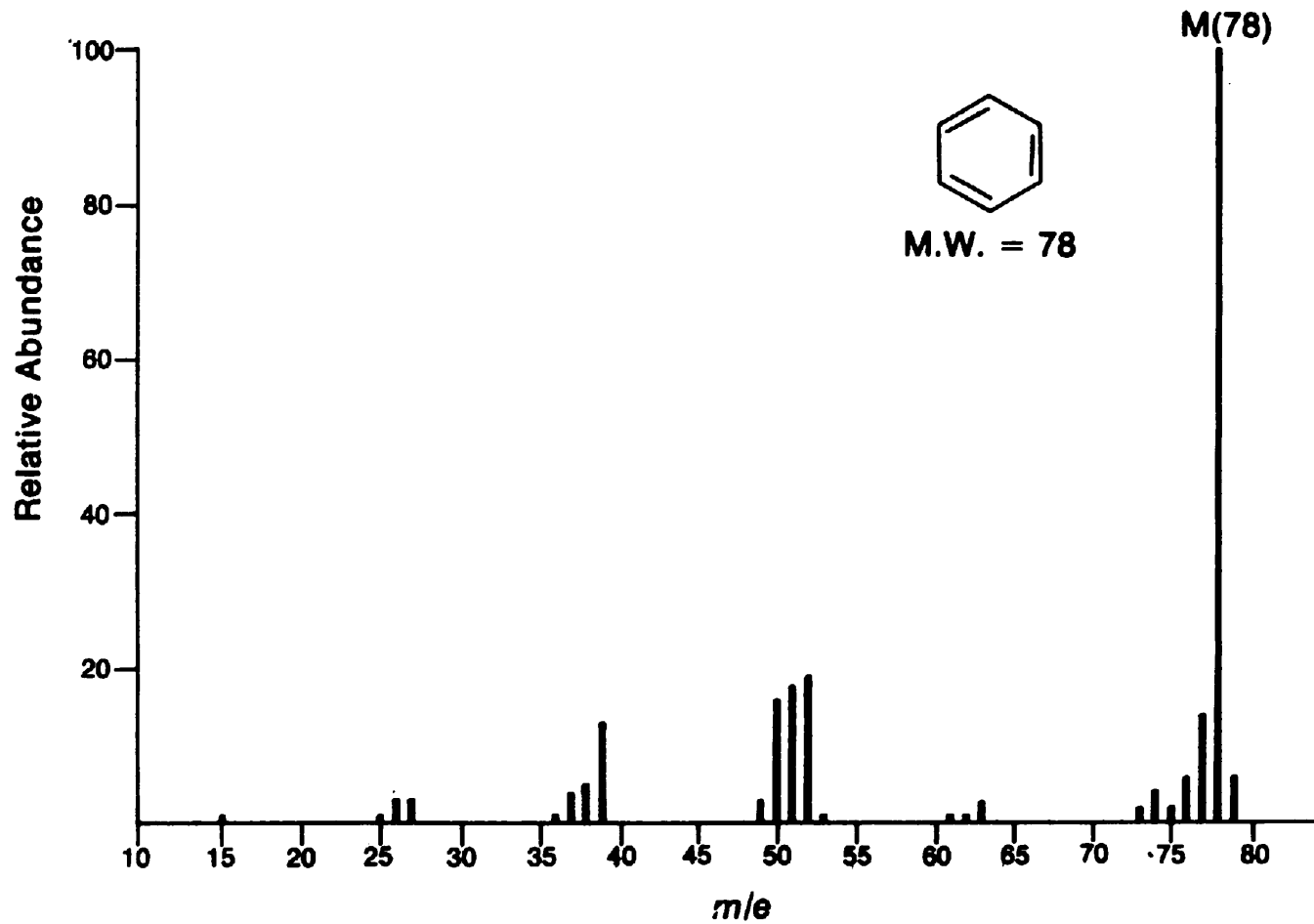
# Alkyne Fragmentation

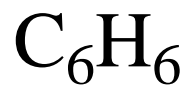
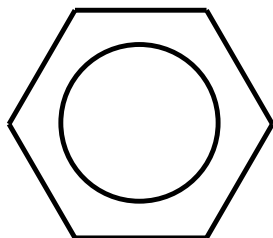
- Molecular ion readily visible
- terminal alkynes readily lose hydrogen atom
- terminal alkynes lose propargyl cation if possible

# Aromatic Hydrocarbon Fragmentation

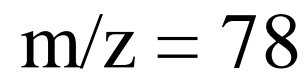
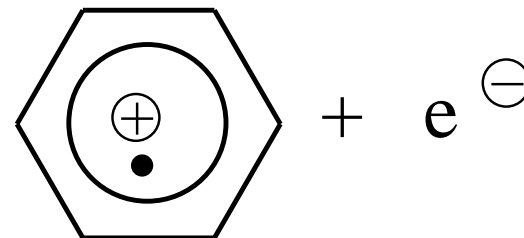
- Molecular ion usually strong
- alkylbenzenes cleave at benzylic carbon  
tropylium ion formation
- McLafferty rearrangement of aromatics  
need  $\gamma$ -hydrogens

# benzene



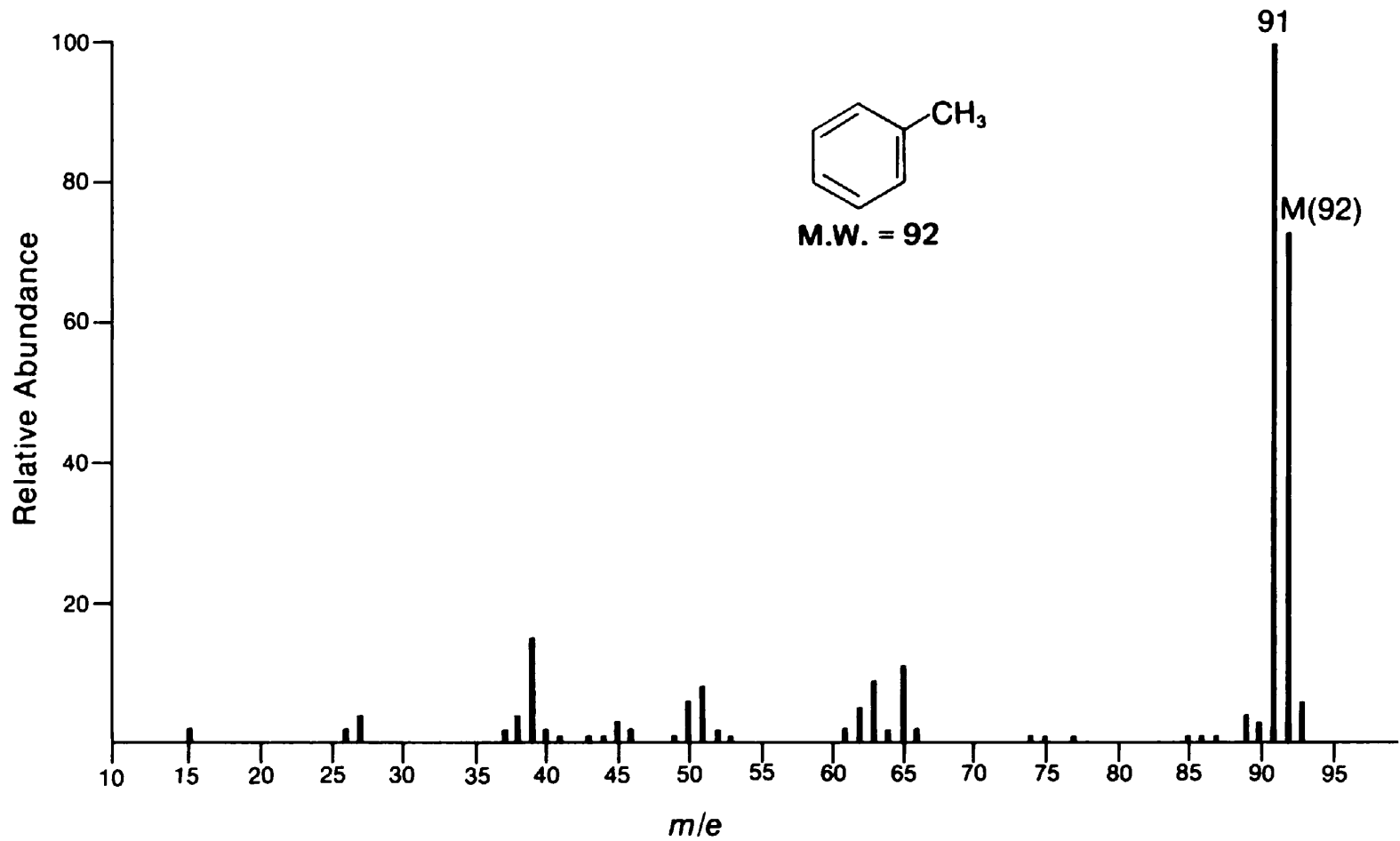


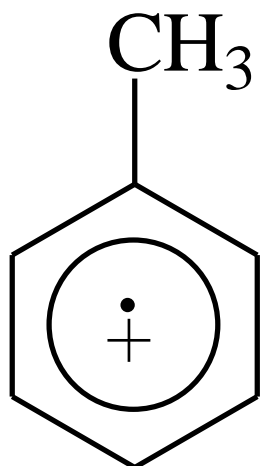
**closed shell**  
**(paired electrons)**



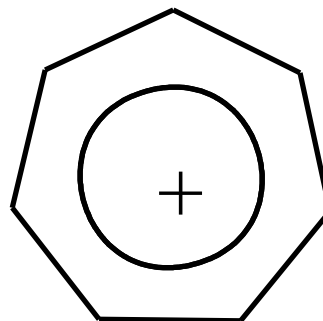
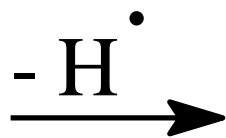
**open shell**  
**(odd electron ion)**

# toluene





$m/z = 92$

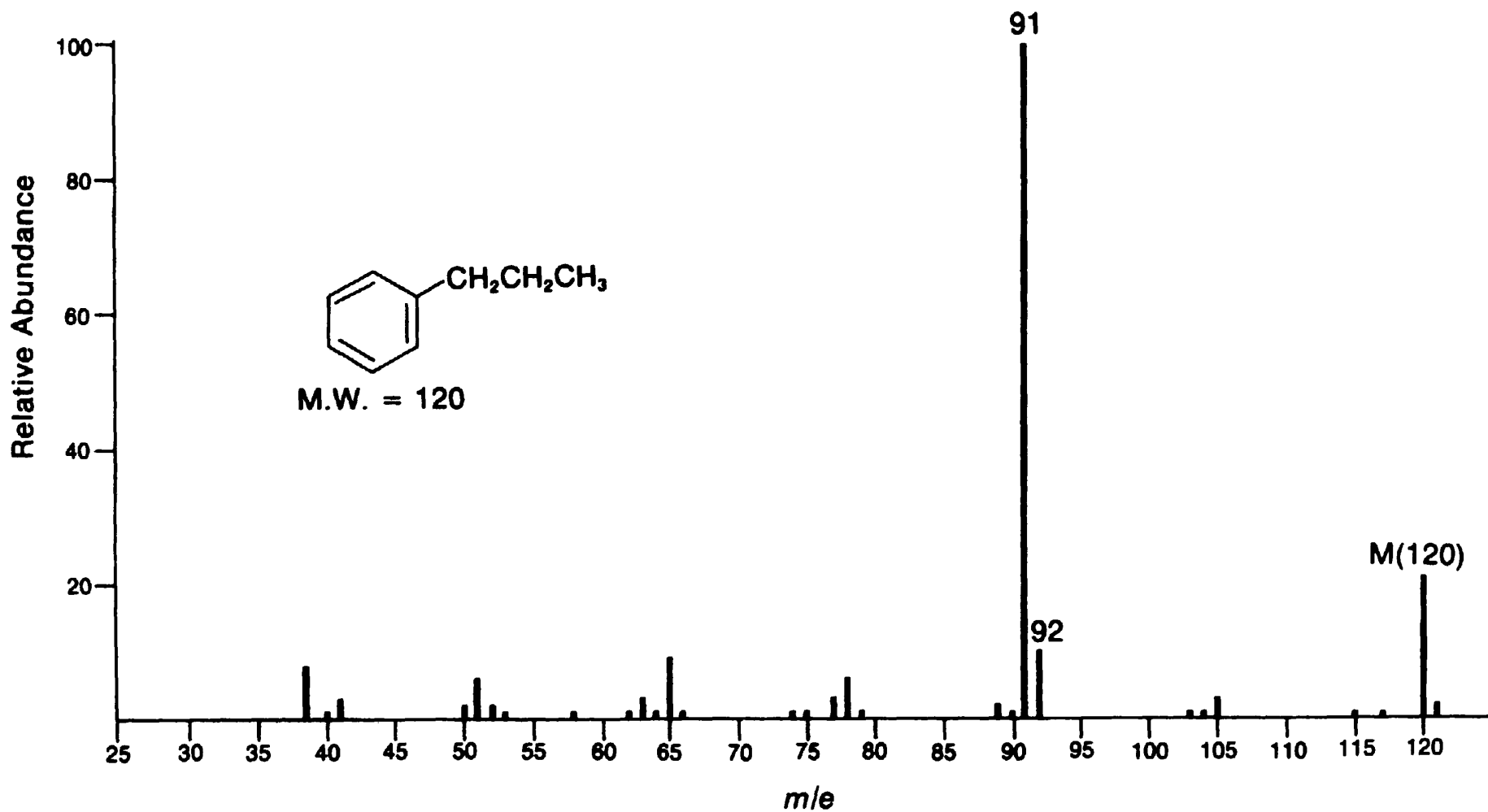


$m/z = 91$

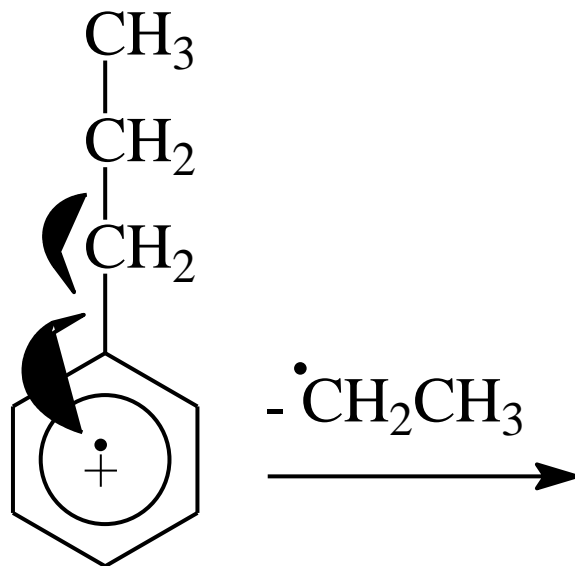
$C_7H_7$

tropylium ion

# n-propylbenzene





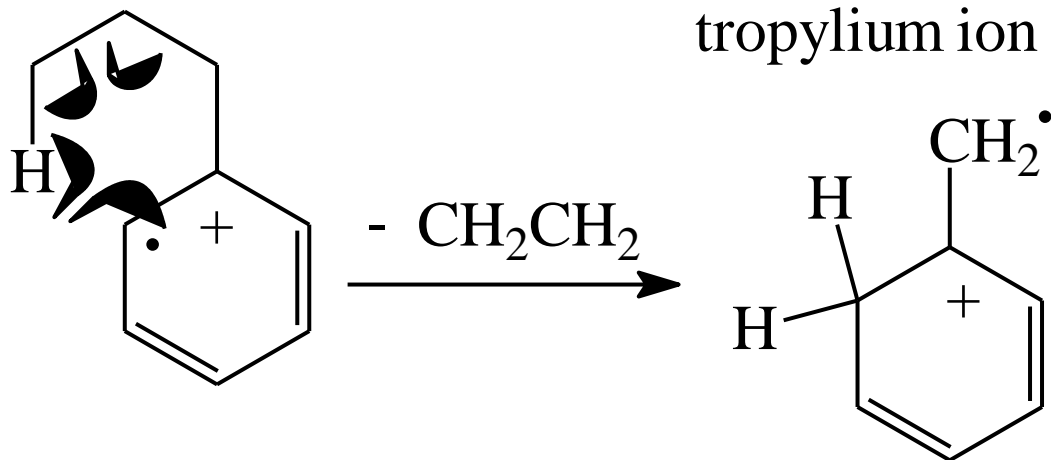


$m/z = 120$

$m/z = 91$

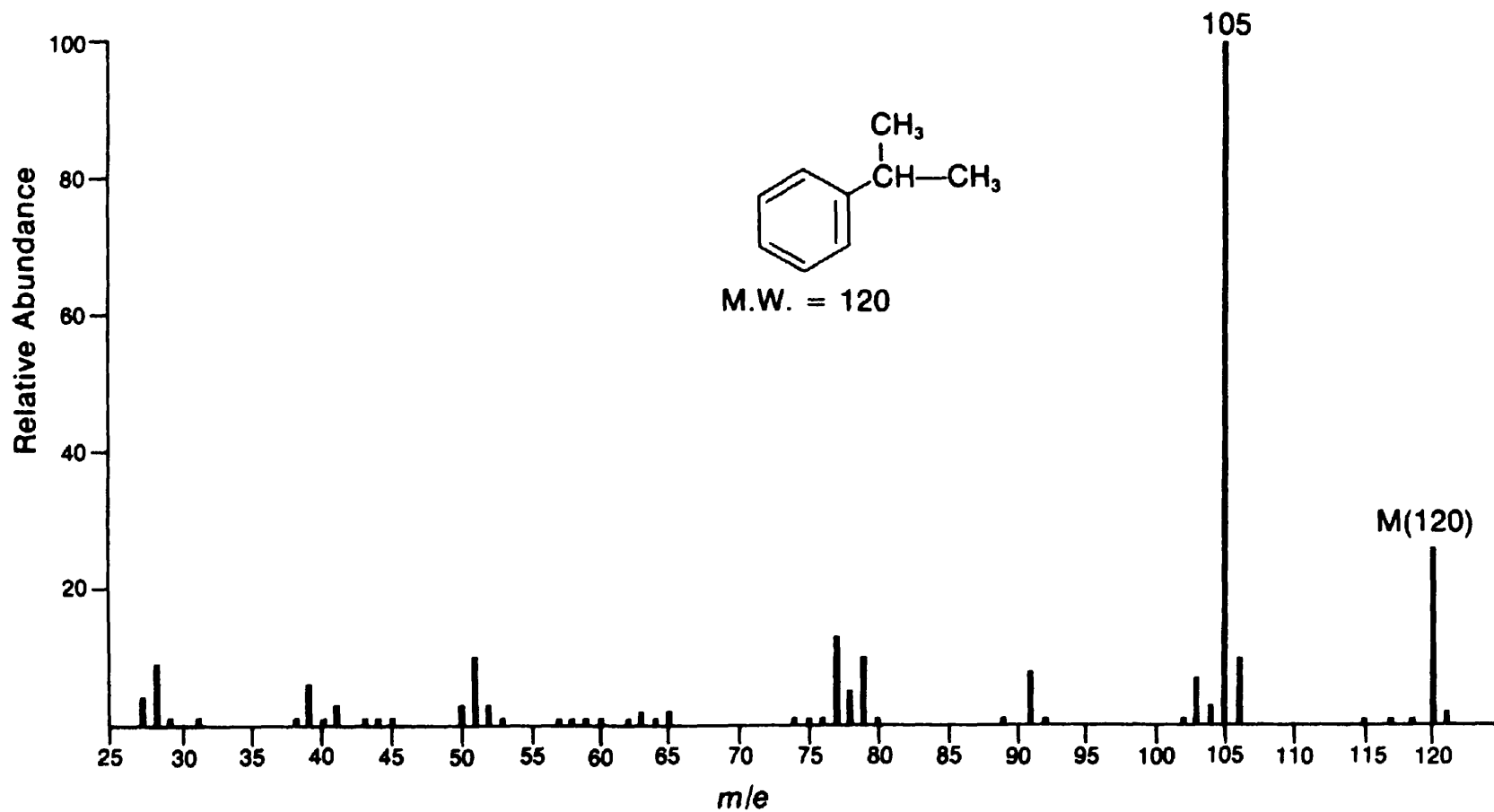
$\text{C}_7\text{H}_7$

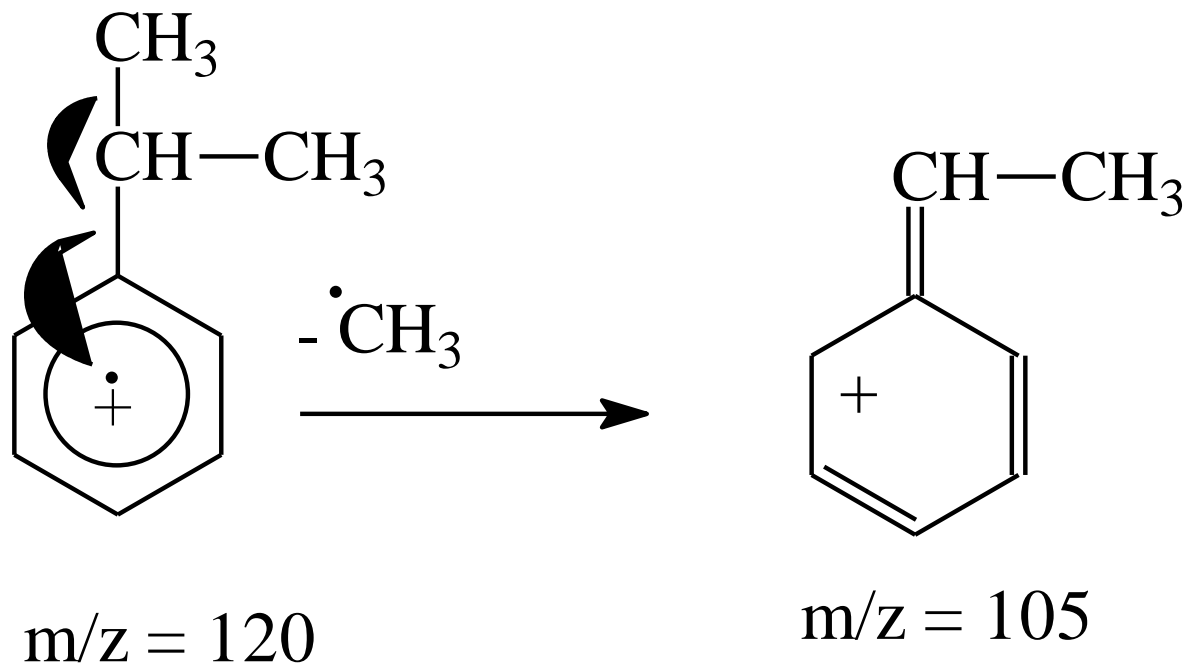
tropylium ion



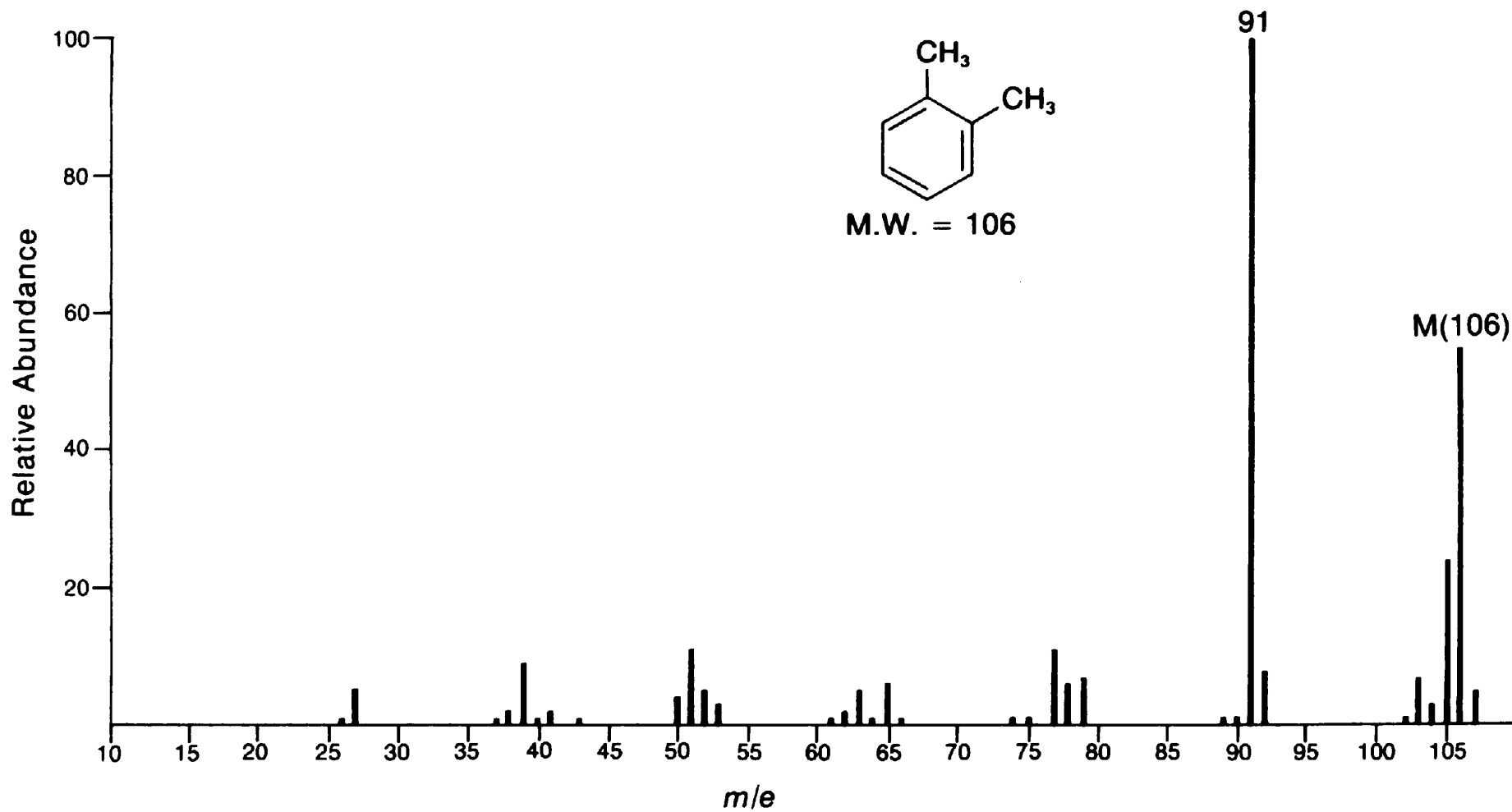
$m/z = 92$

# isopropylbenzene

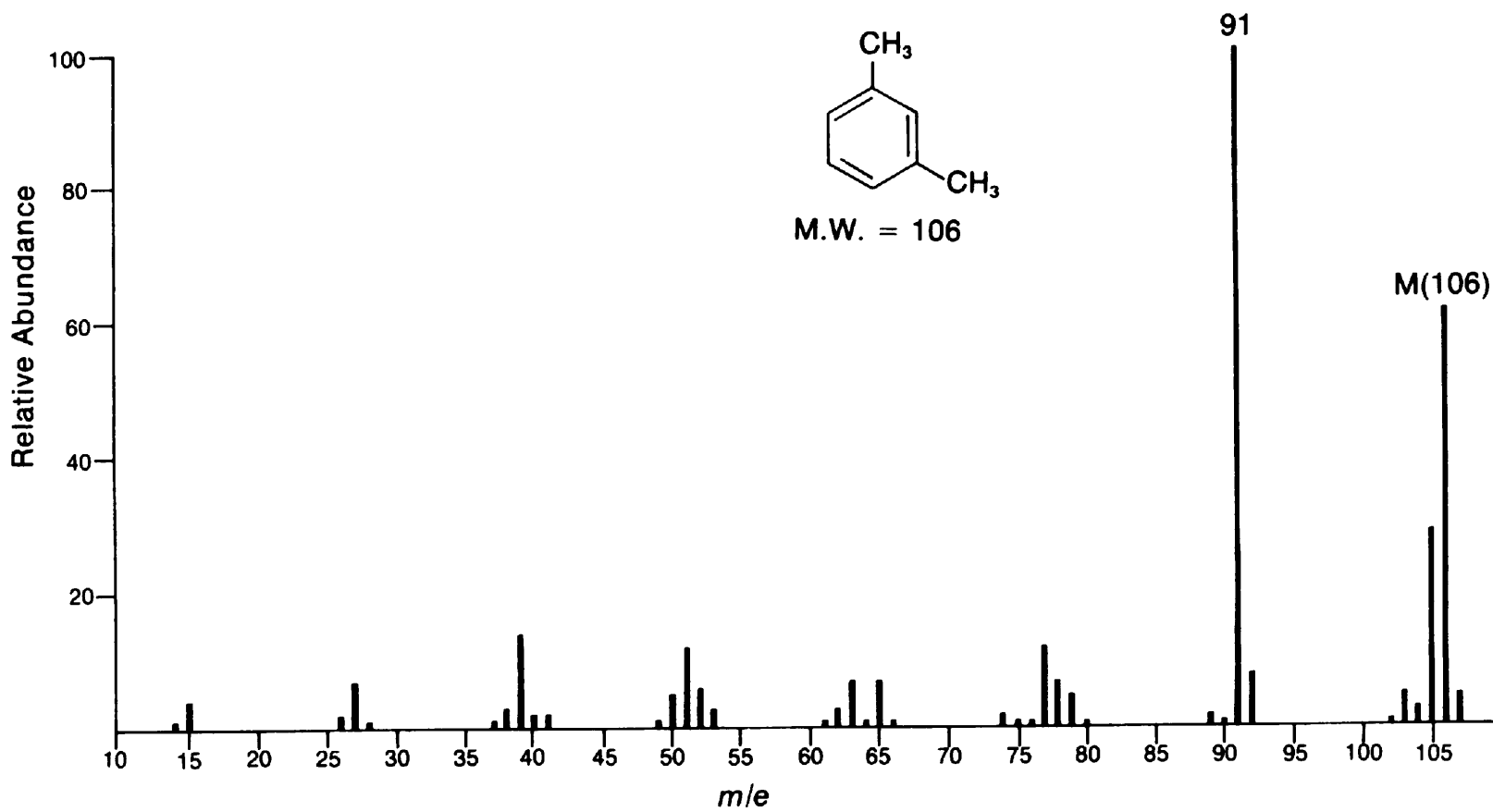




# o-xylene



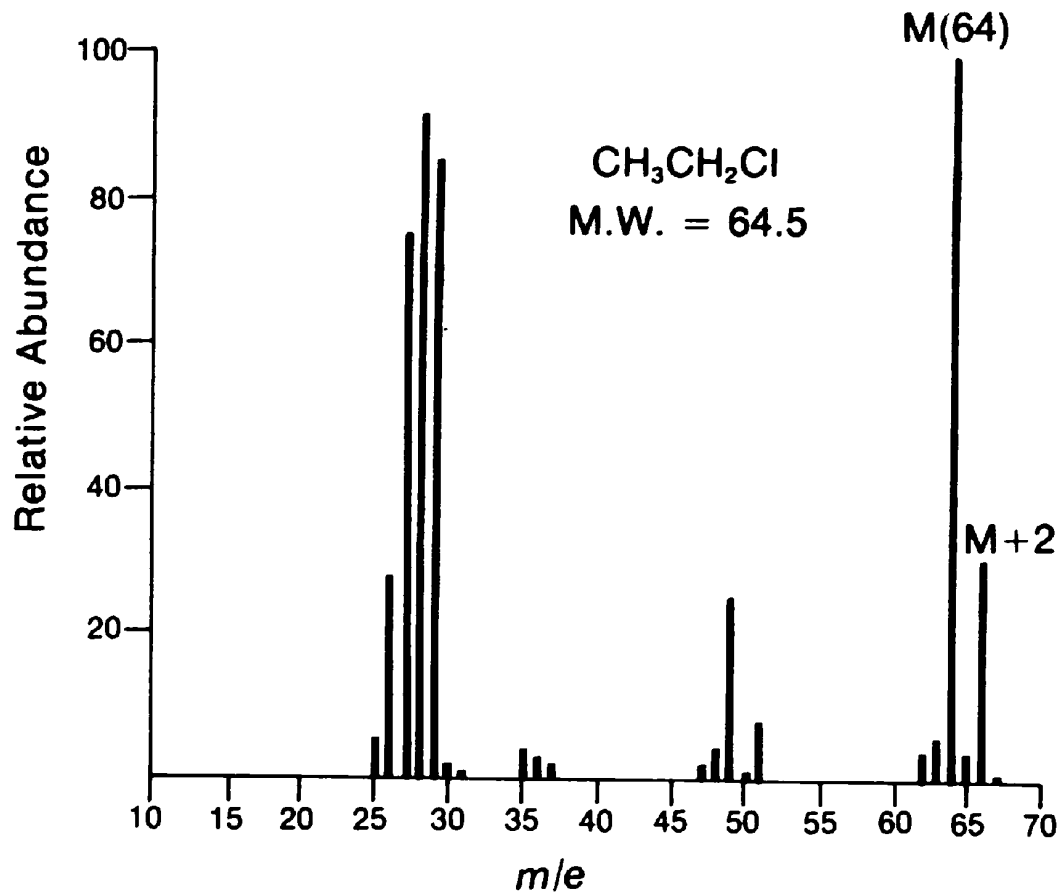
# m-xylene

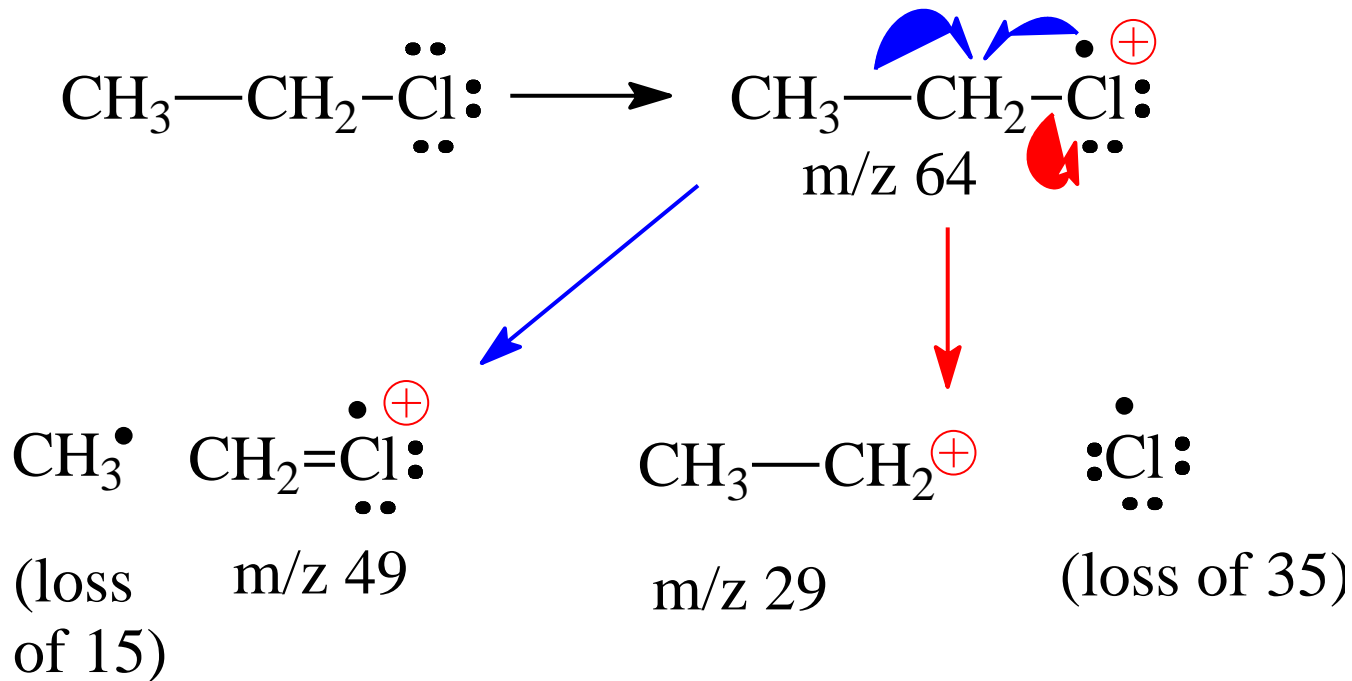


# Halide Fragmentation

- Loss of halogen atom
- Elimination of HX
- alpha-cleavage
- 1,4-rearrangement

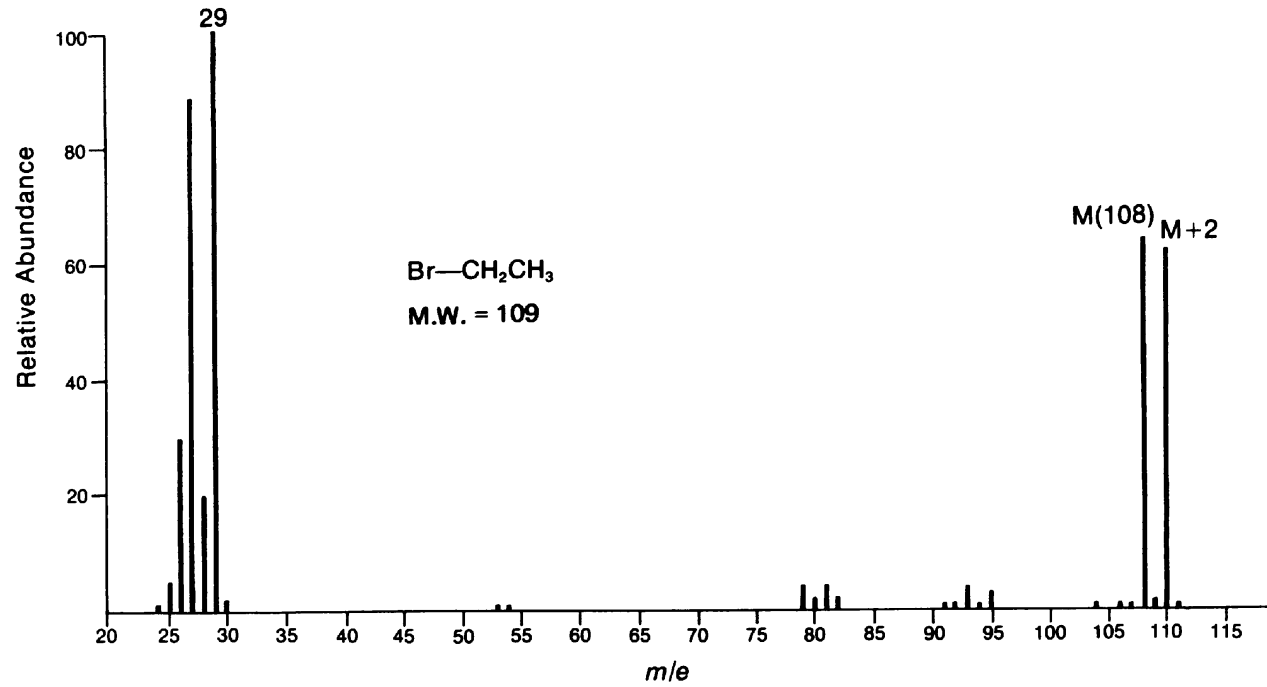
# chloroethane



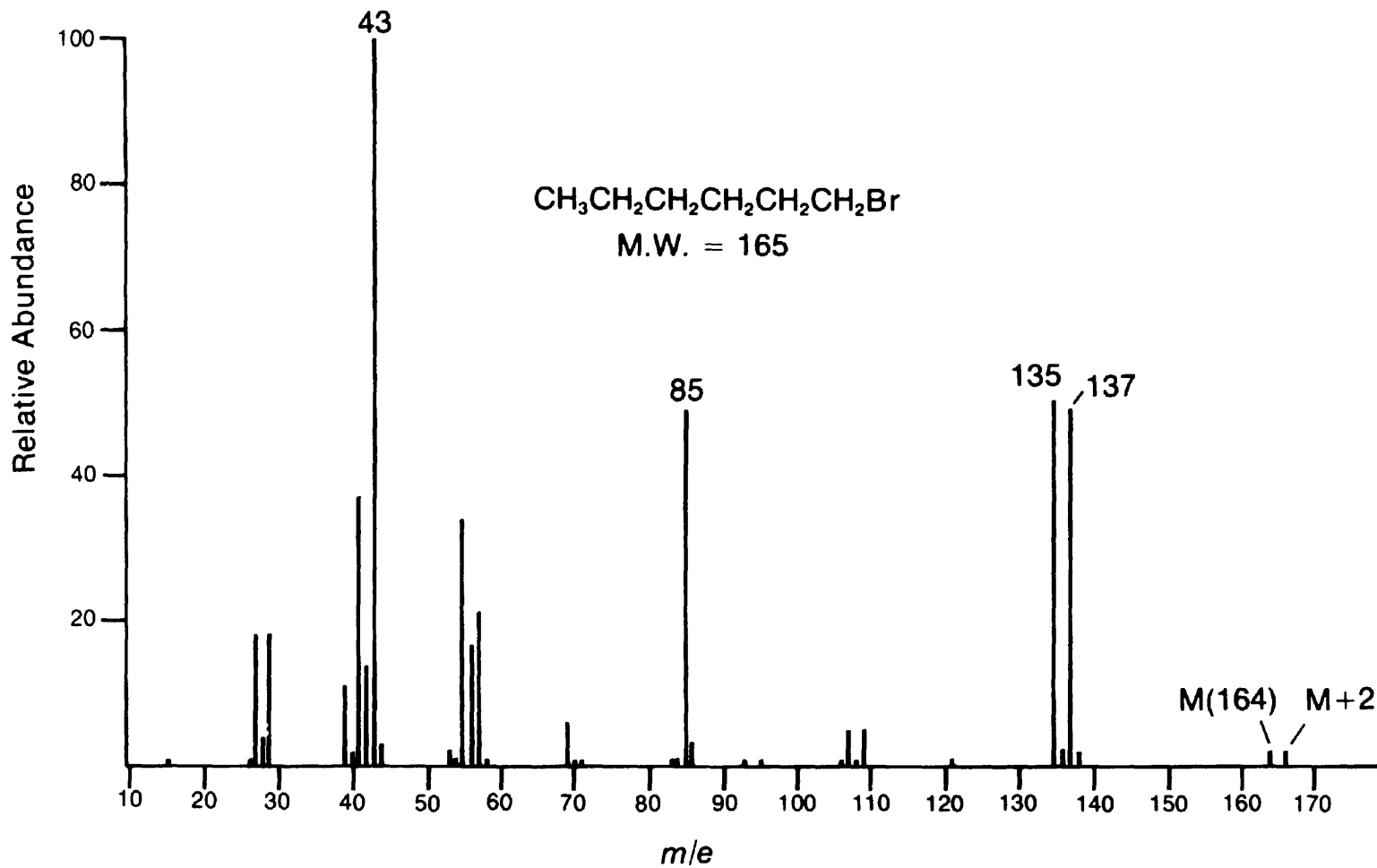




# bromoethane

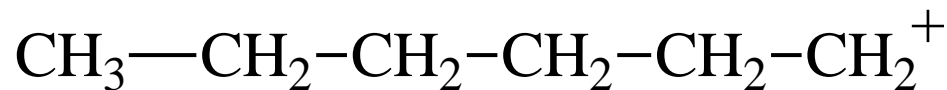
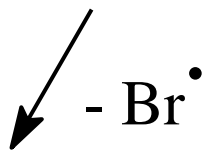


# bromohexane

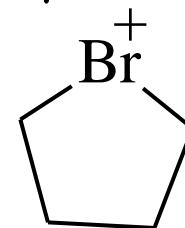
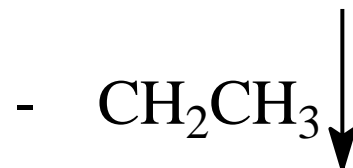
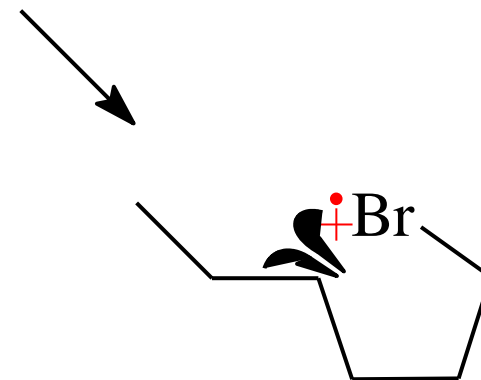




$m/z = 164$



85



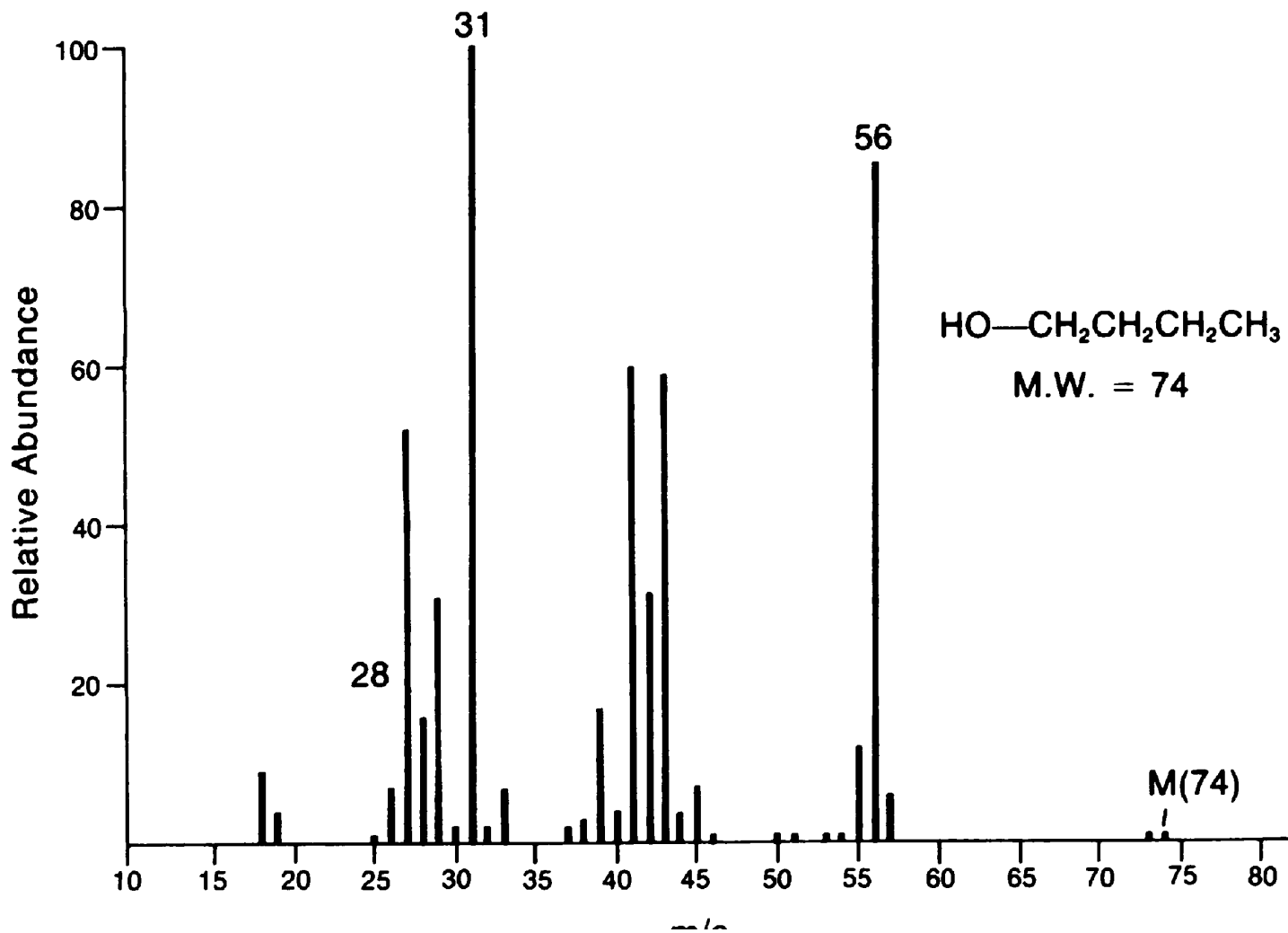
135

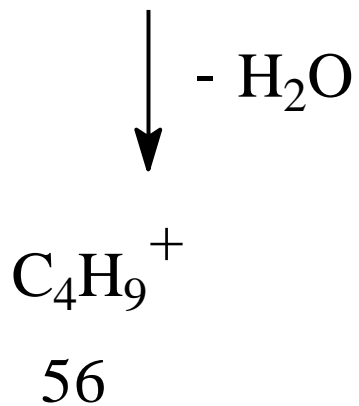
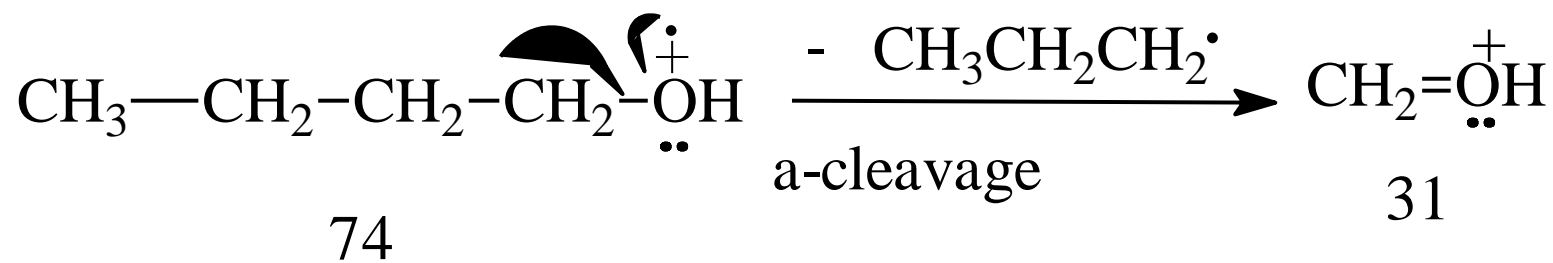
# Alcohol Fragmentation

- Molecular ion strength depends on substitution

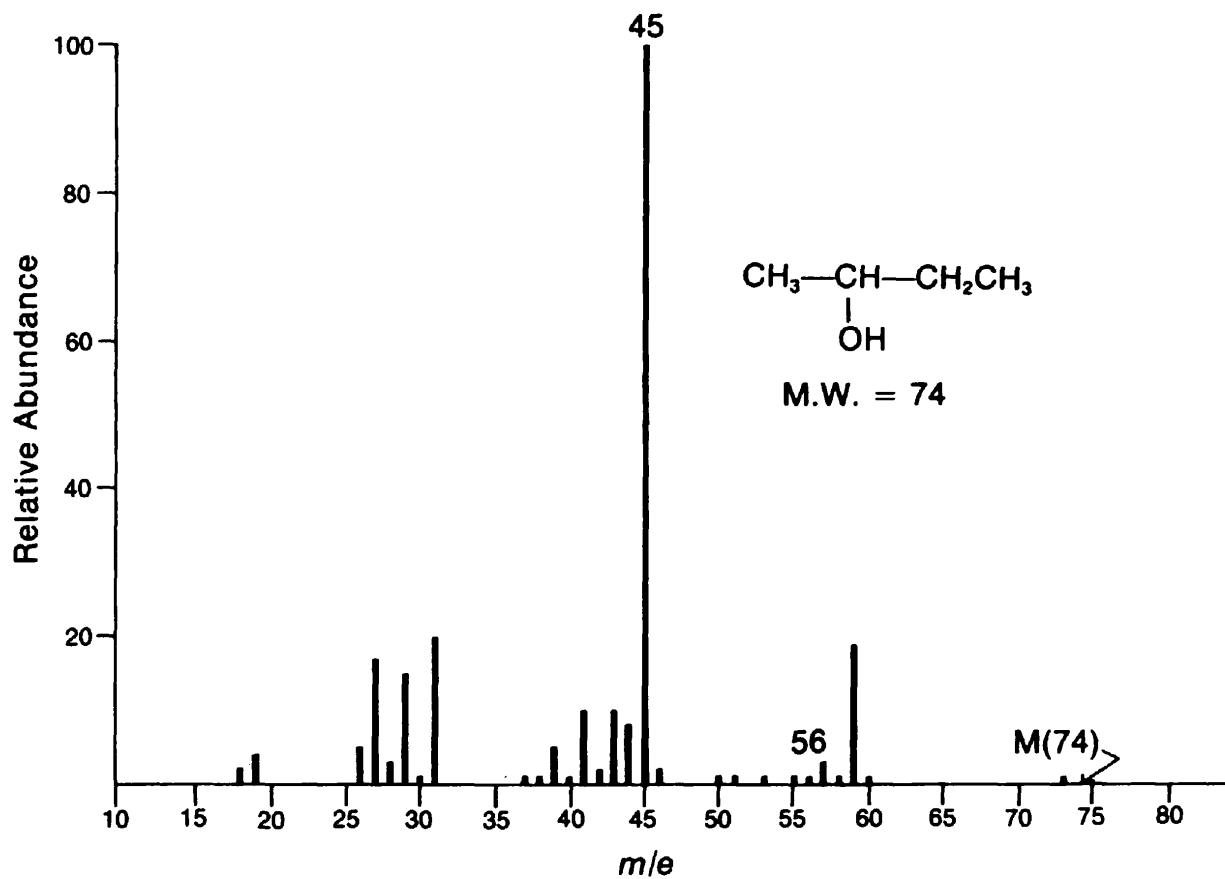
primary alcohol	weak $M^+$
secondary alcohol	VERY weak $M^+$
tertiary alcohol	$M^+$ usually absent
- Dehydration fragmentation
  - thermal vs. 1,4-dehydration of  $M^+$
- Loss of alkyl group
  - largest R group lost as radical

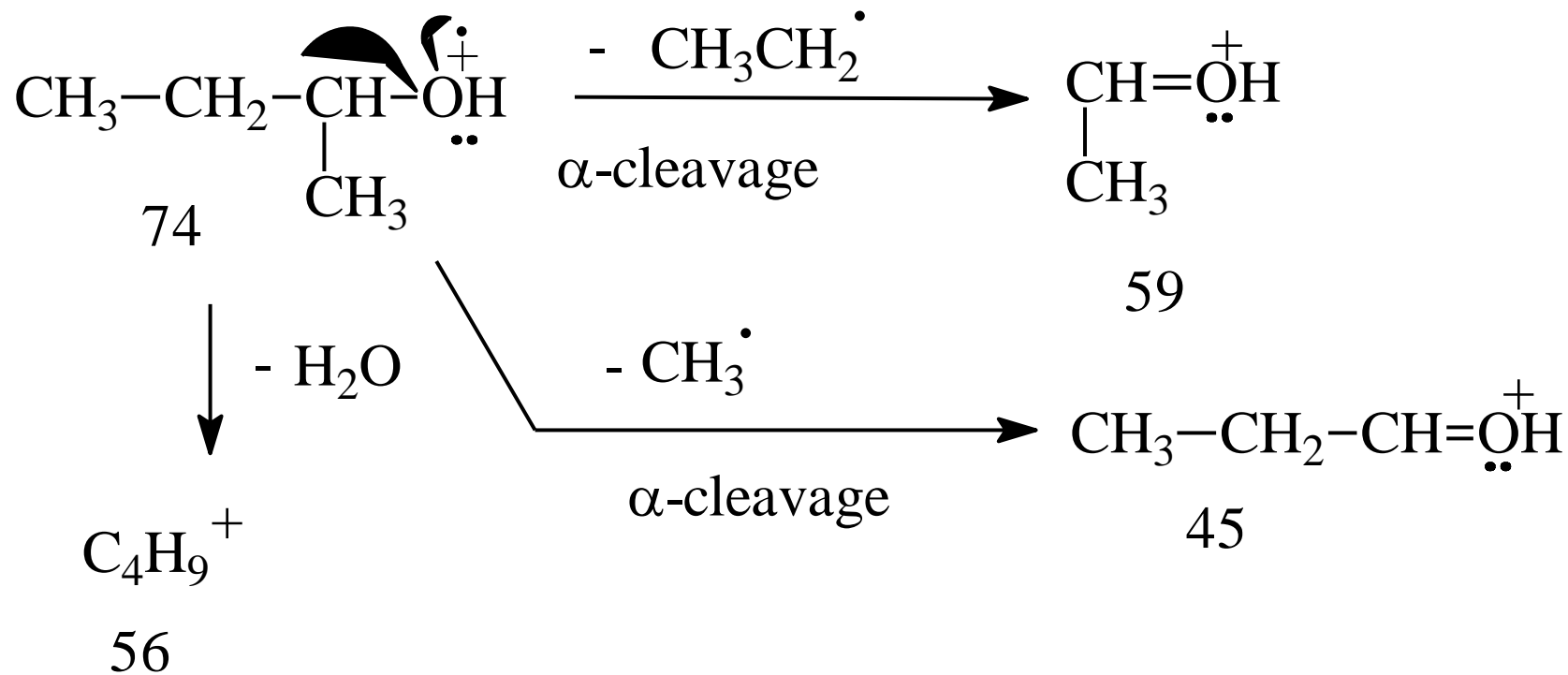
# 1-butanol





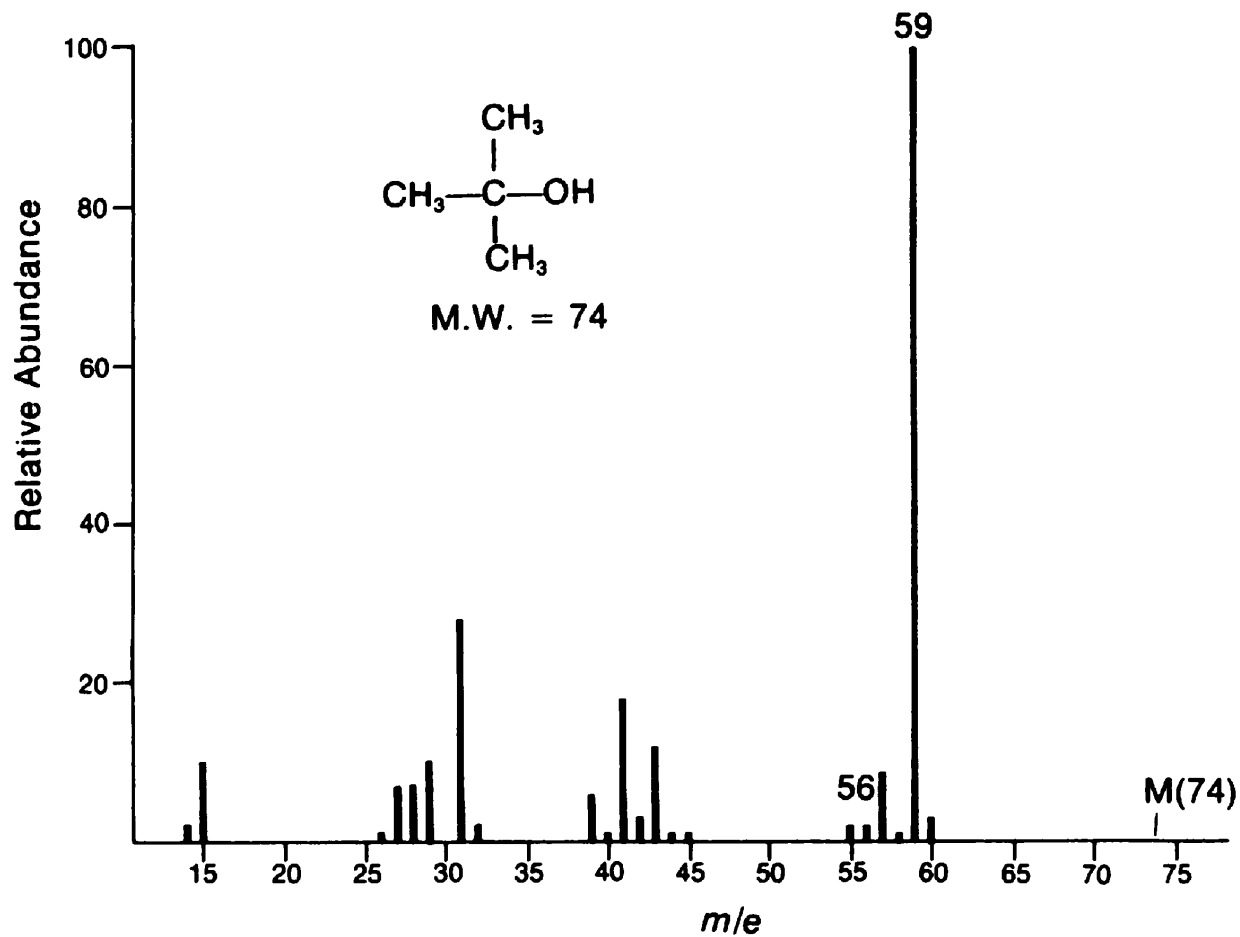
# 2-butanol



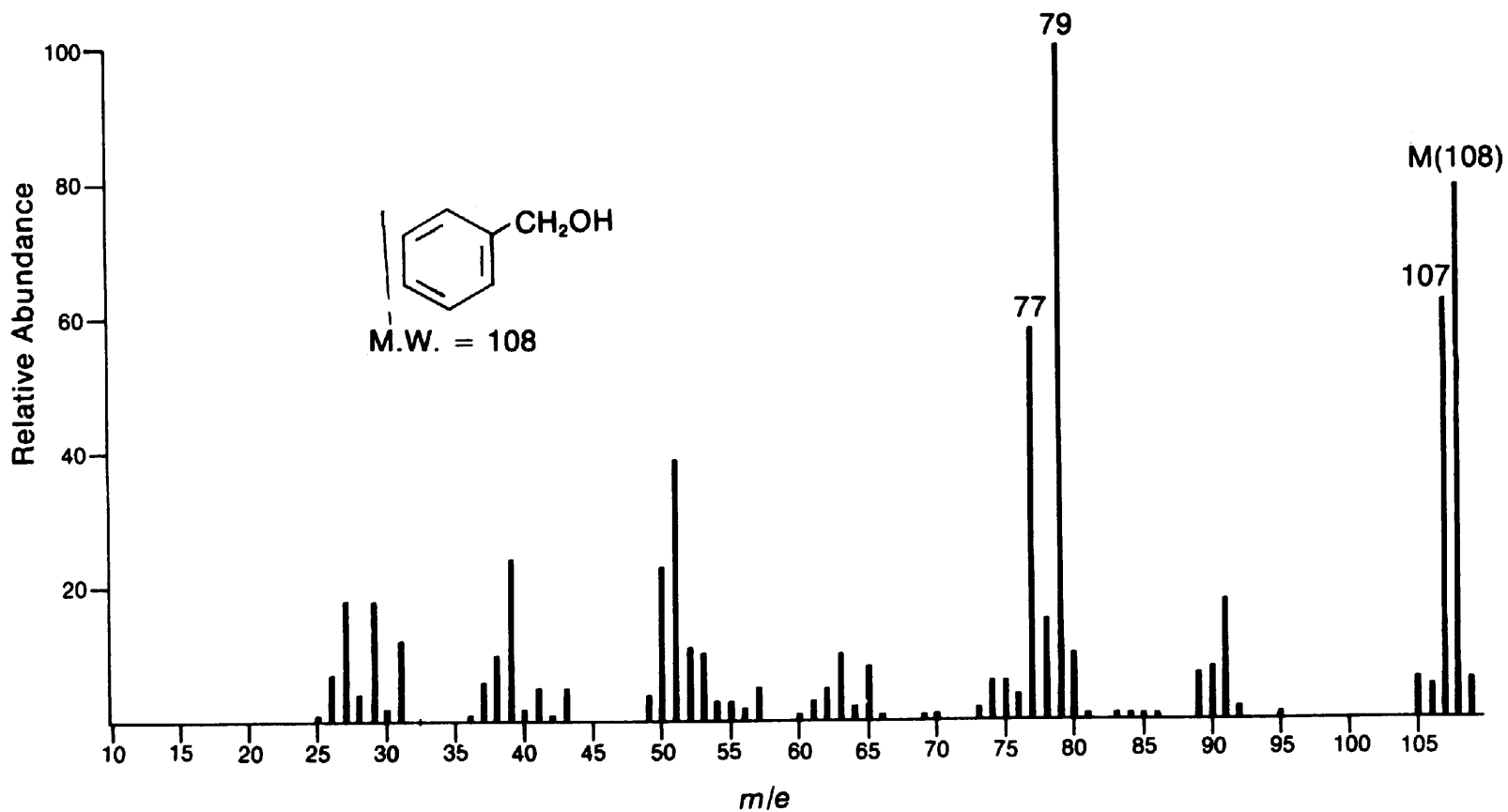


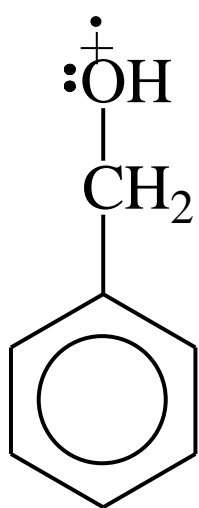


# t-butanol

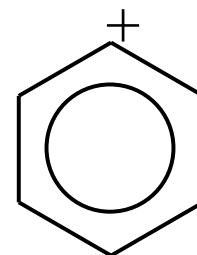
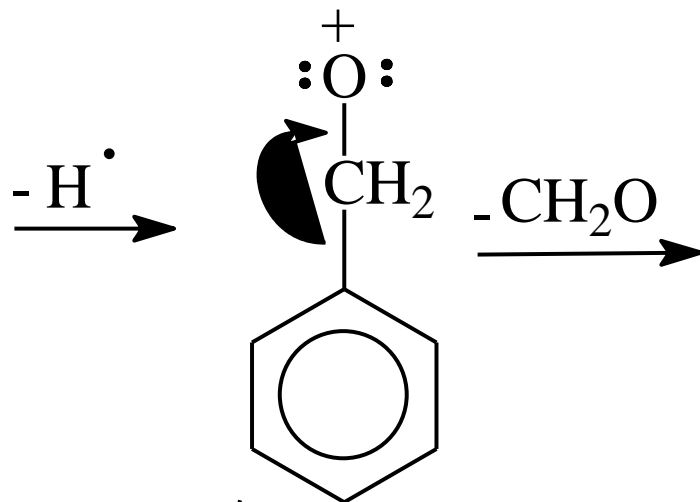


# benzyl alcohol

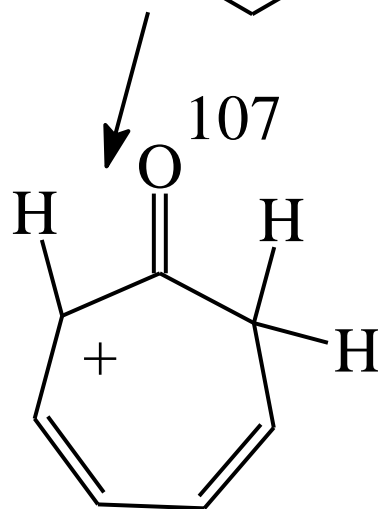




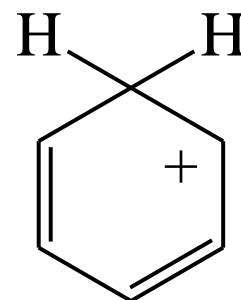
108



77

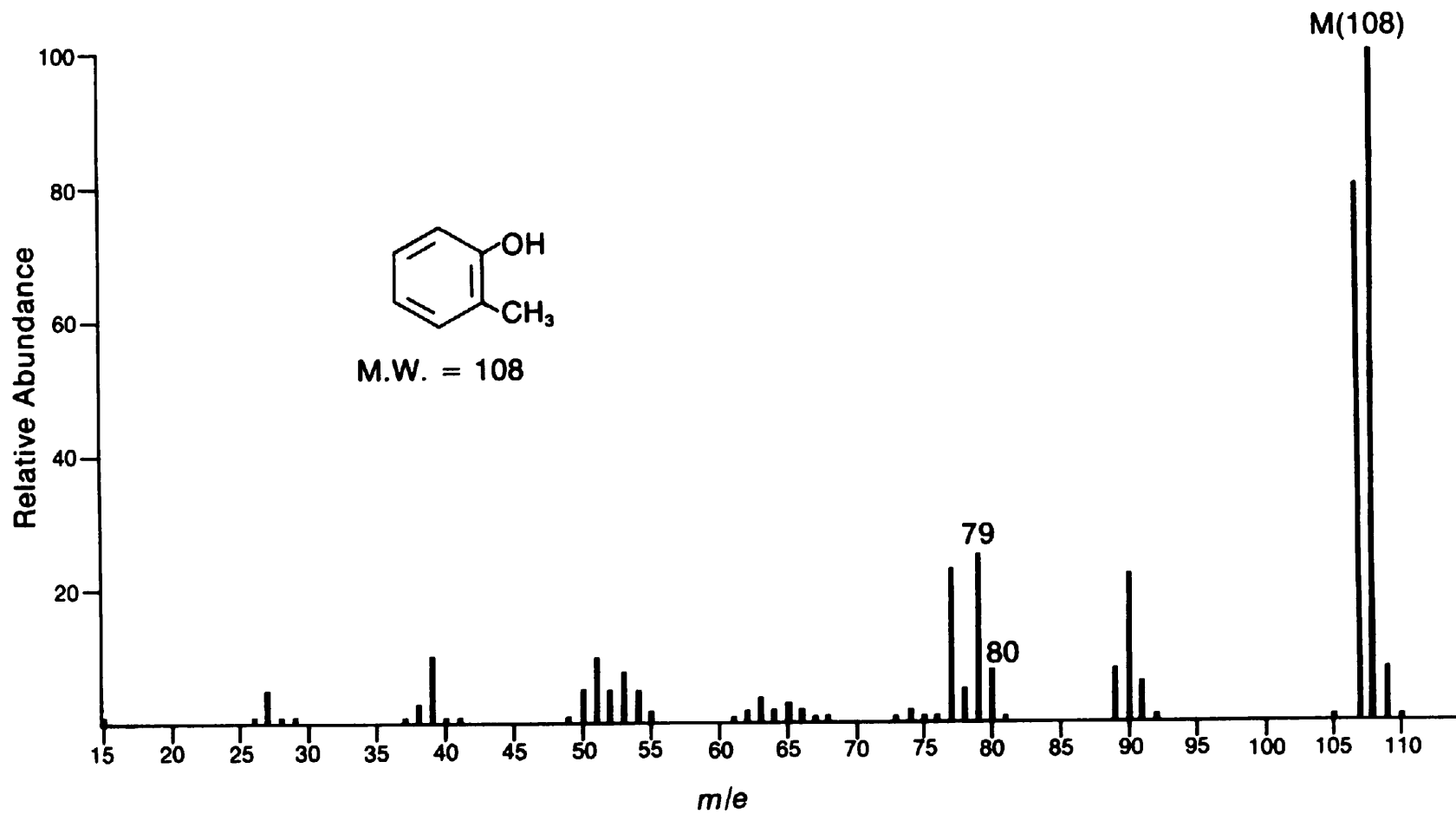


107



79

# o-cresol



# Carbonyl Compounds

Dominant fragmentation pathways:

$\alpha$ -cleavage

$\beta$ -cleavage

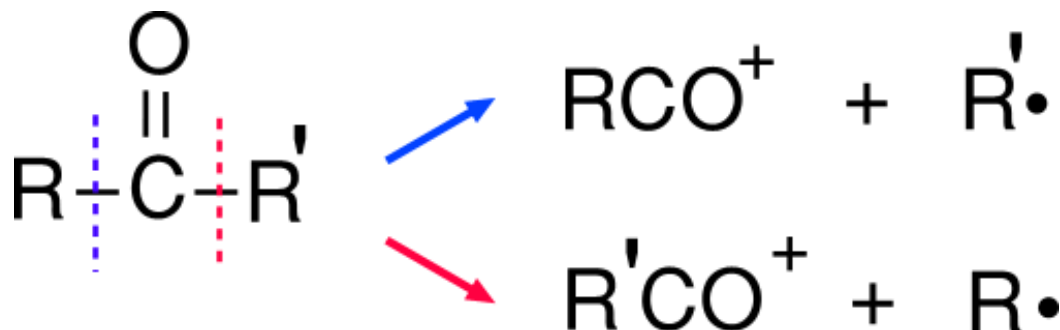
McLafferty rearrangement

# FRAGMENTATION PATTERNS

## ALDEHYDES AND KETONES

Cleavage of bonds next to the carbonyl group (C=O) is a characteristic fragmentation of aldehydes and ketones. A common fragment is carbon monoxide (CO) but as it is a molecule and thus uncharged it will not produce a peak of its own. However, it will produce an m/z drop of 28 somewhere in the spectrum.

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group

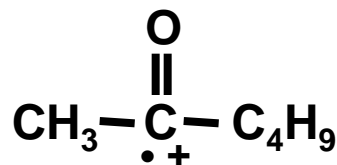


the more stable the acylium ion  $\text{RCO}^+$ , the more abundant it will be and the more abundant the species the taller its peak in the mass spectrum

# FRAGMENTATION PATTERNS

## Aldehydes and ketones

The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group.



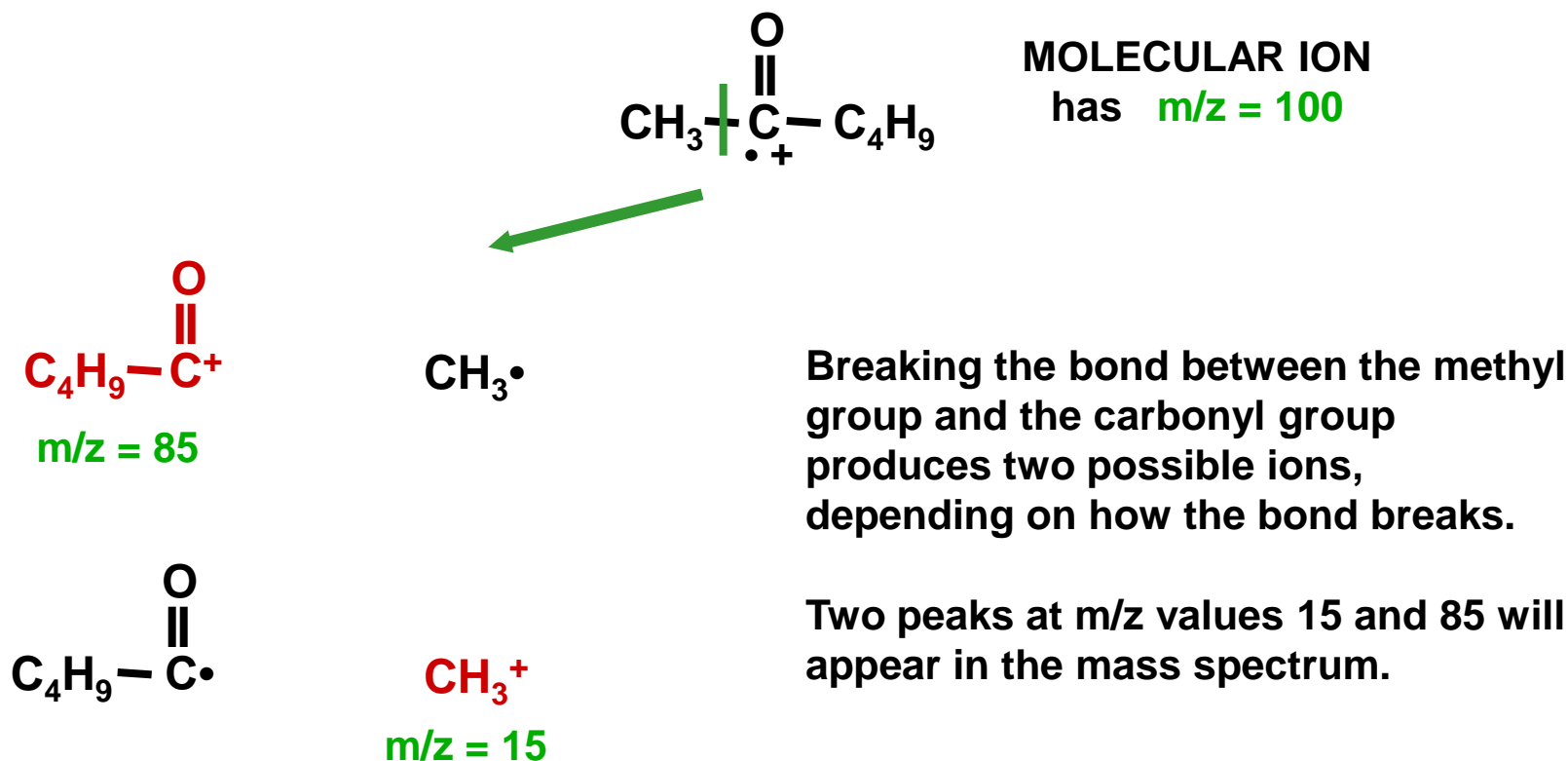
MOLECULAR ION  
has  $m/z = 100$



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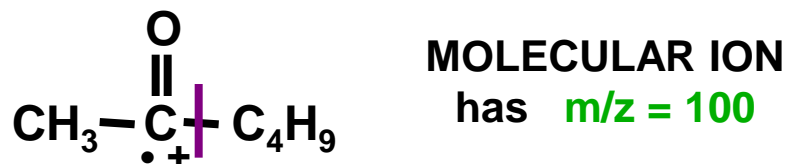




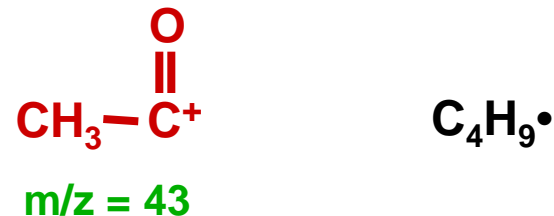
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Breaking the bond between the butyl group and the carbonyl group produces two further ions, depending on how the bond breaks.



Two peaks at  $m/z$  values 43 and 57 will appear in the mass spectrum.

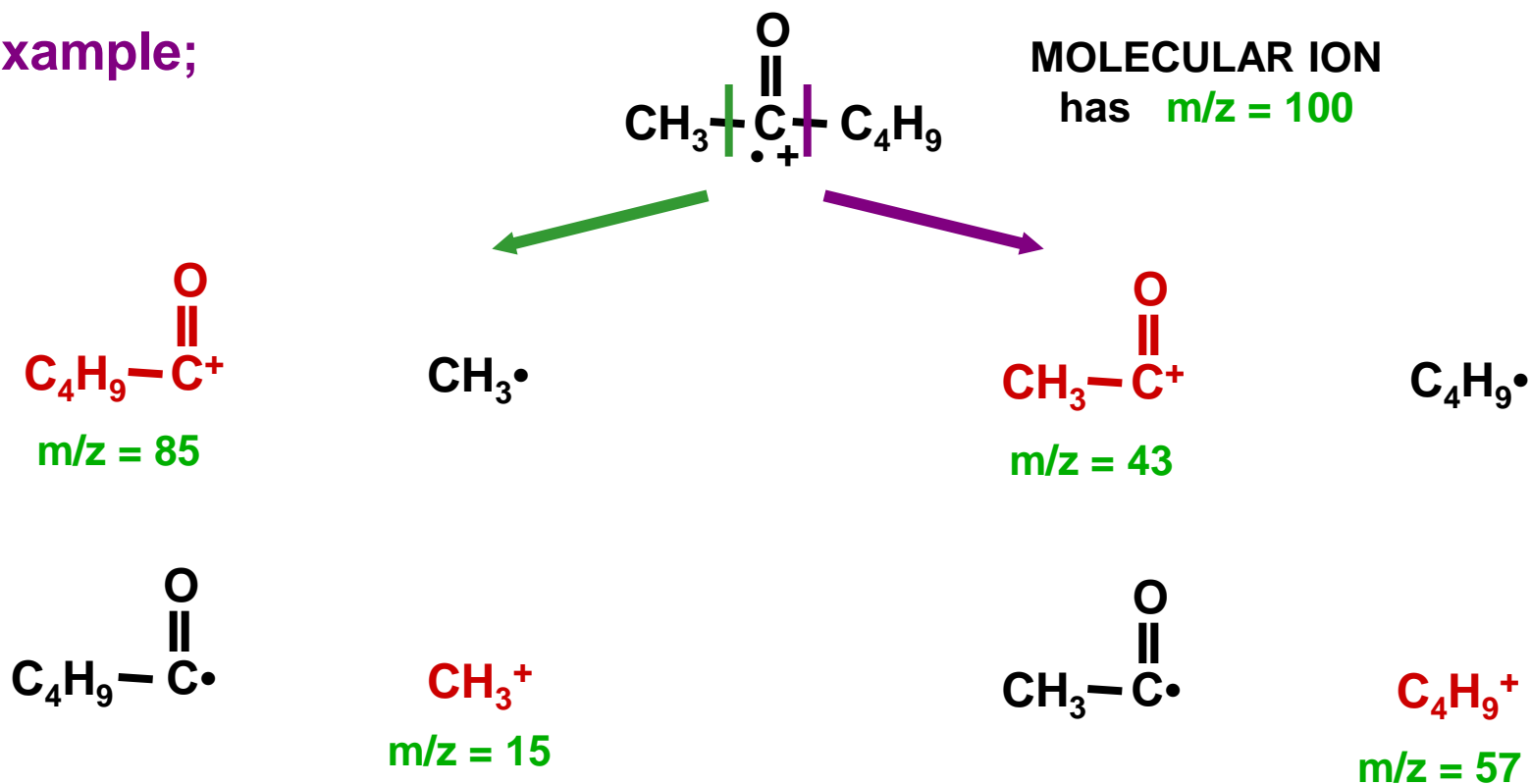


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## Aldehydes and ketones

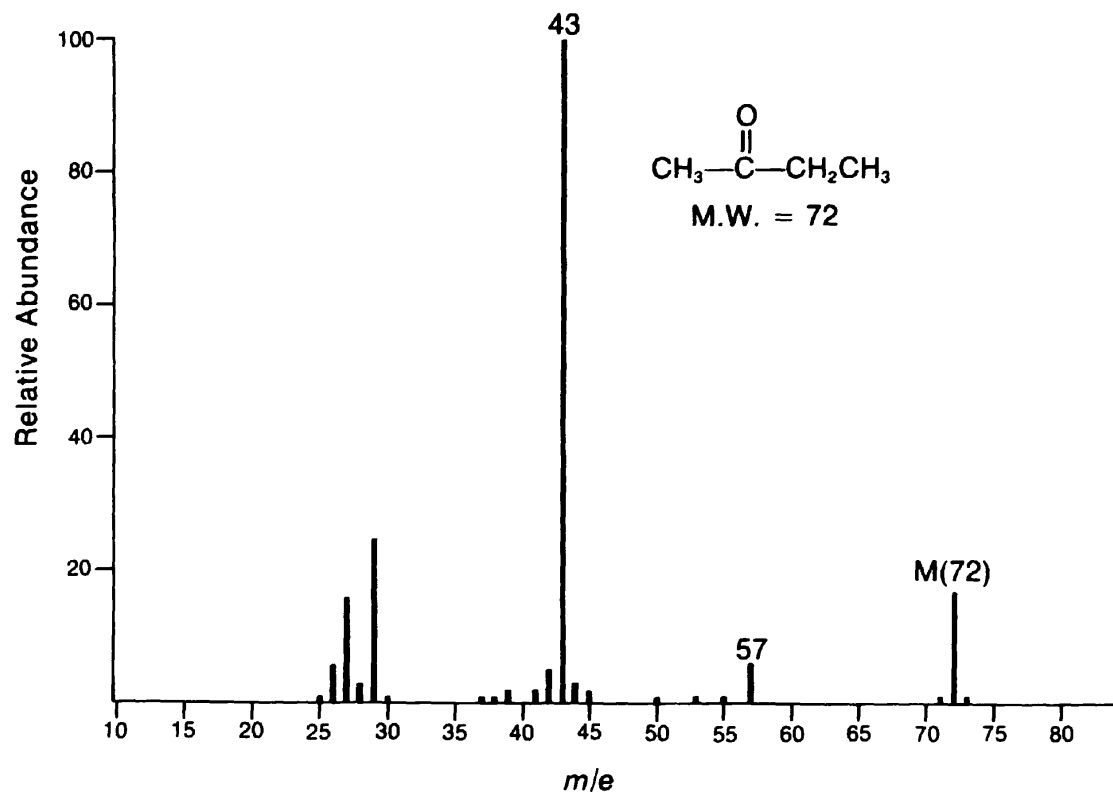
The position of the carbonyl group influences the fragmentation pattern because the molecular ion fragments either side of the carbonyl group.

Example;

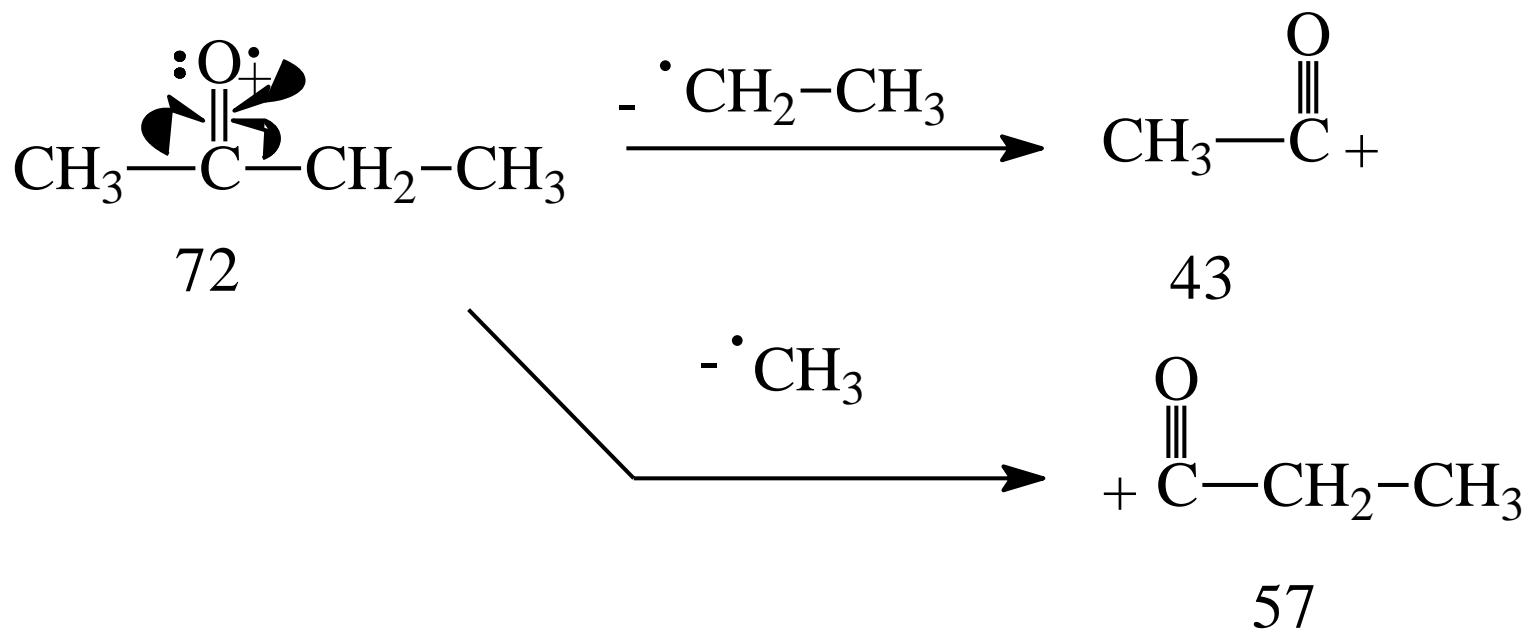


A further peak occurs at  $m/z = 72$  ( $100 - 28$ ) due to loss of CO

# 2-butanone

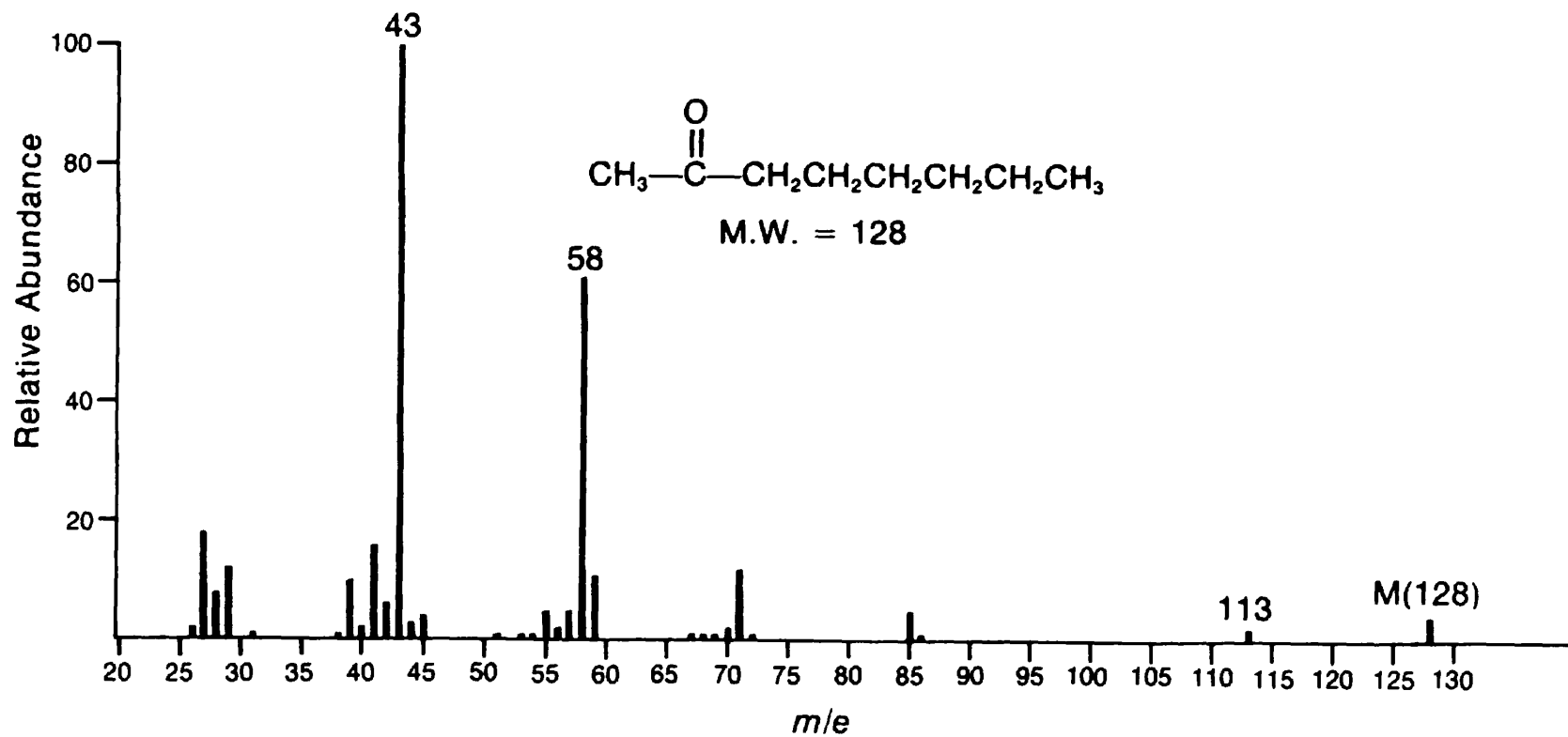


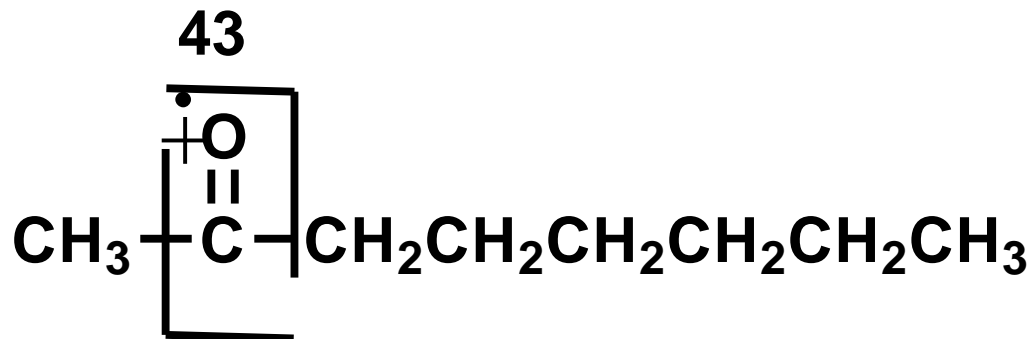
# $\alpha$ -cleavage



favor loss of larger radical

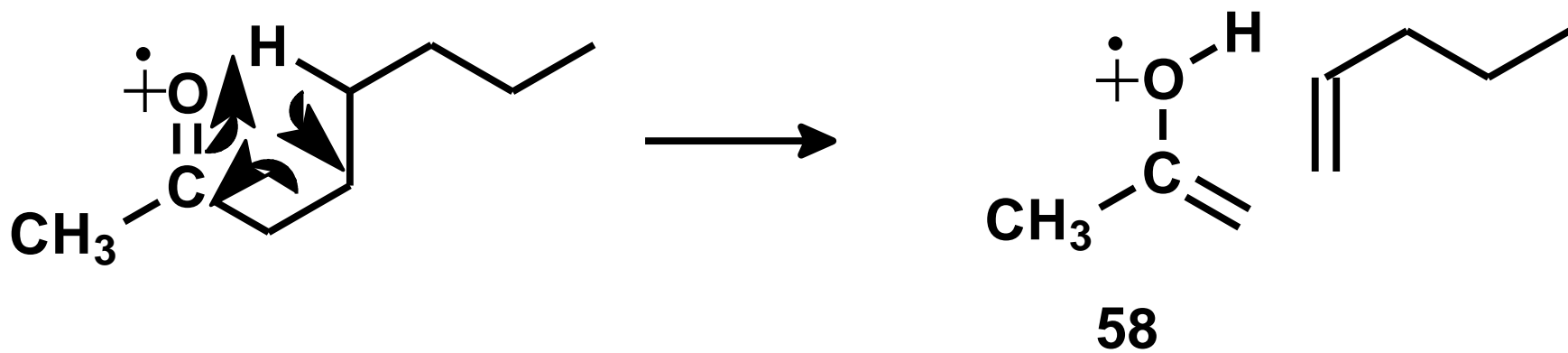
# 2-octanone





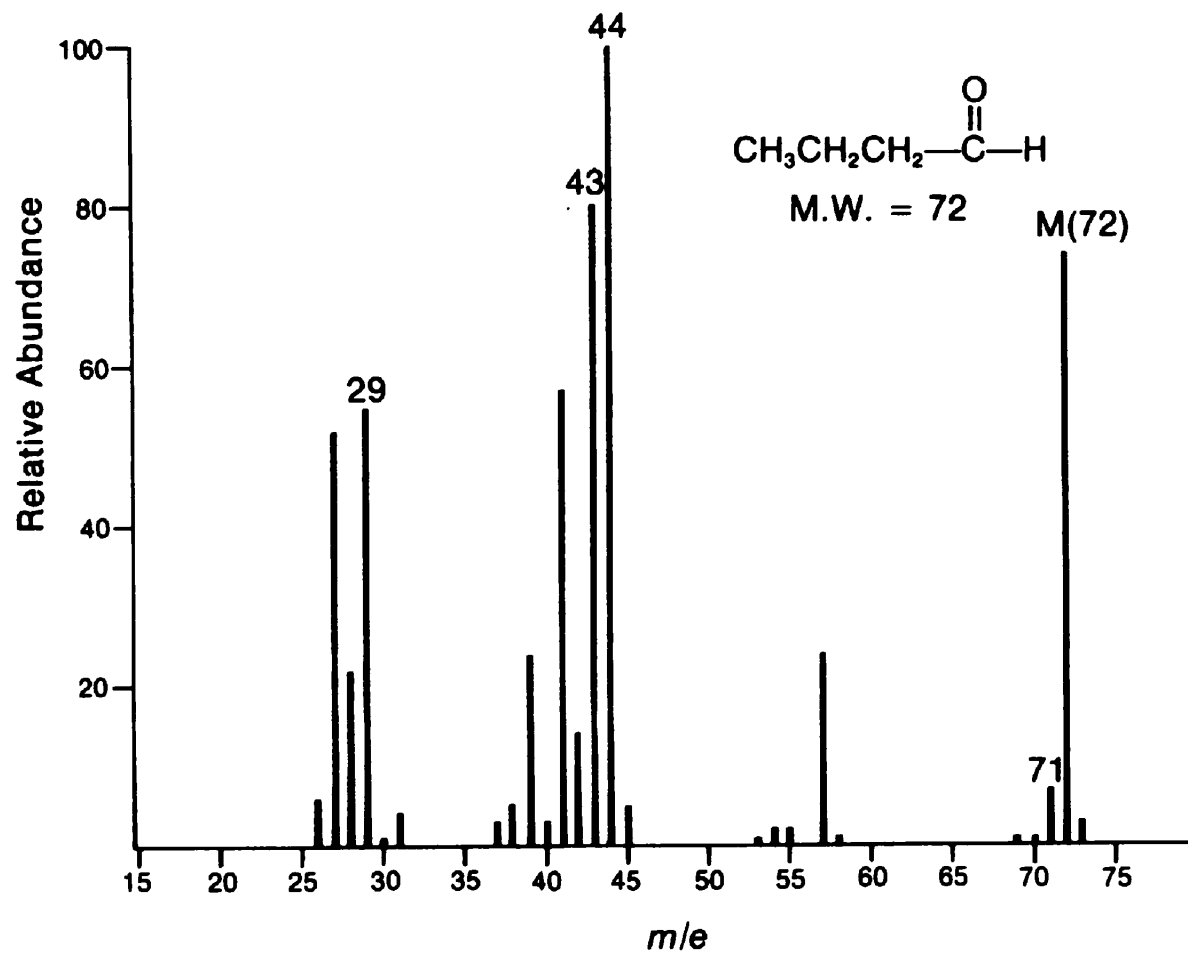
113

128

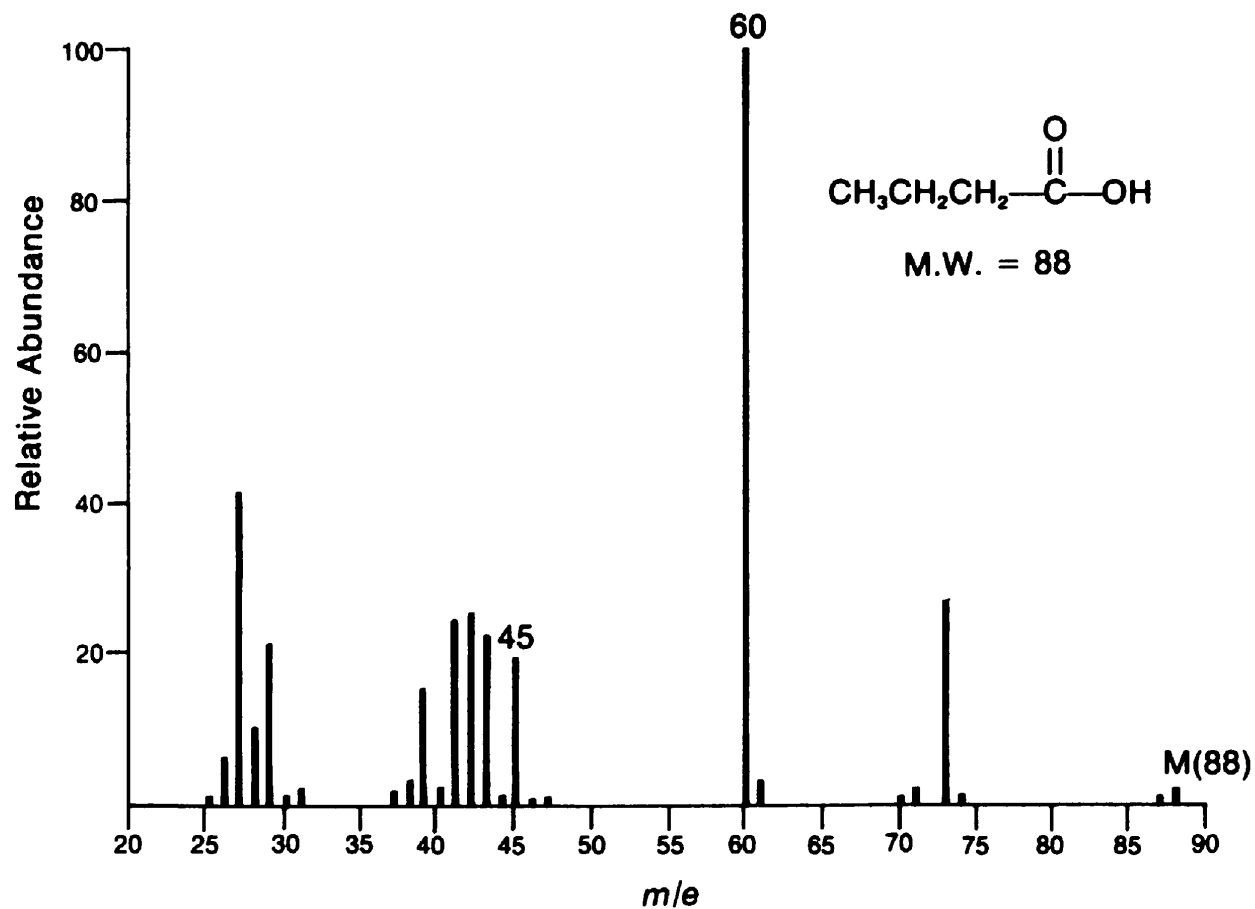


McLafferty Rearrangement

# butyraldehyde

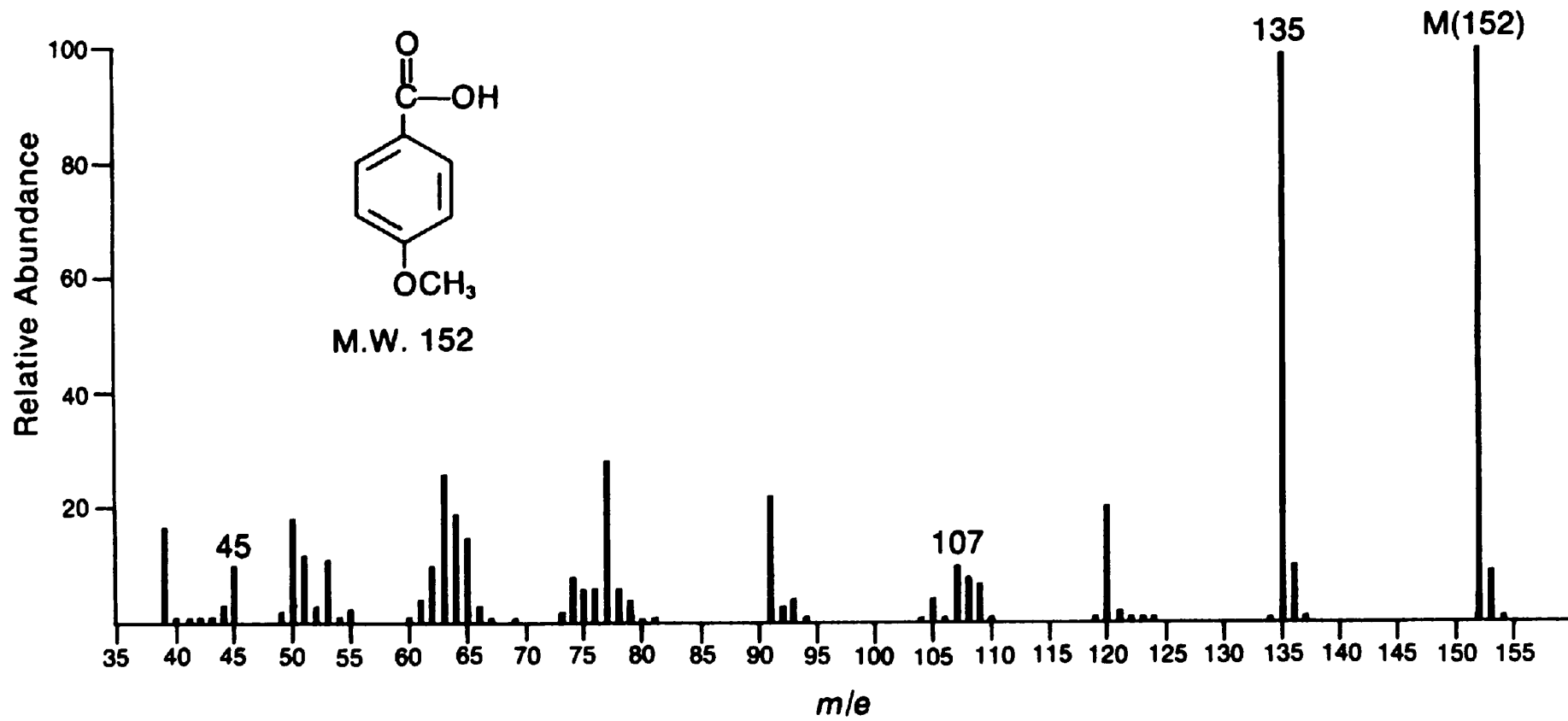


# butyric acid

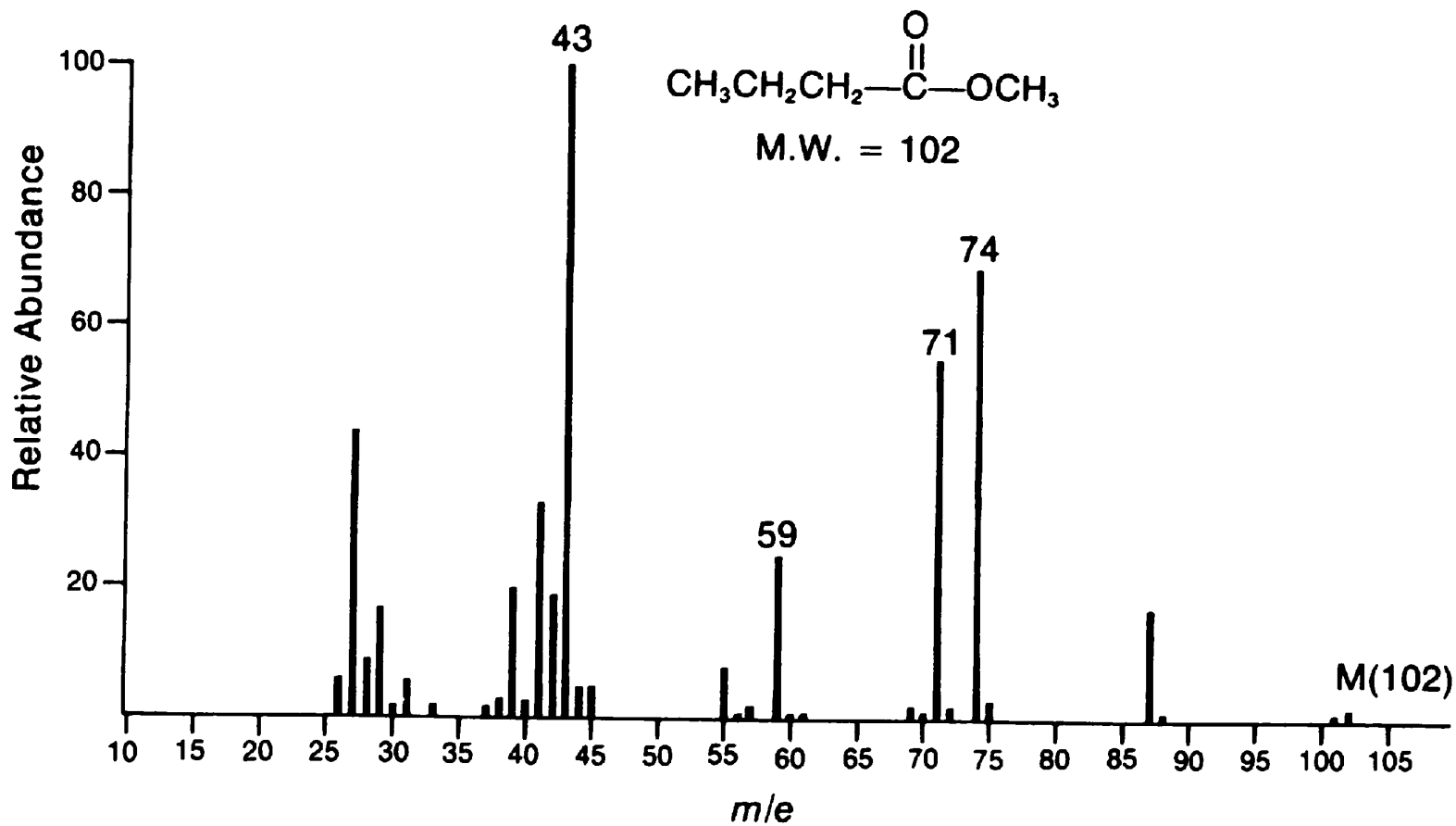


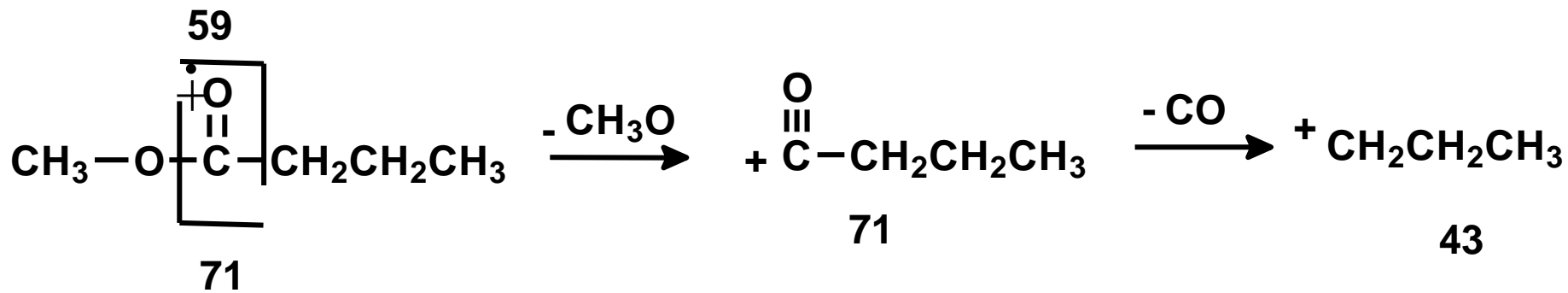


# p-anisic acid

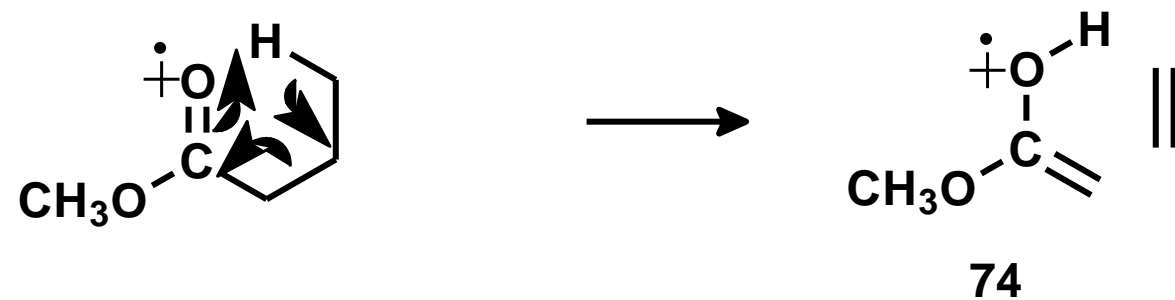


# methyl butyrate



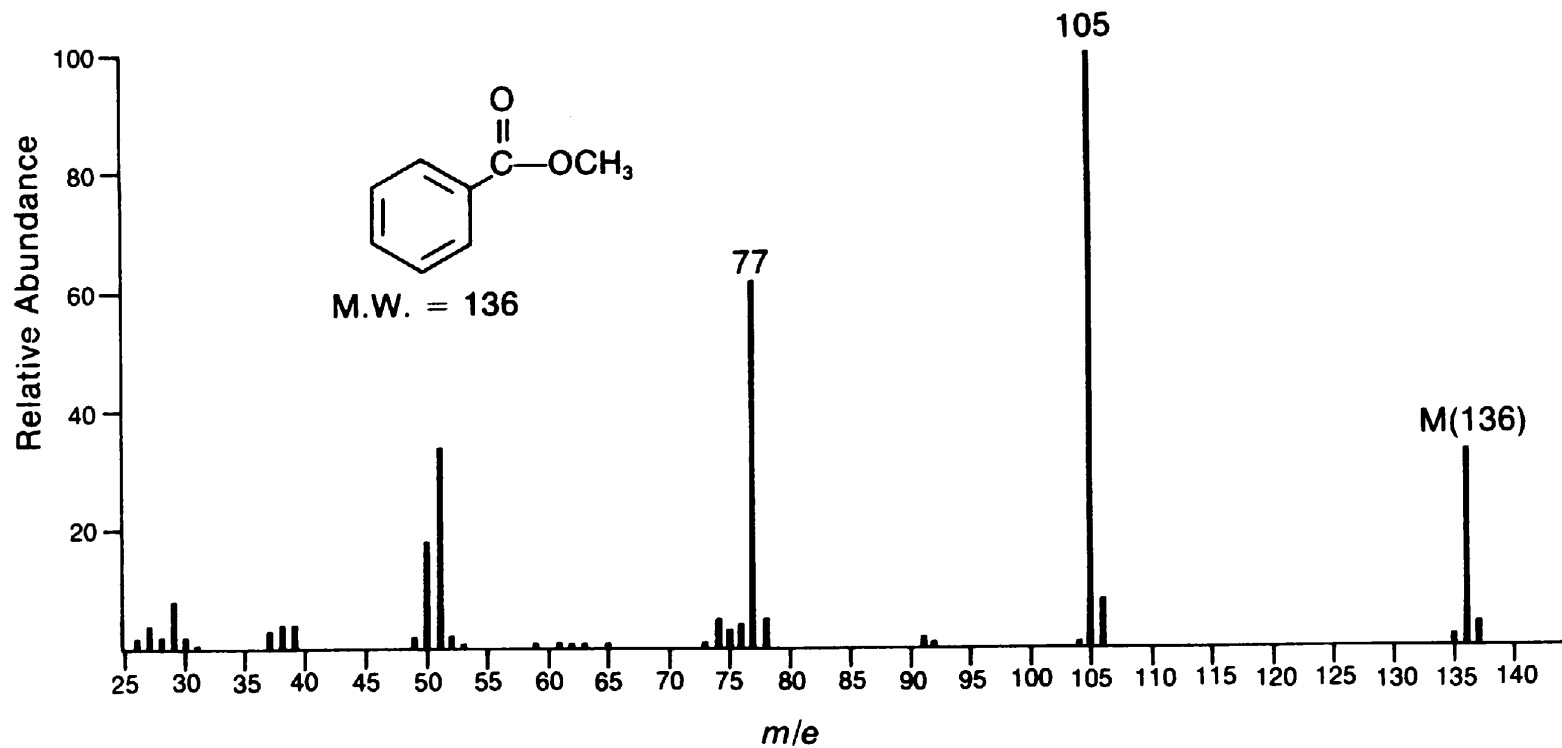


|||

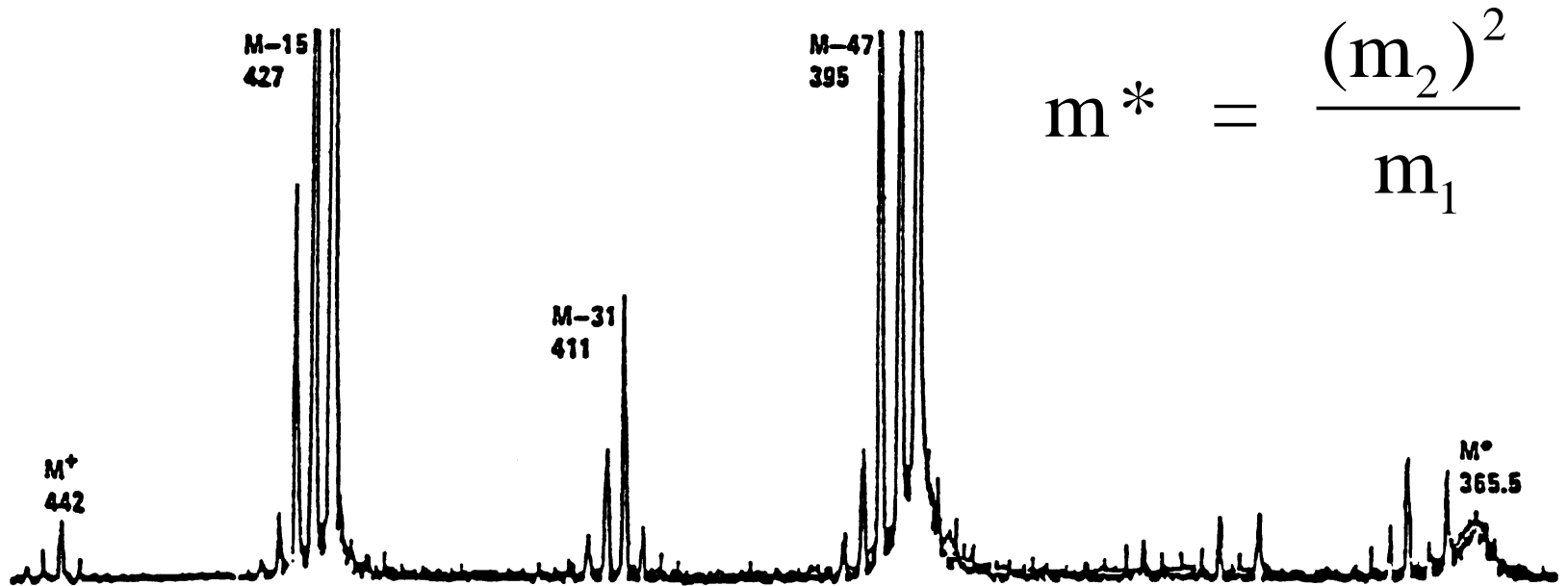


McLafferty Rearrangement

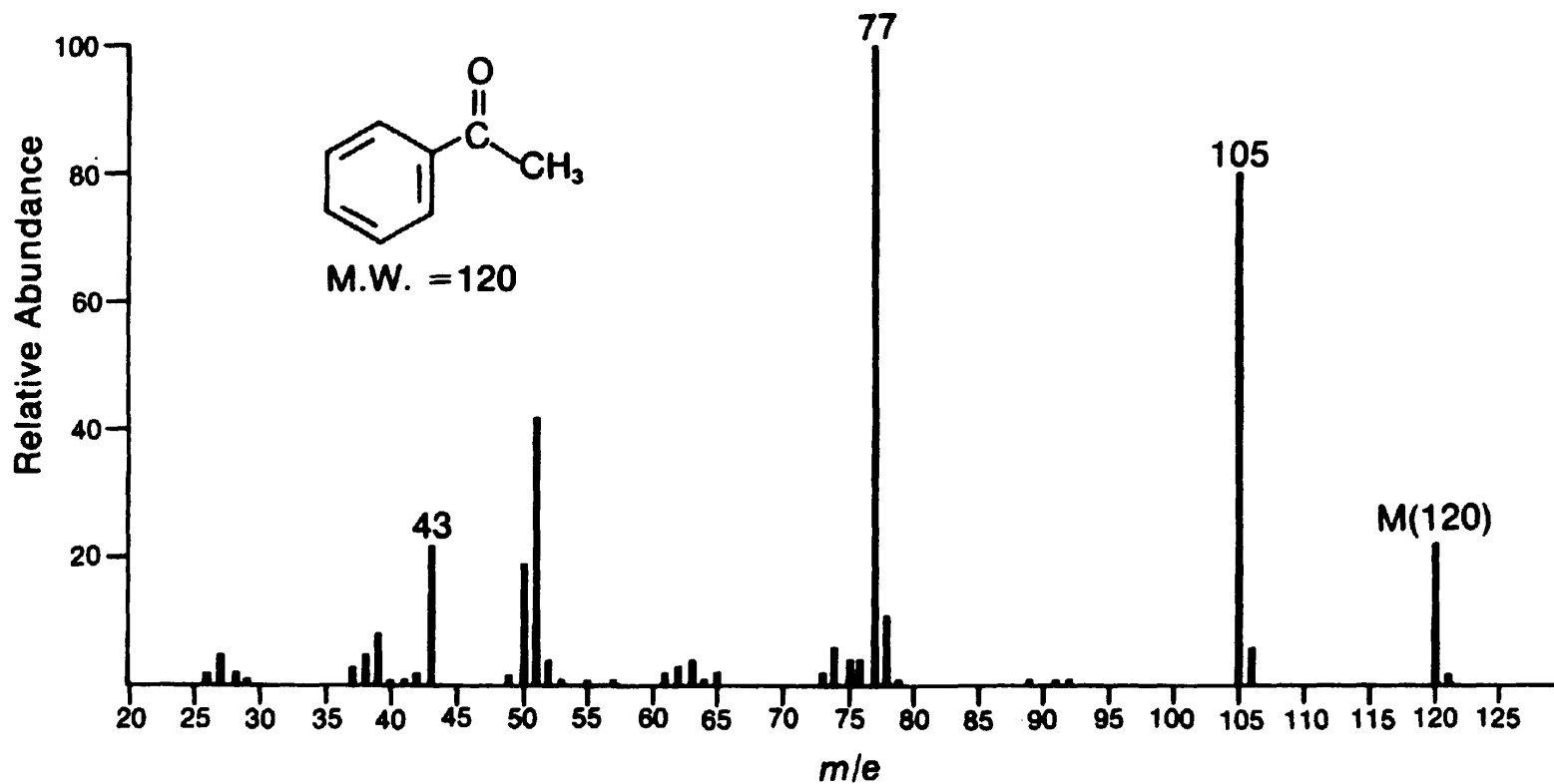
# methyl benzoate

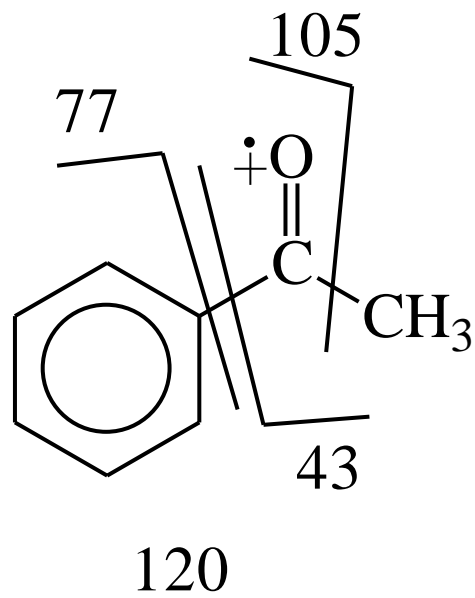


# metastable



# acetophenone





metastable peaks at 91.9, 56.4, 33.8

$$m^* = \frac{(m_2)^2}{m_1}$$

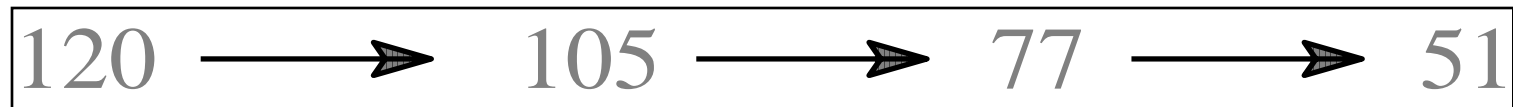
$$m^* = \frac{(105)^2}{120} = 91.875$$

$$m^* = \frac{(77)^2}{120} = 49.4$$

$$m^* = \frac{(77)^2}{105} = 56.47$$

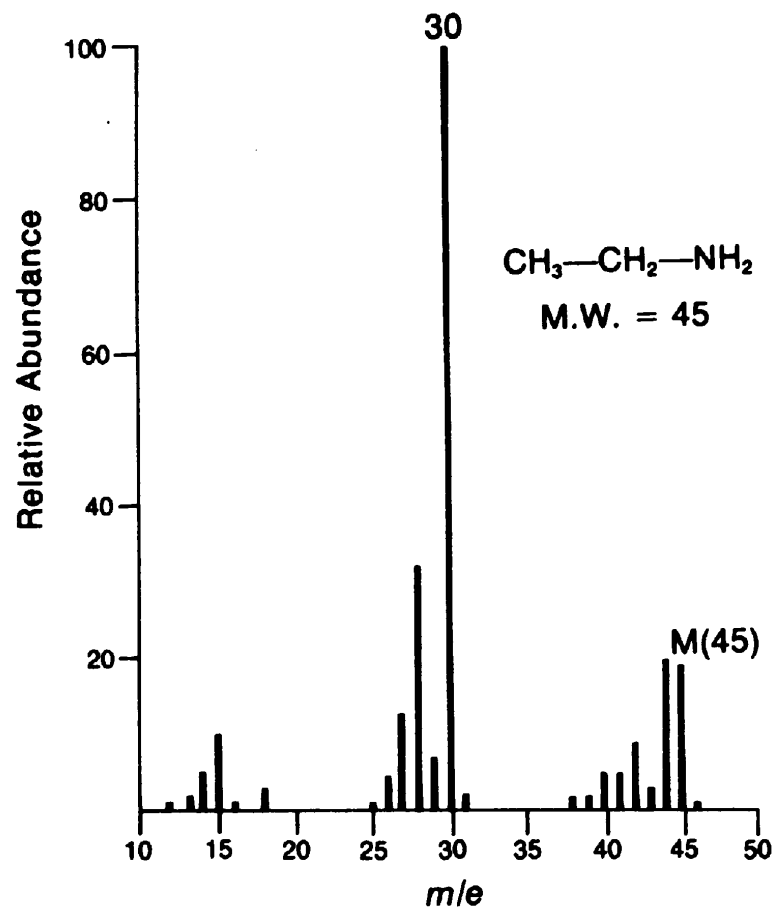
$$m^* = \frac{(51)^2}{77} = 33.8$$

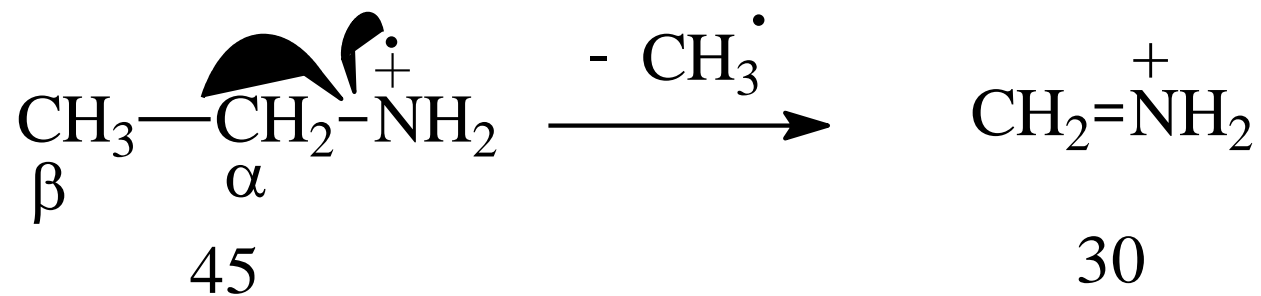
timing of fragmentation





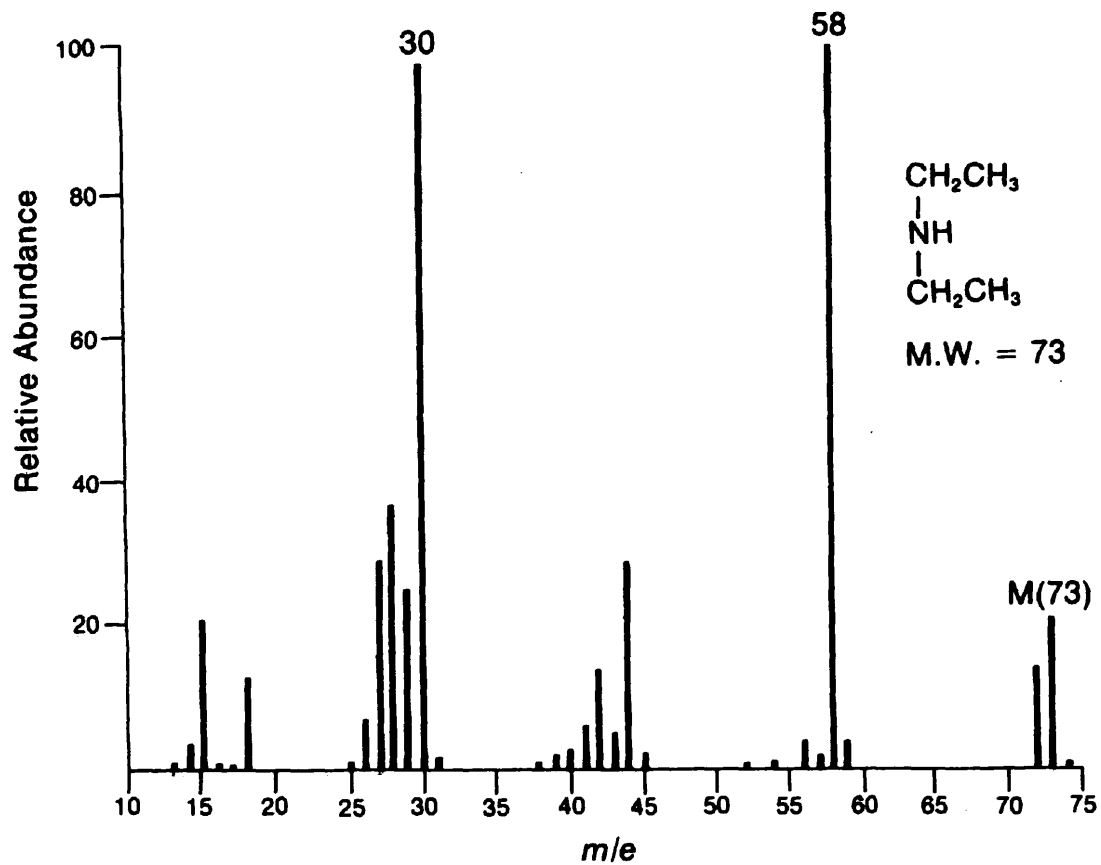
# ethylamine

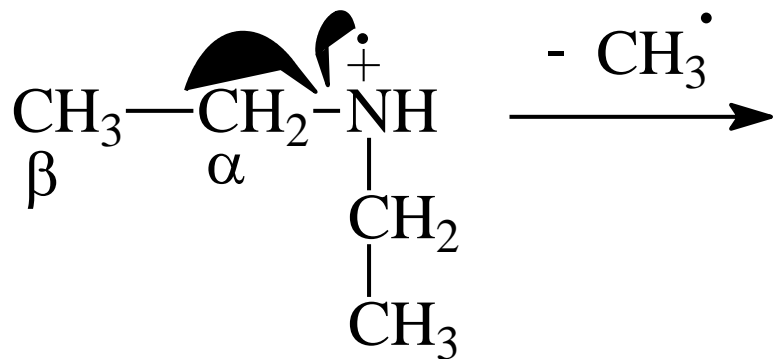




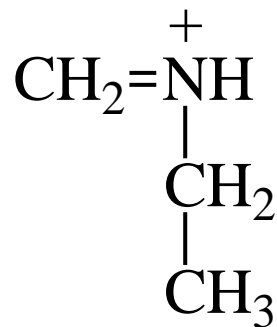
$\alpha$  - cleavage

# diethylamine



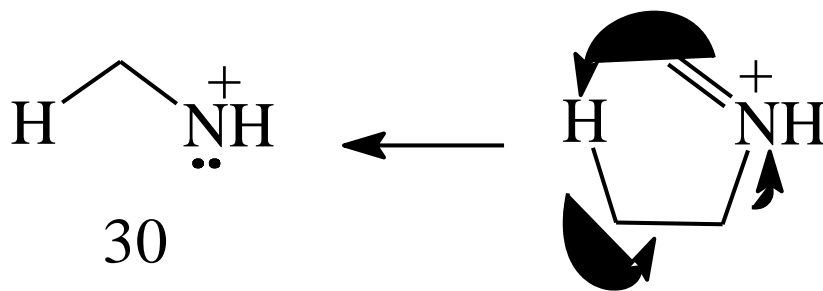
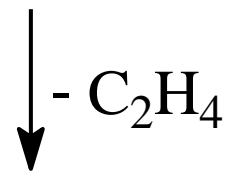


73



58

$\alpha$  - cleavage



# triethylamine

