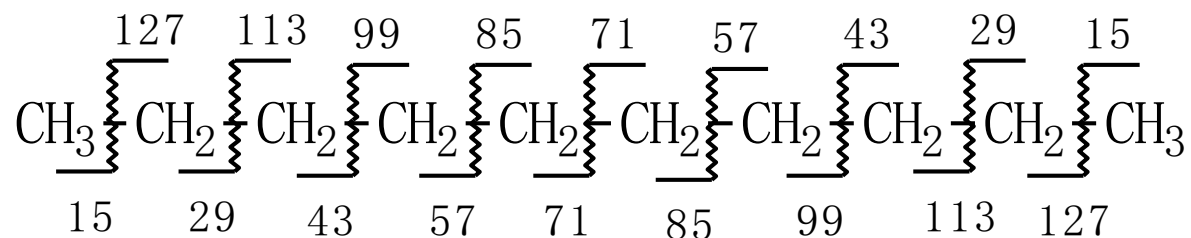


# MS Spectra of Organic Compounds

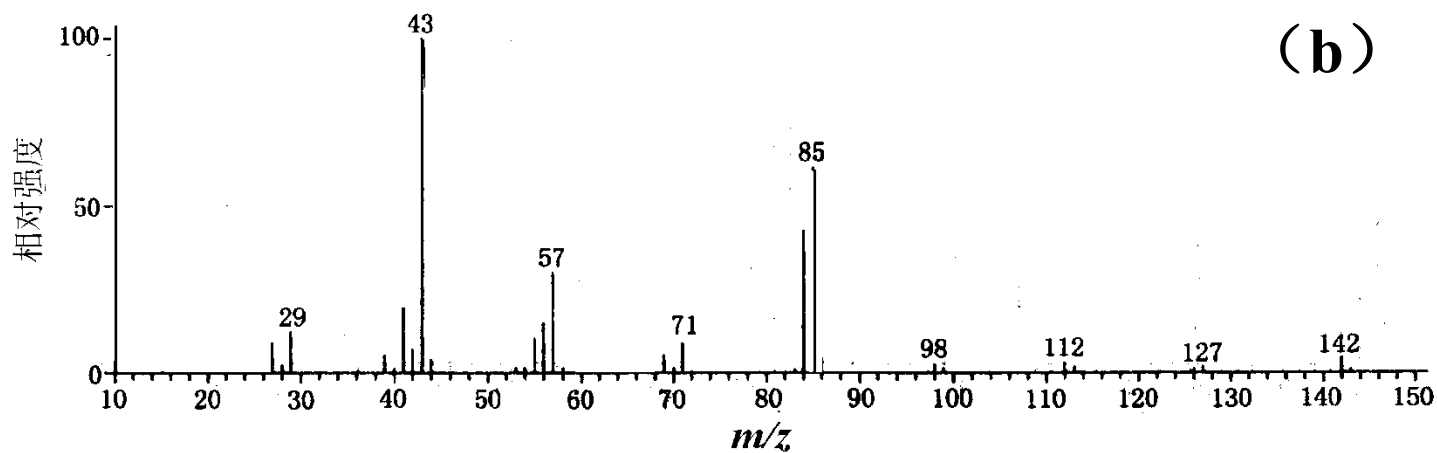
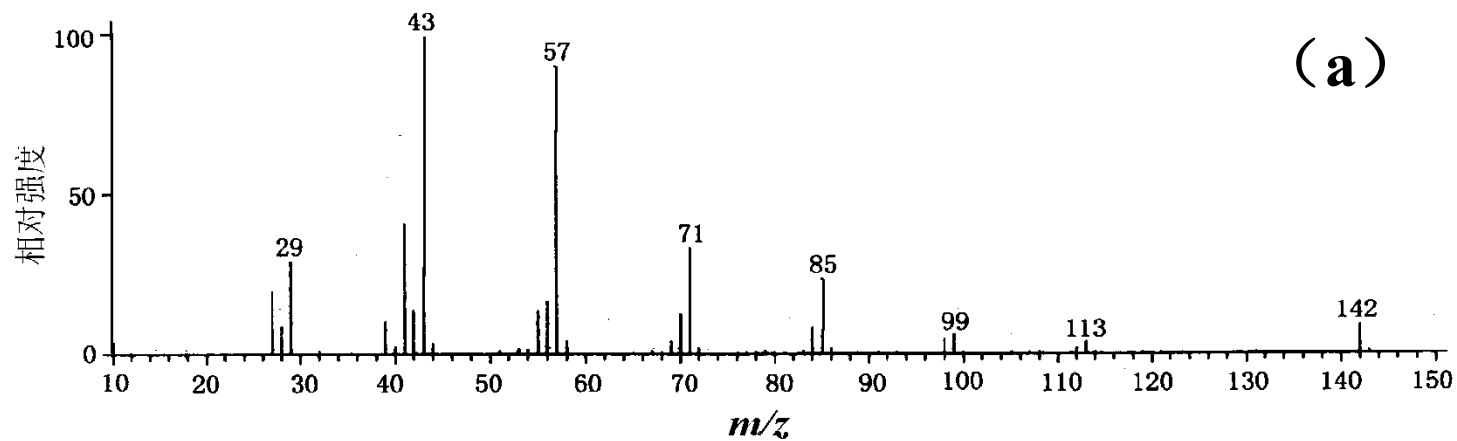
# 1. Carbon Hydrates ( $C_mH_n$ )

## a. Alkane

- C-C  $\sigma$ - fragmentation,  $C_nH_{2n+1}^{1+}$  cations



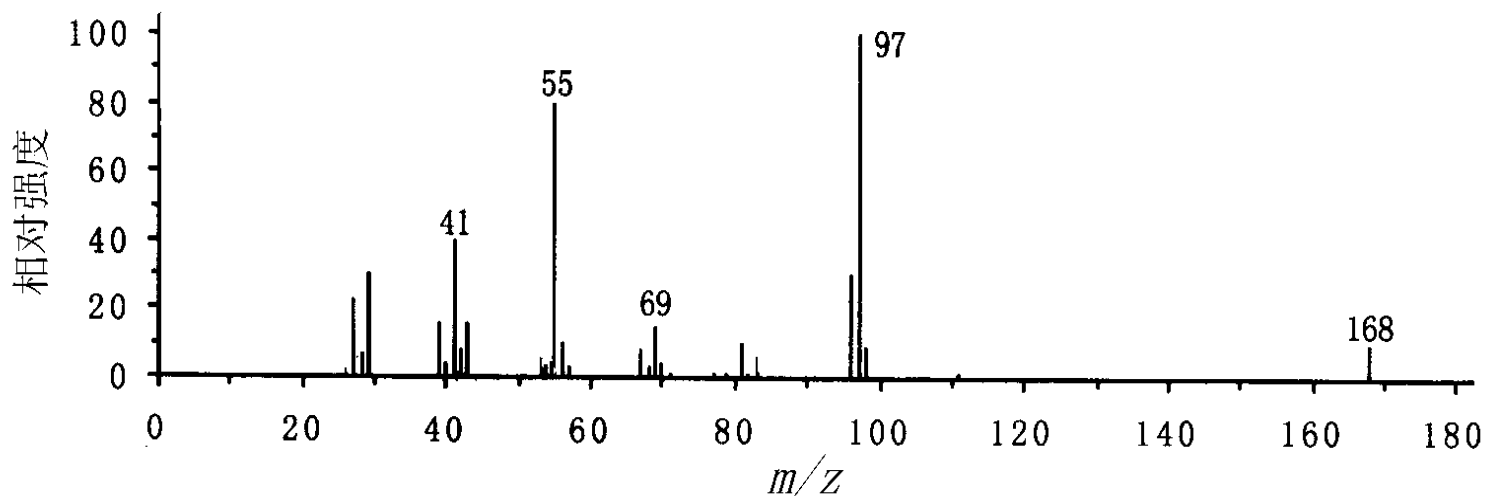
- Most abundance (Base peak):  $C_3H_7^+$  (  $m/z$  43 ) and  $C_4H_9^+$  (  $m/z$  57 )
- **Branched C-C favors cleavage** and **lose the most weighted alkyl**, forming stable secondary/tertiary carbon cations
- **Weak molecular ion peak**



**n-decane(a) vs 5-methylnonane(b)**

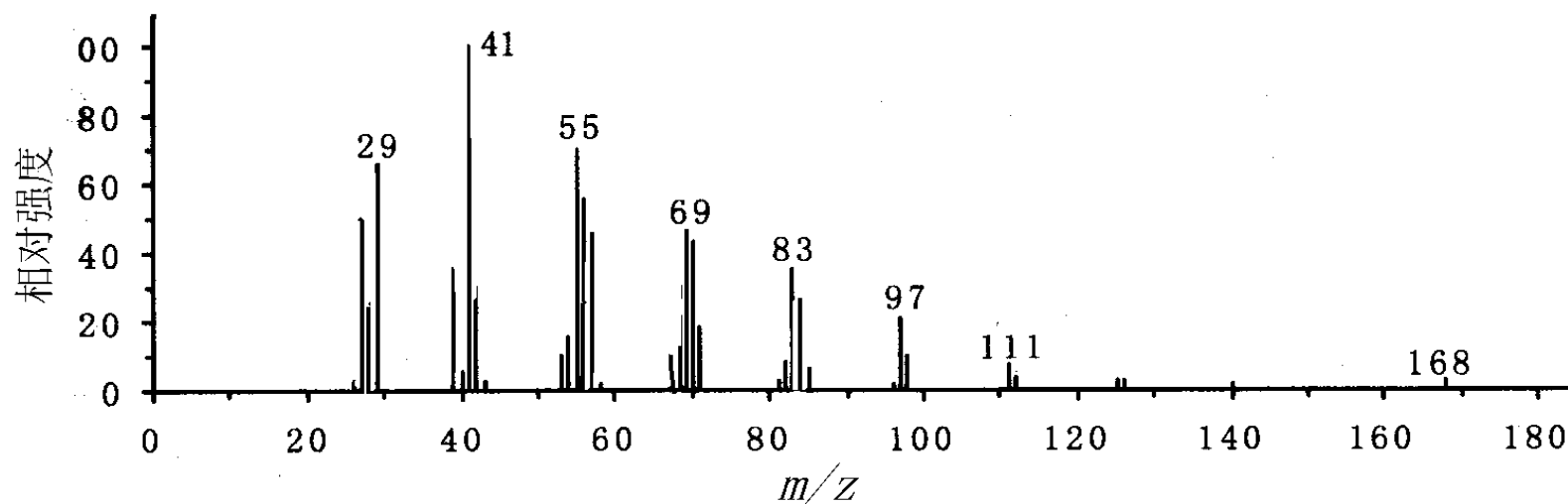
## b. cycloalkane

- Strong molecular ion peaks
- Side chain cleavage is favored
- $C_nH_{2n-1}^{+}$  cations in the low-weight side



**1-methyl-3-pentylcyclohexane**

## c. Alkene

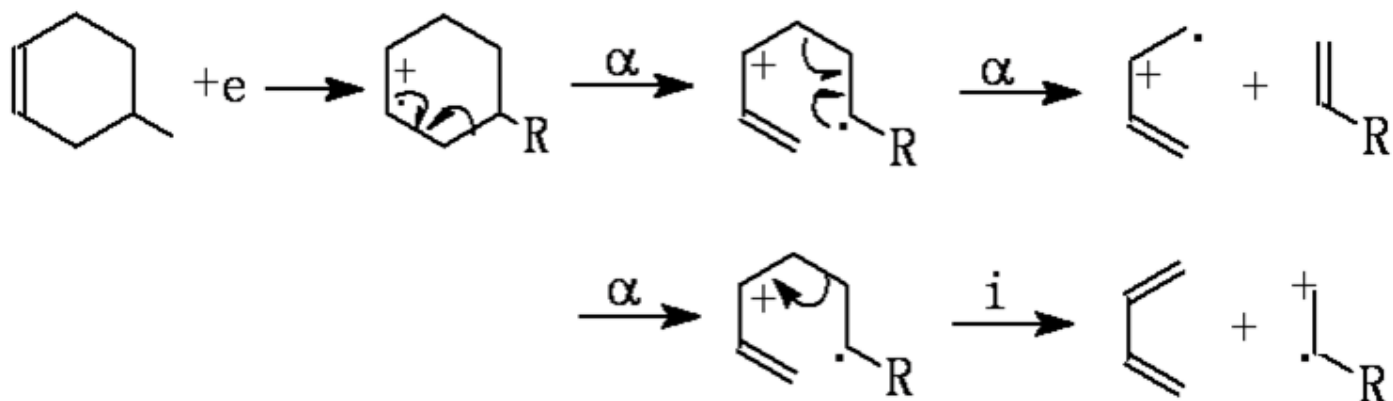


### 1-dodecene

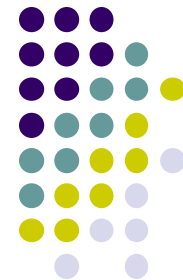
- Stronger molecular ion peak than alkane
- $C_nH_{2n-1}^{+}$  with difference of 14
- Allyl cleavage ( $\alpha$ -cleavage)

## d. cycloalkene

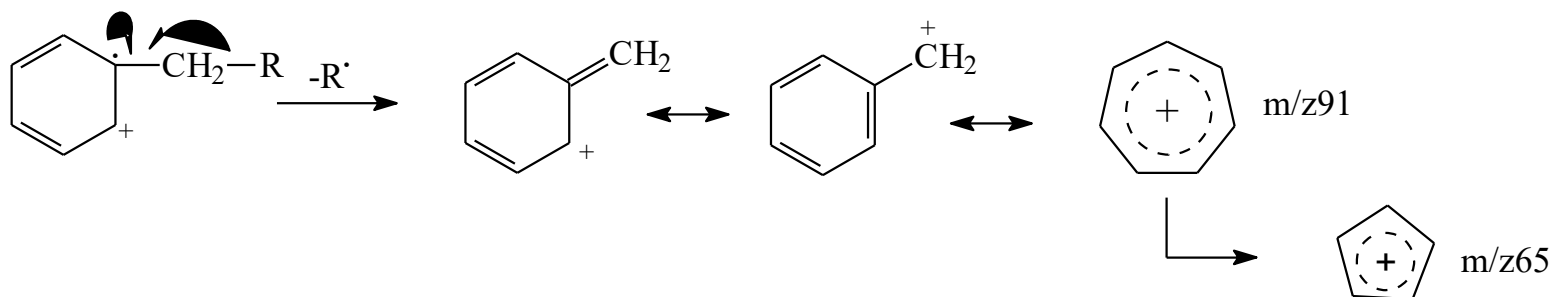
### Retro-Diels-Alder



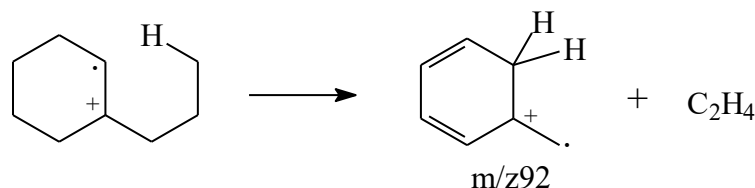
## e. Benzene

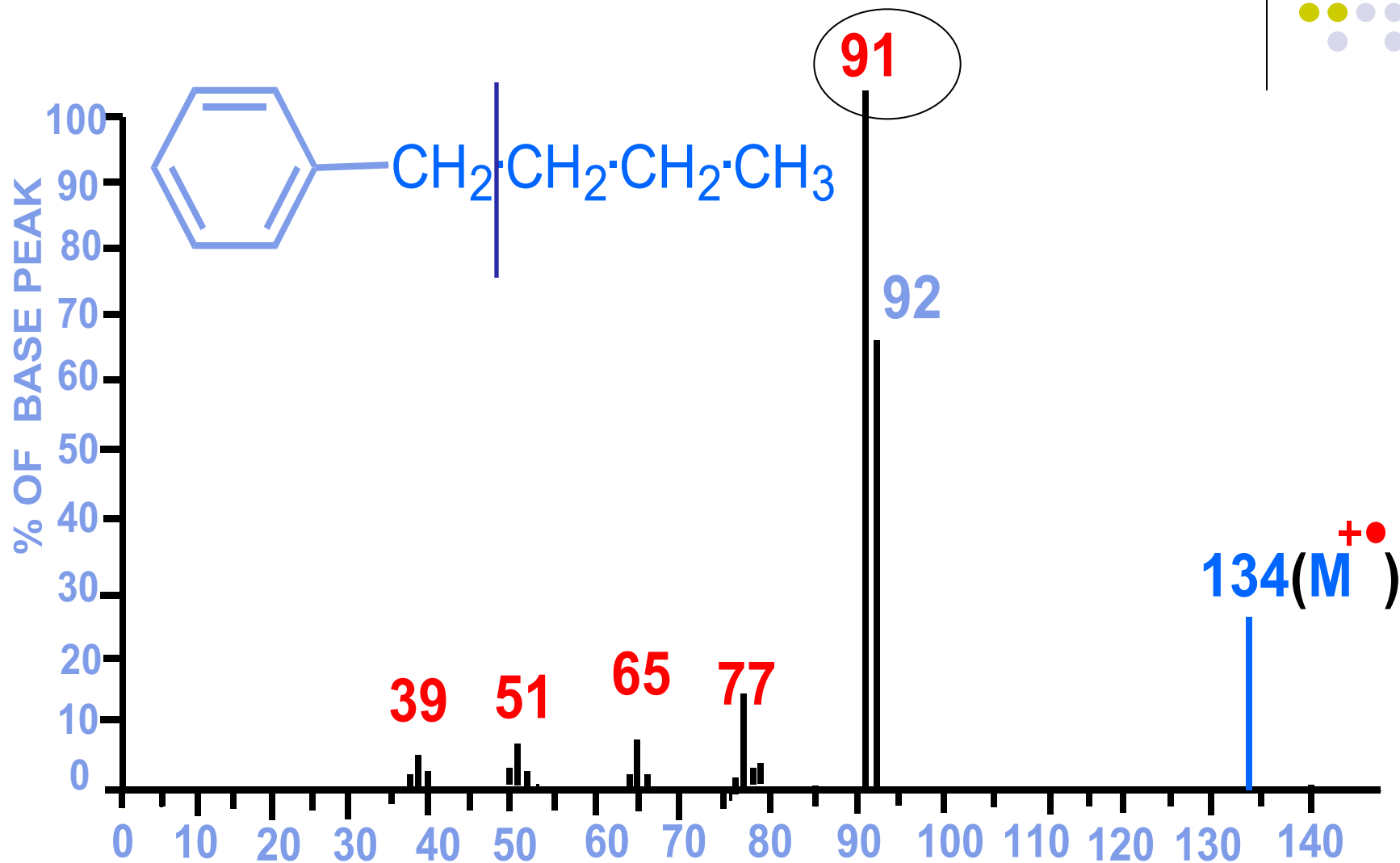


- **Strong  $M^{+\bullet}$  , low fragments**
- **$m/z$  39, 50 - 52 , 63 - 65 , 75-77 fragment ion peaks** for benzene , but weak intensity
- **Benzyl cleavage** for alkyl substituted benzenes ( **$m/z$  91**)



- **McLafferty rearrangement** for alkylbenzenes with  $\gamma\text{-H}$





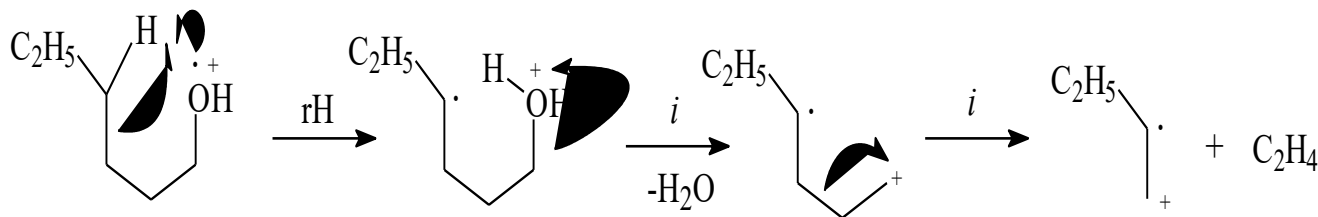




## 2. Alcohols (-OH)

### a. Aliphatic alcohols

- **Very low molecular ion peaks**
- Long **primary and secondary alcohols** would perform hydrogen rearrangement and **lose one H<sub>2</sub>O**.

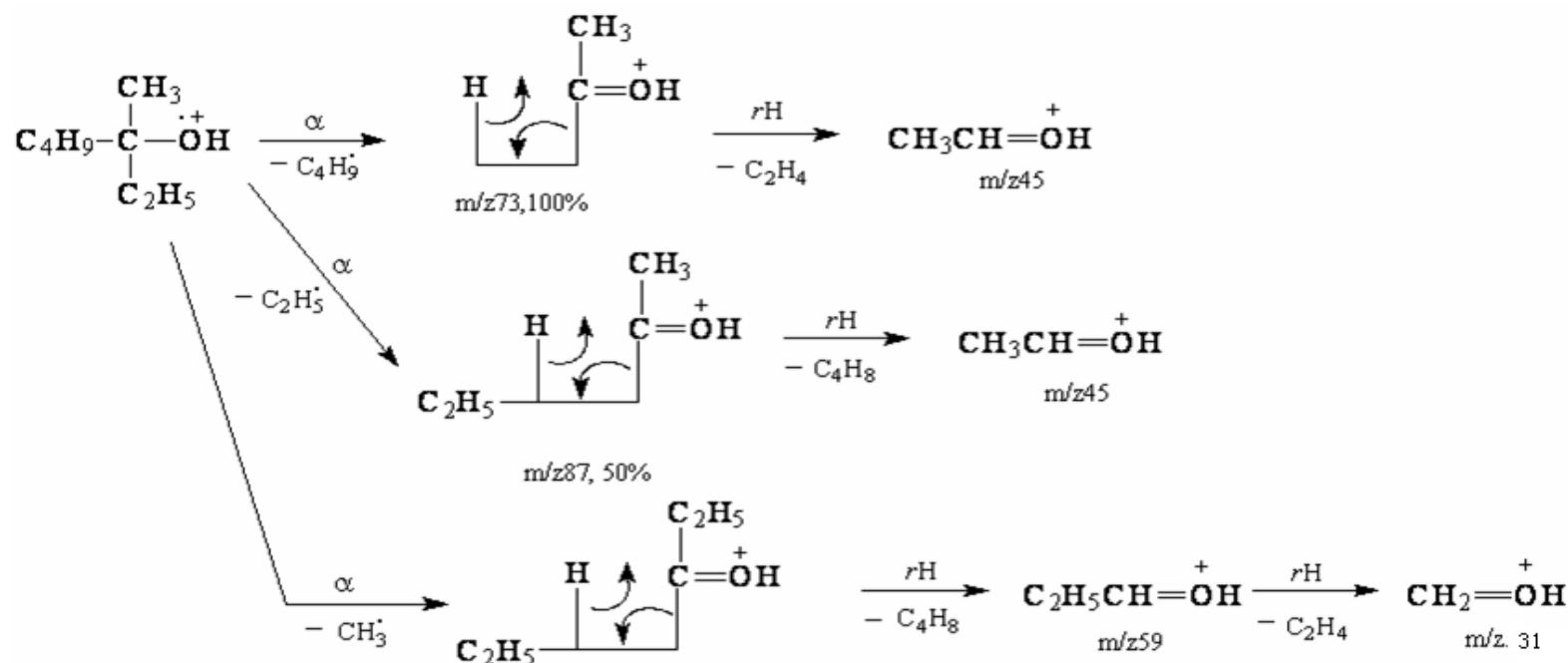


- The base peak sequentially cleaves and **loses one C<sub>2</sub>H<sub>4</sub>** to produce **C<sub>n</sub>H<sub>2n-1</sub><sup>+</sup>** fragment cations.



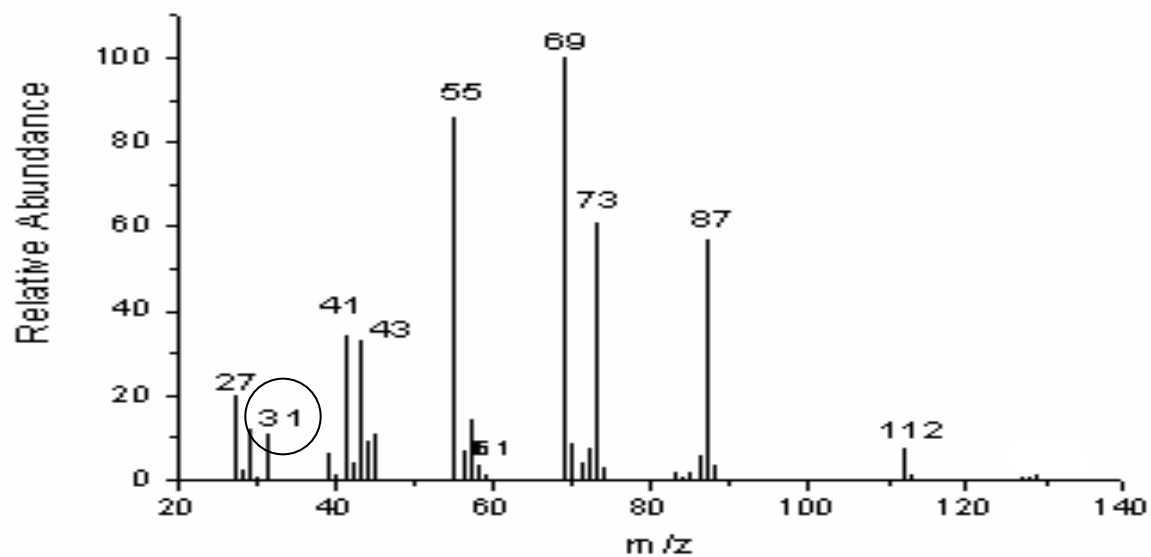
➤ Featured **oxonium ion** via  **$\alpha$ -cleavage**.  **$m/z$  31** for **primary alcohols**

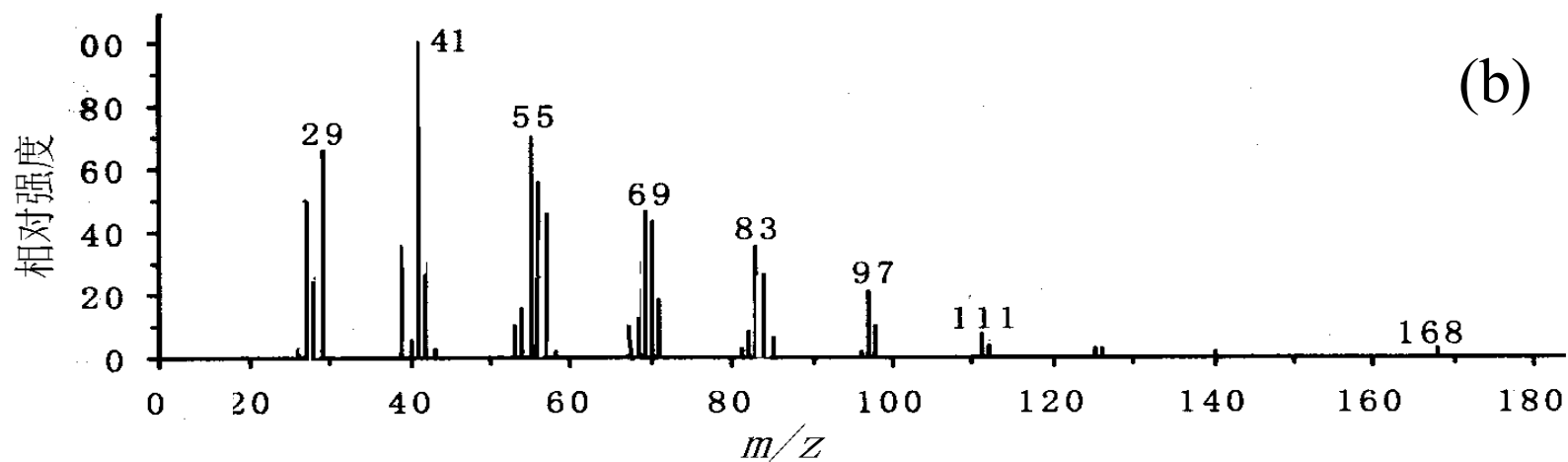
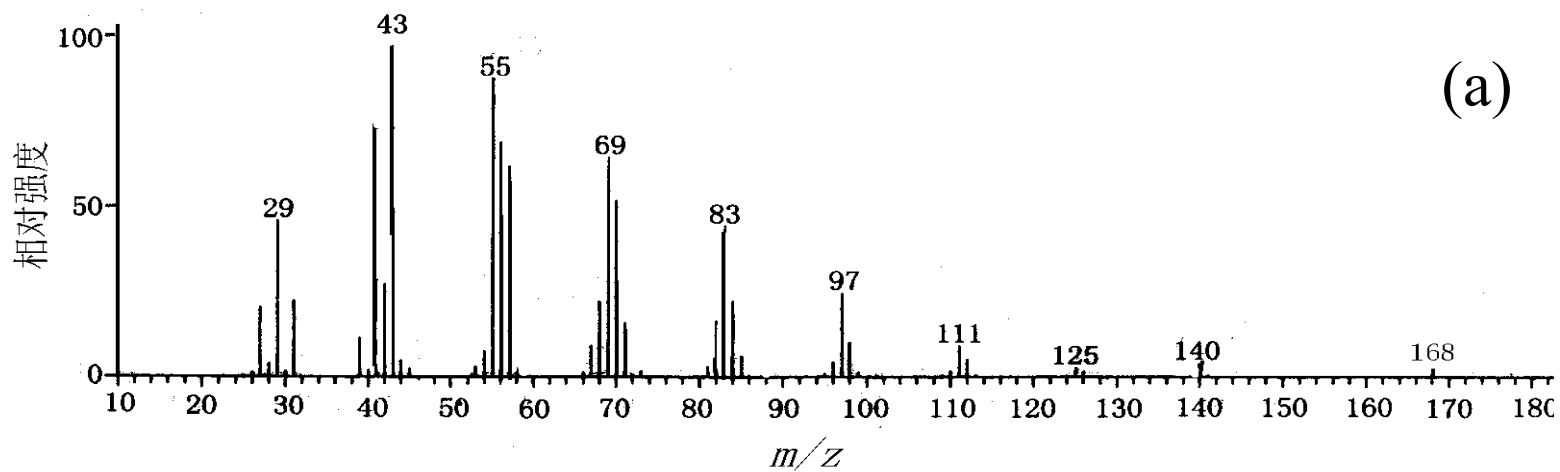
➤  **$m/z$  31+14n** for **secondary and tertiary alcohols** via H rearrangement and elimination of  $C_nH_{2n}$  from oxonium ion  $RR'C=O^+H$ .





## 4-octanol

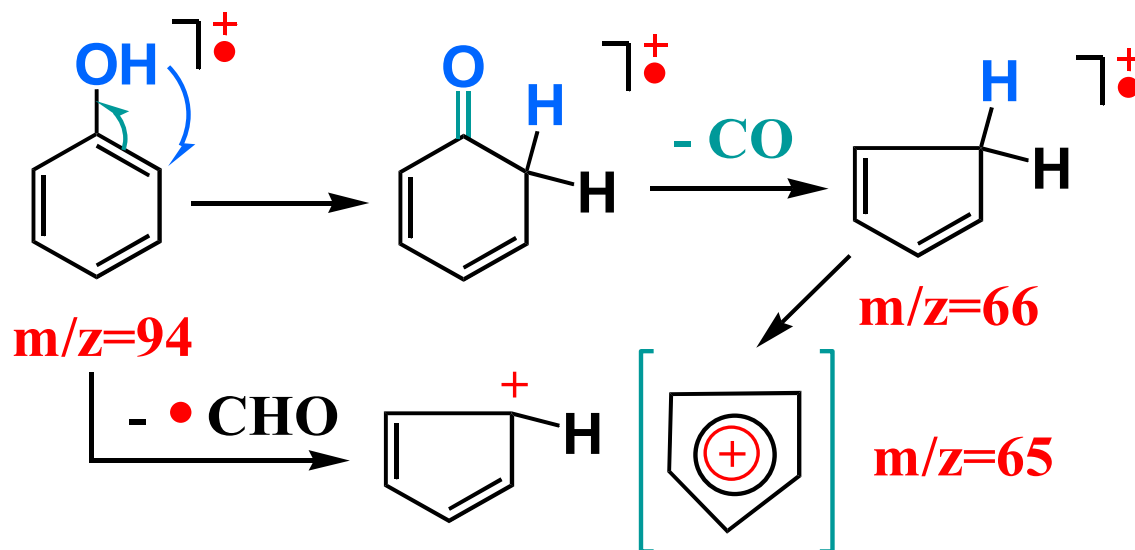




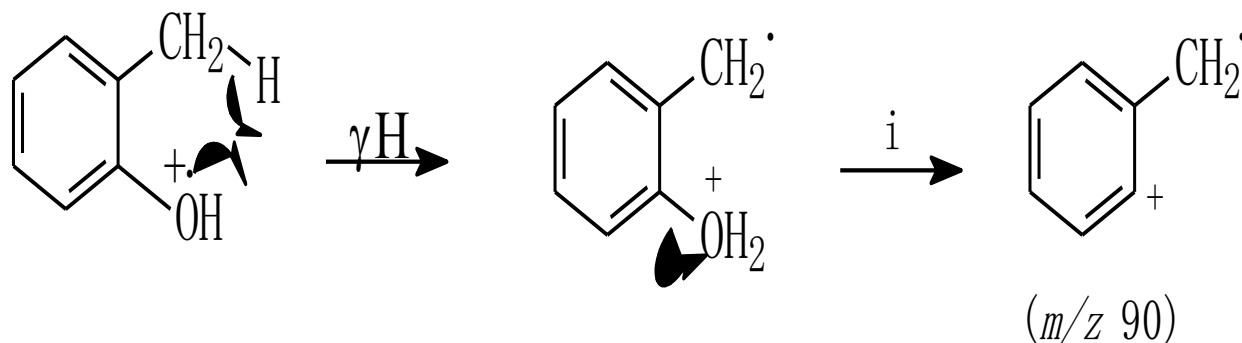
**1-dodecanol(a) vs 1-dodecene(b)**

## b. Phenol

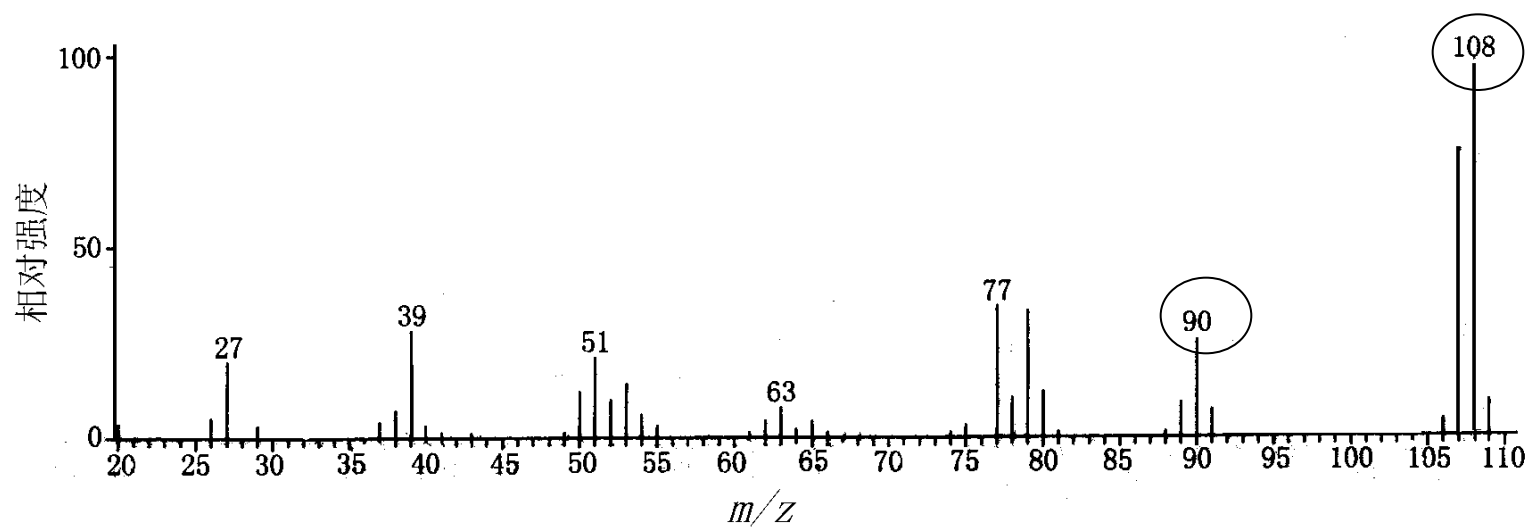
- Strong molecular ion peak
- - CO and - CHO,  $[M-28]^+$  and  $[M-29]^+$



➤ Ortho-substituted phenol, lose neutral molecule via ortho-effect



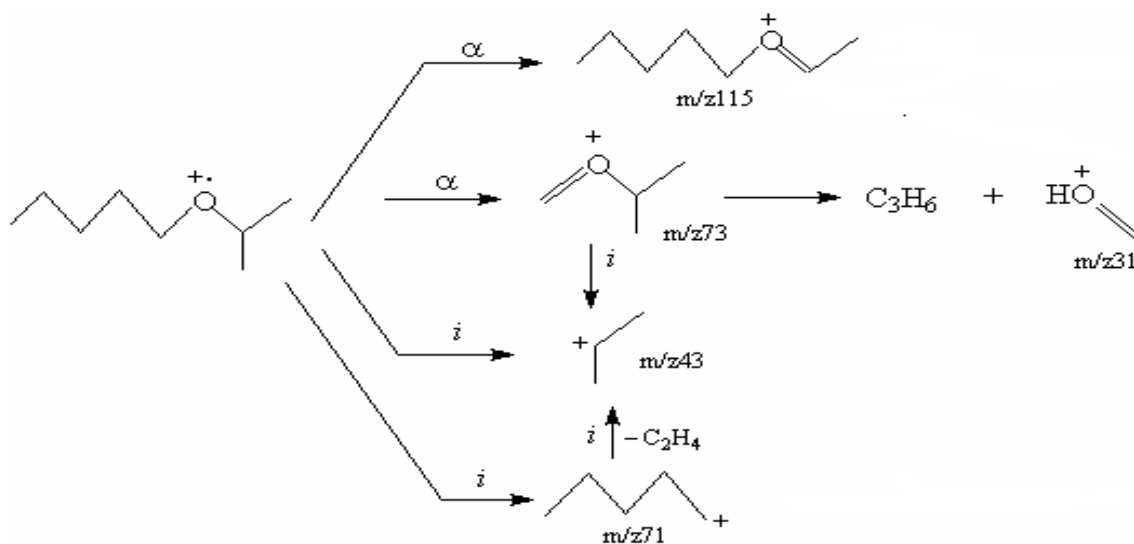
➤ **Strong  $[M-1]^+$  peak** for methylphenol and benzyl alcohol



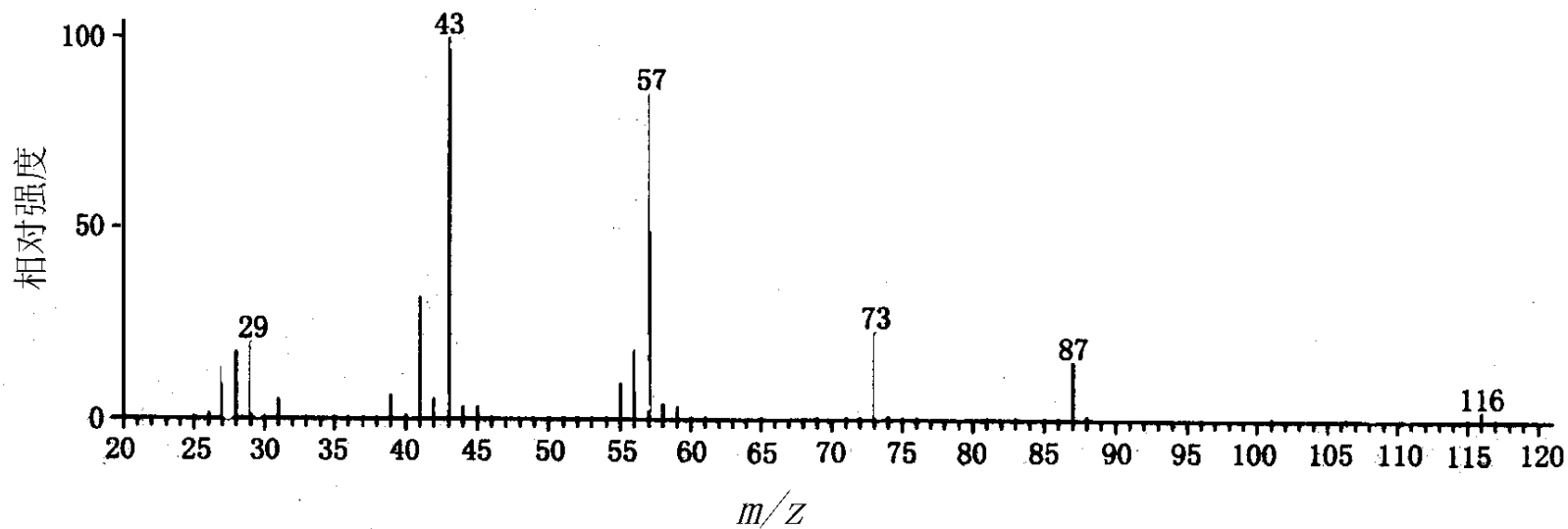
**o-methylphenol**

### 3. Ether

- Low molecular ion peak, higher than alcohol
- **$R-O^+=CR'R''$  fragment ion (  $m/z$  45,59,73,87... ) via  $\alpha$ -cleavage**; the larger alkyl, easier to lose.
- **Alkyl cation via i-cleavage**



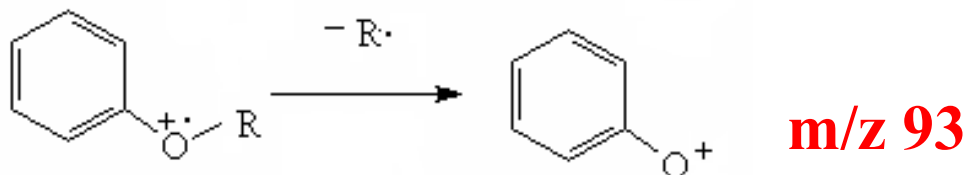




**propylbutyl ether**

## For aromatic ether:

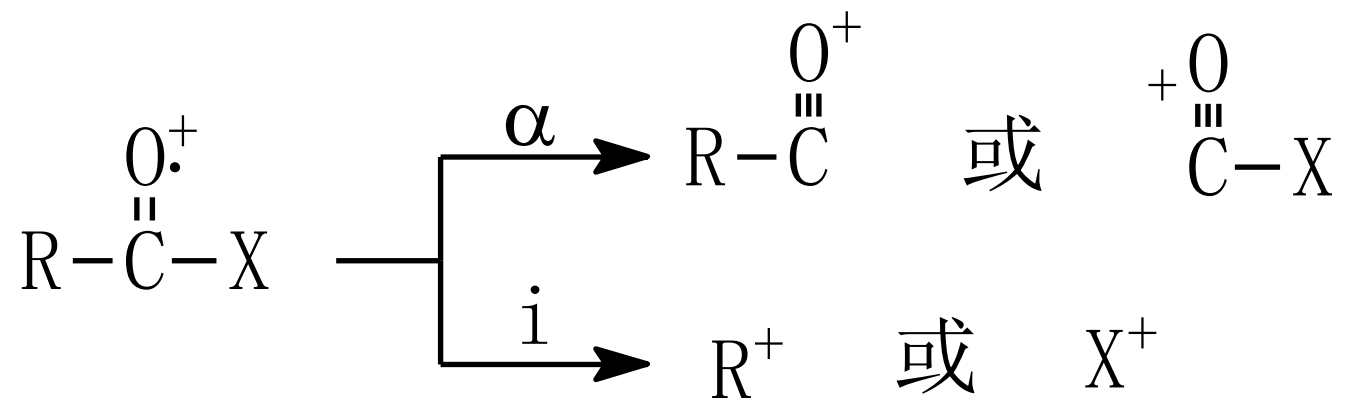
- Strong molecular ion peak.
- Most fragmentation:



- For R is long chain, McLafferty rearrangement would occur; For no other substitution of benzene, **m/z 94** as feature fragment ion

## 4. Carbonyl derivatives

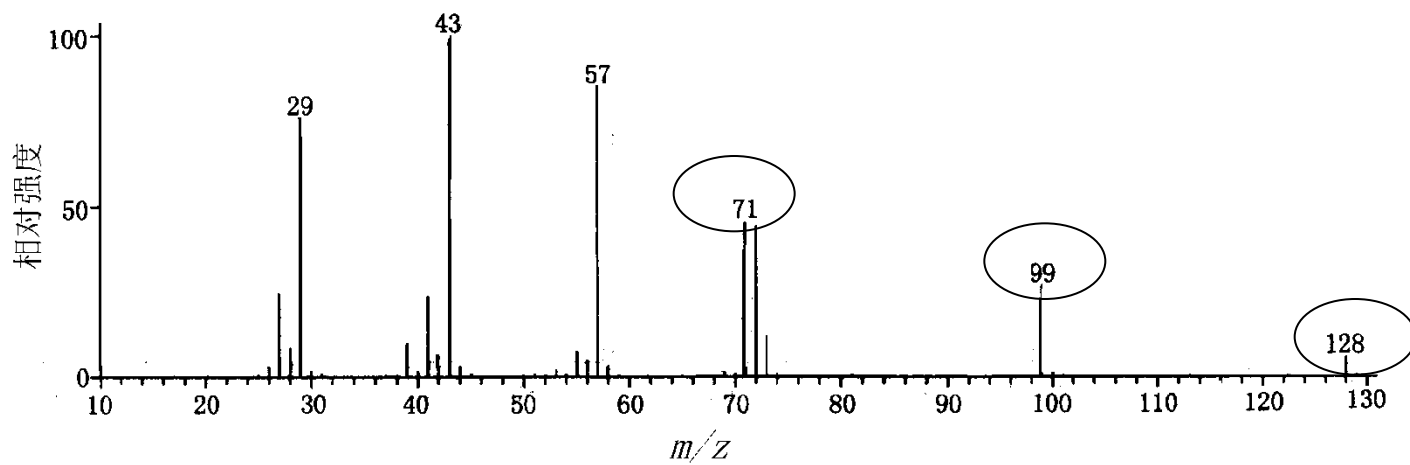
### 1) $\alpha$ -cleavage and i-cleavage



2) R is long chain and with  $\gamma$ -H: **McLafferty Rearrangement**

## a. Aliphatic ketone

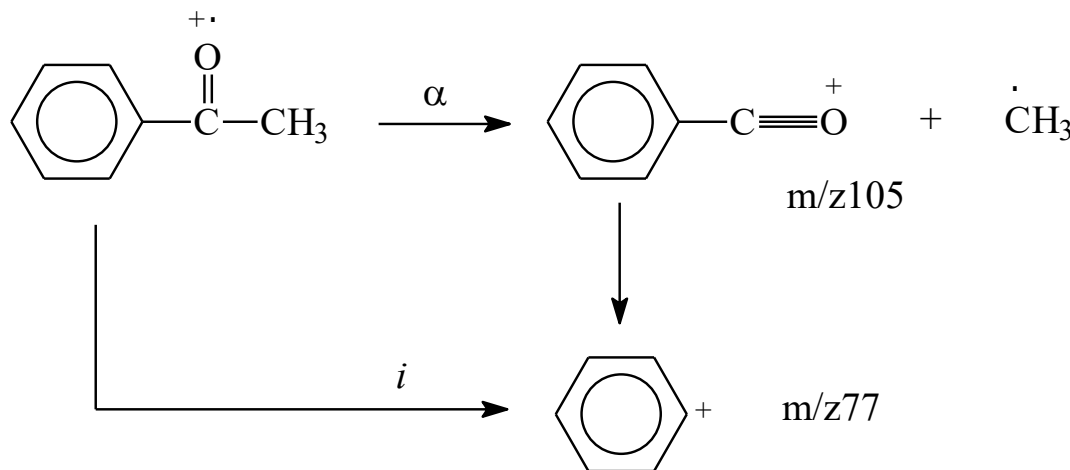
- **Obvious molecular ion peak**
- **Carbonyl cation** via  $\alpha$ -cleavage:  $\text{C}_n\text{H}_{2n-1}\text{O}^{\cdot+}$
- **Alkyl cation** via  $\beta$ -cleavage:  $\text{C}_n\text{H}_{2n+1}^{\cdot+}$
- **Methyl ketone (no  $\alpha$ -substitution )** shows a **m/z 58** via McLafferty rearrangement



**5-methyl-3-heptanone**

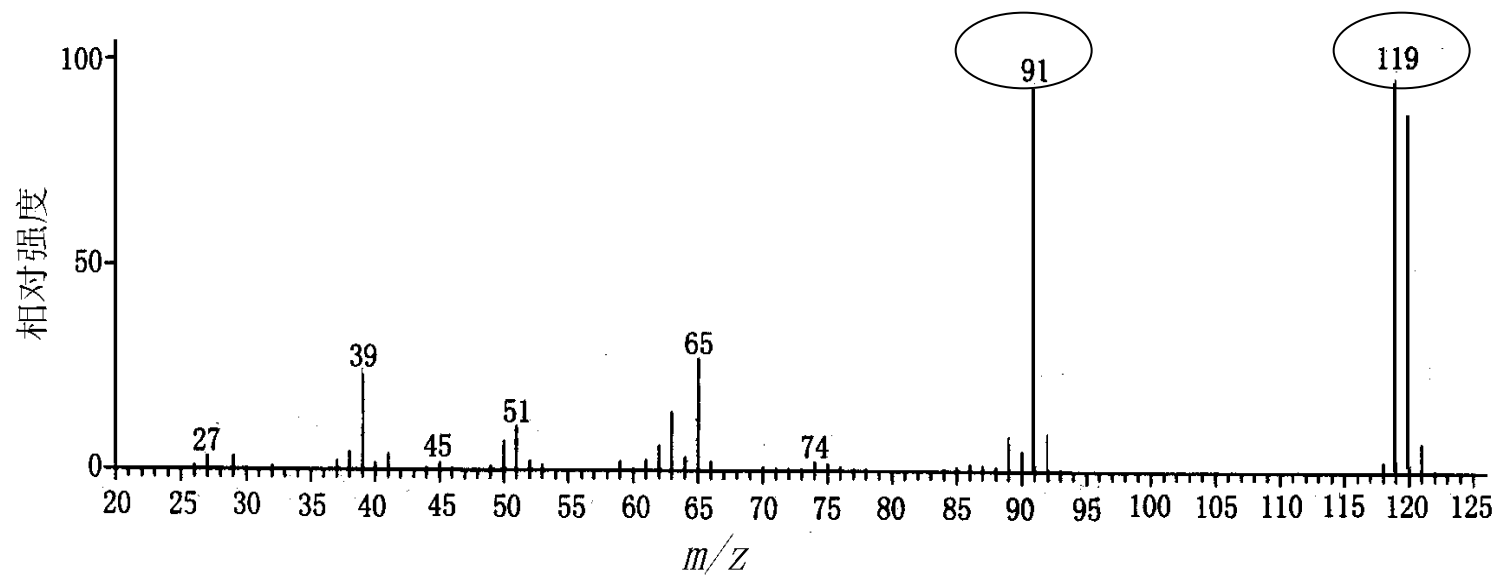
## b. Aromatic ketone

- Strong molecular ion peak
- High abundance of aromatic carbonyl cation ( $\text{Ar-C}\equiv\text{O}^+$ )  $m/z$  105.
- Sequential elimination of CO produces phenyl cation  $m/z$  77



## c. Aldehyde

- Obvious molecular ion peak for aliphatic aldehyde; **strong for aromatic aldehyde**
- Carbonyl cation  $[M-1]^+$  and  $\text{HC}\equiv\text{O}^+$  ( $m/z$  29) via  $\alpha$ -cleavage. **Carbonyl cation  $[M-1]^+$  is feature ion peak for aldehyde, especially aromatic aldehyde.**
- $[M-29]^+$  via  $i$ -cleavage is for high molecular weight aldehyde.
- **$m/z$  44 via McLafferty rearrangement if no  $\alpha$ -substitution of aldehyde.**



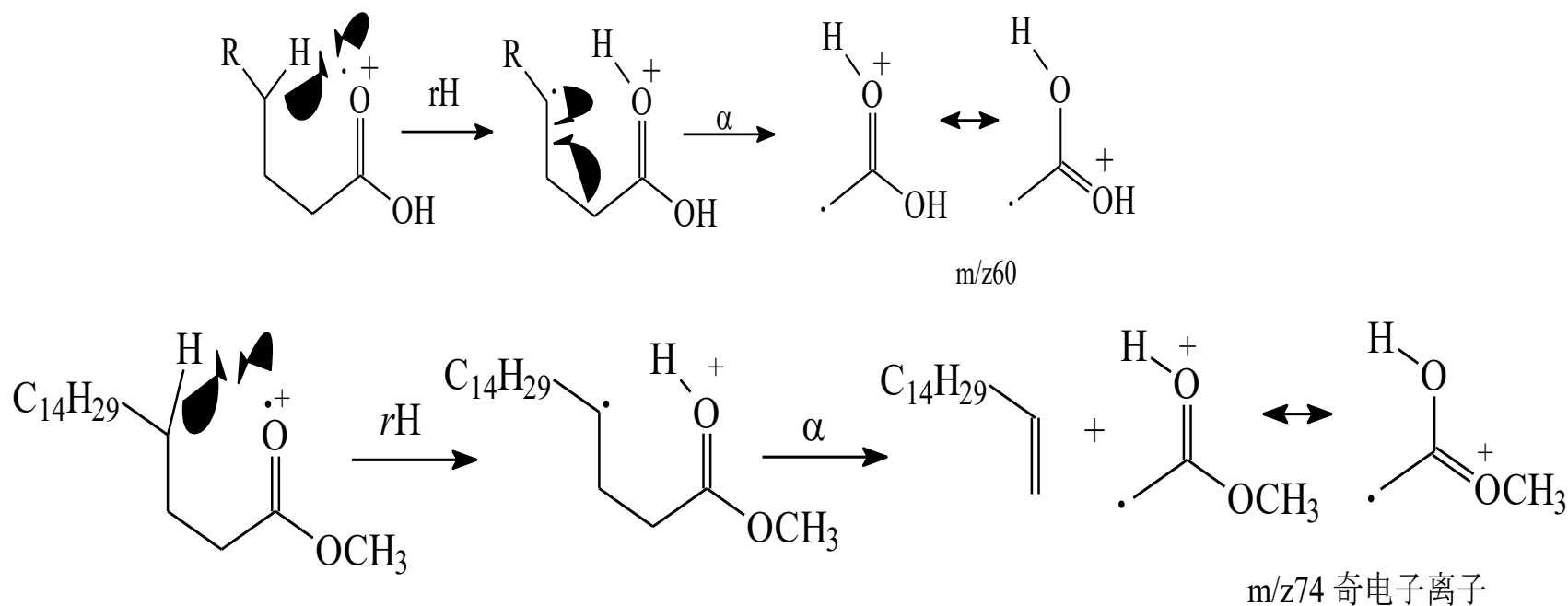
**p-methylbenzaldehyde**



## d. Ester and Carboxylic acid

- Obvious molecular ion peak for aliphatic ester and carboxylic acid; **strong for aromatic ones.**
- $[M-OH]^+$  and  **$OH-C\equiv O^+$  (m/z 45)** via  $\alpha$ -cleavage for low molecular weight acids, for higher ones only m/z 45.
- **$[M-OR]^+$  and  $[COOR]^+$**  via  $\alpha$ -cleavage for esters.

➤ **McLafferty rearrangement:  $m/z60$  for carboxylic acid,  $m/z60+14n$  for esters.**



➤  **$m/z 59+14n$  for long chain aliphatic acid.**

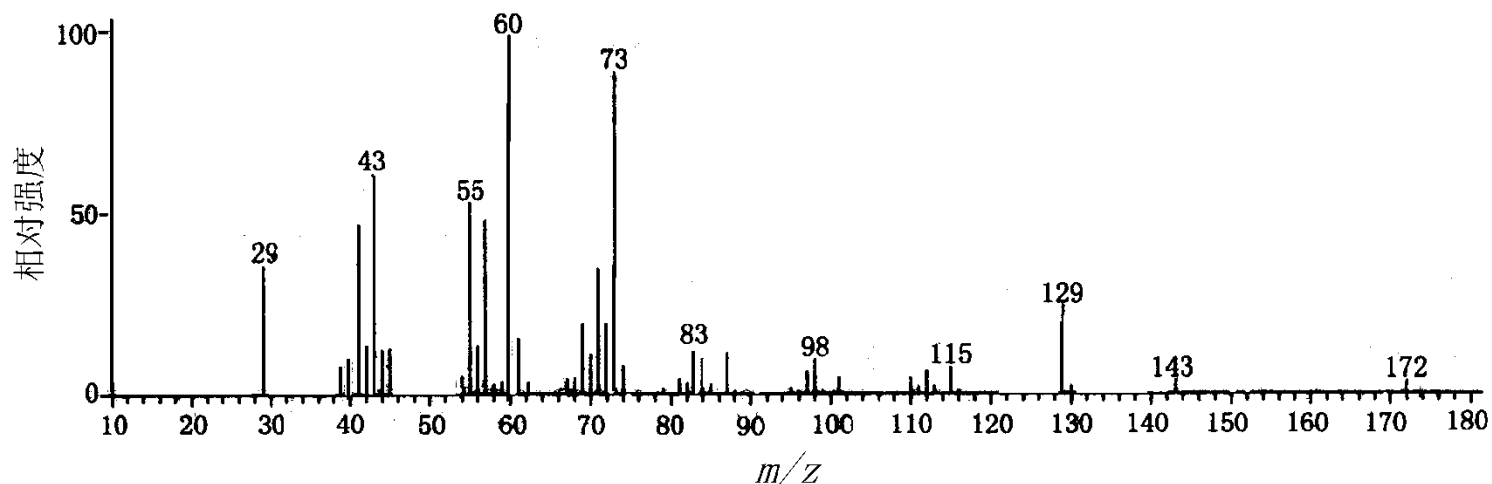
➤  **$m/z 61$  for long chain acetate (Page 40)**

## e. Aromatic Ester and Carboxylic acid

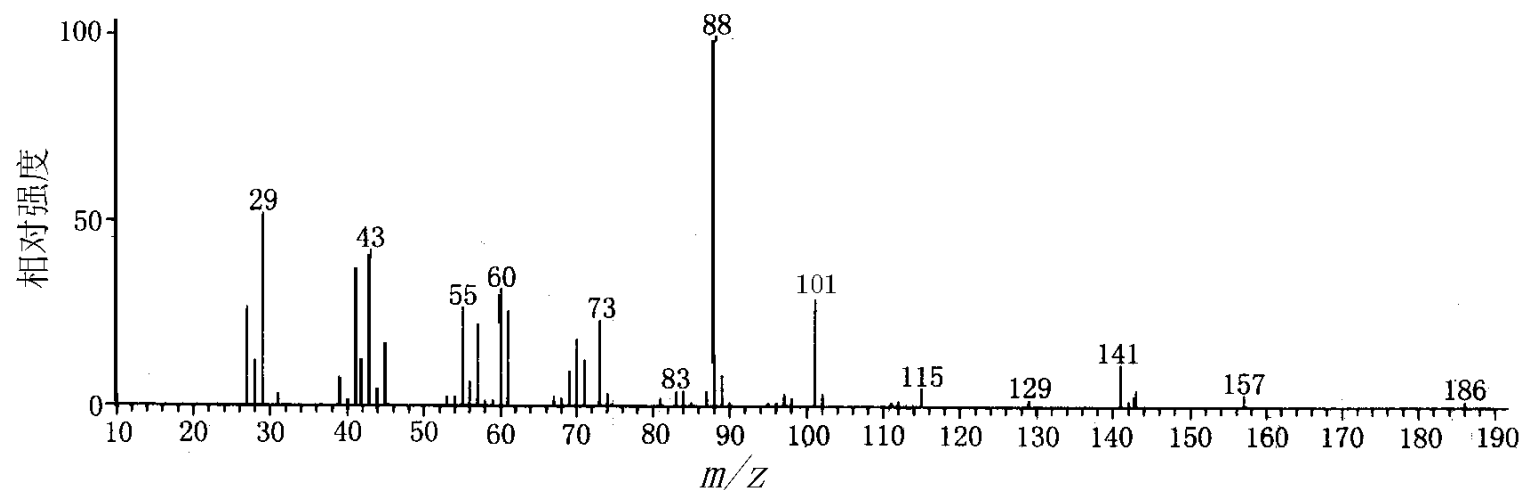
➤ **Phenyl carbonyl cation (  $\text{Ar-C}\equiv\text{O}^+$  )** via  $\alpha$ -cleavage is feature fragment ion for aromatic ester and acid

➤ **ortho-effect would occur when benzene is substituted with  $\text{CH}_3$  and  $\text{OH}$  in the ortho-position.**

Sequentially elimination of  $\text{H}_2\text{O}$  and alcohol would occur and relative fragment ions would be produced.



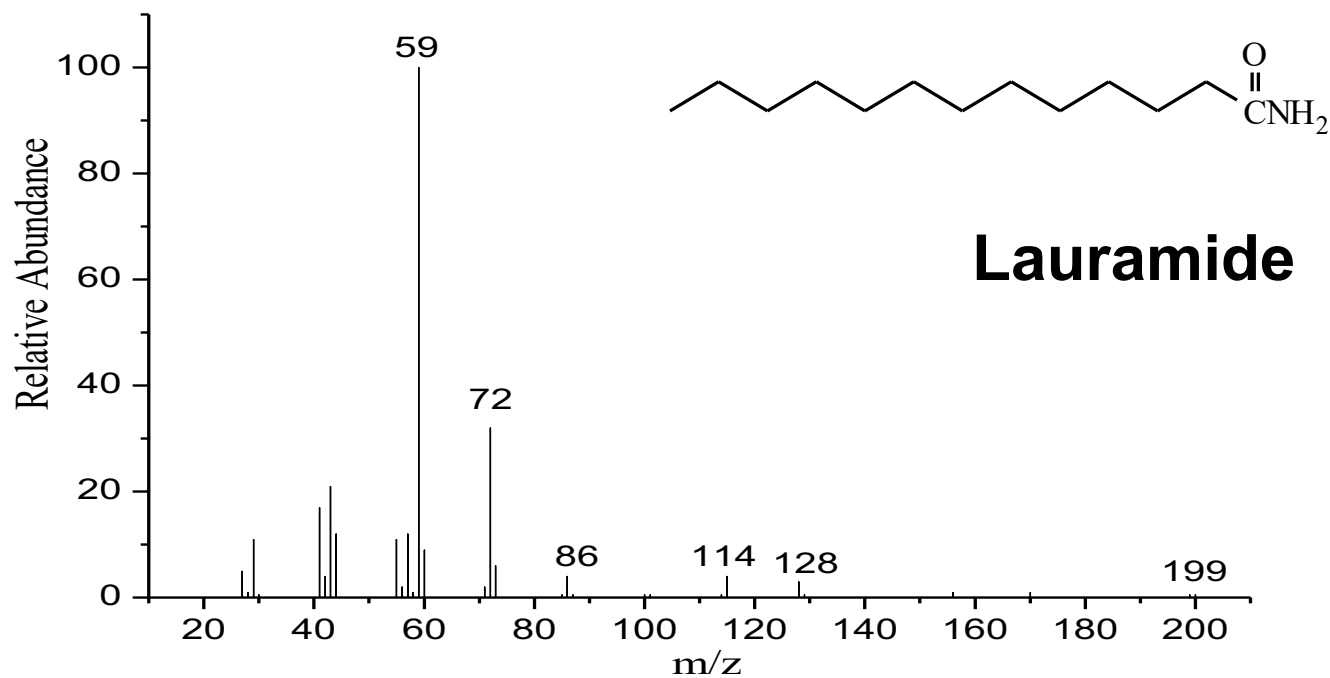
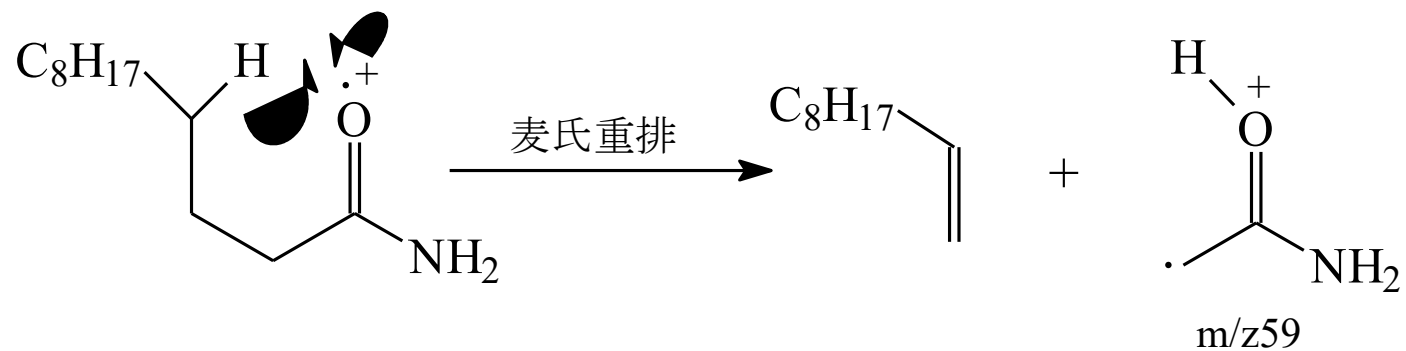
自丁酸开始以上的各羧酸，都有强峰  $m/z$  73 ( $-\text{CH}_2\text{CH}_2\text{COOH}$ )，随着烷链的加长，由  $m/z$  73 开始，每增加 4 个亚甲基，即出现 1 个较强的含羧基的离子，这些离子可用通式  $-(\text{CH}_2)_n\text{COOH}$  表示， $n=2, 6, 10, 14$  等，分别为  $m/z$  73, 129, 185, 241, 297... 各离子相差  $56u$ 。



**Decanoic acid (a) and Ethyl nonanoate(b)**

## f. Amide

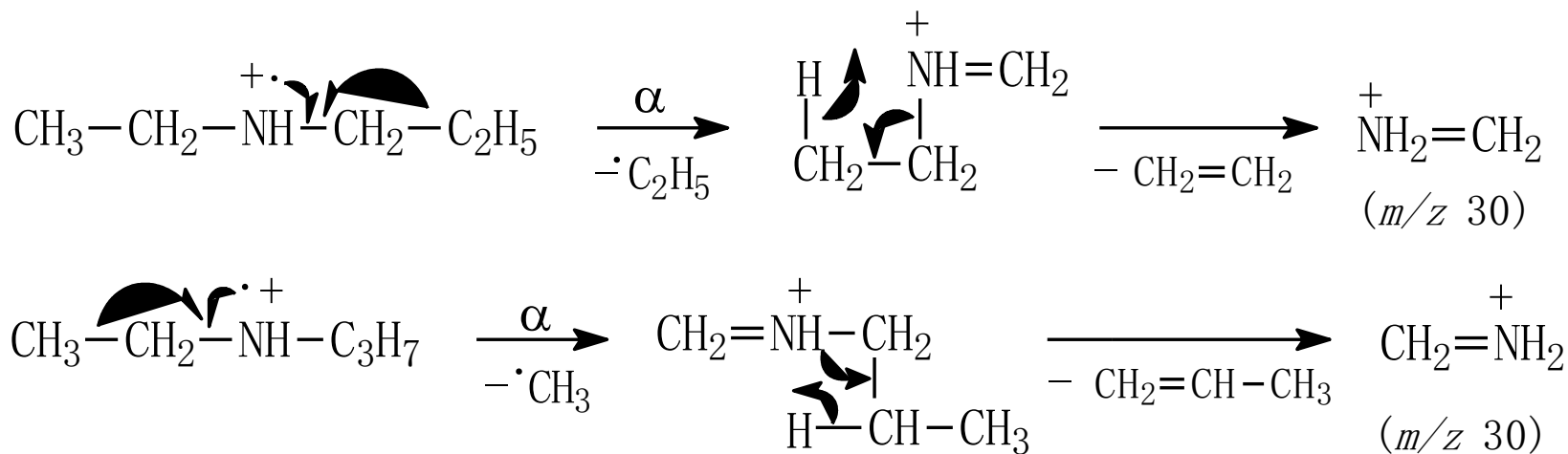
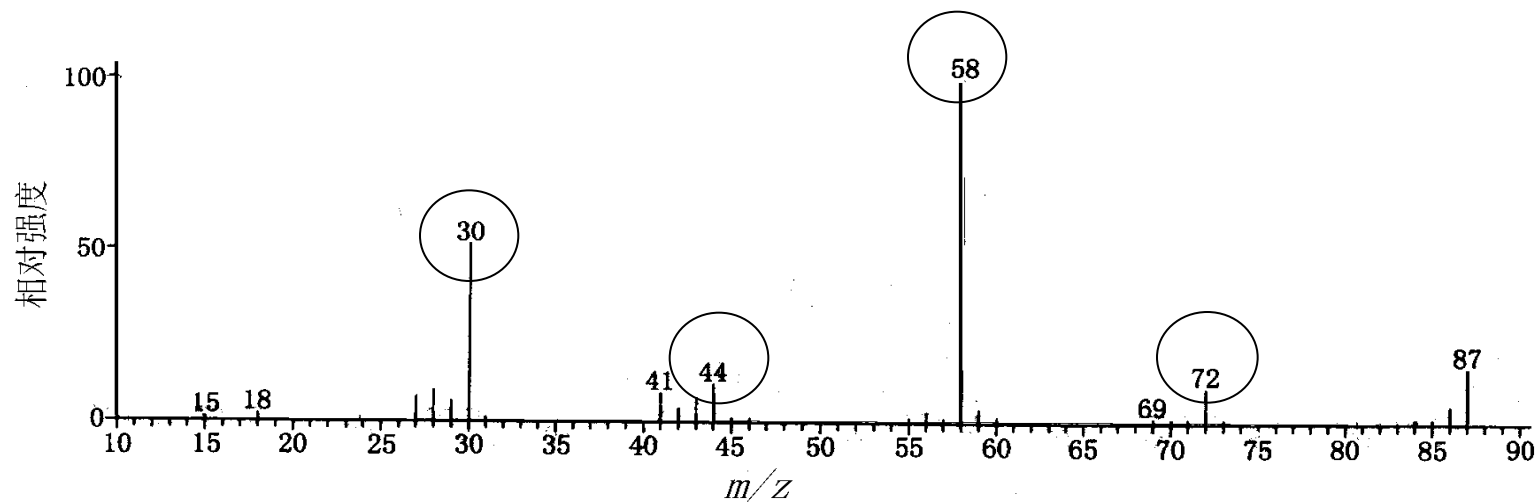
- $\text{R}-\text{C}\equiv\text{O}^+$  and  $\text{O}\equiv\text{C}-\text{NR}_2$  via  $\alpha$ -cleavage , **m/z 44** for **primary amides**.
- **McLafferty rearrangement** for long chain aliphatic amides: **m/z 59 + 14n**
- $\text{C}_n\text{H}_{2n}\text{ON}^{\gamma+}$  for C-C cleavage of long chains.
- **Strong phenyl carbonyl cation (  $\text{Ar}-\text{C}\equiv\text{O}^+$  )** via  $\alpha$ -cleavage and **molecular ion peak** for aromatic amides.



## 5. Amine

- Weak molecular ion peak for aliphatic amines;  
**Strong for aromatic amines.**
- Feature fragment ion peak **m/z 30+14n** via **α-cleavage**; high weight alkyl prefers to be cleaved.
- Sequential rearrangement after α-cleavage and eliminate one ethene to form secondary fragment ions.
- For anilines, **[M-1]<sup>+</sup> (lose H·)** and **[M-27]<sup>+</sup> (-HCN)** are characteristic peaks, similar with phenols.
- For nitriles and nitro compounds, see Page 42.

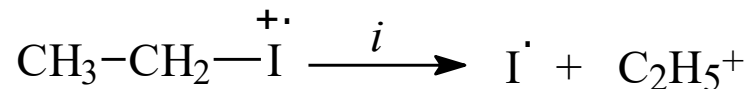
# ethylpropylamine



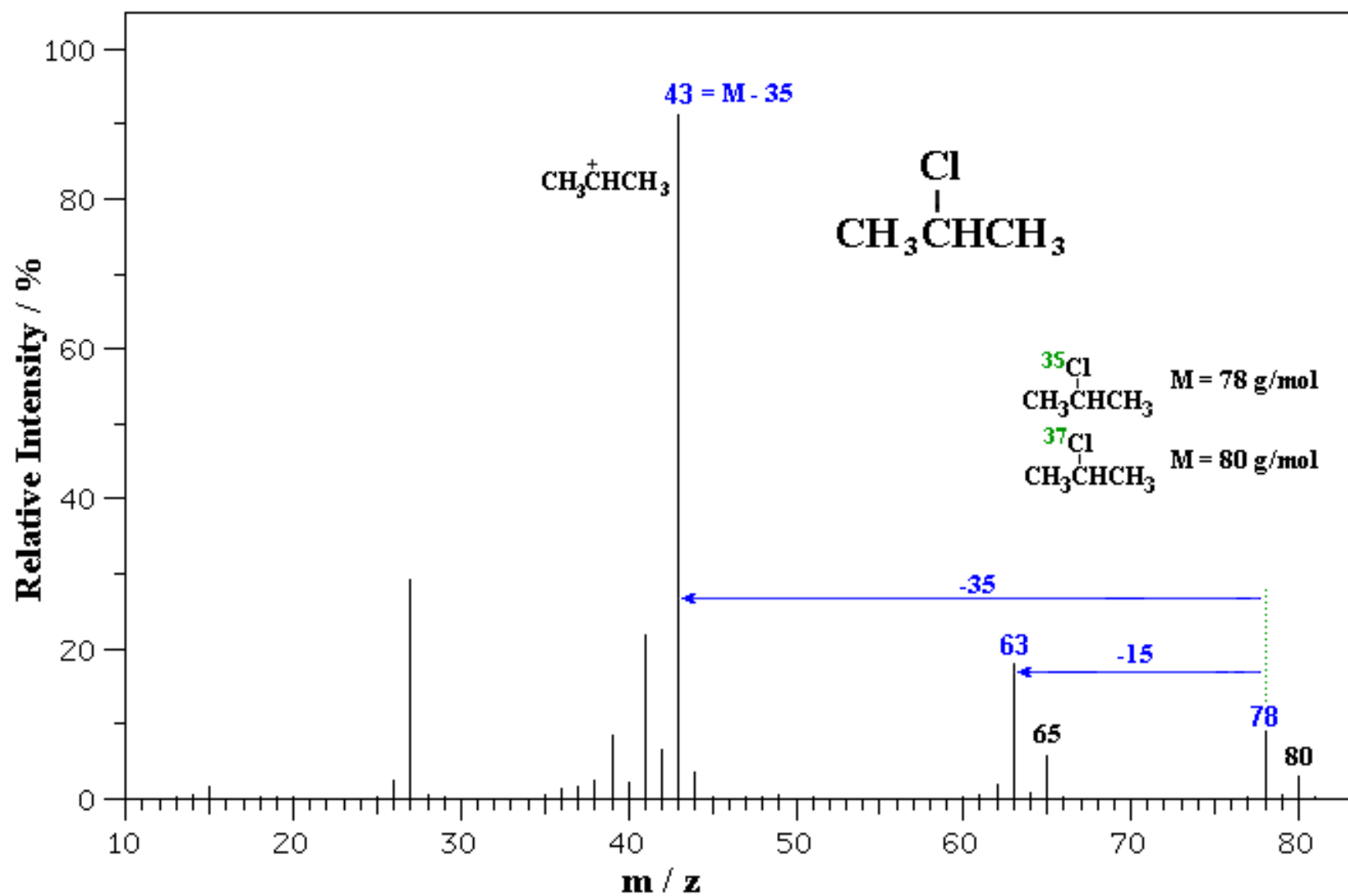


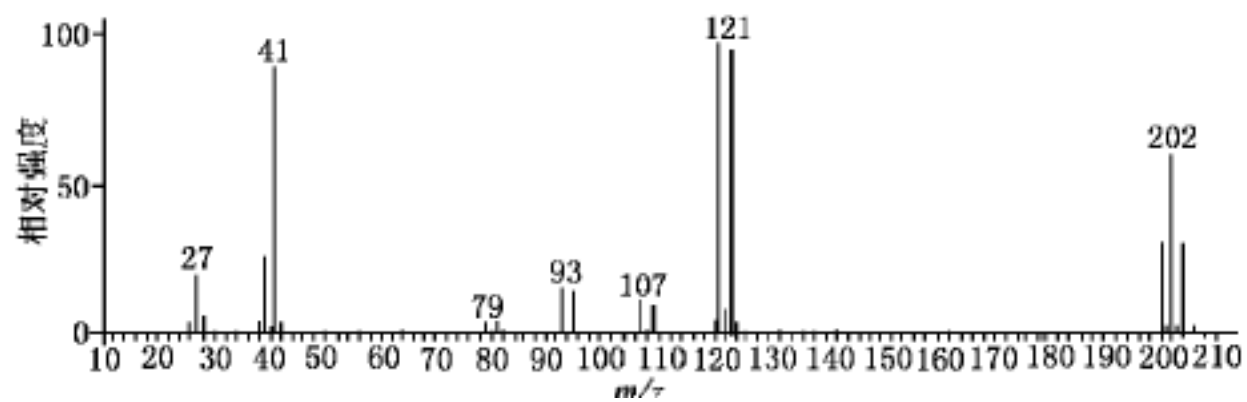
## 6. Halides

- Feature fragment ion peak **[M-X]<sup>+</sup>** via i-cleavage for Cl, Br and I derivatives , but not for F.



- [M-H]<sup>+</sup>
- 1,3-elimination for long chain halides, loses one HX
- Feature **Isotope peaks** for molecular ion peak.





**1,3-dibromopropane**

## 7. Sulfides

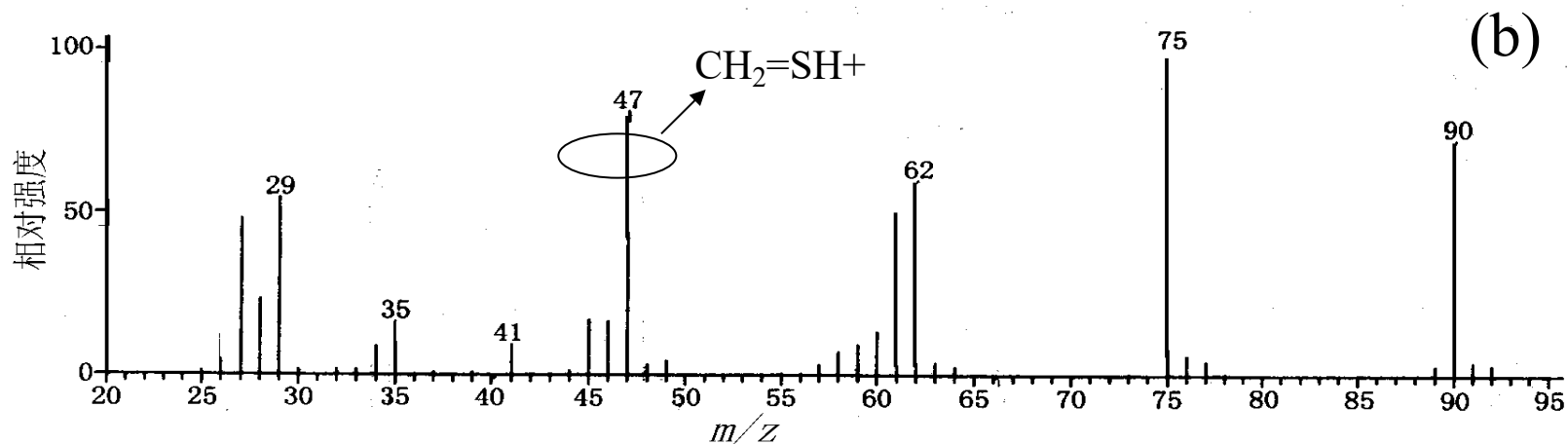
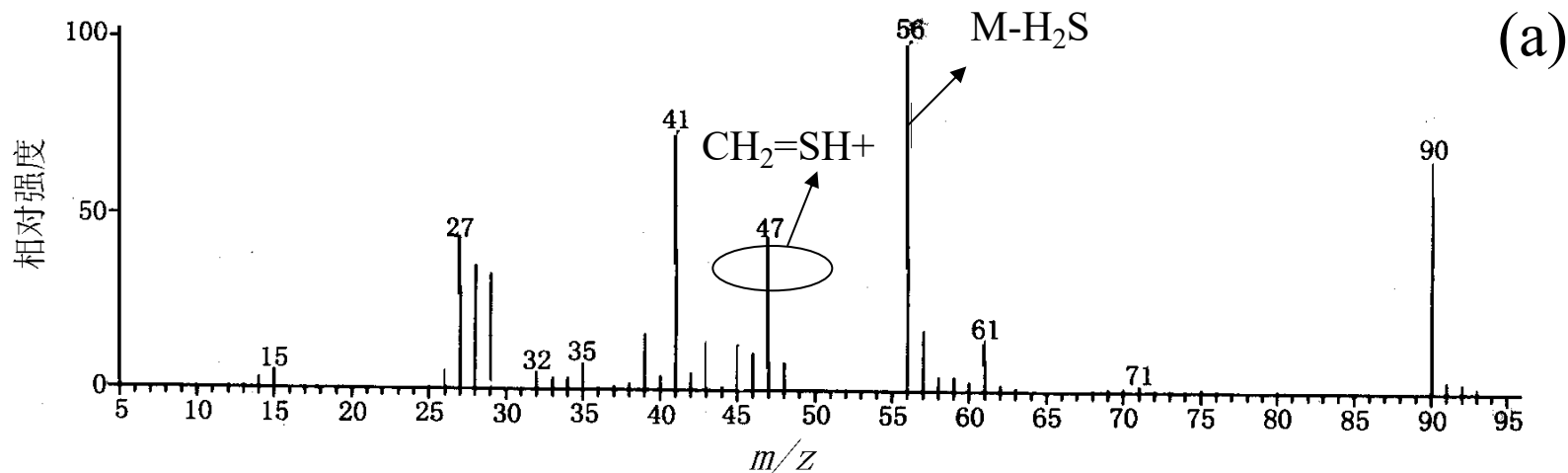
- Isotope peak  $[M+2]^+$ ;
- Obvious molecular ion peak ;
- $m/z\ 33 + 14n$

## a. Thiol

- Fragment ion  $\text{CH}_2=\text{SH}^+$  (m/z 47) for **primary thiols** via  $\alpha$ -cleavage. For secondary and tertiary thiols, higher molecular weight alkyls prefer to cleavage.
- Fragment ion  $[\text{M}-\text{H}_2\text{S}]^+$  via 1,4-elimination for **primary thiols** and sequentially lose  $\text{C}_2\text{H}_4$ . For secondary and tertiary thiols, alkyl cations are tends to formed after losing HS.

## b. Thioether

- $\alpha$ -cleavage would occur at the alkyls besides S with the larger alkyl leaves first.  $\text{R-S}^+=\text{CH}_2$  is produced and may rearrange and eliminate  $\text{C}_n\text{H}_{2n}$ .
- alkyl cation is produced after i-cleavage.
- $\text{RS}^+$  cation is produced after  $\sigma$  –cleavage of C-S bond.



**Mercapto-butane(a) vs Diethyl sulfide(b)**