Rearrangements

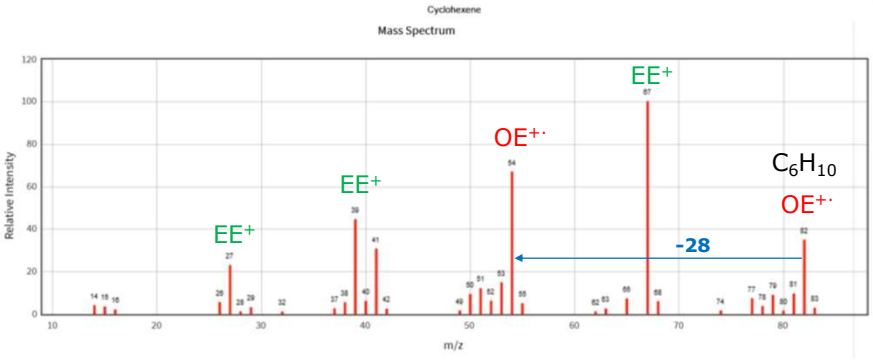
Standard interpretation procedure for EI spectra

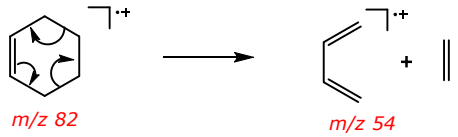
1. ***Known information*** *(other spectra, history of the sample), clear requirements for the MS measurement, control the m/z assignment (calibration)*
2. ***Elemental composition*** *– isotopic pattern (for all peaks in the spectrum)*
3. ***Molecular ion*** *(largest mass in the spectrum, odd number of electrons, logic neutral losses). Comparison with spectra obtained with CI or other soft-ionization method*
4. ***Important ions****: odd number of electrons, largest abundance, high mass, largest abundance in a group of the peaks*
5. ***Appearance of the spectrum****: stability of molecular ion, labile bonds*
6. **Possible sub-structures**
   1. Important series of ions with low masses
   2. Important neutral losses from $M^{+\cdot}$ (fragment with high masses)
   3. Characteristic ions
7. **Suggest molecular structure**

   Comparison with a reference spectrum, with spectra of similar compounds, check with fragmentation mechanisms expected for the suggested molecular ion

Literature - Fred W. McLafferty, František Tureček: Interpretation of mass spectra

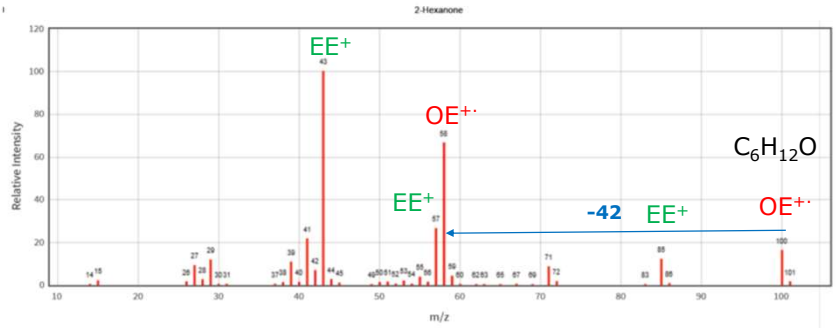
Retro-Diels-Alder reaction

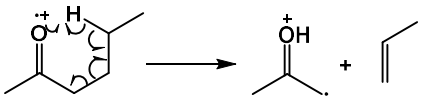




m/z 82 *m/z 54*

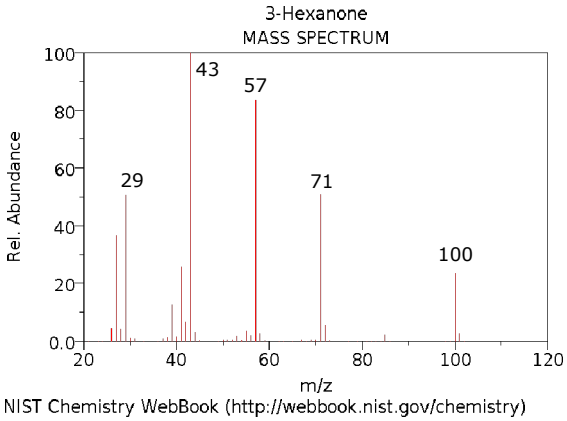
McLafferty rearrangement

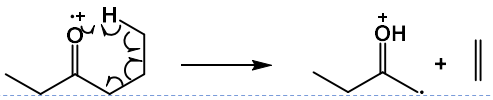




m/z 100 *m/z 58*

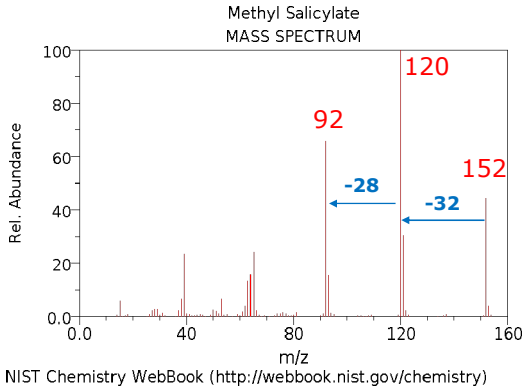
McLafferty rearrangement

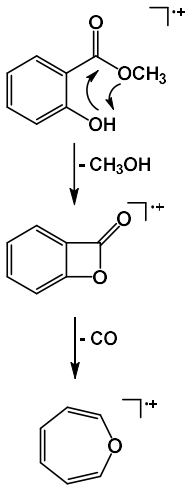




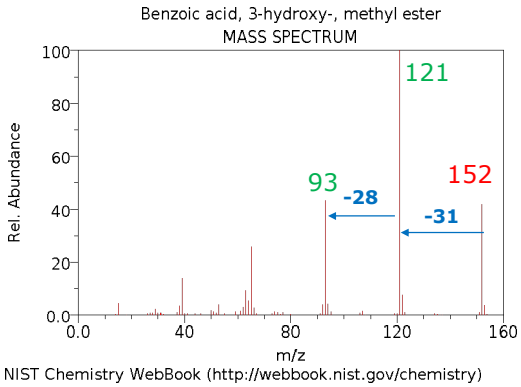
m/z 100 *m/z 72*

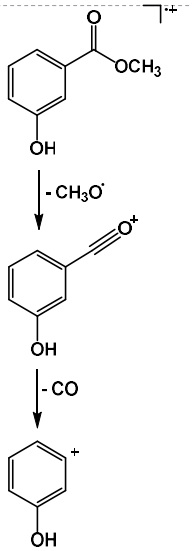
Ortho effect





Ortho effect





Stable sub-structures

Stable sub-structures are connected with a weak bond →
A simple spectrum with prominent peaks

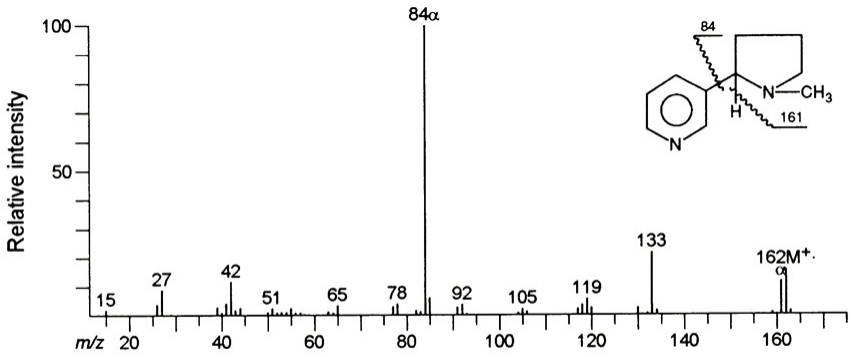


Figure 5.1. Mass spectrum of nicotine.

Common Ion Series

Table 5.1. *Common ion series* (see Tables A.6 and A.7)

Function[a]	Formula	Index, Δ[b]	*m/z* values
Nitriles	$C_nH_{2n-2}N^+$	−1	40 54 68 82
Alkenyl, cycloalkyl	$C_nH_{2n-1}^+$	0	27 41 55 69 83
Alkenes, cycloalkanes, alkyl-Y[c]	$C_nH_{2n}^{+\cdot}$	+1	28 42 56 70 84
Alkyl	$C_nH_{2n+1}^+$	+2	15 29 43 57 71 85
Aldehydes, ketones	$C_nH_{2n-1}O^+$	+2	29 43 57 71 85
Amines	$C_nH_{2n+2}N^+$	+3	30 44 58 72 86
Alcohols, ethers	$C_nH_{2n+1}O^+$	+4	31 45 59 73 87
Acids, esters	$C_nH_{2n-1}O_2^+$	+4	45 59 73 87
Thiols, sulfides	$C_nH_{2n+1}S^+$	+6	33[d] 47 61 75 89
Chloroalkyl	$C_nH_{2n}Cl^+$	−6	35 49 63 77 91
Aromatic	$C_nH_{\leq n}$	−2 to −8	38, 39, 50–52, 63–65, 75–78[e]

[a] Connected to a saturated aliphatic substructure
[b] Δ = mass − 14*x* + 1 (Dromey 1976); an odd number corresponds to an *N*-containing or $OE^{+\cdot}$ series.
[c] For which HY is a molecule of low proton affinity.
[d] HS^+ ion
[e] All of these peaks may not be of significant abundance in a particular spectrum, and neighboring peaks are sometimes observable.