Mass Spectrometry (MS)

from chapter(s) _____ in the recommended text

A. Introduction

B. Components Of Mass Spectrometers

molecules on the basis of the ratio of *mass-to-charge*.

primary objective of MS is to determine the *molecular mass* of that entity
from the complete molecule *without* fragmentation).

Most mass spectrometers are able to

- create ions in the gas phase
- separate ions on the basis of *m/z* (*ie* an analyzer)
- detect the number of ions of each *m/z*

three basic components to a mass spectrometer *an ionization source / an analyzer / a detector*.

Electrospray (ESI) is a form of *ionization*.

Quadrupoles are components used for *analysis*.

Time-of-flight (TOF) is a form *analysis*.

Quadrupole ion traps are components used for *analysis*.

Matrix assisted laser desorption (MALD) is a form of *ionization*.

Fourier transform (FT) is a form of *analysis*.

Electron Impact (EI) is a form of *ionization*.

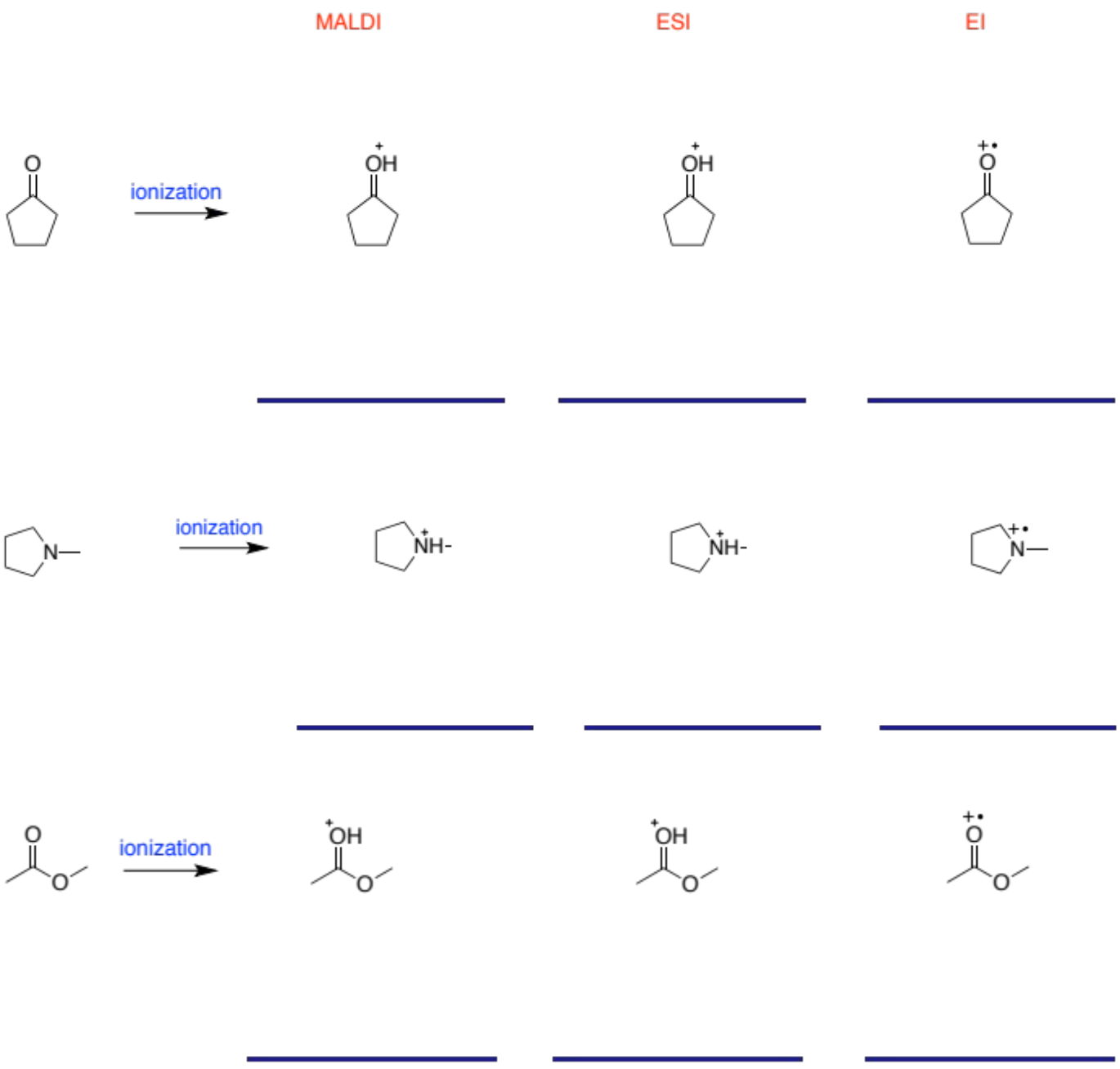
Detectors in MS are usually *electron multipliers*.

Thus*, MALDI-TOF* is a valid description but *ESI-MALDI* is not.

C. Primary Ions Formed In Different Ionization Techniques

In *matrix-assisted lased desorption ionization*, or _MALDI_, the sample is adsorbed
The matrix transfers energy to the sample and mainly *protonates* it to give a cation, *ie* $[M + H]^+$.

In *electrospray ionization*, or _ESI_, the sample in a solvent (*eg* water) is sprayed
be protonated by the solvent giving $[M + 1]^+$ and ions with more than one proton.



Electron impact, removes *an electron* from molecules to give *radical cations*

MM as the sample, provided there is no fragmentation, *ie* $[M]^{+\bullet}$.

Resolution is important in MS when trying to distinguish two materials of similar molecular weights.

Observation of signals when working with tiny amounts of substrate is a question of *sensitivity*.

It is one of the *most* sensitive forms of MS.

D. Isotopes In Mass Spectrometry

Element	Isotope	Abundance (%)	Mass number	Exact mass
hydrogen	^{1}H	99.99	1	1.00783
carbon	^{12}C	98.89	12	12.00000
carbon	^{13}C	1.11	13	13.00335
nitrogen	^{14}N	99.64	14	14.00307
oxygen	^{16}O	99.76	16	15.99492
fluorine	^{19}F	100	19	18.99840
phosphorus	^{31}P	100	31	30.97376
sulfur	^{32}S	95.00	32	31.97207
chlorine	^{35}Cl	75.77	35	34.96886
chlorine	^{37}Cl	24.23	37	36.96590
bromine	^{79}Br	50.69	79	78.91835
bromine	^{81}Br	49.31	81	80.91635
iodine	^{127}I	100	100	126.904468

CO	C_2H_4	$C_2H_5{}^{35}Cl$
27.99492	28.03132	64.00801
exact mass	*exact mass*	*exact mass*

$CH_3{}^{79}Br$	$CH_3{}^{81}Br$	$C_2H_5{}^{37}Cl$
93.94184	95.93984	66.00505
exact mass	*exact mass*	*exact mass*

A *high resolution* mass spectrometer *can* distinguish

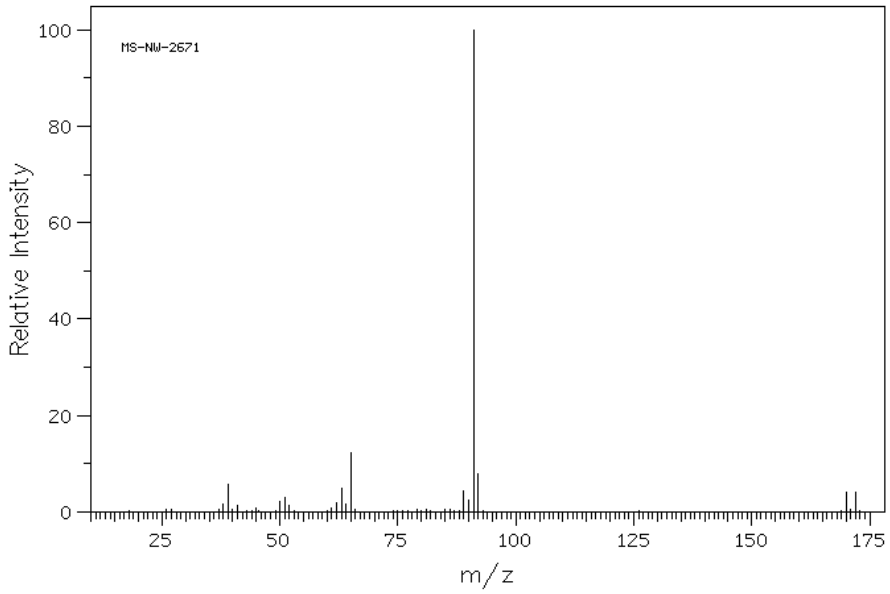
containing natural chlorine are separated by 1.99704 atomic mass units (amu's) in a ratio of 3.13:1, and compounds containing natural bromine are separated by 1.99800 amu's in a ratio of 1.03:1.

containing *two* bromines will have 3 molecular ions in a 1:2:1
containing *three* bromines will have 4 molecular ions in a 1:3:3:1

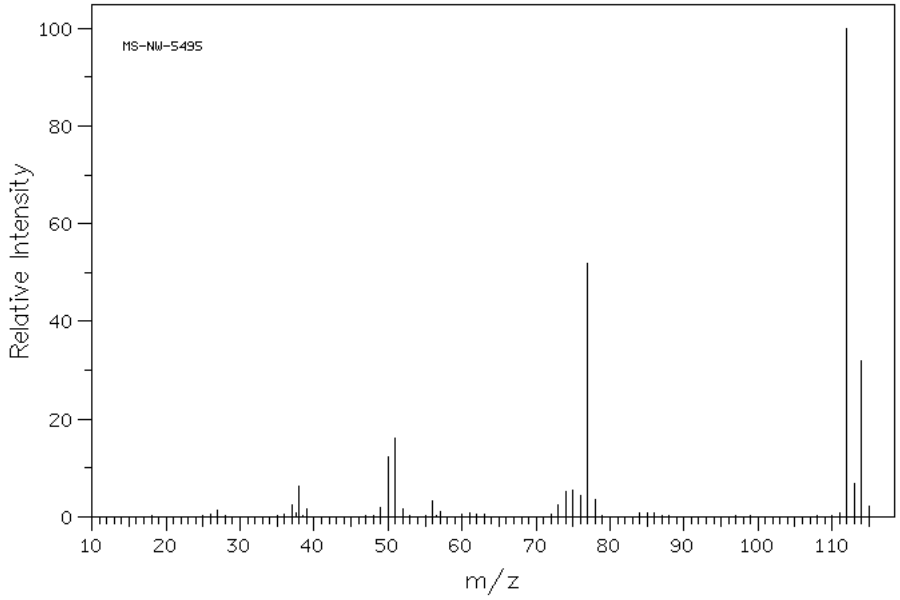
Illustrative Interpretation Of Isotopes In MS

the chlorine-containing compound A is number: __*2*_____
the bromine-containing compound B is number: __*1*_____
the non-halogenated compound C is number: ____*3*_____

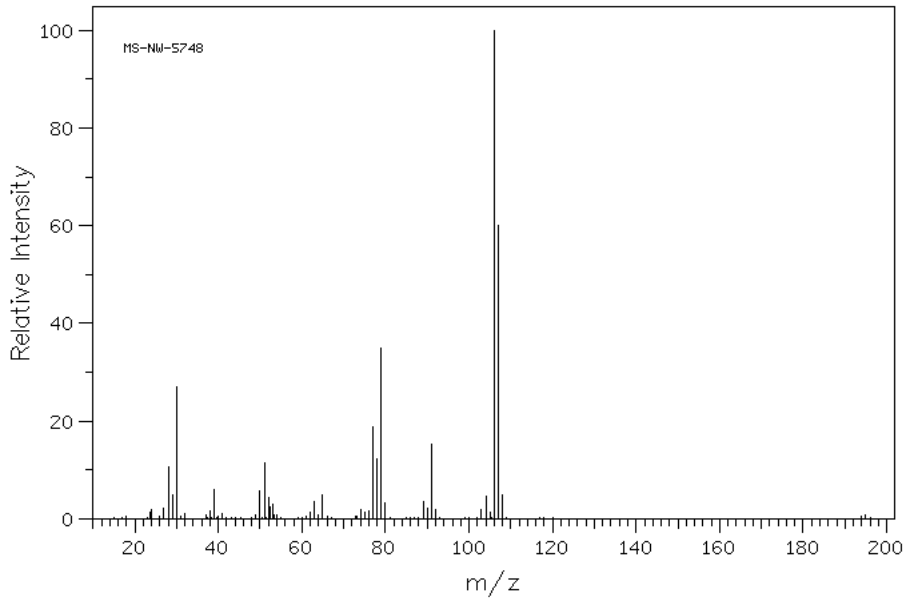
1 (m/z = 170 and 172):



2 (m/z = 112 and 114):



3 (m/z = 107):



containing odd numbers of nitrogen atoms (1, 3, 5 *etc*) *always* have odd molecular ion m/z values.

E. Fragmentation

dissociate into smaller cations and *radicals*

the *most* stable one that is most likely to be observed.

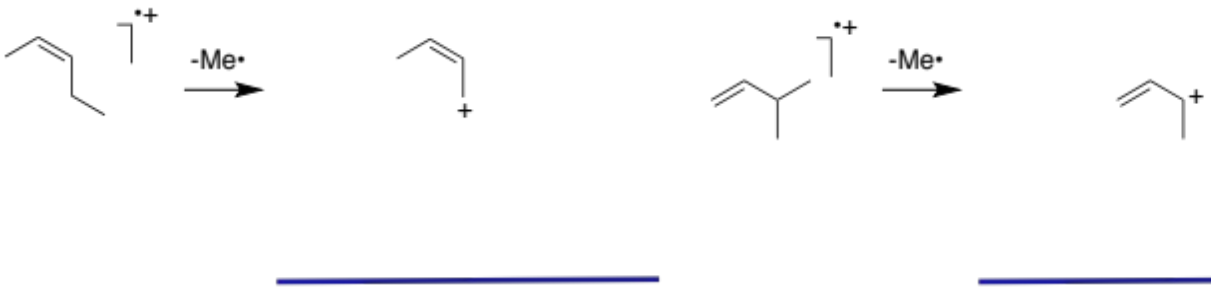
Electron impact methods *usually* show fragmentation, but *ESI* does not.

ESI is widely used in contemporary MS, but *EI* instruments are becoming less important.

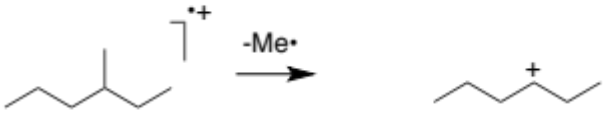
Fragmentation is usually *undesirable* because observation of the molecular ion is the most important and this *is* useful when complementary methods

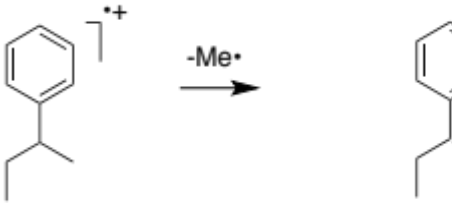
observing molecular ions *and* fragmentation patterns is *MS/MS.*

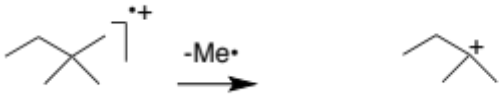
Tandem mass spectrometry allows observation of molecular ions from peptides and proteins

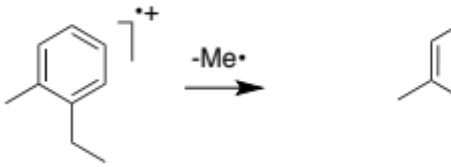


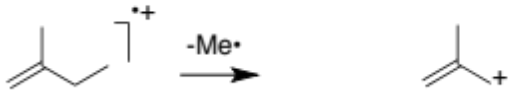

-Me•

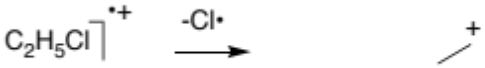

-Me•

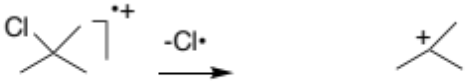

-Me•

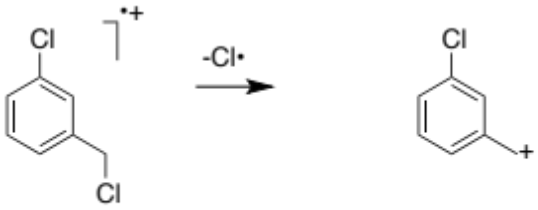

-Me•

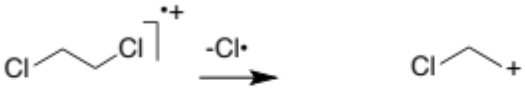

-Me•


-Me•

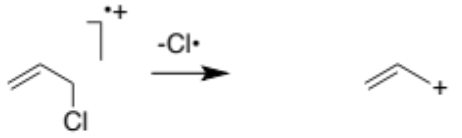

C2H5Cl
-Cl•


Cl
-Cl•

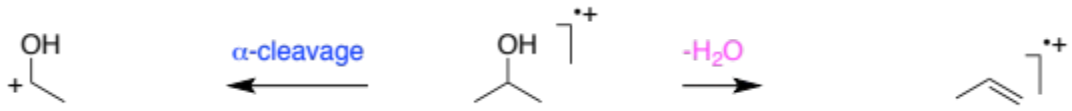

Cl
-Cl•
Cl
Cl

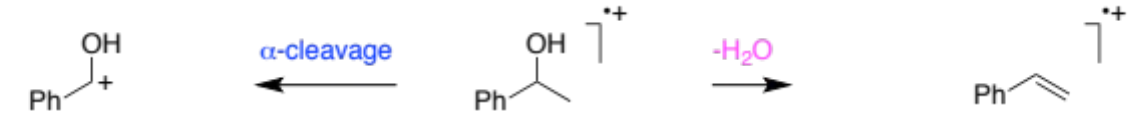

Cl
Cl
-Cl•
Cl

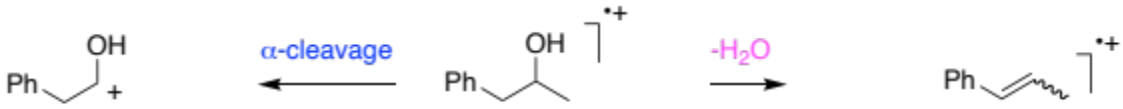

Cl
-Cl•
Cl
Cl

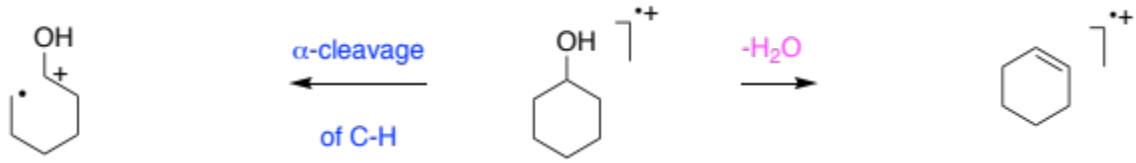

-Cl•
Cl

-Cleavage

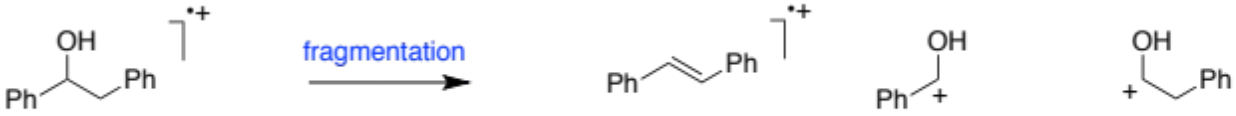

OH
α-cleavage
OH
-H2O


OH
Ph
+
α-cleavage
OH
Ph
•+
-H2O
Ph
•+

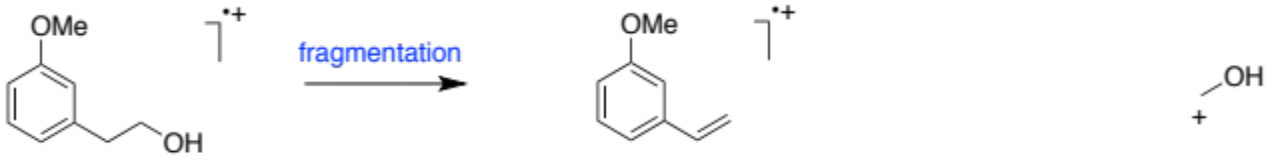

OH
Ph
+
α-cleavage
OH
Ph
•+
-H2O
Ph
•+


OH
+
α-cleavage
of C-H
OH
•+
-H2O
•+


OH
Ph
Ph
fragmentation
OH
Ph


OH
Ph
Ph
fragmentation
Ph
OH
Ph
OH
Ph


HO
fragmentation
HO

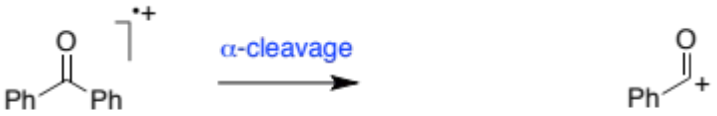

OMe
OH
fragmentation
OMe
OH

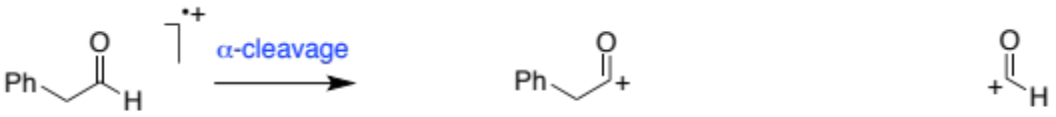

NH2
Ph
Ph
α-cleavage
NH2
Ph
Ph
NH2
Ph

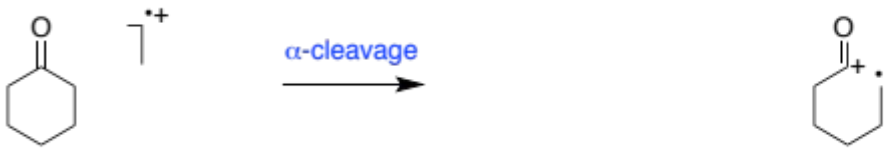

NH
α-cleavage
NH
NH


NH
α-cleavage
NH
NH


NEt3
α-cleavage
N
N

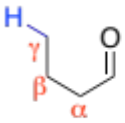

α-cleavage

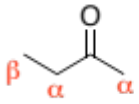

α-cleavage

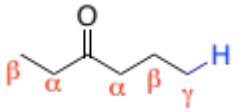

α-cleavage

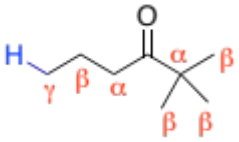

α-cleavage

The McLafferty Rearrangement



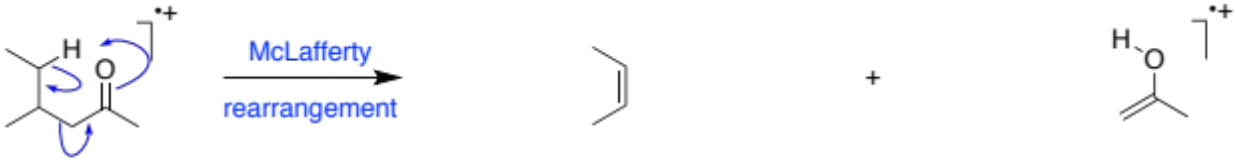




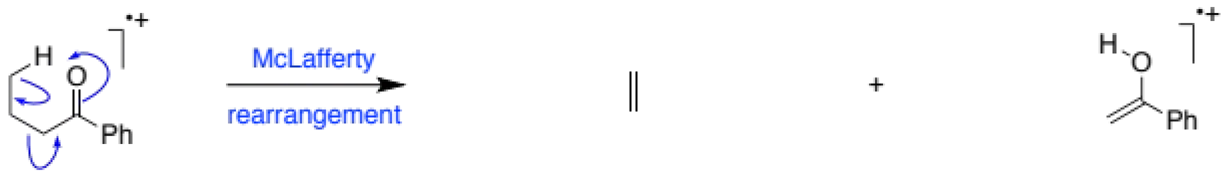


This gives cleavage of the bond between the *and* fragments

All these answers can also be shown as a movement in single electron steps corresponding to radical reactions and using fishhook arrows.

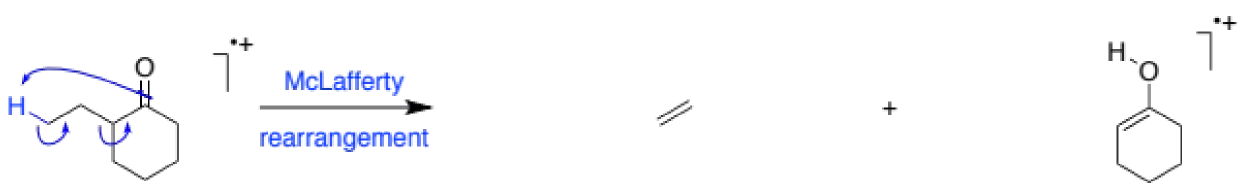


alkene *radical cation*



alkene

radical cation



Molecule on the left can undergo *McLafferty rearrangement* since it has -hydrogen whereas molecule on the right does not.