Mass Spectrometry (MS)

from chapter(s) _____ in the recommended text

A. Introduction

B. Components Of Mass Spectrometers

mass-to-charge.

mass
without fragmentation).

- 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*

an ionization source / an analyzer / a detector.

ionization.

for *analysis*.

or *analysis*.

for *analysis*.

or *ionization*.

Fourier transform (FT) *analysis*.

Electron Impact (EI) *ionization*.

Detectors in MS *electron multipliers*.

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

C. Primary Ions Formed In Different Ionization Techniques

MALDI
ie $[M + 1]^+$.

ESI
$[M + 1]^+$

MALDI ESI EI

an electron from molecules to give *radical cations*
ie $[M]^{+}$.

Resolution
sensitivity.

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*

can distinguish

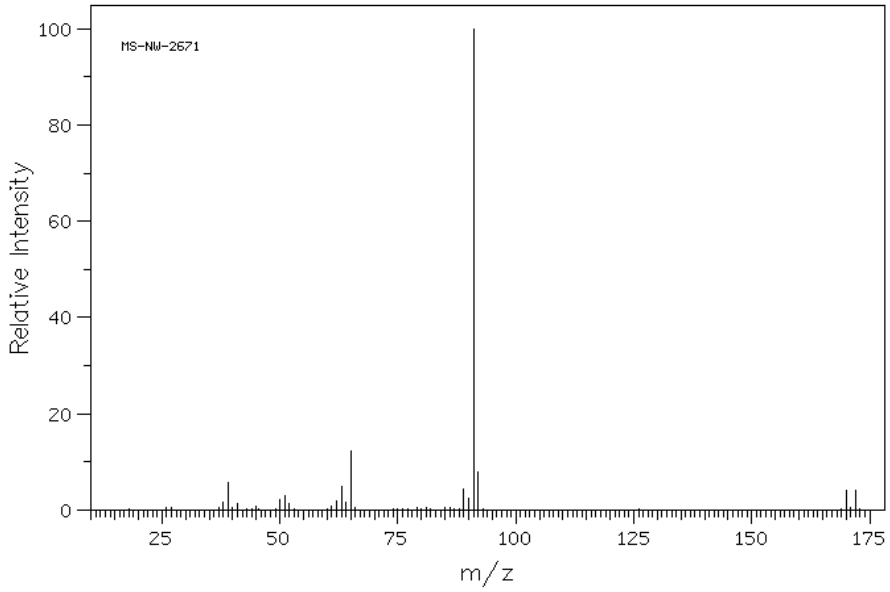
1.99704 atomic mass units (amu's) in a ratio of 3.13:1
1.99800 amu's in a ratio of 1.03:1.

3 molecular ions in a 1:2:
4 molecular ions in a 1:3:3:1

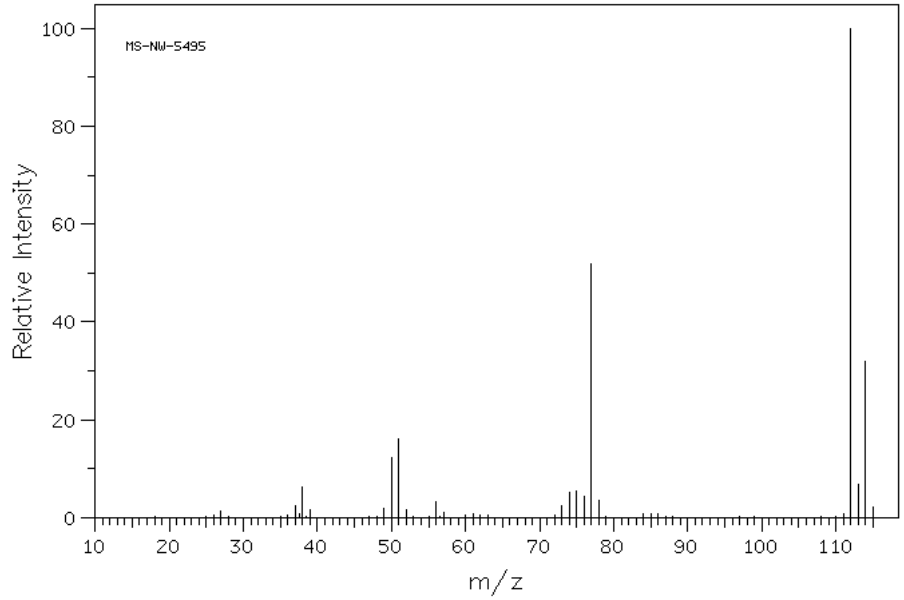
Illustrative Interpretation Of Isotopes In MS

the chlorine-containing compound A is number: __2_____
the bromine-containing compound B is number: __1_____
the non-halogenated compound C is number: ____3_____

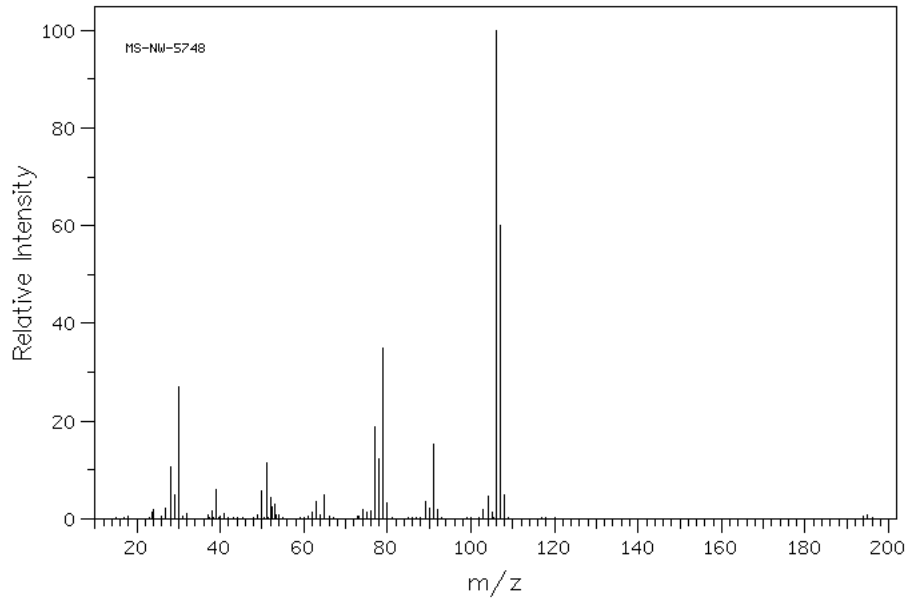
1 (m/z = 170 and 172):



2 (m/z = 112 and 114):



3 (m/z = 107):



always have odd molecular ion m/z values.

E. Fragmentation

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

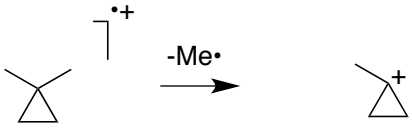
electron impact
ESI does not.

ESI is widely used in contemporary MS, but *EI*

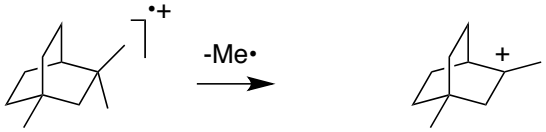
Fragmentation is usually *undesirable*
is useful when complementary methods

MS/MS

tandem


-Me•


-Me•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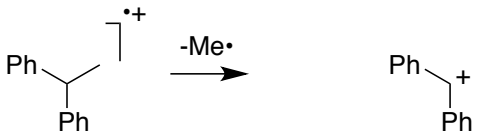
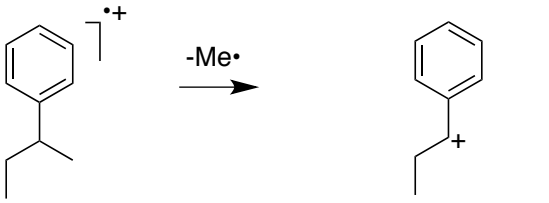

Ph
Ph
-Me•
Ph
Ph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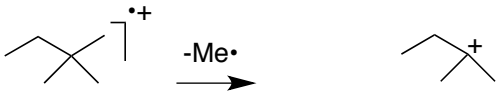
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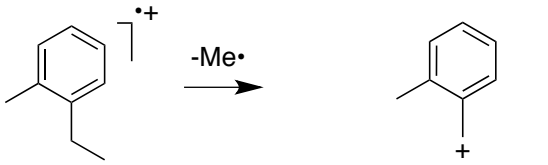
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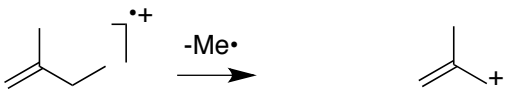
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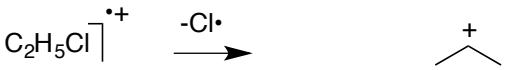
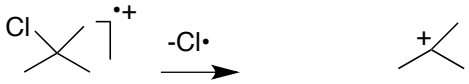
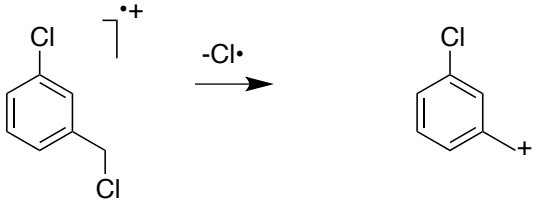
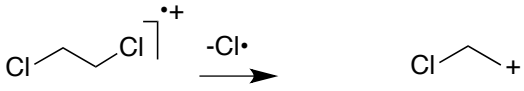
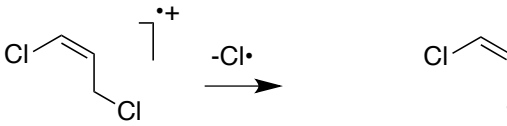
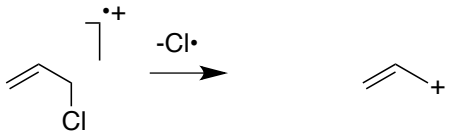

C2H5Cl
-Cl•


Cl
-Cl•

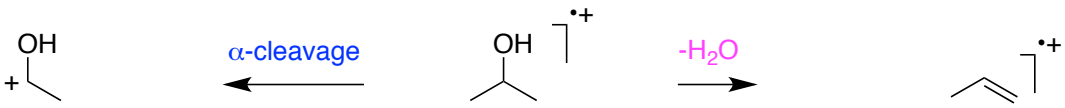

Cl
-Cl•
Cl
Cl

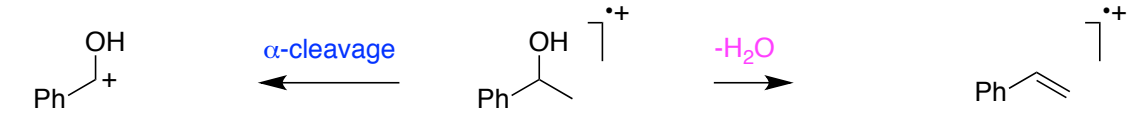

Cl
Cl
-Cl•
Cl

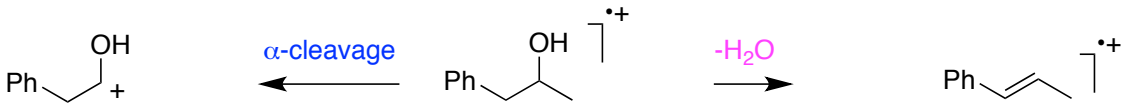

Cl
-Cl•
Cl

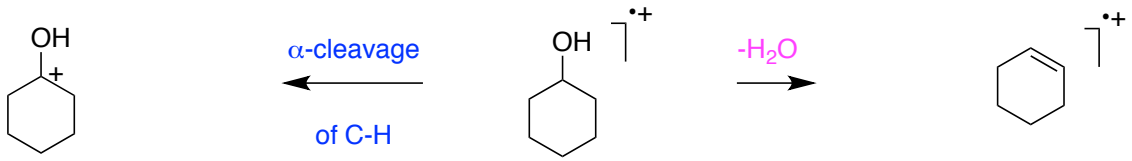

-Cl•
Cl

α-Cleavage

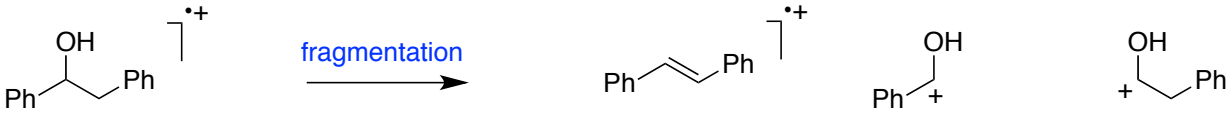

OH
α-cleavage
OH
-H2O


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

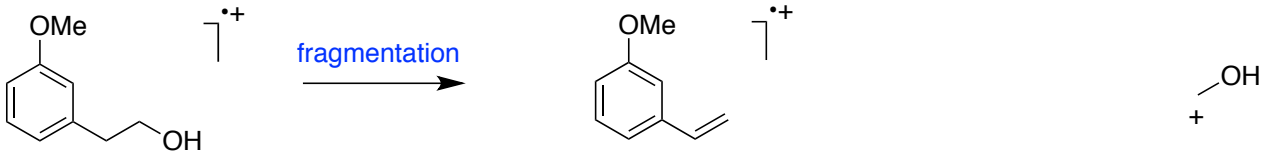

OH
Ph
+
α-cleavage
OH
Ph
•+
-H2O
Ph
•+


OH
+
α-cleavage
of C-H
OH
•+
-H2O
•+


OH
Ph
Ph
fragmentation
OH
Ph


OH
Ph
Ph
fragmentation
Ph
Ph
OH
Ph
OH
Ph


HO
fragmentation
HO

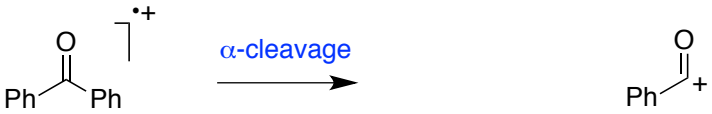

OMe
OH
fragmentation
OMe
OH

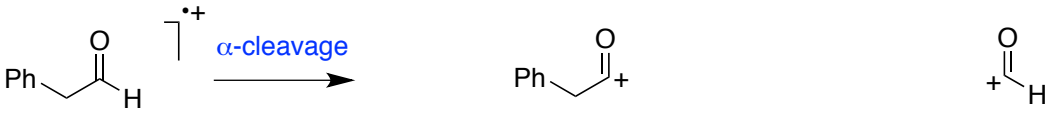

NH2
Ph
Ph
α-cleavage
NH2
Ph
Ph
NH2
Ph

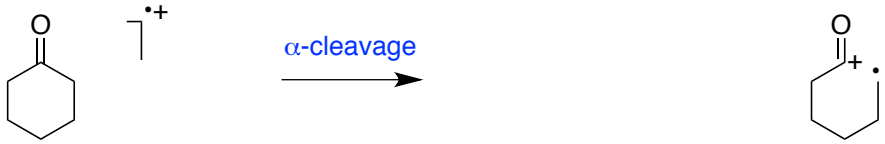

NH
α-cleavage
NH
NH


NH
α-cleavage
NH
NH


NEt3
α-cleavage
N

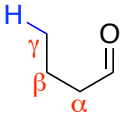

α-cleavage

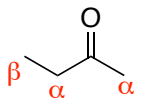

α-cleavage

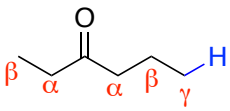

α-cleavage

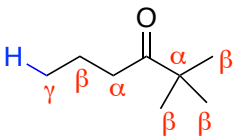

α-cleavage

The McLafferty Rearrangement

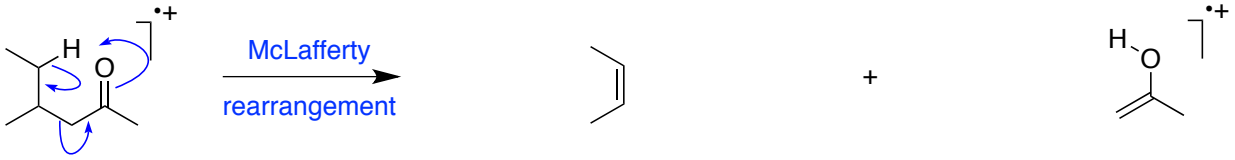




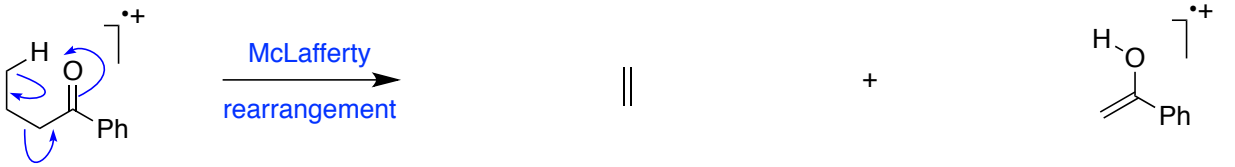




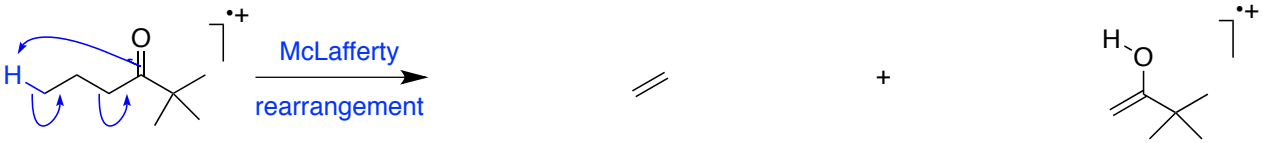
α and β fragments

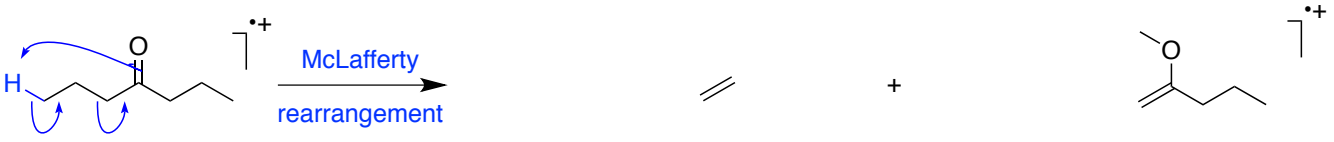


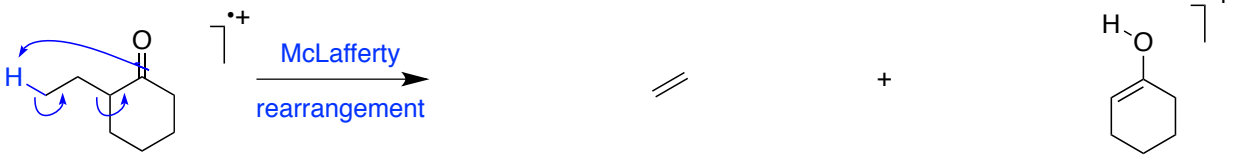
alkene *radical cation*



alkene *radical cation*







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