344 | Organic Chemistry Laboratory
Fall 2013

Lecture 3 Gas Chromatography and Mass Spectrometry
June 19 2013

Chromatography

Chromatography – separation of a mixture into individual components

Paper, Column, Thin Layer (TLC), High-Pressure Liquid (HPLC)

All feature a **stationary phase** and a **mobile phase**

Focus on **Gas Chromatography (GC)** (coupled with mass spec. – see later)

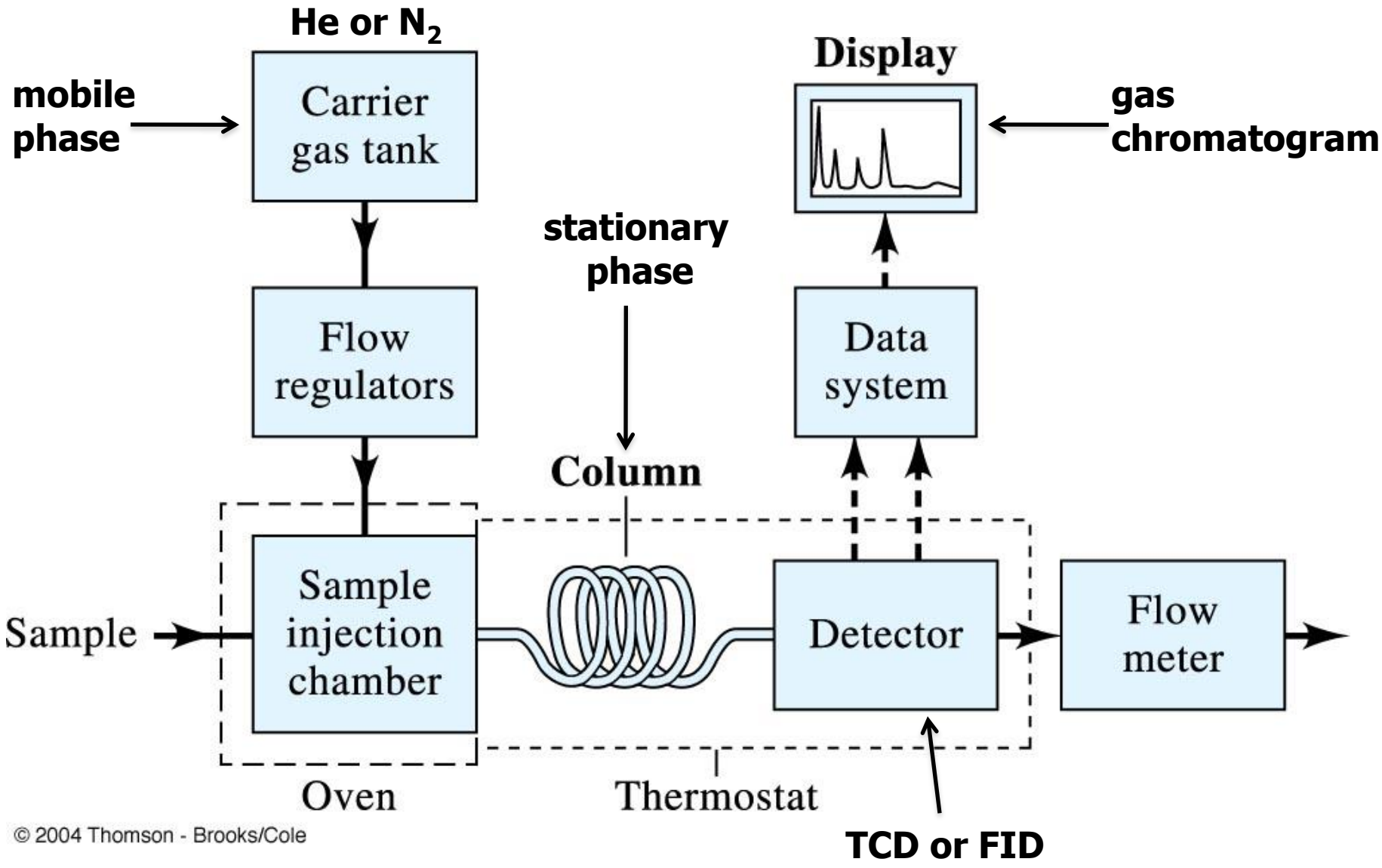
Stationary phase is a packed column (non-volatile liquid on a solid support)

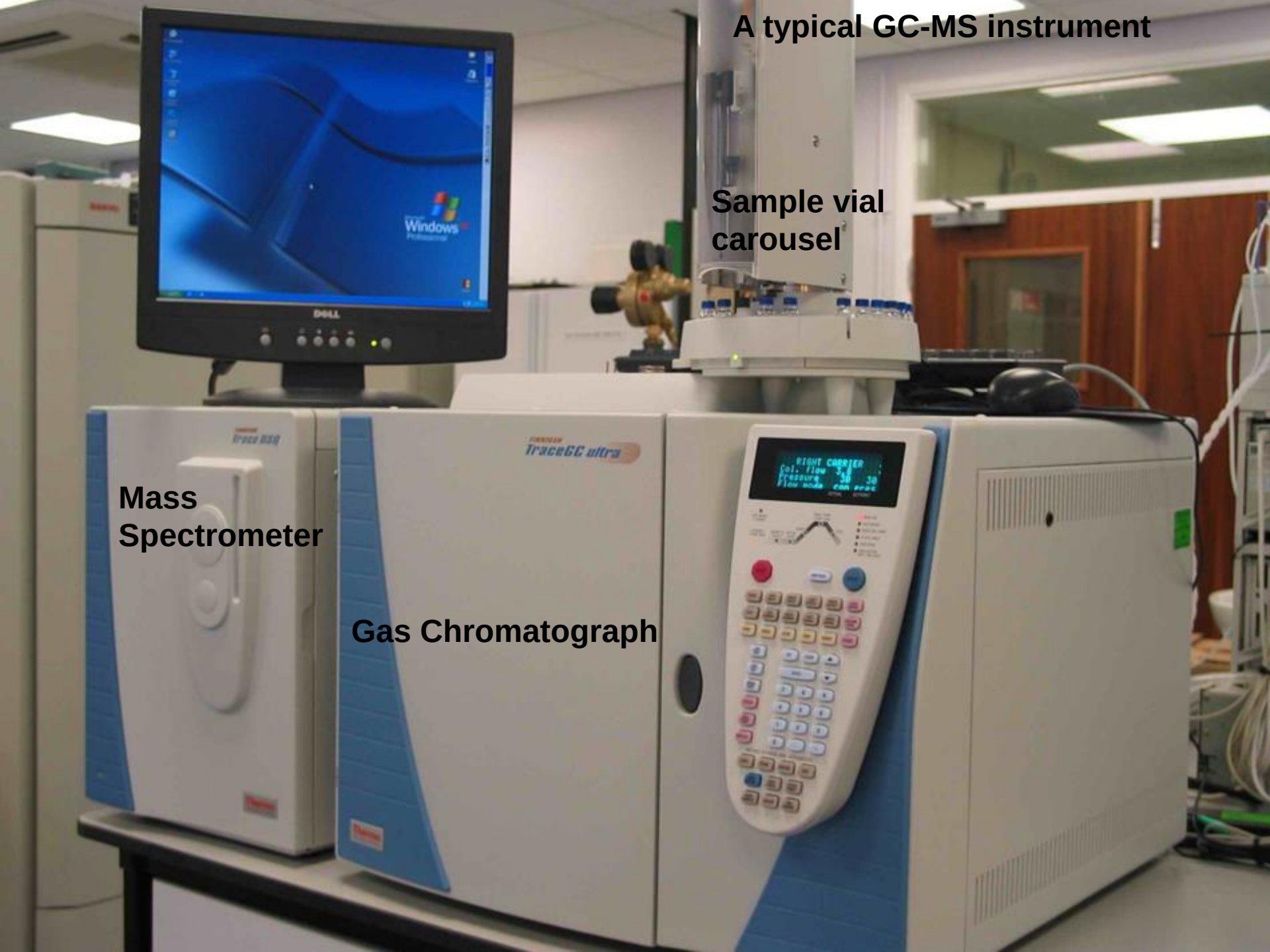
Mobile phase is a gas

Sample needs to be volatile

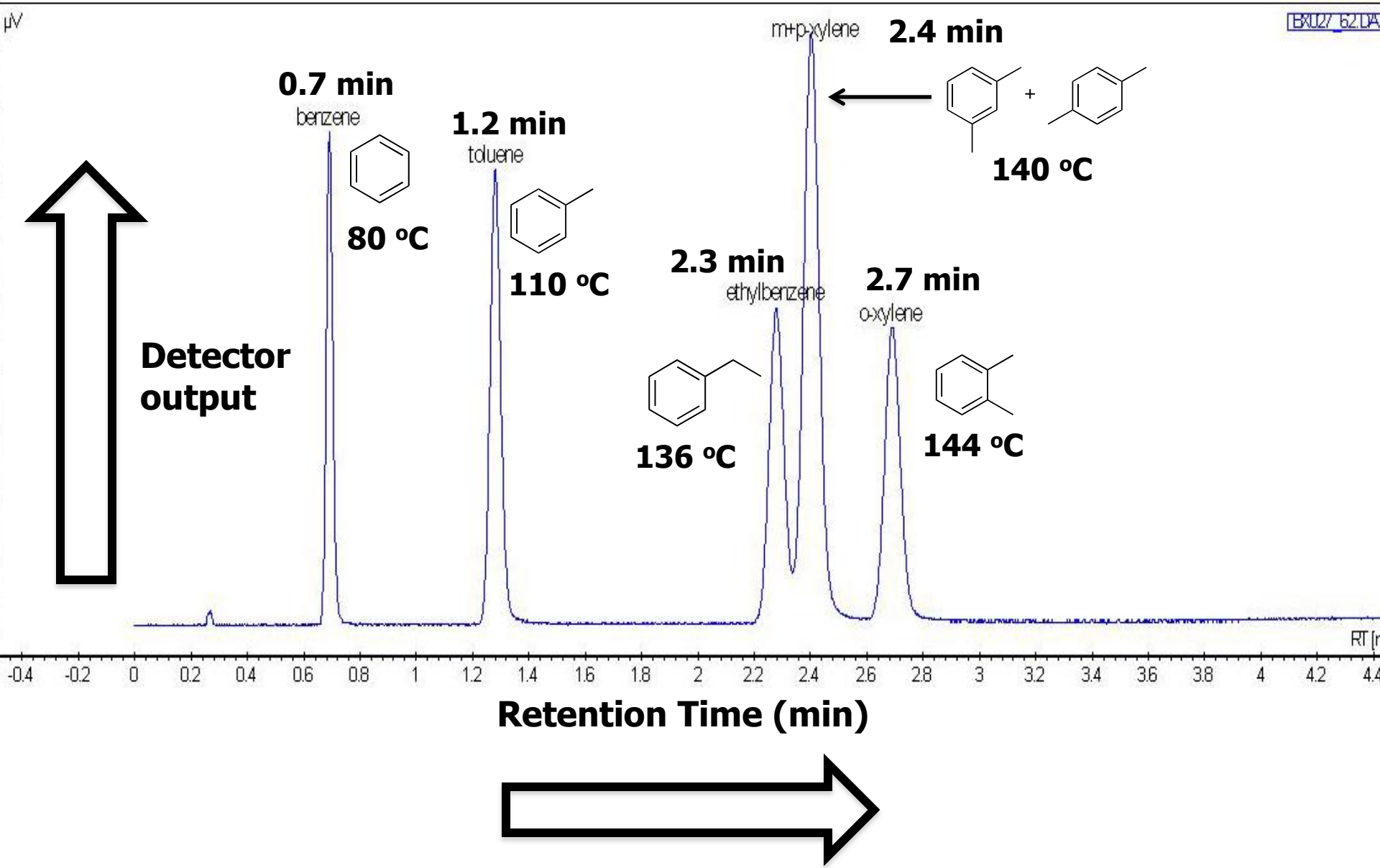
(You will use **TLC** in the lab to monitor the progress of reactions)

GC instrument schematic




A typical GC-MS instrument
Sample vial carousel
Mass Spectrometer
Gas Chromatograph

GC trace – mixture of aromatic hydrocarbons



Features of the GC trace

Number of signals
Corresponds to number of resolvable components in mixture

Order of elution
Components are eluted according to their retention time

Retention time
Governed by extent of interaction with stationary phase
For our purpose, this follows the relative order of boiling points

Other considerations
Peak area approximates amount of each compound

Compound polarity (polar compounds move slower than non/less-polar cpds)

Column polarity (compounds move slower on polar columns)

Column temperature (raising column temperature speeds up elution of all cpds)

Column length (longer columns lead to better separation/resolution of signals).

EI-MS

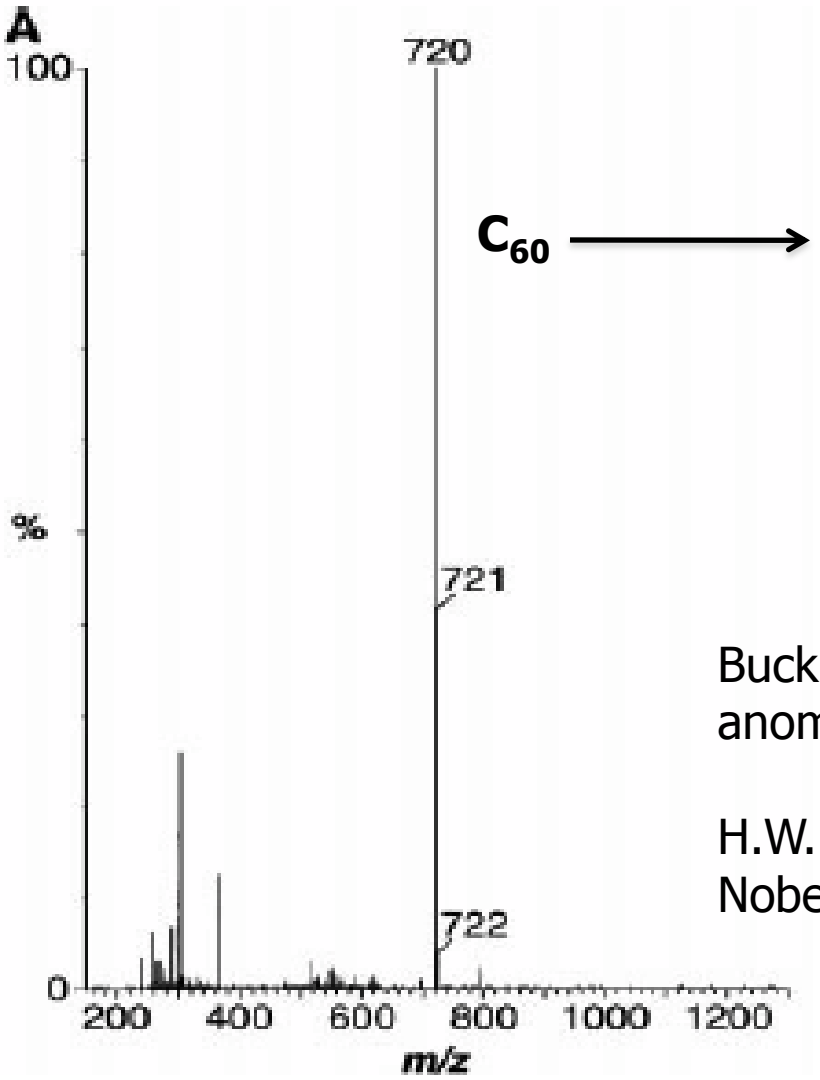
Electron Impact or Electron Ionization Mass Spec (both OK to use)

Uses high energy electron beam (70 eV), sample in gas phase

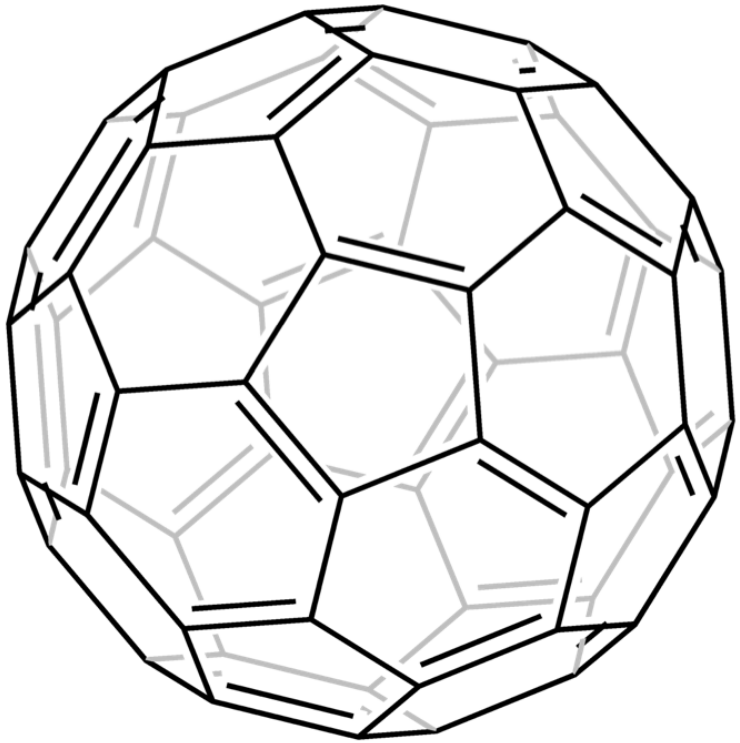
Ionization energy for most organic molecules 8-15 eV

Gives info on molecular mass and formula of compound (m/z, isotopes)

Gives info on connectivity of molecule (fragmentation pattern)



C_{60} →



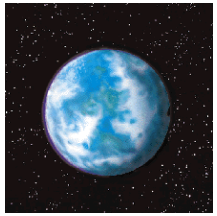
Buckminsterfullerene (C_{60}) was discovered as an anomalous signal in a mass spec experiment!

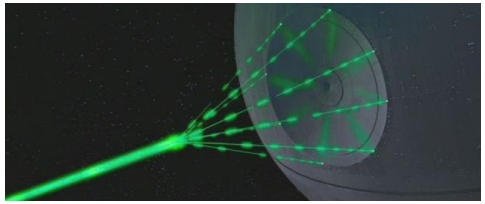
H.W. Kroto, R. E. Smalley and R. F. Curl won the 1996 Nobel Prize in Chemistry for the discovery of C_{60}.

Nature, **1985**, *318*, 162-163

Molecular Ion $[M]^{\cdot+}$

$[M]^{\cdot+}$ gives the mass (m) of the molecule





$$M + e^- \longrightarrow [M]^{\cdot+} + 2\,e^-$$

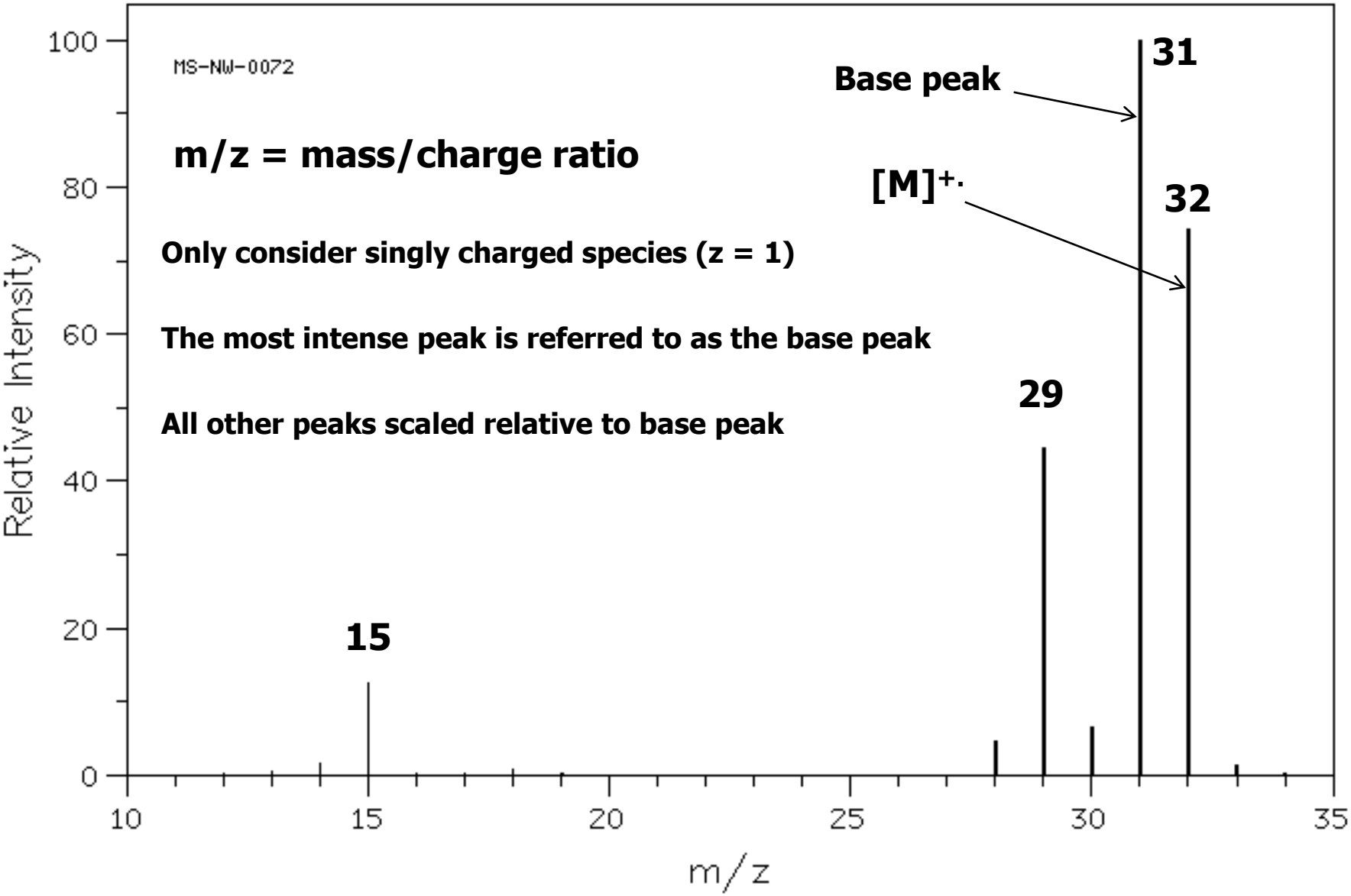
Molecule

Molecular Fragments

Fragments give info on connectivity of the molecule

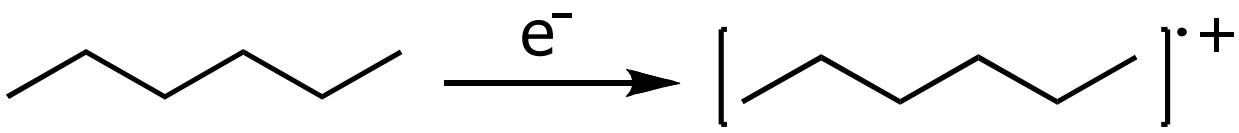
You've all seen Star Wars, right?

Mass Spectrum of Methanol CH_3OH

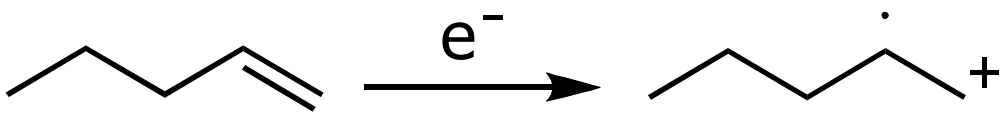


From where on the molecule is the electron lost?

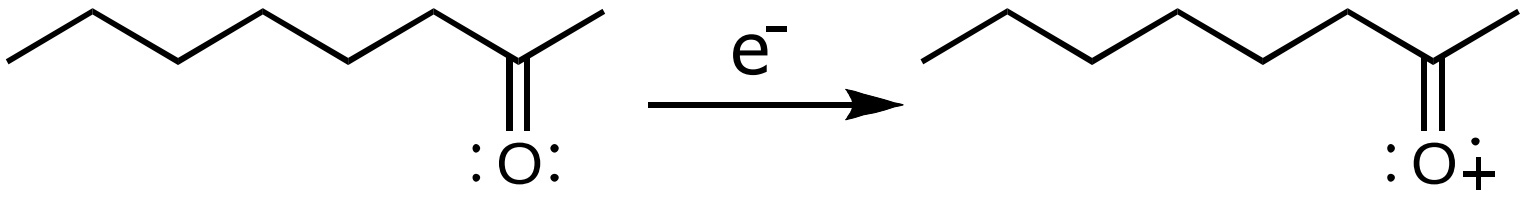
Alkanes – sigma bond

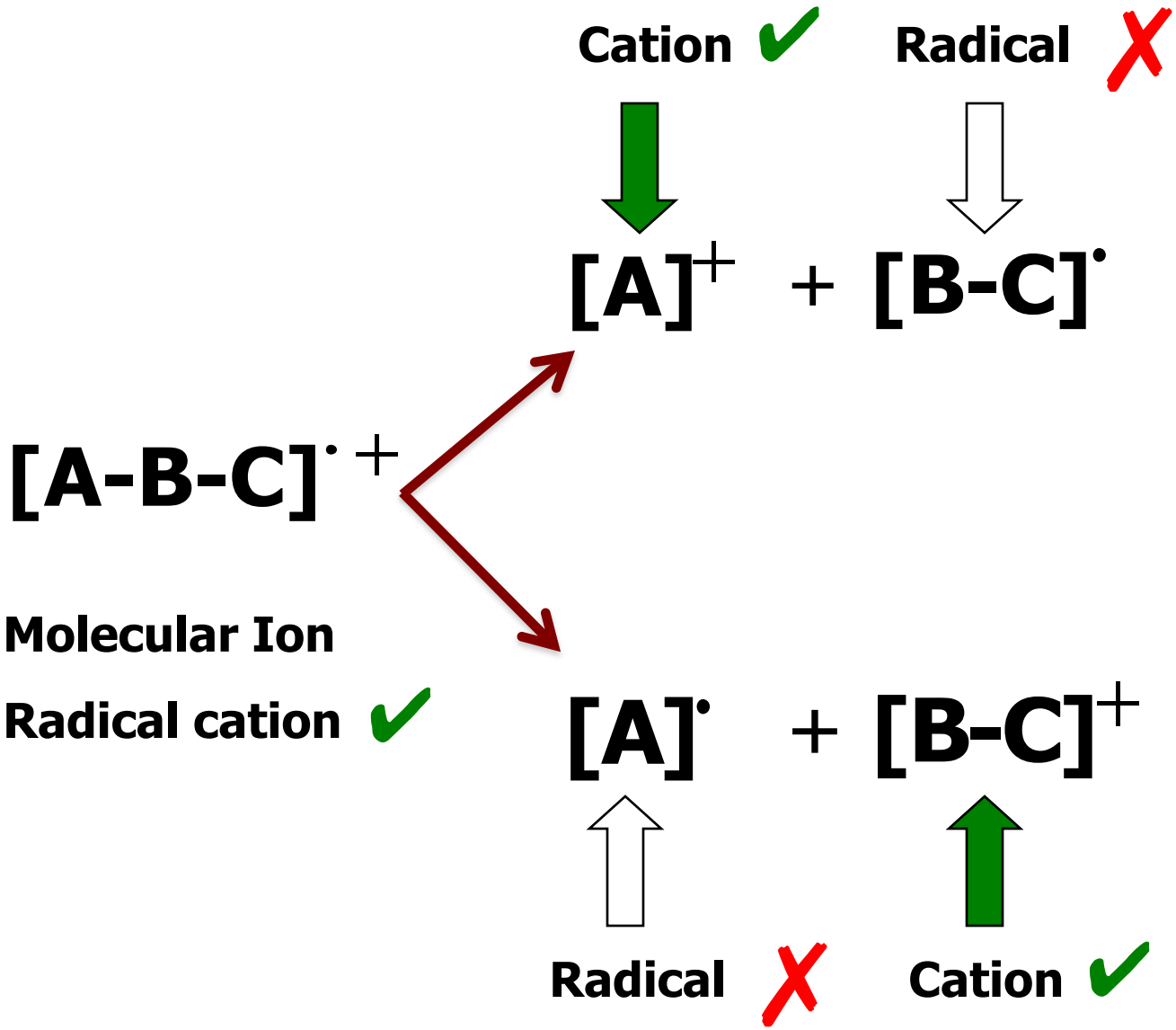


Alkenes – pi bond

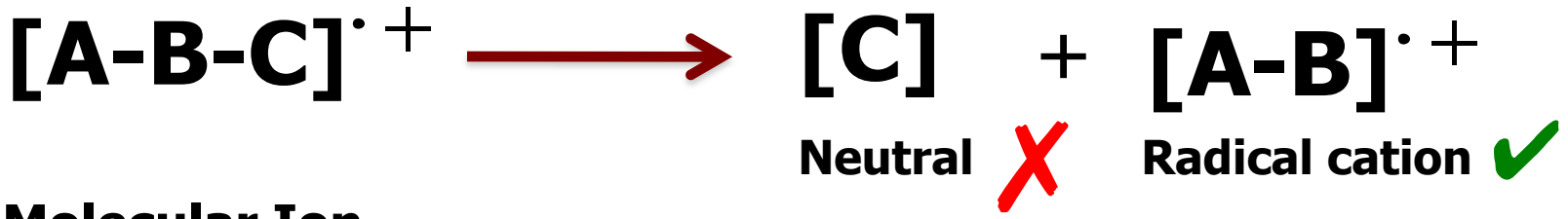


Heteroatom compounds (O, N, S, etc.) – non-bonding lone pairs





Even electron fragments [EE]+



Molecular Ion

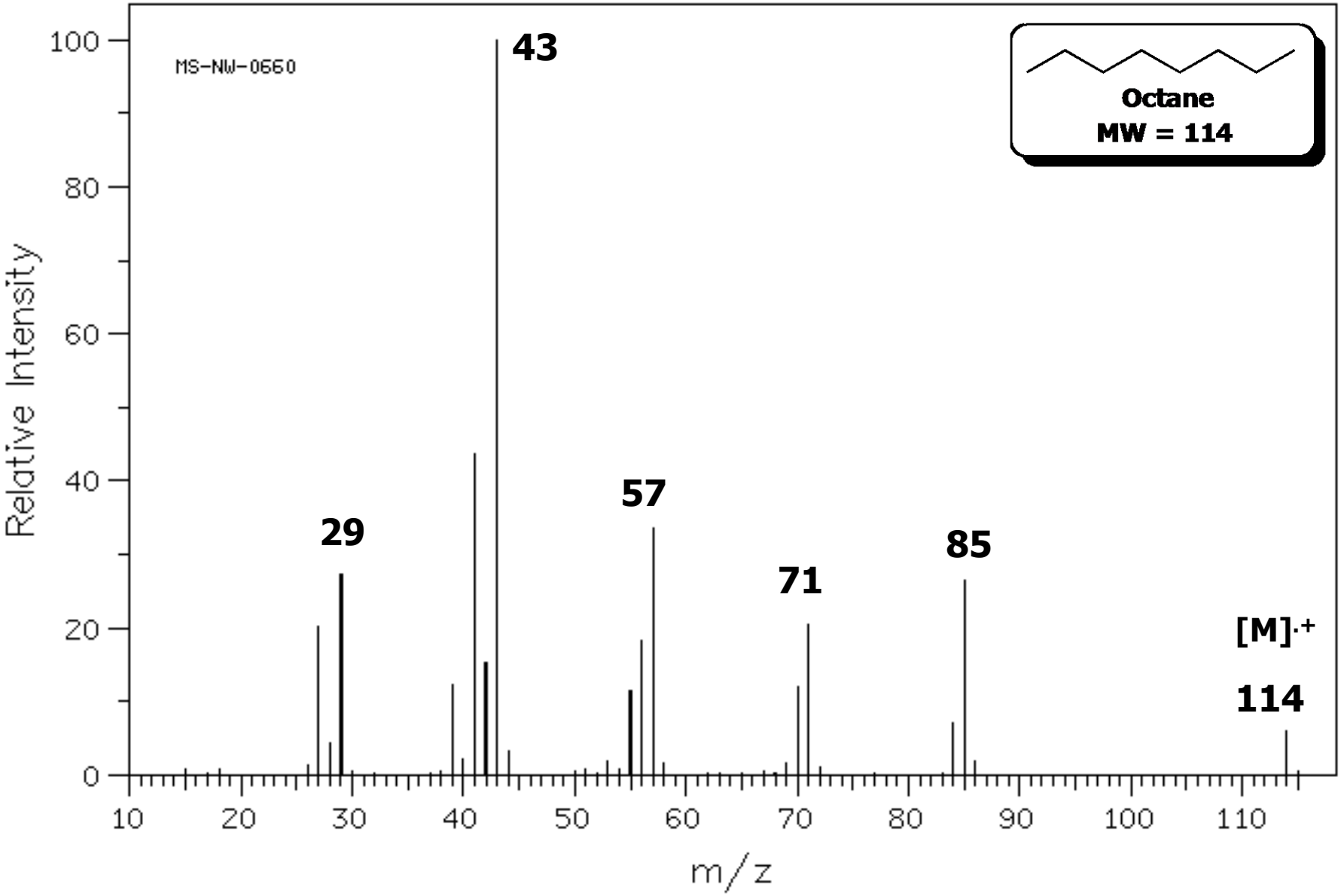
Radical cation ✔

Only CATIONS and RADICAL CATIONS detected by Mass Spec

Radicals and other neutrals (CO, H_2O) <u>NOT</u> detected by Mass Spec

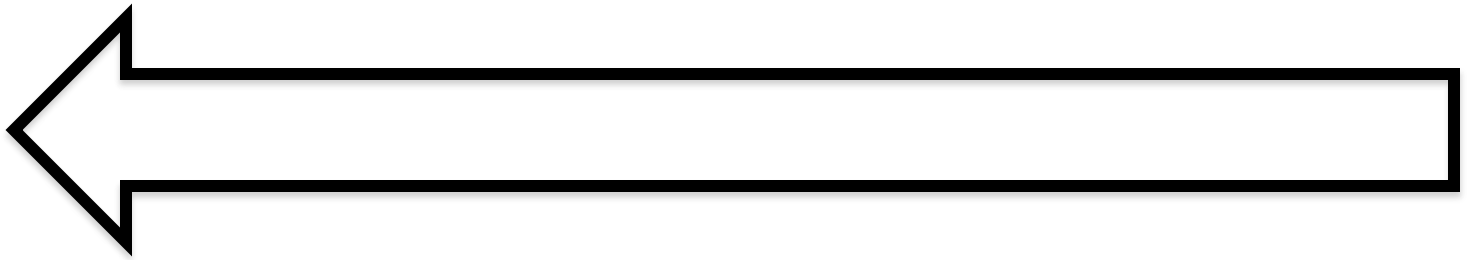
Odd electron fragments [OE]·+

Mass Spectrum of Octane

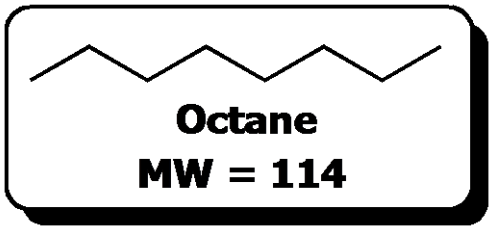


$3^{o} > 2^{o} > 1^{o} > Me$

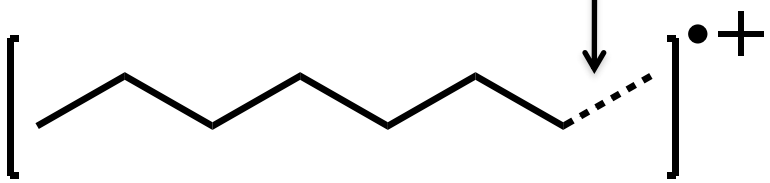
R_3C R_2CH RCH_2 CH_3

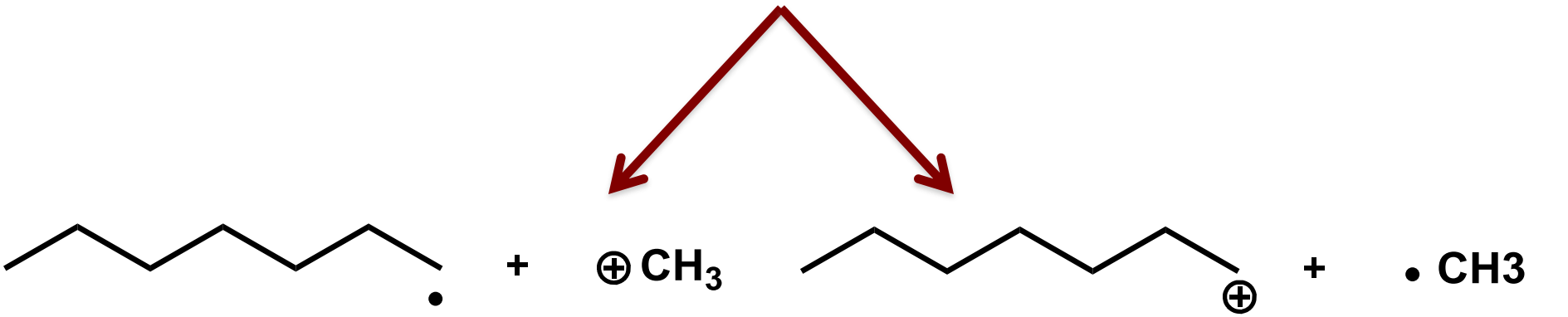


Increasing stability of cation or radical

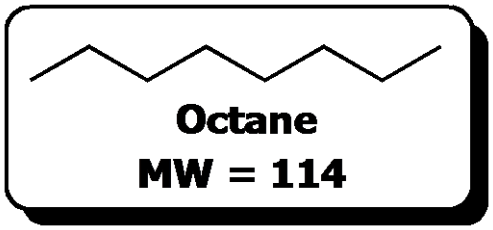


Electron lost from **this** C-C bond

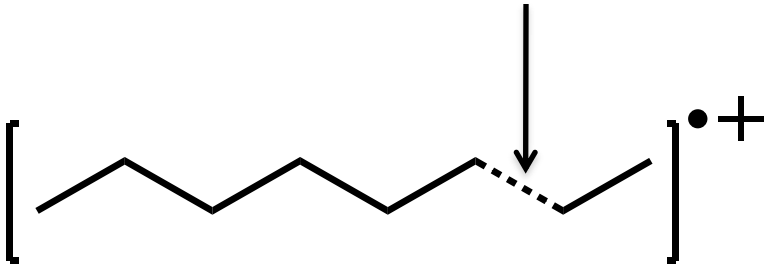


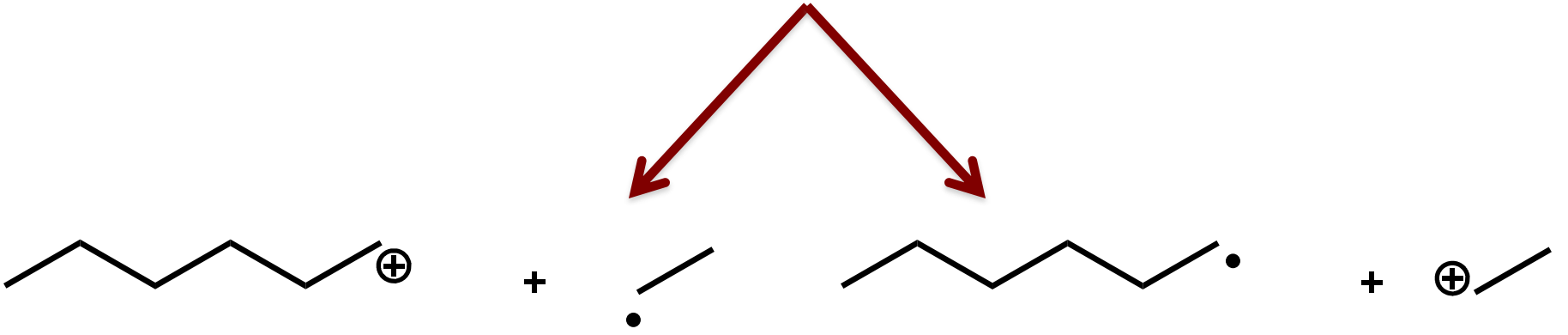


Both fragmentations involve formation of a Me radical or a Me cation



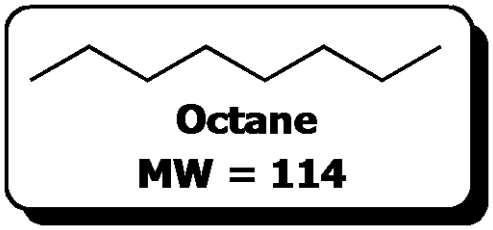
Electron lost from **this** C-C bond

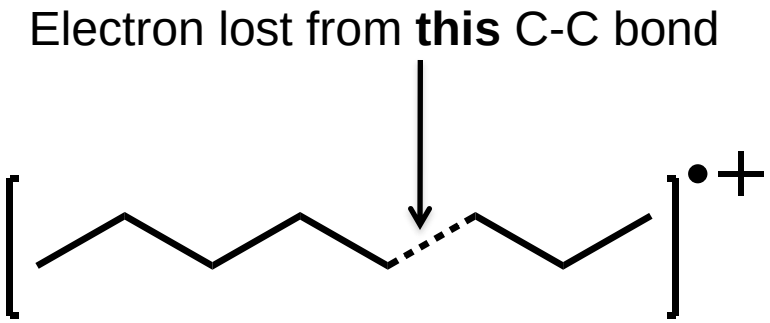


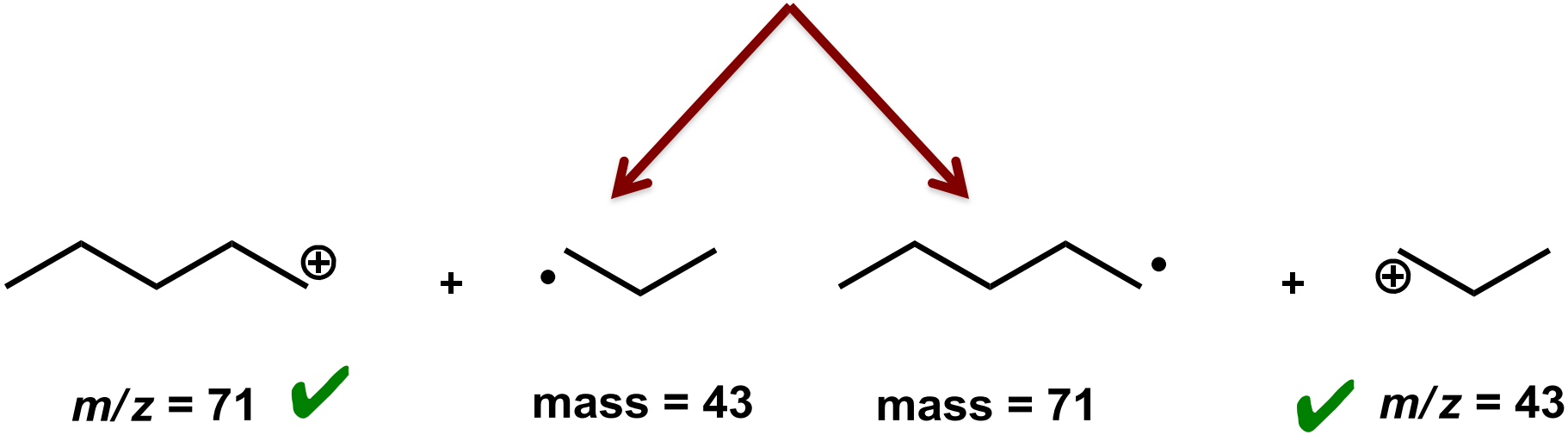


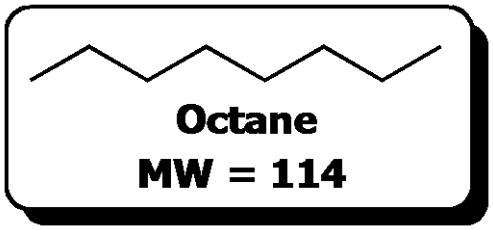
m/z = 85 ✔ mass = 29 mass = 85 ✔ *m/z* = 29

Stability of cation and radical is important

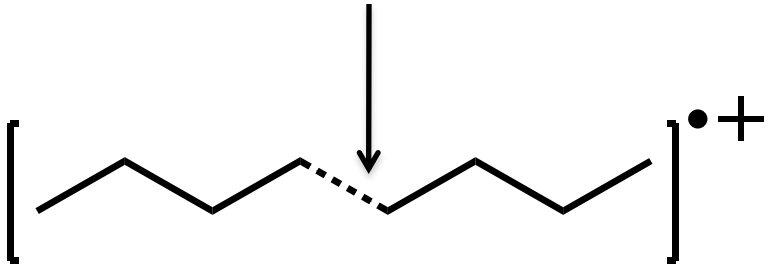

Octane
MW = 114


Electron lost from **this** C-C bond


m/z = 71
mass = 43
mass = 71
m/z = 43



Electron lost from **this** C-C bond



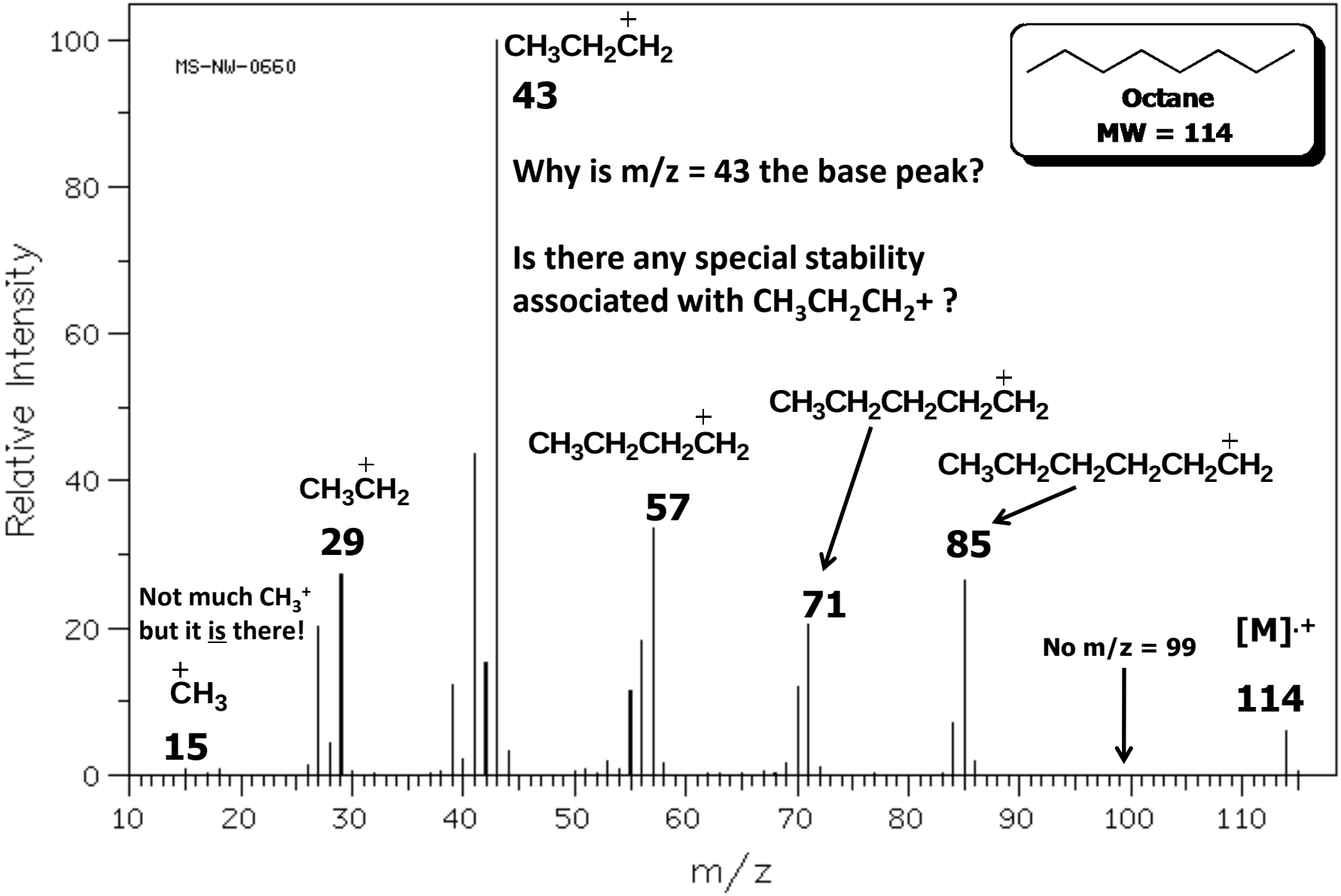
mass = 57

✔ *m/z* = 57

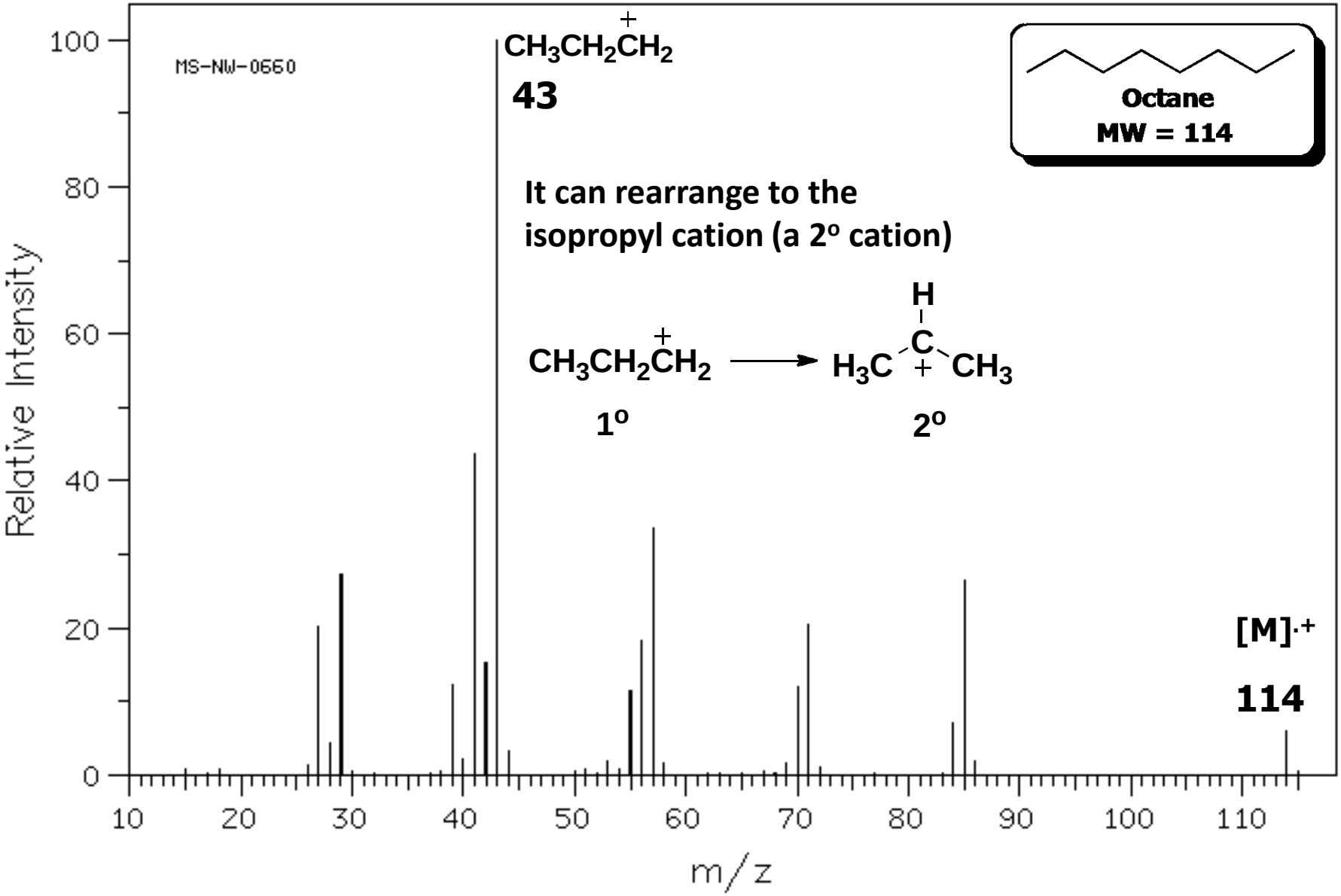
Stability of cation and radical is important

Fragmentations involving formation of a Me species are disfavored

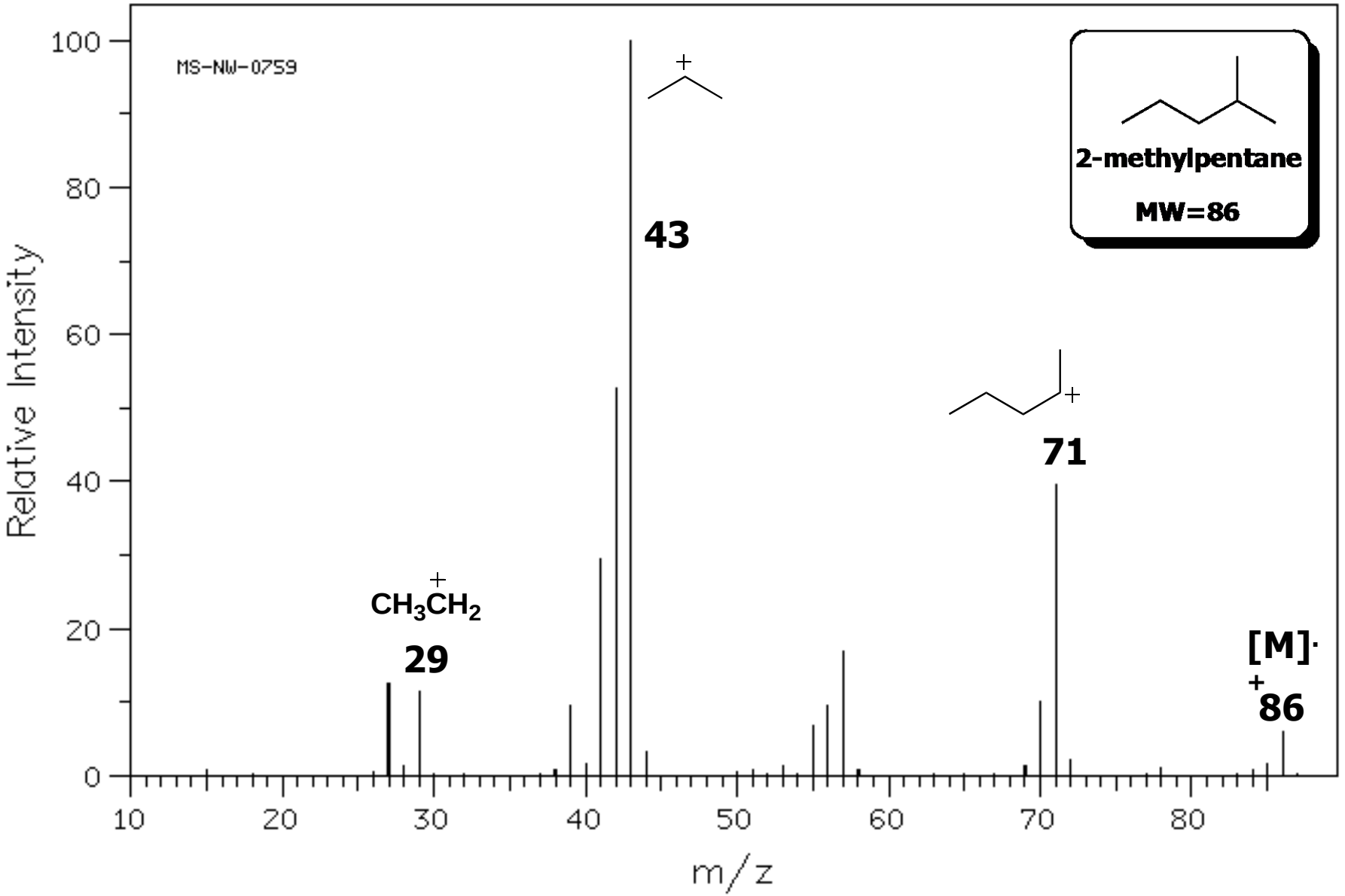
Mass Spectrum of Octane

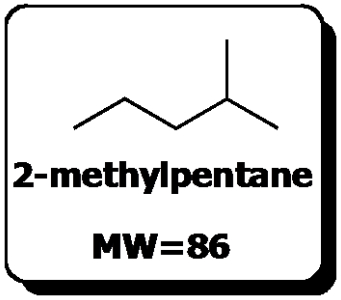


Mass Spectrum of Octane



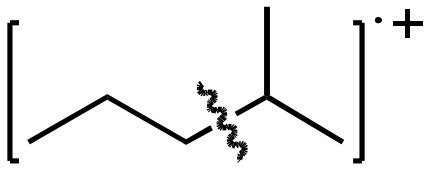
Mass Spectrum of 2-methylpentane

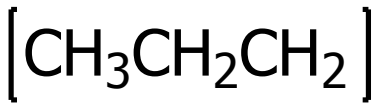


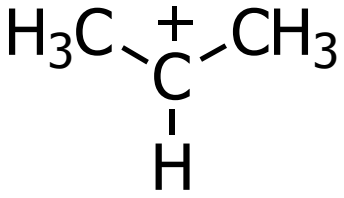


Branched alkanes fragment either side of the branch point(s)

The m/z = 43 fragment is the base peak – why?

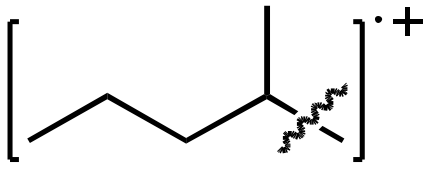


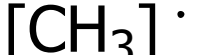


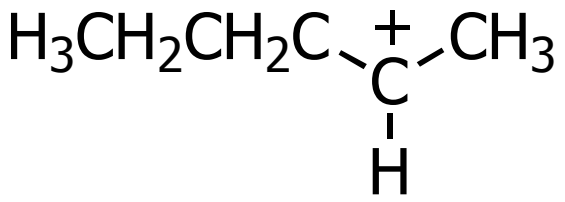


mass = 43 *m/z* = 43 ✔

As in octane, $CH_3CH_2CH_2^+$ will rearrange to Me_2CH^+







mass = 15 *m/z* = 71 ✔

Isotopes

Atoms exist as isotopes (different # neutrons, same # protons)

^{12}C is most abundant isotope of carbon

~1.08 % of C-atoms in a sample are ^{13}C isotope (NMR active, useful)

~0.016% of H-atoms in a sample are ^{2}H isotope (D)

~0.38% of N-atoms in a sample are ^{15}N isotope

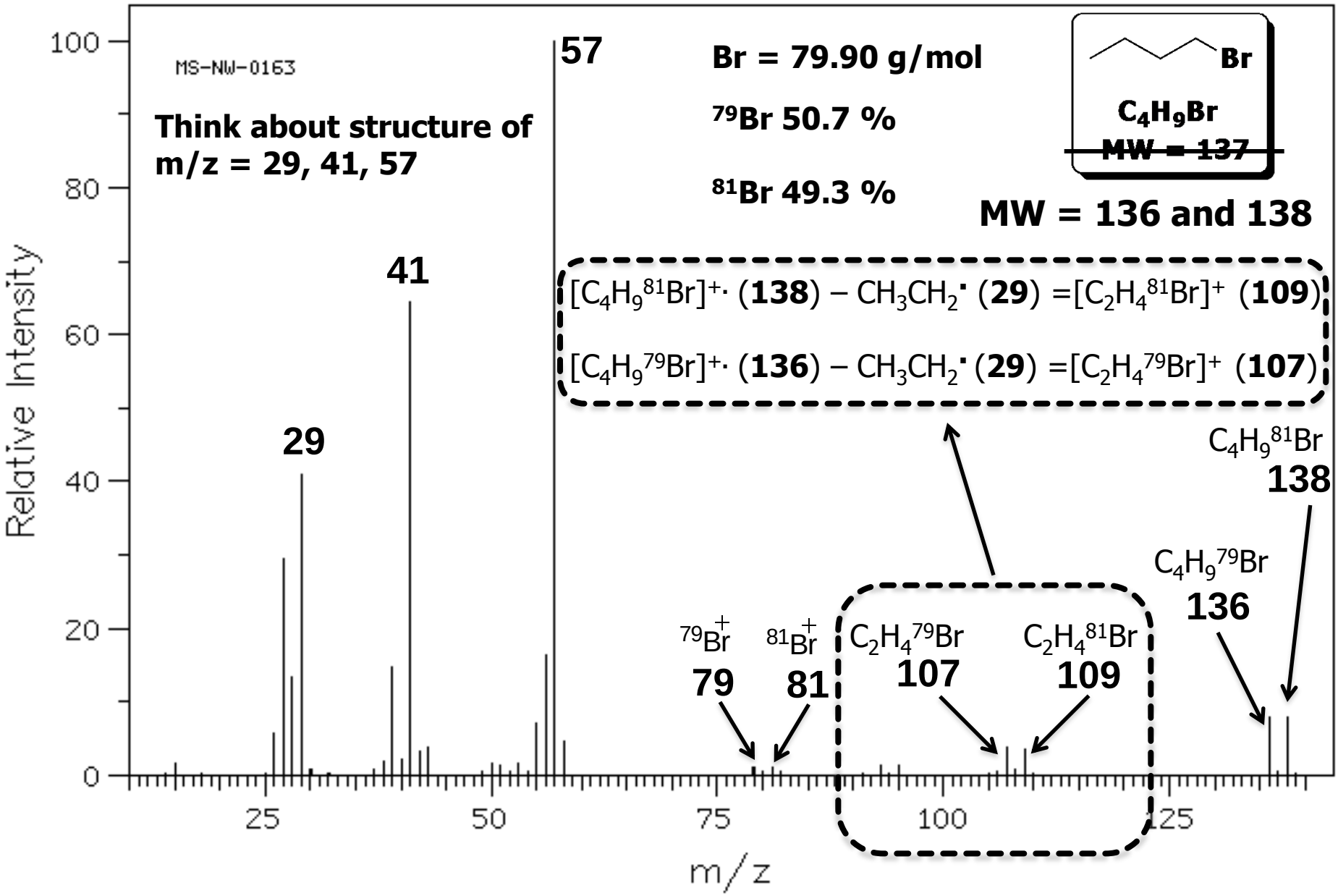
Atomic weight Cl = 35.48 g/mol

^{35}Cl 75.8 % ^{37}Cl 24.2 % ~3:1 ratio of isotopes

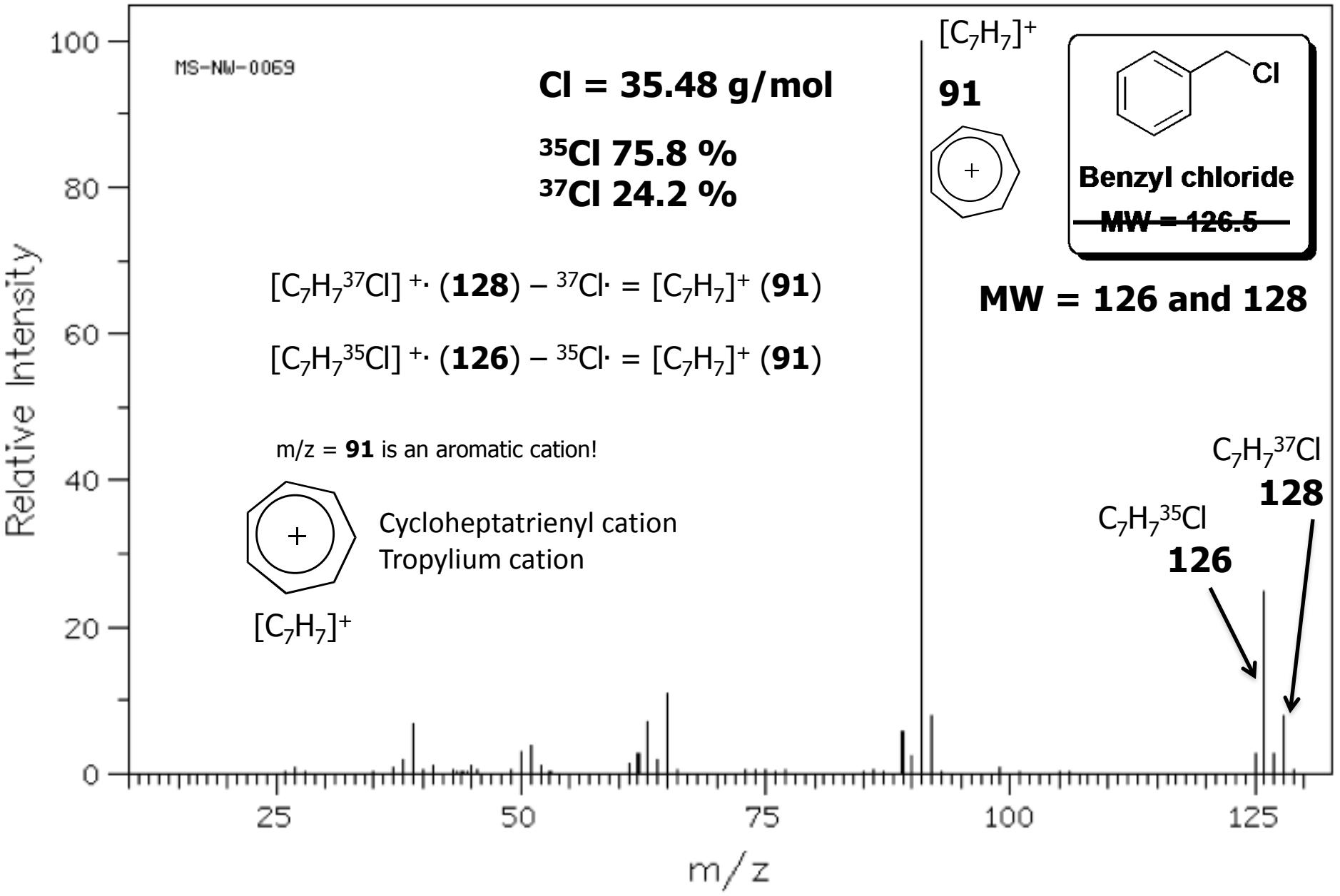
Atomic weight Br = 79.90 g/mol

^{79}Br 50.7 % ^{81}Br 49.3 % ~1:1 ratio of isotopes

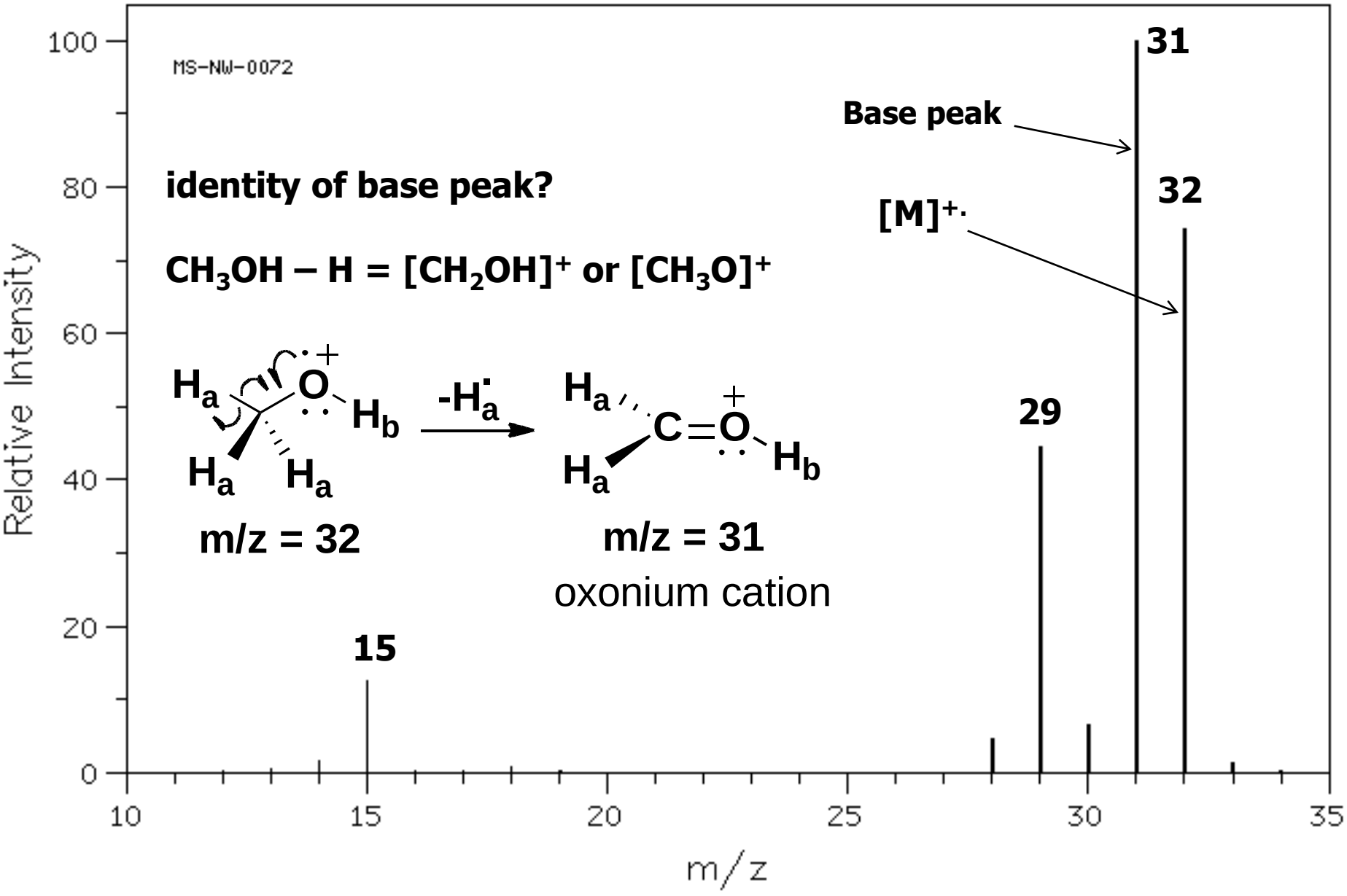
Mass Spectrum of 1-Bromobutane



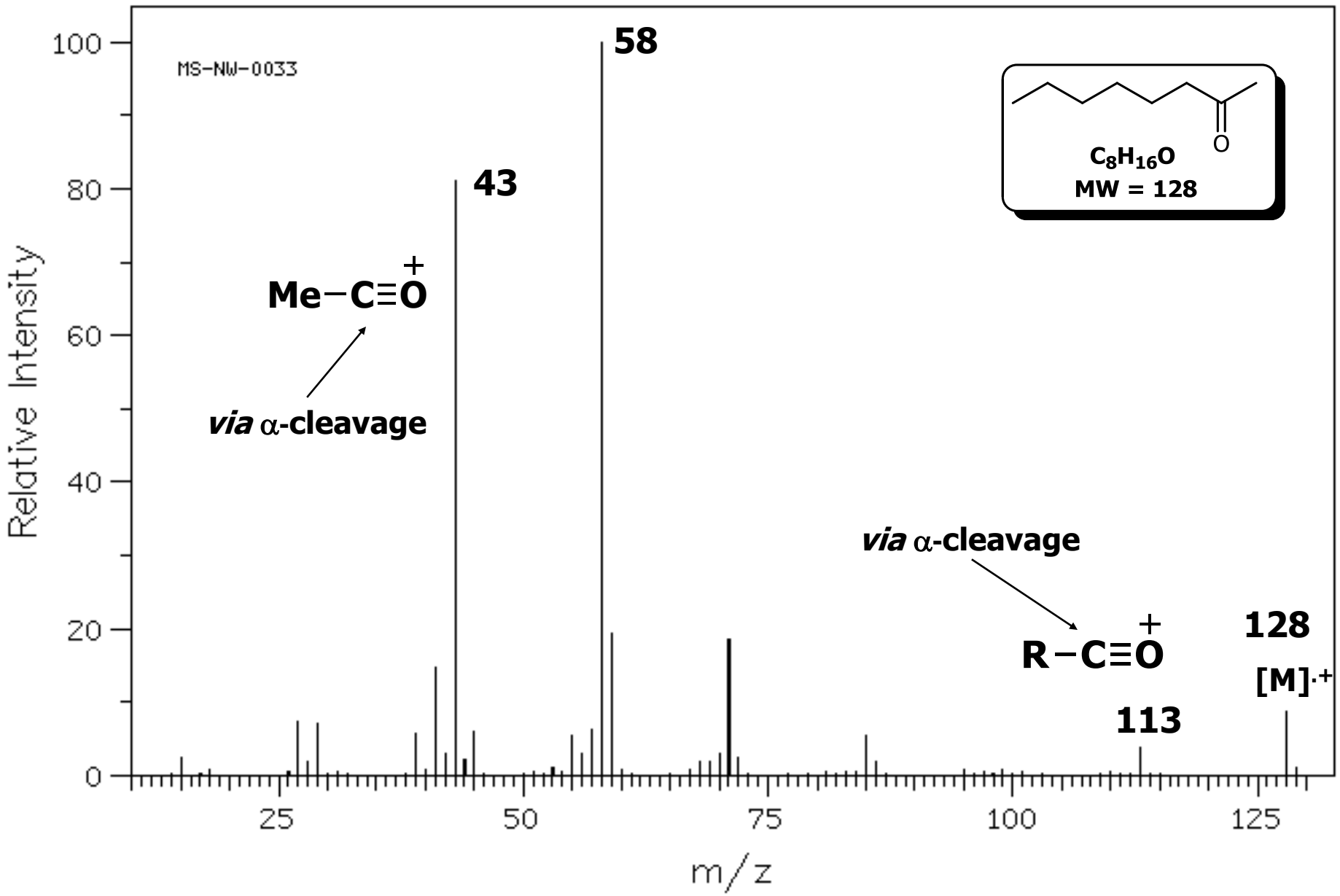
Mass Spectrum of Benzyl chloride



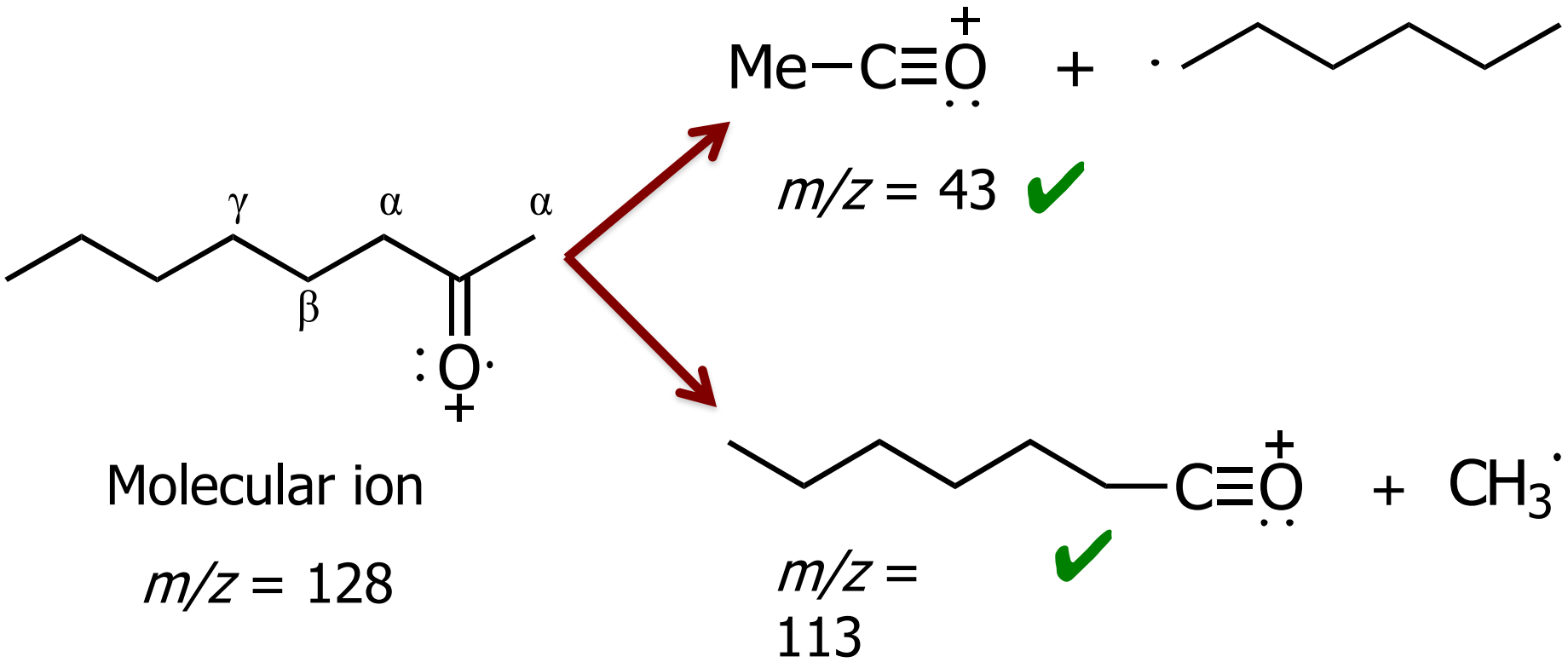
Mass Spectrum of Methanol CH_3OH



Mass Spectrum of 2-octanone

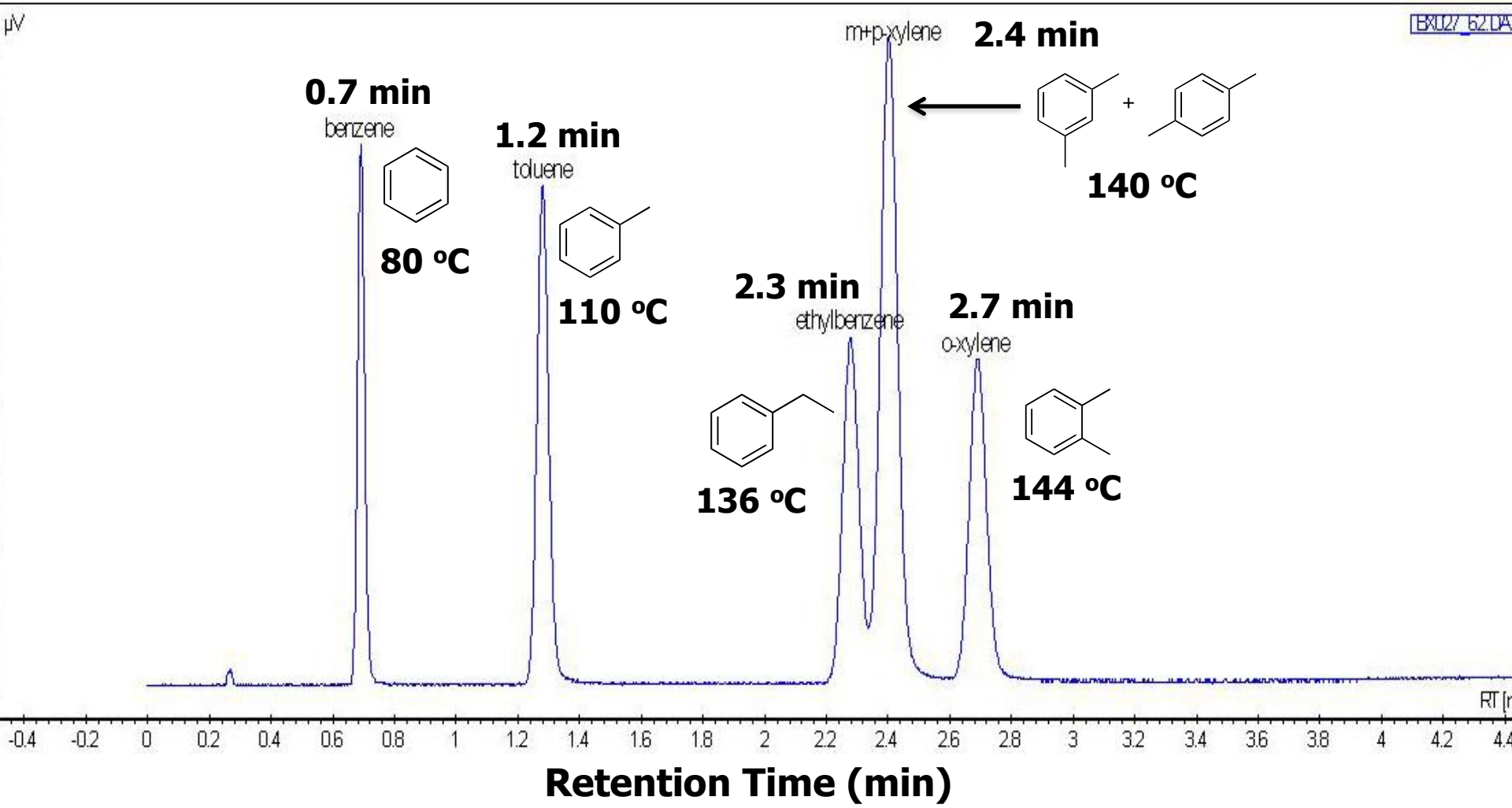


α-cleavage at a C=O group



Practice drawing the fragmentation pattern for α-cleavage

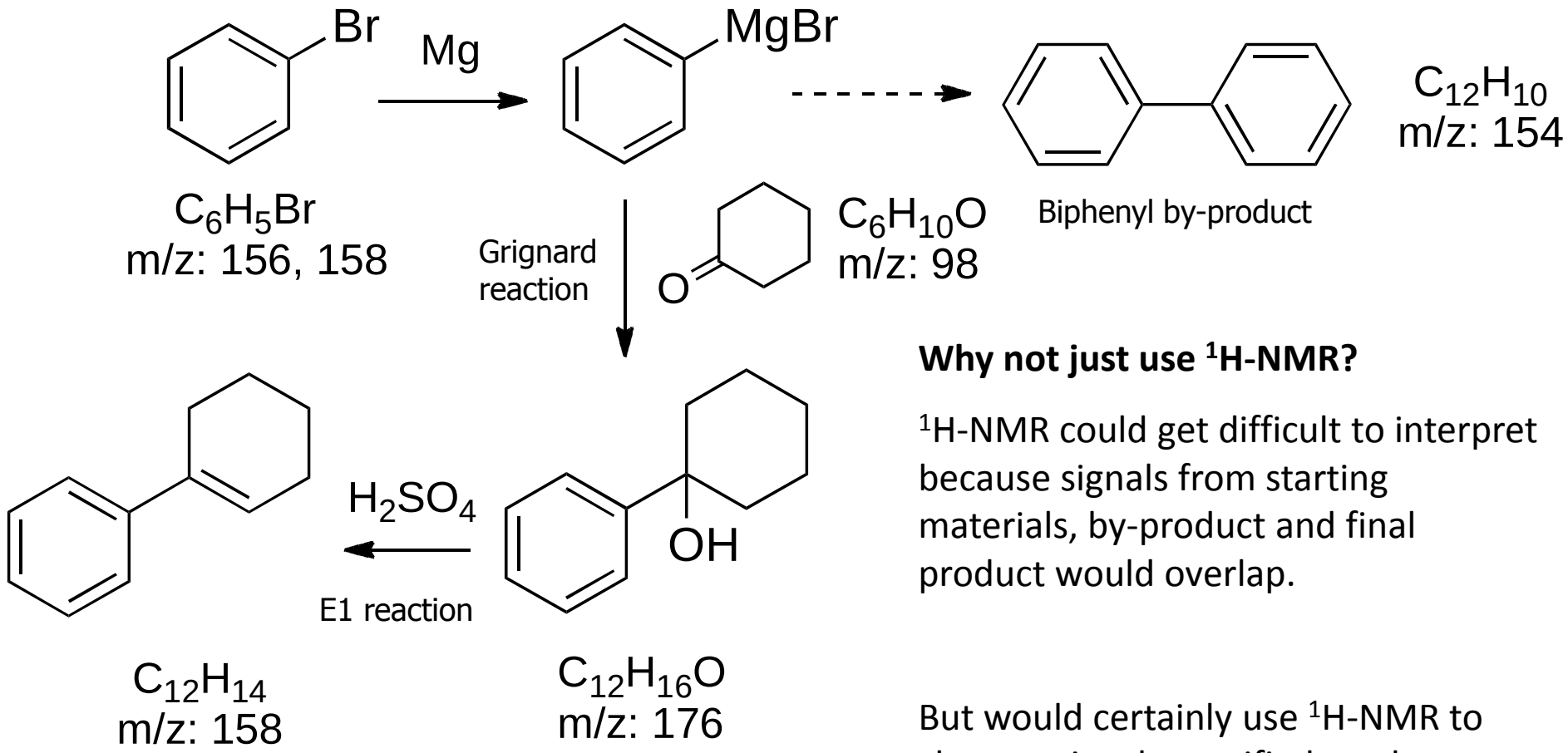
GC trace – mixture of aromatic hydrocarbons



GC-MS - a mass spectrum is obtained for each compound as it elutes

Synthesis of 1-phenylcyclohexene

Use GC-MS to gauge success of reaction/purification



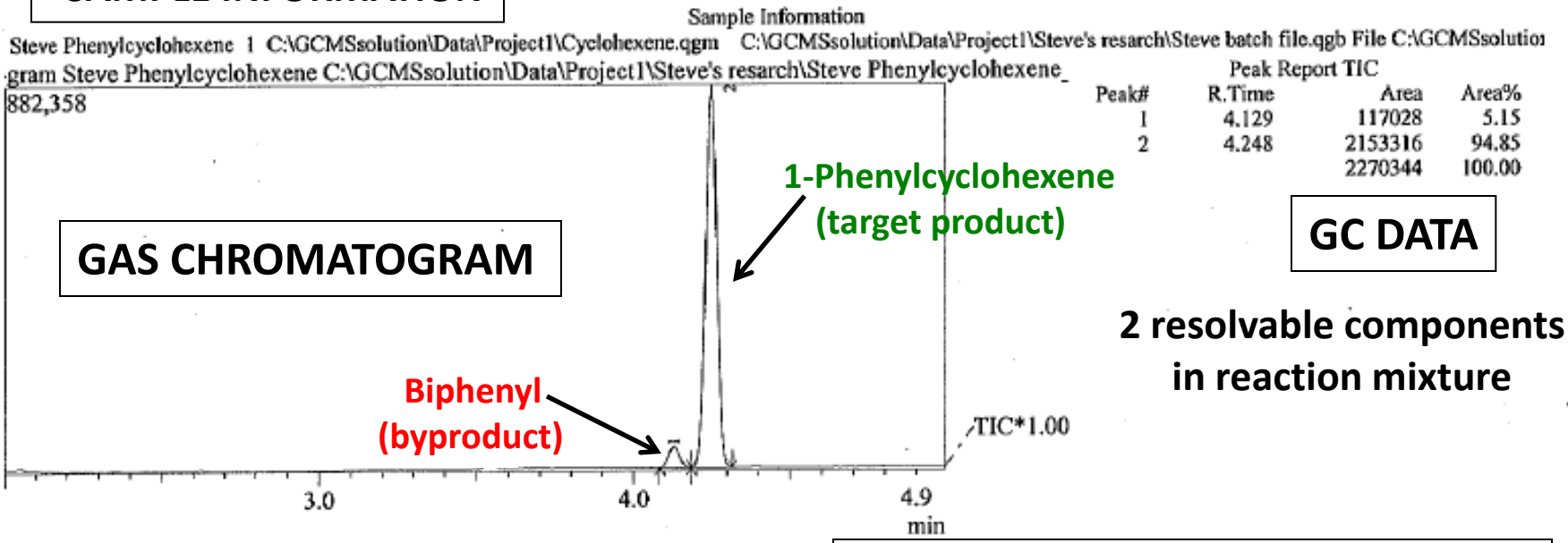
Why not just use ^{1}H-NMR?

^{1}H-NMR could get difficult to interpret because signals from starting materials, by-product and final product would overlap.

But would certainly use ^{1}H-NMR to characterize the purified product.

You will perform both an E1 and a Grignard reaction in CHEM 344 lab!

SAMPLE INFORMATION



GAS CHROMATOGRAM

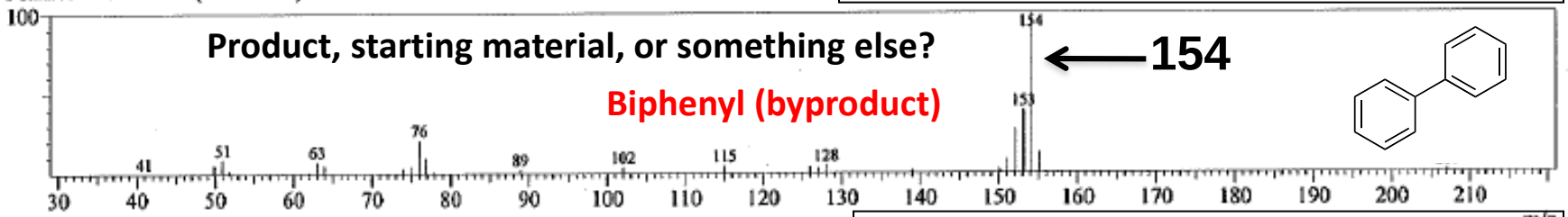
Peak Report TIC

Peak#	R.Time	Area	Area%
1	4.129	117028	5.15
2	4.248	2153316	94.85
		2270344	100.00

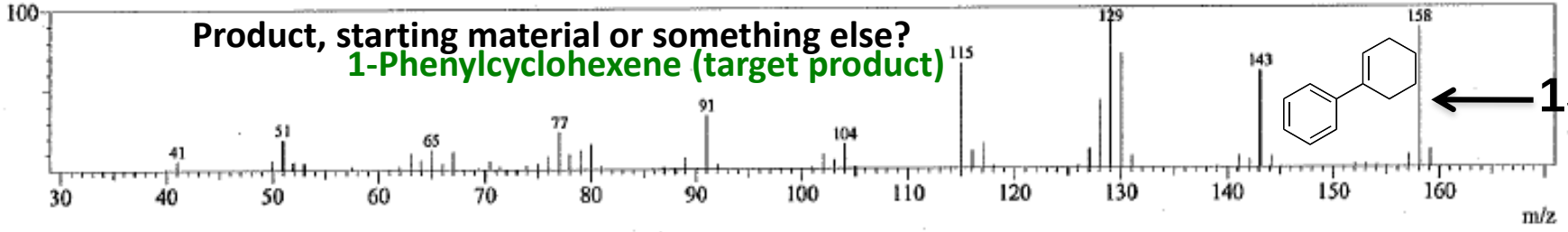
GC DATA

2 resolvable components in reaction mixture

MASS SPECTRUM OF COMPONENT 1



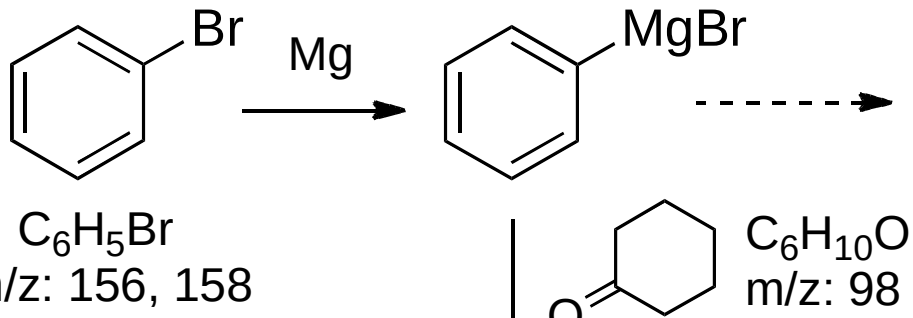
MASS SPECTRUM OF COMPONENT 2



Synthesis of 1-phenylcyclohexene

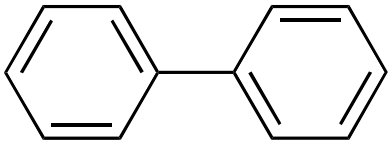
Did the reaction work?

<u>YES</u>…..but we need to purify the product a little more.



C_6H_5Br
m/z: 156, 158

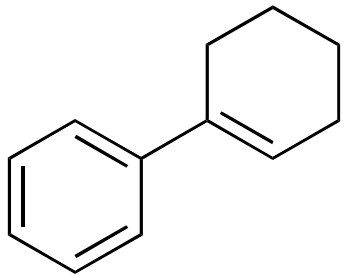
$C_6H_{10}O$
m/z: 98



$C_{12}H_{10}$
m/z: 154

Biphenyl

Component 1 is indentified as biphenyl based on the molecular ion m/z = 154



$C_{12}H_{14}$
m/z: 158

$C_{12}H_{16}O$
m/z: 176

The absence of a $^{79}Br/^{81}Br$ isotope pattern tells us that bromobenzene is **not** present

Component 2 is identified as 1-phenylcyclohexene based upon the molecular ion m/z = 158.

GC shows that the reaction mixture is ~95% 1-phenylcyclohexene