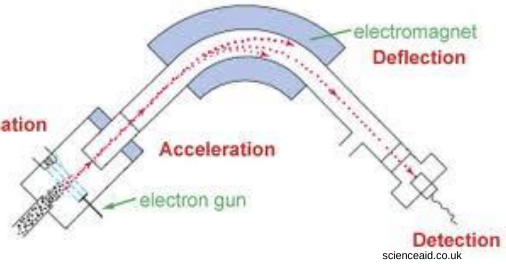
MASS SPECTROMETRY: BASIC EXPERIMENT

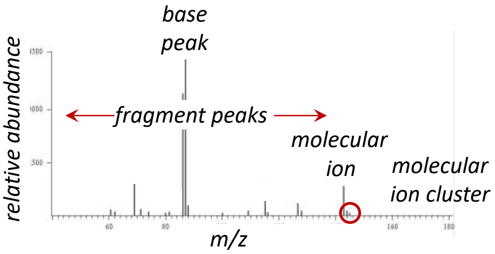
Pavia 8.1-8.5



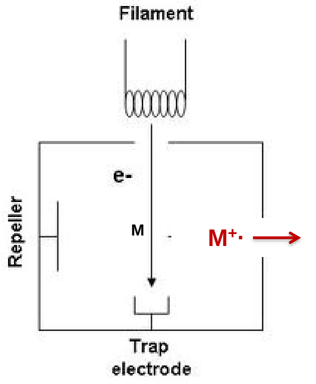
$$\text{Molecule} \xrightarrow{-e^-} \textbf{Molecule}^{+\cdot} + 2e^-$$

$$\downarrow$$

$$\textbf{[Fragments]}^{+\cdot}$$



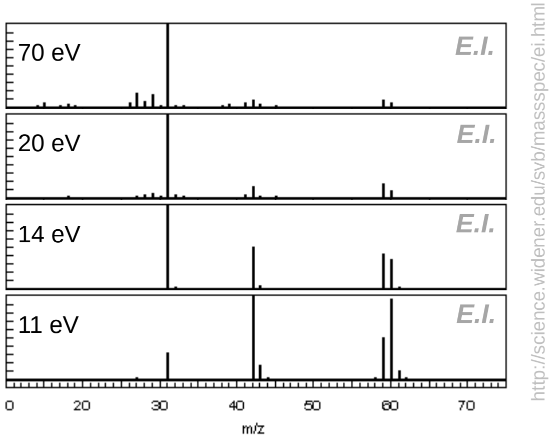
Electron Ionization



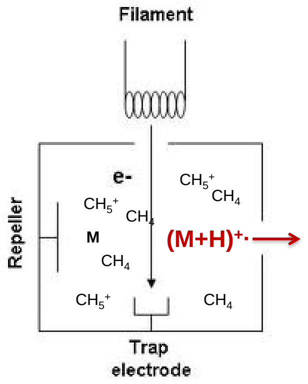
$$M + e^- \longrightarrow \mathbf{M^+} + 2e^-$$

Effect of ionizing energy on spectrum

1-propanol (C_3H_8O, M = 60)



Chemical Ionization

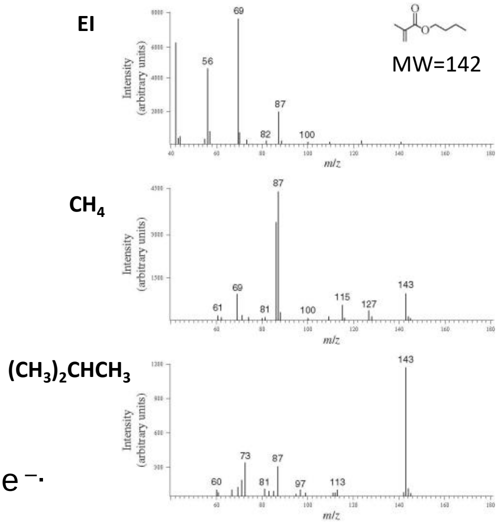


$$CH_4 + e^{-\cdot} \longrightarrow CH_4^{+\cdot} + 2e^{-\cdot}$$

$$CH_4^{+\cdot} + CH_4 \longrightarrow CH_5^{+\cdot} + CH_3\cdot$$

$$M + CH_5^{+} \longrightarrow (M+H)^{+\cdot} + CH_4$$

Effect of ionization on spectrum



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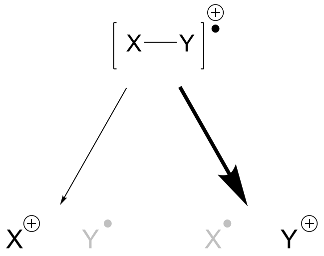
FRAGMENTATION

Radical cations formed upon electron impact are unstable!



One or the other of these process will predominate

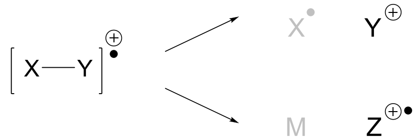
Large peaks result from fragmentations that are energetically most favorable

Remember:

You will only see peaks for positively charged species (cations and radical cations), X^+ and Y^+

not neutral molecules or radicals.

Fragmentation of Radical Cations



Molecular ion

Radical Cation

even m/z

loss of radical (odd MW)

Fragment: **Cation**

odd m/z

loss of molecule (even MW)

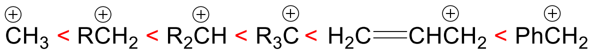
Fragment: **Radical Cation**

even m/z

Radical cations are very reactive species

Radical cations are very unstable. Fragmentations are unimolecular chemical reactions. The relative stability of cations and radical cations can often be understood in terms of substitution patterns and resonance.

Remember: Ease of formation of carbocations



less stable $\overset{+}{C}H_3 < R\overset{+}{C}H_2 < R_2\overset{+}{C}H < R_3\overset{+}{C} < H_2C{=}CH\overset{+}{C}H_2 < Ph\overset{+}{C}H_2$ more stable

c.f. ease of S_N1 reactions of R-Hal, or E1 dehydration of ROH

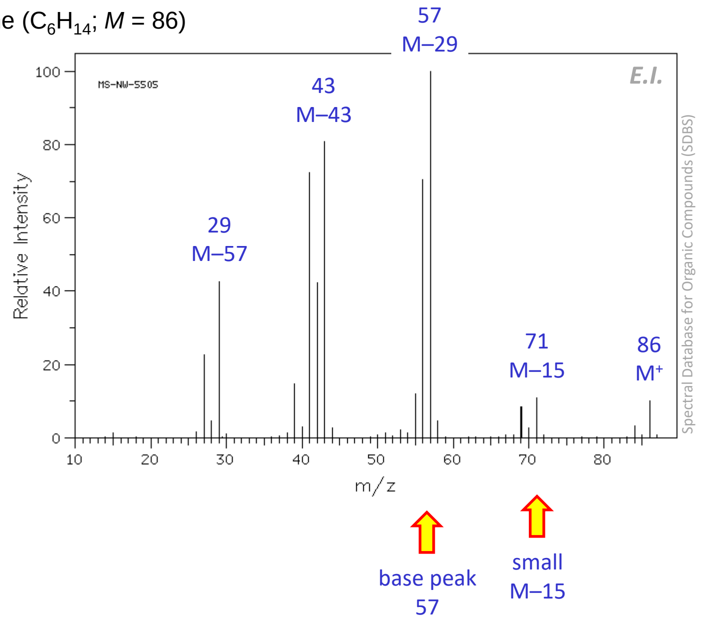
Alkyl groups are *inductive electron donating substituents*

Allylic and benzylic cations are *resonance stabilized*

Alkanes

Pavia 8.8 I

hexane (C_6H_{14}; M = 86)

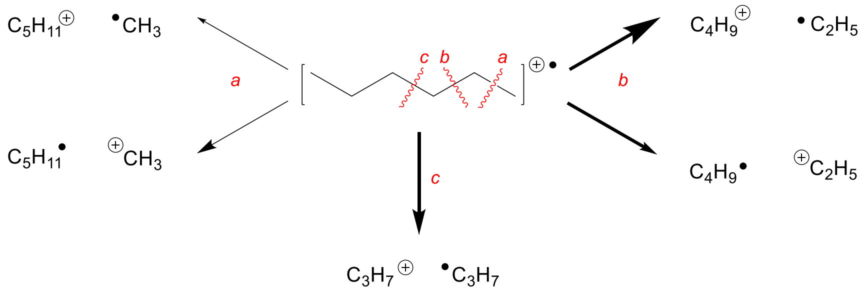


Spectral Database for Organic Compounds (SDBS)

base peak
57

small
M–15

Molecular ions fragment by cleavage of C-C bonds to give one cation and one radical. The *cations* are detected.

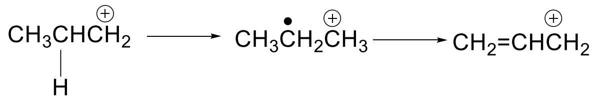


29	43	57	71	86
M–57	M–43	M–29	M–15	M+

Peaks appear in clusters separated by 14 mass units ….

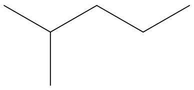
M**–15**, M**–29**, M**–43**, M**–57**, M**–71**, M**–85**, M**–99**, ….

…with other fragments corresponding to 1 and 2 mass units fewer by lose hydrogen atoms (radicals):

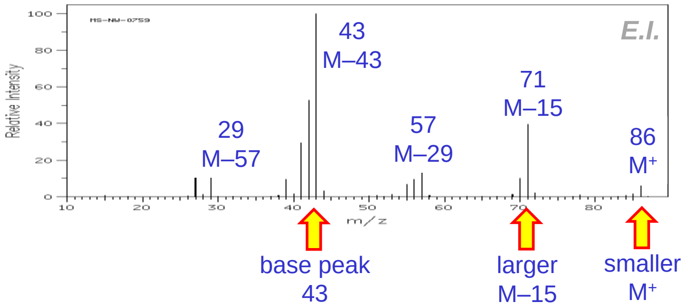


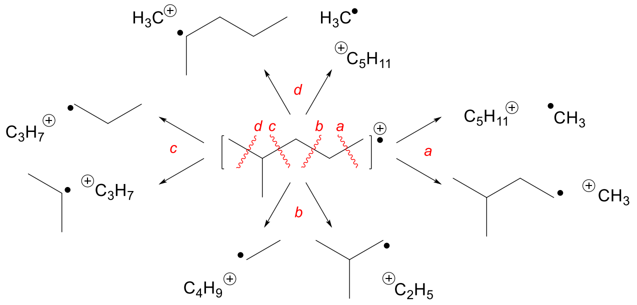
$$\mathrm{CH_3\underset{\displaystyle\overset{|}{H}}{C}H\overset{\oplus}{C}H_2 \longrightarrow CH_3\overset{\bullet}{C}H_2\overset{\oplus}{C}H_3 \longrightarrow CH_2{=}CH\overset{\oplus}{C}H_2}$$

2-methylpentane

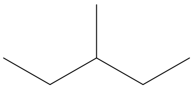


M**–15**, M**–29**, M**–43**, M**–57**, M**–71**, M**–85**, M**–99**, ….

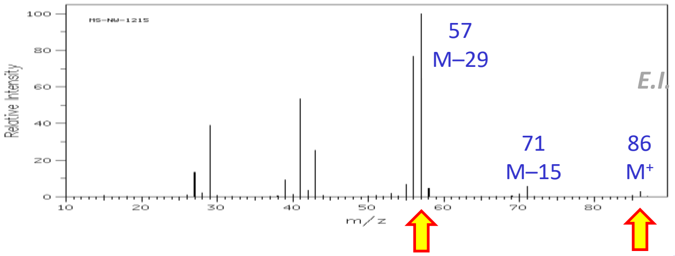




3-methylpentane

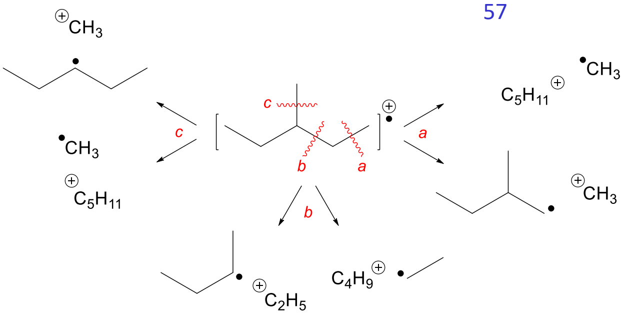


M**–15**, M**–29**, M**–43**, M**–57**, M**–71**, M**–85**, M**–99**, ….

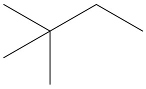


base peak
57

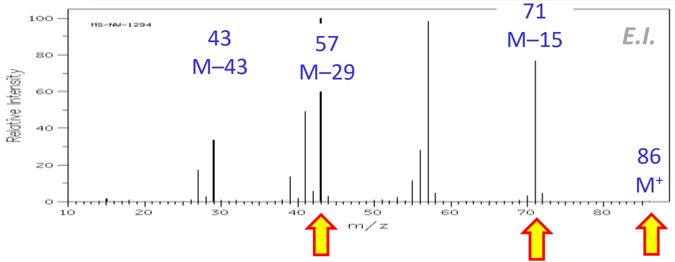
even smaller
M^+



2,2-dimethylbutane



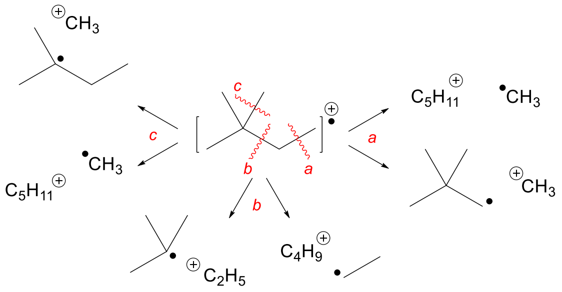
M**–15**, M**–29**, M**–43**, M**–57**, M**–71**, M**–85**, M**–99**, ….



M-43
?!?

Prominent
M-15

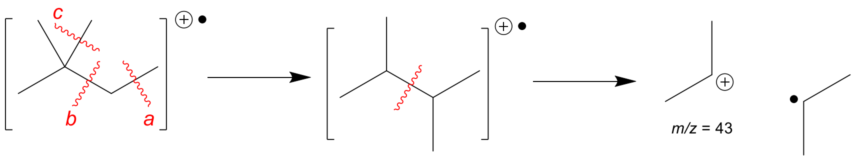
No M^+ ***!!***

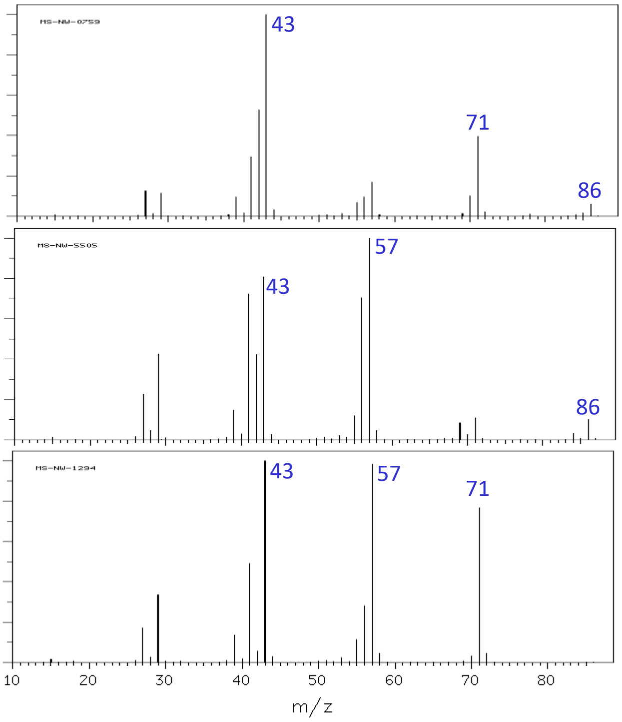


Branched alkanes undergo more fragmentation

- small M^+ peak, more predominant M-15

Carbocations rearrange

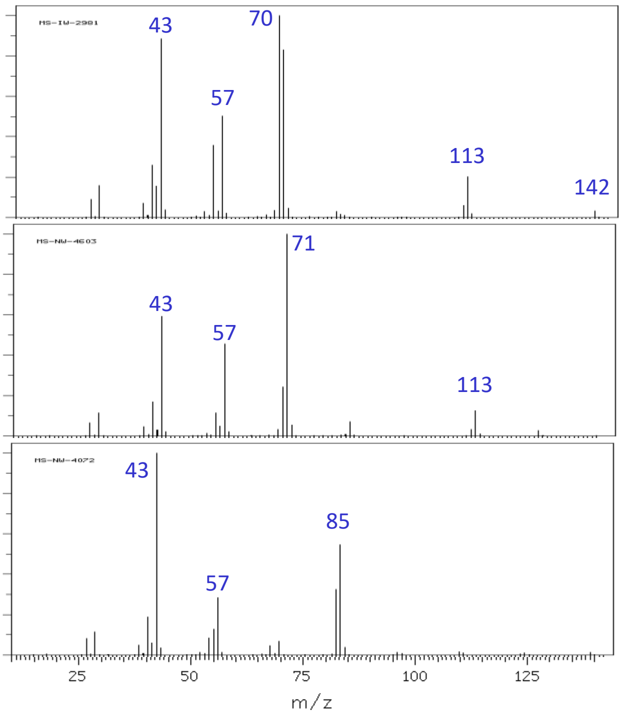




Which is which?

(all C_6H_{14})

hexane
2-methylpentane
2,2-dimethylbutane



Which is which?

(all $C_{10}H_{22}$; $M = 142$)

3,4-diethylhexane
3,3-dimethyloctane
5-methylnonane

Summary: Alkanes

For straight chain alkanes

- Molecular ion peak is usually present but weak (esp. for branched alkane)
- Clusters of fragments appear spaced by *m*/*z* of 14
- The largest peak in each cluster corresponds to an alkyl radical cation, C_nH_{2n+1}
- A peak for $M - CH_3$ is often weak or absent
- More fragmentation at highly branched positions

Cycloalkanes

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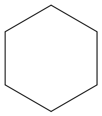
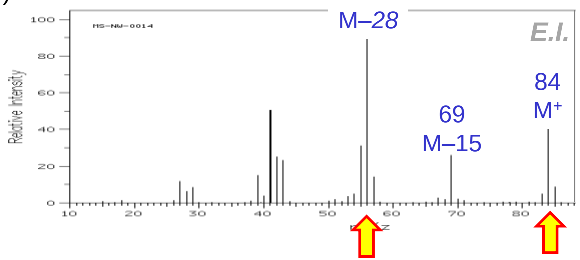
cyclohexane (C_6H_{12}; *M* = 84)





56
M–*28*

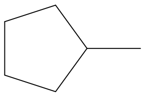
69
M–15

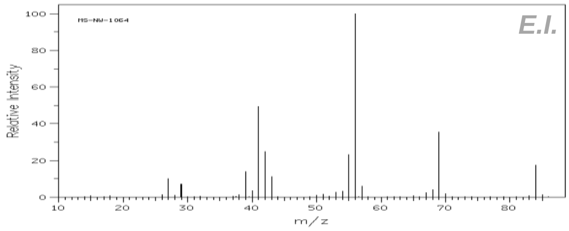
84
M^+

base peak
even *m/z,* M–28
from rearrangement

strong M^+ ***!!***

methylcyclopentane (C_6H_{12}; *M* = 84)





Alkenes

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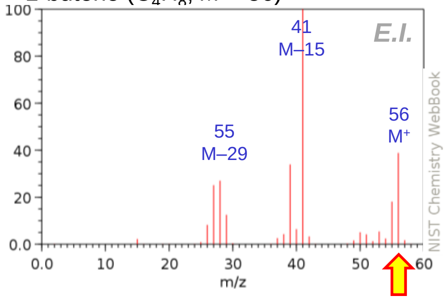
1-butene (C_4H_8; *M* = 56)



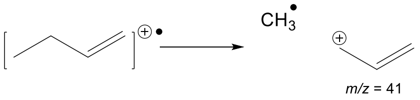
41
M–15

55
M–29

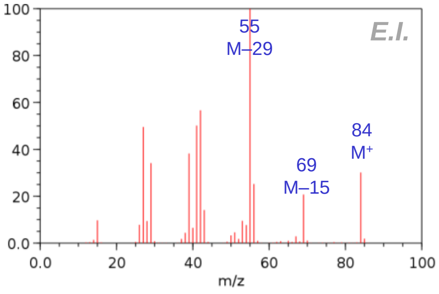
56
M^+

strong M^+ peak

Fragmentation to give allylic cation



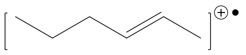
E-2-hexene (C_6H_{12}; *M* = 84)



55
M–29

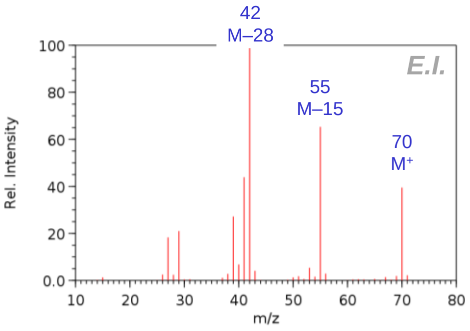
69
M–15

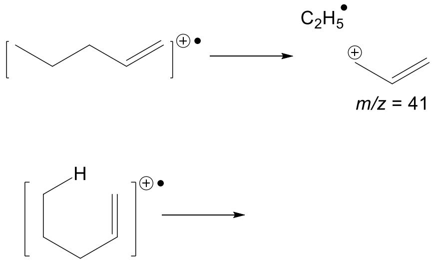
84
M^+



Pavia 8.8 K

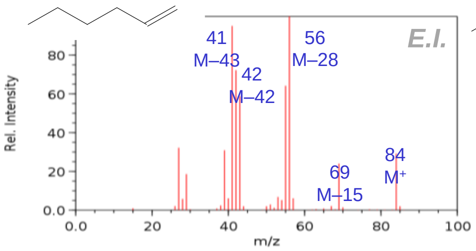
1-pentene (C_5H_{10}; M = 70)

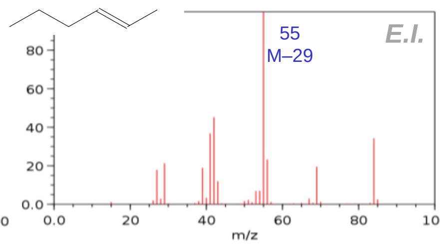


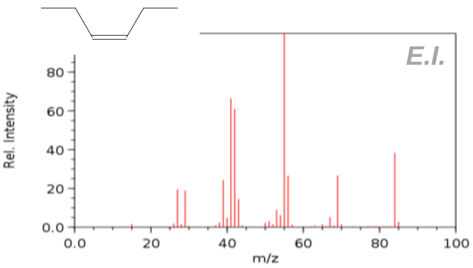


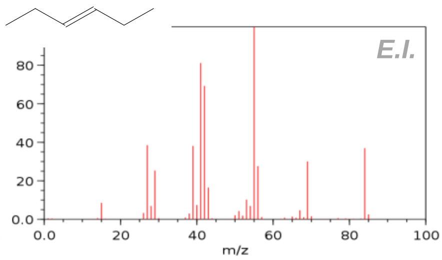
Pavia 8.8 K

Hexenes (C_7H_{12}; M = 84)

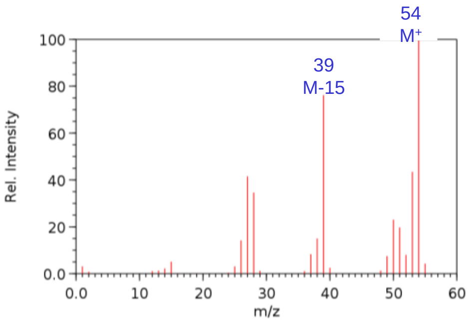


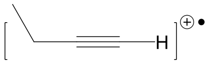


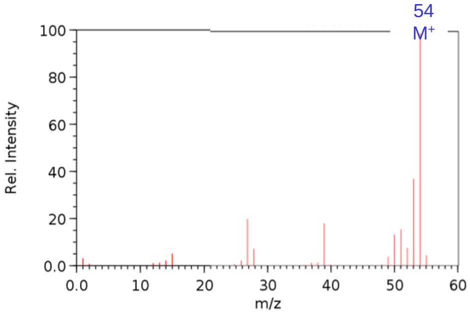


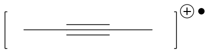


Not possible to determine location or E/Z stereochemistry of C=C


54
M⁺
39
M-15
Rel. Intensity
100
80
60
40
20
0.0
0.0
10
20
30
40
50
60
m/z


H
⊕•


54
M⁺
Rel. Intensity
100
80
60
40
20
0.0
0.0
10
20
30
40
50
60
m/z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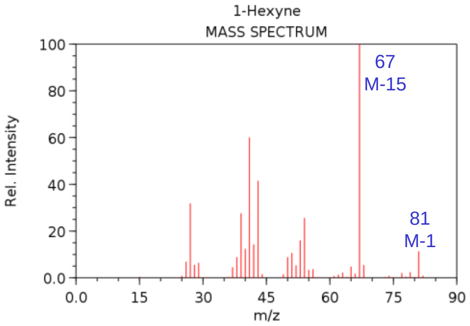
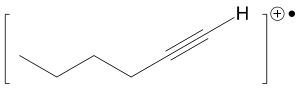

1-Hexyne
MASS SPECTRUM
67
M-15
81
M-1
Rel. Intensity
100
80
60
40
20
0.0
0.0
15
30
45
60
75
90
m/z


H
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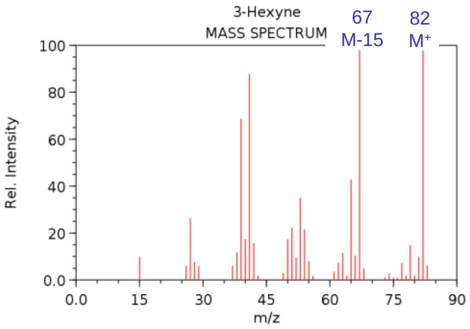
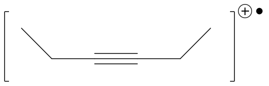

3-Hexyne
MASS SPECTRUM
67
M-15
82
M⁺
Rel. Intensity
100
80
60
40
20
0.0
0.0
15
30
45
60
75
90
m/z


⊕•

Summary: Alkenes and Alkynes

1. Relatively strong M^+ ion (removal of π electron does not result in bond breaking
2. Strong peak arises from cleavage of alkyl radical to form a resonance stabilized allylic cation (M-15, M-29, M-43, …)

terminal alkene → $^{\oplus}CH_2{-}CH{=}CH_2$ (*m/z* = **41**)

3. McLafferty rearrangement – loss of alkene

M–**28**, M–**42**, M–**56**, M–**70**, M–**84**, M–**98**, ….

3. Difficult to identify position of π bond since the double bond migrates easily. No information about *E/Z* isomers.

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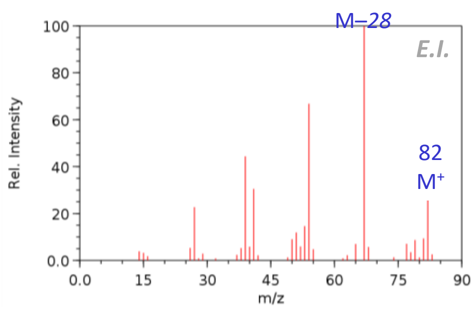
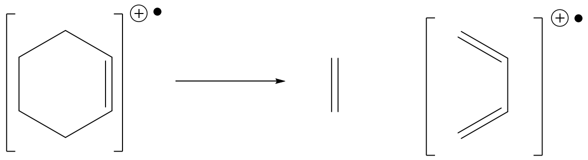
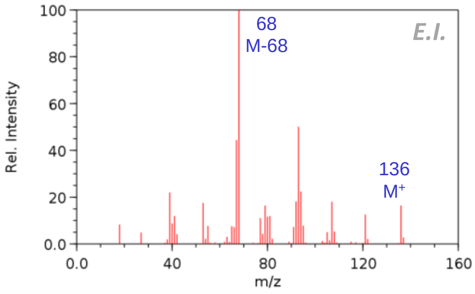
cyclohexene (C_6H_{10}; *M* = 82)

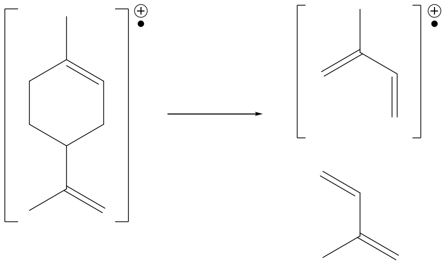


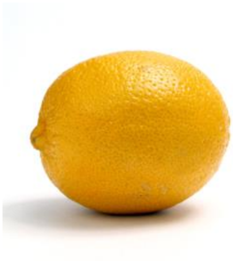
Retro-Diels-Alder Reaction

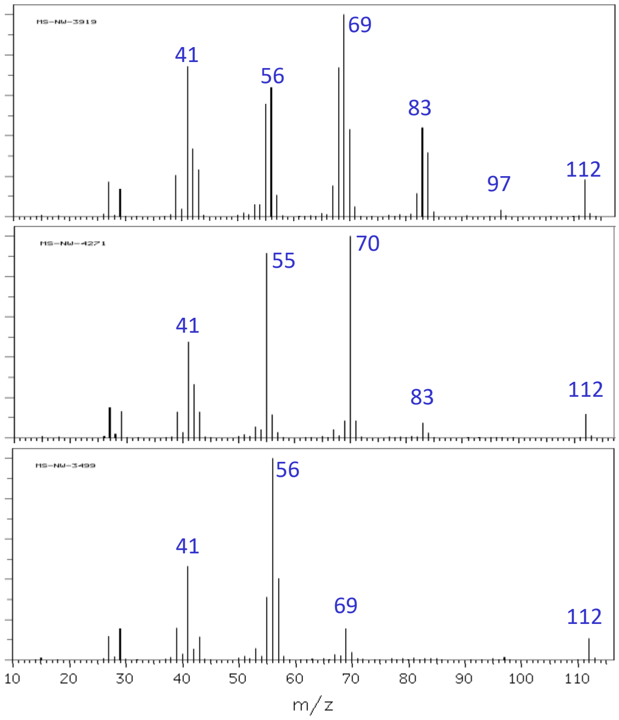


limonene ($C_{10}H_{16}$; M = 136)









Which is which?

(all C_8H_{16}; M = 112)

propylcyclopentane
2-ethyl-1-hexene
2.5-dimethyl-1-hexene

Aromatic Hydrocarbons

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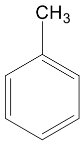
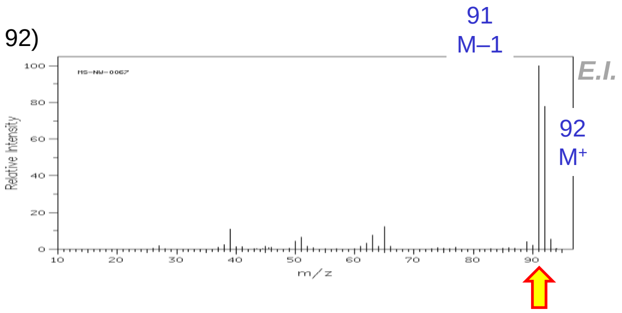
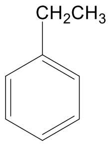
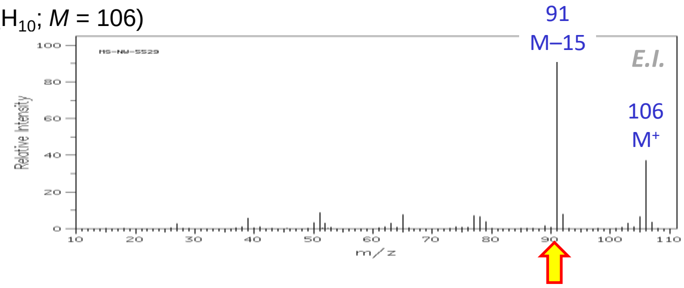
toluene (C_7H_8; *M* = 92)



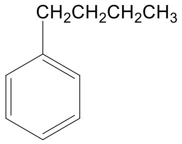


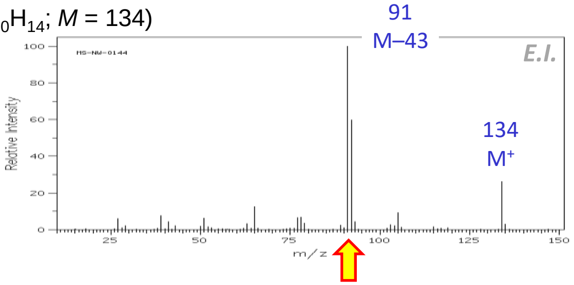
ethylbenzene (C_8H_{10}; *M* = 106)



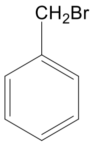


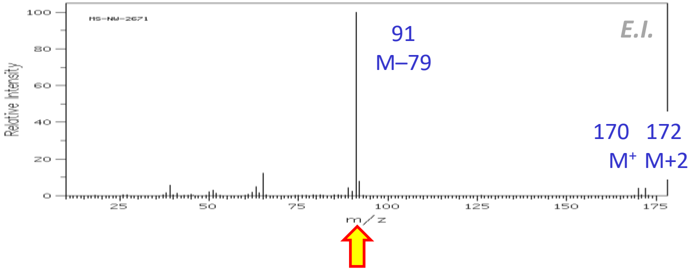
1-butylbenzene ($C_{10}H_{14}$; *M* = 134)





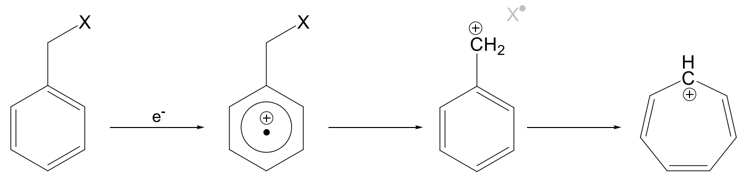
α-bromotoluene (C_7H_7Br, *M* = 170[^{79}Br])

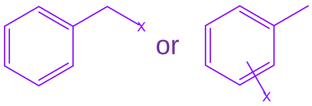




What are all those *m/z* = 91 peaks for PhCH$_2$X?

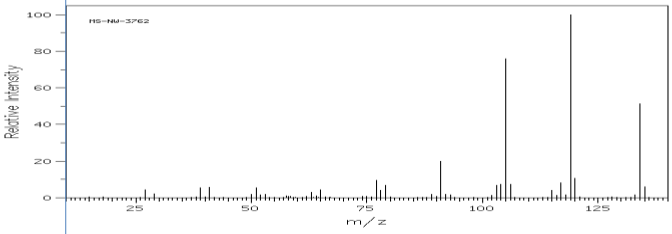
X = H, R, Hal, OH(R)

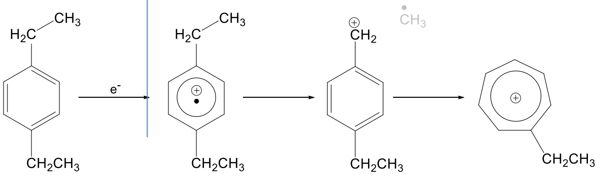




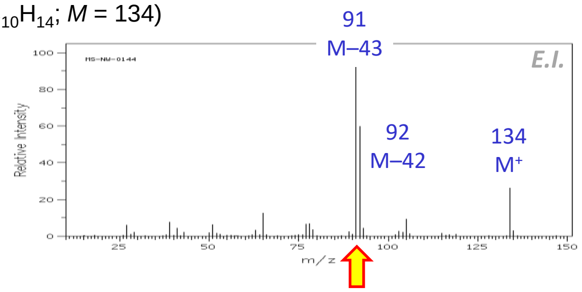
$\rightarrow$ $C_7H_7^{+}$ (*m/z* = 91)

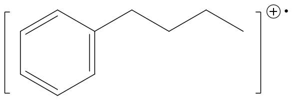
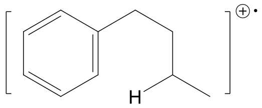
1,4-diethylbenzene, *M* =134





1-butylbenzene ($C_{10}H_{14}$; *M* = 134)

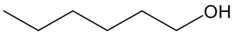


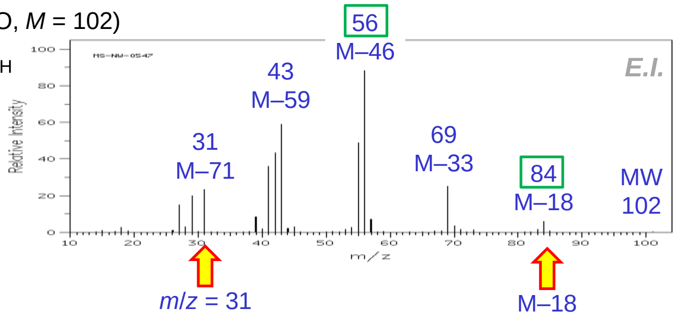



Alcohols, Ethers and Amines

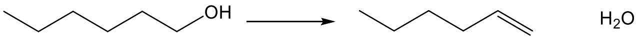
Pavia 8.8 N,O,T

1-hexanol ($C_6H_{14}O$, *M* = 102)

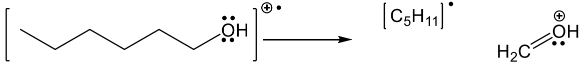




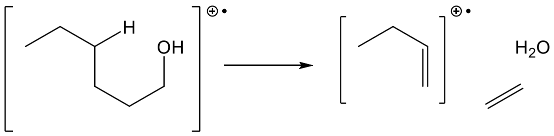
M–18: Dehydration



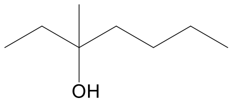
m/z = 31 (M-71): α-cleavage of an alkyl radical

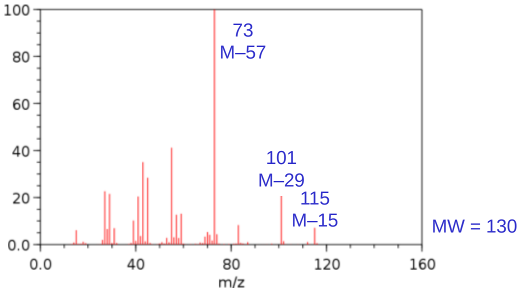


M–46: Dehydration with loss of alkene

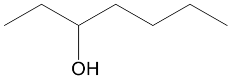


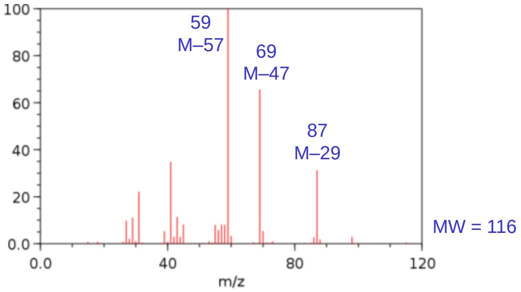
3-methyl-3-heptanol ($C_8H_{18}O$, *M* = 130)



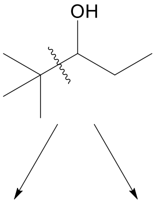


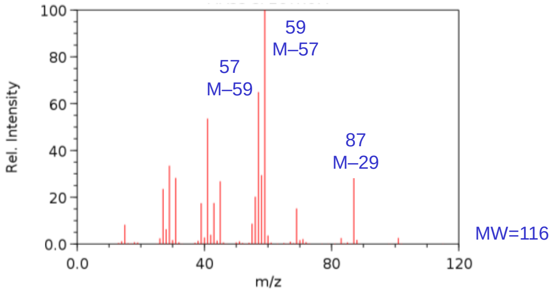
3-heptanol ($C_7H_{16}O$, *M* = 116)



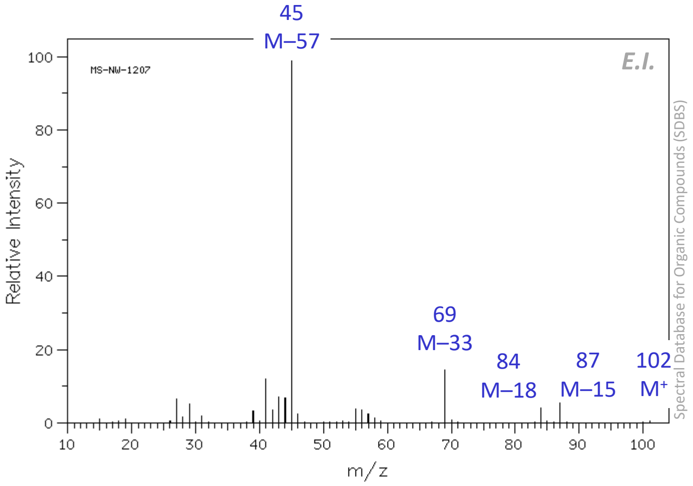


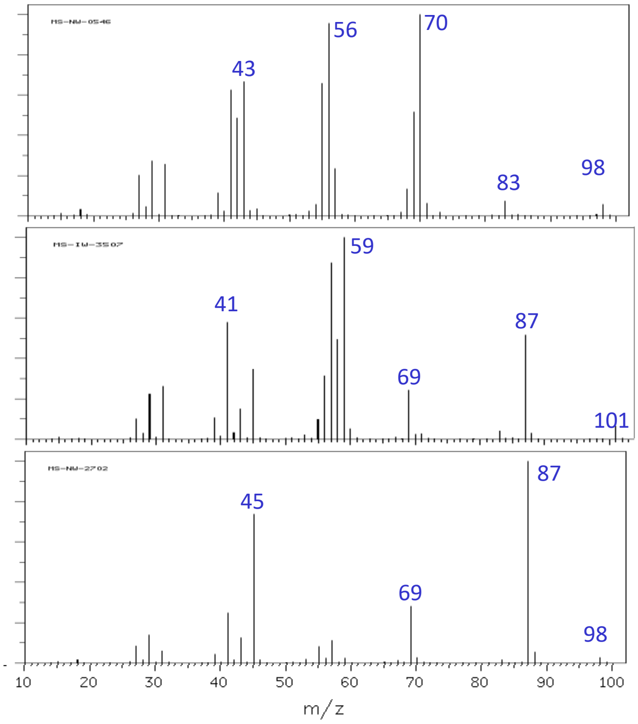
2,2-dimethyl-3-pentanol ($C_7H_{16}O$, M = 116)





Which $C_6H_{12}O$ alcohol?



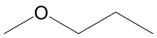


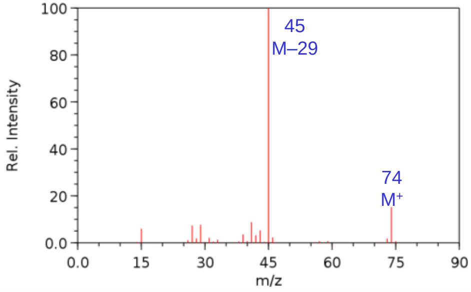
Which is which?

(all $C_7H_{16}O$; *M* = 116)

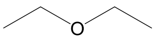
1-heptanol
2,2-dimethyl-3-
pentanol
3-ethyl-3-pentanol

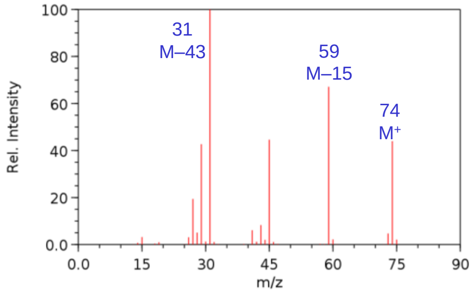
Methyl 1-propyl ether ($C_4H_{10}O$, *M* = 74)



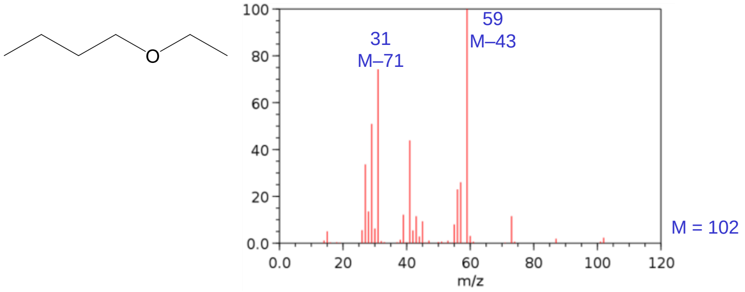


Diethyl ether ($C_4H_{10}O$, *M* = 74)

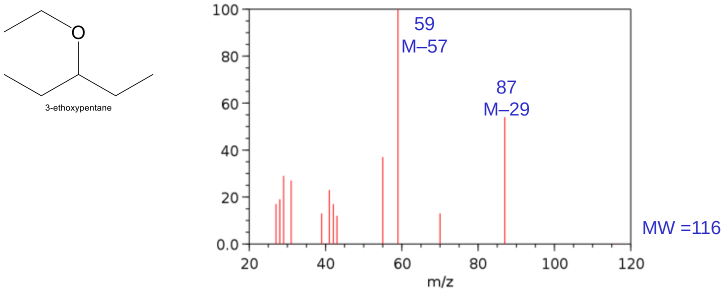




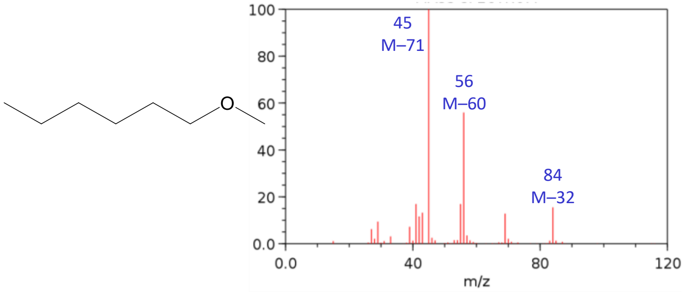
ethyl 1-butyl ether ($C_6H_{14}O$, *M* = 102)

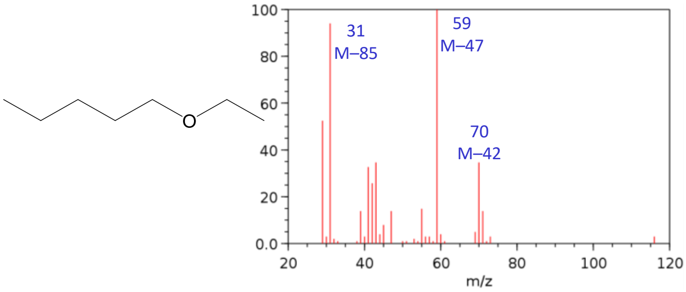


3-ethoxypentane ($C_7H_{16}O$, *M* = 116)

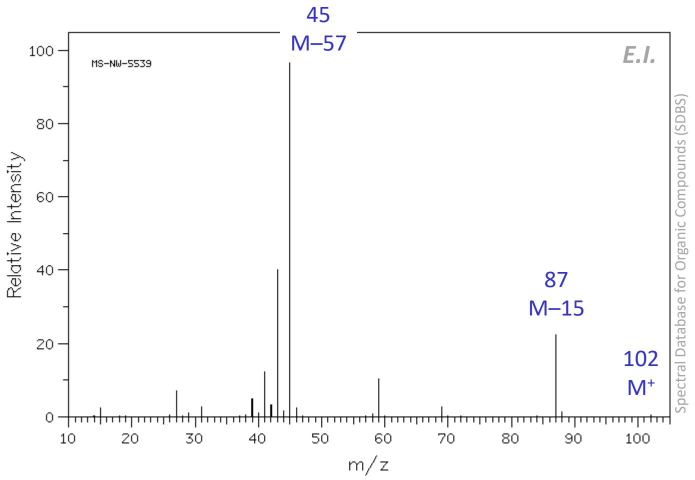


What are the formulas of each labeled fragment?
Explain how these fragments are formed.

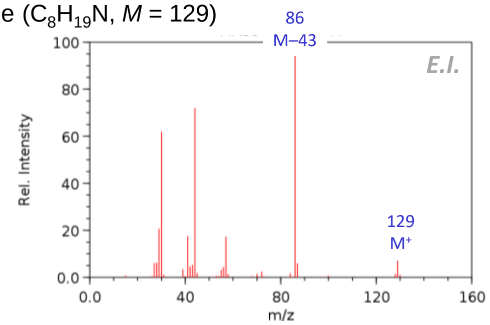


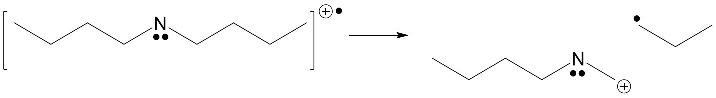


Which $C_6H_{12}O$ ether? Bear in mind that methyl ethers do not fragment by cleavage of the CH_3-O bond.

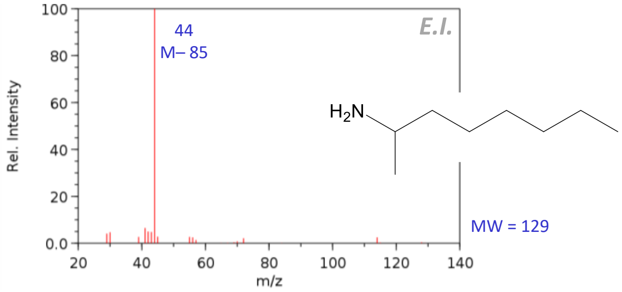


N,*N*-dibutylamine ($C_8H_{19}N$, $M = 129$)

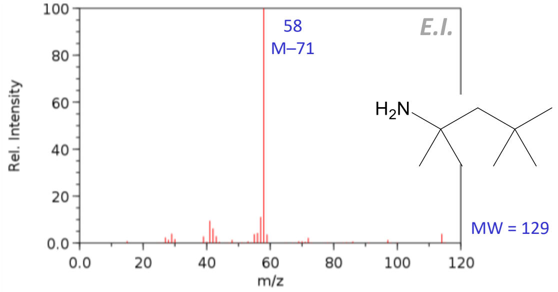


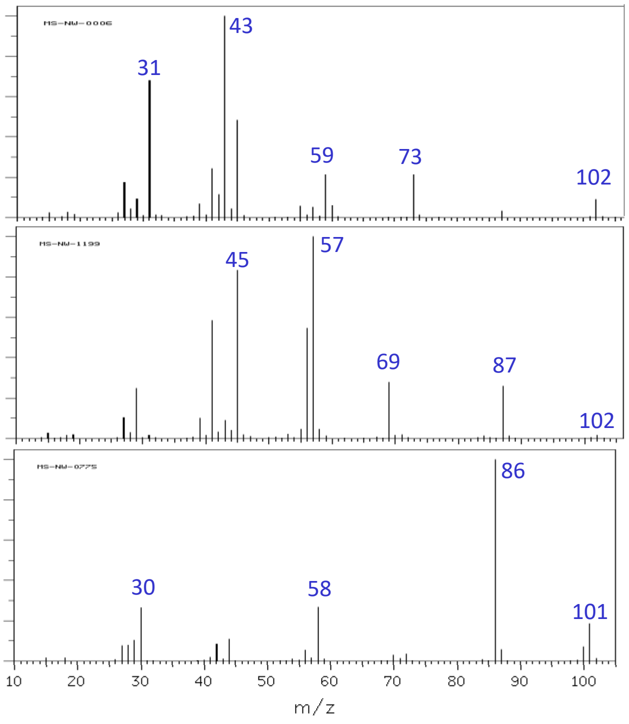


2-octanamine ($C_8H_{19}N$, M = 129)



2,4,4-trimethylpentan-2-amine ($C_8H_{19}N$, M = 129)





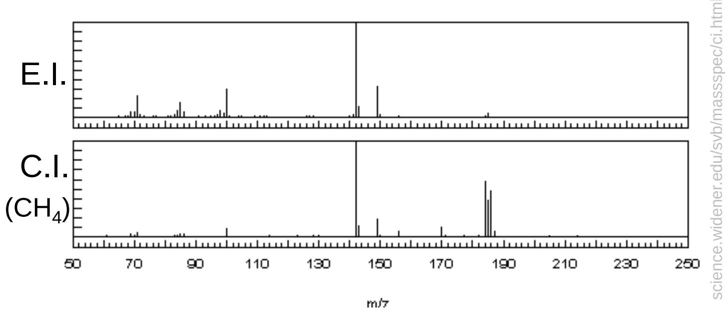
Identify each compound

There is one alcohol, one ether and one amine

dipropylether
3,3-dimethyl-2-butanol
triethylamine

E.I and C.I of tri-*n*-butylamine

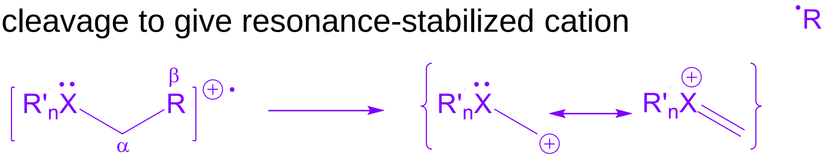
$C_{12}H_{27}N$ (*MW* = 185)



science.widener.edu/svb/massspec/ci.html

Summary: Alcohols, Ethers and Amines

α-cleavage to give resonance-stabilized cation



Dehydration (M-H_2O)

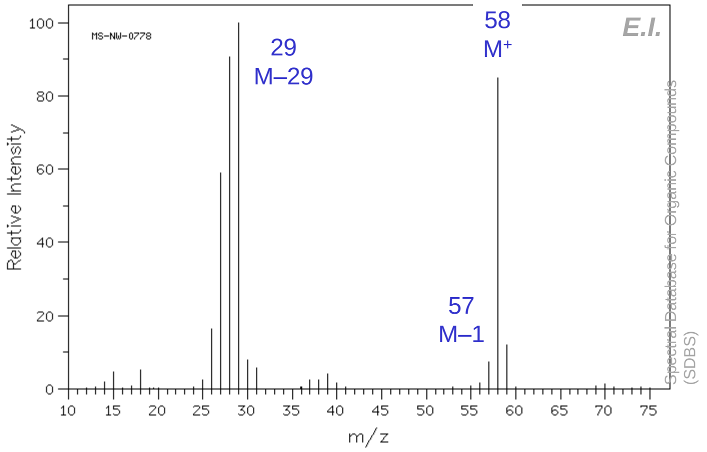
McLafferty (-H_2O, -CH_2=CH_2)

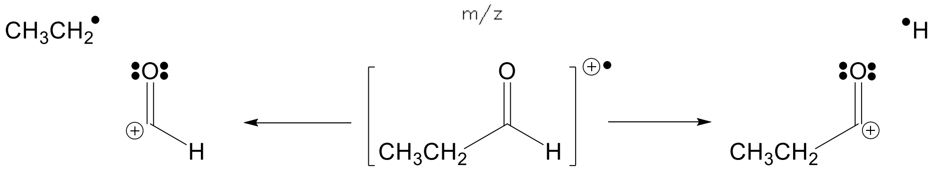
α-cleavage (-R·) followed by elimination (-C_nH_{2n}) from another substitutent (ethers, 2°/3° amines)

Aldehydes and ketones

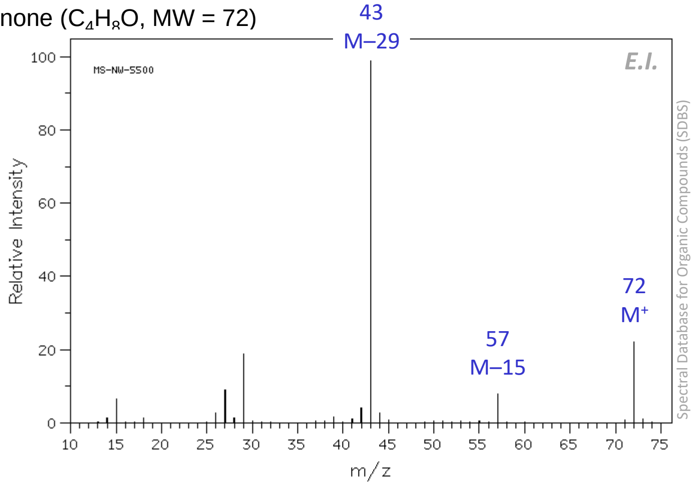
Pavia 8.8 P-Q

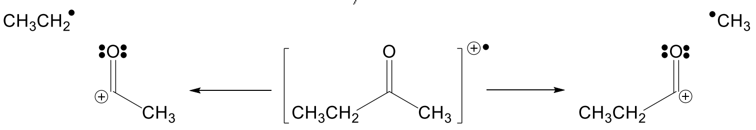
propanal (C_3H_6O, MW = 58)



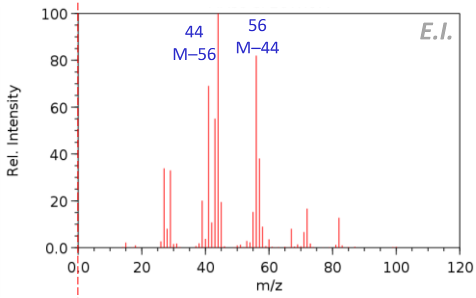


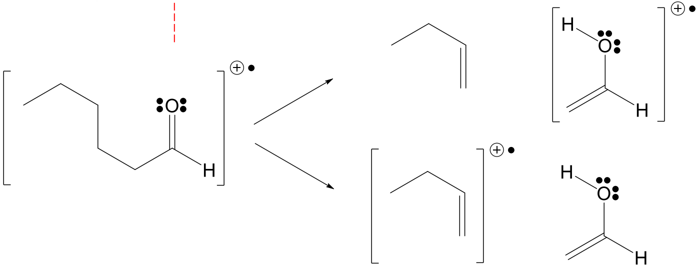
2-butanone (C_4H_8O, MW = 72)



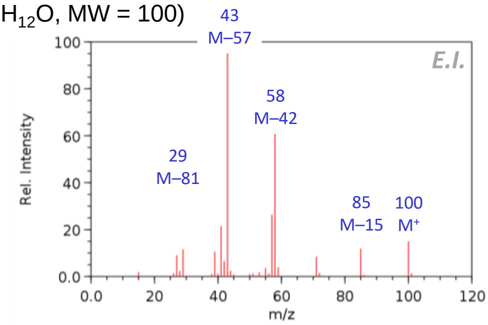


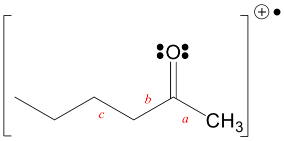
hexanal ($C_6H_{12}O$, MW = 100)



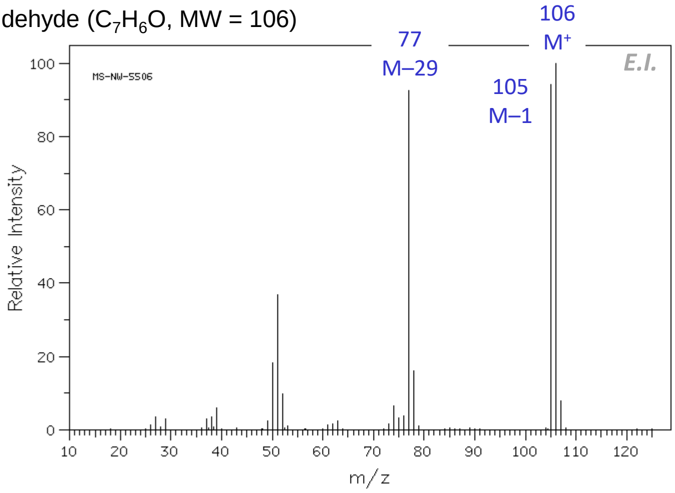


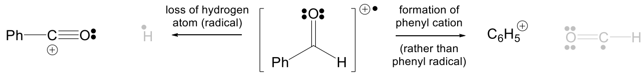
2-hexanone ($C_6H_{12}O$, MW = 100)





benzaldehyde (C_7H_6O, MW = 106)





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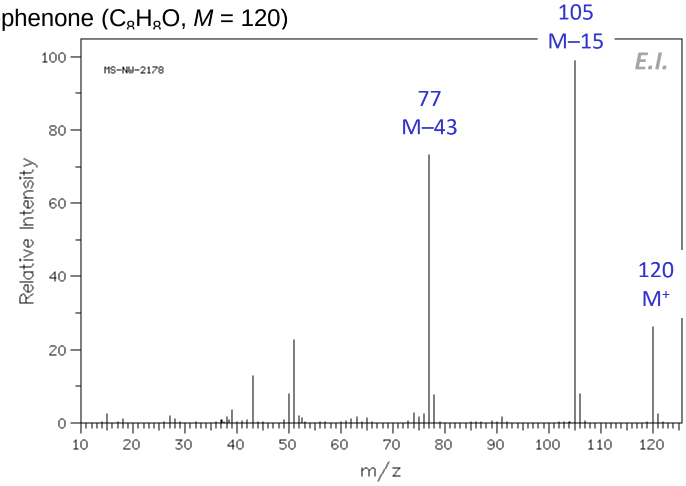
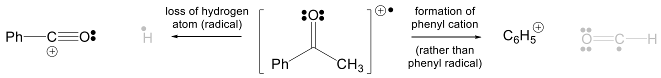
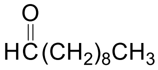
acetophenone (C_8H_8O, *M* = 120)

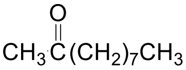


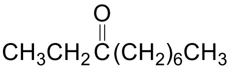
Spectral Database for Organic Compounds (SDBS)

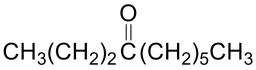


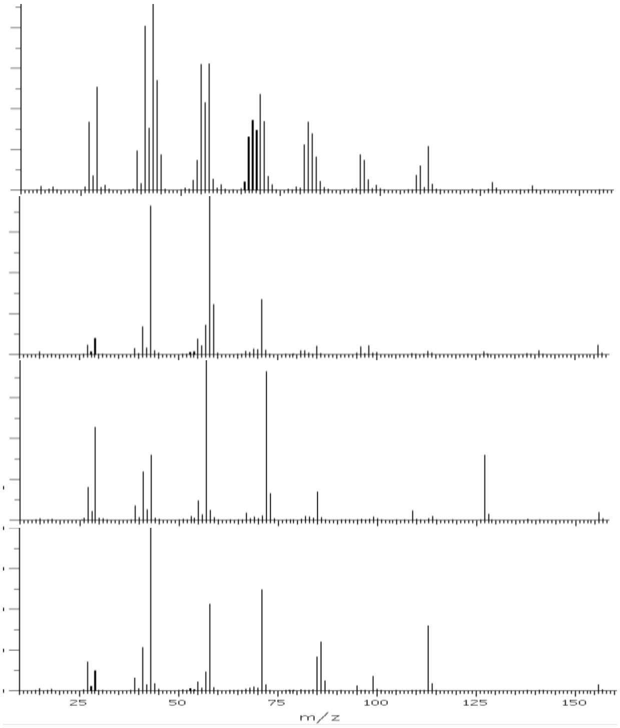
Which is which?


$H\overset{\overset{O}{\|}}{C}(CH_2)_8CH_3$

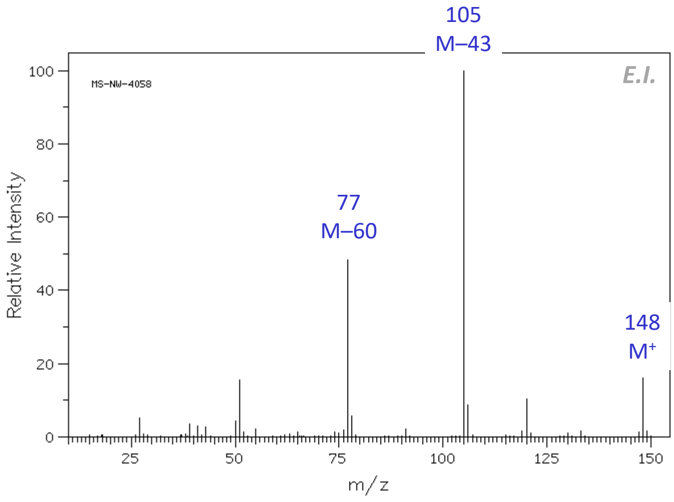

$CH_3\overset{\overset{O}{\|}}{C}(CH_2)_7CH_3$


$CH_3CH_2\overset{\overset{O}{\|}}{C}(CH_2)_6CH_3$


$CH_3(CH_2)_2\overset{\overset{O}{\|}}{C}(CH_2)_5CH_3$



Which ketone?



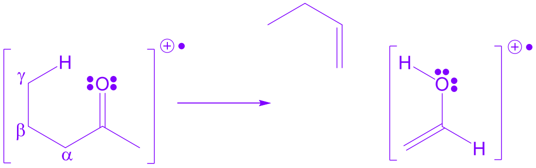
Spectral Database for Organic Compounds (SDBS)

Summary: Aldehydes and Ketones

1. α-cleavage: C–C(=O)
   Loss of larger R· predominates

   M-**1**, M-**15**, M-**29**, M-**43**, ….

2. McLafferty rearrangement: transfer of γ-H to C=O
   Becomes more important as R↑

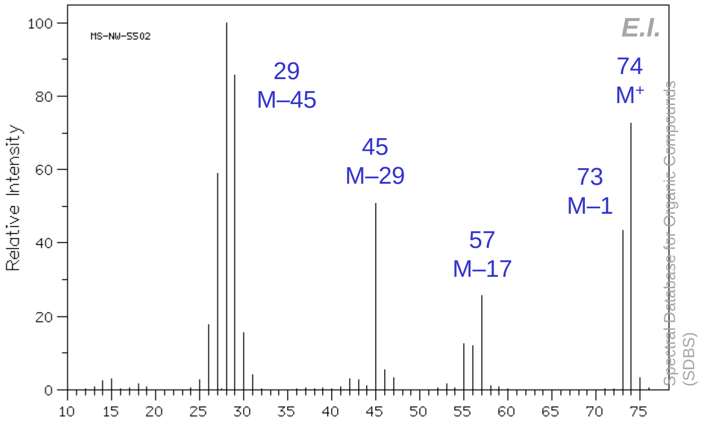


   M-**28**, M-**42**, M-**56**, ….

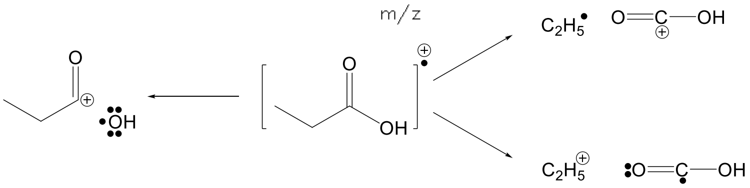
Carboxylic acids

Pavia 8.8 R,S

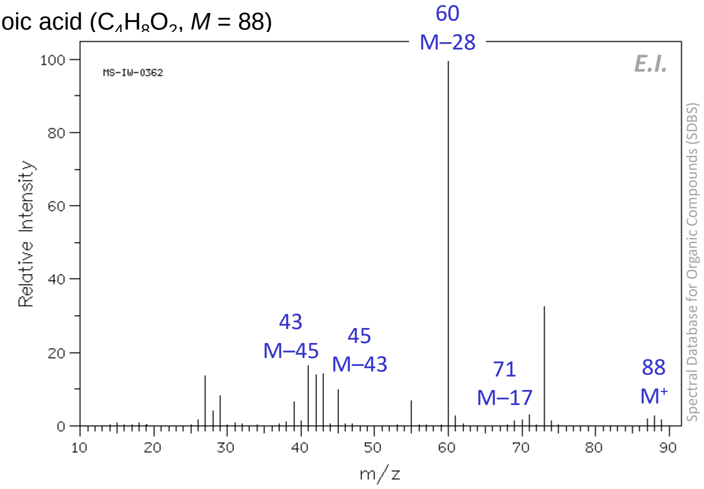
propanoic acid ($C_3H_6O_2$, *M* = 74)

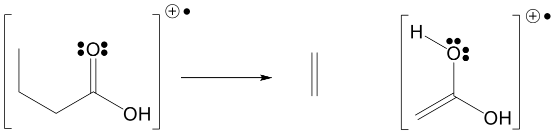


m/z



butanoic acid ($C_4H_8O_2$, M = 88)





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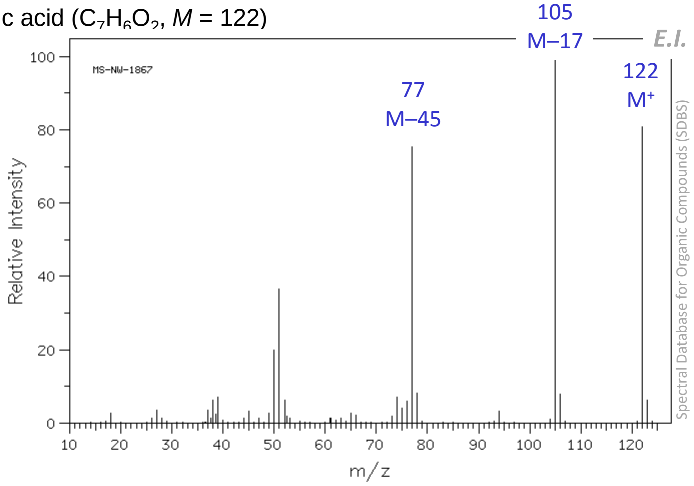
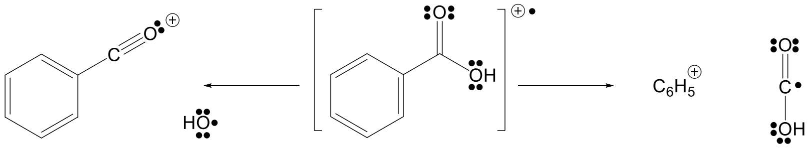
benzoic acid ($C_7H_6O_2$, M = 122)





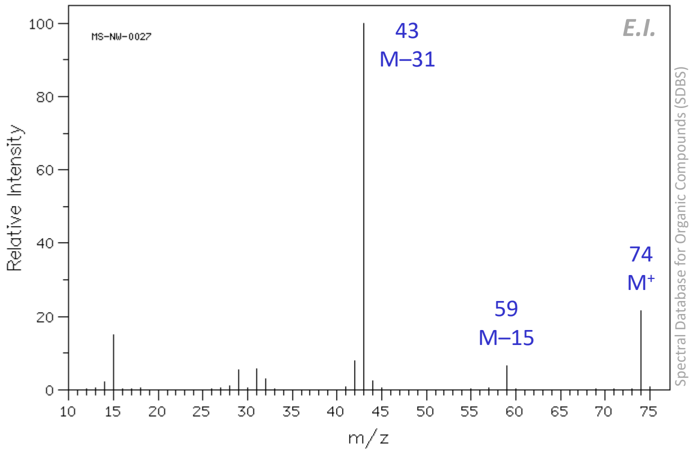
Summary: Carboxylic acids

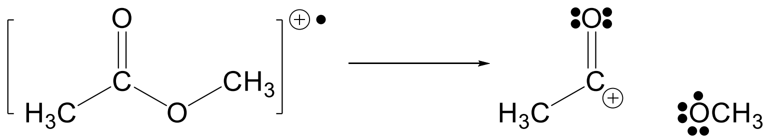
1. M-1
2. Cleavage of C(O)-OH
3. Cleavage of R-C(O) → $[M\text{-}R]^+$
   and $[CO_2H]^{+\cdot}$ m/z = 45

4. McLafferty rearrangement for CH-C-C-C(=O)OH

Esters

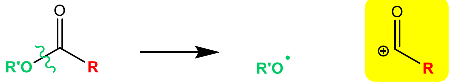
methyl acetate ($C_3H_6O_2$, *M* = 74)





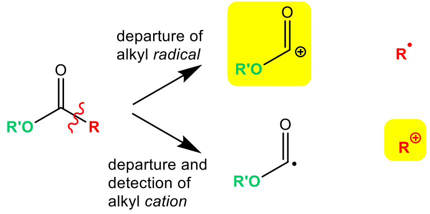
Modes of fragmentation of esters

Cleavage of alkoxy radical (**R'O·**) from carbonyl



[M–OR']$^+$
m/z = M–31, M–45, M–59, ...

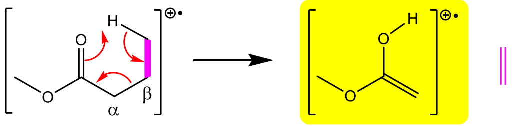
Cleavage of alkyl (**R**) radical or cation from carbonyl



[M–R]$^+$
m/z = M–15, M–29, M–43, …

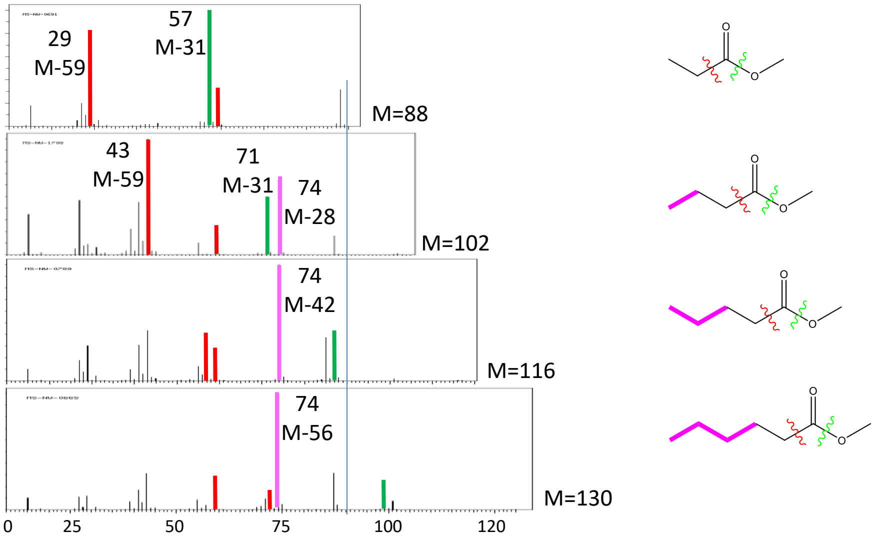
R$^+$
m/z = (15,29), 43, 57, 71, ...

McLafferty rearrangement - Elimination of an alkene (**C_nH_{2n}**) <u>from the alkyl substituent</u> to give **M–$C_nH_{2n}$$^{+\cdot}$**



[M–C_nH_{2n}]$^{+\cdot}$
m/z = 28, 42, 56, 70, 84, ...

Alkyl (–R·) versus alkoxy cleavage (–OR·) and McLafferty rearrangement (–C_nH_{2n}) of alkyl substituent

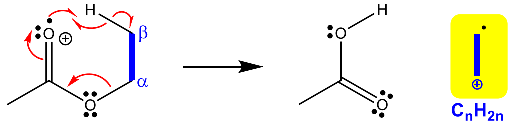


α-cleavage of **R·** increases as R↑; but McLafferty begins to dominate
α-cleavage of **CH_3O·** becomes less important

More modes of fragmentation of esters

McLafferty rearrangement on alkoxy side of the ester

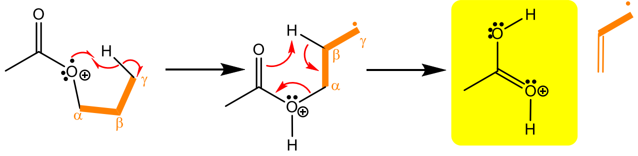
Elimination of a carboxylic acid from the alkoxy substituent to give **$C_nH_{2n}^{+\cdot}$**



$[C_nH_{2n}]^{+\cdot}$
m/z = 28, 42, 56, 70, ...

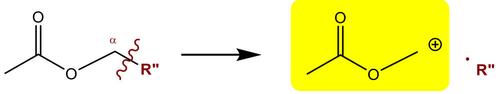
"McLafferty plus one" rearrangement

Transfer of two hydrogen atoms from the alkoxy group. Loss of $C_nH_{2n-1}\cdot$ to give **$RCO_2H_2^+$**

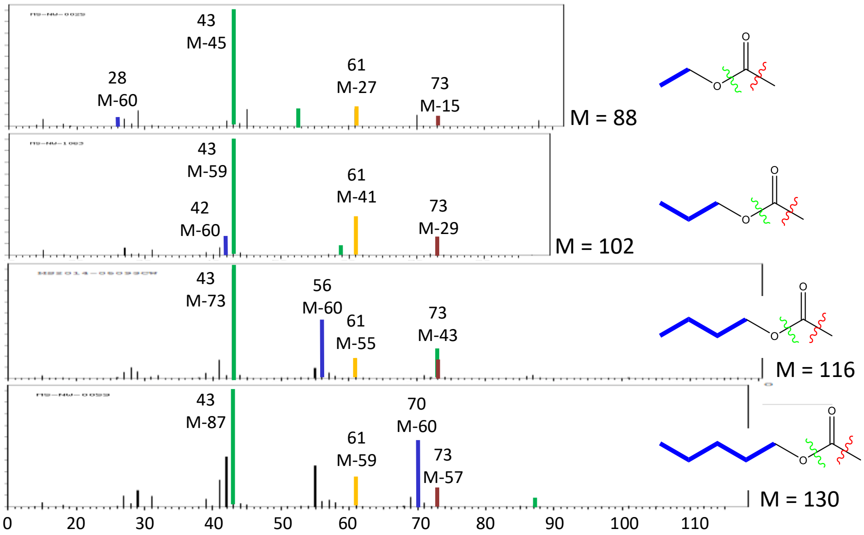


$[M-C_nH_{2n-1}]^+$
m/z = M–41, M–55,
M–69, M–83, ...

… and finally, fragmentation from –OR’ by loss of alkyl from α-position

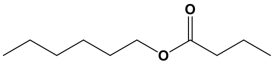


Alkoxy cleavage, McLafferty rearrangement, McLafferty+1 rearrangement and a-cleavage of R”O-C(=O)R

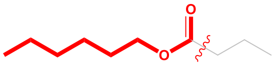


α-cleavage of **$R'O\cdot$** predominates. *McLafferty rearrangement with elimination* of RO_2H becomes more important as **R’**↑

Predict the peaks that appear in the MS of hexyl butanoate, $C_{10}H_{20}O_2$ (MW=172)

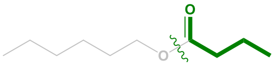


Cleavage of R^+ and R· from C=O
Loss of $C_nH_{2n+1}O$ (M–31,45,59, …)



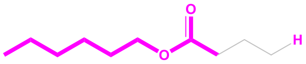
43
M–43 = 129

Loss of RO· from C=O
Loss of $C_nH_{2n+1}O$ (M–31,45,59, …)



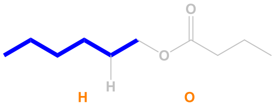
M–101 = 71

McLafferty rearrangement (alkyl)
Loss of C_nH_{2n} (M–28,42,56,70, …)



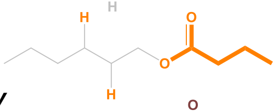
M–28 = 144

McLafferty rearrangement (alkoxy)
Loss of $C_nH_{2n}O_2$ (M–48,62,76, …)



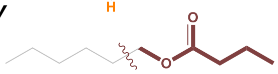
84

"McLafferty + 1"
Loss of C_nH_{2n-1} (M–41,55,69, …)

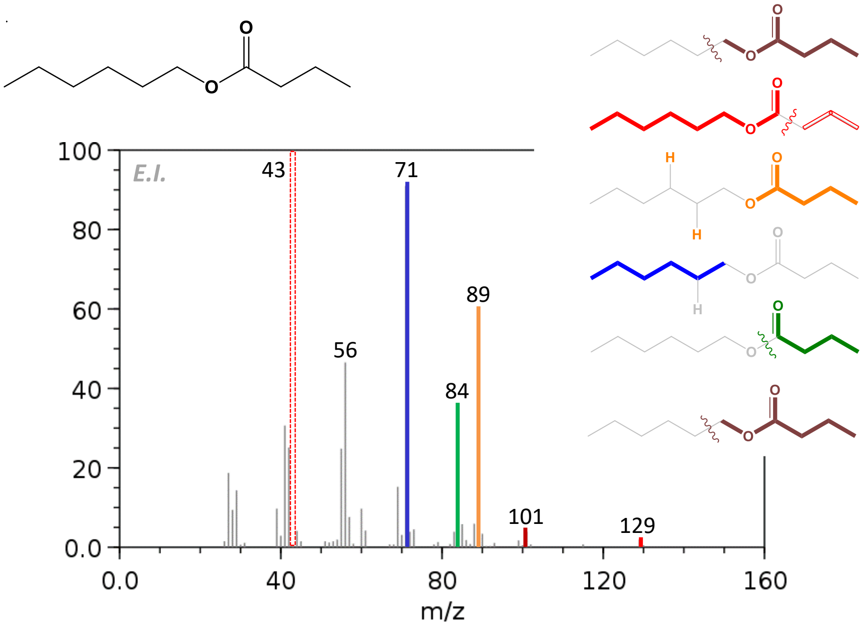


M–83 = 89

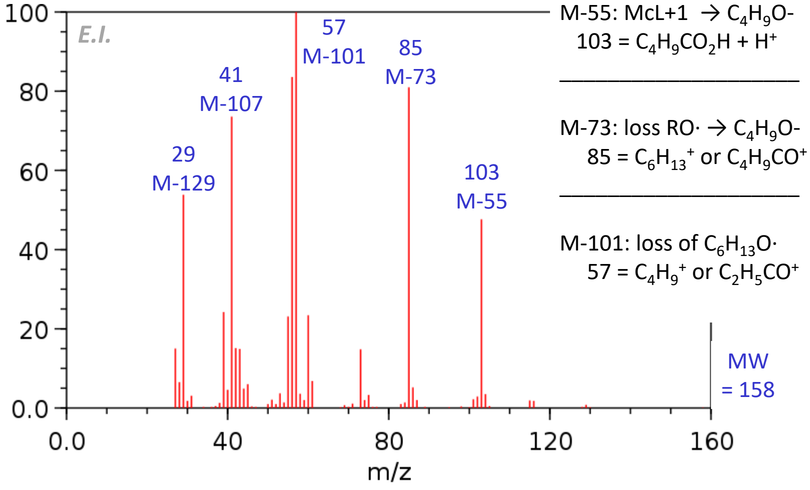
α-cleavage of α-β C-C bond of alkoxy
Loss of C_nH_{2n+1} (M–15,29,43,57,…)



M–71 = 101



Which ester?



M-55: McL+1 → C_4H_9O-
103 = $C_4H_9CO_2H + H^+$

M-73: loss RO· → C_4H_9O-
85 = $C_6H_{13}^+$ or $C_4H_9CO^+$

M-101: loss of $C_6H_{13}O$·
57 = $C_4H_9^+$ or $C_2H_5CO^+$

---

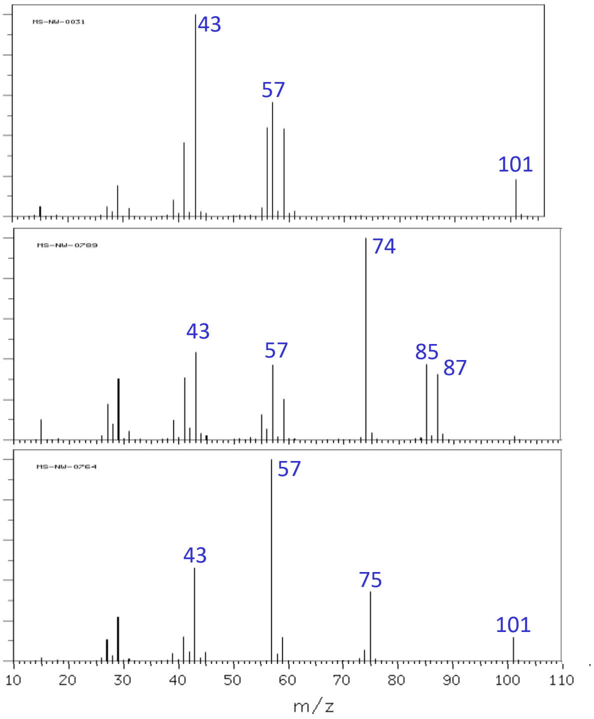
n	**Alkyl groups C_nH_{2n+1} M**	**Acyl groups $C_nH_{2n+1}CO$ M**
1	15	43
2	29	57
3	43	71
4	57	85
5	71	99
6	85	113
7	99	127

-2: C_nH_{2n-1}
lost: “McLafferty+1”

-1: alkene C_nH_{2n}
lost: McLafferty
observed: McLafferty
(alkoxy substituent of ester)

0: alkyl C_nH_{2n+1}
observed: alkyl cation, R^+
or
$C_nH_{2n+1}CO^+$

+2:
lost: alkoxy $C_nH_{2n+1}O$·



Identify each ester

$C_6H_{12}O_2$ esters, MW = 116

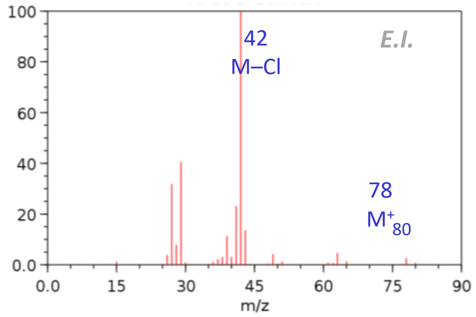
tert-butyl acetate
$CH_3C(=O)OC(CH_3)_3$

Methyl pentanoate
$CH_3CH_2CH_2CH_2COOCH_3$

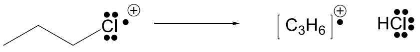
Isopropyl propionate
$CH_3CH_2COOCH(CH_3)_2$

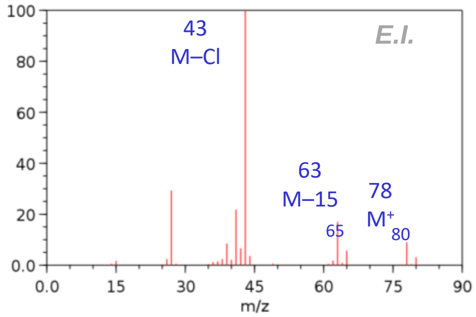
Halogen Containing Compounds

Pavia 8.8 V

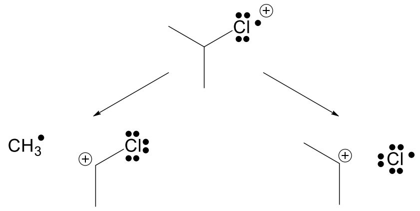


1-chloropropane (C_3H_7Cl, M = 78 [^{35}Cl])

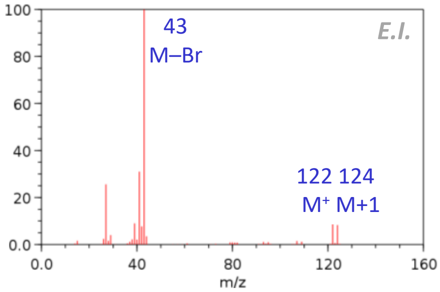




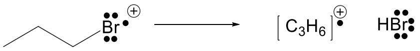
2-chloropropane (C_3H_7Cl, M = 78 [^{35}Cl])

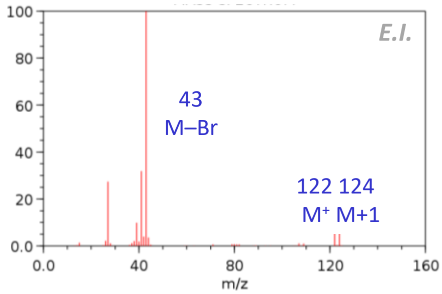


Pavia 8.8 V

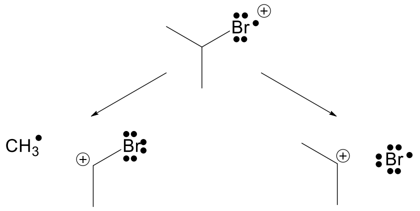


1-bromopropane (C_3H_7Br, M =122 [^{79}Br])





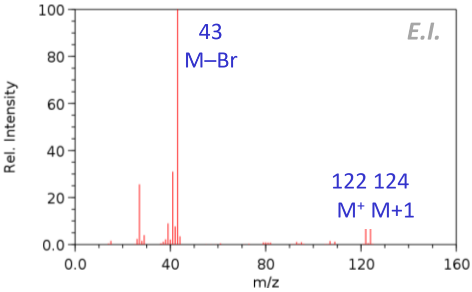
2-bromopropane (C_3H_7Br, M =122 [^{79}Br])

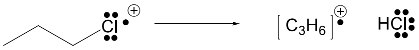


Halogen Containing Compounds

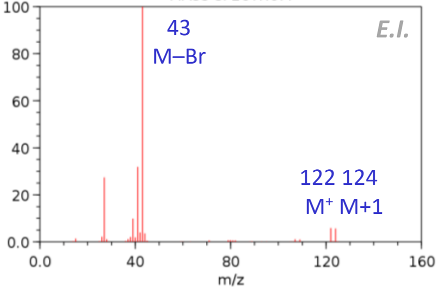
Pavia 8.8 V

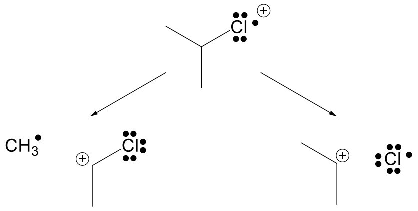
1-bromopropane (C_3H_7Br, M =122 [^{79}Br])



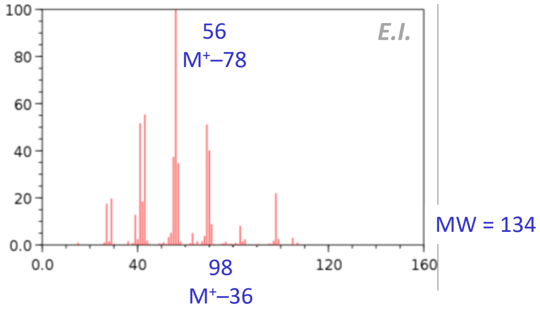


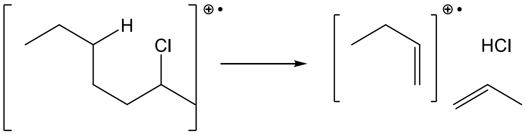
2-bromopropane (C_3H_7Br, M =122 [^{79}Br])



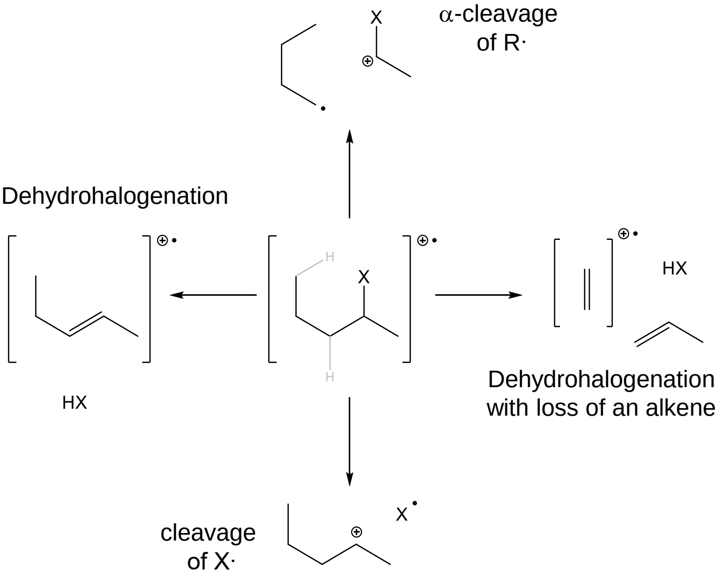


2-chloroheptane ($C_7H_{15}Cl$, M = 134 [^{35}Cl])





Summary: Alkyl halides



SUMMARY: SOME COMMON FRAGMENT PEAKS

Pavia Appendix 12

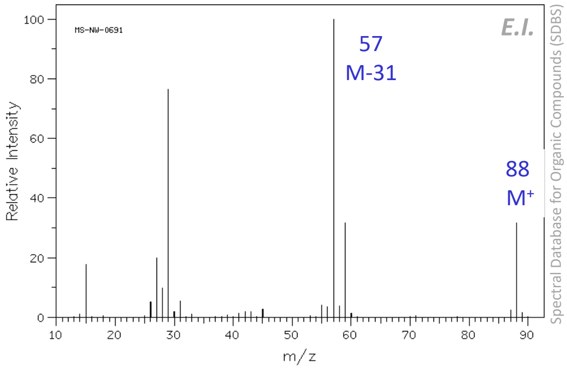
Peak	*Fragment lost*	*Interpretation*
M–1	$\mathrm{H}^{\bullet}$	aldehydes, 3° alcohols, cyclic amines
M–2	Multiple $\mathrm{H}^{\bullet}$	2° alcohols
M–3	Multiple $\mathrm{H}^{\bullet}$	1° alcohols
M–15	CH3$^{\bullet}$	methyl groups
M–17	$\mathrm{HO}^{\bullet}$	alcohols, phenols, carboxylic acids
M–18	H_2O	alcohols
M–26	HC≡CH	
M–27	$^{\bullet}\mathrm{HC{=}CH_2}$	
M–28	$CH_2=CH_2$	cyclic alkanes, alkenes $CH_3CH_2CH_2C(=O)X$ [McLafferty rearr.]
M–19,35/37,79/81	$^{\bullet}$halogen	
M–15,29,43,57,71…	$^{\bullet}$alkyl	
M–31,45,59,73,87…	$^{\bullet}$alkoxy	esters, ethers

Pavia Appendix 11

Peak	*Fragment observed*	*Interpretation*
39	$\mathrm{H_2\underset{+}{C}{-}C{\equiv}CH}$ *propargyl cation*	from alkyne
41	$\mathrm{H_2C{-}CH{=}CH_2}$ *allyl cation*	from terminal alkene
42	$\mathrm{H_2\overset{+}{C}{=}C{=}NH_2}$	from 1° amine ($R–CH_2NH_2$)
43	$\mathrm{H_2C{=}C{=}\underset{+}{OH}}$	from 1° alcohol
77	$C_6H_5^+$	from substituted phenyl
91	+ $C_7H_7^+$ *tropylium cation*	from C-substituted phenyl

Compound X revisited, yet again

Analysis of fragmentation ⇒ STRUCTURAL information



Spectral Database for Organic Compounds (SDBS)

Fragmentation:

Structure contains:

Reporting MS Spectra in Papers and Progress Reports

Ⓐ

MS (EI, 70 kV):

molecular ion

m/z 91 (tropilium, 100%), 205 (M-29, 64%), 234(M^+, 35%), …

Ⓑ Ⓒ Ⓓ

base peak

Fragments *that help in structure determination*

… 235 (M+1, 4.6%).

M+1 peak (or others) *that indicate something about molecular structure* based on isotope distribution

- Ⓐ Ionization technique/method (e.g., EI, CI, FAB, MALDI).
- Ⓑ Mass
- Ⓒ Assignment of the peak to a particular ion
- Ⓓ Height of the peak relative to the base peak (100%)

Reporting HRMS Spectra in Papers and Progress Reports

Ⓐ

HRMS (EI, 70 kV):

m/z 100.0639, 39%; Calc. for $C_4H_8N_2O$, Δ = 2 ppm.

Ⓑ Ⓒ Ⓓ Ⓔ

- Ⓐ Ionization technique/method (e.g., EI, CI, FAB, MALDI).
- Ⓑ Mass
- Ⓒ Height of the peak relative to the base peak (100%)
- Ⓓ Suggested formula
- Ⓔ The difference between the experimental value of molecular weight and the value calculated for the putative molecular formula, in ppm:

$$\Delta = |\, M_{exp} - M_{calc} \,| \times 10^6 / M_{exp}$$

WORK AS MANY PROBLEMS AS POSSIBLE!

Pavia, chap 8 questions:

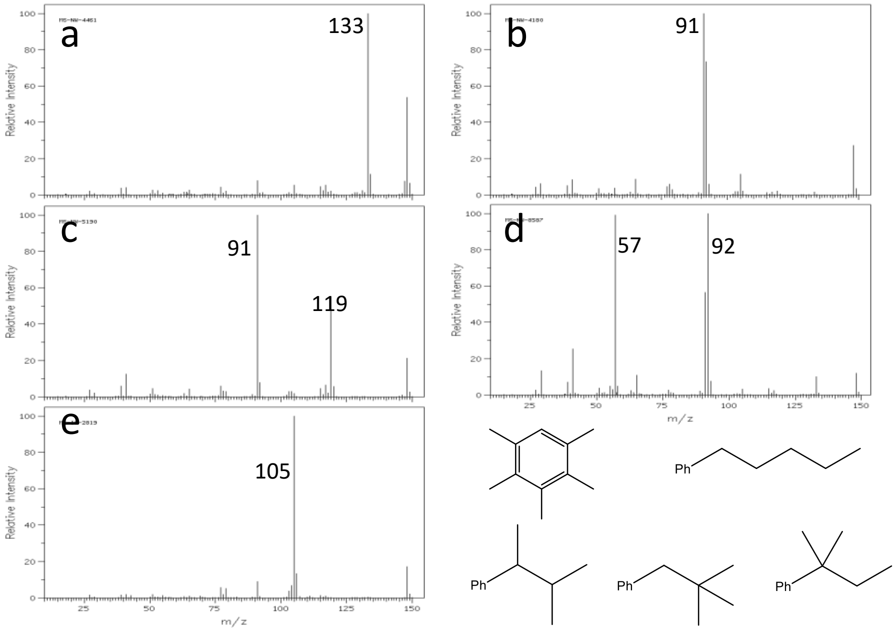
7 (a)-(x), 8, 9, 10, (a)-(f), 11, (a)-(g), 12 (a)-(c), 13, 14, 15 (a)-(b)

Online tool Problem sets based on M.S. alone
http://science.widener.edu/~svanbram/chem465/htmldocs/ms_unk.html
Intensities of peaks are provided, you need to download free spectral visualization software to view actual spectra

Determine the ***structures*** of the compounds for which the mass spectra and IR spectra are provided on the following slides. In some cases you might be able to identify a single compound. For others, a ^{1}H NMR would really help!!

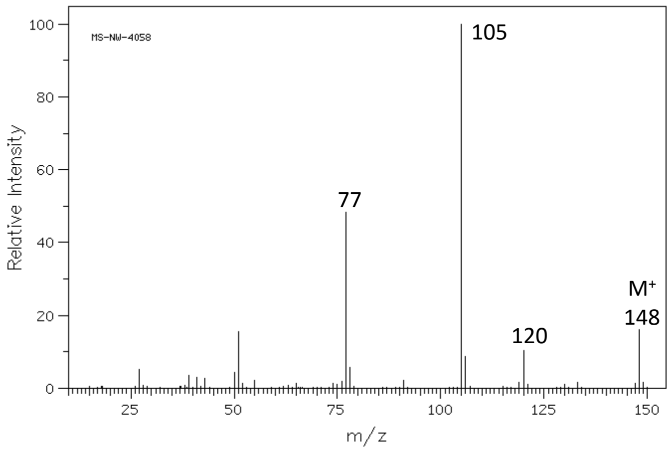
---

1. *[10 points]* Match spectra *a-e* to the following compounds (all $C_{11}H_{16}$).

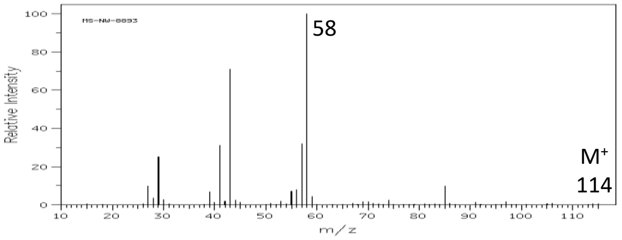


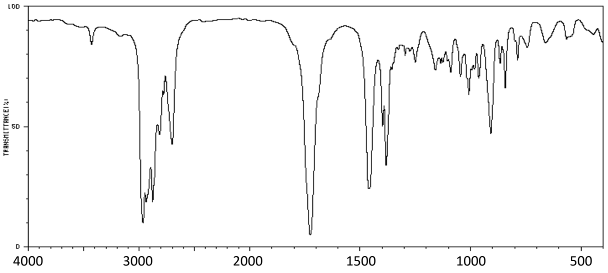
2. *[80 points]* Provide the structures of compounds **F**, **G**, **H** and **I**. Partial credit will be assigned for correct structural information that you provide (e.g., formula, functional groups, presence of specific alkyl groups, benzene substitution patterns, etc.)

H

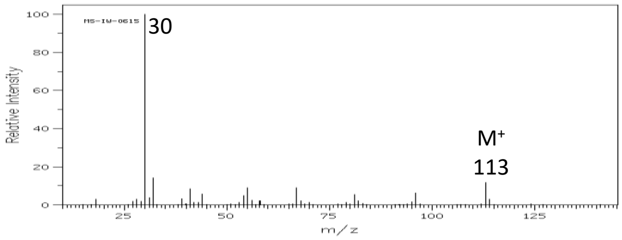


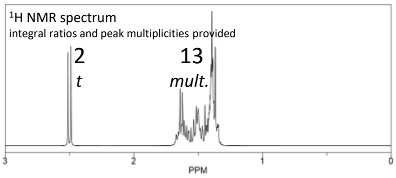
F

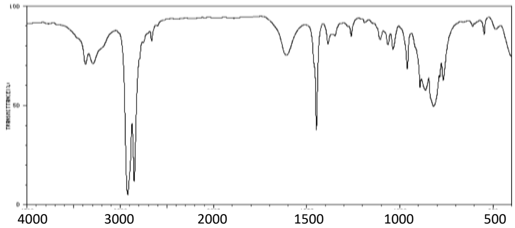




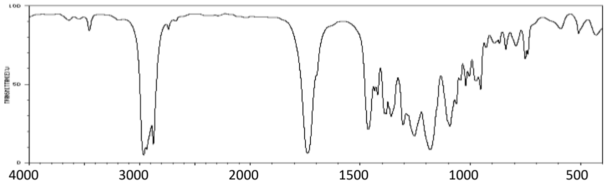
G

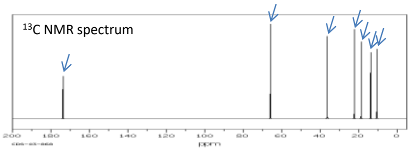

MS-IW-0615
30
M+
113
Relative Intensity
100
80
60
40
20
0
25
50
75
100
125
m/z

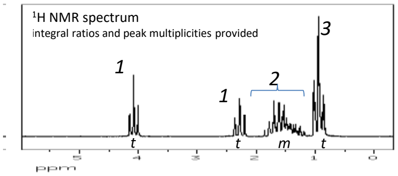

1H NMR spectrum
integral ratios and peak multiplicities provided
2
t
13
mult.
3
2
1
0
PPM

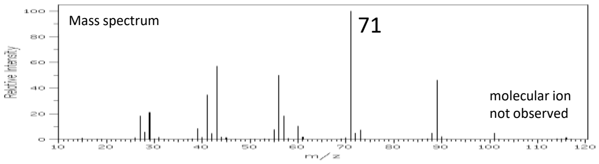

100
50
0
4000
3000
2000
1500
1000
500

I

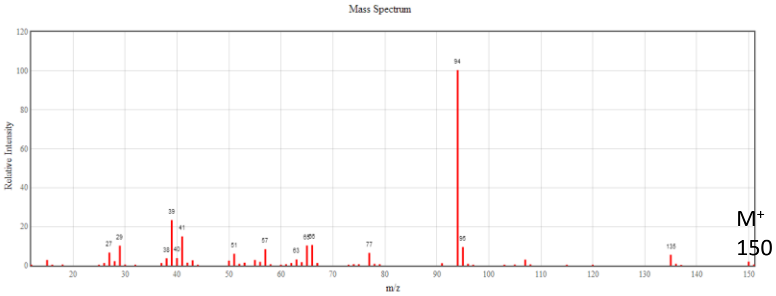

100
50
0
4000
3000
2000
1500
1000
500


13C NMR spectrum
200
180
160
140
120
100
80
60
40
20
0
ppm


1H NMR spectrum
integral ratios and peak multiplicities provided
1
1
2
3
t
t
m
t
5
4
3
2
1
0
ppm


Mass spectrum
71
molecular ion
not observed
Relative Intensity
100
80
60
40
20
0
10
20
30
40
50
60
70
80
90
100
110
120
m/z

tert-butyl phenyl ether, Ph-O-C(CH_3)$_3$



1(a) Spectra **a**-**d**, four monosubstituted benzenes, $C_{11}H_{16}$ (MW = 148)