

# CHEMISTRY 552

Lecture 04

# Mass Spectrometry - Fragmentation

The molecular ion may possess a large amount of internal energy which causes it to undergo chemical reactions leading to smaller fragments.

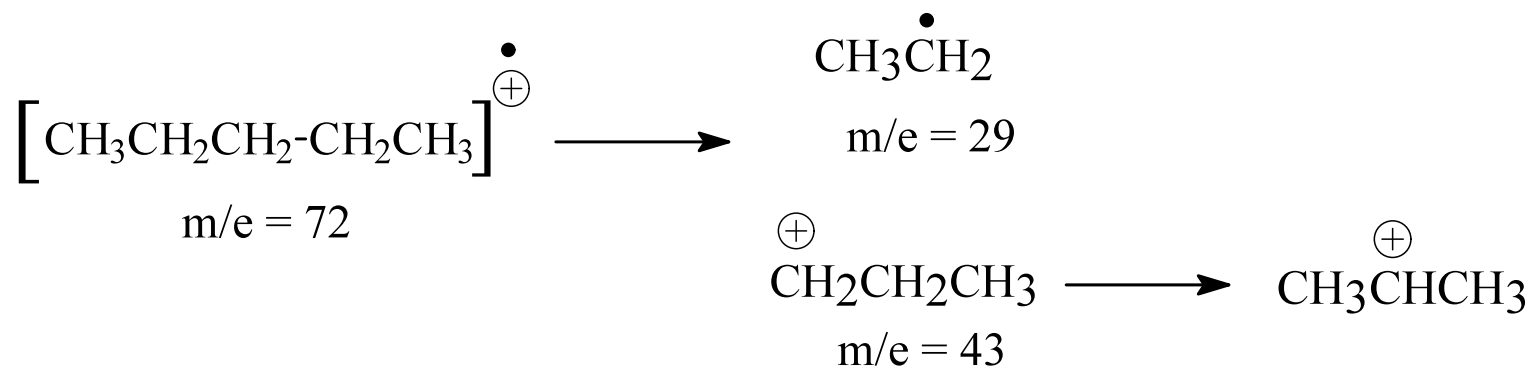
- The pressure in a mass spectrometer is very low which means that collisions are rare. Fragments are formed by unimolecular reactions.

Typically only one fragment will be charged and observed in the mass spectrum. Its mass will be recorded by the instrument.

By subtracting the mass of an observed fragment from the mass of the molecular ion we can obtain the mass of the unobserved fragment.

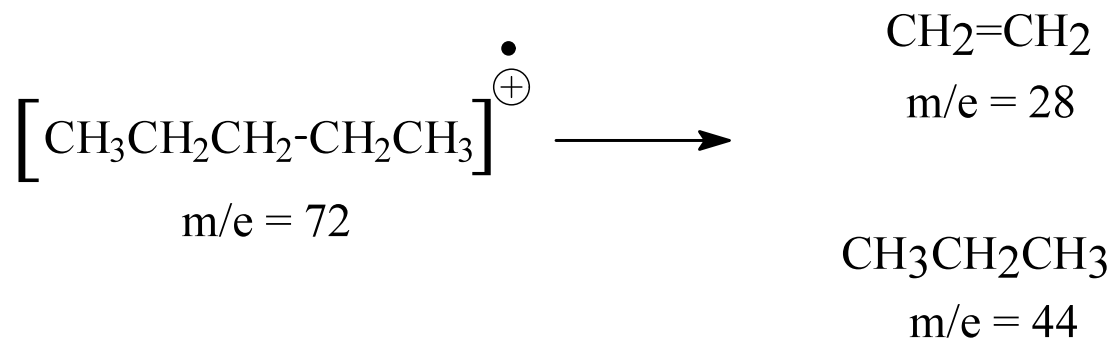
Fragmentation may occur by cleaving one bond or two.

A one bond cleavage with an even number molecular ion produces odd numbered fragments.

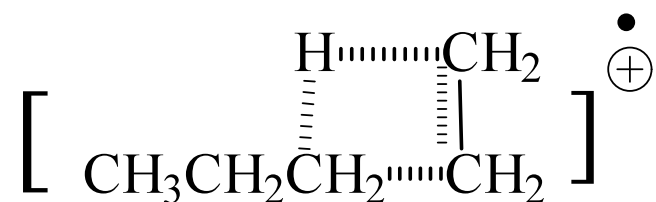


Once formed a fragment ion may undergo subsequent reactions.

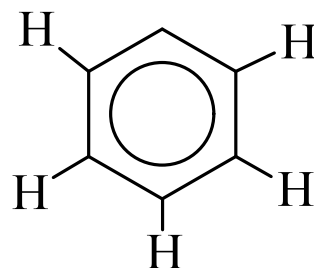
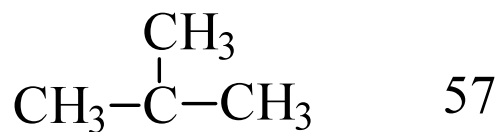
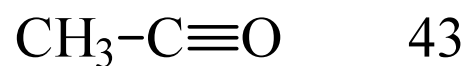
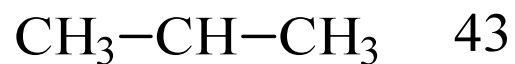
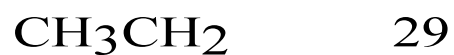
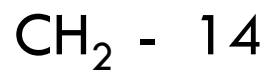
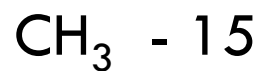
A two bond cleavage of an even-number ion produces even-numbered fragments.



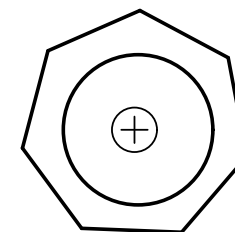
A two bond cleavage will often require a cyclic transition state.



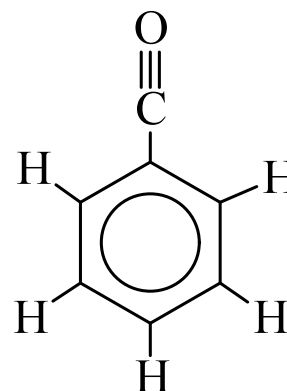
Certain numbers show up often in mass spectra.



77




91



105



Reactions in a mass spectrometer are subject to most of the same criteria as reactions in solution.

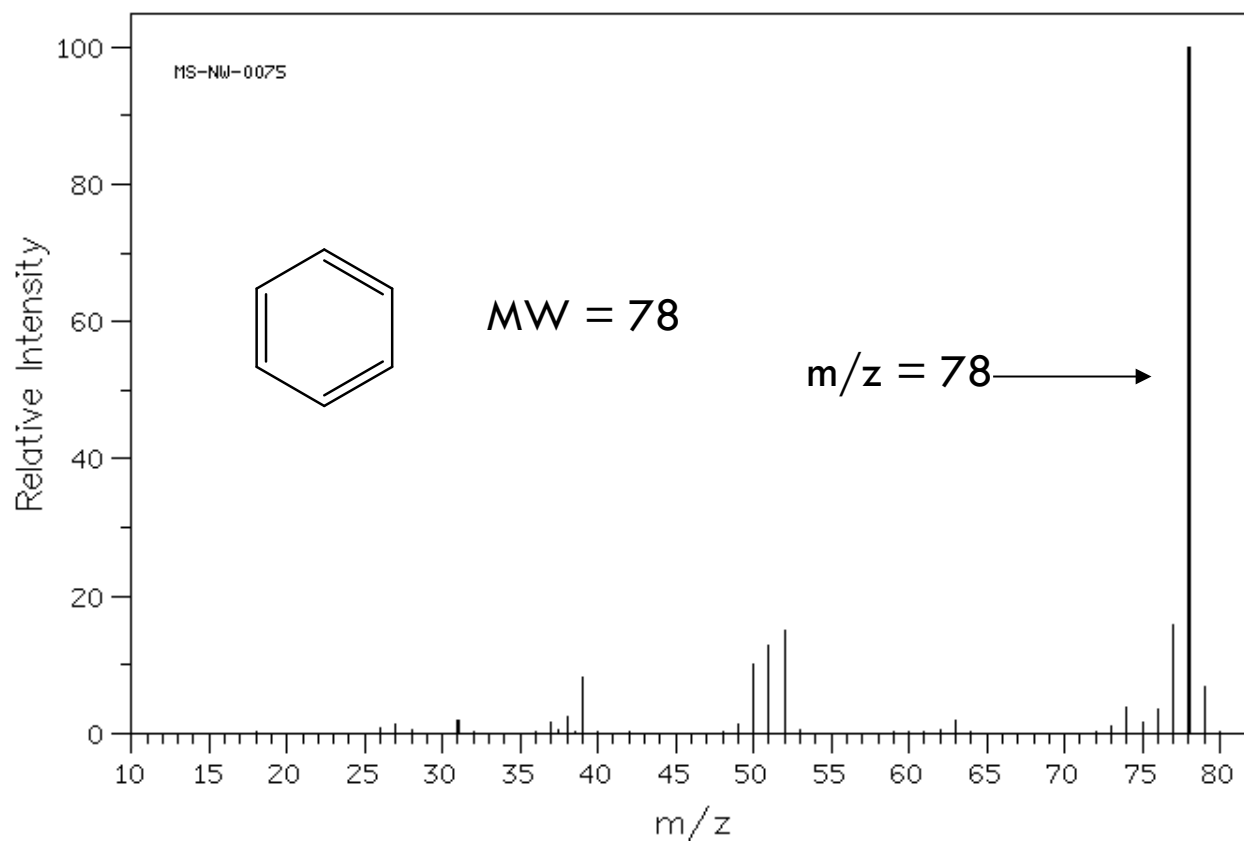


- Molecules with strong bonds react slower.
- Reactions with lower energies of activation occur faster.
- Hammond's postulate applies, that is:

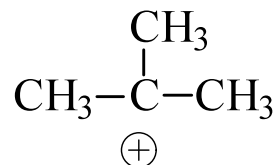
Reactions that produce more stable ions will have lower energies of activation and will occur faster.

Remember that the primary factor in determining the stability of ions is the distribution of the electrical charge over a larger amount of space.

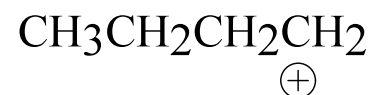
The  $M^+$  peak is very strong in aromatics because of the tremendous stability of aromatic rings



The more alkyl groups attached to a charged atom, the more stable the ion.

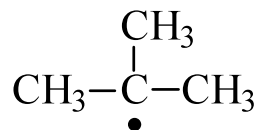


tertiary (3<sup>o</sup>) - most stable

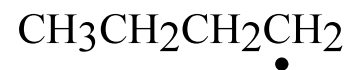


primary (1<sup>o</sup>) - least stable

The same order of stability exists for radicals, but the differences in stability are much less.

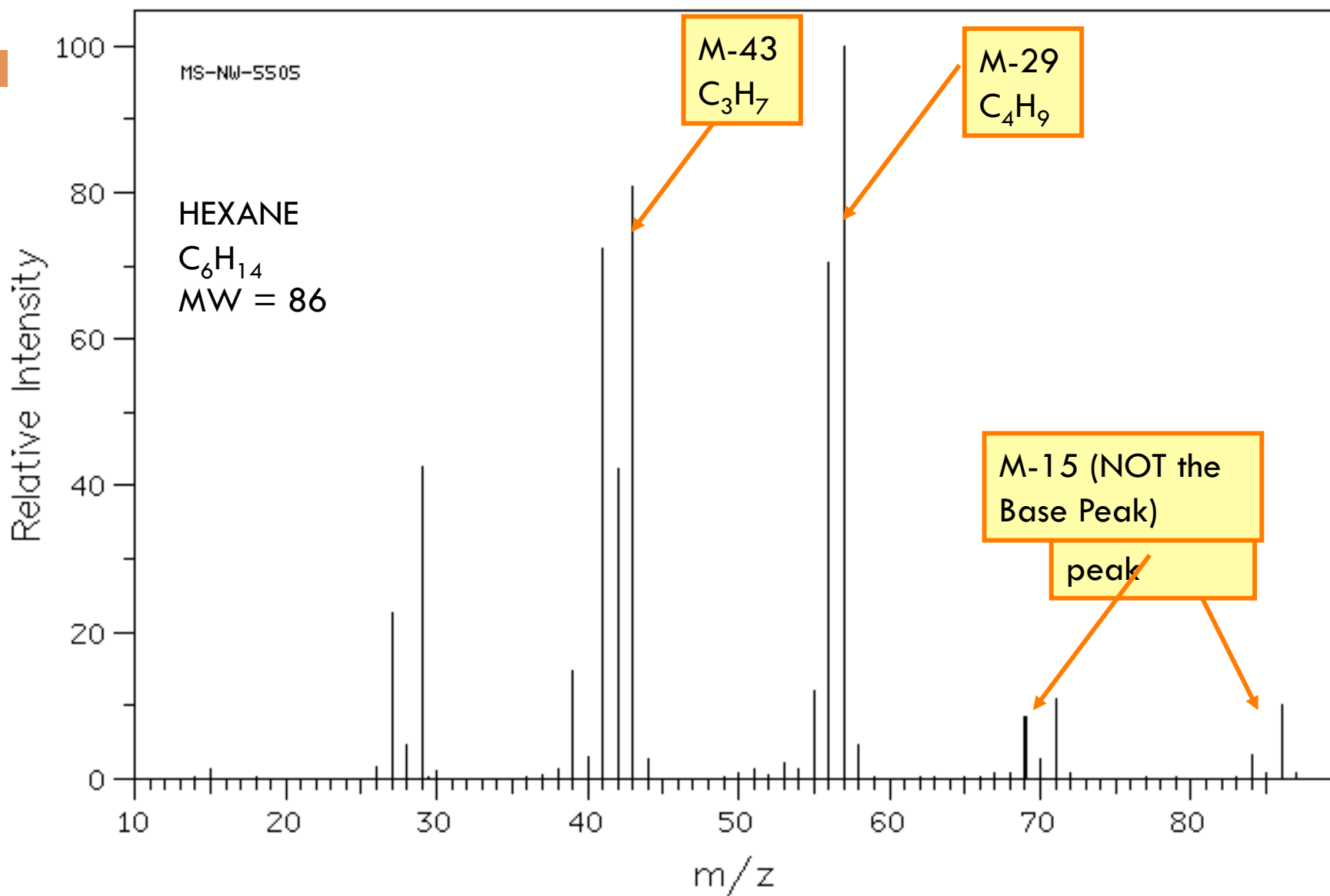


tertiary (3<sup>o</sup>) - most stable



primary (1<sup>o</sup>) - least stable

# Fragmentation of Straight Chain Hydrocarbons



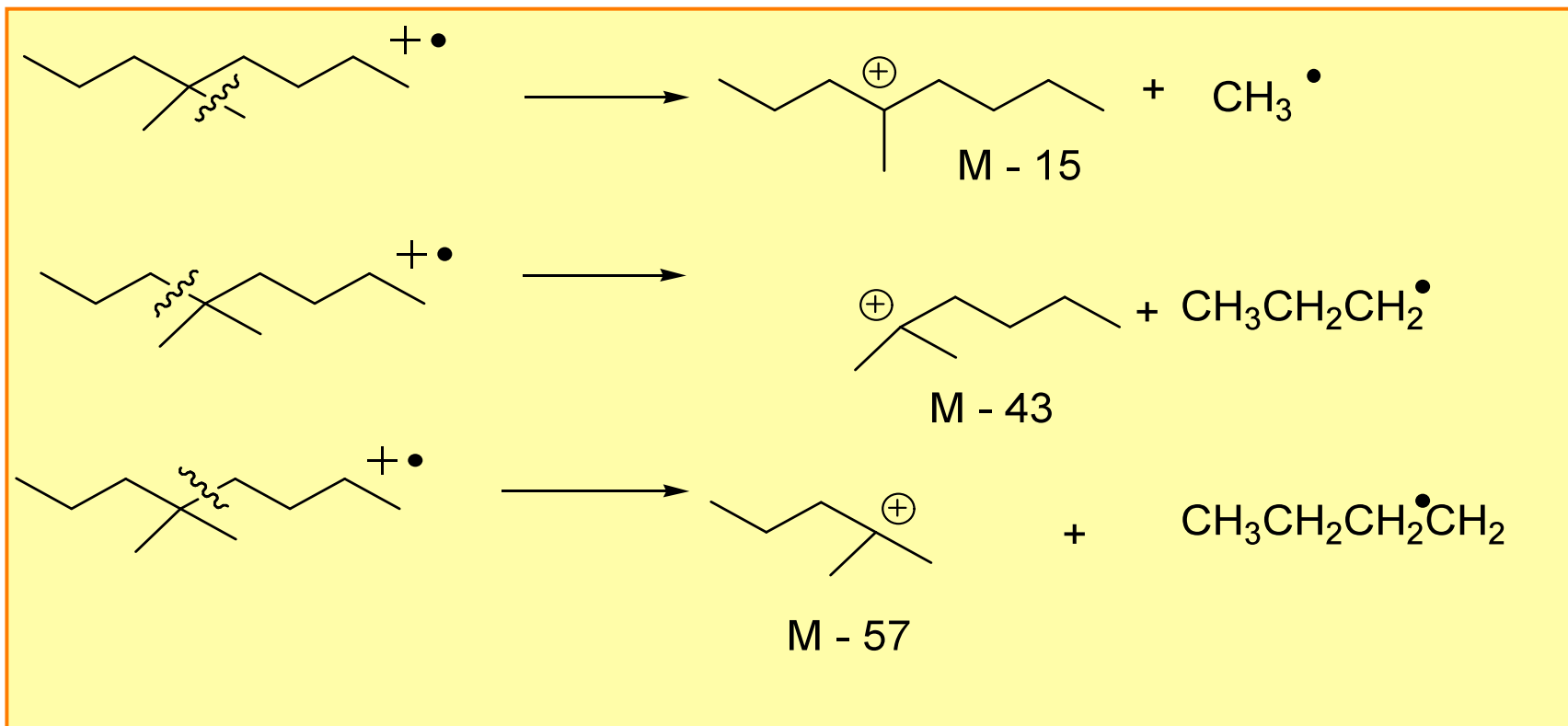
# Fragmentation of Branched Alkanes



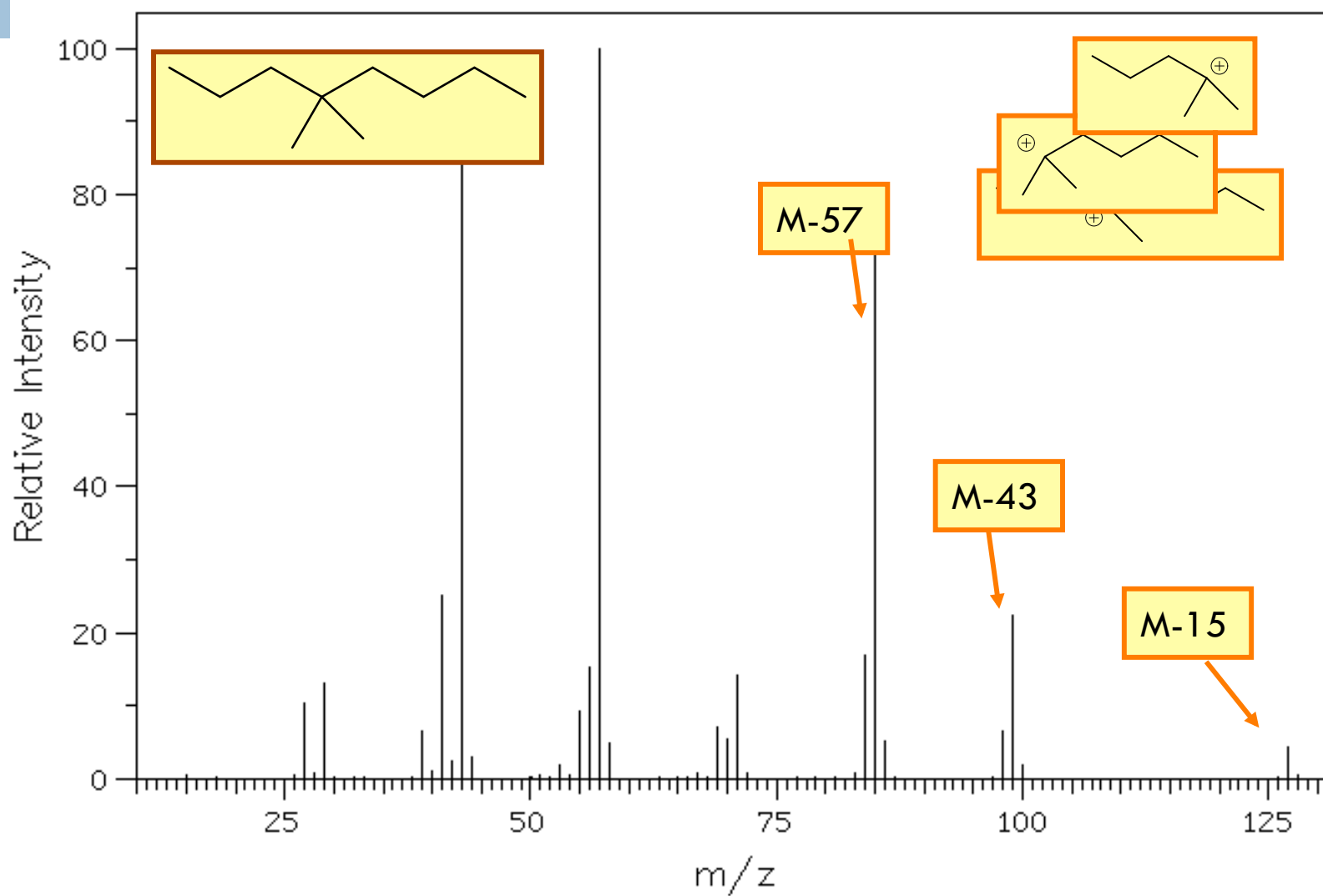
- Branch points can lead to relatively stable carbocations, so molecular ion peak is not always present


- Fragmentation will lead to the most stable carbocations, which then will lose CH<sub>2</sub> groups as before

# Predicted Fragmentation of 4,4-dimethyloctane

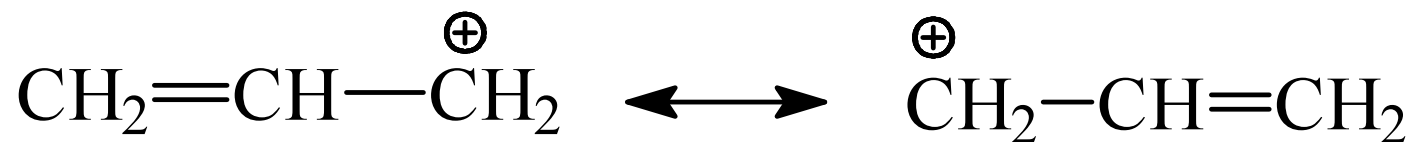
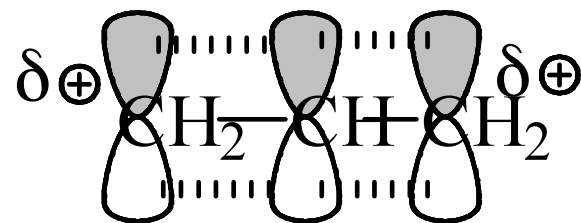
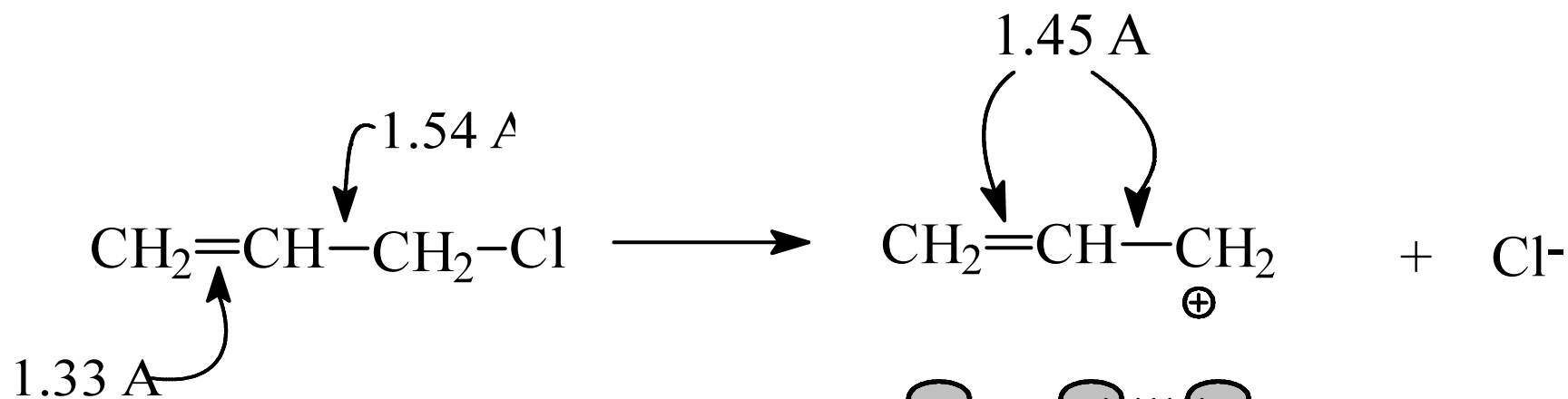


# Fragmentation of Branched Alkanes: 4,4-dimethyloctane (MW = 142)

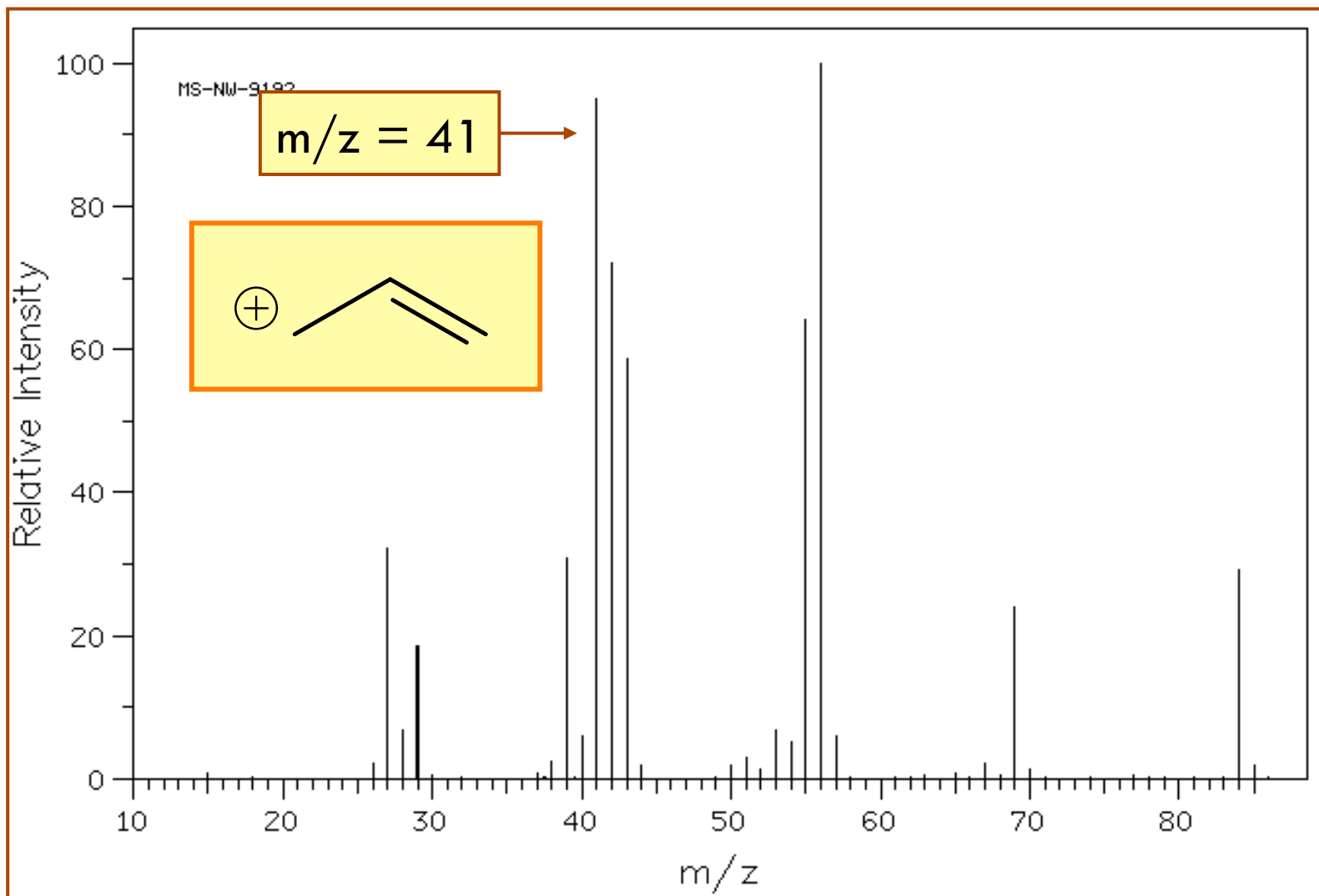
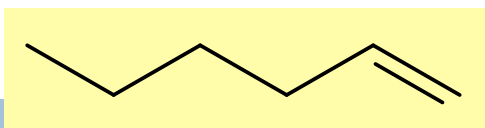




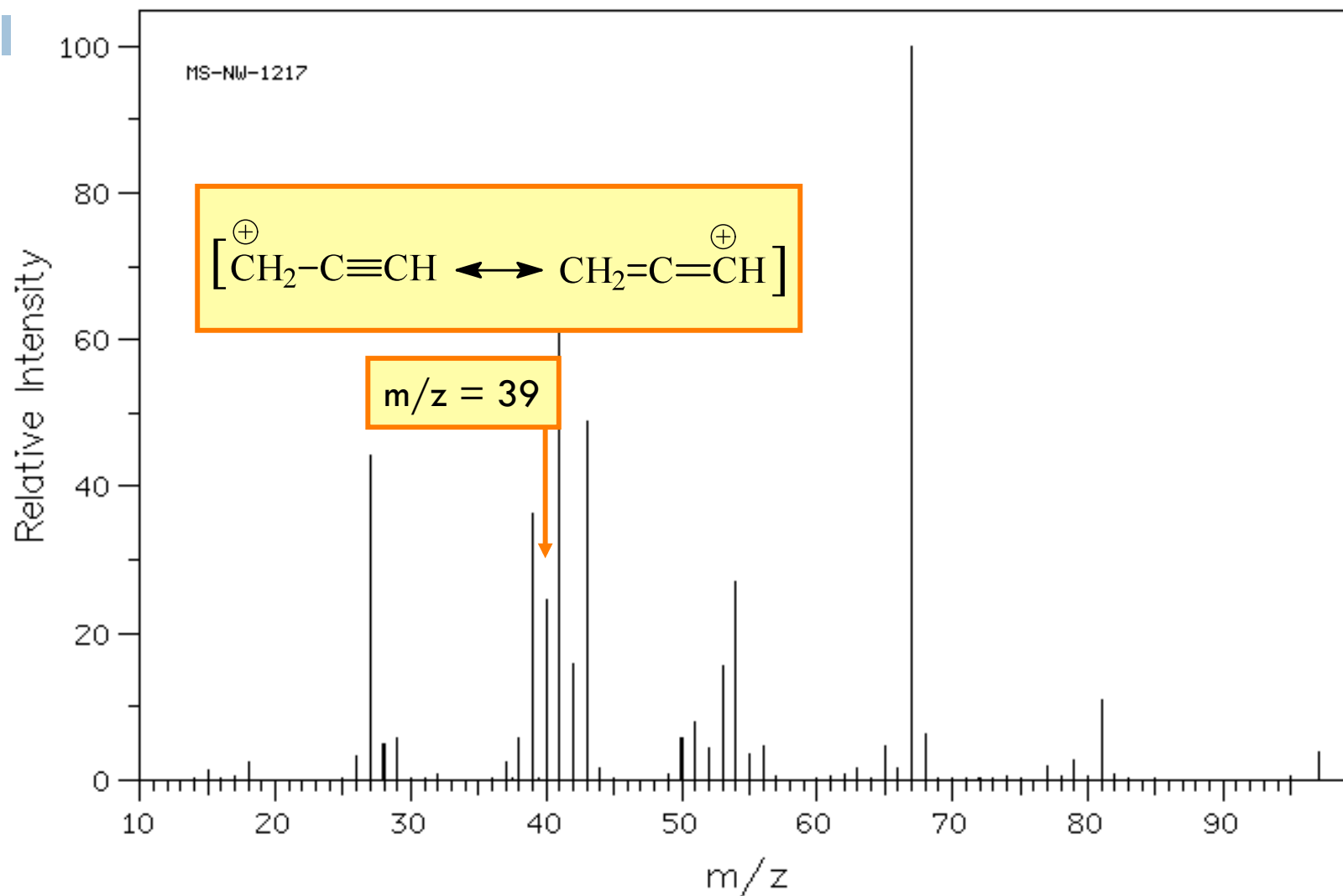
Ions for which resonance structures may be drawn are often very stable since their electrical charge may be distributed over several different atoms.



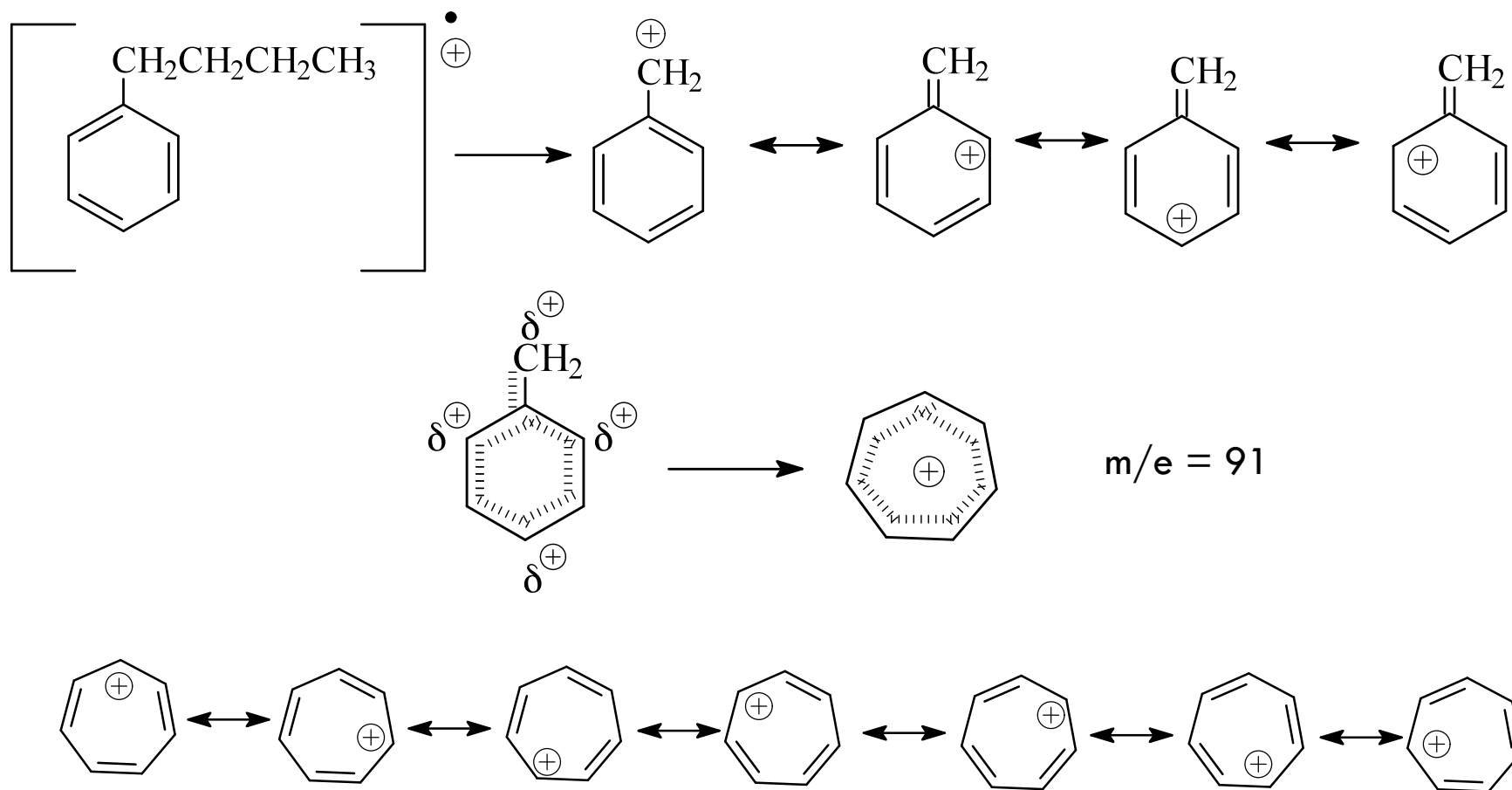
# Fragmentation of 1-hexene (MW = 84)

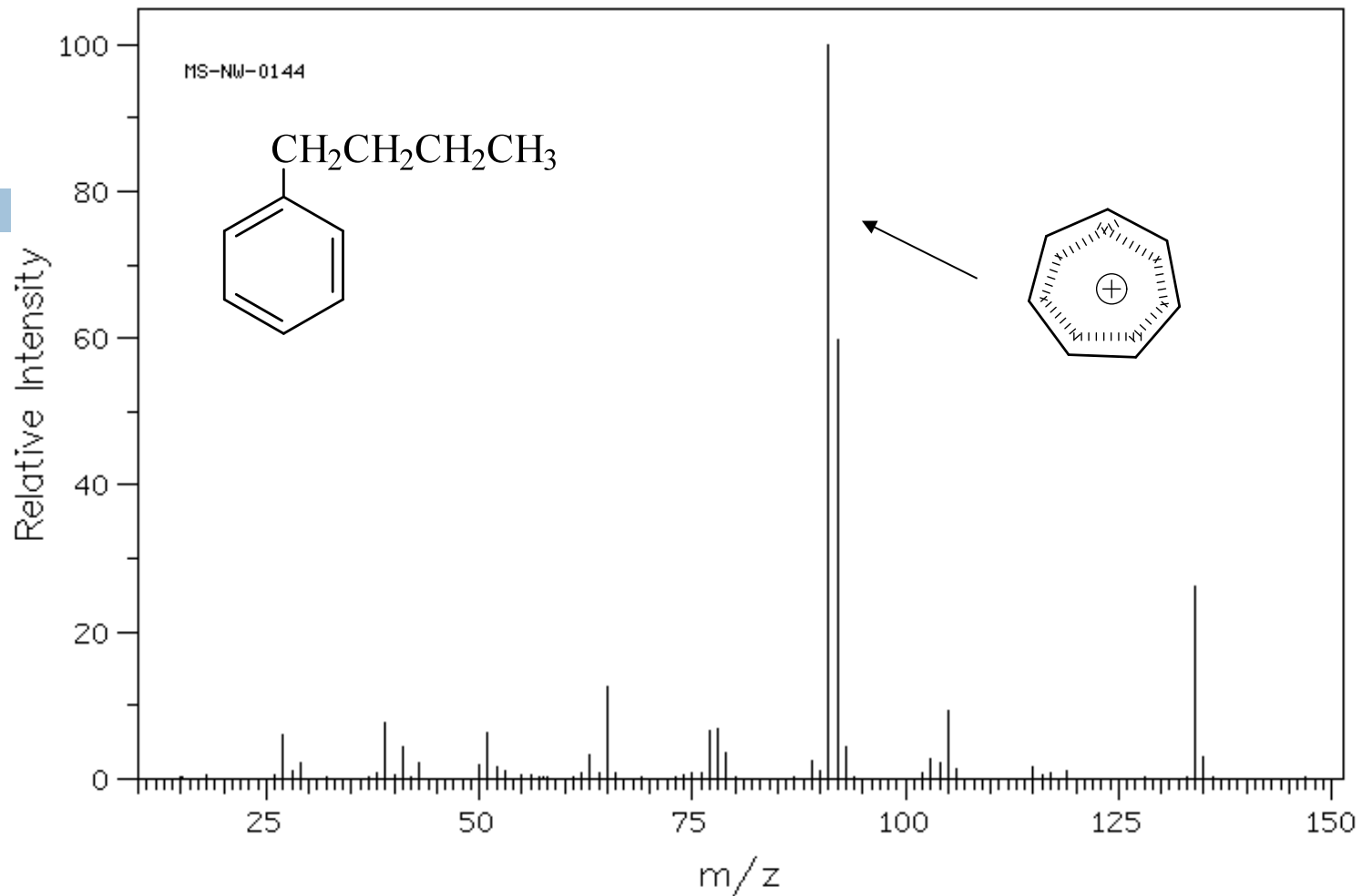


# 1-Hexyne MW = 82

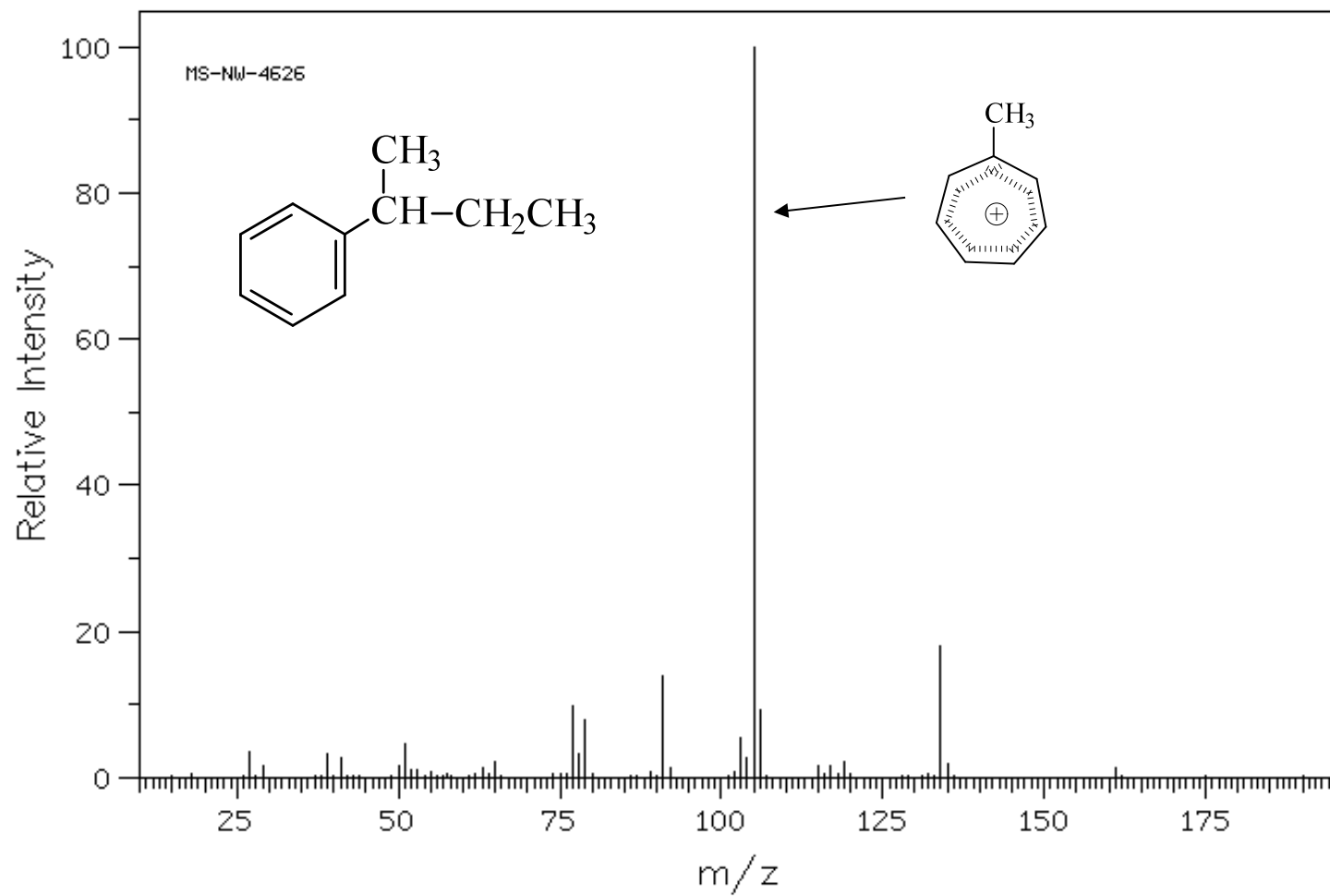


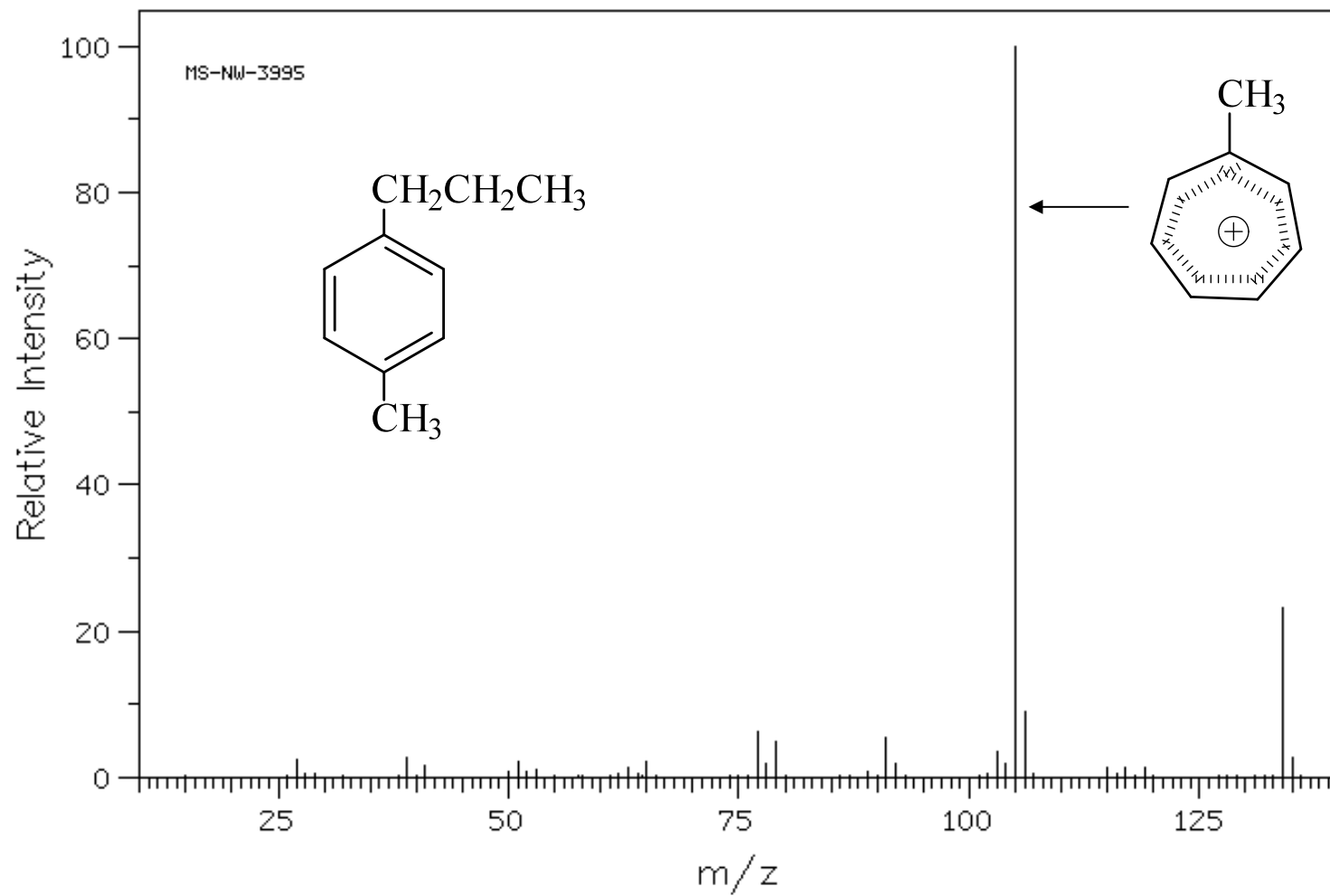
Benzene derivatives produce a variety of resonance stabilized ions.

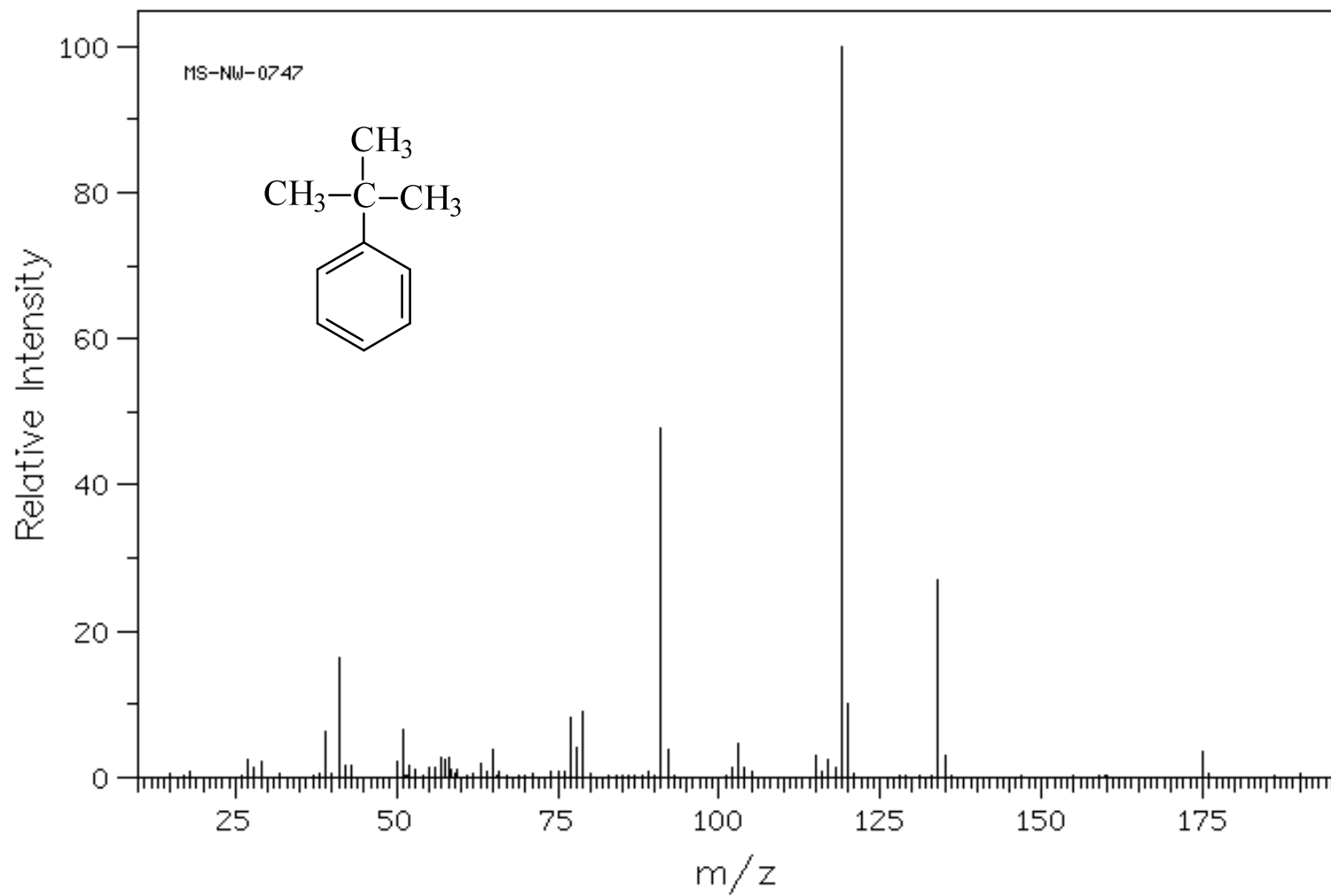




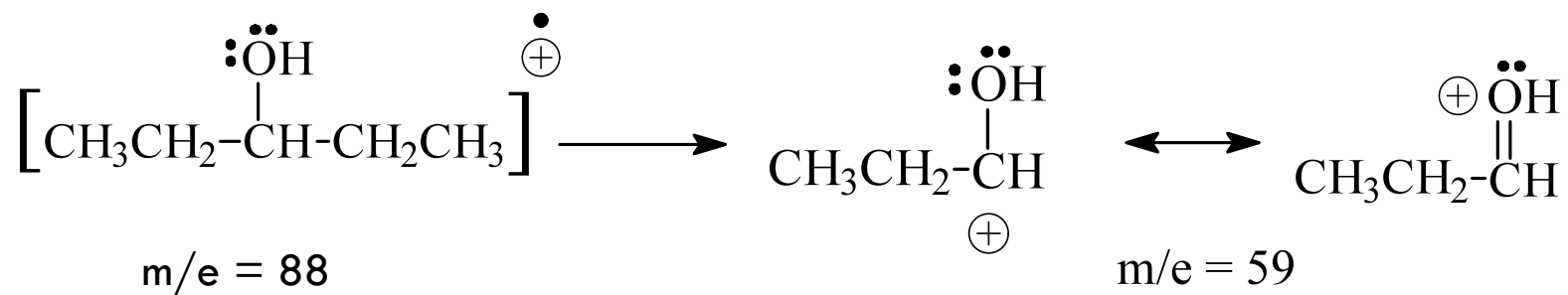
What can you say about the peak at  $m/e = 92$ . We will come back to it later.

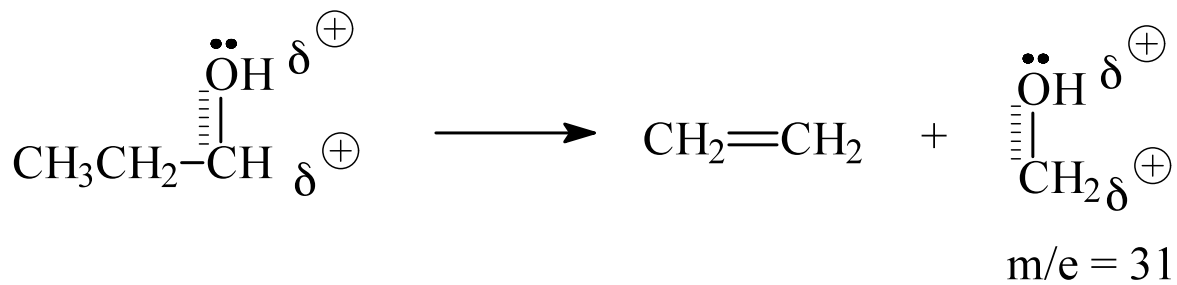
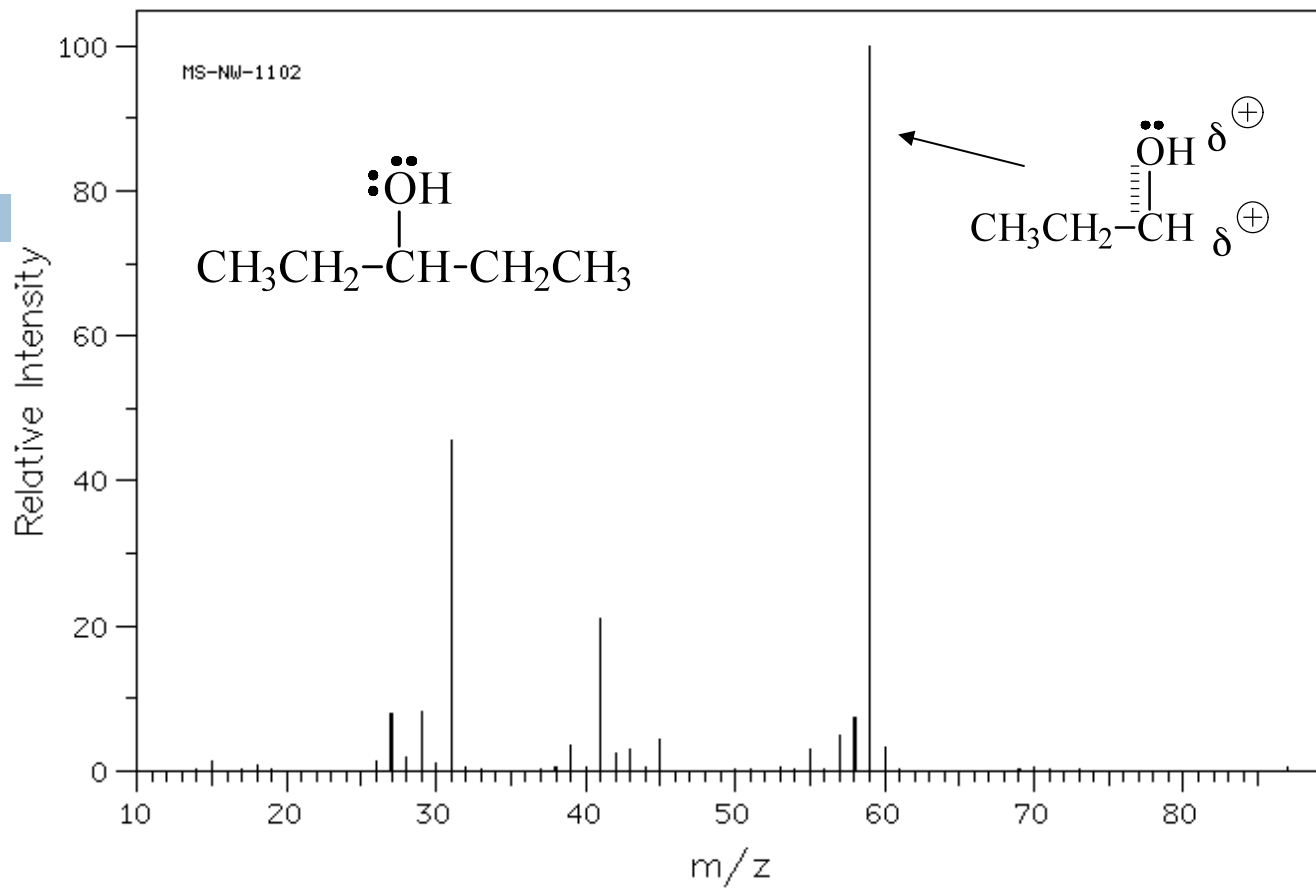




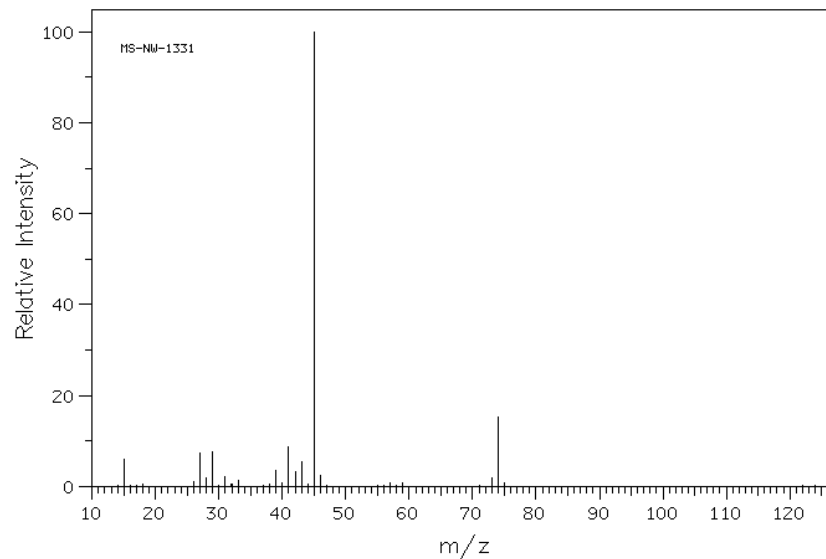
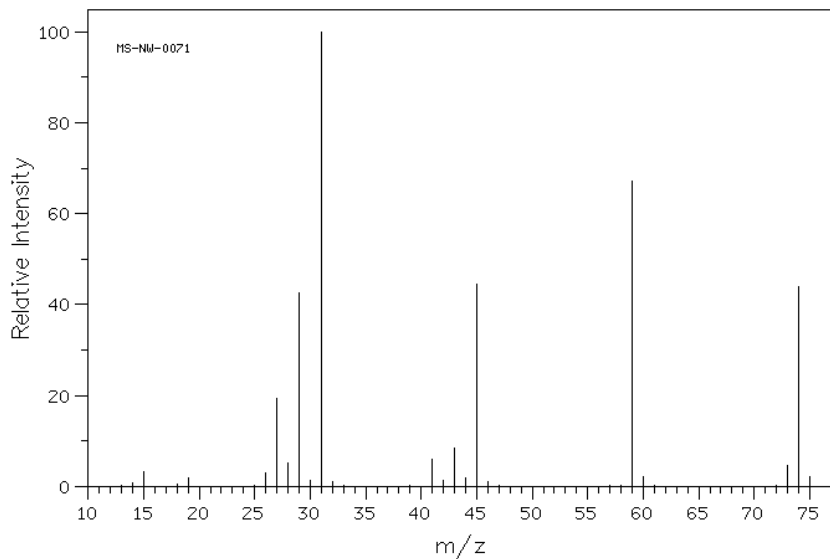


Positive ions are stabilized by an adjacent heteroatom with a nonbonded pair of electrons.

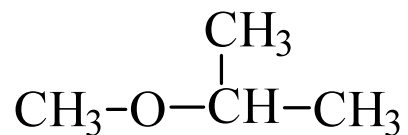
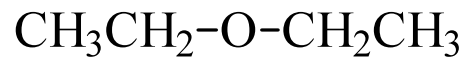




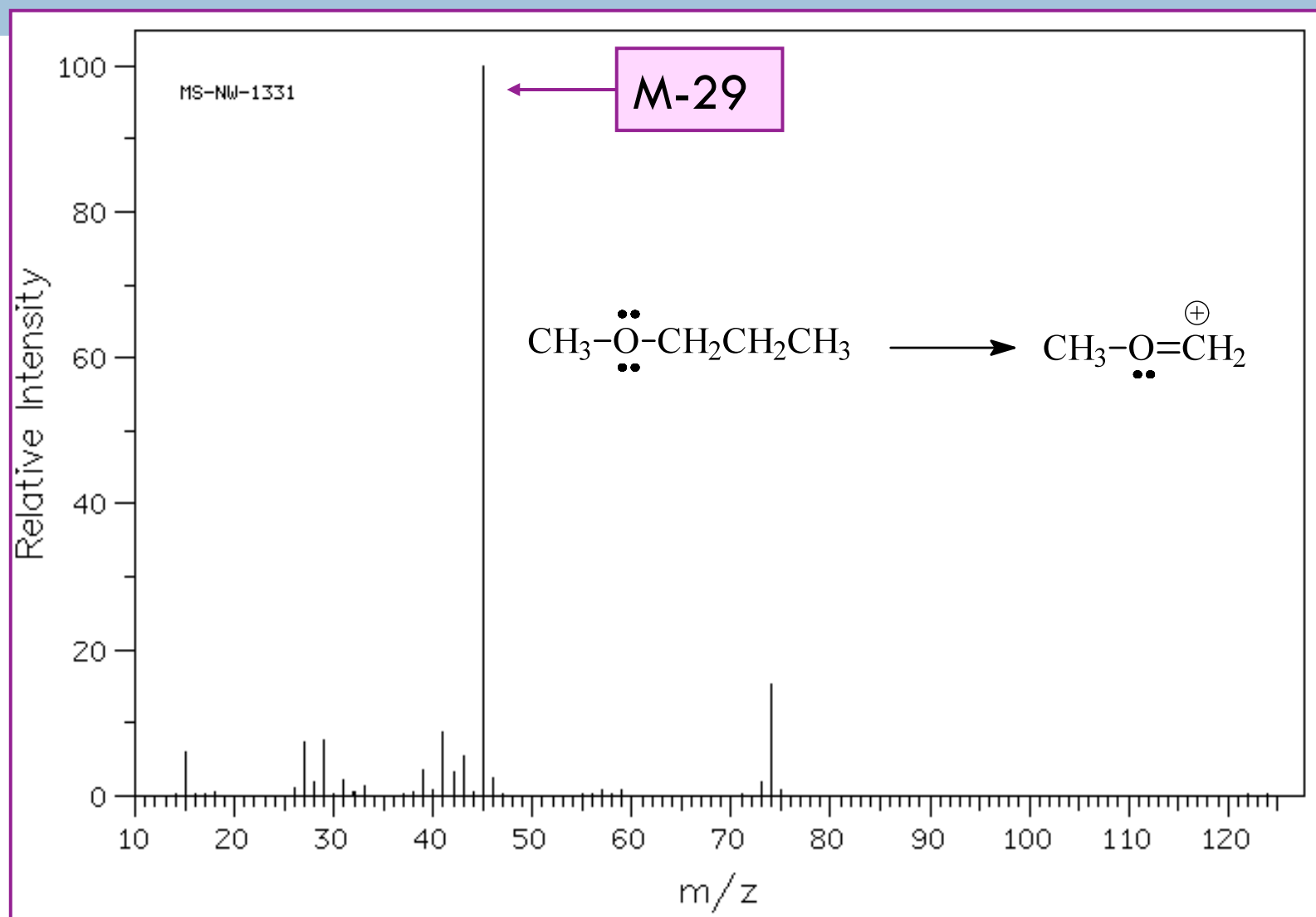
# Identify these ethers, MW=74



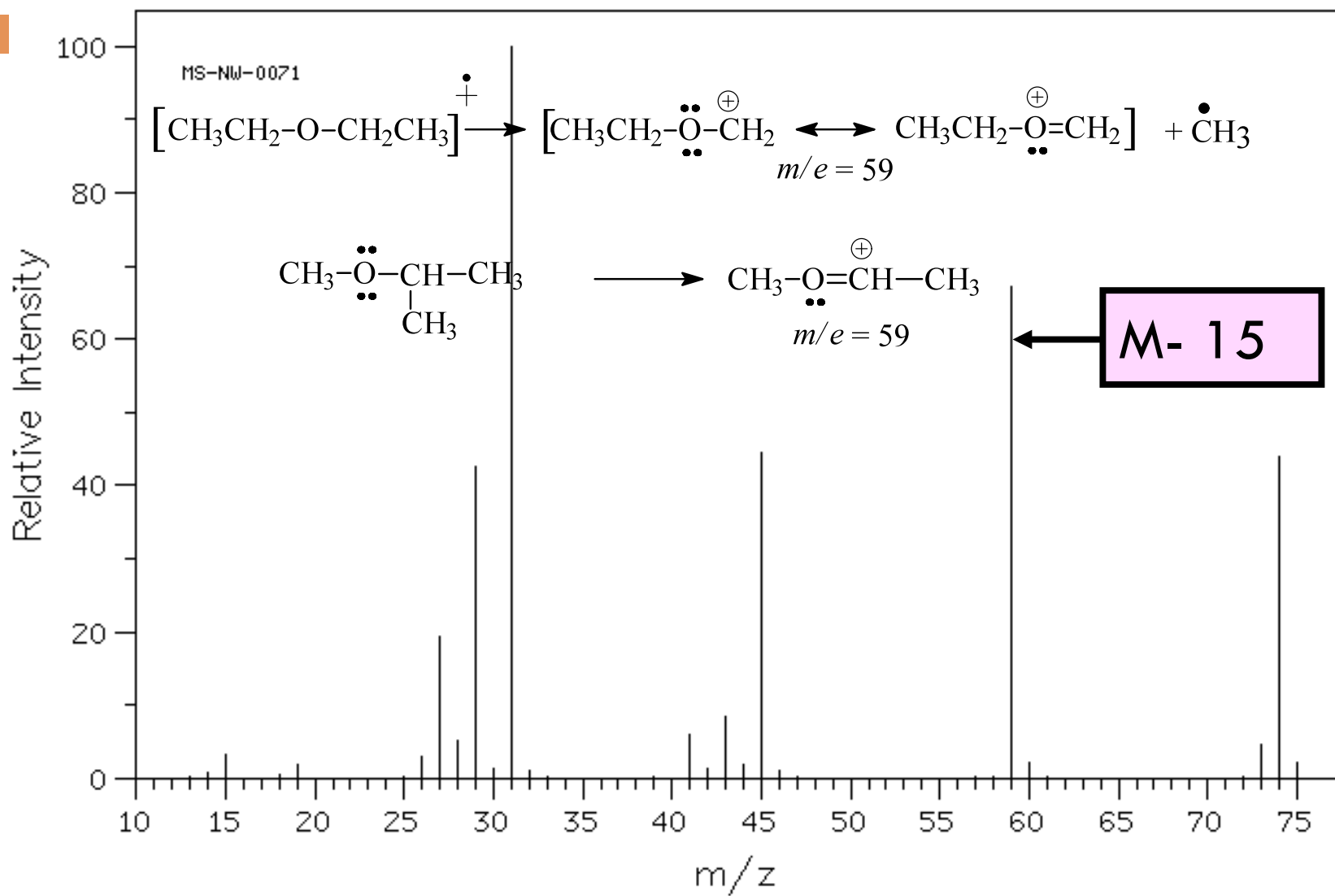
There are 3 possible structures



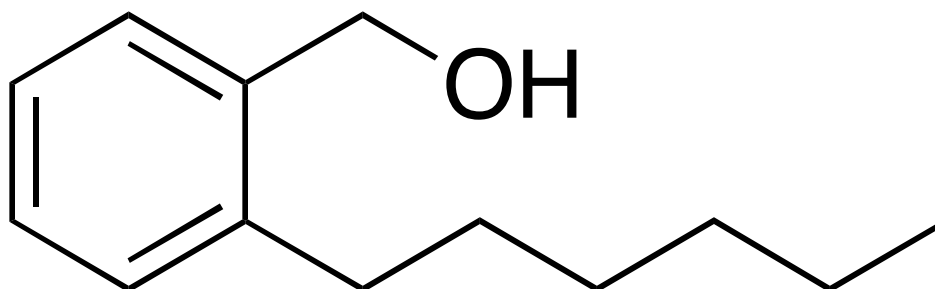
# Loss of an ethyl group



# Loss of a Methyl Group fits two of the structures!

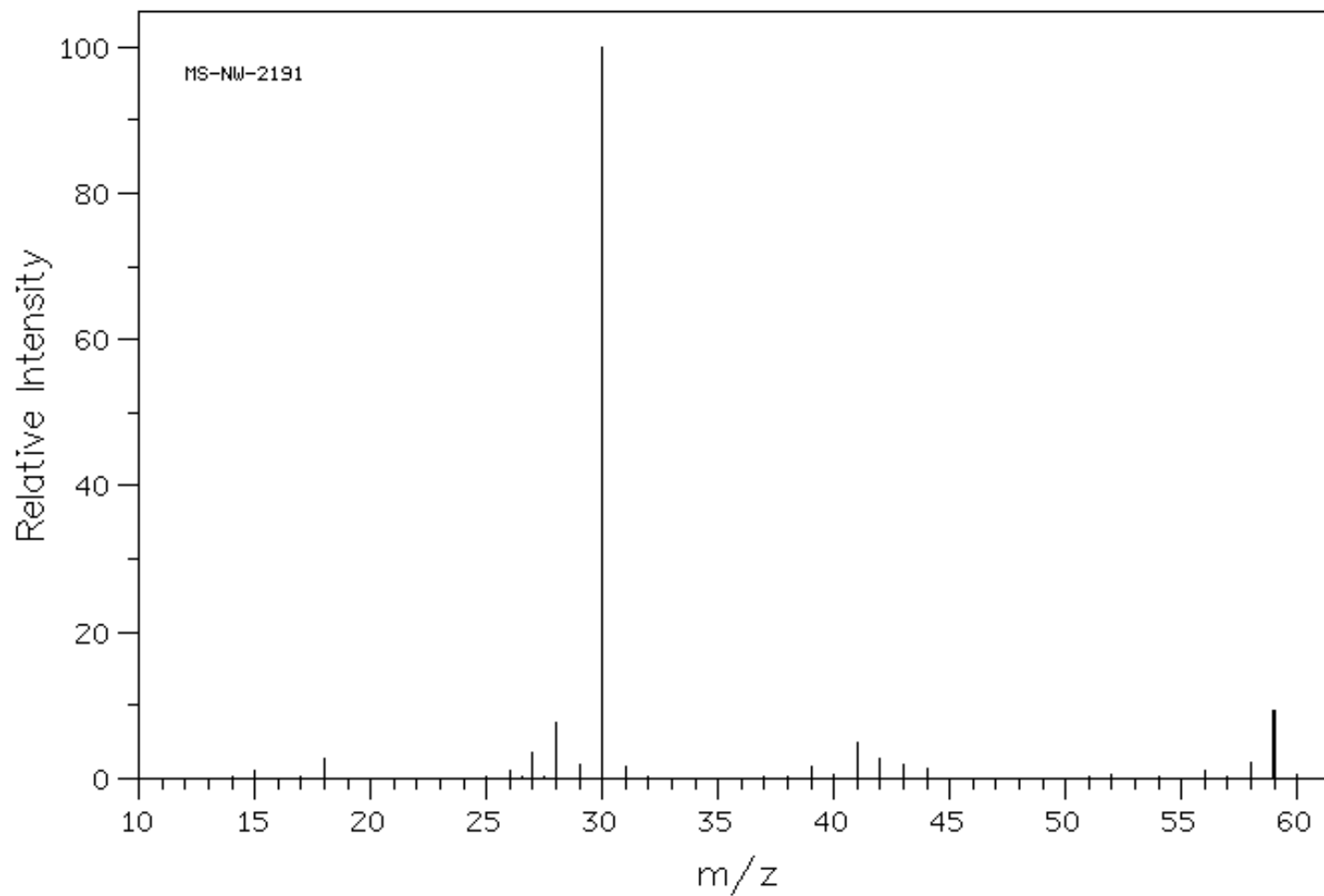
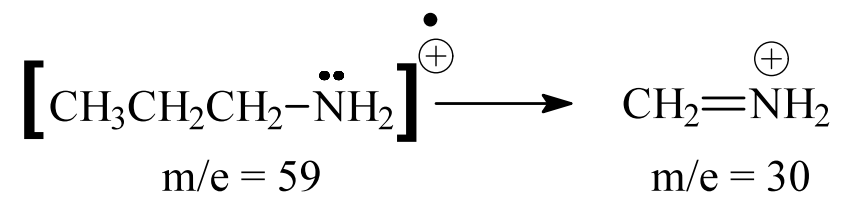


# Let's do a problem...together...

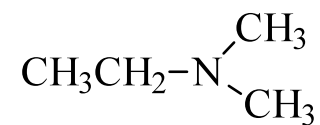
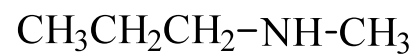
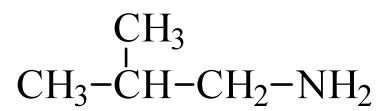
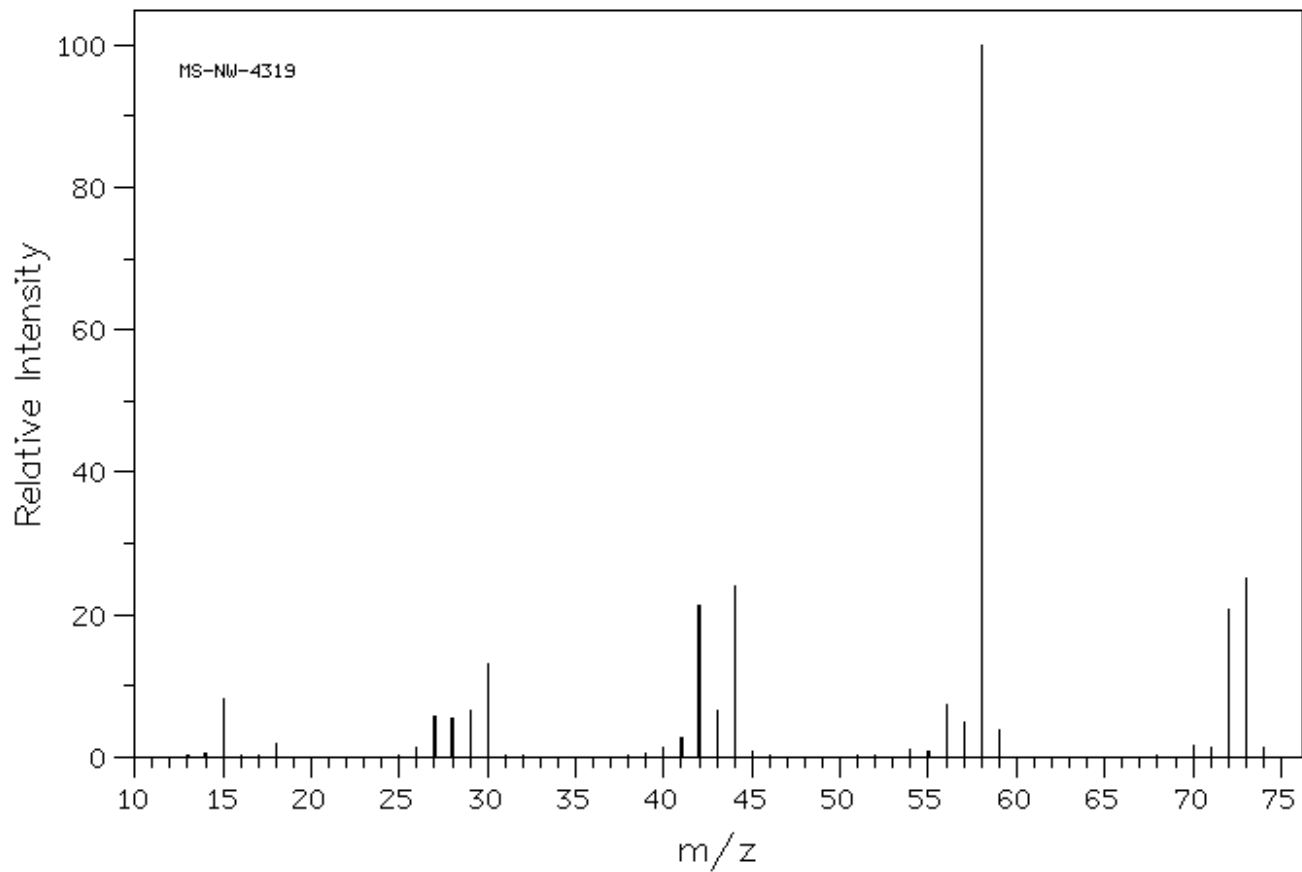


Assume EI:

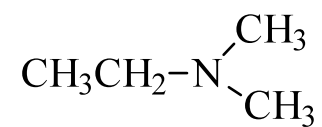
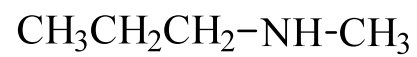
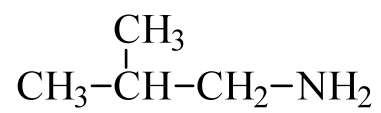
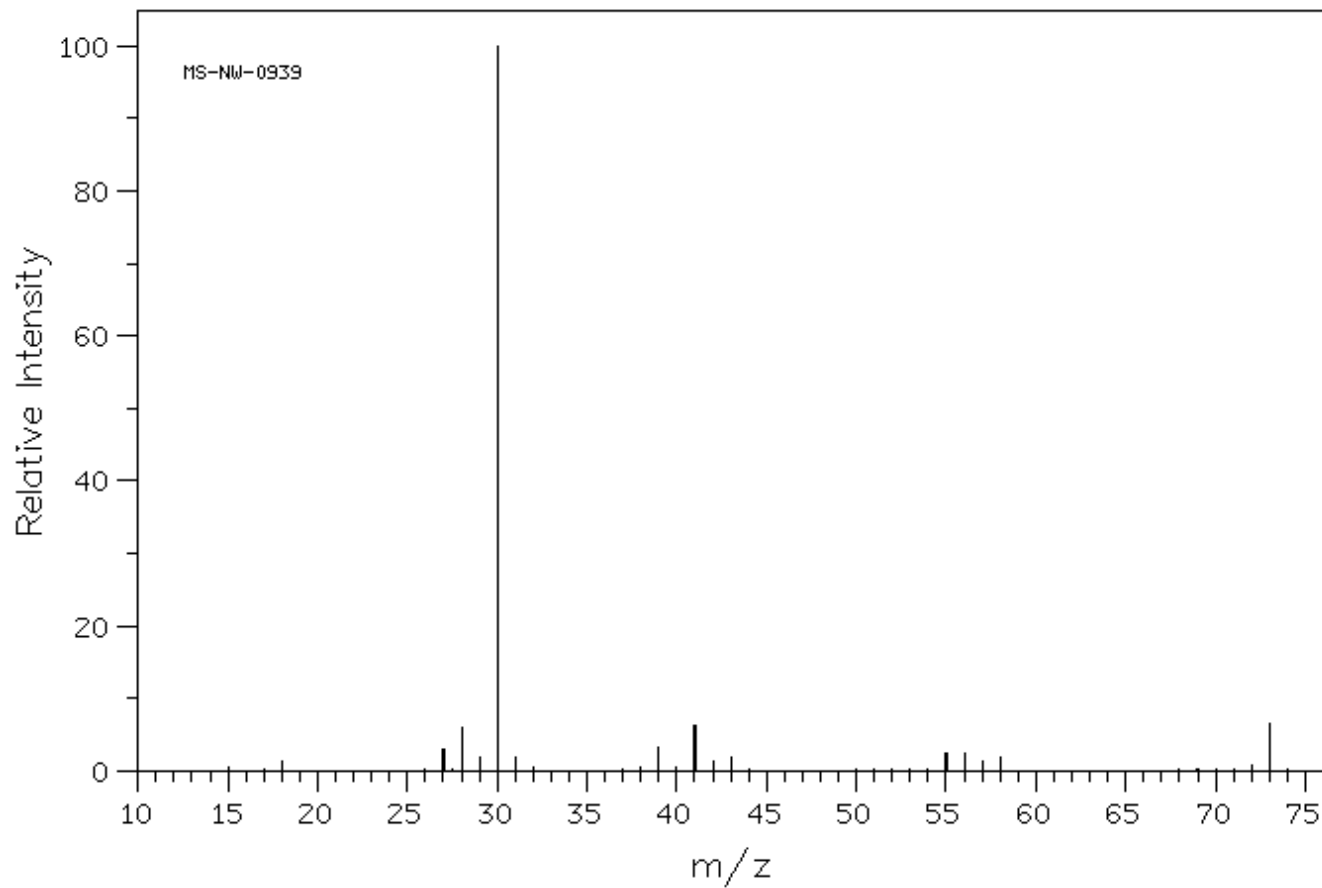
- Structure of molecular ion, showing location of radical cation.
- Predict three major fragmentation/rearrangement pathways.
- For each fragmentation/rearrangement, use detailed single- or double-barbed arrows to describe mechanism.



Which amine produces this mass spectrum?

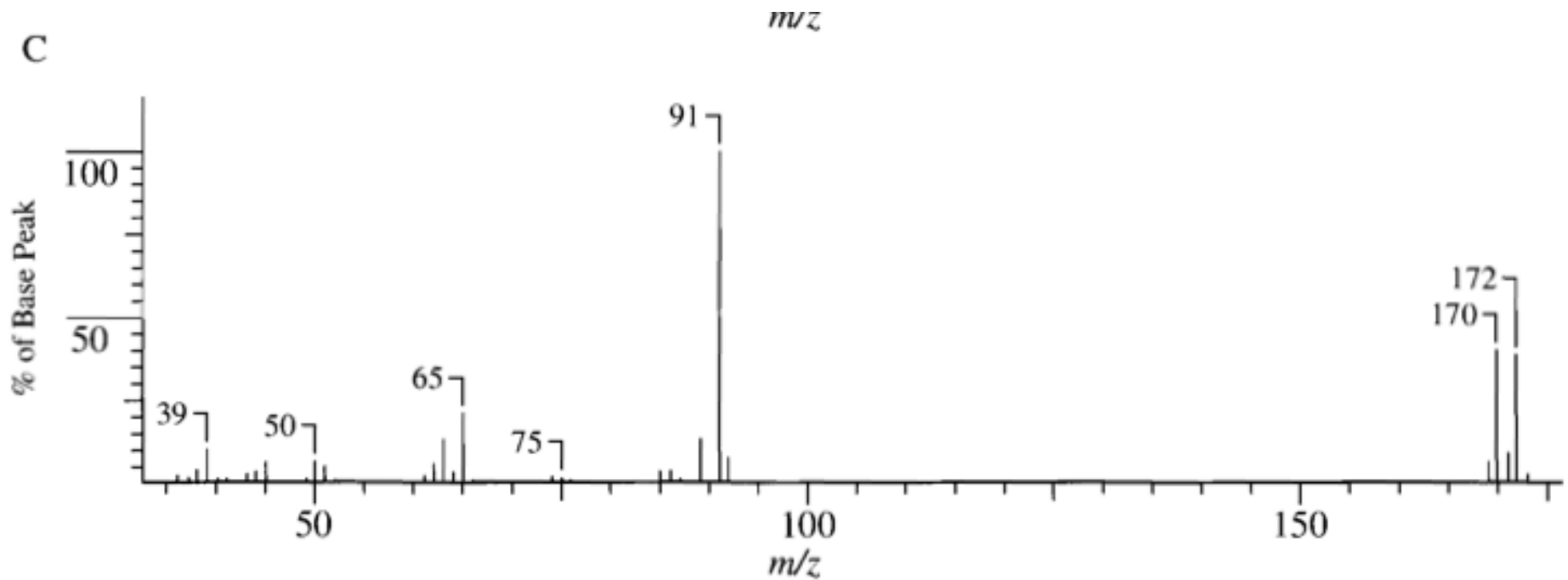


Which amine produces this mass spectrum?



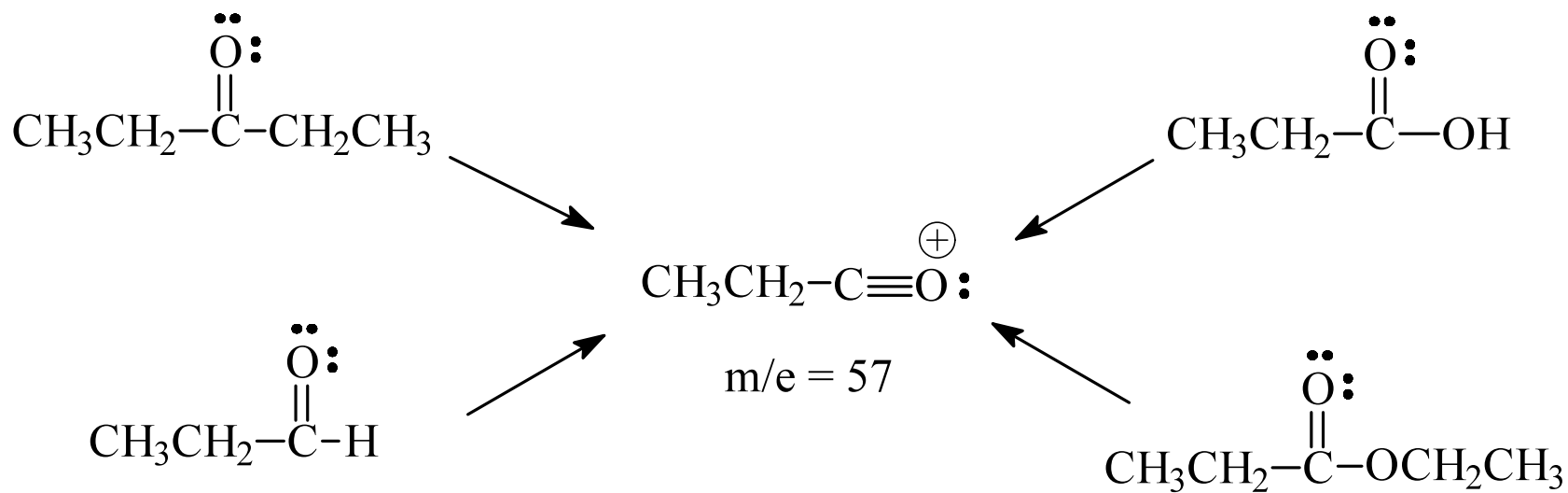
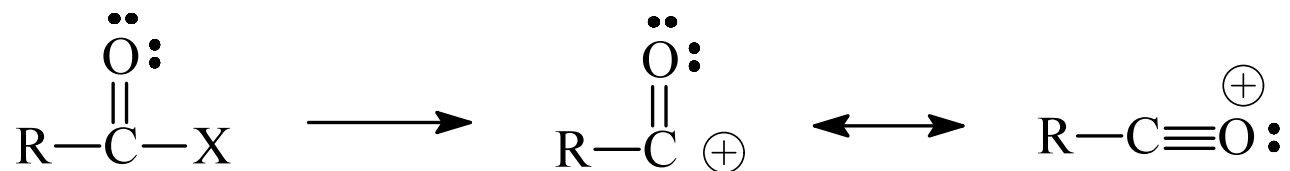
# Question...

What is the molecular ion and the base peak of this spectrum?

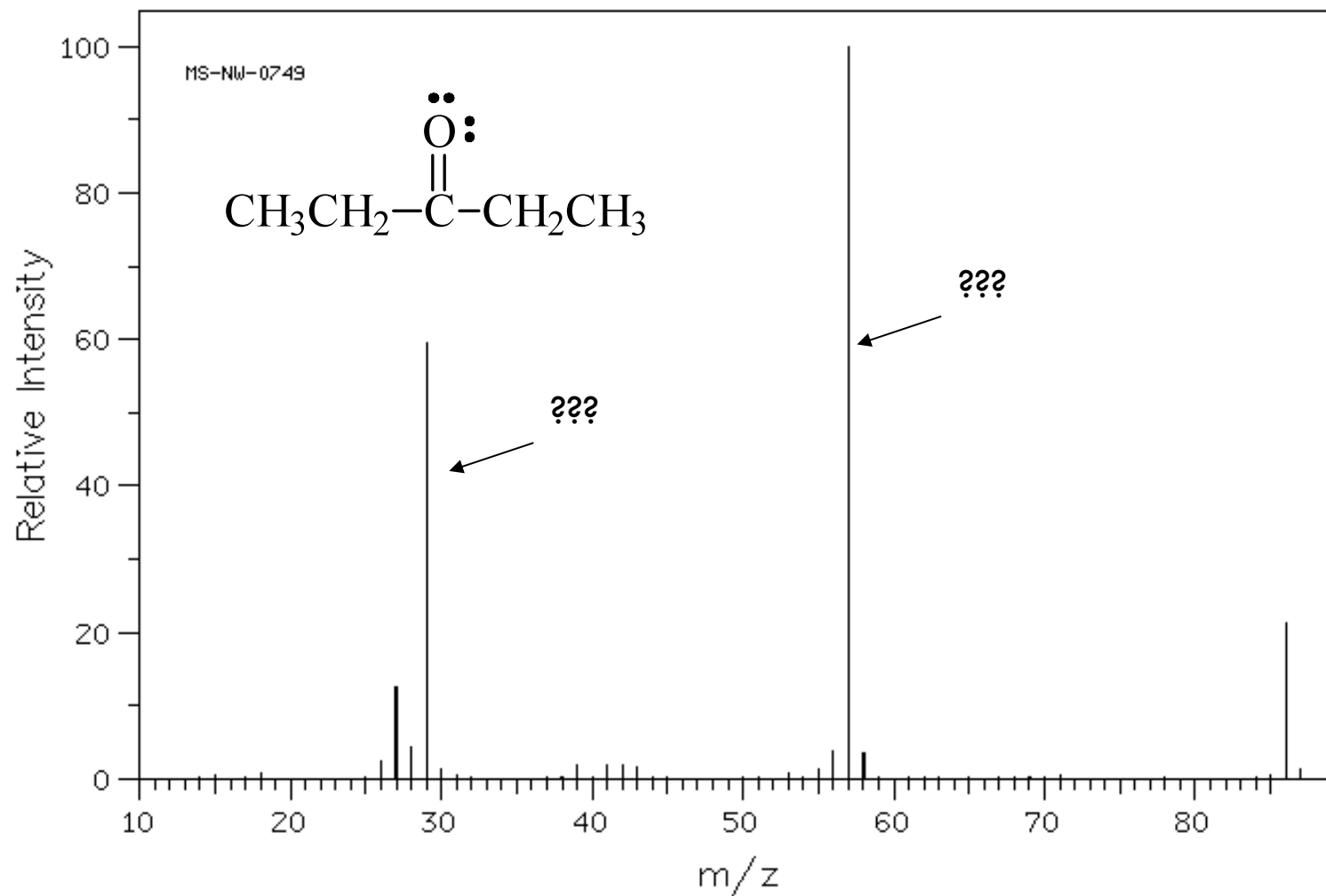


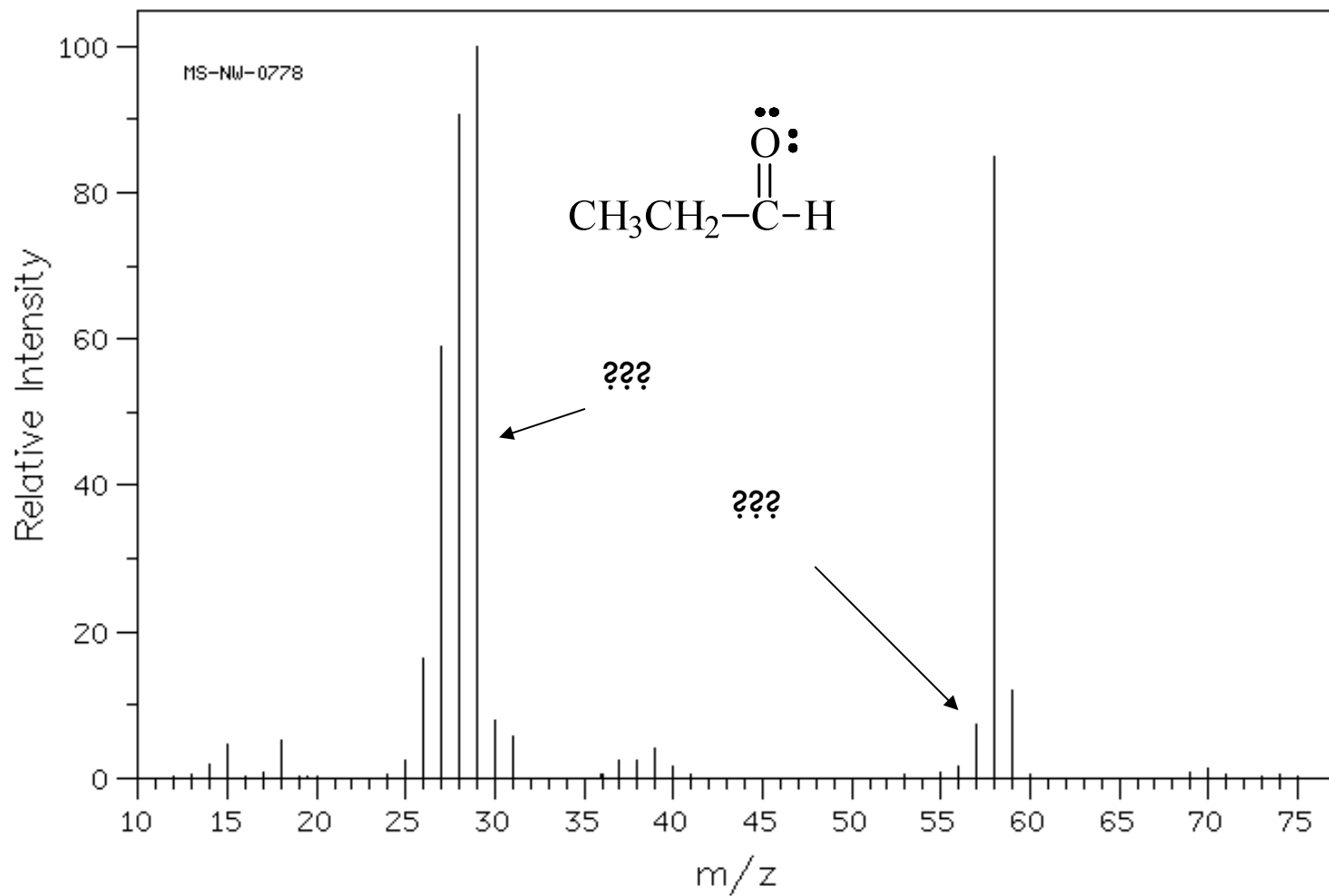
How can you explain peaks at 170 and 172?

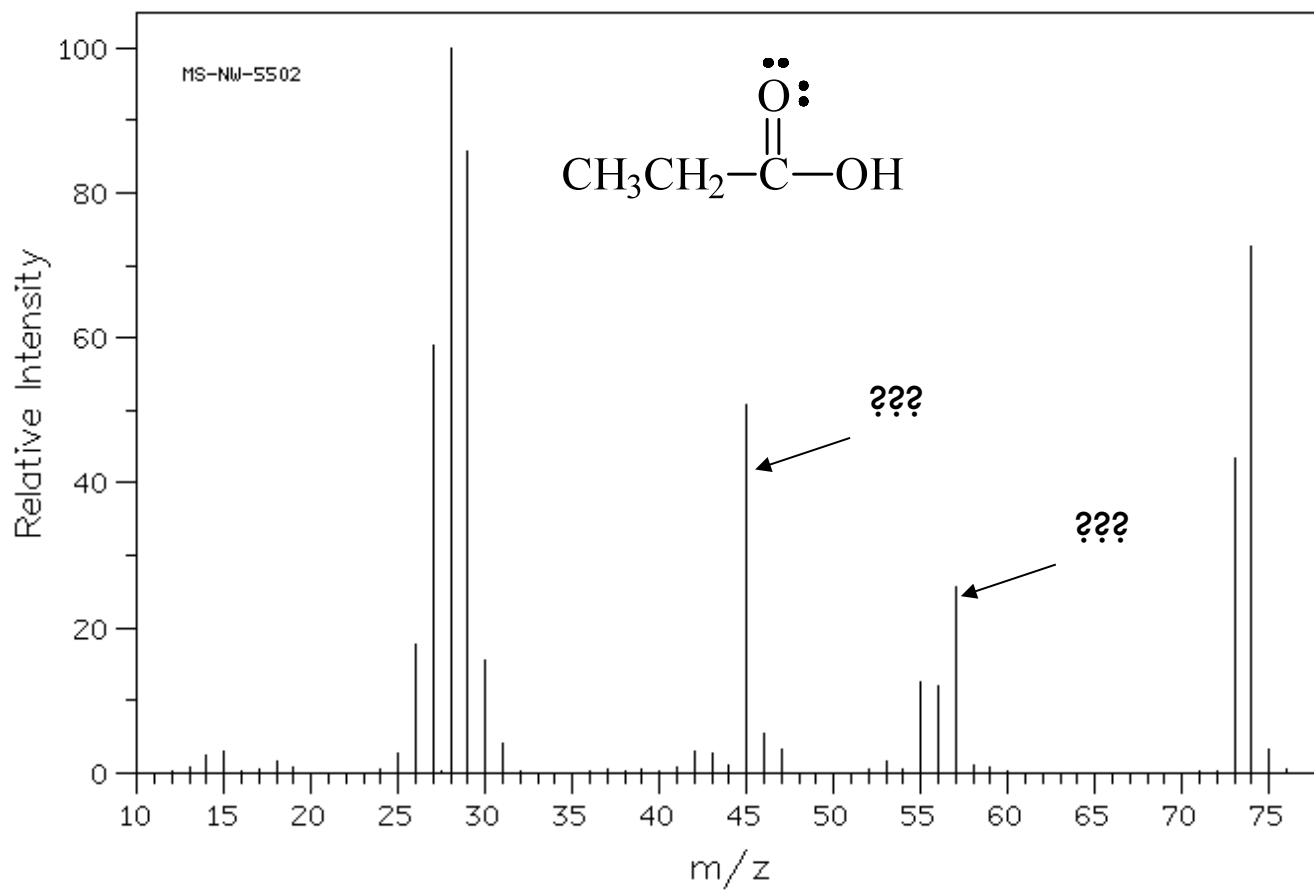
## Carbonyls

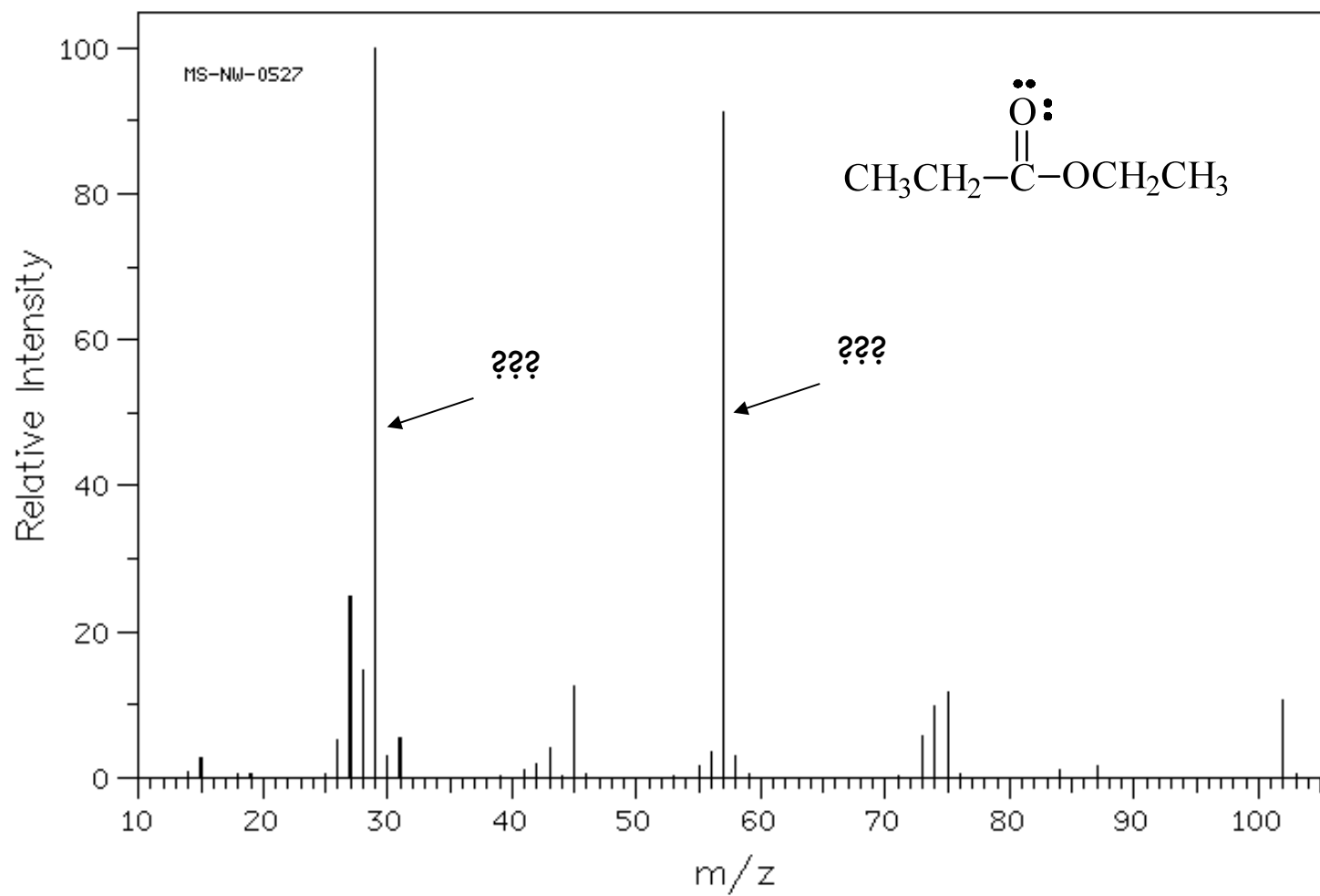


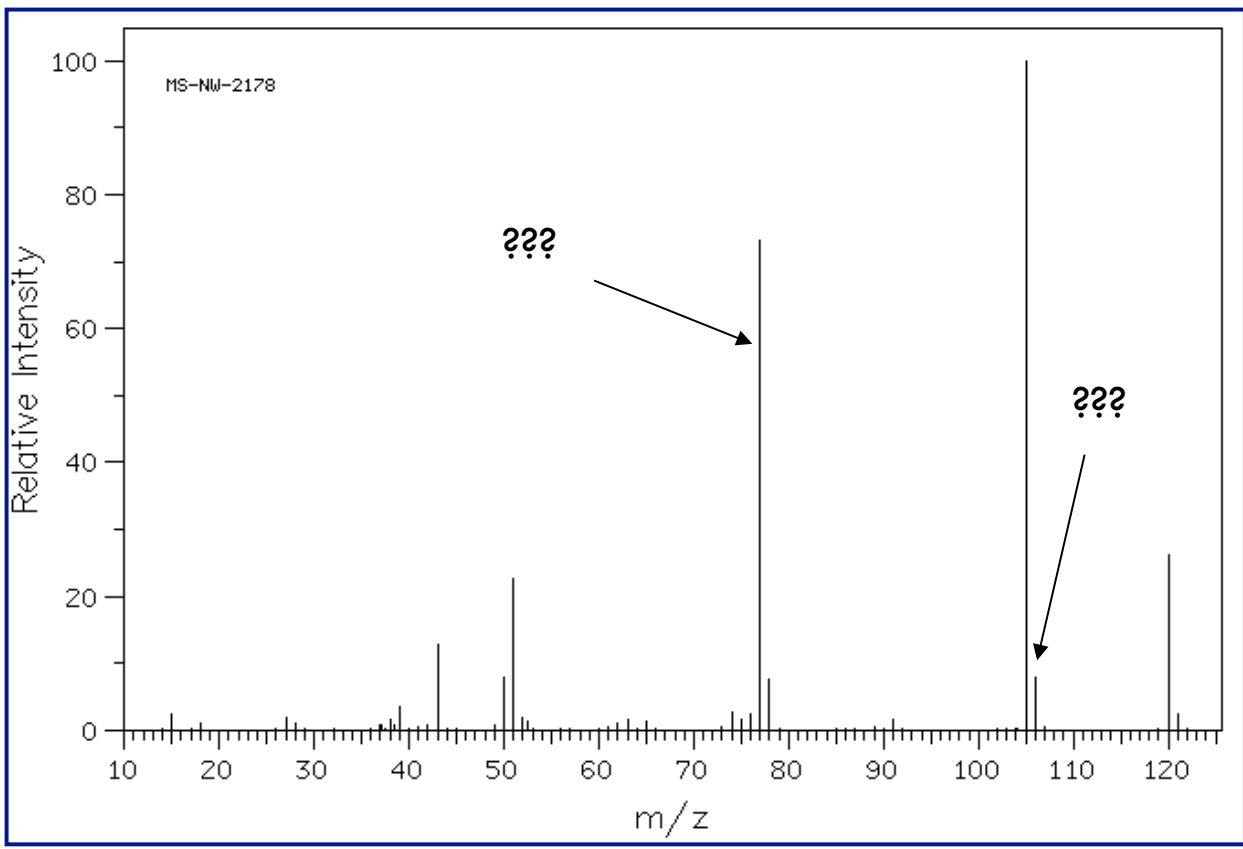
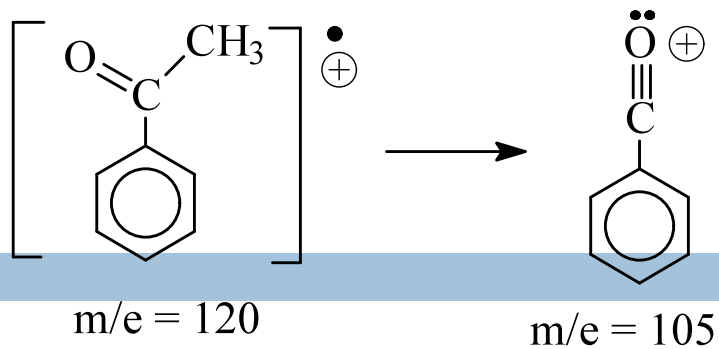
# What are these peaks?





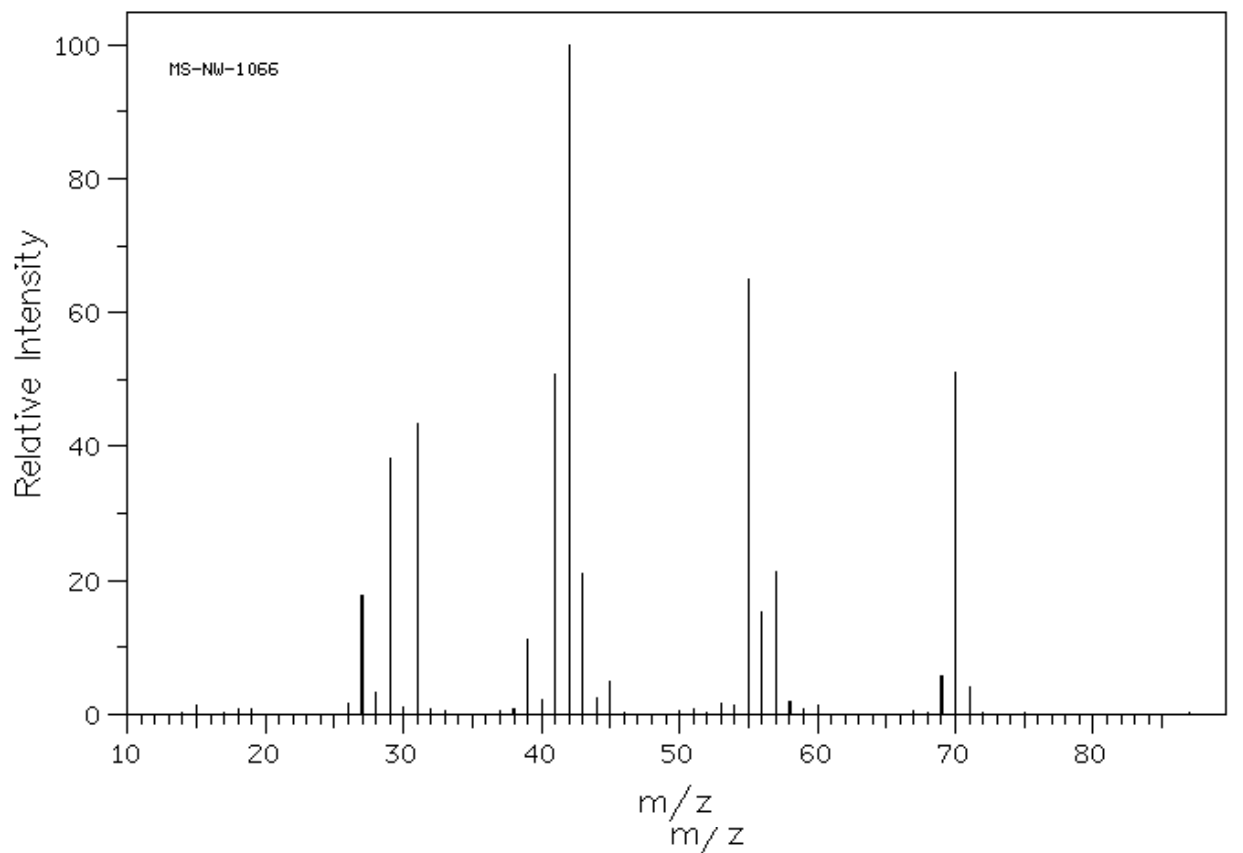
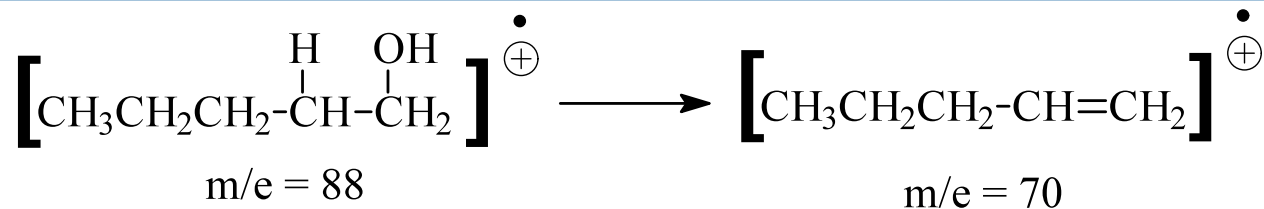






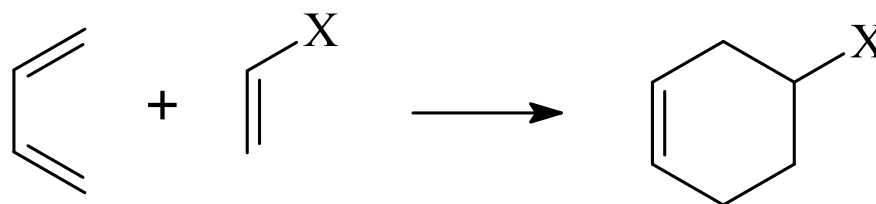
## Two-bond cleavage

Alcohols often undergo dehydration (loss of water)

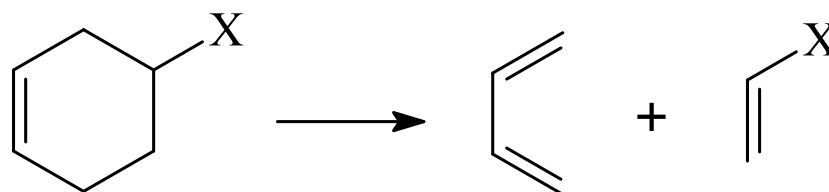


Cyclohexenes undergo reverse Diels-Alder reactions.

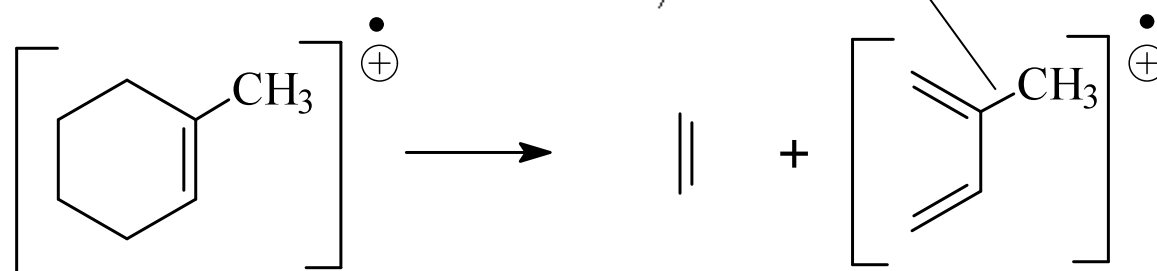
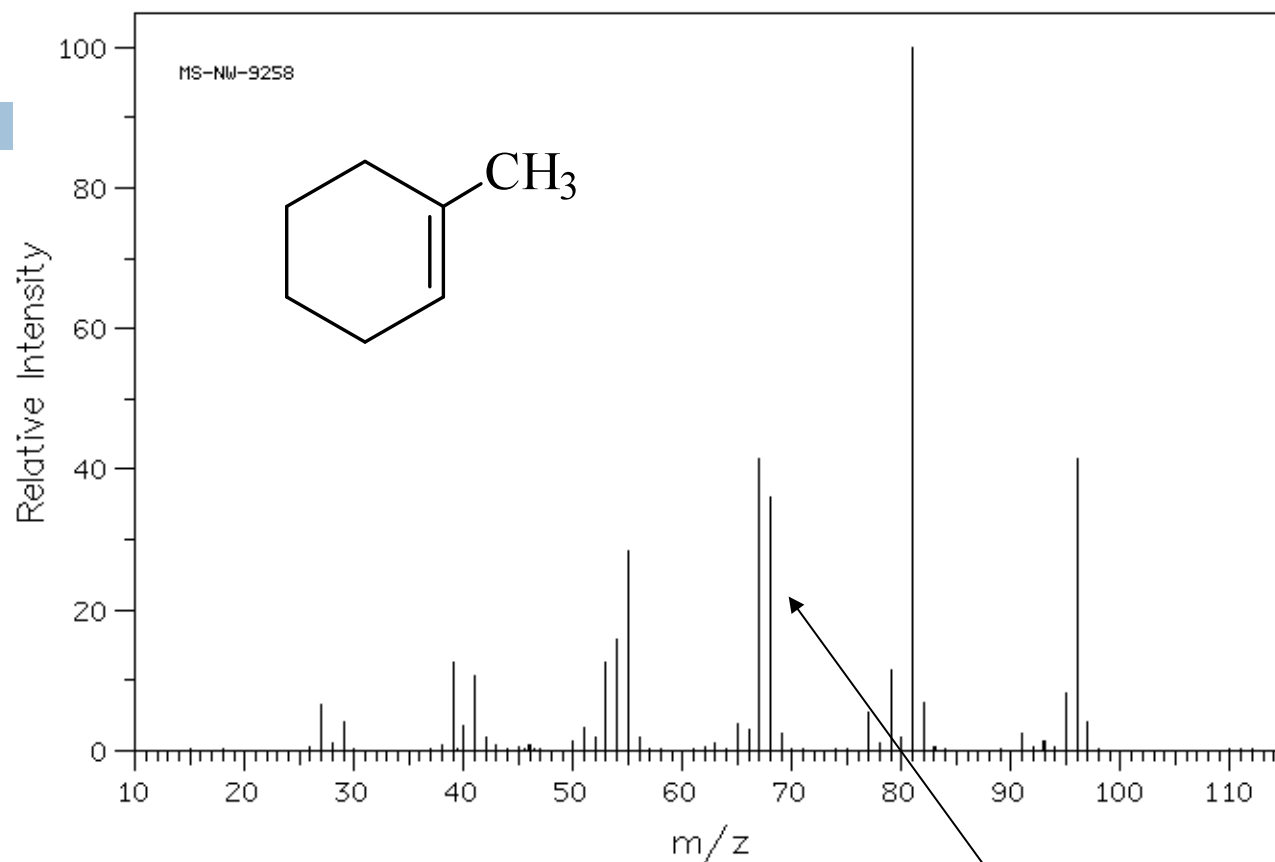
Diels-Alder reaction



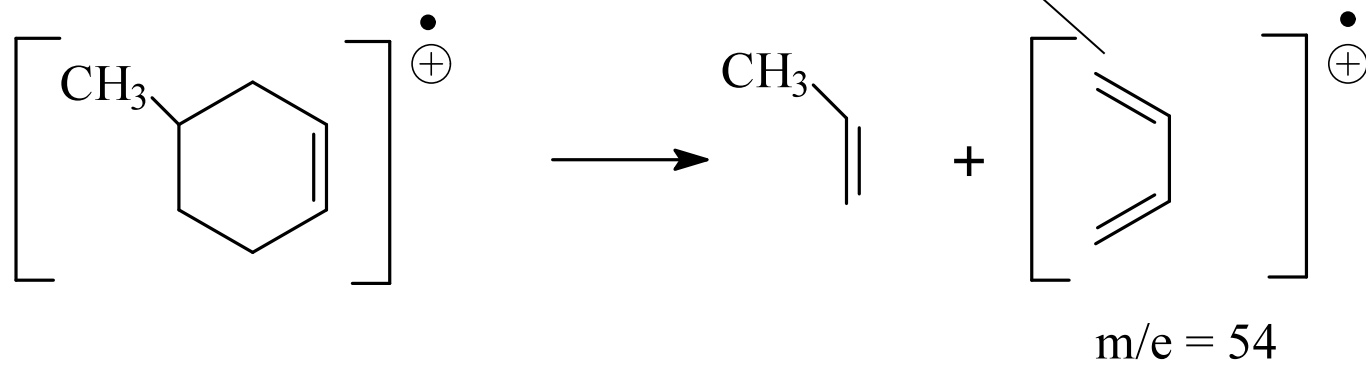
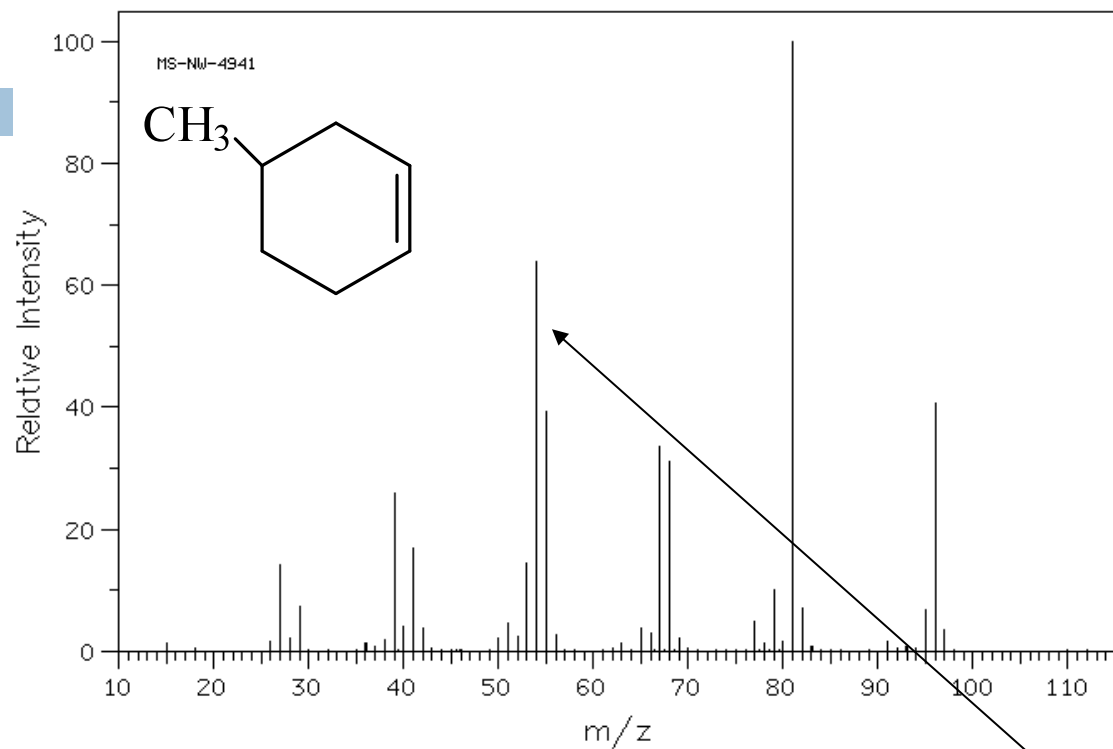
Reverse Diels-Alder



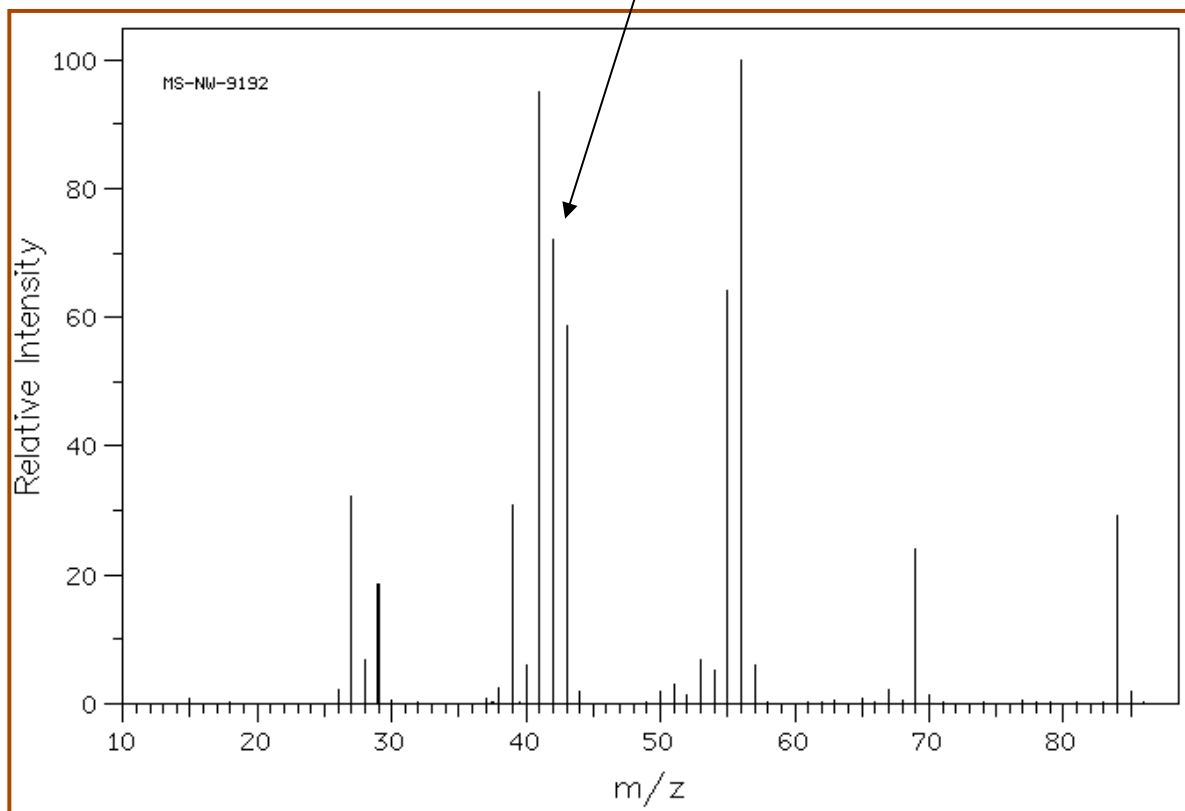
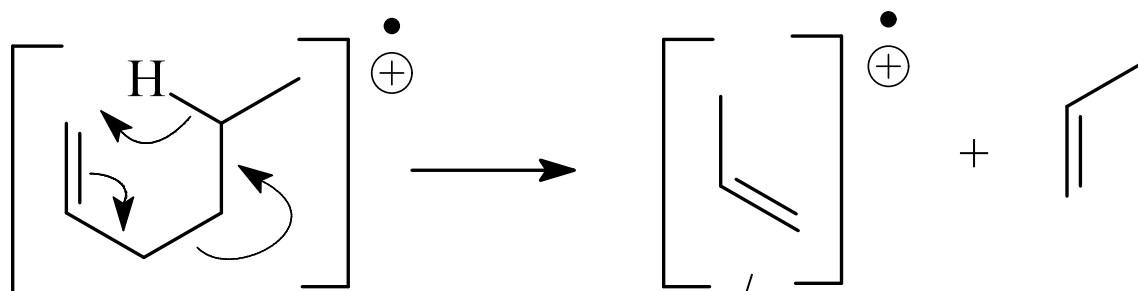
Identify the fragment produced by a reverse Diels-Alder reaction.

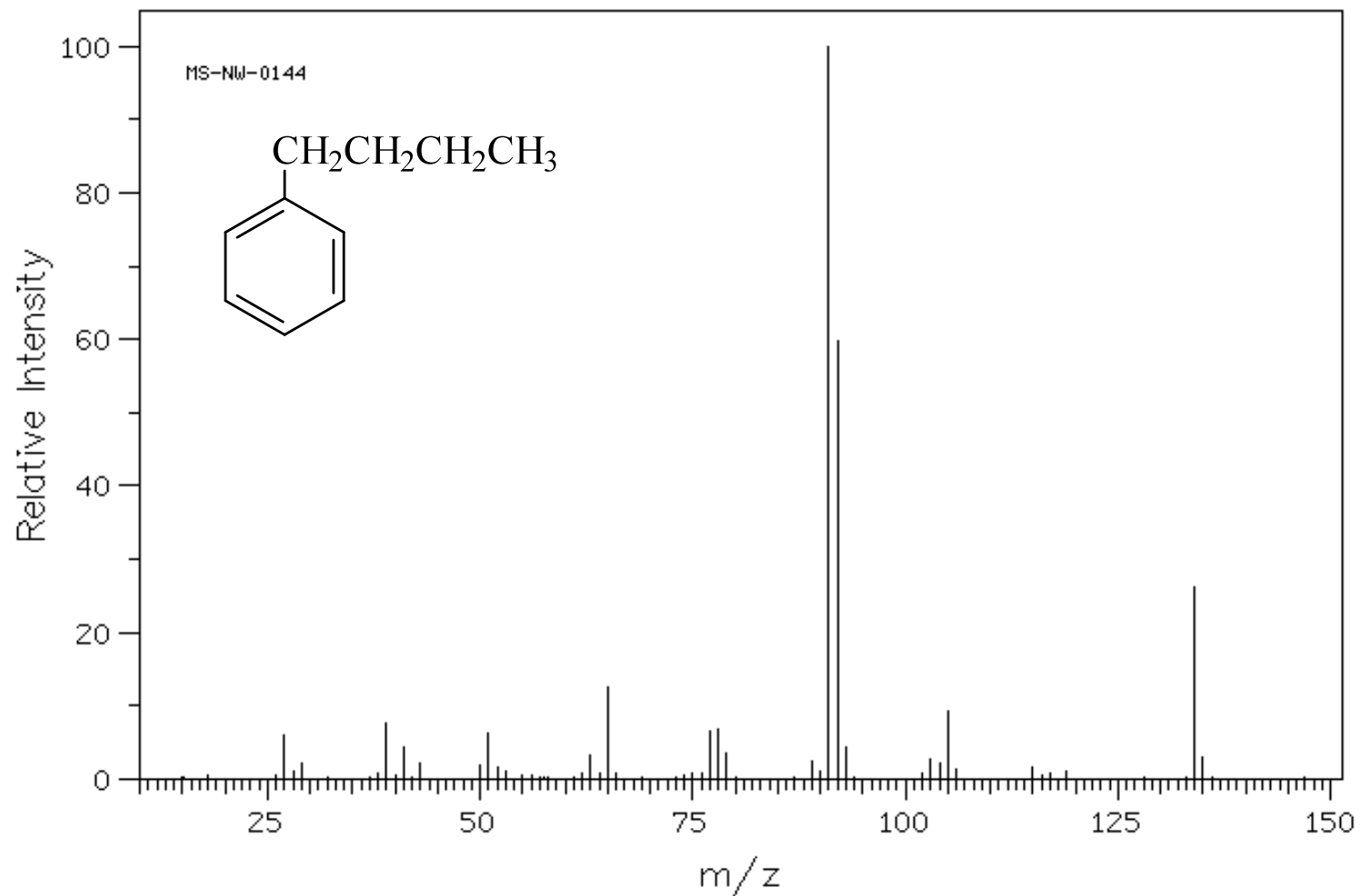


Identify the fragment produced by a reverse Diels-Alder reaction.

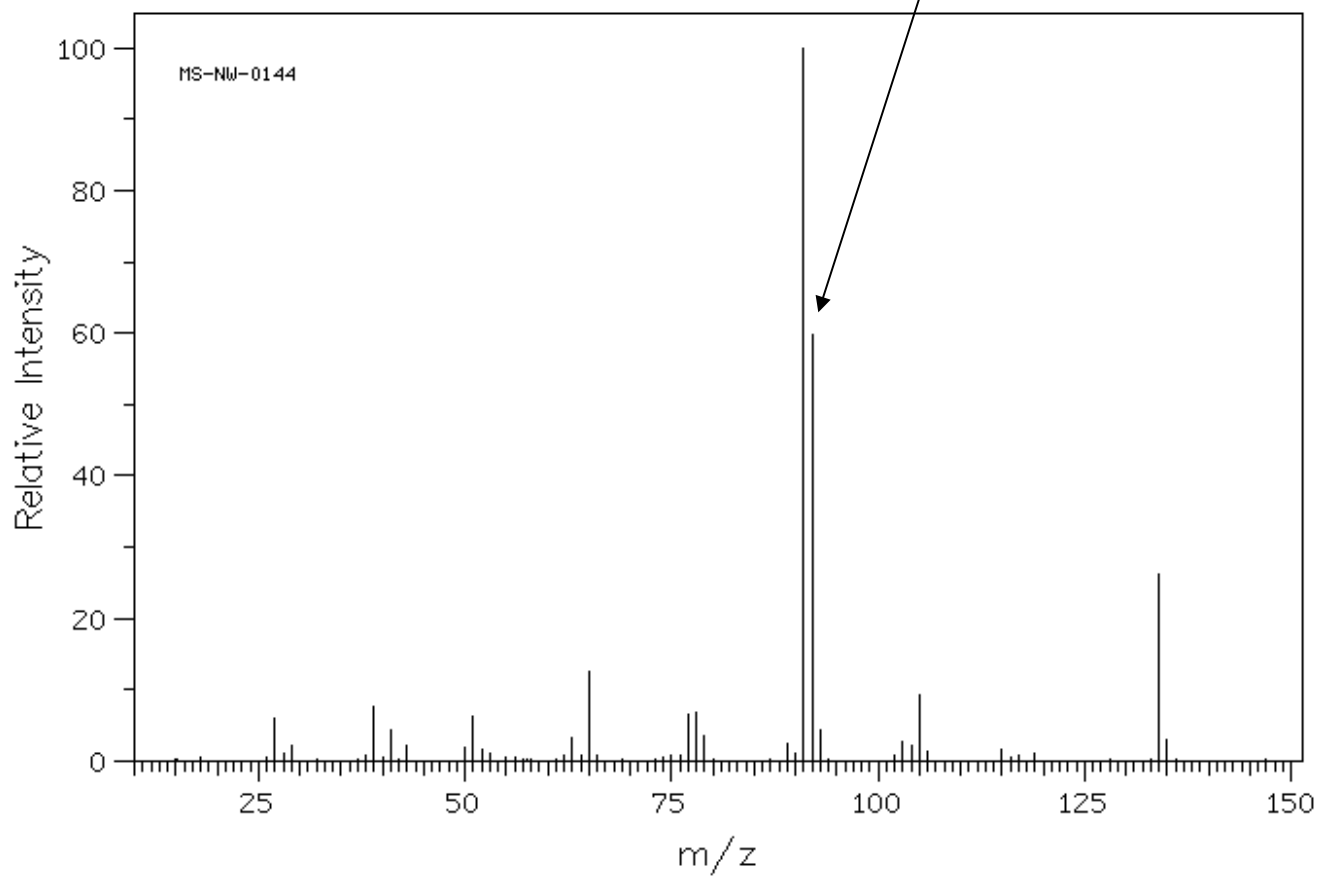
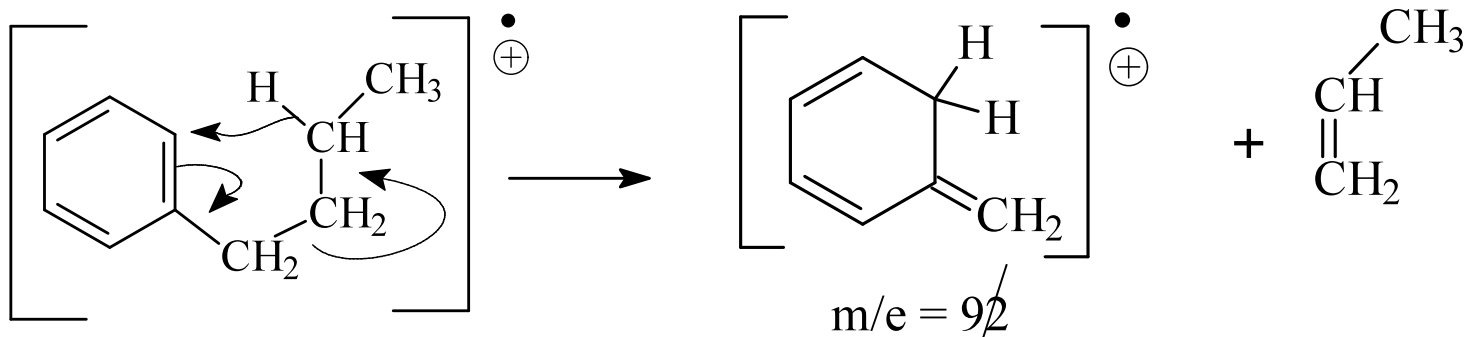


# McLafferty fragmentation

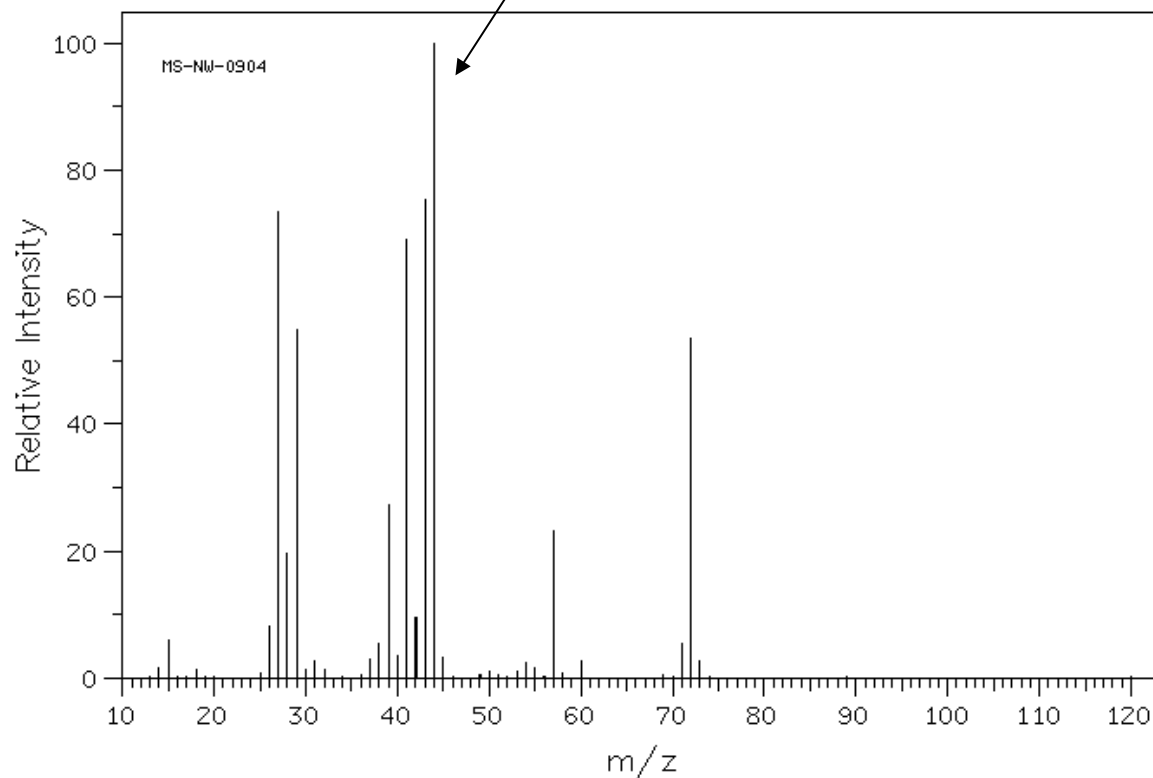
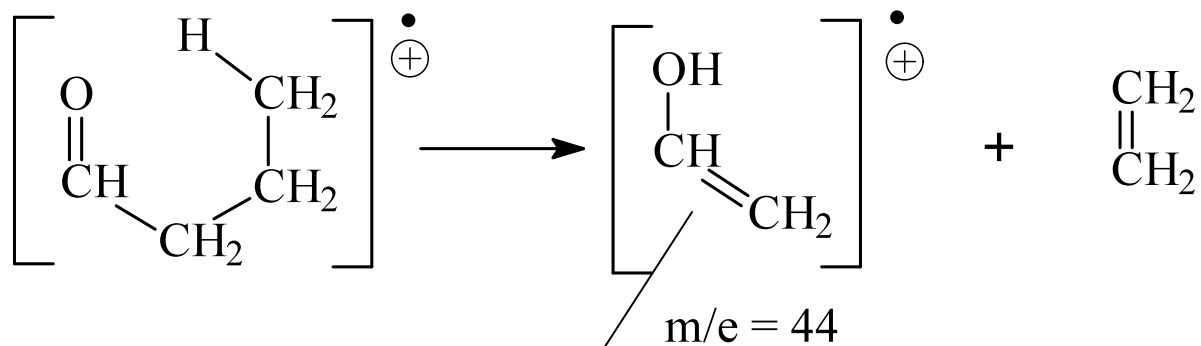




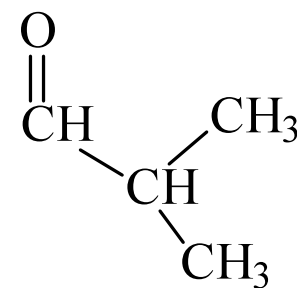
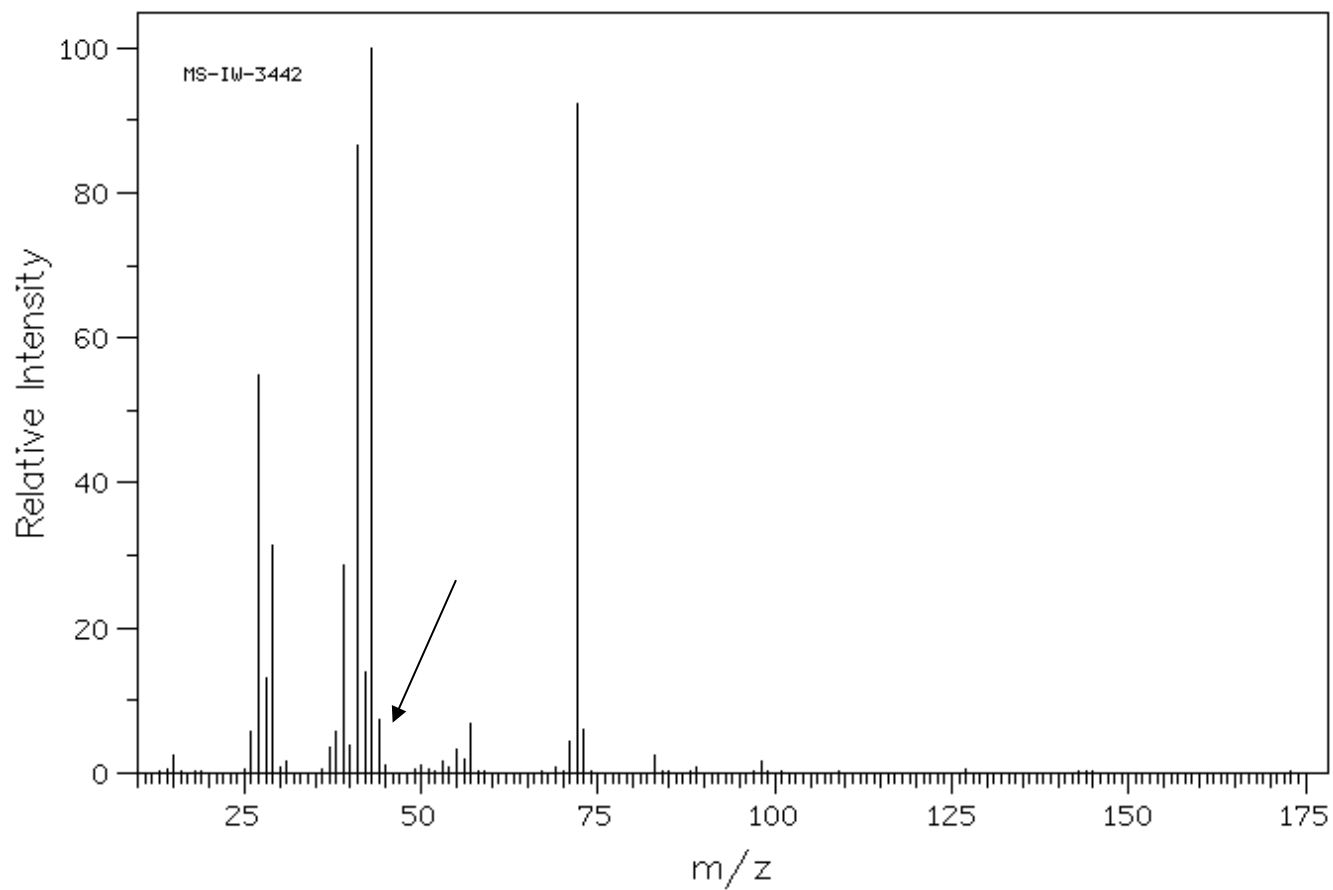
What can you say about the peak at  $m/e = 92$ . We will come back to it later.



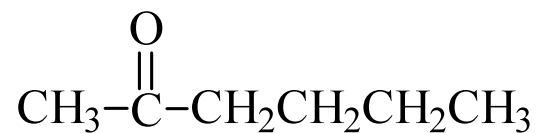
Noticed that there must be at least 3 carbon atoms attached to the double bond in order for McLafferty fragmentation to occur?



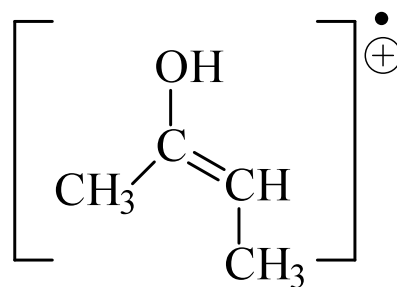
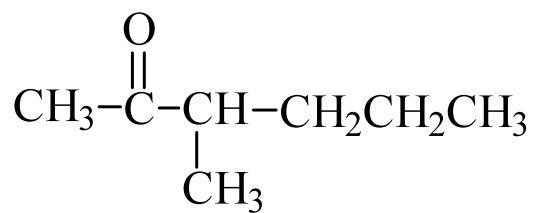
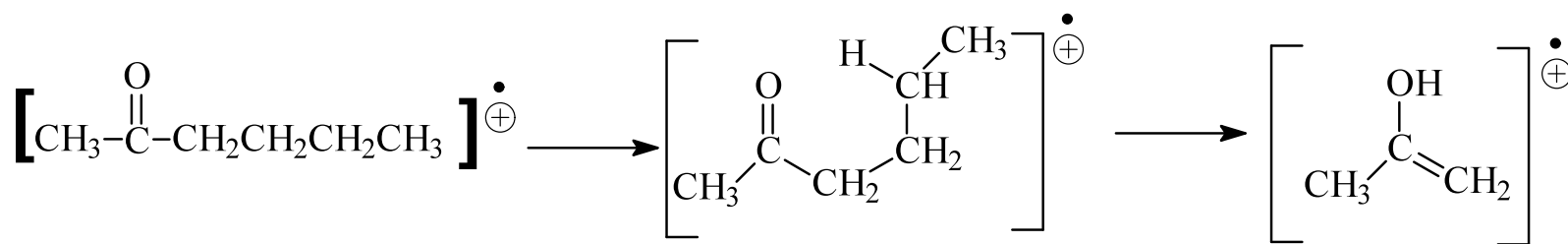
No McLafferty fragmentation is possible for shorter chains.



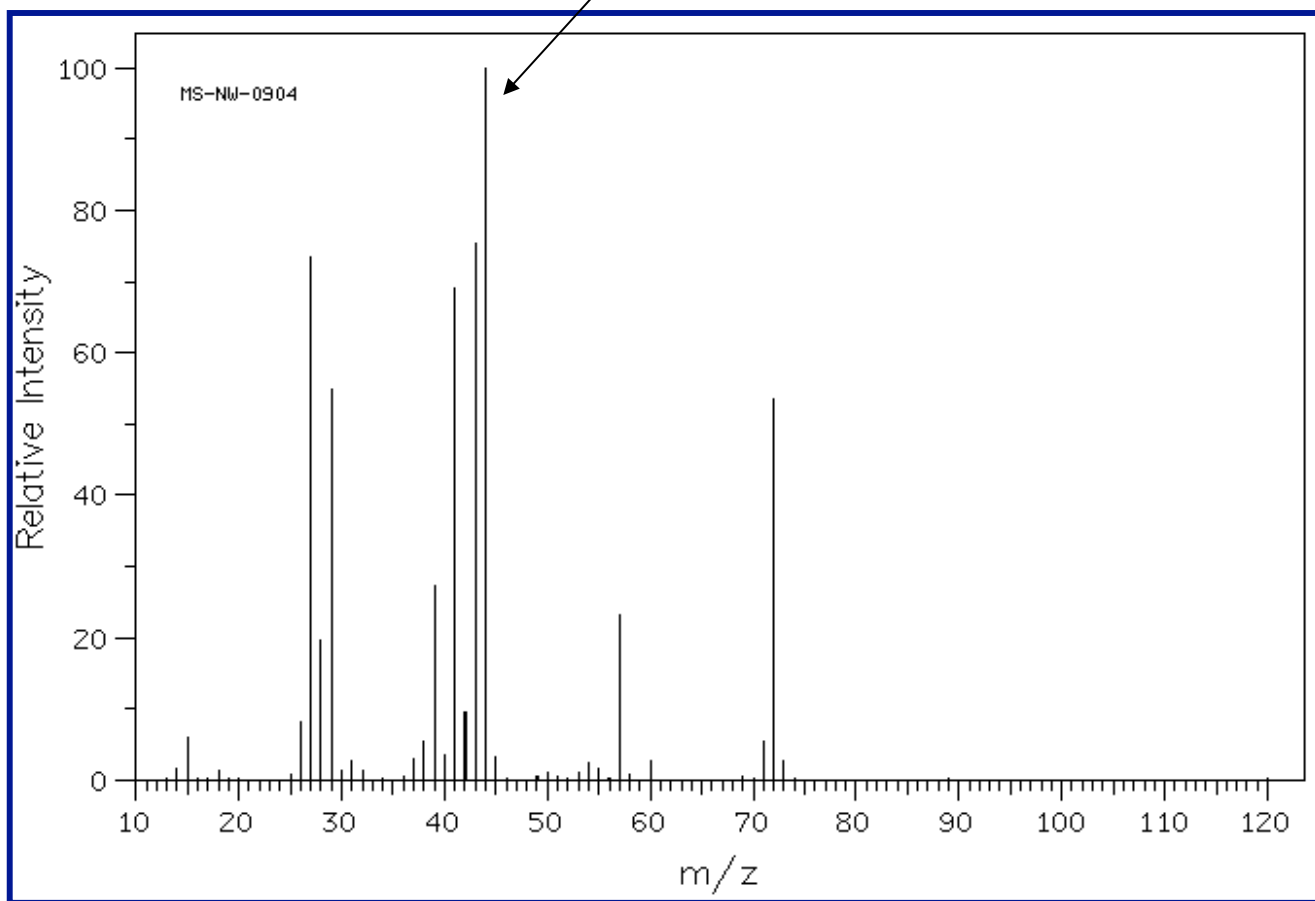
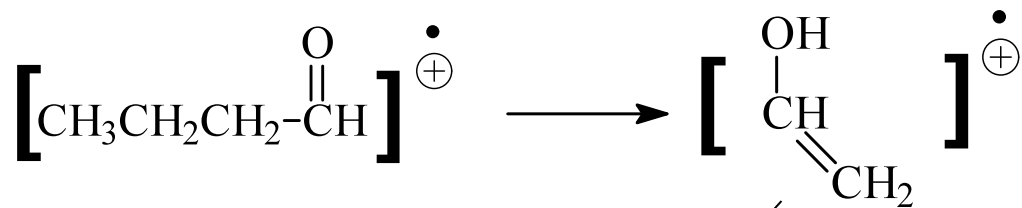
Identify McLafferty fragment (and its mass) for each of the following.

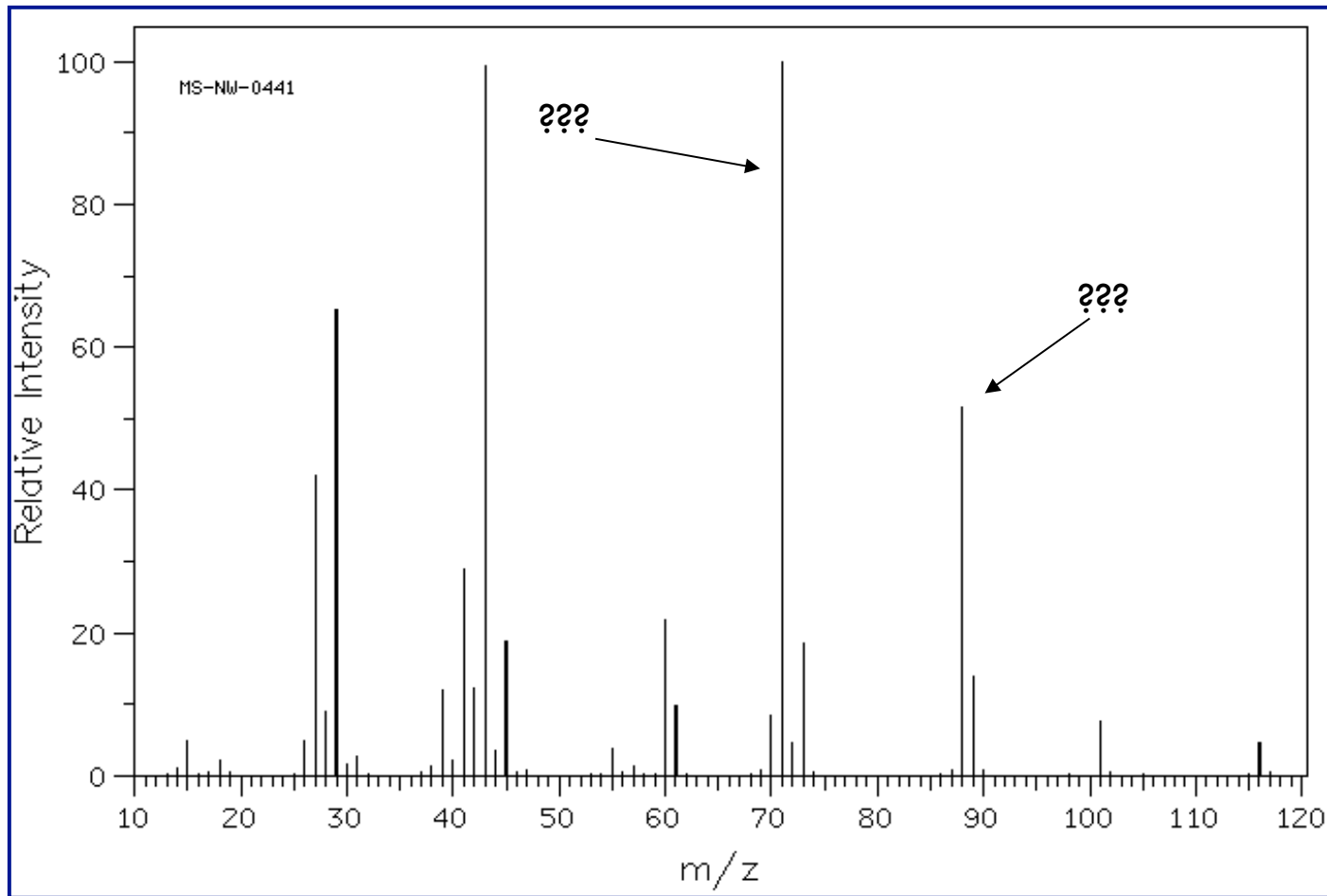
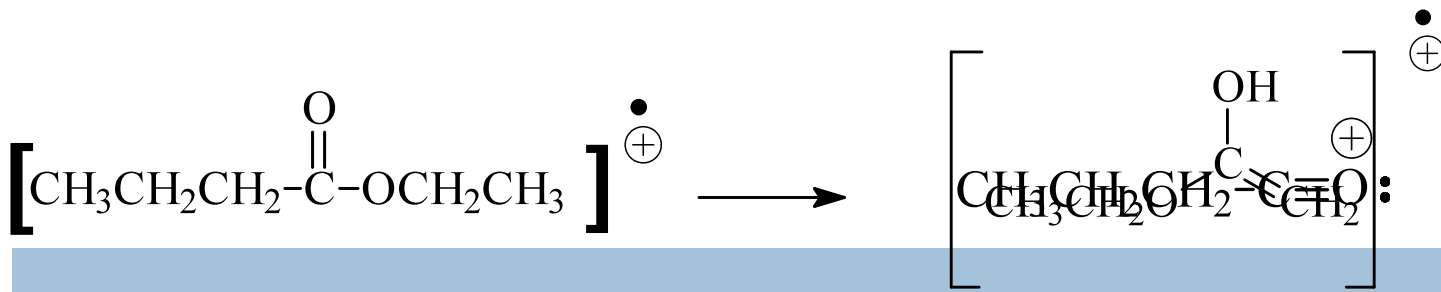


$m/e = 58$



$m/e = 72$





What would be the mass of the McLafferty fragment produced by each of the following?

A methyl ester

74

2,4-dimethyl-1-hexene

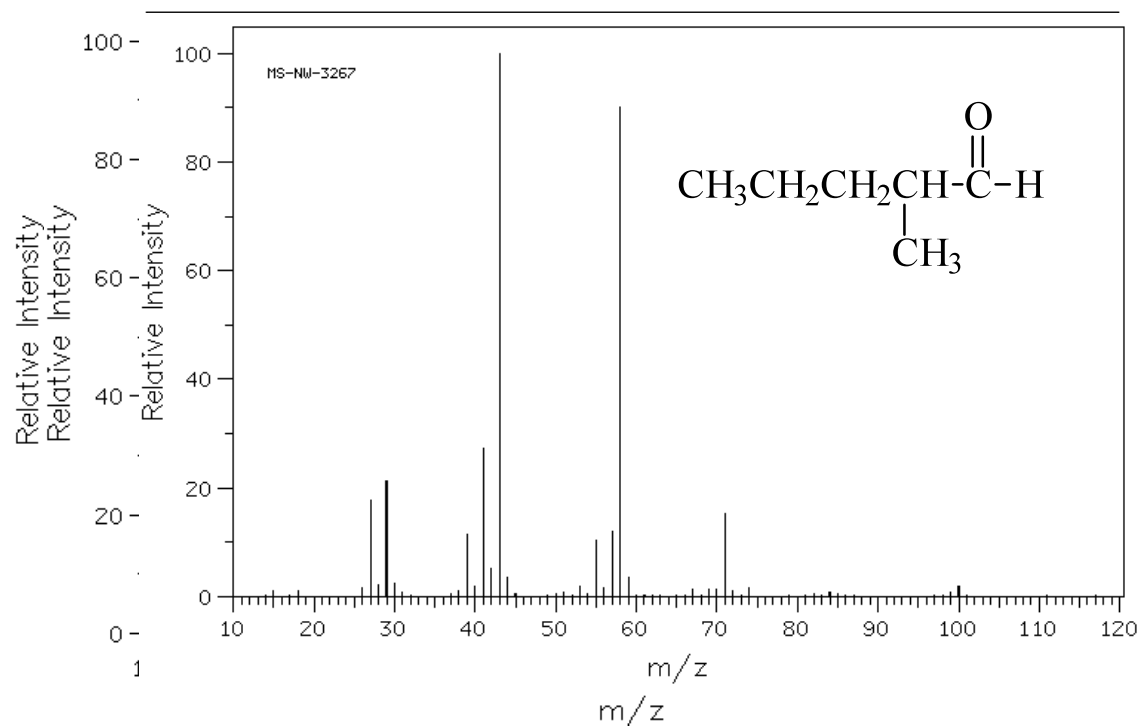
56

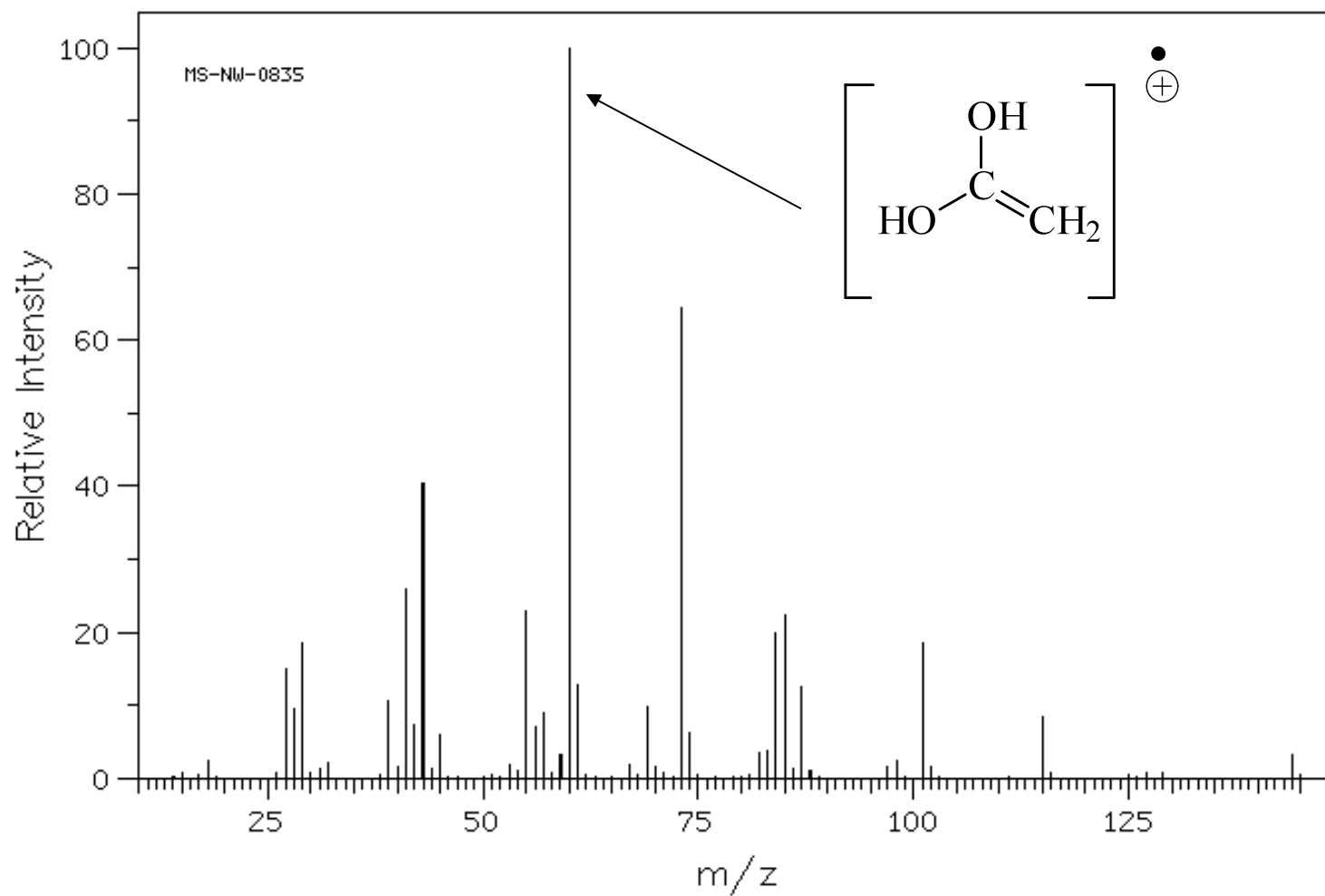
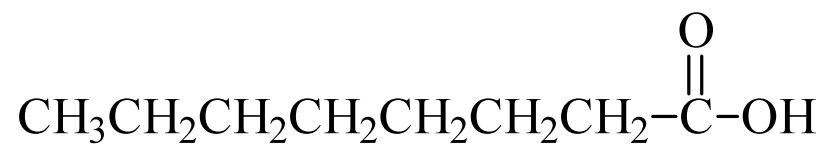
An alpha-methyl aldehyde

58

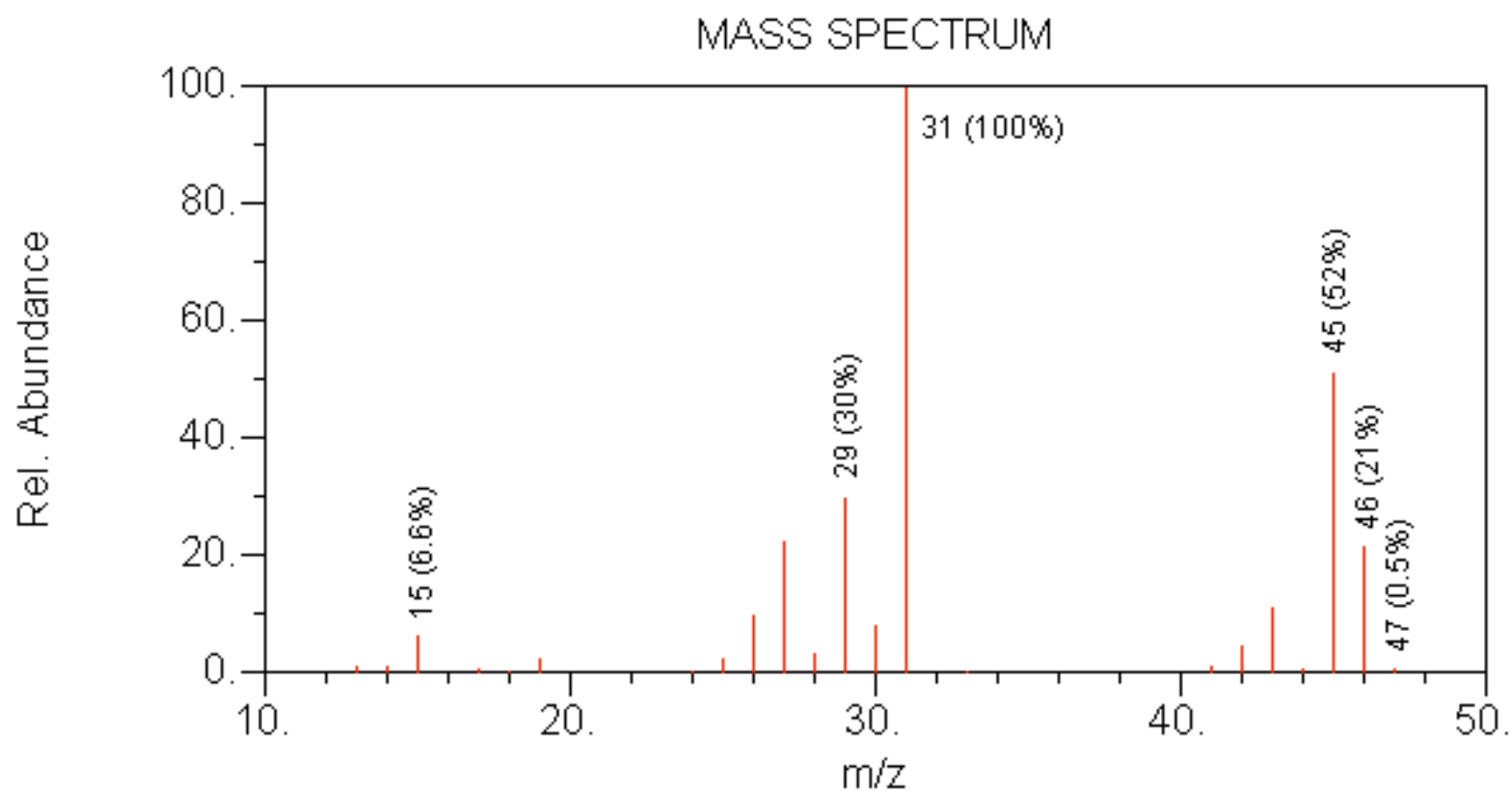
Octanoic acid

60





# What molecule produced this EI spectrum?



# Update



Hand back quizzes and homework.

Next week - NMR begins

You will be receiving an email shortly from the in-house NMR guru.

Reading – read chapter on IR