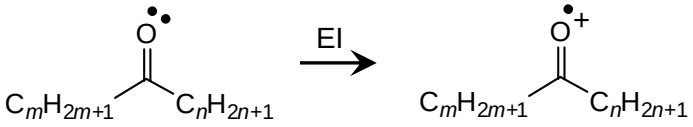
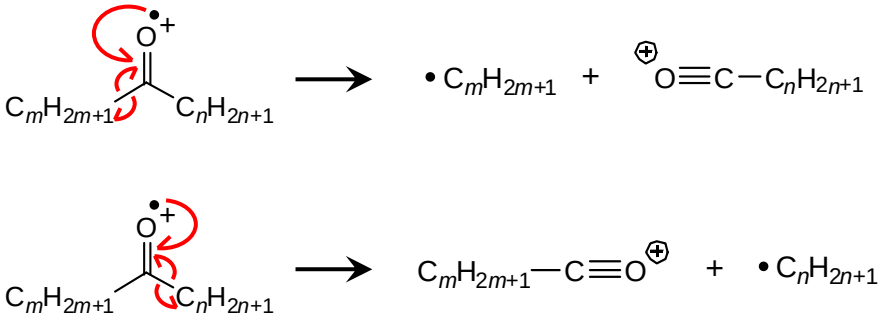
In-Class Exercise Solutions:
Ketone Radical Cation Fragmentation

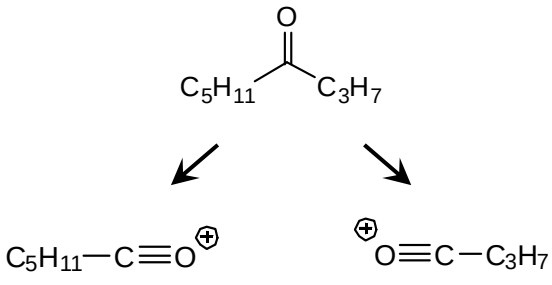
a. The highest-energy electrons in this structure are the oxygen lone-pair electrons, and these are the easiest to remove by EI.



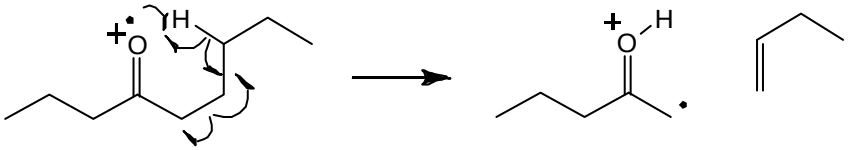
b. α-cleavage occurs on either side of the carbonyl:



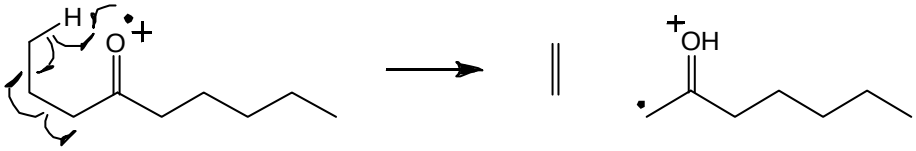
In each of these cases, our even-mass parent fragments into two odd masses, only one of which (the cation) is visible by mass spectrometry. The odd-mass peaks are 99, 71, and 43 amu. If any of these corresponded to the ions above, those ions' C_nH_{2n+1} parts would be 28 amu (the CO group) less than the daughter itself, so C_nH_{2n+1} would be 71, 43, or 15 amu. Two of these three numbers have to add up to 114 to make the whole *m* = 144 molecule, and only 71 + 43 does that. So that means our molecule has 5 carbons on one side and 3 on the other.



c.

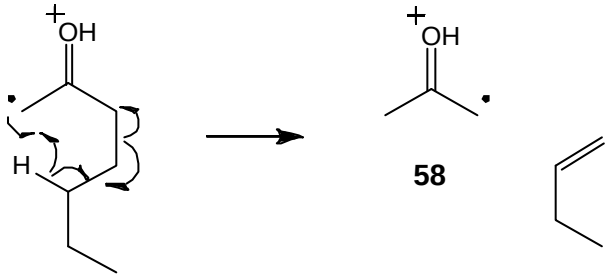


86



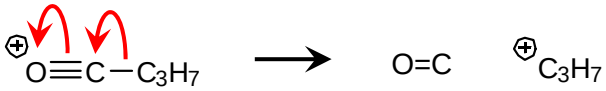
114

d. Okay, this question was pretty hard. The *m* = 58 peak comes from a second McLafferty rearrangement on top of the first one:



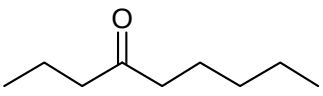
114 **58**

The *m* = 43 peak comes from loss of CO from the *m* = 71 ion:



71 **43**

e. All of my drawings above show a linear ketone, but I think that the same fragmentations could also be drawn if the C_5H_{11} part were branched at the end. Either of these structures is possible.



or