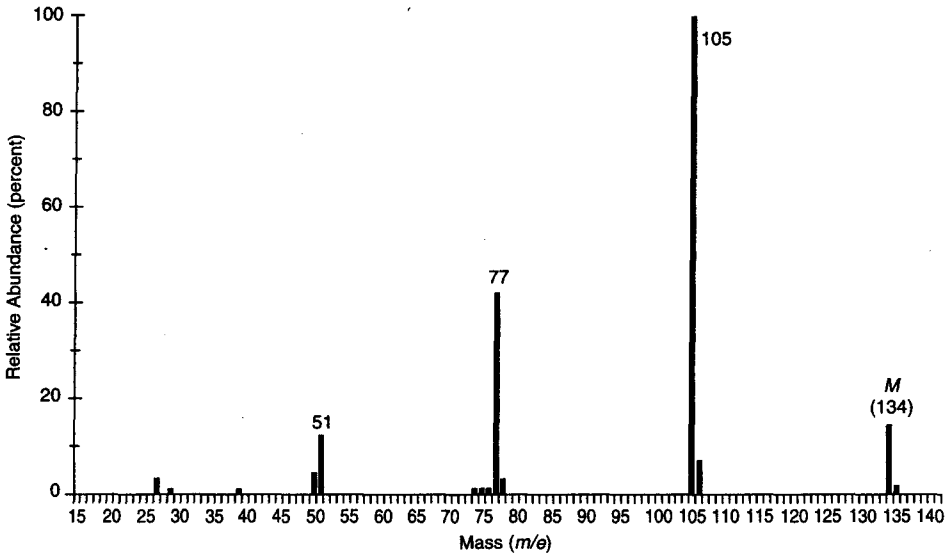
■ SOLVED EXAMPLE

An unknown compound has the mass spectrum shown. The infrared spectrum of the unknown shows significant peaks at

3102 cm^{-1}	3087	3062	3030	1688
1598	1583	1460	1449	1353
1221	952	746	691	

There is also a band from aliphatic C–H stretching from 2879 to 2979 cm^{-1}.



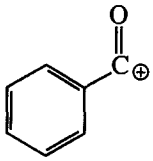
■ SOLUTION

1. The molecular ion appears at an *m/e* value of 134. Applying the Rule of Thirteen gives the following possible molecular formulas:

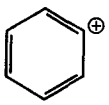
$$C_{10}H_{14} \qquad U = 4$$
$$C_9H_{10}O \qquad U = 5$$

2. The infrared spectrum shows a C=O peak at 1688 cm^{-1}. The position of this peak, along with the C–H stretching peaks in the 3030–3102 cm^{-1} range and C=C stretching peaks in the 1449–1598 cm^{-1} range, suggests a ketone where the carbonyl group is conjugated with a benzene ring. Such a structure would be consistent with the second molecular formula and with the index of hydrogen deficiency.

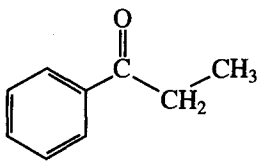
3. The base peak in the mass spectrum appears at $m/e = 105$. This peak is likely due to the formation of a benzoyl cation.



Subtracting the mass of the benzoyl ion from the mass of the molecular ion gives a difference of 29, suggesting that an ethyl group is attached to the carbonyl carbon. The peak appearing at $m/e = 77$ arises from the phenyl cation.

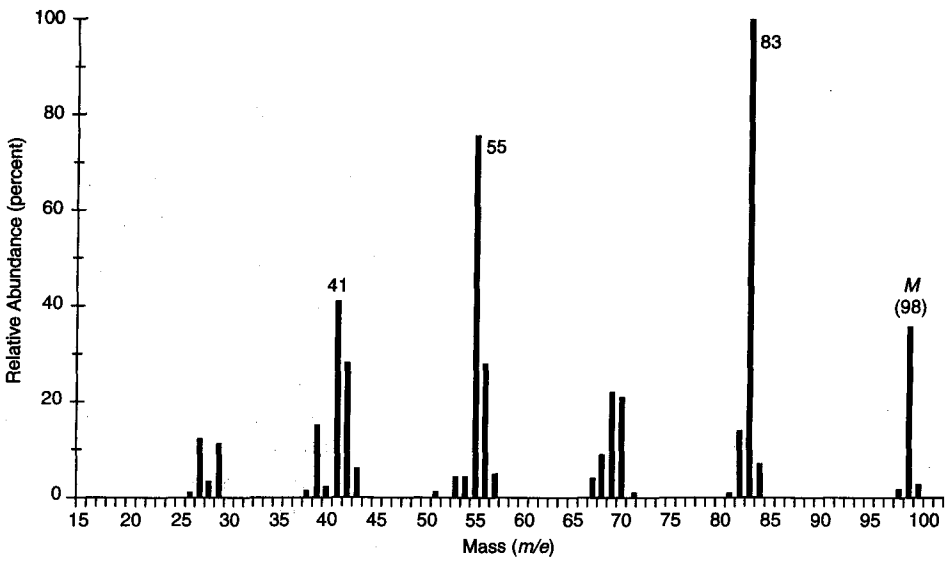


4. If we assemble all of the "pieces" suggested in the data, as described above, we conclude that the unknown compound must have been **propiophenone (1-phenyl-1-propanone).**

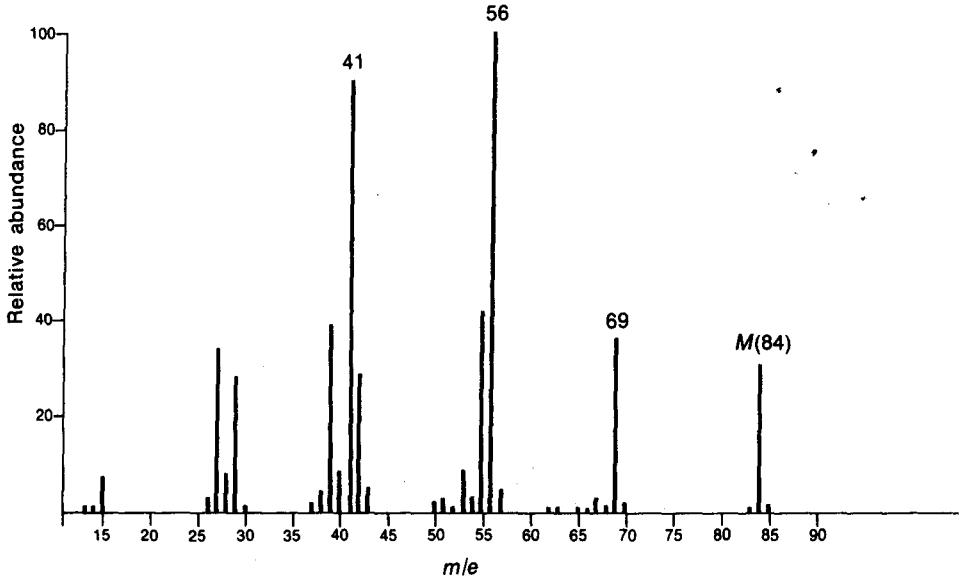


Problem 7 (continued)

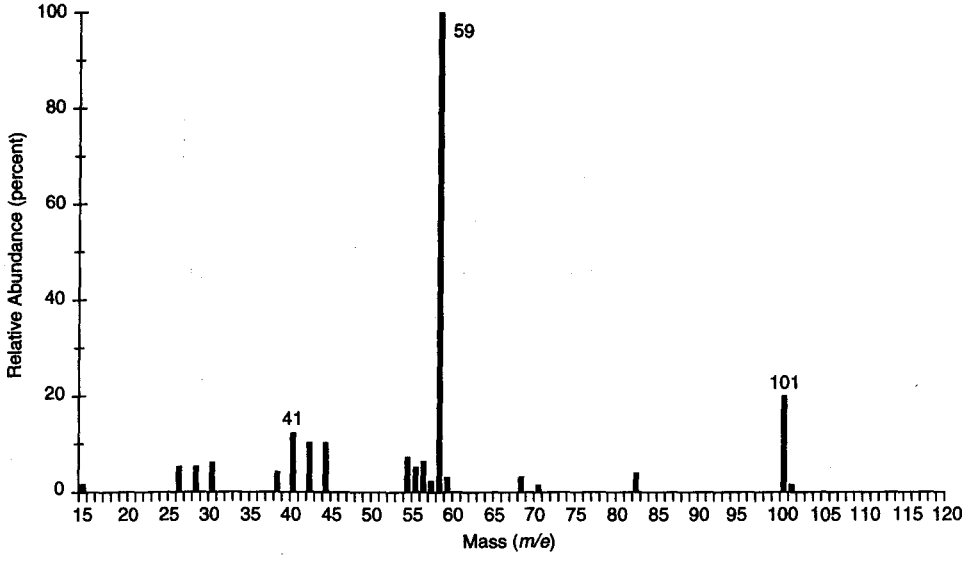
*(a) The infrared spectrum has no interesting features except aliphatic C—H stretching and bending.



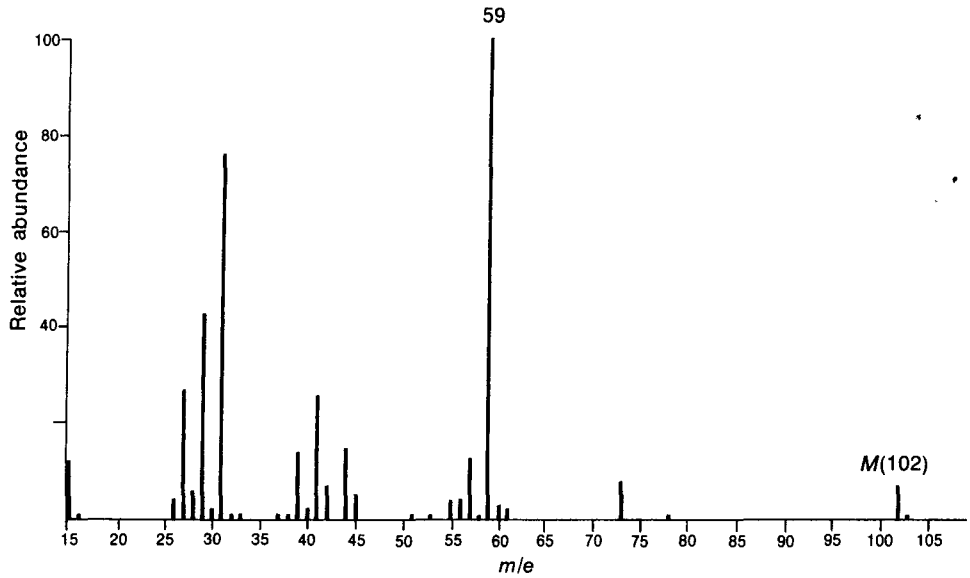
*(b) The infrared spectrum has a medium-intensity peak at about 1650 cm^{-1}. There is also a C—H out-of-plane bending peak near 880 cm^{-1}.



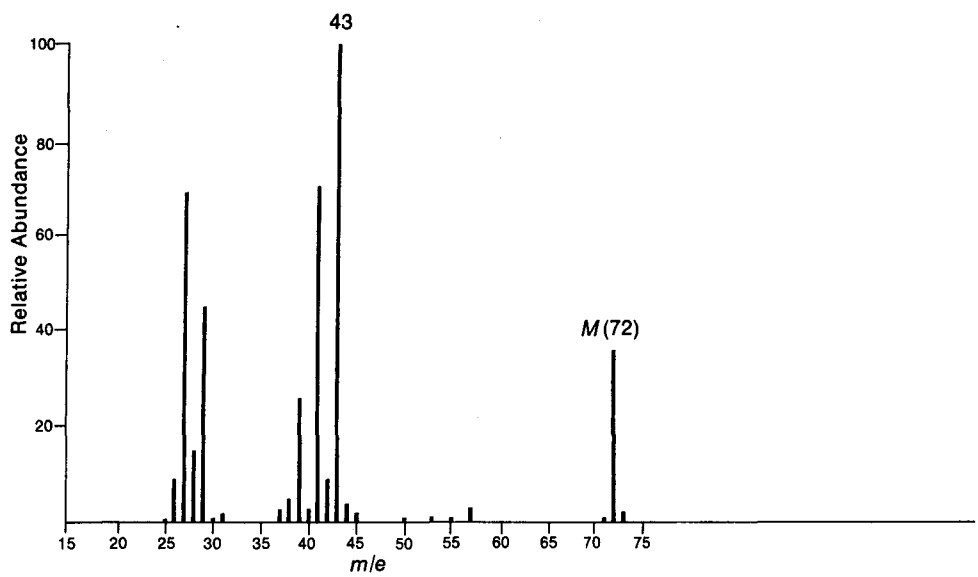
*(c) The infrared spectrum of this unknown has a prominent, broad peak at 3370 cm^{-1}. There is also a strong peak at 1159 cm^{-1}. The mass spectrum of this unknown does not show a molecular ion peak. You will have to deduce the molecular weight of this unknown from the heaviest fragment ion peak, which arises from the loss of a methyl group from the molecular ion.



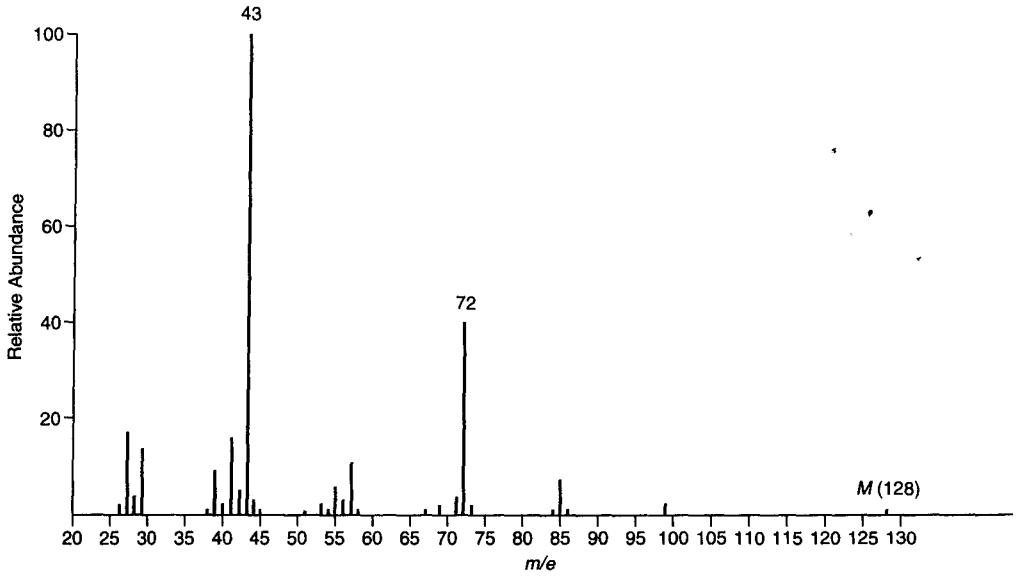
*(d) This unknown contains oxygen, but it does not show any significant infrared absorption peaks above 3000 cm^{-1}.



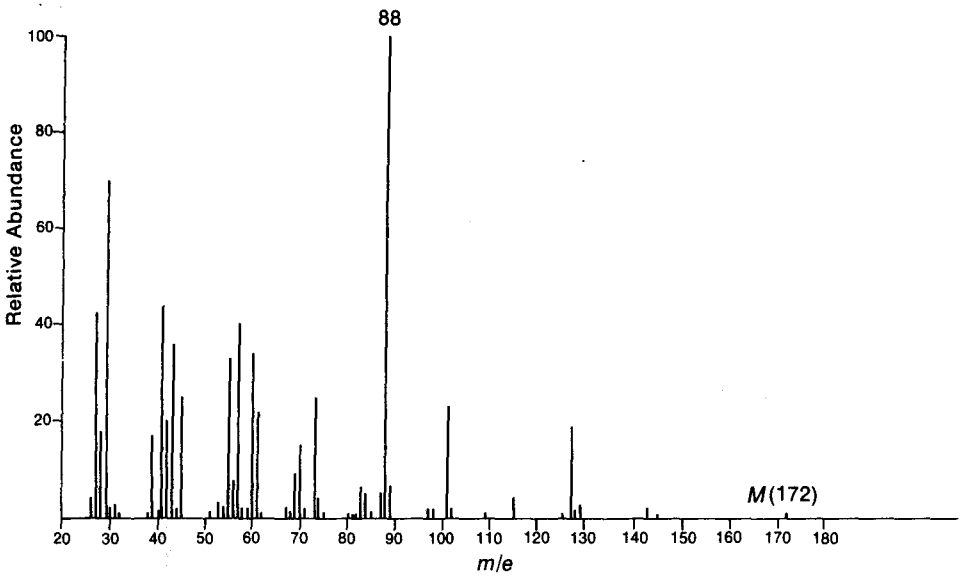
*(e) The infrared spectrum of this unknown shows a strong peak near 1725 cm^{-1}.



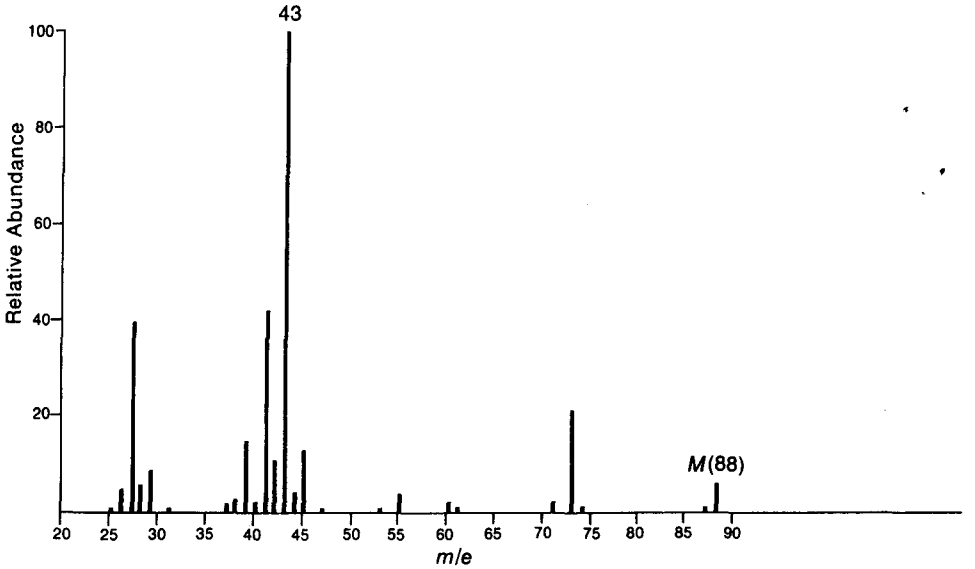
*(f) The infrared spectrum of this unknown shows a strong peak near 1715 cm^{-1}.



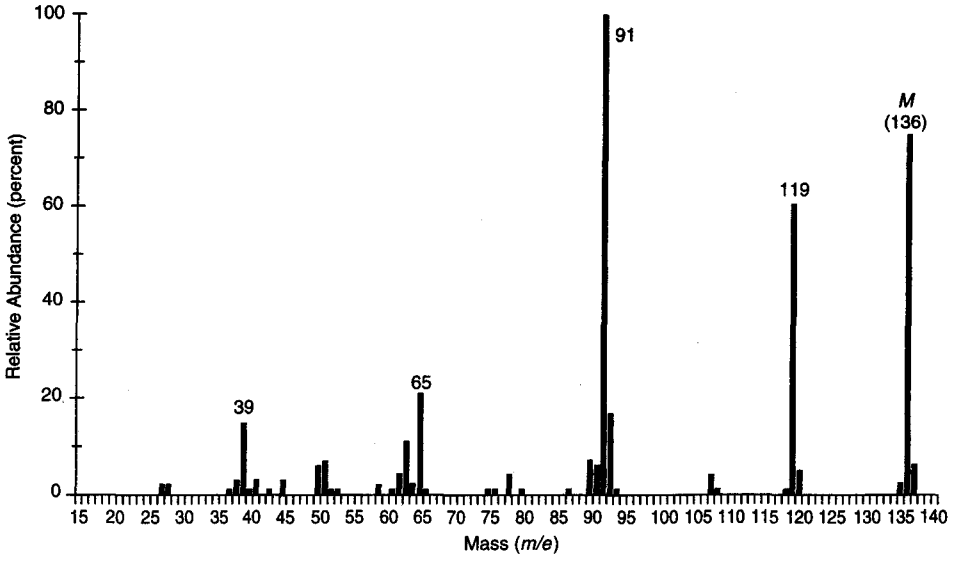
*(g) The infrared spectrum of this compound lacks any significant absorption above 3000 cm^{-1}. There is a prominent peak near 1740 cm^{-1} and another strong peak near 1200 cm^{-1}.



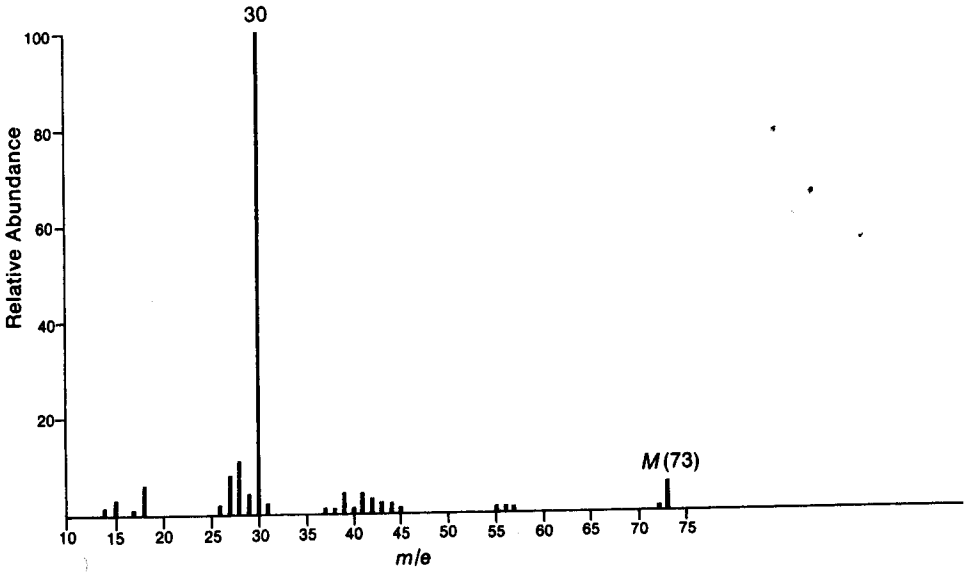
*(h) The infrared spectrum of this substance shows a very strong, broad peak in the range of 2500–3000 cm^{-1}, as well as a strong, somewhat broadened peak at about 1710 cm^{-1}.



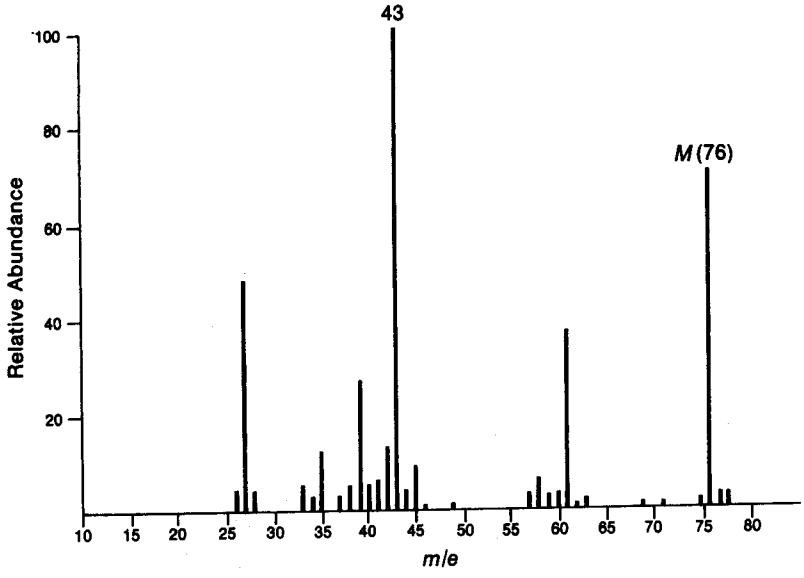
*(i) The ^{13}C NMR spectrum of this unknown shows only four peaks in the region 125–145 ppm (there are six peaks in the entire spectrum). The infrared spectrum shows a very strong, broad peak extending from 2500 to 3500 cm^{-1}, as well a strong and somewhat broadened peak at 1680 cm^{-1}.



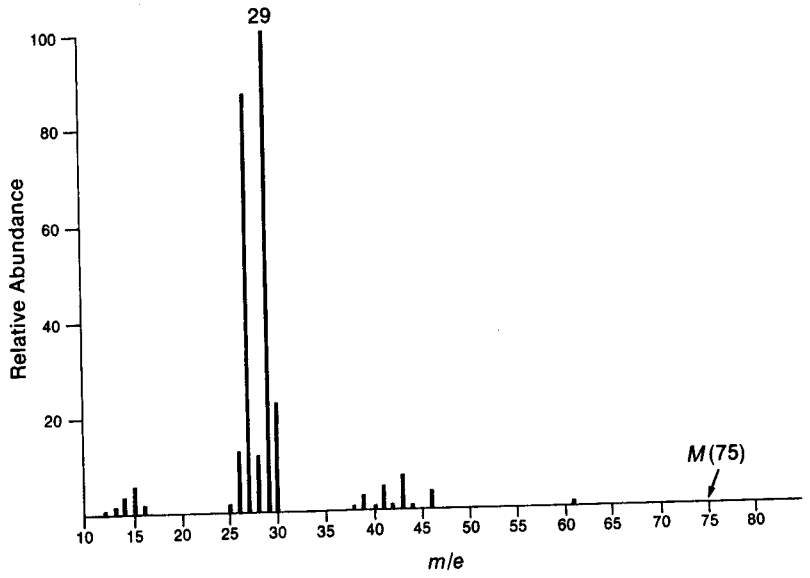
*(j) Note the odd value of mass for the molecular ion in this substance.



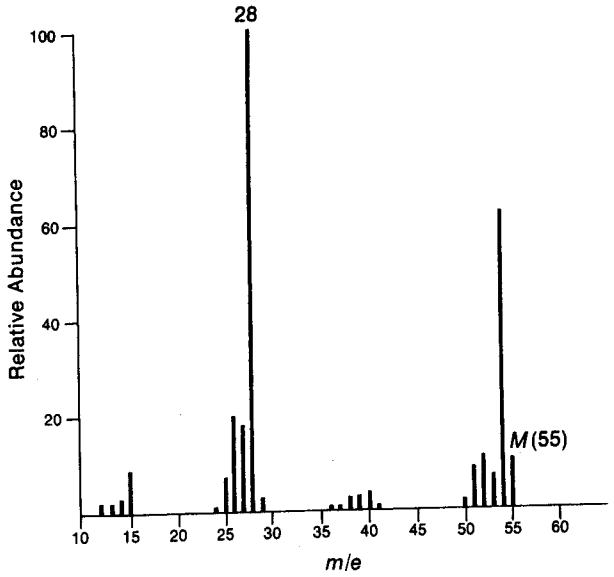
*(k) Notice the ***M* + 2** peak in the mass spectrum.



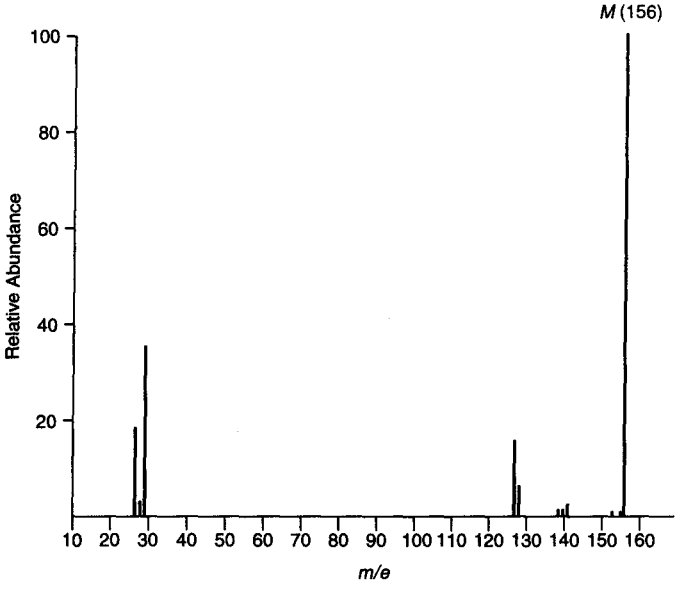
*(l) The infrared spectrum of this unknown shows two strong peaks, one near 1350 cm^{-1} and the other near 1550 cm^{-1}. Notice that the mass of the molecular ion is *odd*.



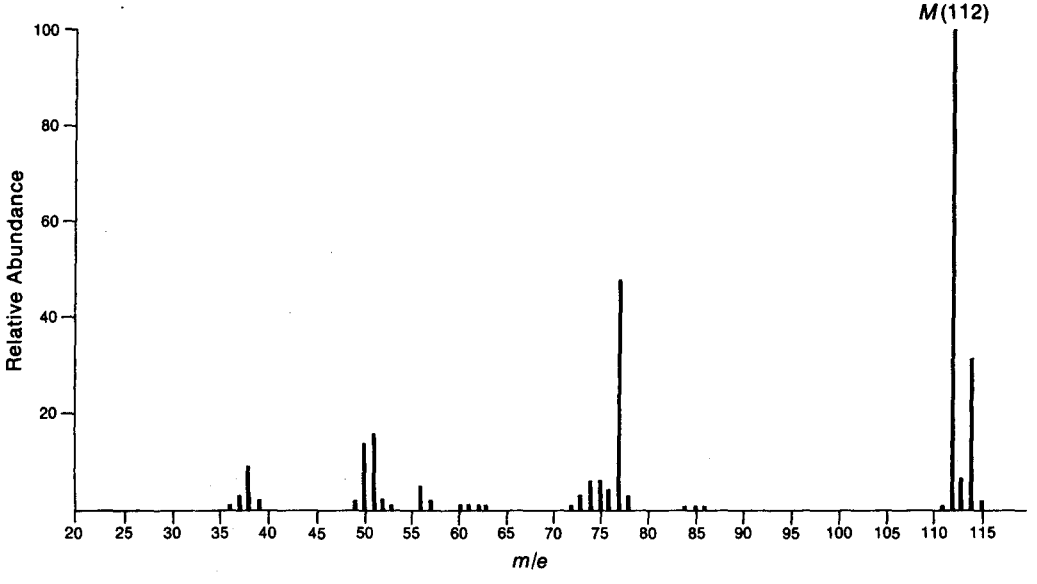
*(m) There is a sharp peak of medium intensity near 2250 cm^{-1} in the infrared spectrum of this compound.



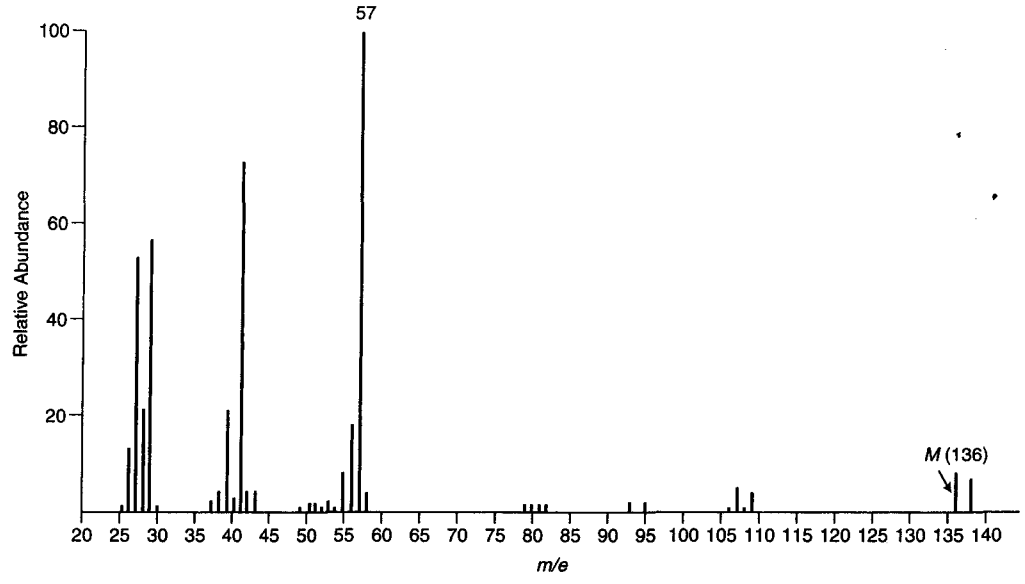
*(n) Consider the fragment ions at $m/e = 127$ and 128. From what ions might these peaks arise?



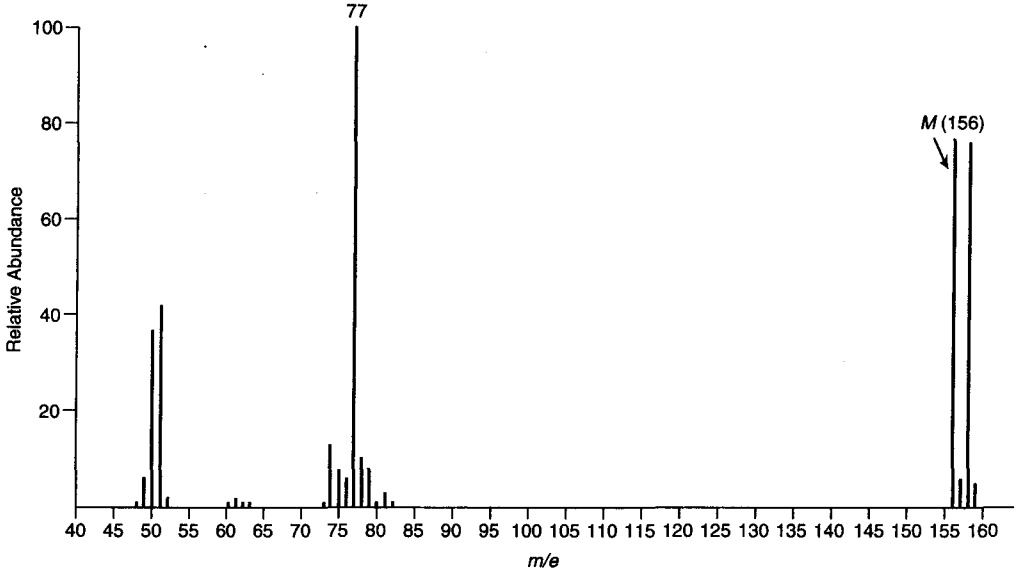
*(o)



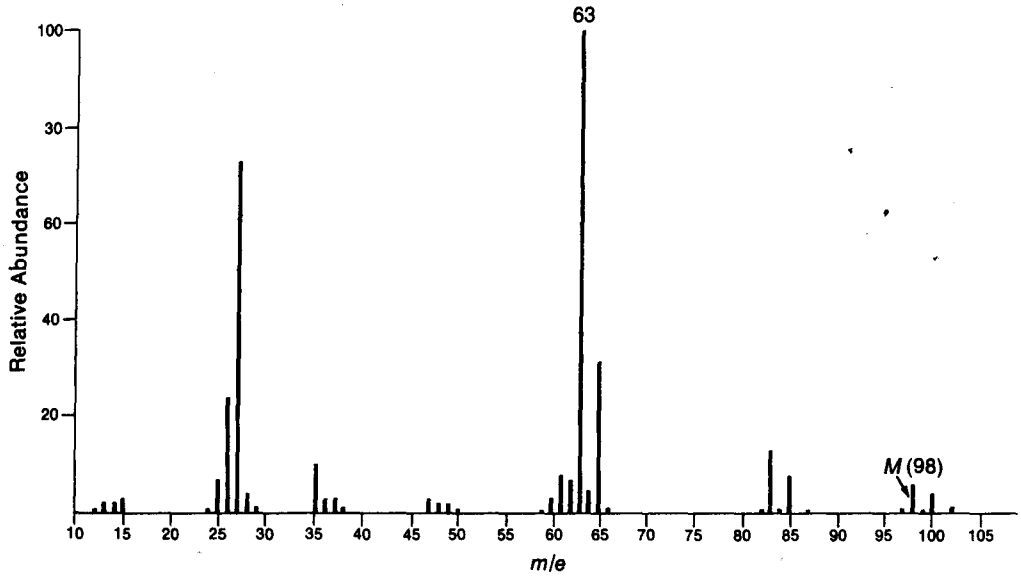
*(p)


57
100
80
60
40
20
Relative Abundance
M (136)
20 25 30 35 40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140
m/e

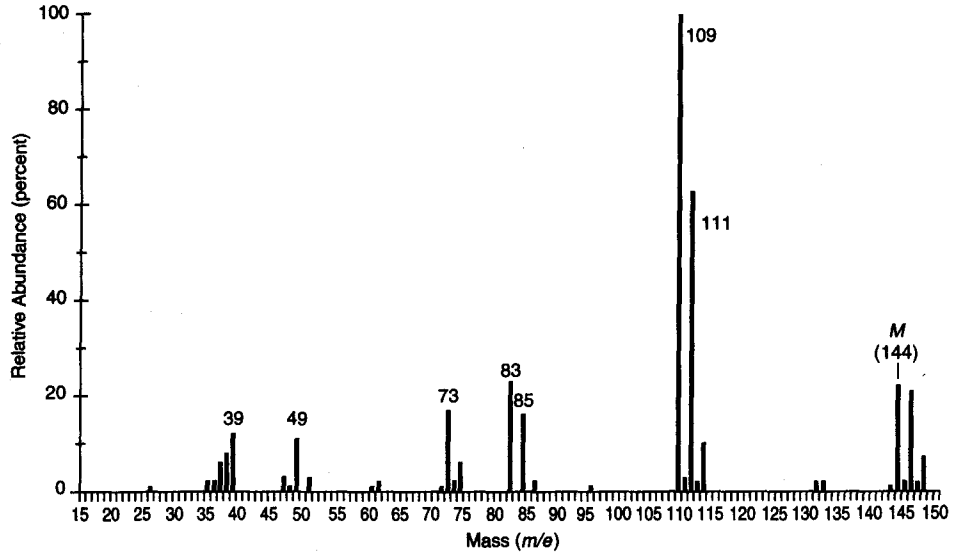
*(q)


77
100
80
60
40
20
Relative Abundance
M (156)
40 45 50 55 60 65 70 75 80 85 90 95 100 105 110 115 120 125 130 135 140 145 150 155 160
m/e

*(r)



*(s) The infrared spectrum of this unknown shows a sharp peak at 3087 cm^{-1}, and a sharp peak at 1612 cm^{-1}, in addition to other absorptions. The unknown contains chlorine atoms, but some of the isotopic peaks ($M + n$) are too weak to be seen.



8. The mass spectrum of 3-butyn-2-ol shows a large peak at $m/e = 55$. Draw the structure of the fragment and explain why it is particularly stable.