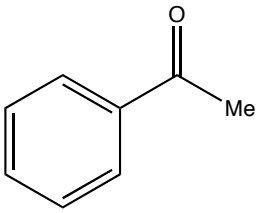
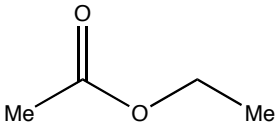
Answers to Problem Set 9

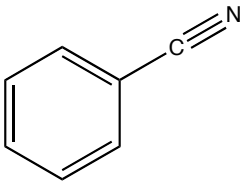
1.

a) 

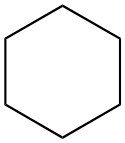
(acetophenone) There is a strong 1690 absorbance, definately a carbonyl & probably conjugated (which lowers the absorbance about 20 cm^{-1}. The peak at 1590 is indicative of a benzene ring (probably also conjugated) and the aromatic overtones are also visible. This is not an aldehyde, since there are no signals at 2850 and 2750 cm^{-1}.

b) 

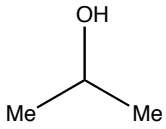
(ethyl acetate) The strong carbonyl absorbance at 1745 cm^{-1} is typical of an ester. Since there was only one ester on the list, that is all the data we need.

c) 

(benzonitrile) The strong signal at 2220 cm^{-1} indicates a triple bond of some sort. We could probably guess that it was a C-N triple bond because the signal is so strong (remember: bigger dipole change, bigger signal!). However, we can also see a signal at 1595 cm^{-1} and the aromatic overtones, indicating the presence of a benzene ring.

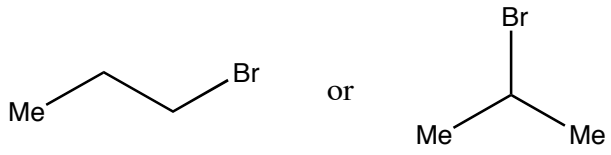
d) 

(cyclohexane) This spectrum contains only C-H bonds that absorb below 3000 cm^{-1}, and clearly does not contain any double, triple or O-H bonds. It must therefore be the only alkane on the list.

e) 

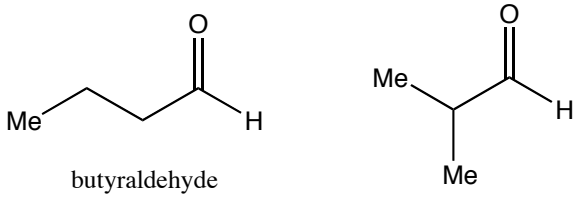
(isopropanol) The strong, broad signal at 3300 cm^{-1} is from an alcohol O-H (not an acid, since there is no C=O singal and the signal at 3300 cm^{-1} does not extend below 3100 cm^{-1}. The molecule also does not have any signals indicative of a benzene ring.

2a. The peaks at 122 and 124 in a 1:1 ratio are indicative of a bromine isotope pattern. Subtracting 79 mass units from 122 (for ^{79}Br) or 81 mass units from 124 (for ^{81}Br) leaves us with 43 mass units remaining, which we have seen before is probably a propyl (C_3H_7) group (unfortunately, the "M+1 trick" for determining the number of carbons doesn't work very well here, because the signal is so small). Our best guesses for the unknown structure that are consistent with this spectrum are *n*-propyl bromide or *iso*-propyl bromide:



2b. The IR spectrum shows a strong absorption at 1725 cm^{-1} – indicating a ketone, aldehyde or carboxylic acid carbonyl. The peaks at 2850 and 2750 cm^{-1} confirm that the molecule contains an aldehyde.

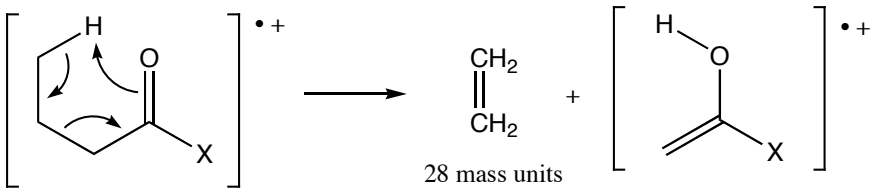
The parent ion is 72, and the M+1 peak is about 6% of the parent ion. Subtracting one oxygen atom (for the carbonyl) from 72 leaves us with 56. We can't possibly have five carbon atoms (12 X 5 = 60, too high), so we probably have four carbon atoms and a molecular formula of C_4H_8O. Since we know there is an aldehyde, only two arrangements are possible (I consider either of these answers "correct"):



butyraldehyde

isobutyraldehyde

Note: To distinguish between these two possibilities (yes, this is tricky with just MS/IR – NMR would make it so much easier!), we would have to use a characteristic fragmentation that is discussed on pgs. 377-378 of the textbook called the *McLafferty rearrangement* [no, you will not be tested on this]. Notice that the base peak at 44 is 28 mass units less than the molecular ion peak at 72. This is most commonly due to loss of ethylene, which results from the McLafferty rearrangement as shown below:



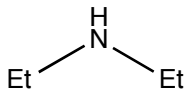
28 mass units

Since only butyraldehyde is able to undergo this fragmentation (because the McLafferty rearrangement requires a 3-carbon chain with hydrogen atoms at the γ-position), that is the correct answer.

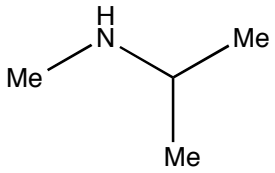
2c. The molecular ion peak for this compound is 73 – an odd number. This means that the compound contains an odd (nonzero) number of nitrogen atoms (let's assume one, since the molecule only weighs 73).

The IR spectrum shows a single (moderately strong) absorption at 3300 cm^{-1}, indicating that we have a secondary amine (it bears one hydrogen atom). We also can note the absence of carbonyl groups, double bonds, etc.

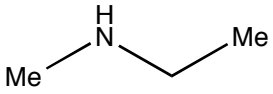
The M+1 peak is 4.7% of the molecular ion, hinting that we have approximately four carbon atoms, so we very likely have a molecular formula of $C_4H_{11}N$. There are several possibilities, and we cannot easily distinguish between them without NMR:



diethylamine

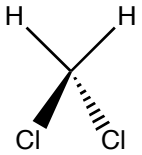


isopropylmethylamine



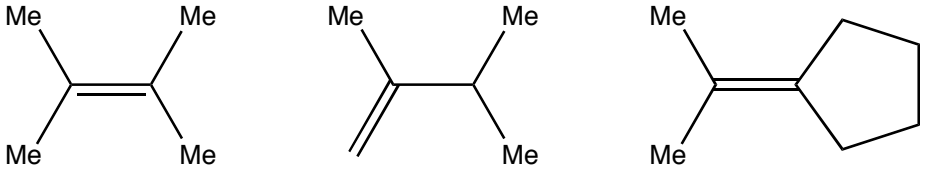
propylmethylamine

3. (Yes, getting the number of chlorine atoms right on this one is very tricky) This compound has a very strange looking region where the molecular ion peak should be: the peaks at 84, 86, and 88 (all 2 mass units apart) are in approximately a 6:4:1 ratio. This looks like a halogen isotope pattern of some sort (Cl or Br). We know that if we have one Cl atom, we should see a 3:1 ratio of peaks. What if we have two Cl atoms? Statistics say we should see a 100:65:10 ratio of three peaks (spaced two mass units apart). <u>The fragment ions at 49 and 51 also give us a big hint</u>. They are in a 3:1 ratio, and result from the loss of 35 or 37 mass units from the molecular ion peaks (the loss of one Cl atom). If we subtract 70 (the mass of two ^{35}Cl atoms) from 84 (our molecular ion peak containing two ^{35}Cl atoms), we are left with 14, which is either N (but it can't be, because we have an even mass!) or CH_2. The identity of our compound is:

$2\ Cl + CH_2 =$ 

dichloromethane

4.



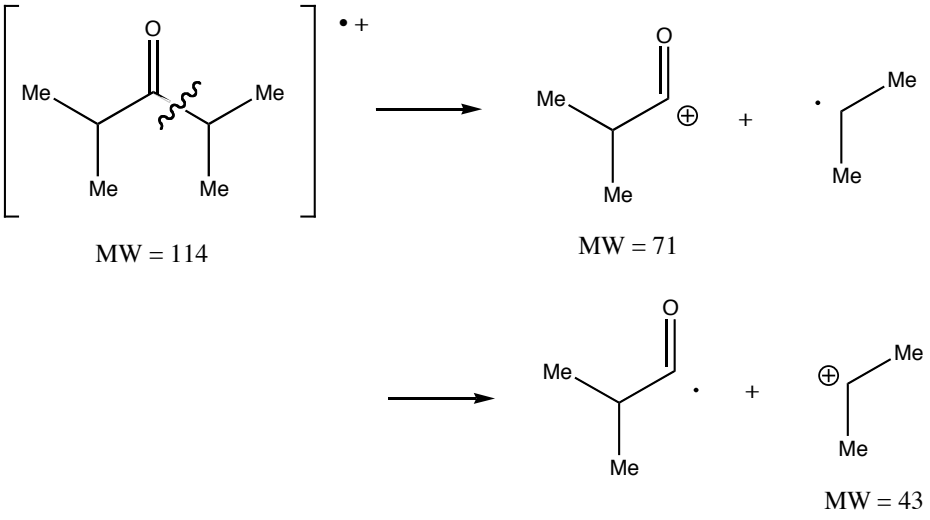
1 **2** **3**

Compound **1** will not show a C=C absorbance, because that stretch causes no dipole change.

Compound **2** will be the only compound with C-H stretching signals above 3000 cm^{-1} (it has C_{sp2}-H bonds).

Compound **3** will show a C=C stretching signal, but contains no C-H bonds that absorb above 3000 cm^{-1}.

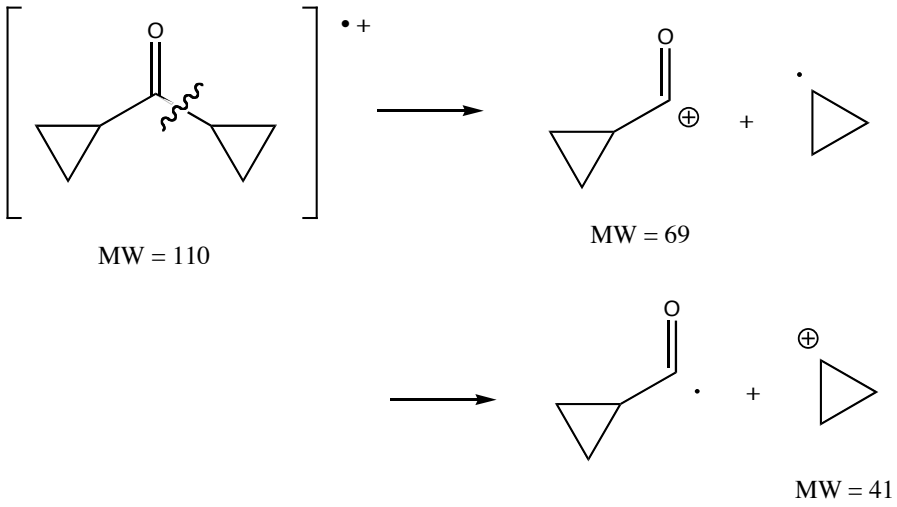
5a.



MW = 114

MW = 71

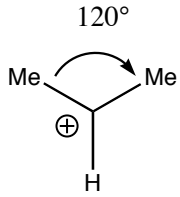
MW = 43

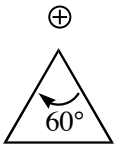


5b. The base peak profile is different because of the difference in stability between the isopropyl cation and the cyclopropyl cation:

a typical secondary carbocation

this secondary carbocation is less stable due to ***angle strain***





A typical carbocation has 120° bond angles. As we make this angle smaller, we destabilize the carbocation. Since cyclopropane has 60° bond angles, the carbocation is much less readily formed.