Problem Set 10 Answers
S343 Summer 2009

Smith Text chapter 13: See text

Techniques in Organic Chemistry

2. The *m/z* base peak for 1-bromopropane is $C_3H_7^+$, the propyl cation.

3. The most stable cations are the base peaks. The base peak at *m/z* 31 for 1-pentanol is $CH_2{=}OH^+$, and the base peak at *m/z* 45 for 2-pentanol is $CH_3CH{=}OH^+$.

4. The ratio of 3:1 for the *m/z* 139 and 141 peaks suggests that each fragment contains a chlorine atom. Both have the formula *p*-$ClC_6H_4C{\equiv}O^+$. The base peak at *m/z* 105 is due to $C_6H_5C{\equiv}O^+$.

6. The odd number molecular-ion peak suggests an odd number of nitrogen atoms, and the broad infrared band of medium intensity at 3300 cm^{-1} is diagnostic for a secondary amine. The compound is *N*-methylbenzylamine, $C_6H_5CH_2NHCH_3$. The *m/z* peak at 120 probably results from loss of $H^\bullet$ from the molecular ion to give $(C_6H_5CH{=}NHCH_3)^+$. The *m/z* peak at 91, $C_7H_7^+$, is the tropylium cation. The base peak at *m/z* 44 is the $(CH_3NH{=}CH_2)^+$ cation.

8. It is likely that the major component of clove oil is eugenol, hit 6. Except for the height of the 149 fragment, the fragmentation peaks are smaller than the peaks in the MS of the major component of clove oil (hit 0); however, they have comparable ratios of heights in all cases, except in the mass range below 30. Hits 1 and 2 have some peaks that are too large and others that are too small, compared to hit 0.

Hit #1: No 163 peak; small 137, 122, and 94 peaks; large 91 peak; small 66, 55, and 39–43 peaks.

Hit #2: Large 136, 133, 43, and 41 peaks; small 103 and 91 peaks.

However, this is not conclusive proof. Subtle changes in the GCMS experimental conditions can cause minor changes in mass spectral fragmentation patterns. The identity of the clove oil component would have to be confirmed by NMR analysis, which would show definitive differences in the alkene signals of eugenol, compared to the other two isomers.

Additional problems:

1. Explain why there is a small peak at m/z=32 for the compound CH_3NH_2.

   A heavy isotope such as ^{13}C could cause a $M^+ + 1$ peak.

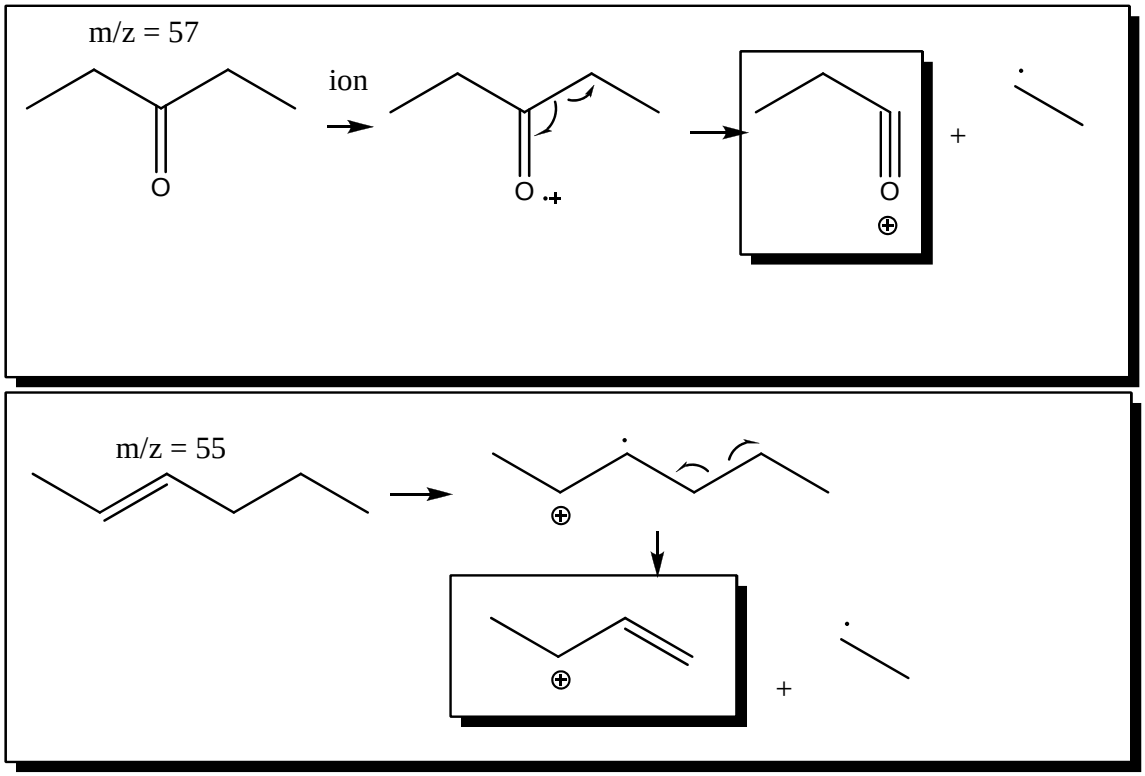
2. What do the following abbreviations stand for?

   a. EI: electron impact (electron ionization)
   b. CI chemical ionization
   c. FAB: fast-atom bombardment

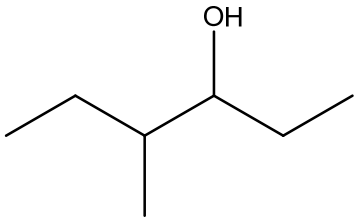
3. Use the rule of 13 to come up with 3 likely formulas that fit $M^+ = 128$.

   C_9H_{20}, $C_8H_{16}O$, $C_7H_{12}O_2$

4. Provide mechanisms to account for the fragments seen in the mass spectrum of these compounds.



5. Give the m/z values of two major fragments you would expect to see in the mass spectrum of the following compound. Mark the one that is most likely to show up as the base peak, and explain.



m/z = 59 most common

m/z = 87

Alpha fragmentation of the left branch will give the more stable secondary radical.

6. What two circumstances lead to fragments with even m/z values?

   a. contains nitrogen
   b. McLafferty rearrangement

7. Give three important pieces of information about the molecular formula of the compound (other than the molecular weight) that you can obtain from this mass spec data.

m/z	Relative abundance
34	21
52	35
91	100
102	22
111 (M^+)	10
113	3.3

   a. odd MW means odd number of nitrogen atoms
   b. $M^+ + 2$ with 33% abundance relative to M^+ means Chlorine
   c. 91 means trypollium, which arises from a benzyl group