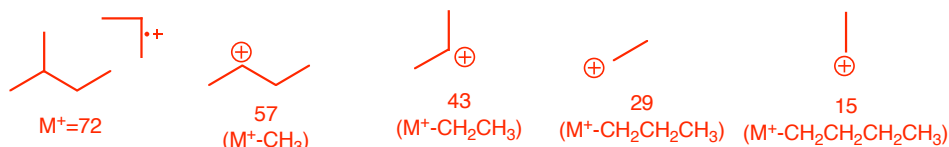


Chem. 218 Problem Set 2

Recommended Problems from the text: 13.1-13.4, 13.21, 13.23, 10.4-10.8, 10.12-10.24, 10.34-10.35, 10.37-10.38, 10.44-10.45, 10.46-10.47 (a-f), 10.48-10.49, 10.50 (a, b, d, e, h), 10.51, 10.53 (a, b, c, e, f, h), 10.55, 10.56 part a, 10.57-10.60, 10.61 part a, 10.62, 10.65-10.67

(Recommended Problems from the first edition: 13.1-13.4, 13.21, 13.23, 10.4-10.7, 10.11-10.24, 10.33-10.36, 10.42-10.43, 10.44-10.45 (a-f), 10.46-10.47, 10.48 (a, b, d, e, h), 10.49, 10.51 (a, b, c, e, f, h), 10.54, 10.55-10.58, 10.59 part a, 10.60, 10.63-10.65)

1. Identify the structure of the ion which is responsible for each of the following peaks in the mass spectrum of 2-methylbutane: 72, 57, 43, 29, 15.



2. For each of the following fragmentation peaks in the mass spectrum of 1-butanol, determine what was lost from the parent in order to form that peak. (For example, a peak at 59 would be characterized as $M^+ - CH_3$): 56, 43, 41, 31

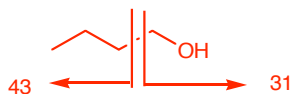
The M^+ is 74.

56 = 74 - 18 so this peak is due to a fragment which has lost water: $M^+ - H_2O$

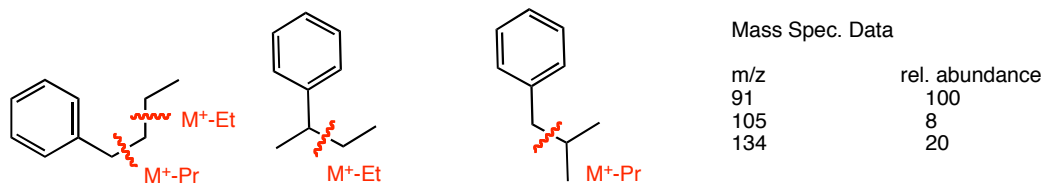
43 is a propyl group. To form a propyl group, which results from loss of CH_2OH

41 is notably 15 lower than 56, so this results from loss of H_2O and CH_3

31 = 74 - 43 so this peak is due to loss of a propyl group. Note that this fragment and the fragment at 43 are the two halves of the molecule.



3. Determine which isomer below corresponds to the mass spectral data.



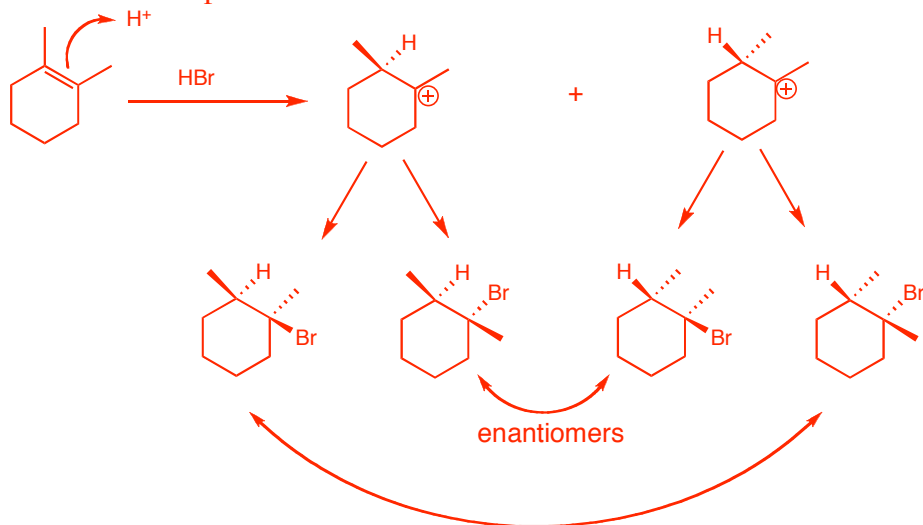
134 is the M^+ peak for each one. 105 results from loss of a methyl, and 91 loss of a propyl. Only the compound on the left can lose both a methyl and a propyl group, so the mass spectral data is for the first compound.

4. Explain why the molecular weight of a compound may be different than the mass of the parent ion.

The molecular weight of a compound is calculated by adding up all atomic weights. But, atomic weights take in to consideration other isotopes and their natural abundances (ex. atomic weight of carbon = 12.011 not 12 because ^{13}C adds a small amount to the atomic weight. Likewise, the atomic weight of bromine is 79.904, because ^{78}Br is only slightly more abundant than ^{80}Br). However, in MS, we are plotting the mass of each molecule, not an average of all molecules. So, the mass of the parent ion may not be exactly the same as the molecular weight.

5. None of the addition reactions we have studied so far is enantioselective, in that the products are always formed as a racemic mixture. Why?

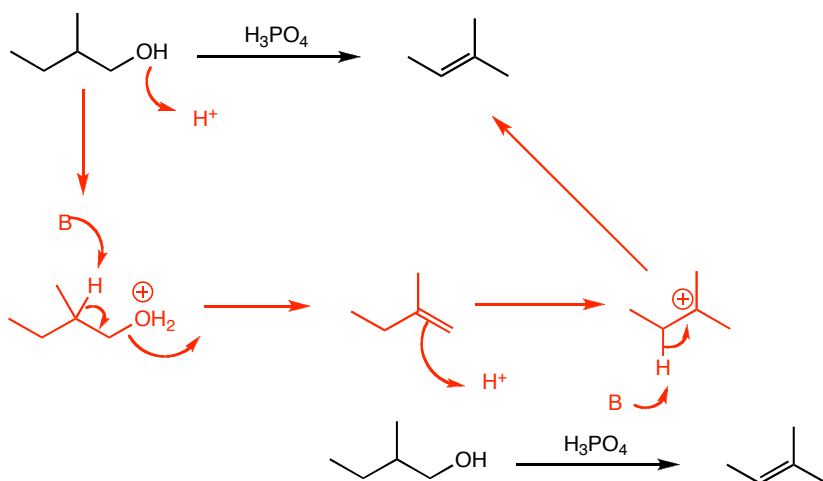
In every case, the initial addition to the alkene can occur from either the top or the bottom face. For example:



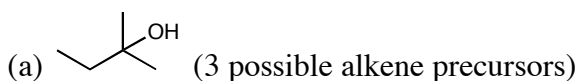
6. Make sure you can do all assigned problems in chapter 10, and that you can draw the mechanism for all transformations in the assigned problems.

7. Unlike 2° and 3° alcohols, 1° alcohols cannot undergo cationic shifts during dehydration reactions (why?). However, they can appear to have undergone a shift. Based on what you now know about alkenes in the presence of acid, propose a mechanism for the following transformation without using a hydride shift.

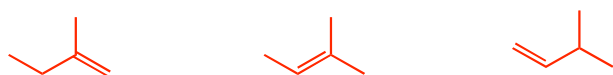
Primary alcohols are dehydrated by an E2 mechanism. In this case, the dehydration occurs without a shift (because there are no carbocation intermediates). Then, the alkene is re-protonated to give the most stable carbocation, which eliminates a hydrogen to give the most stable alkene:



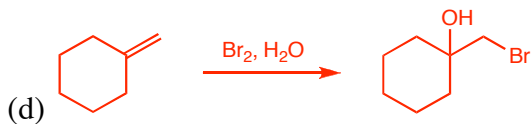
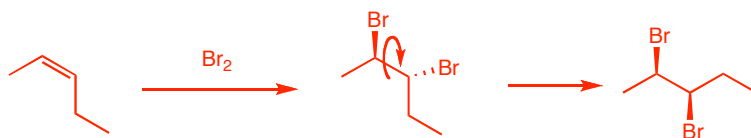
8. Give an alkene precursor and the reagents necessary to form the following compounds:



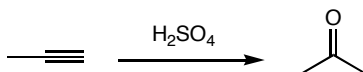
When any of the three alkenes below are treated with H_2SO_4 , they give the desired product. The third would give the desired product after a hydride shift.



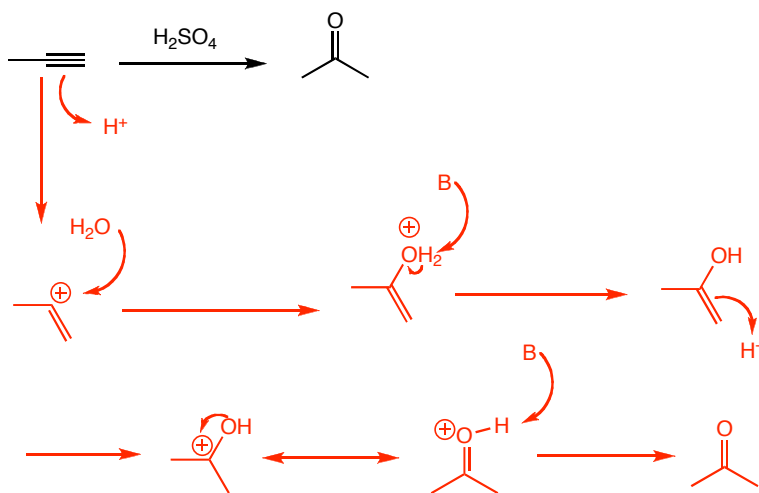
(c) The dibromide appears to be cis, so rotate the sigma bond to make them trans, which is the product of the bromination.



9. Hydration of an alkyne actually results in a ketone rather than an alcohol. Propose a mechanism to account for this transformation.



First the alkyne undergoes acid catalyzed hydration in the same way that alkenes do. Then, protonation of the resulting alkene is protonated once again, leaving a carbocation intermediate. This cation has a resonance form with a C=O double bond, which is simply deprotonated to give the ketone. See section 11.9 for additional information.



10. Propose two syntheses of the following bromide from any alkene. You may use a different alkene for each synthesis.

This problem cannot be done using chemistry you currently know. Sorry...we'll come back.