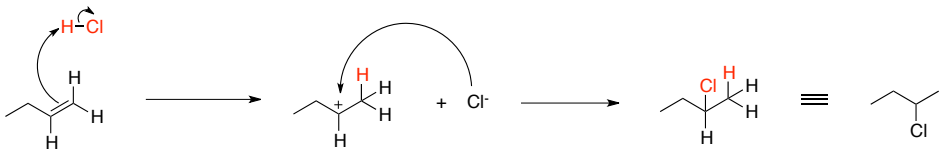
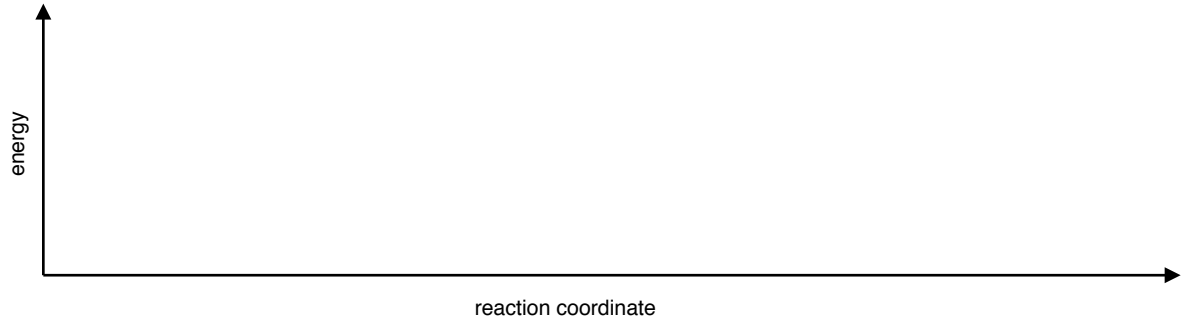
CHAPTER 7: AN OVERVIEW OF ALKENE REACTIVITY



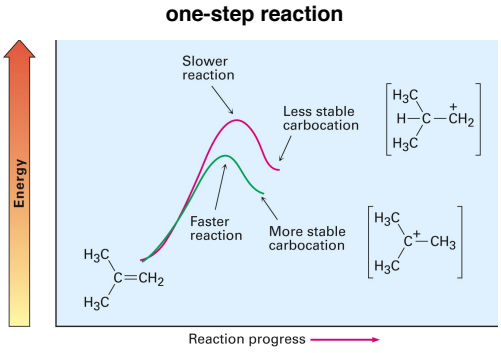
starting material, SM intermediate, I product, P

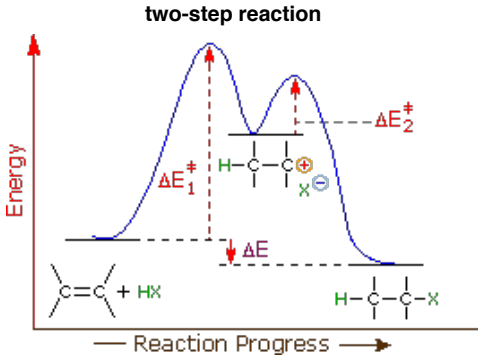
Draw a qualitative energy diagram for this entire reaction. This is a two step reaction, so make sure there are TWO transition states.



The highest point in that energy diagram should be for the first transition state. Getting over that energy barrier is of utmost importance for the success of the reaction, so stabilizing the transition state is very important!

Hammond Postulate. *The structure of a transition state resembles the structure closest to it in free energy.*

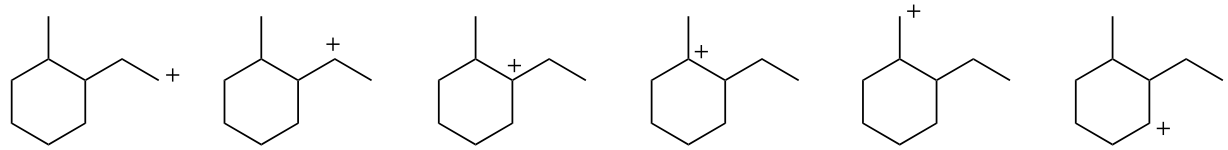




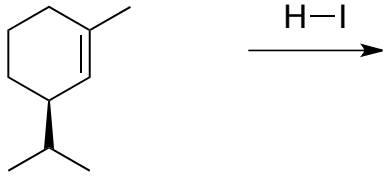
How does this apply to electrophilic addition reactions? For a TWO-STEP exergonic reaction (like electrophilic addition to an alkene), the first and second transition states will resemble the carbocation intermediate (see figure, upper right).

Still not getting it? Any factor that stabilizes the carbocation intermediate will also stabilize the transition state; and hence will accelerate the reaction. The Hammond Postulate supports the carbocation stability trend of 3° > 2° > 1°.

Carbocation Stability. Label the molecules below as having 1°, 2° or 3° carbocations. Circle the two that represent the most stable molecules.

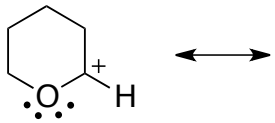


For the next four reactions, draw a stepwise arrow-pushing mechanism that predicts the major product. Do any of these reactions form a mixture of enantiomers or diastereomers?

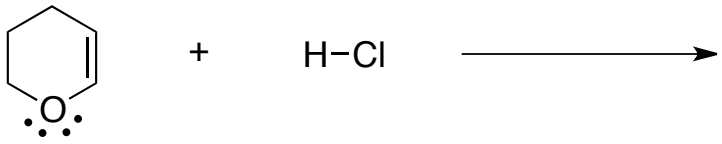


Resonance Delocalization of Charge

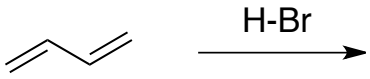
Draw a resonance structure of this molecule that shows *delocalization* of the positive charge. Remember, delocalization of charge is a good thing - it lowers energy and creates stability.



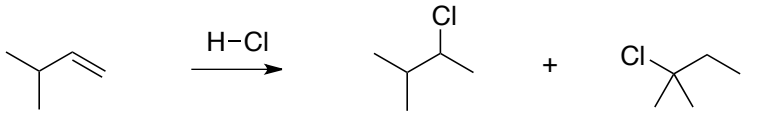
Now draw the mechanism for the following reaction, and predict the major organic product. Can you defend the *regioselectivity* of the reaction?



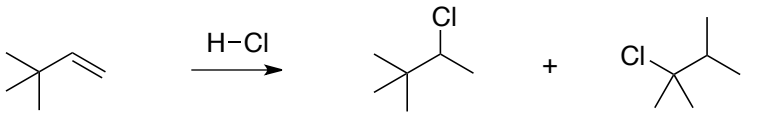
There are two products of the following addition of hydrogen bromide to 1,3-butadiene - what are they?



Carbocation rearrangement. Carbocation intermediates prefer to be stable rather than unstable; period. Hence the trend, 3° > 2° > 1°. If you were to predict the major products of the following reactions, you probably would NOT choose what is labeled as the major organic product, below:



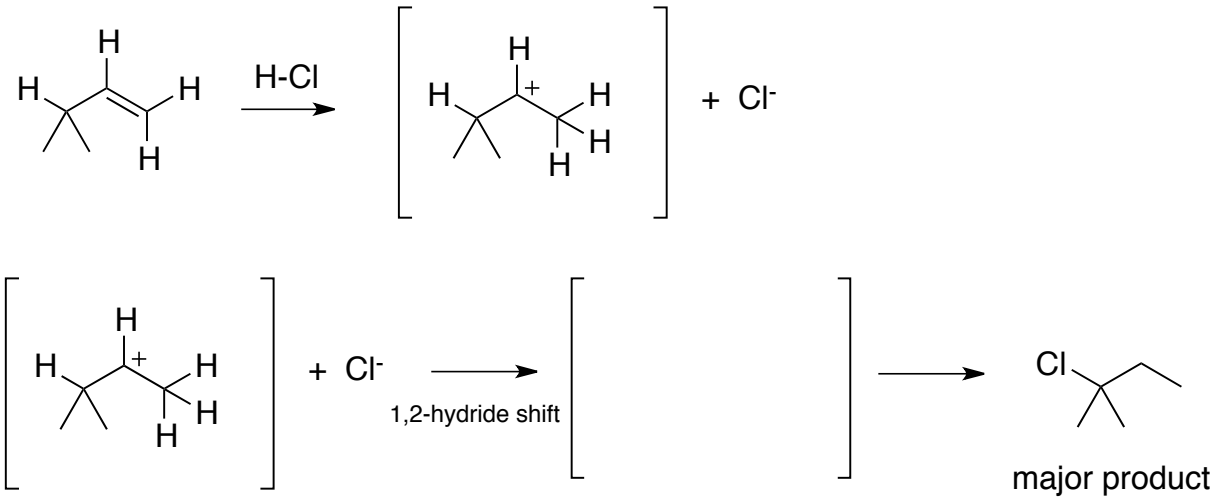
minor product major product



minor product major product

Let's look more closely and see how that happened:

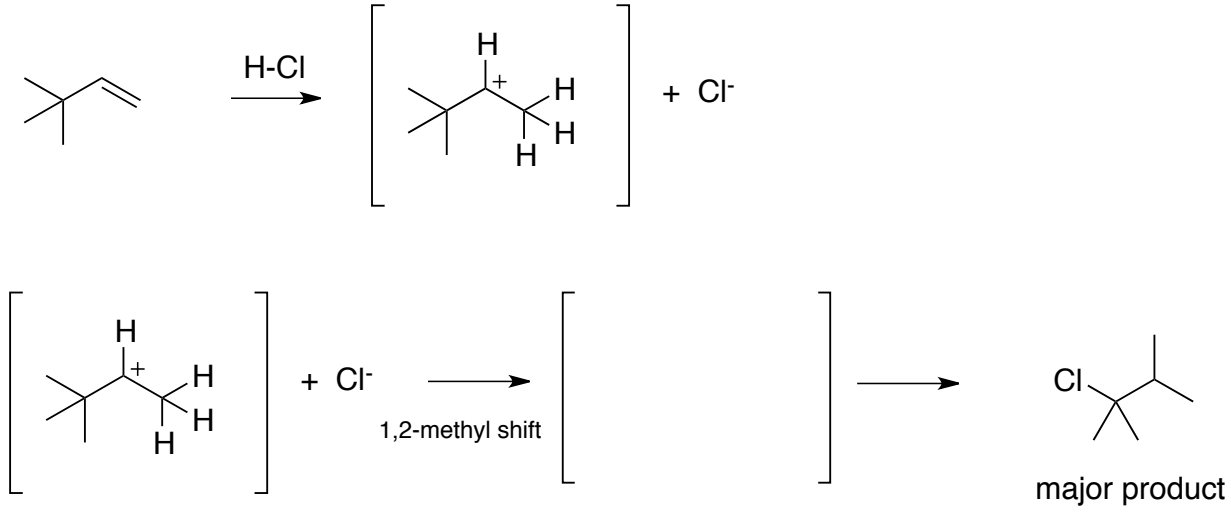
For the first reaction, we know a carbocation intermediate will be formed (I've drawn it for you). However, what MUST the carbocation intermediate look like if we are to form what is identified as the major product (draw it within the empty brackets)? Why did the rearrangement happen?



what must this structure be?

Draw a curved arrow on the intermediate, above, showing this 1,2-hydride shift.

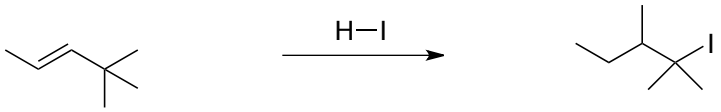
Now let's try a 1,2-methyl shift. Again, predict what the intermediate is in the blank brackets below, and draw a curved arrow that shows the 1,2-methyl shift. Why did the rearrangement happen?

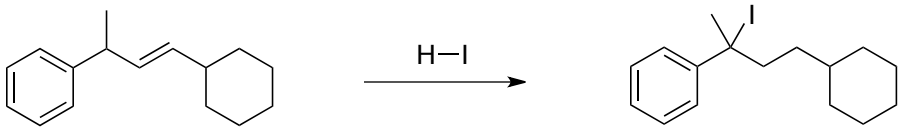


what must this structure be?

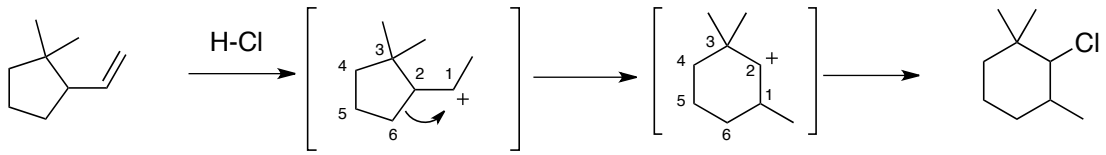
1,2-Hydride and 1,2-alkyl shifts are common IF the resulting intermediate is more stable than before the rearrangement. There's a reason for everything, and usually it boils down to a reaction pathway seeking a lower energy.

For each intermediate below, draw an arrow-pushing mechanism that details product formation, as shown.

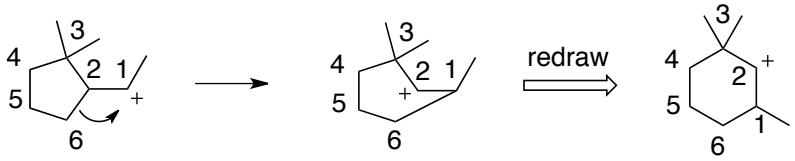




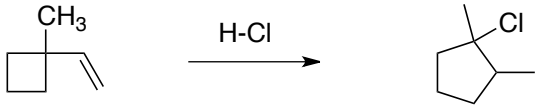
Rearrangement Resulting in Change in Ring Size. Rearrangements are common when a lower energy intermediate can be reached. In some cases, the carbocation energy isn't the major factor to consider, but the ring size.



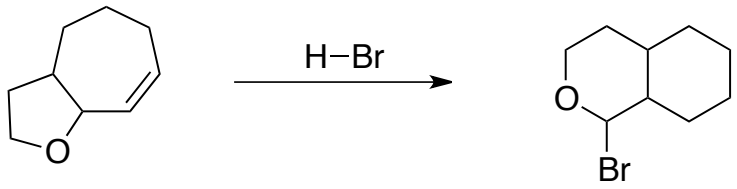
Although drawing a mechanism for this rearrangement involves one arrow, correctly drawing the rearranged intermediate can be tricky. NUMBERING YOUR ATOMS will help immensely; like this:



You try. Draw a mechanism that involves rearrangement of the initially formed carbocation intermediate to form a lower-energy carbocation intermediate.



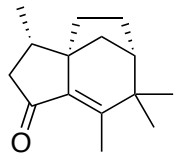
Challenge: Draw a mechanism that accounts for the following transformation.



Biological Rearrangements.

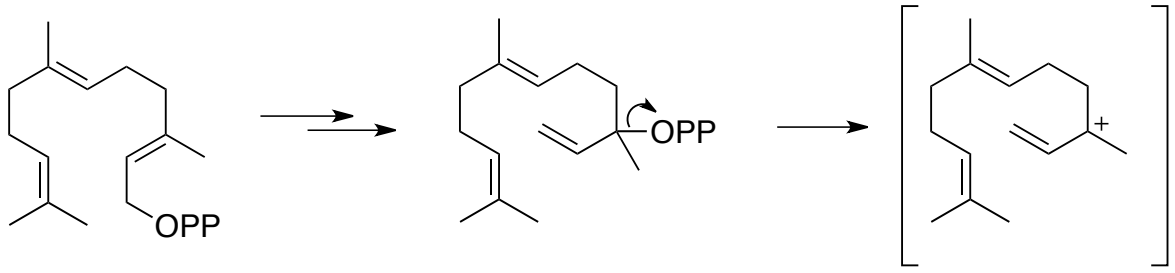
Farnesyl pyrophosphate (FPP), a sesquiterpene, is a common intermediate synthesized by organisms (animal and plant) in the process of synthesizing terpenoids and steroids.

The tricyclic sesquiterpene albaflavenone, which has been isolated from the gram-positive soil bacteria *Streptomyces coelicolor* and *S. albidoflavus*, exhibits antibacterial activity. In the process of studying the biosynthesis of albaflavenone in *S. coelicolor*, a detailed GC-MS analysis of the organic extracts resulting from the incubation of FPP with wild-type epi-isozizaene synthase revealed the formation of at least 6 additional sesquiterpene hydrocarbons; one of which is α-neocallitropsene.



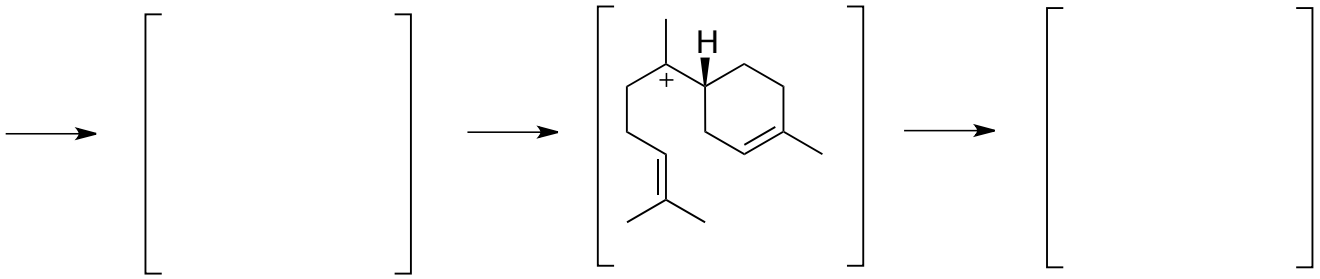
albaflavenone

Draw an arrow-pushing mechanism, and add structures where needed (empty brackets).

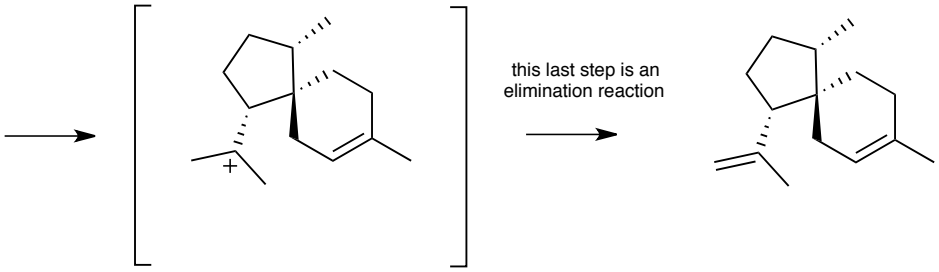


farnesyl diphosphate

nerolidyl diphosphate



bisaboyl cation



acorenyl cation

α-neocallitropsene