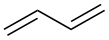
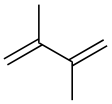
Organic Chemistry I Jasperse
Test 4: Extra Practice with HBr addition to Dienes (p 1,2) and Allylic NBS Brominations (p3,4).

Review on predicting products when H-X adds to a diene.

1. Always protonate first on an outside rather than inside carbon.
   - This will give an allylic rather than isolated cation
2. Is the diene symmetric or asymmetric?
   - If it's symmetric, it doesn't matter which outside carbon you add to first.
   - If it's asymmetric, then protonating at different ends will likely give allylic cations of unequal stability. Thus you should decide which protonation site will give the best allylic cation.
3. Is the allylic cation (once you have protonated) symmetric or asymmetric?
   - If it's symmetric, you'll get one structural isomer.
   - Is it's asymmetric, you'll get two structural isomers.

A. For each of the following:
   a. Predict products following HBr addition. (Will there be just one, or more than one?)
   b. Draw mechanisms. Be sure to draw both versions of the allylic cation.
   c. Identify 1,2 versus 1,4 addition products.
   d. Identify thermodynamic product.

1. 

2. 

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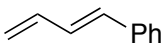
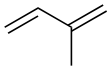
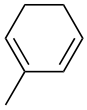
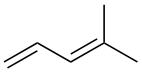
4. 

5. 

6. 

7. 

Practice with NBS bromination of Alkenes.

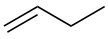
Review on predicting products for NBS allylic radical bromination of an alkene.

1. Any allylic spot with an H could give up an H to product an allylic radical. How many allylic spots are there?
2. If there is more than one allylic spot, is the alkene symmetric or asymmetric? In other words, will the different allylic spots give the same allylic radical or unequal allylic radicals?
   - If there is more than one allylic radical, they may be of unequal stability. So one might lead to more product than the other. Still, you should expect to get at least some product from each of the allylic radicals.
3. One you have made an allylic radical, is it symmetric or asymmetric?
   - If it's symmetric, you'll get one structural isomer from it.
   - If it's asymmetric, you'll get two structural isomers out.
   - Note that if you your allylic radicals are asymmetric, you'll get two bromide products for each one. So if you have two different allylic sites each offering asymmetric allylic radicals, you'll get 2 x 2 = 4 isomer products.

B. For each of the following:
   a. Predict products following allylic NBS reaction. (Will there be just one, or two, or four?)
   b. Draw all allylic radicals that could be intermediates.
   c. For each allylic radicals, draw all resonance structures.
   d. Be sure to note whether allylic radicals and allylic resonance structures are the same or different.

Draw products following NBS/peroxides bromination. Identify radicals, and draw all resonance structures for the radicals.

1. 

2. 

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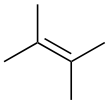
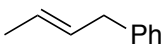
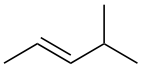
4. 

5. 

6. 

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