Practice with HBr addition to Dienes.
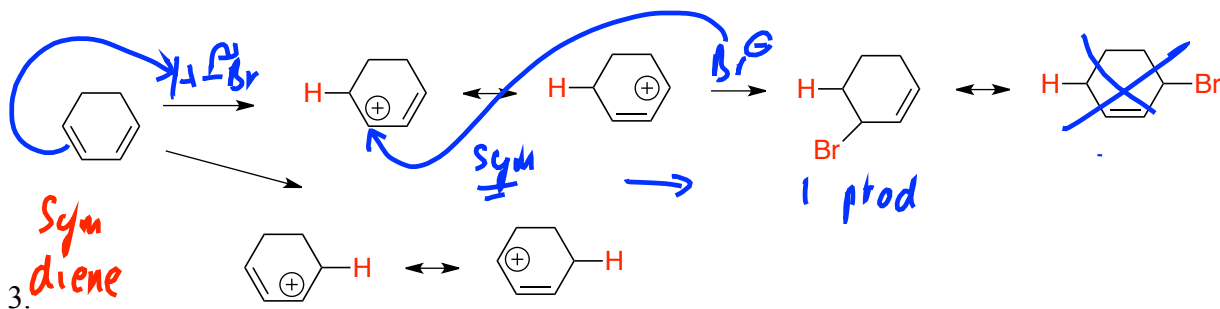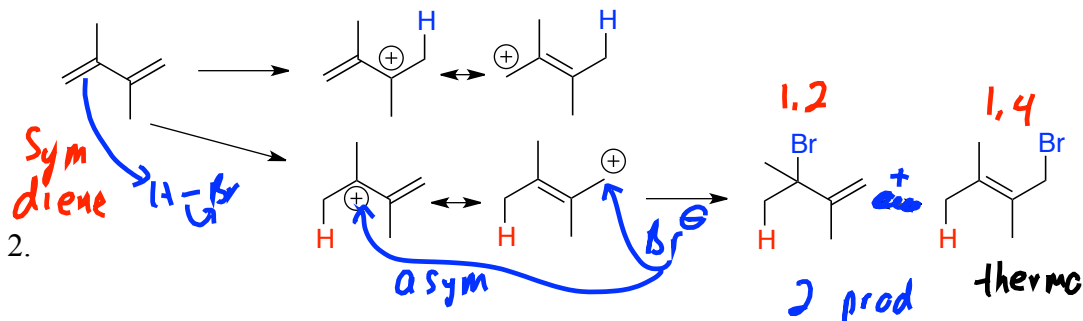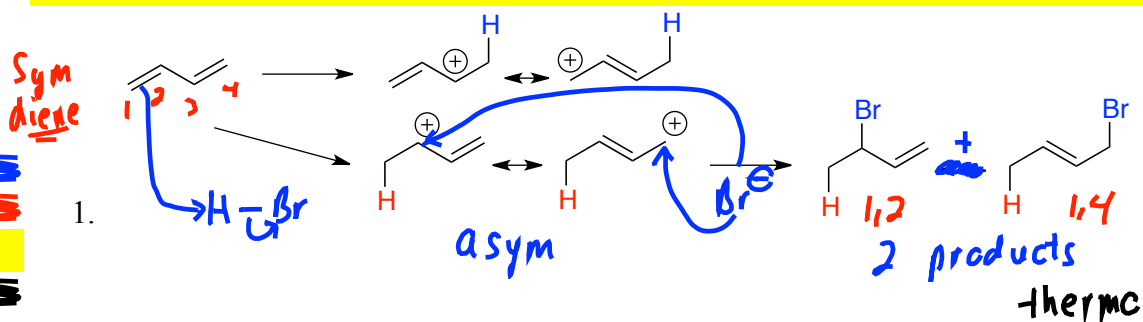
Review on predicting products when H-X adds to a diene.
1. Always protonate first on an outside rather than inside carbon.
   - This will give an allylic rather than isolated cation
2. Is the diene symmetric or asymmetric?
   - If it's symmetric, it doesn't matter which outside carbon you add to first.
   - 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.
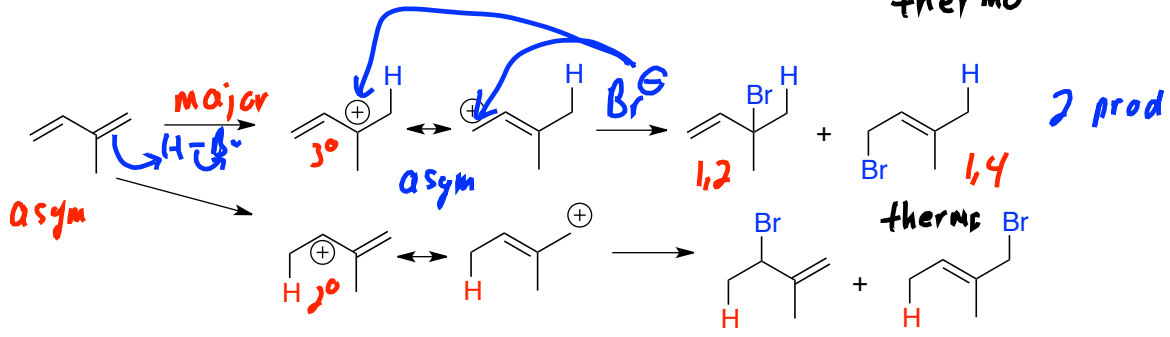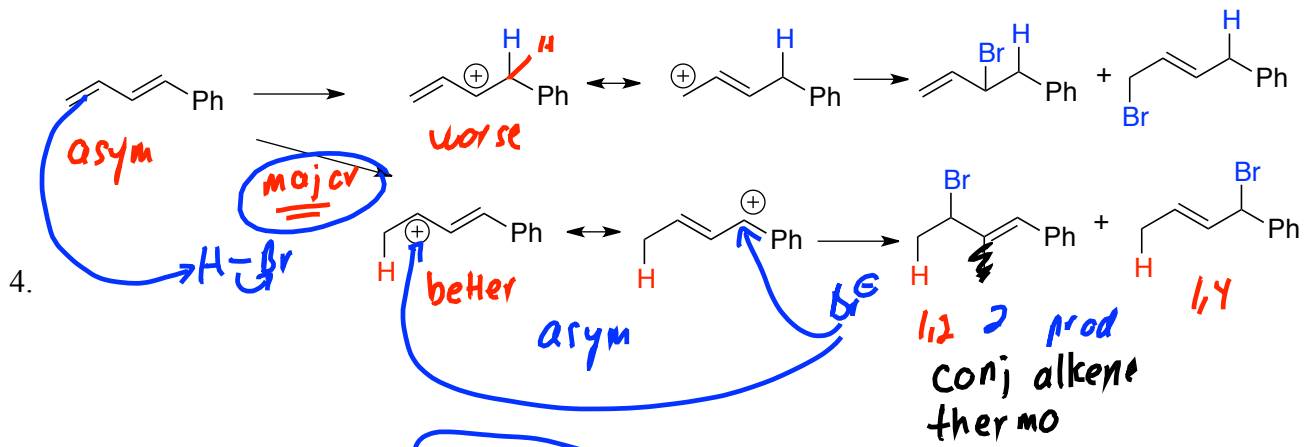3. Is the allylic cation (once you have protonated) symmetric or asymmetric?

*Problems 1-3 involve symmetric dienes. I have drawn the allylic cations that would result from protonation on either end, but this is only for illustration sake only. On a real test question, either cation would be fine.
*Problems 1 and 2 represent cases where the diene is symmetric, but the resulting allylic cation is not symmetric. Thus two structure isomers would be produced.
*Problem 3 represents a case where not only is the diene symmetric, but so too is the allylic cation. Thus only one isomer will form.
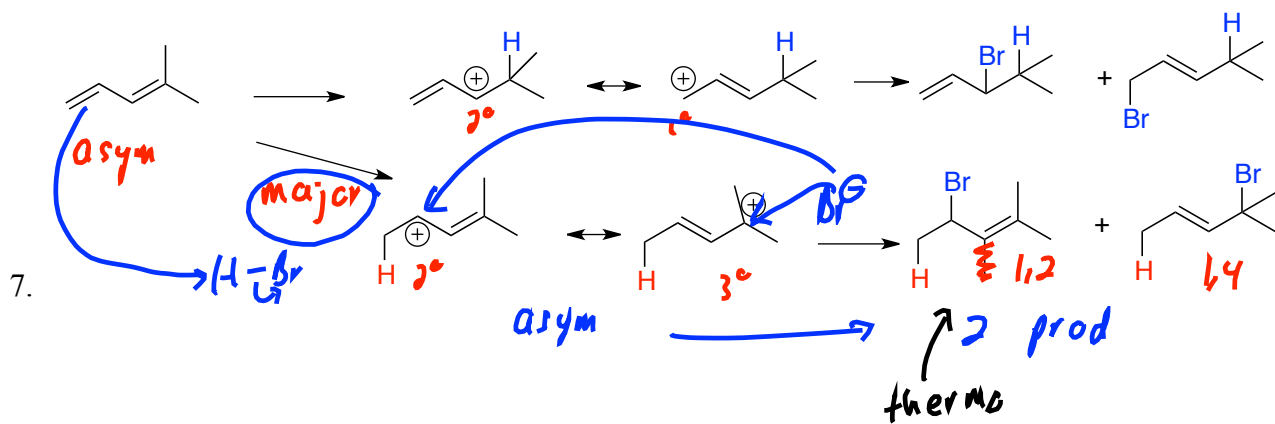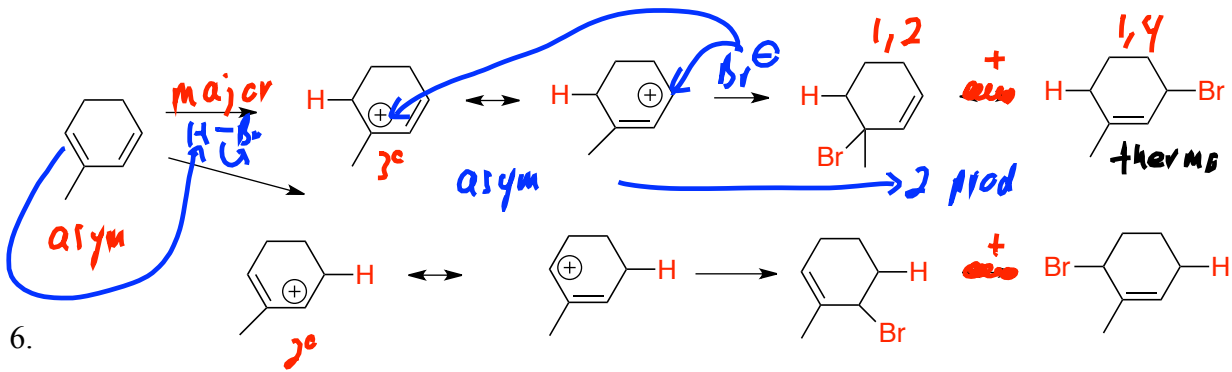
1.

Sym diene

H—Br

asym

1,2   1,4
2 products
thermo

2.

Sym diene

H—Br

asym

1,2   1,4
2 prod   thermo

3.

Sym diene

Sym

1 prod

4. asym · H—Br · worse · major · better · asym · Ph · Ph · Ph · Ph · Br · H · 1,4

1,2 · 2 prod · conj alkene · thermo

major · H—Br · asym · 3° · asym · Br⁻ · H · Br · Br · 1,2 · 1,4 · 2 prod · thermo · 2° · H · Br · Br

5.

major · H—Br · asym · 3° · asym · br⁻ · 1,2 · 1,4 · H · Br · H · Br · + · can · 2 prod · therms · 2° · Br · H

6.

asym · H—Br · major · H · 2° · 2 prod · 1,2 · 1,4 · Br · thermo · + · can · Br · H

**7.** asym · H—Br · major · 2° · 2° · asym · Br⁻ · 3° · H · H · Br · Br · 1,2 · 1,4 · + · 2 prod · thermo

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.

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

1.
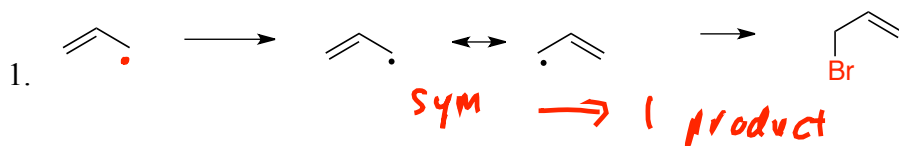
==*This illustrates the simplest case. There is only one allylic position, and the allylic radical is symmetric leading to a single product.==
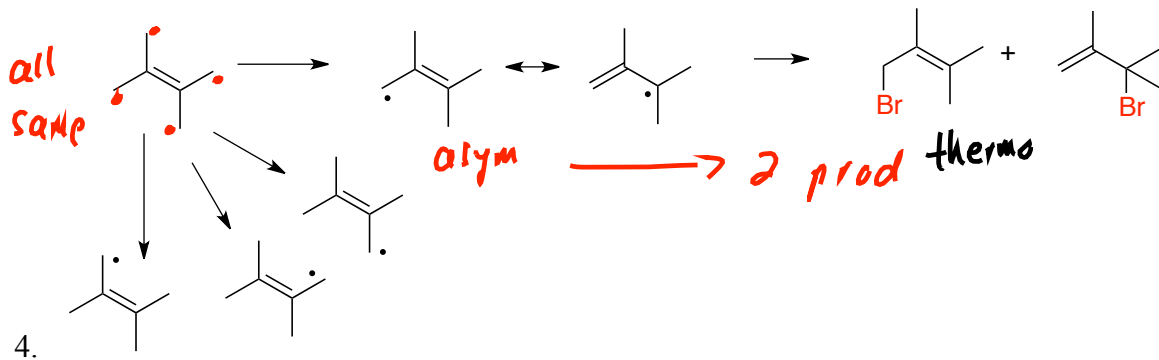
2.
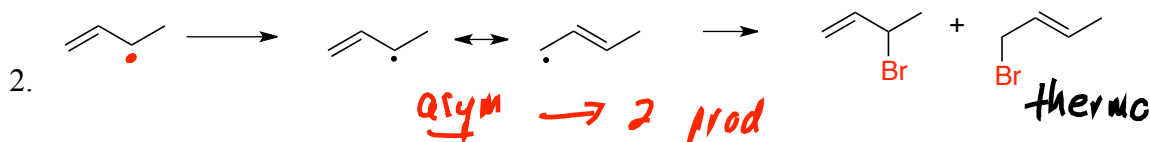
==*Problem 2 has only a single allylic position, but proceeds via an asymmetric radical which leads to two products.==
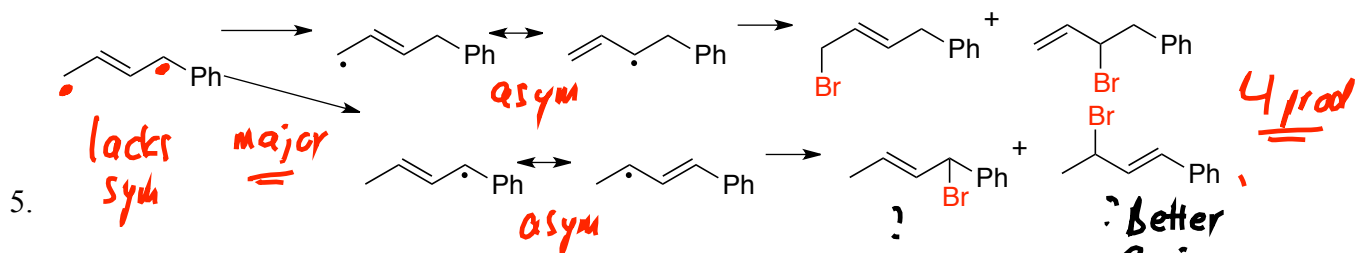
3.
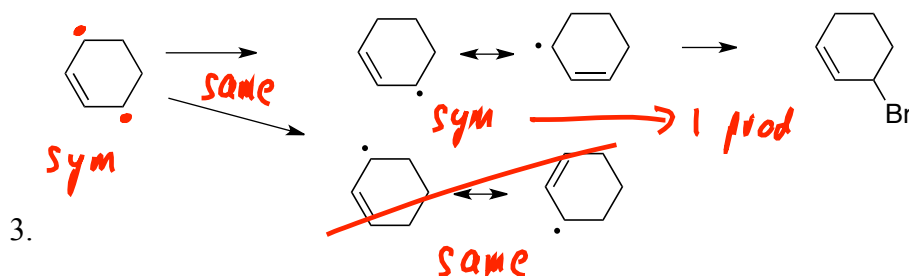
==*Problem 3 represents a symmetric alkene.==
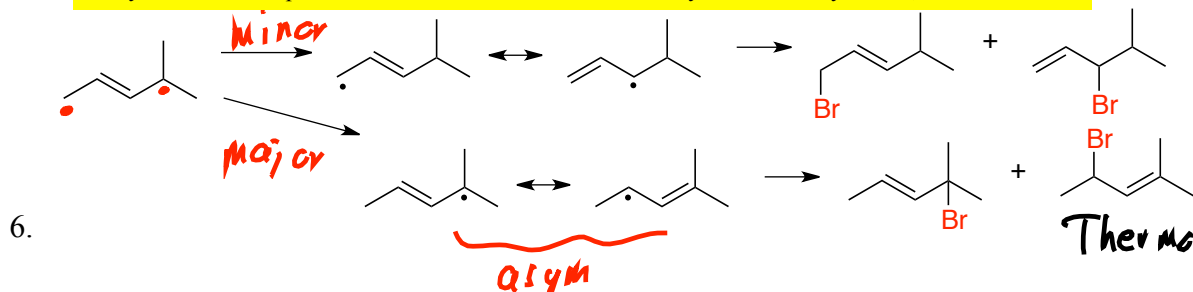==It has two allylic positions, but due to symmetry they are both equivalent.==
==The allylic radical formed is symmetric, thus only a single isomer is produced.==

all
same

asym

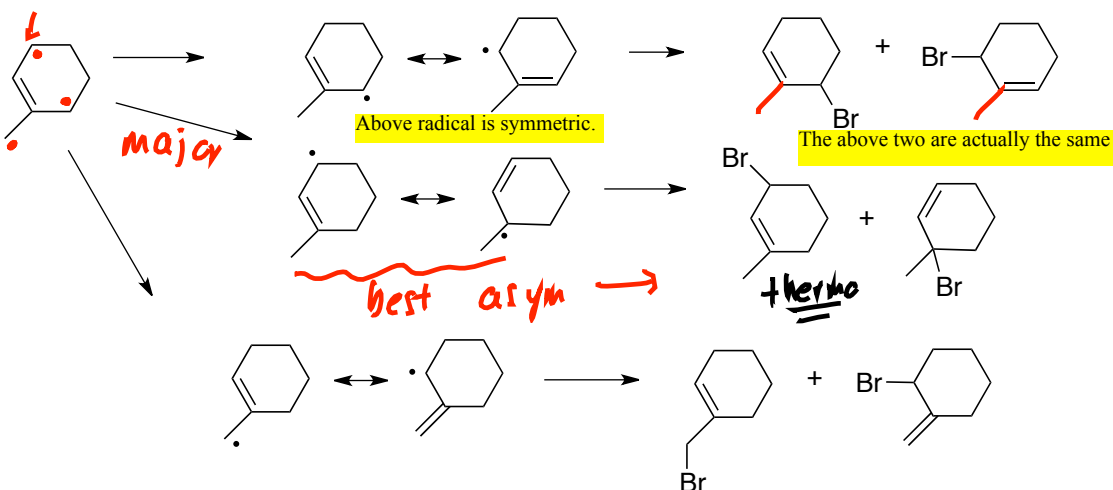→ 2 prod thermo

Br   Br

4.

*Problem 4 represents a symmetric alkene.
It has four allylic positions, but due to symmetry they are all equivalent.
*The allylic radical formed is asymmetric, thus two isomers are produced.

Ph   Ph   Ph +   Ph

asym   Br   Br
                               Br   4 prod

lacks   major
sym   better
5.   Conj
        Ph   Ph   Ph +   Ph   Thermo
        asym   Br   Br

*Problem 5 represents an asymmetric alkene.
It has two allylic positions, and they are not equivalent.
*Each allylic radical formed is asymmetric, thus each produces two isomers.
*2 isomers x 2 products from each => 4 isomeric products.
*The yield of the two products born from less stable "minor" allylic radical may be low, but is not zero.

Minor

+

Br   Br
                Br

Major

+

Br   Br

6.   Thermo
     asym

*Problem 6 represents another asymmetric alkene.   It has two allylic positions, and they are not equivalent.
*Each allylic radical formed is asymmetric, thus each produces two isomers.
*2 isomers x 2 products from each => 4 isomeric products.
*The yield of the two products born from less stable "minor" allylic radical may be low, but is not zero.

+   Br

major   Br
               Above radical is symmetric.
                                        The above two are actually the same
          Br

                                +

best asym →

              thermo   Br

+   Br

7.

*Problem 7 represents another asymmetric alkene, with 3 non-equivalent allylic positions

Br