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?
   - If it’s symmetric, you’ll get one structural isomer.
   - If it’s asymmetric, you’ll get two structural isomers.

Predict products. Draw mechanisms. Identify 1,2 versus 1,4 addition products. Identify thermodynamic product.

---

*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.*
Problems 4-8 all involve asymmetric dienes. I have drawn the allylic cations that would result from protonation on either end, and have drawn the products that would result. But the yields of products resulting from the "minor" allylic cation may be low.

*In each case the major allylic cation is asymmetric, leading to two structural isomers.

*Problems 4 and 7 both illustrate cases where the 1,2 addition is the more stable "thermodynamic" product.
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. Once 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 $2 \times 2 = 4$ isomer products.

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

1. \[ \text{Sym} \rightarrow 1 \text{ product} \]
   *This illustrates the simplest case. There is only one allylic position, and the allylic radical is symmetric leading to a single product.

2. \[ \text{Asym} \rightarrow 2 \text{ prod} \]
   *Problem 2 has only a single allylic position, but proceeds via an asymmetric radical which leads to two products.

3. \[ \text{Sym} \rightarrow 1 \text{ prod} \]
   *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.
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.

5. *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.

6. *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.

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