Workshop 17 Solutions **Unpaired Electron Pushing**

a. First product:





Second product:



subsequent cycles)

b. You might expect that the more substituted bromide would be preferred-that the first product, a secondary halide, would predominate over the second product, a primary halide-because that's the usual pattern for radical halogenations. Remember, however, that this preference is caused by the difference in energies between the secondary and primary radical intermediates. In this problem, the secondary and primary radical intermediates don't have a difference in energy; they are the same radical, just different resonance structures. So the usual justification for favoring the more substituted bromide cannot apply here.

So then what other criterion can we use to argue for one product over the other? The more substituted alkene is more stable, and the transition state leading to it should also be most stable. So I would expect the second product to predominate. (What might that look like in a potential energy diagram?)