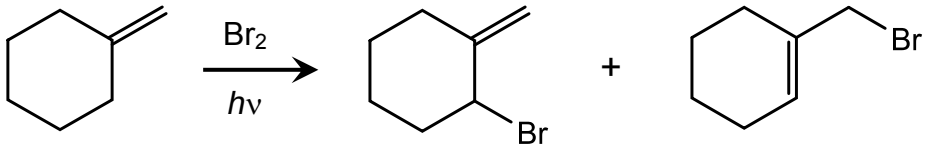
Chemistry 2301

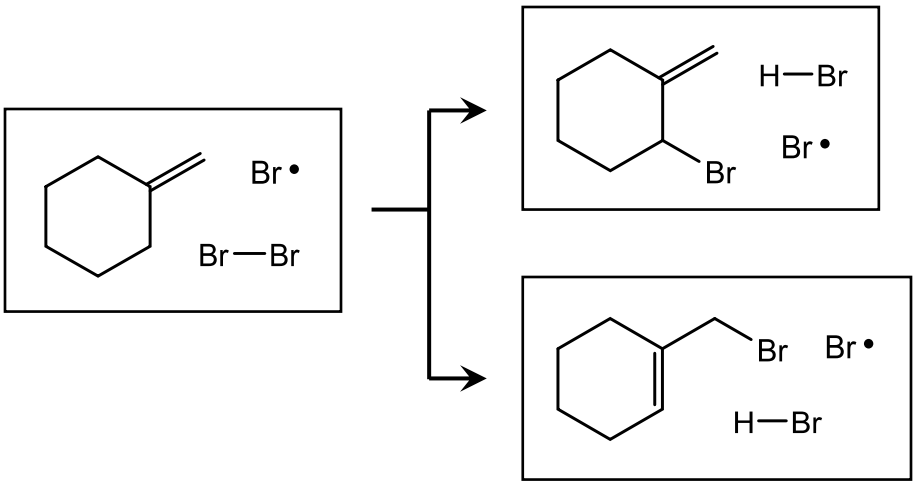
Workshop 21
Unpaired Electron Pushing

1. a. Radical halogenation is especially favored at allylic C-H bonds—C-H bonds adjacent to double bonds—because the organic radical intermediate is stabilized by resonance. For example, the alkene starting material below undergoes radical halogenation very selectively, to give the two products shown.



Draw a mechanism that explains both of these products. Keep in mind that radical mechanisms require an initiation step and propagation steps; make sure your mechanism includes both. (You do not need to draw any termination steps in this problem—they are not typically responsible for products.)

b. Draw a potential energy diagram that illustrates the two propagation steps that turn starting material into each product. Or, put another way, draw energy curves that show how a “box” of starting molecules become each “box” of products:



c. Based on your potential energy diagram, which of the two products would you expect to predominate?

2. Light ("*h*ν") can be used to initiate Br_2 halogenation, but another method is to use a thermal initiator like benzoyl peroxide. The O-O bond in benzoyl peroxide is sensitive to heat, and is homolytically cleaved to produce benzoyl radicals in an initiation step. Draw a mechanism for bromination that uses benzoyl peroxide as the initiator, again showing how the first product above gets made.