

2022 CHAPTER 19 Advanced Topics in Organic Chemical Reactions

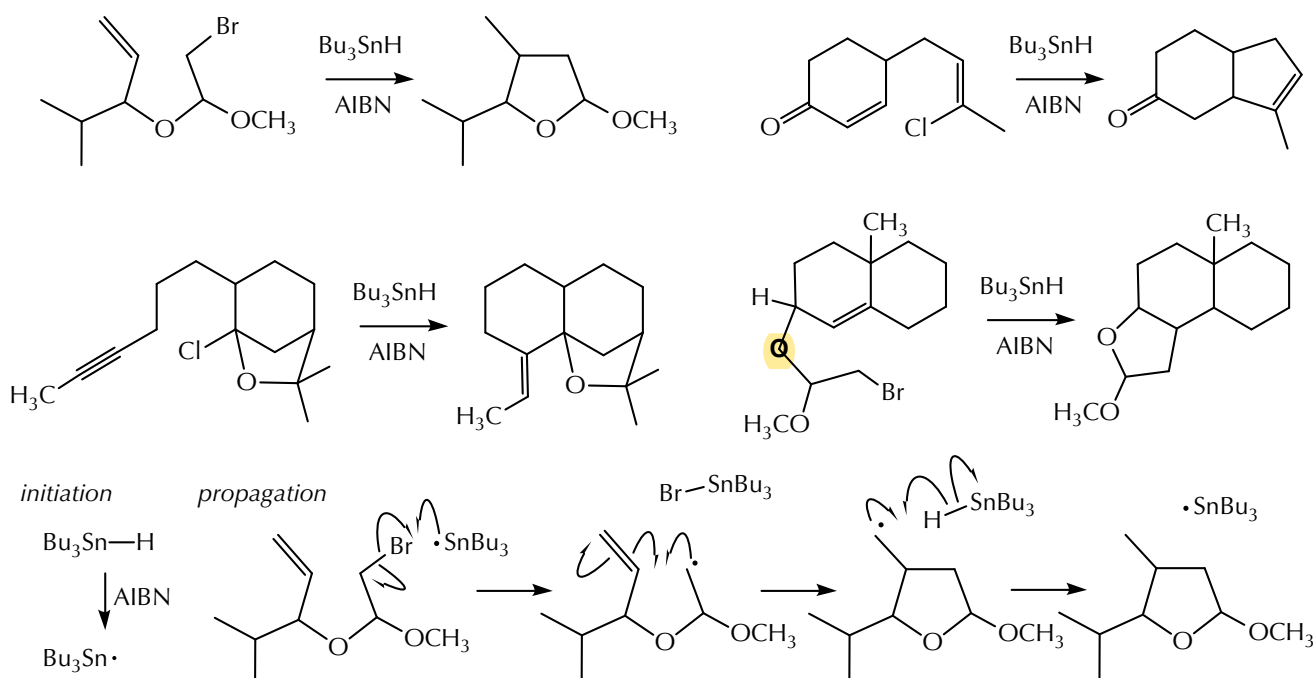
The same mechanism operates for all these cases.

- I. The tributyltin radical, formed from the reaction between tributyltin hydride and radical initiator, is the outcome from the initiation step.
- II. Radical substitution forms a carbon radical from the carbon-halogen bond, which adds to the pi bond of the other reacting partner, giving the second intermediate carbon radical that completes the propagation by reacting with tributyltin hydride.
- III. The standard termination steps are anticipated, with byproducts derived from the statistical coupling of any radicals present in the reaction.

The intramolecular version of these same addition reactions take place readily when there is a double or triple bond accessible to the initially formed radical (Figure 1991).

Figure 1991

Intramolecular radical addition reactions.



These ring-forming reactions between radicals and pi bonds tend to make 5-membered rings. As is true for intramolecular reactions generally, the regioselectivity of the addition reaction is driven by more than the one factor (i.e., the Markovnikov Rule) that governed the intermolecular reaction. Proximity of the reacting centers, ring strain, and the trajectory of the bond-forming step are all additional factors that have been observed to play a role in the regioselectivity of the intramolecular addition reactions.

As you look at the examples, as well as the sample mechanism, notice that the steps are all completely comparable with those in the intermolecular cases.

D. Cascade Reactions

Chemists recognized that the intramolecular addition reactions could be extended to form multiple rings in a single experimental step if, after the first intramolecular addition reaction, a second pi bond was strategically situated for a second addition to occur prior to the termination. Extending the propagation