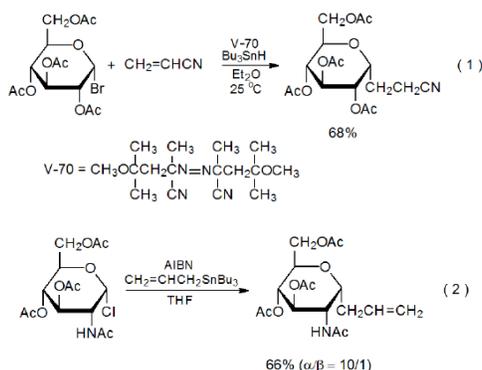


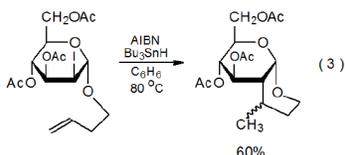
II. Ease of Reaction between a Carbon-Centered Radical and a Multiple Bond

Once structural requirements have been met, successful radical cyclization depends on reaction rates. The basic question is “Will ring formation occur before competing reactions intervene?” The answer to this question depends upon the nature of the radical center and multiple bond and on the separation between these two. The ability of a radical to add to a multiple bond to form a new ring will be addressed first; then, the effect of the separation between the radical center and the multiple bond will be considered.

A beginning point for discussing reactivity between a radical center and a multiple bond during internal addition is to recall some of the findings in Chapter 18 about addition reactions that are not internal. Such reactions take place rapidly when a radical is nucleophilic (as are most carbon-centered radicals) and a multiple bond is electron-deficient. This description fits the reaction shown in eq 1.^{1,2} If a multiple bond is not electron-deficient, radical addition normally is too slow to compete with hydrogen-atom abstraction; however, minimizing or eliminating effective hydrogen-atom transfers from a reaction mixture can enable addition to occur even when the multiple bond is not electron-deficient. An example of this type of reaction is shown in eq 2, where Bu_3SnH is not present in the reaction mixture even though $\text{Bu}_3\text{Sn}\cdot$ is there and acts as the chain-carrying radical.^{3,4}



Addition of a radical to a multiple bond is potentially much faster when the reaction is intramolecular. If a radical center and a multiple bond in a molecule are positioned so that they frequently come within bonding distance, the rate of internal addition increases to the point that even for a multiple bond that is not electron-deficient, cyclization competes effectively with hydrogen-atom abstraction. In the reaction shown in eq 3, internal addition to a double bond that is not electron-deficient takes place even in the presence of Bu_3SnH .⁵



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