

III. Formation of Organosamarium Compounds

At some point after its formation a carbohydrate radical will combine with a molecule of SmI_2 to produce an organosamarium compound. The radical combining with SmI_2 sometimes is the one initially formed and other times is one produced by reaction of the initially formed radical. Because carbon-centered radicals react rapidly with SmI_2 ($k = 7.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$ for reaction of the 5-hexenyl radical with SmI_2 at 25 °C in the presence of five equiv of HMPA),¹⁰ only a limited number of radical reactions are fast enough to take place before an organosamarium compound forms. (Even those that are fast enough produce new radicals that are destined to be captured by SmI_2 .) Organosamarium compounds are quite reactive and, consequently, rarely isolated. Evidence for their existence takes the form of characteristic reactions (e.g., proton transfer, β elimination, and addition to a carbonyl compound). To understand the outcome of reactions begun by transfer of an electron from SmI_2 to a carbohydrate derivative, it is necessary to be familiar with the reactions of organosamarium compounds.

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