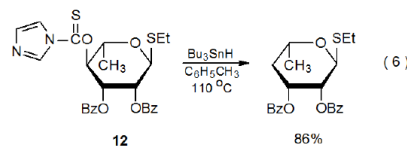
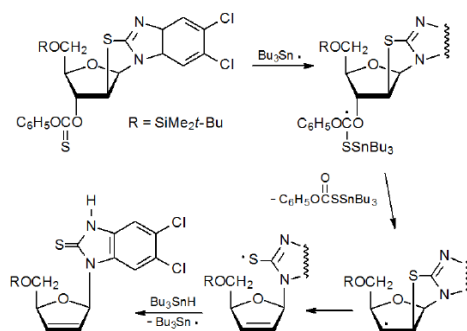


VI. O-Thiocarbonyl Compounds

Compounds with carbon–sulfur single bonds are substantially less reactive with tin- and silicon-centered radicals than are compounds with C–S double bonds. Among carbohydrates these double bonds are almost always part of *O*-thiocarbonyl groups. (The reactions of *O*-thiocarbonyl carbohydrate derivatives are discussed in [Chapter 12](#).) The reaction shown in eq 6 illustrates the greater reactivity of a C–S double bond when compared to a C–S single bond because only the *O*-thiocarbonyl group in the 1-thioglycoside **12** reacts even though an ethylthio group is present in the molecule.³⁹ Greater reactivity of a carbon–sulfur double bond also can be seen in the reaction shown in Scheme 13, where $\text{Bu}_3\text{Sn}\cdot$ reacts only with the *O*-thiocarbonyl group.²⁶ A quantitative measure of the reactivity of C–S single and double bonds comes from comparing absolute rate constants for their reactions; thus, rate constants for reaction of $(\text{Me}_3\text{Si})_3\text{Si}\cdot$ with $\text{C}_{10}\text{H}_{21}\text{SC}_6\text{H}_5$ and $\text{C}_6\text{H}_{11}\text{OC}(=\text{S})\text{SMe}$ are less than 5×10^6 and $1.1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$, respectively, at 21 °C.⁴⁰ The reactions in Schemes 12 and 13 also illustrate the ease of fragmentation of a carbon–sulfur single bond when a radical is centered on an adjacent carbon atom.



Scheme 13



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