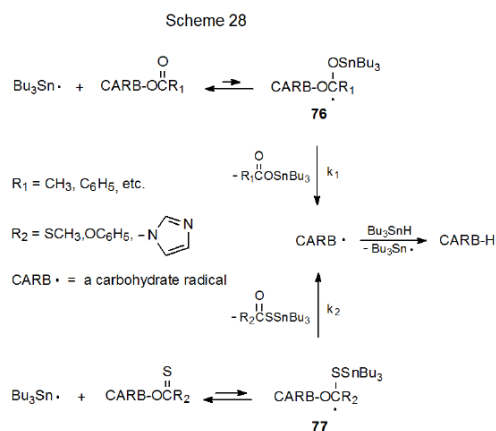


V. Comparing the Reactivity of O-Thiocarbonyl and O-Carbonyl Carbohydrates

When one considers the success of *O*-thiocarbonyl compounds as substrates in the Barton- McCombie reaction, a reasonable question to ask is “Why don’t *O*-carbonyl carbohydrate derivatives (in particular, *O*-acylated compounds) exhibit similar reactivity?” An answer to this question can be framed in terms of the reactions shown in Scheme 28.^{223–225} According to this explanation, the equilibrium involving addition of $\text{Bu}_3\text{Sn}\cdot$ to a compound with an *O*-thiocarbonyl group produces a far greater concentration of the adduct radical **77** than the concentration of the radical **76** produced by addition of $\text{Bu}_3\text{Sn}\cdot$ to the corresponding *O*-carbonyl carbohydrate. The dramatically greater equilibrium concentration of **77** leads to a corresponding increased rate of carbohydrate radical (CARB·) formation.^{223–225}



Detectable reaction of simple esters with $\text{Bu}_3\text{Sn}\cdot$ becomes possible only if the low equilibrium concentration of **76** can be increased in some manner or compensated for by rapid further reaction of this radical (k_1 large). Due to these requirements, no reaction takes place under normal Barton-McCombie conditions, but replacement of an acyloxy group with a hydrogen atom does occur when acylated carbohydrates react with $(\text{C}_6\text{H}_5)_3\text{Si}\cdot$ under vigorous conditions [$(\text{C}_6\text{H}_5)_3\text{SiH}$, 140 °C, 12 h, benzoyl peroxide].²²⁶ Also, under quite different conditions (HMPA, H_2O , UV light, room temperature) photochemical electron transfer leads to reduction of acylated carbohydrates to the corresponding deoxy compounds.²²⁷ These and other reactions of esterified carbohydrates are discussed in detail in [Chapter 8](#).

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