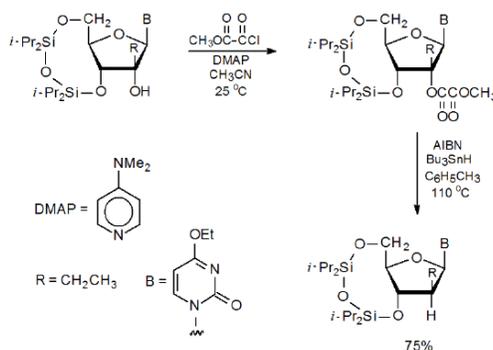


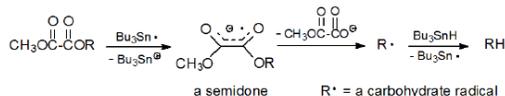
has been esterified. Many of these compounds are nucleosides.^{4,7-16} One reason that most methyl oxalyl esters are formed from tertiary alcohols is that the *O*-thiocarbonyl compounds commonly used for deoxygenation in the Barton-McCombie reaction- (Section II in Chapter 12) sometimes have difficulty forming when an alcohol is tertiary.⁶ Methyl oxalyl chloride typically esterifies tertiary alcohols without difficulty.^{4,6-19} Another reason for selecting methyl oxalyl esters is that they are less likely to experience the thermal elimination (Chugaev reaction) that is common for tertiary *O*-thiocarbonyl compounds. In molecules with the proper structure cyclization can precede hydrogen-atom abstraction.¹³

Scheme 2



A proposed mechanism for reaction of methyl oxalyl esters with tri-*n*-butyltin hydride is shown in Scheme 3. According to this mechanism the tri-*n*-butyltin radical transfers an electron to the π system of the ester to produce a highly stabilized radical anion (a semidione).²⁰ (Supporting the idea that such a transfer takes place is the observation that $\text{Bu}_3\text{Sn}\cdot$ reacts with oxalate esters to produce intermediates with ESR spectra characteristic of radical anions.²¹) Fragmentation of such a radical anion then generates a carbon-centered radical that abstracts a hydrogen atom from Bu_3SnH (Scheme 3).

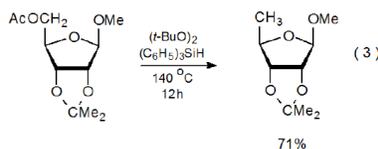
Scheme 3



There are two significant problems associated with the synthesis and reaction of methyl oxalyl esters. One of these is the difficulty in starting- material purification that arises because these esters hydrolyze readily, in particular, during chromatography on silica gel.^{4,22} A second problem has to do with alcohol regeneration, a significant side reaction from treatment of some methyl oxalyl esters with tri-*n*-butyltin hydride.^{5,20}

C. Acetates and Trifluoroacetates

Acetylated carbohydrates do not react with tri-*n*-butyltin hydride under normal conditions (80-110 °C, 2 h, AIBN initiation), but under different, more vigorous conditions (triphenylsilane, 140 °C, 12 h, two equivalents of benzoyl peroxide) these compounds produce the corresponding deoxy sugars (eq 3).²³ These more vigorous conditions cause similar reaction in *O*-trifluoroacetyl substituted carbohydrates.²⁴ The need for two equivalents of benzoyl peroxide in the reaction shown in eq 3 indicates that a nonchain process is taking place.



D. *p*-Cyanobenzoates

Replacement of the benzoyl group in compound 2 with a *p*-cyanobenzoyl group converts an unreactive compound (2) into a reactive one (3) (eq 4).²⁵ One explanation for this difference in reactivity is that because a cyano group is quite effective at stabilizing a radical anion, electron transfer to compound 3 is taking place where analogous transfer to the unsubstituted benzoate 2 does not occur. Since radical anions can form by electron transfer from the tri-*n*-butyltin radical to easily reduced organic com-

