

VI. Summary

An effective procedure for deoxygenation begins with the conversion of a hydroxyl group in a carbohydrate into an *O*-thiocarbonyl group and ends with a radical reaction (the Barton- McCombie reaction) that replaces the *O*-thiocarbonyl group with a hydrogen atom. Xanthates, (thiocarbonyl)imidazolides, and thionocarbonates are the most common substrates for the Barton- McCombie reaction. Although a number of hydrogen-atom donors can be used in this reaction, the usual choice is tri-*n*-butyltin hydride. Safety concerns about tin hydrides and problems with product purification have caused chemists to turn increasingly to other hydrogen atom sources, in particular, tris(trimethylsilyl)silane. Barton-McCombie reaction is sometimes complicated by competing reactions, the most common of which regenerates the partially protected carbohydrate from which the *O*-thiocarbonyl-containing substrate was synthesized.

Differences in reactivity sometimes favor selecting a particular type of *O*-thiocarbonyl compound. Phenyl thionocarbonates are particularly valuable for hydroxyl group replacement by a hydrogen atom during nucleoside synthesis, and they are the least likely *O*-thiocarbonyl derivative to undergo alcohol regeneration. If reaction of a xanthate is attempted with a hydrogen-atom donor much less effective than tri-*n*-butyltin hydride, xanthate-dithiocarbonate rearrangement can take place. Reactions of tertiary xanthates can be complicated by Chugaev elimination unless these reactions are conducted at low temperature.

Deoxygenation involving cyclic thionocarbonates differs from that of other *O*-thiocarbonyl compounds because reaction involves ring opening. The direction of ring opening determines which of the two carbon atoms in the ring system will become the radical center. A high yield of a single product, therefore, depends on high regioselectivity in the ring-opening process. Cyclic thionocarbonates generally react to give deoxy compounds resulting from formation of the more stable intermediate radical. In some instances release of ring strain during ring opening becomes a factor in determining where the radical center will be located. Mixtures of products are a common result when the two radicals produced by ring opening are comparable in stability.

Radicals produced by reaction of *O*-thiocarbonyl compounds undergo addition reactions when a compound with a reactive multiple bond is present, and they undergo cyclization when the radical itself has a properly positioned multiple bond. In either situation the reactions that take place are of the addition-abstraction or addition-elimination type. The latter includes reactions with double bond migration and those without. Observed radical cyclizations are all addition- abstraction reactions. Most of these involve addition of a framework radical to either a framework multiple bond or to a substituent multiple bond.

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