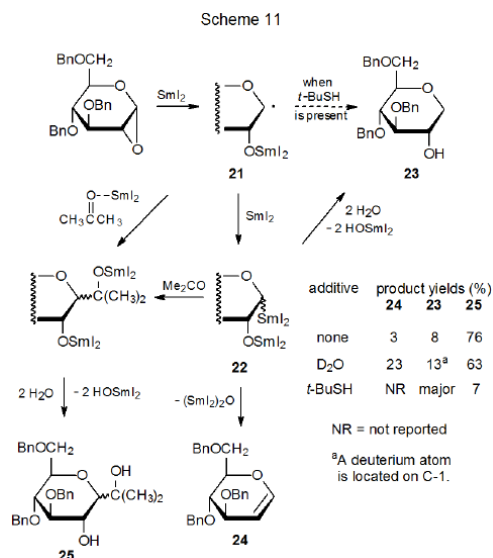


VI. Radical Addition and Hydrogen-Atom Abstraction

The reaction shown in Scheme 11 describes the formation of the C-glycoside **25** by addition of the oxygen-stabilized radical **21** or the organosamarium compound **22** (or both) to a molecule of acetone.⁹⁵ There is evidence for participation of both of these intermediates at some stage in this reaction. Conducting the reaction in the presence of *t*-BuSH quenches the addition process and dramatically increases the yield of the reduction product **23**. Such a change would be expected from hydrogen-atom abstraction by the radical **21**. In the absence of *t*-BuSH, formation of **23** and the elimination product **24** provide evidence for the organosamarium compound **22** also being present in the reaction mixture. Since conducting the reaction in the presence of D₂O decreases the yield of the C-glycoside **25** in favor of the reduction and elimination products **23** and **24**, respectively, the organosamarium compound **22** appears to be a likely intermediate in the addition process, but since a large excess of D₂O only modestly reduces the yield of **25**, radical addition remains a possible (perhaps major) pathway to C-glycoside formation.



The radical-addition pathway shown in Scheme 11 involves the nucleophilic, carbon-centered radical **21** adding to the carbonyl carbon atom in acetone. The carbonyl carbon atom is rendered quite electron deficient by complexation of acetone with SmI₂. This combination of a reactive radical adding to a double bond with a decidedly electron-deficient atom is found in other reactions promoted by SmI₂.^{96,97}

This page titled [VI. Radical Addition and Hydrogen-Atom Abstraction](#) is shared under a [All Rights Reserved \(used with permission\)](#) license and was authored, remixed, and/or curated by [Roger W. Binkley and Edith R. Binkley](#).