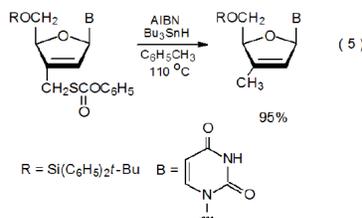
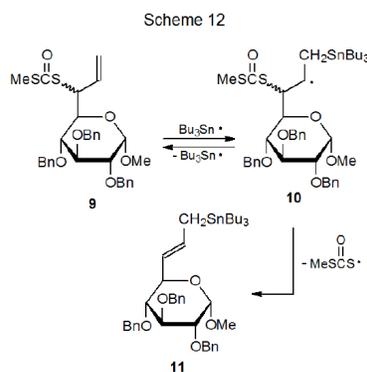


V. Thiocarbonates and Dithiocarbonates

Thiocarbonates and dithiocarbonates are compounds in which at least one sulfur atom is bonded to the carbon atom of a carbonyl group. The reactivity of these compounds is similar to that of the sulfur-containing compounds already discussed in that reaction begins with carbon–sulfur bond cleavage producing the more stable of the possible carbon-centered radicals; thus, in the reaction shown in eq 5, product identity is consistent with forming an intermediate allylic radical from reaction of a thiocarbonate.³⁶



Addition of Bu₃Sn· to the dithiocarbonate **9** is the first step in an addition-elimination reaction that produces the tin-containing compound **11** (Scheme 12).³⁷ The stability of CH₃SC(=O)S· is critical to this type of reaction because it, rather than Bu₃Sn·, is expelled when a radical such as **10** forms a tin-containing product.^{37,38} Since Bu₃Sn· addition to a double bond often is reversible, **10** sometimes may break a carbon–tin bond causing an undetectable regeneration of Bu₃Sn· and the substrate **9**.



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