

## IX. Summary

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Tin-centered radicals react with carbohydrates that contain methylthio, ethylthio, or phenylthio groups to produce carbon-centered radicals. Two mechanisms have been proposed for such a reaction. The first is a concerted  $S_H2$  process, and the second is a stepwise reaction that forms an intermediate with a hypervalent sulfur atom. Molecular orbital calculations favor the concerted process.

Compounds with alkylthio or arylthio groups break the C–S bond that produces the more stable, carbon-centered radical. This means that when fragmentation takes place in a carbohydrate containing a methylthio, ethylthio, or phenylthio substituent, a carbohydrate radical forms rather than an alkyl or aryl radical. Reactions that begin with carbon–sulfur bond cleavage often lead to either simple reduction or radical cyclization. Similar reactions occur when the sulfur atom is part of a dithioacetal, thiocarbonate, or dithiocarbonate.

When the carbon–sulfur bonds in a carbohydrate are part of a sulfone and when an electron-donor (usually  $SmI_2$ ) is present, bond cleavage occurs via an electron-transfer reaction. The resulting radical combines rapidly with a second molecule of  $SmI_2$  to produce an organosamarium intermediate that undergoes reactions typical of an organometallic compound (e.g., proton abstraction,  $\beta$  elimination, or addition to an aldehyde or ketone). Radical cyclization is one of the few reactions fast enough to occur before this combination takes place.

If a compound has a hydrogen–sulfur bond, the major reaction pathway usually is hydrogen-atom abstraction to form a sulfur-centered radical. This radical adds readily to a carbon–carbon double bond.

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