

CHAPTER OVERVIEW

4: Selenides & Tellurides

Carbohydrates containing selenium–carbon bonds react with tin and silicon hydrides to generate carbon-centered radicals. Phenyl selenides are the most common type of selenium-containing carbohydrate used in radical formation. As radical precursors, phenyl selenides rival the reactivity of bromides and iodides. (Absolute rate constants for reaction of simple organic iodides,¹ phenyl selenides,² and bromides^{2,3} with $(\text{CH}_3\text{Si})_3\text{Si}\cdot$ are 4.0×10^9 , 9.6×10^7 , and $2.0 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, respectively.)

Selenophenyl glycosides have a distinct advantage over the corresponding iodides and bromides when it comes to radical formation because anomeric phenyl selenides are thermally more stable than the corresponding anomeric halides. Anomeric iodides are, in fact, too unstable to have a significant role in generating pyranos-1-yl or furanos-1-yl radicals. Anomeric bromides are acceptable radical precursors in many instances, but when they are too unstable, phenyl selenides become attractive alternatives. Phenyl selenide advantage is apparent in the generation of furanos-1-yl radicals where glycosyl bromides typically are unable to survive the heating at reflux in benzene or toluene that normally is used in such reactions. Selenophenyl glycosides are stable enough under these conditions to avoid nonradical, thermal decomposition and, therefore, they are able to form the desired radicals.^{4,5}

Organotellurium compounds represent another source of carbohydrate radicals. Although selenides are used much more frequently as starting materials for radical formation, tellurides undergo many of the same types of reaction. A problem with many tellurium-containing compounds is that they decompose so readily that they can be difficult to purify and store.

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