

## V. Summary

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Halogen-atom abstraction by a tin-centered radical is a common reaction in carbohydrate chemistry. Ample evidence supporting radical intermediates in this type of reaction comes from chemical reactivity and from direct radical observation by ESR spectroscopy. Iodides are the most reactive of the halogenated carbohydrates. Bromides are slightly less so, but the reactivity of chlorides is considerably reduced. Fluorides are essentially unreactive. In dehalogenation reactions the transition-state structure is thought to involve partial tin–halogen and carbon–halogen bonds.

Simple reduction (replacement of a halogen atom with a hydrogen atom) occurs under mild reaction conditions. The halogen atom being abstracted can be attached to any carbon atom in the carbohydrate framework. Although the primary role of simple reduction is in the synthesis of deoxy sugars and deoxy nucleosides, this reaction also can be used to modify the reactivity of halogenated protecting groups. Replacement of halogen atoms with hydrogen atoms can convert a group that is difficult to hydrolyze into one that does so more easily.

Simple reduction of anomeric halides must compete with group migration when there is an acyloxy group at C-2. This migration, which is useful in the synthesis of 2-deoxy sugars, is most likely to occur when the concentration of the hydrogen-atom transfer (e.g., tri-*n*-butyltin hydride) is held at a very low level.

Halogen-atom abstraction often is the first step in the addition of a carbohydrate radical to a compound containing a multiple bond. Such addition will occur in an intramolecular fashion if the multiple bond is electron-deficient because under the proper conditions a nucleophilic carbohydrate radical adds to an electron-deficient multiple bond more rapidly than it abstracts a hydrogen atom. When the radical center and the multiple bond are in the same molecule and easily come within bonding distance, cyclization takes place so readily that it will occur even if the multiple bond is not electron-deficient. A characteristic of cyclization reactions is that formation of the new carbon–carbon bond often occurs in a highly stereoselective fashion.

Halogenated carbohydrates participate in a variety of less common reactions. These include double bond formation, internal hydrogen-atom abstraction, addition to molecular oxygen, cyclopropane ring opening, and radical anion formation.

Free-radical bromination produces several types of brominated carbohydrates. Bromination of benzylidene acetals leading to formation of bromodeoxy benzoates is a standard reaction in carbohydrate synthesis. Modifications of this reaction also are known; thus, the cation produced following benzylidene acetal bromination can be intercepted by water to give a hydroxy benzoate. Carbohydrates protected as benzyl ethers react with bromine to produce unstable bromides that, in turn, react with water to give benzaldehyde and the deprotected carbohydrate. Reaction with bromine of carbohydrates that do not contain benzyl or benzylidene protection regioselectively replaces a hydrogen atom on one of the carbon atoms attached to the ring oxygen atom.

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