A. Halogen-Atom Abstraction

Halogen-atom abstraction can take place both in forming a halogenated carbohydrate and in removing a halogen atom from such a compound. When abstraction is from a halogenated carbohydrate, it produces a carbohydrate radical (eq 1). The abstracting radical typically is tin-centered or silicon-centered. In the reaction shown in eq 2, for example, a carbohydrate radical forms when a tin-centered abstracts an iodine atom from a deoxyiodo sugar. Abstraction that generates a halogenated carbohydrate takes place when I₂, Br₂, or another halogen donor reacts with a carbohydrate radical (eq 3). Equation 4 describes a reaction of this type.

\[
\text{CARB-}X + R^\cdot \rightarrow \text{CARB}^\cdot + RX \quad (1)
\]

\[X = \text{Cl, Br, I}\]

\[\text{CARB} = \text{carbohydrate moiety}\]

\[R = \text{Bu}_3\text{Sn}, (\text{Me}_3\text{Si})_2\text{Si}, (\text{C}_9\text{H}_3)_2\text{Sn}\]

\[
\begin{array}{c}
\text{CH}_2\text{OBn} \\
\text{I} \\
\text{OAc} \\
\text{OR} \\
\end{array}
\rightarrow

\begin{array}{c}
\text{CH}_2\text{OBn} \\
\text{OAc} \\
\text{OR} \\
\end{array}
+ \text{Bu}_3\text{Sn} \quad (2)

\[
R^\cdot + XY \rightarrow RX + Y^\cdot \quad (3)
\]

\[XY = I_2, Br_2, BrCCl_3\]

\[R^\cdot = \text{a carbohydrate radical}\]

\[
\begin{array}{c}
\text{Ar} \\
\text{O} \\
\text{OBz} \\
\text{O} \\
\text{OMe} \\
\end{array}
\rightarrow

\begin{array}{c}
\text{Br} \\
\text{Ar} \\
\text{OBz} \\
\text{OBz} \\
\end{array}
+ \text{Br}^\cdot \quad (4)
\]

\[\text{Ar} = \text{C}_9\text{H}_5\]

B. Hydrogen-Atom Abstraction

Hydrogen-atom abstraction is an elementary reaction that permeates the free-radical chemistry of carbohydrates. Because it is the final propagation step in many chain reactions, hydrogen-atom abstraction often converts a carbon-centered radical into a stable product. The hydrogen-atom donor in such reactions usually is a tin or silicon hydride, but sometimes a thiol or selenol serves in this role (eq 5). The final step in the simple reduction shown in eq 6 is a typical,
hydrogen-atom-abstraction reaction.  \(^3\)

\[ \text{R} \cdot + \text{HX} \rightarrow \text{RH} + \text{X} \cdot \quad (5) \]

\( \text{R} \cdot = \text{a carbohydrate radical} \)

\( \text{HX} = \text{a hydrogen donor, usually} \text{Bu}_3\text{SnH} \quad \text{or} \quad (\text{Me}_3\text{Si})_3\text{SiH} \quad \text{but sometimes} \quad (\text{C}_6\text{H}_{13})_2\text{SnH, C}_6\text{H}_5\text{SH, or C}_6\text{H}_5\text{SeH} \)

\[ \begin{array}{c}
\text{CH}_2\text{OBn} \\
\text{HOAc} \\
\text{OR} \\
\text{OAc}
\end{array} + \quad \text{Bu}_3\text{SnH} \rightarrow \quad \begin{array}{c}
\text{CH}_2\text{OBn} \\
\text{HOAc} \\
\text{OR} \\
\text{OAc}
\end{array} \quad (6) \]

Carbohydrates also can serve as hydrogen atom donors (eq 7). A radical centered on a bromine, chlorine, or oxygen atom (and, sometimes, on a sulfur or carbon atom) is able to abstract a hydrogen atom from a carbohydrate in an elementary reaction that can be highly regioselective. For intermolecular reactions this selectivity is due to radicals preferentially abstracting the hydrogen atoms that produce the most stable carbon-centered radicals. In the reaction shown in eq 8, for example, the bromine atom abstracts only the hydrogen atom that produces the highly resonance-stabilized radical 1.  \(^4\)

\[ \text{X} \cdot + \text{CARB-H} \rightarrow \text{XH} + \text{CARB-} \quad (7) \]

\( \text{X} = \text{Br, Cl, C, O, S} \)

\[ \begin{array}{c}
\text{CH}_2\text{OBz} \\
\text{OBz} \\
\text{OBz} \\
\text{OBz}
\end{array} + \text{Br} \cdot \rightarrow \begin{array}{c}
\text{Ar} \cdot \\
\text{OBz} \\
\text{OBz} \\
\text{OBz}
\end{array} + \text{HBr} \quad (8) \]

If a radical is centered on an oxygen or carbon atom in a carbohydrate, internal abstraction becomes a possibility. Such abstraction is regioselective not only because a more stable radical is being produced but also because the radical center is able easily to come within bonding distance of a limited number of hydrogen atoms (sometimes only one). In the reaction shown in eq 9, the only hydrogen atom abstracted is the one that is 1,6-related to the radical center.  \(^5\) Although an oxygen-centered radical (e.g., 2 in eq 9) is reactive enough to abstract a hydrogen atom from any carbon-hydrogen bond in a carbohydrate, \(^6\) only the most reactive carbon-centered radicals (e.g., primary and vinylic ones) are capable of such reaction (eq 10).  \(^7\)
Contributors

Roger W. Binkley (Cleveland State University) and Edith R. Binkley (Cleveland Heights-University Heights school system)