A. Synthesis

When tert-butyl isonitrile reacts with a carbon-centered radical, an addition-elimination process takes place that results in the formation of a nitrile (Scheme 8).\textsuperscript{16–23} This type of nitrile synthesis is illustrated by the reaction shown in eq 5.\textsuperscript{20} (Scheme 10 in Chapter 2 describes another example of this type of reaction.\textsuperscript{22})

\begin{scheme}
\begin{align*}
R \cdot + & \cdotC=NC(CH_3)_3 \rightarrow R\overset{\cdot}{C}=NC(CH_3)_3 \\
R\overset{\cdot}{C}=NC(CH_3)_3 & \rightarrow R\overset{\cdot}{C}=N + \cdotC(CH_3)_3 \\
\cdotC(CH_3)_3 + & (\text{Me}_3)_3\text{SiH} \rightarrow HC(CH_3)_3 + (\text{Me}_3)_3\text{Si} \cdot \\
(\text{Me}_3)_3\text{Si} \cdot + & RX \rightarrow R \cdot + (\text{Me}_3)_3\text{SiX} \\
\end{align*}
\end{scheme}

B. Reactions

1. Addition to a Cyano Group

Radical reactions of carbohydrate nitriles usually involve internal addition in which a carbon-centered radical generated in close proximity to a cyano group forms a new ring system.\textsuperscript{24–31} An example is shown in Scheme 9, where the radical centered on C-6 in 11 adds to the cyano group as a part of this sequential process.\textsuperscript{24} Carbohydrate radical formation in this type of reaction typically begins with the tri-n-butyltin radical abstracting a halogen atom or an O-thiocarbonyl group. After cyclization, the radical abstracts a hydrogen atom from Bu$_3$SnH to produce an imine, which in some cases is isolated and in others is hydrolyzed to the corresponding carbonyl compound before isolation.
2. Cyano Group Migration

When a cyclic imino radical forms during carbon-centered radical addition to a cyano group, the possibility exists that ring opening will lead to cyano group migration (Scheme 10). Such a reaction is shown in Scheme 11, where migration accompanies ring opening of a benzylidene acetal.

![Scheme 9](image)

![Scheme 10](image)
Contributors

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