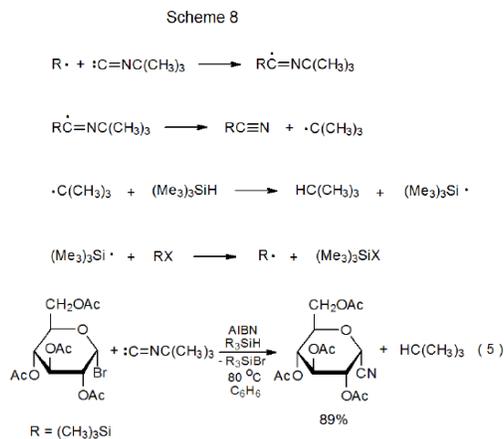


### III. Nitriles

#### A. Synthesis

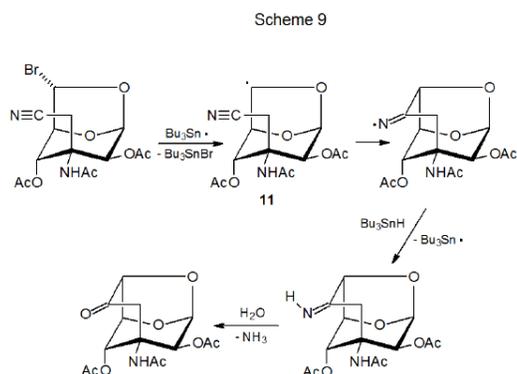
When *t*-butyl isonitrile reacts with a carbon-centered radical, an addition-elimination process takes place that results in the formation of a nitrile (Scheme 8).<sup>16–23</sup> This type of nitrile synthesis is illustrated by the reaction shown in eq 5.<sup>20</sup> (□ Scheme 10 in Chapter 2 describes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



#### B. Reactions

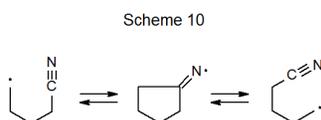
##### 1. Addition to a Cyano Group

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.<sup>24–31</sup> 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.<sup>24</sup> 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<sub>3</sub>SnH to produce an imine, which in some cases is isolated and in others is hydrolyzed to the corresponding carbonyl compound before isolation.

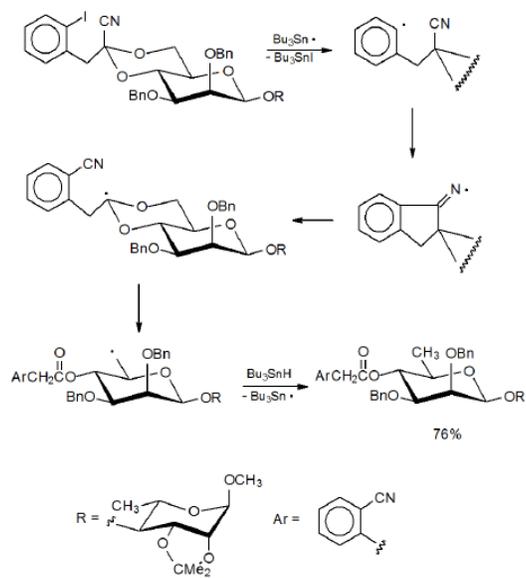


##### 2. Cyano Group Migration

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).<sup>32–34</sup> Such a reaction is shown in Scheme 11, where migration accompanies ring opening of a benzylidene acetal.<sup>32</sup>



Scheme 11



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