IV. Ring Opening of Specially Designed Acetals

Search for compounds with more versatile reactivity than that provided by a 4,6-*O*-benzylidene group has stimulated development of some specially designed structures.[14–18] The acetal **23**, which fits into this "specially designed" category, reacts with $Bu_3Sn\cdot$ to form the aryl radical **24**. The iodine-atom abstraction that generates **24** is the first step in a sequence of radical reactions that culminates in producing the protected glycoside **25** (Scheme 9).[14–16] An example of the synthetic usefulness of this reaction is found in the conversion of a tetrasaccharide containing four such protecting groups into one in which each group is transformed into an *O*-benzoyl group.[15] The glycoside **26** is another cyclic benzylidene acetal with an aromatic iodo substituent that undergoes a sequential radical reaction that leads to the corresponding deoxy benzoate **27** (eq 10).[17] The reactions pictured in Scheme 9 and eq 10 are two more examples (in addition to those shown in equations 2 and 3) where *trans*-fused rings open to produce primary rather than a secondary radicals. Ring opening of the 4,6-*O*-benzylidene acetal **28** to give a secondary radical (eq 11) further supports the proposal made for the acetal **11** (eq 4) that for a more flexible, *cis*-fused ring system the direction of ring opening is controlled by radical stability rather than ring strain at the transition state.

Scheme 9