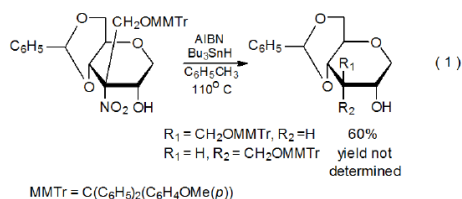


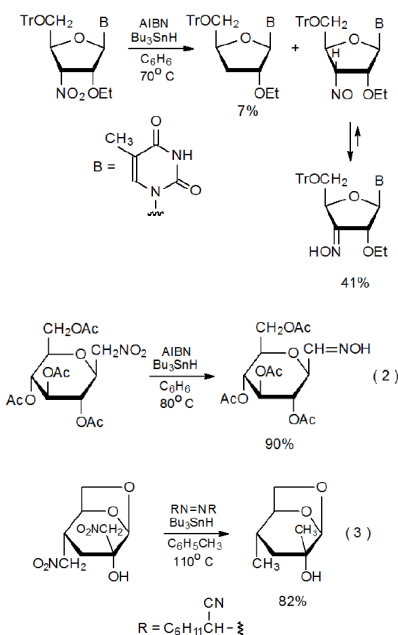
### III. C-Nitro Carbohydrates

#### A. Group Replacement

Since in the reaction of a C-nitro compound the stability of the developing radical ( $R\cdot$ ) affects the ease of cleavage of the carbon–nitrogen bond (□ Scheme 2), group replacement occurs more easily for tertiary nitro compounds<sup>9–14</sup> than for secondary<sup>15–19</sup> and, especially, primary ones.<sup>20–22</sup> Reaction of  $Bu_3SnH$  with a compound containing a tertiary nitro group is given in eq 1.<sup>9</sup> If the nitro group in the substrate is secondary, reaction usually follows the same pathway and replaces this group with a hydrogen atom,<sup>15–18</sup> but sometimes breaking a C–O bond leading to a nitroso compound (which isomerizes to an oxime) offers significant competition (Schemes 2 and 5).<sup>19</sup> When a nitro group is primary, the elimination phase of the reaction is more likely to produce only the nitroso compound (eq 2),<sup>20,21</sup> even though replacement of a primary nitro group with a hydrogen atom has been observed (eq 3).<sup>22</sup>

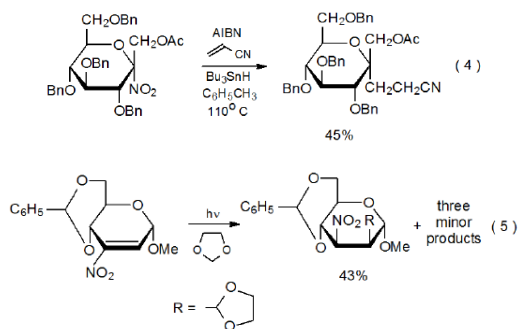


Scheme 5

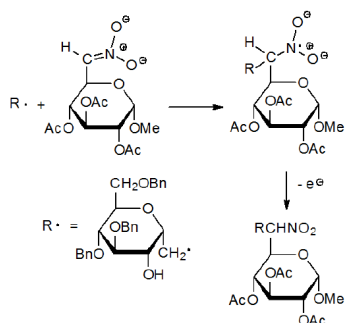


#### B. Addition Reactions

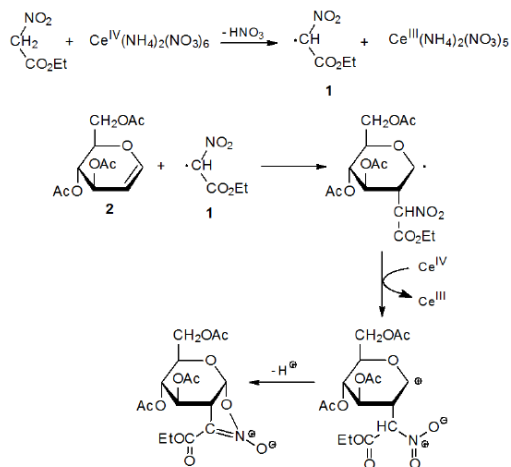
A nitro group in a reactant molecule can be involved in radical addition in several ways. First, denitration can produce a carbon-centered radical that undergoes typical addition to an electron-deficient multiple bond (eq 4).<sup>3</sup> In a different role, nitro groups activate multiple bonds toward addition by nucleophilic radicals and affect the regioselectivity of such reactions (eq 5).<sup>23</sup> Deprotonation of a carbon atom bearing a nitro group creates an unsaturated system to which a carbon-centered radical can add to form a new, C–C bond (Scheme 6<sup>24</sup>).<sup>24–26</sup> Finally, the electron-withdrawing character of a nitro group can contribute to turning a normally nucleophilic radical into one that is electrophilic; thus, the philicity of the radical **1**, which has both nitro and ethoxycarbonyl groups attached to the radical center, is reflected in its ability to add to the electron-rich double bond in the glycol **2** (Scheme 7).<sup>27</sup>



Scheme 6

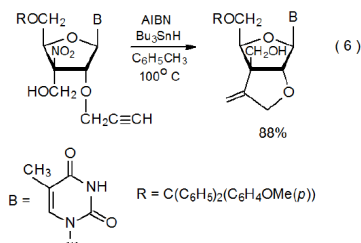


Scheme 7



## C. Cyclization Reactions

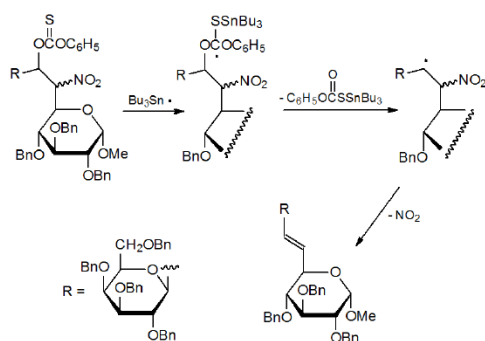
A cyclization reaction that begins with a C-nitro carbohydrate is shown in eq 6.<sup>28</sup> The high yield of this reaction, which involves a radical centered on a tertiary carbon atom adding to a multiple bond, illustrates that radical addition can be relatively insensitive to steric congestion at the radical center.<sup>28,29</sup>



## D. Elimination Reactions

A deoxynitro sugar can undergo an elimination reaction, if a radical center develops on a carbon atom adjacent to that bearing the nitro group.<sup>30–32</sup> In the reaction shown in Scheme 8,<sup>30</sup> such a radical forms and then eliminates nitrogen dioxide to give an unsaturated compound.

Scheme 8



This page titled [III. C-Nitro Carbohydrates](#) is shared under a [All Rights Reserved \(used with permission\)](#) license and was authored, remixed, and/or curated by [Roger W. Binkley and Edith R. Binkley](#).