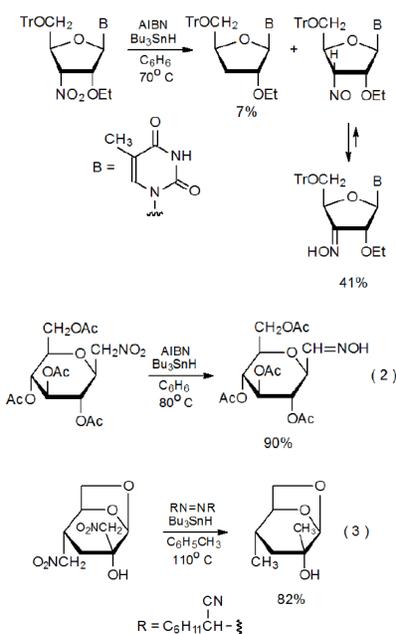
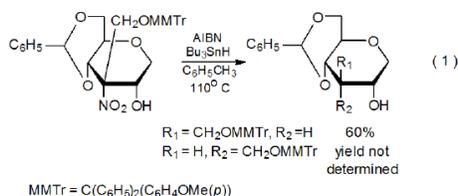


III. C-Nitro Carbohydrates

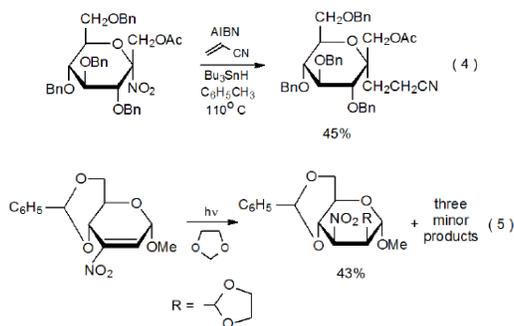
A. Group Replacement

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^{9–14} than for secondary^{15–19} and, especially, primary ones.^{20–22} Reaction of Bu_3SnH with a compound containing a tertiary nitro group is given in eq 1.⁹ If the nitro group in the substrate is secondary, reaction usually follows the same pathway and replaces this group with a hydrogen atom,^{15–18} but sometimes breaking a C–O bond leading to a nitroso compound (which isomerizes to an oxime) offers significant competition (Schemes 2 and 5).¹⁹ When a nitro group is primary, the elimination phase of the reaction is more likely to produce only the nitroso compound (eq 2),^{20,21} even though replacement of a primary nitro group with a hydrogen atom has been observed (eq 3).²²

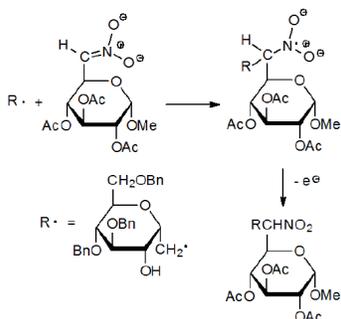


B. Addition Reactions

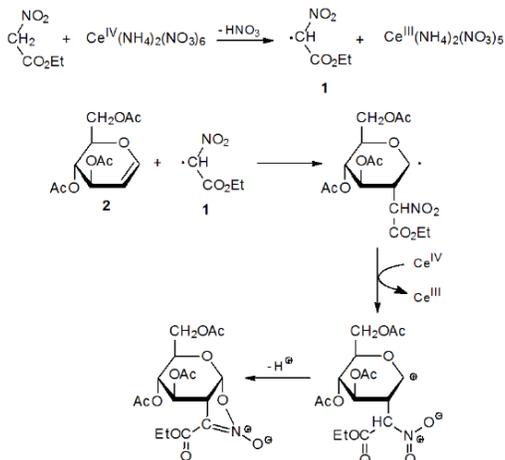
A nitro group in a reactant molecule can be involved in radical addition in several ways. First, denitration can produce a carbon-centered radical that undergoes typical addition to an electron-deficient multiple bond (eq 4).³ In a different role, nitro groups activate multiple bonds toward addition by nucleophilic radicals and affect the regioselectivity of such reactions (eq 5).²³ 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 6²⁴).^{24–26} 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 ethoxy-carbonyl 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).²⁷



Scheme 6

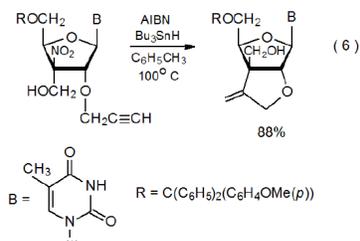


Scheme 7



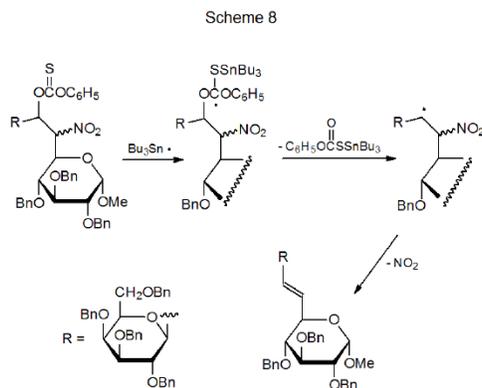
C. Cyclization Reactions

A cyclization reaction that begins with a C-nitro carbohydrate is shown in eq 6.²⁸ 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.^{28,29}



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.^{30–32} In the reaction shown in Scheme 8,³⁰ such a radical forms and then eliminates nitrogen dioxide to give an unsaturated compound.



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