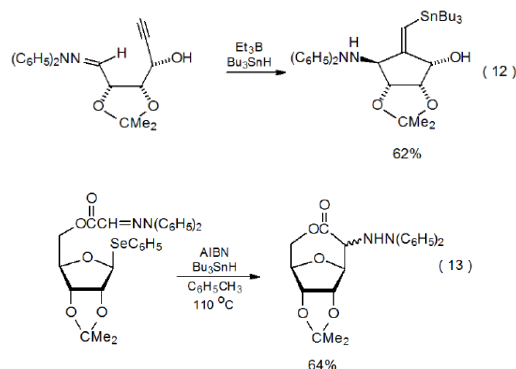


III. Hydrazones and Imines

Radical reactions of carbohydrate hydrazones^{2,43–46} are less common than those of oxime ethers; reactions of imines⁴³ are still more rare. The reported reactions of hydrazones, such as that shown in eq 12,⁴³ all involve radical cyclization. The substrates in most of these reactions are esters derived from (2,2-diphenylhydrazono)acetic acid (eq 13).^{44,45}



The reaction shown in eq 14 pictures a highly stereoselective cyclization involving a carbohydrate hydrazone.⁴⁶ Stereoselectivity in this reaction is determined by the preferred conformation (**37**, Figure 1) of the intermediate produced by a phenylthiyl radical adding to the carbon–carbon double bond in the substrate. Conformation **37** has the carbon–nitrogen bond *anti* to the adjacent carbon–oxygen bond. The conformation **38**, expected to be more stable because it has more pseudoequatorial substituents, is destabilized by dipole-dipole interactions arising from a *gauche* relation between the neighboring C=N and C–O bonds.⁴⁶

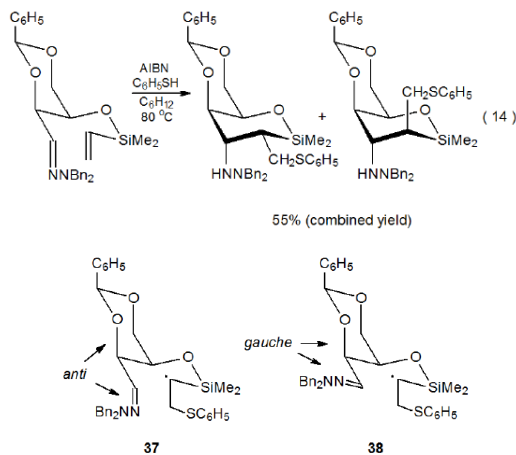


Figure 1. *Anti* and *gauche* conformations of a radical about to form a new ring

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