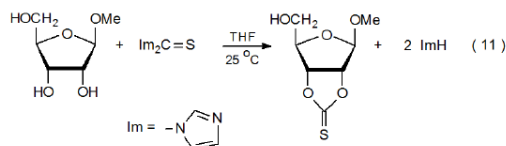
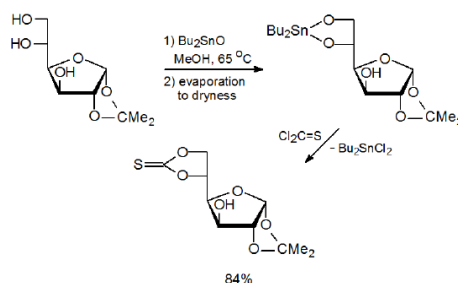


V. Cyclic Thionocarbonates

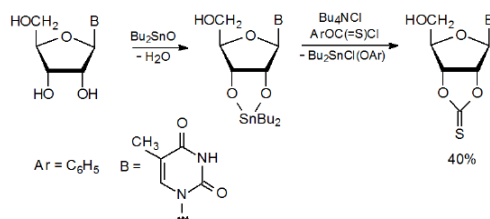
Two basic procedures for the synthesis of cyclic thionocarbonates are in common use. The first involves reacting a compound containing adjacent hydroxyl groups with *N,N*-thiocarbonyldiimidazole (eq 11).⁵⁰ Most cyclic thionocarbonates are synthesized by this procedure. The second approach involves initial formation of a stannylene complex and then treatment of this complex with thiophosgene (Scheme 8)⁵¹ or phenoxythiocarbonyl chloride^{52–54} (Scheme 9)⁵⁴.



Scheme 8

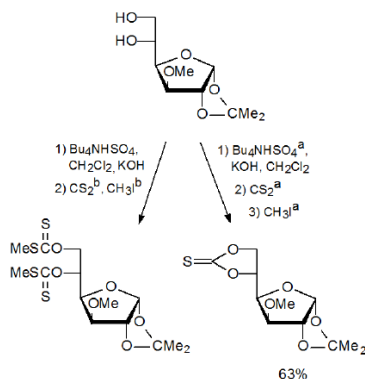


Scheme 9



A third, but seldom used, reaction for cyclic thionocarbonate formation is one conducted under phase-transfer conditions. This synthesis is capable of producing either a bisxanthate⁵⁵ or a cyclic thionocarbonate (Scheme 10).⁵⁶ The critical factors in determining which type of product will be produced are the timing of reagent addition and the relative amounts of the reagents used. To maximize the cyclic-thionocarbonate yield, methyl iodide needs to be added to the reaction mixture after the other reagents; also, the phase-transfer catalyst, and the remaining reagents, need to be limited to molar amounts equal to that of the substrate (Scheme 10).⁵⁶

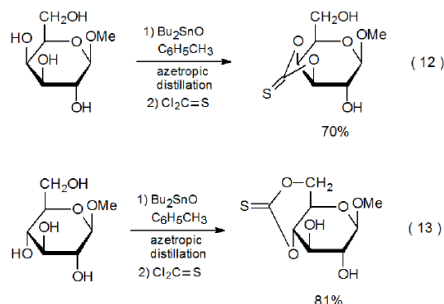
Scheme 10



^aUsed in molar amounts equal to the reactant sugar

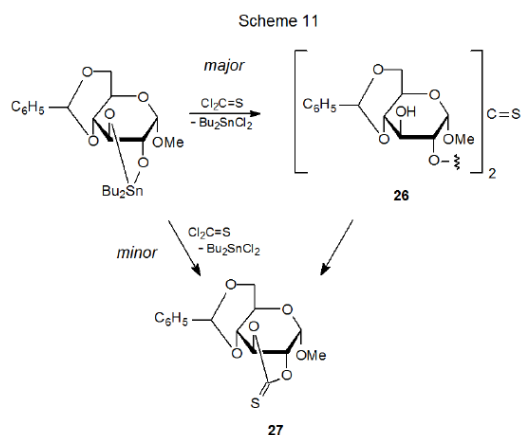
^bUsed in molar amounts greater than twice that of the reactant sugar

Synthesis of a cyclic thionocarbonate by initial stannylene complex formation can be complicated if more than one complex is possible because a dynamic equilibrium will exist between the possible structures.⁵⁷⁻⁵⁹ The equilibrium population of the various complexes is determined by their stability, which is a function of factors such as ring strain, steric hindrance, and inductive effects. The relative amounts of the various complexes do not by themselves determine final product distribution because "the steric inaccessibility of the activated oxygen atoms may retard or prevent a major complex from reacting, thus allowing a minor complex to determine the product".⁵⁷ An illustration of how these factors can cause quite different cyclic thionocarbonates to form from structurally similar compounds is provided by the reactions shown in equations 12 and 13.⁵⁷



Although there can be uncertainty about which cyclic thionocarbonate will form from compounds where more than one stannylene complex is possible, this uncertainty disappears for molecules with *cis*-related, vicinal hydroxyl groups. For such compounds the major (sometimes exclusive) product will come from a complex involving these *cis*-related groups (eq 12⁵⁶).^{51,52,56}

In some situations a competition exists between formation of cyclic and noncyclic thionocarbonates. In the reaction shown in Scheme 11 there is such a competition between the cyclic thionocarbonate **27** and the noncyclic thionocarbonate **26**.⁵⁷ Complete cyclic thionocarbonate formation is only temporarily delayed if reaction is allowed to continue because compound **26** is converted into **27** under the reaction conditions.



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