

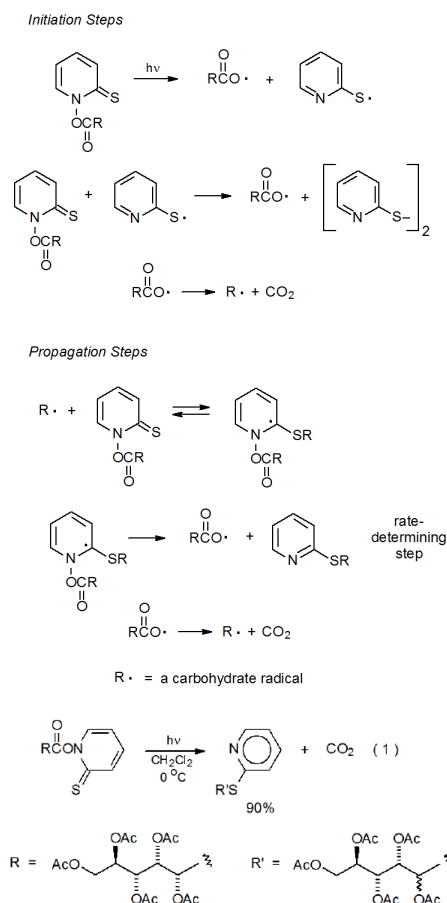
## CHAPTER OVERVIEW

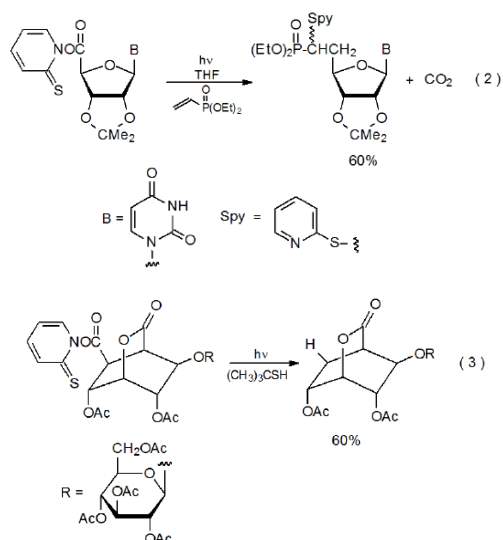
### 13: Carboxylic Acid Esters of N-Hydroxypyridine-2-thione

The discussion in [Chapter 12](#) focused on reactions of *O*-thiocarbonyl compounds prepared by derivatization of hydroxyl groups in partially protected carbohydrates. The current chapter is concerned with reactions of another type of thiocarbonyl compound, one prepared by carboxyl group esterification. The compounds of interest are esters of *N*-hydroxypyridine-2-thione, sometimes referred to as *O*-acyl-*N*-hydroxy-2-thiopyridones or “Barton esters”.

Barton esters generate carbon-centered radicals in photochemically initiated reactions in which the esters themselves produce the chain-carrying radicals needed for the chain reaction to continue (Scheme 1).<sup>1-4</sup> Radical formation from these esters is followed by loss of carbon dioxide and, in the absence of additional reactants (e.g., a compound with an electron-deficient double bond), formation of a product with a sulfur atom bonded to the carbon atom in the carbohydrate framework where the radical was centered (eq 1).<sup>5</sup> The carbon–sulfur bond in the product from Barton ester reaction provides greater flexibility in further synthetic transformation than does the carbon–hydrogen bond that forms when tin or silicon hydrides are present. The synthetic potential of this type of reaction is greater than that indicated in eq 1 because the intermediate, carbon-centered radical also can add to a multiple bond (eq 2),<sup>6,7</sup> abstract a hydrogen atom from a suitable donor (eq 3),<sup>8</sup> or undergo other radical reactions. In effect, through formation and reaction of *N*-hydroxypyridine-2-thione esters it is possible to replace a carboxyl group in a molecule with a carbon-atom chain or with one of a variety of functional groups.

Scheme 1





Since relatively few carbohydrates contain the carboxyl group needed for radical formation by Barton ester photolysis, the requirement that a carbohydrate first be converted into a carboxylic acid places a barrier to the general usefulness of this procedure. In spite of this limitation a number of addition and group replacement reactions exist that are based on radical formation from *N*-hydroxypyridine-2-thione esters of carbohydrates that have been modified to contain a carboxyl group.

### Topic hierarchy

- II. Reaction Mechanism
- III. Group Replacement Reactions
- IV. Addition Reactions
- V. Cyclization Reactions
- VI. Generating Methyl Radicals
- VII. Summary

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