

CHAPTER OVERVIEW

8: Carboxylic Acids & Esters

Carbohydrates containing typical *O*-acyl groups are unreactive under the reduction conditions (AIBN initiation, Bu_3SnH , 80-110 °C) normally used for radical reactions. This lack of reactivity changes when *O*-acyl groups become part of the more complex structures found in α -acyloxy ketones, methyl oxalyl esters, and *p*-cyanobenzoates. For such compounds radical reaction with Bu_3SnH under normal reaction conditions replaces the acyloxy group with a hydrogen atom.

There are conditions under which a less complex *O*-acyl group (e.g., an *O*-acetyl or *O*-benzoyl group) is replaced with a hydrogen atom. One set of conditions includes raising the reaction temperature dramatically, a change with potentially destructive consequences for the compounds involved. A more attractive approach depends upon photochemically promoted electron transfer to an esterified carbohydrate. Electron transfer (both photochemical and nonphotochemical) permeates the radical reactions of carboxylic acid esters; that is, many of these reactions either involve (or may involve) electron transfer.

Another way in which *O*-acyl groups participate in radical reactions is by group migration. When a radical centered at C-1 in a pyranoid or furanoid ring has an *O*-acyl group attached to C-2, this group will migrate to C-1 when the conditions are properly selected. Such migration provides an effective method for producing 2-deoxy sugars.

Although esters of carboxylic acids are rich sources for substrates in radical-forming reactions, the acids themselves also can produce radicals. Under the proper conditions carboxylic acids generate carboxyl radicals, intermediates that lose carbon dioxide to form carbon-centered radicals. Carboxyl radicals are generated by electrolysis of carboxylate anions and by the reaction of carboxylic acids with hypervalent iodine compounds.

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