

## CHAPTER OVERVIEW

### 8: Carboxylic Acids & Esters

Carbohydrates containing typical *O*-acyl groups are unreactive under the reduction conditions (AIBN initiation,  $\text{Bu}_3\text{SnH}$ , 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  $\alpha$ -acyloxy ketones, methyl oxalyl esters, and *p*-cyanobenzoates. For such compounds radical reaction with  $\text{Bu}_3\text{SnH}$  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.

#### Topic hierarchy

- II. Replacement of an Acyloxy Group with a Hydrogen Atom
- III. Photochemical Electron Transfer to Carboxylic Acid Esters
- IV. Nonphotochemical Electron Transfer to Carboxylic Acid Esters
- V. Acyloxy Group Migration
- VI. Reactions of Carboxylic Acids
- VII. Summary

---

This page titled [8: Carboxylic Acids & Esters](#) is shared under a [All Rights Reserved \(used with permission\)](#) license and was authored, remixed, and/or curated by [Roger W. Binkley and Edith R. Binkley](#).