

VII. Summary

Carbohydrates with simple acyloxy groups are unreactive under conditions normally used in reduction reactions. Reduction does occur, however, if the reaction temperature is raised to 140 °C and the reaction time is greatly extended. Esters with special structural features undergo reduction at lower temperatures; thus, both α -acyloxy ketones and methyl oxalyl esters react with tri-*n*-butyltin hydride at or below 110 °C.

Photochemical electron transfer provides a way for acyloxy groups to be replaced by hydrogen atoms under mild reaction conditions (at room temperature in neutral solution). Electron transfer occurs when either excited HMPA or *N*-methylcarbazole donates an electron to an ester to form a radical anion. Fragmentation of the radical anion generates a carbon-centered radical that then abstracts a hydrogen atom to produce a deoxygenated compound. Regeneration of the partially protected carbohydrate from which the ester was synthesized sometimes competes with deoxygenation.

Acyloxy group migration to a radical center on an adjacent carbon atom is a reaction that is useful in the synthesis of 2-deoxy sugars. Early proposals for the mechanism of this reaction turned out not to be correct. The considerable investigation that has taken place since then has shown that this reaction is likely to involve the formation of an intimate ion pair consisting of a carboxylate anion and a radical cation. Recombination of this pair produces a new radical, one that has undergone group migration.

Carboxylic acids produce carboxyl radicals by reaction with hypervalent iodine reagents or electrolysis of carboxylate anions. These radicals expel carbon dioxide to form carbon-centered radicals. Electrochemical reaction results in radical coupling, or if the radical is further oxidized, carbocation formation. Reaction of carboxylic acids with hypervalent iodine reagents often is conducted in the presence of heteroaromatic compounds, where radical addition to the aromatic ring takes place.

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