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Organic Reactions, Volume 81

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Synopsis

Volume 81 represents the confluence of two rare and important phenomena for chapters in the Organic Reactions series, namely, it is a single-chapter volume, and it contains a name reaction coauthored by the inventor. Of the 261 chapters published thus far, only seven have been of sufficient impact to appear as single-chapter volumes. The single chapter in this volume entitled "The Krapcho Dealkoxycarbonylation Reaction of Esters with α -Electron-Withdrawing Substituents" has been coauthored by A. Paul Krapcho together with Organic Reactions' long-time contributor Engelbert Ciganek. The "Krapcho Decarboxylation," as it is known in common parlance, is an extraordinarily useful alternative to the classical hydrolysis-decarboxylation of esters bearing α -electron-withdrawing substituents. This process replaces the strongly basic or acidic conditions normally required for ester saponification with the neutral cleavage of the ester group by a BAC2 mechanism through the combination of water and a dipolar aprotic solvent at high temperature. However, another popular variant involves the use of inorganic salts such as lithium chloride, sodium iodide, or sodium cyanide in a dipolar aprotic solvent which can open a second mechanistic pathway (dependent upon the ester) through BAL2 cleavage. Drs. Krapcho and Ciganek expertly outline the broad substrate scope of this reaction and identify the preferred conditions for various substrate classes. The 371 pages of tables containing all known examples of this simple but important transformation, together with the 1,908 references cited in this Chapter, are testimony to the synthetic usefulness of the Krapcho reaction.

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