

PREFACE TO VOLUME 77

To the student and practitioner of organic chemistry, the caché associated with a “name reaction” carries a special significance. Apart from the convenience of being able to identify a given transformation by a simple name and assign credit (whether deserved or not!) to specific individual or individuals, the designation of a name reaction implies a high standard of utility, generality or uniqueness. In the early history of organic chemistry, before a unifying mechanistic understanding, naming a reaction was part of the taxonomy of organizing newly discovered transformations. With the advent of physical organic chemistry, this practice was discouraged as it obfuscated the fundamental similarities of many transformations. Nevertheless, some reactions are just so special as to warrant an eponymous designation. The two chapters in this volume represent unique and important name reactions. The *Organic Reactions* series is also extremely fortunate because these chapters are composed, in part, by their inventors.

The first chapter by Jin Kun Cha and Oleg G. Kulinkovich describes a truly remarkable transformation of carboxylic acid derivatives (esters, amides, carbonates, nitriles) into heteroatom-substituted cyclopropanes. This reaction now bears the name “Kulinkovich Cyclopropanation” and is unique because it constitutes the assembly of the three-membered ring by the formation of two bonds to a carboxyl group (or equivalent) from a 1,2-dimetallic reagent. The dimetallic agent is formed in situ by the action of an organomagnesium reagent on titanium(IV) alkoxide. Cyclopropanols ensue from carboxylic esters whereas cyclopropylamines are formed from amides or nitriles. The synthetic usefulness of cyclopropyl derivatives is easily deduced from their presence in many naturally occurring compounds and therapeutic agents. Indeed, three previous chapters in *Organic Reactions* are dedicated to the formation of cyclopropanes by now classical methods of carbenoid transfer to alkenes. The broad generality of the Kulinkovich cyclopropanation is illustrated by the development of both inter- and intramolecular variants as well as modifications that allow for high degree of stereocontrol in the formation of substituted cyclopropanes.

The second chapter by Stuart W. McCombie, William B. Motherwell, and Matthew J. Tozer represents an homage to one of the giants of organic chemistry in the 20th century, Sir Derek H. R. Barton. Throughout his distinguished career, Derek Barton made innumerable contributions to structure determination, stereochemistry, and synthetic methods development for which he was awarded the Nobel Prize (together with Odd Hassal) in 1969. Barton was a pioneer in the application of radical chemistry to organic synthesis; one of the most useful applications of radical chemistry is the deoxygenation of alcohols, i.e., replacement of the hydroxyl group with a hydrogen atom. During his postdoctoral stint with Barton at Imperial College, Stu McCombie discovered and developed the radical deoxygenation of secondary alcohols that has become known as

the “Barton-McCombie Reaction.” Subsequently, Willie Motherwell (who was then a graduate student) significantly extended the process to include primary and tertiary alcohols as well as free-radical deamination. It is our great fortune that Stu McCombie is a member of the *Organic Reactions* editorial board and together with Willie and Matthew Tozer has composed the definitive treatise on this important transformation. To effect the deoxygenation of an alcohol requires prior activation of the hydroxyl group into an *O*-thio acyl derivative (ester, carbonate, or carbamate) that facilitates the capture of the radical species (usually derived from tin, silicon, phosphorus, or boron reagents) and allows the formation of the key carbon-centered radical, which abstracts a hydrogen atom from the reducing agent. Because of the intermediacy of radicals, the scope of the reaction is extremely broad and the compatibility with many other functional groups (for which ionic or hydridic reducing agents would not be suitable) is excellent. All classes of alcohols can be deoxygenated and polyols such as sugars are particularly well represented in the applications of the reaction. The authors provide an exhaustive survey of the current procedure, including newly developed catalytic methods that obviate the use of tin in stoichiometric quantities. Moreover, the massive tabular survey amply illustrates the true generality and usefulness of this transformation.

It is appropriate here to acknowledge the expert assistance of the entire editorial board, in particular Michael J. Martinelli, who shepherded both of the chapters in this volume. The contributions of the authors, editors, and the publisher were expertly coordinated by the responsible secretary, Robert Bittman. In addition, the *Organic Reactions* enterprise could not maintain the quality of production without the dedicated efforts of its editorial staff, Dr. Linda S. Press and Dr. Danielle Soenen. Insofar as the essence of *Organic Reactions* chapters resides in the massive tables of examples, the authors’ and editorial coordinators’ painstaking efforts are highly prized.

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