

PREFACE TO VOLUME 92

*Something old,
something new,
something borrowed,
something blue,*

Old English Rhyme, Lancaster Version

No, this volume is not a marriage in the traditional sense, but the union of “old” and “new” in the form of two chapters, one of which represents some of the most classical methods for the synthesis of indoles, pyrroles, and carbazoles together with a second chapter that describes some of the most modern methods for the construction of extraordinarily complex polycyclic compounds. To create this volume we have “borrowed” the expertise of one of our longest-serving editors (and a previous author at that), namely, Stuart W. McCombie. And of course, those familiar with the series will appreciate that since 1942, our bound volumes have maintained the same classic “blue” covers that at one time were proudly featured in libraries and researchers offices around the world.

The first chapter, authored by Antonio M. Echavarren, Michael E. Muratore, Verónica López-Carrillo, Ana Escribano-Cuesta, Núria Huguet, and Carla Obradors, represents a family of reactions that are truly the product of modern methods development, namely the remarkable ability of gold catalysts to effect a bewildering array of structural reorganizations in reactions between alkynes and alkenes or arenes. The ascendancy of gold catalysis over the past 15 years can be traced to an early report by Teles on the hydration of alkynes to ketones. The recognition that cationic gold complexes have a special ability to bind to alkynes and to catalyze addition reactions has led to a “gold rush” of developments that leverage this potential in a wide range of settings. Allied to the hydrofunctionalization of alkynes is the landmark report by Echavarren on the cycloisomerization reactions of enynes in 2004. When the field grew to the point where an authoritative overview of this remarkable family of transformations was warranted, naturally, we turned to Prof. Echavarren and were delighted that he agreed to invest the effort together with an impressive team of collaborators to accomplish this task. The result is the first comprehensive treatment of these reactions that introduces the reader to the broad scope of substrate patterns, their myriad mechanistic pathways, and the stunning diversity of product structures that can be generated under mild conditions. Because the structural reorganizations effected by gold catalysis in this family are so deep-seated and diverse, we have, for the first time in the history of the *Organic Reactions* series, incorporated color into a chapter to aid the readers in keeping track of the carbon atoms in these reactions. Creating a logical organization for the wide variety of structural settings and outcomes is extremely challenging, but the

authors have done an outstanding job in guiding the reader through the complexities of these reactions and aiding the identification of conditions and catalysts that are recommended for the various permutations. The Tabular Survey comprises 23 tables organized by substrate structure with such a fine granularity as to facilitate with ease the identification of product types sought by those interested in using these methods. Even those not interested in executing this chemistry will find a “gold mine” of fascinating mechanistic puzzles for use in problem sessions.

The second chapter authored by William F. Berkowitz and Stuart W. McCombie details one of the most powerful methods for the construction of the privileged heterocycles, pyrroles, indoles, and carbazoles from vinyl and aryl azides. This classical transformation, sometimes known as the Hemestberger-Knittel reaction involves the controlled decomposition of azides into the corresponding nitrenoids by the agency of heat, light, and catalysis by metals as well as Brønsted and Lewis acids. Although a number of different mechanistic pathways are possible, the end result is the formation of a new carbon-nitrogen bond that forms a pyrrole ring either in isolation or fused to one or more aromatic nuclei. The scope of the reaction is remarkably broad and as nicely presented by the authors, the ease of introduction of the azide moiety using many different protocols greatly facilitates the implementation of this process. Given the possibility of effecting the azide decomposition by numerous methods, the authors have provided expert guidance for the preferred reaction conditions depending upon the structural setting and neighboring functionality. In view of the ubiquitous appearance of indoles and carbazoles in natural products and therapeutic agents, this process has found extensive application in synthesis which is thoroughly illustrated in the applications section. This chapter extends our indole synthesis franchise to three, including the most recent chapter in Volume 76 on palladium-catalyzed cyclizations to indoles and the chapter in Volume 20 on the classic Nenitzescu Reaction that forms 5-hydroxyindoles.

It is appropriate here to acknowledge the expert assistance of the entire editorial board, in particular Steven Weinreb who oversaw the early development of Chapter 1 as well as Dale Boger and Marisa Kozlowski who teamed up to shepherd Chapter 2 to completion. The contributions of the authors, editors, and the publisher were expertly coordinated by the board secretary, Robert M. Coates. In addition, the *Organic Reactions* enterprise could not maintain the quality of production without the dedicated efforts of its editorial staff, Dr. Danielle Soenen, Dr. Linda S. Press, Ms. Dena Lindsey, and Dr. Landy Blasdel. Insofar as the essence of *Organic Reactions* chapters resides in the massive tables of examples, the author's and editorial coordinators' painstaking efforts are highly prized.

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