Science of Synthesis
Hetarenes and Related Ring Systems
Five-Membered Hetarenes with Two Nitrogen or Phosphorus Atoms

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Science of Synthesis

Science of Synthesis is the authoritative and comprehensive reference work for the entire field of organic and organometallic synthesis.

Science of Synthesis presents the important synthetic methods for all classes of compounds and includes:
- Methods critically evaluated by leading scientists
- Background information and detailed experimental procedures
- Schemes and tables which illustrate the reaction scope
Science of Synthesis

Houben–Weyl Methods of Molecular Transformations

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Hetarenes and Related Ring Systems
Five-Membered Hetarenes with Two Nitrogen or Phosphorus Atoms

Volume Editor
R. Neier

Responsible Member of the Editorial Board
D. Bellus

Authors
M. R. Grimmett
G. Hajos
K. Karaghiosoff
F. Mathey
Z. Riedl
A. Schmidpeter
W. Stadlbauer
B. Stanovnik
J. Sverte

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Preface

As our understanding of the natural world increases, we begin to understand complex phenomena at molecular levels. This level of understanding allows for the design of molecular entities for functions ranging from material science to biology. Such design requires synthesis and, as the structures increase in complexity as a necessity for specificity, puts increasing demands on the level of sophistication of the synthetic methods. Such needs stimulate the improvement of existing methods and, more importantly, the development of new methods. As scientists confront the synthetic problems posed by the molecular targets, they require access to a source of reliable synthetic information. Thus, the need for a new, comprehensive, and critical treatment of synthetic chemistry has become apparent. To meet this challenge, an entirely new edition of the esteemed reference work *Houben–Weyl Methods of Organic Chemistry* will be published starting in the year 2000.

To reflect the new broader need and focus, this new edition has a new title, *Science of Synthesis, Houben–Weyl Methods of Molecular Transformations*. *Science of Synthesis* will benefit from more than 90 years of experience and will continue the tradition of excellence in publishing synthetic chemistry reference works. *Science of Synthesis* will be a balanced and critical reference work produced by the collaborative efforts of chemists, from both industry and academia, selected by the editorial board. All published results from journals, books, and patent literature from the early 1800s until the year of publication will be considered by our authors, who are among the leading experts in their field. The 48 volumes of *Science of Synthesis* will provide chemists with the most reliable methods to solve their synthesis problems. *Science of Synthesis* will be updated periodically and will become a prime source of information for chemists in the 21st century.

*Science of Synthesis* will be organized in a logical hierarchical system based on the target molecule to be synthesized. The critical coverage of methods will be supported by information intended to help the user choose the most suitable method for their application, thus providing a strong foundation from which to develop a successful synthetic route. Within each category of product, illuminating background information such as history, nomenclature, structure, stability, reactivity, properties, safety, and environmental aspects will be discussed along with a detailed selection of reliable methods. Each method and variation will be accompanied by reaction schemes, tables of examples, experimental procedures, and a background discussion of the scope and limitations of the reaction described.

The policy of the editorial board is to make *Science of Synthesis* the ultimate tool for the synthetic chemist in the 21st century.

We would like to thank all of our authors for submitting contributions of such outstanding quality, and, also for the dedication and commitment they have shown throughout the entire editorial process.

**The Editorial Board**

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October 2000
Volume Editor's Preface

This volume covers the synthesis of five-membered heterocyclic compounds with either two nitrogen or phosphorus atoms or five-membered heterocycles containing both one nitrogen and one phosphorus atom. The oxidation state of the described heterocycles corresponds to the maximum unsaturation. Maximum unsaturation means that the cyclic conjugation in the five-membered ring must not be interrupted by either a $sp^3$-hybridized carbon atom or a heteroatom incapable of $\pi$-conjugation. In accordance with the common principle of the series, the benzoannulated systems are treated directly after the monocyclic systems. The indazoles and benzimidazoles, the benzoannulated systems of pyrazoles and imidazoles, are so important that they are treated in separate chapters. In fusing a five-membered heterocycle containing two heteroatoms to a six-membered ring, one of the heteroatoms can be common to both rings. For these systems, the heterocyclic systems and their analogues containing one or more heteroatoms in the six-membered ring were combined in the same chapter, as long as the synthesis of these compounds proceeded via a ring-closure of the five-membered ring. The same rule was observed for the phosphorus and arsenic analogues: the azaphospholes, the azaarsoles, and the diprophospholes.

Most of the ring systems covered in Volume 12 are stable compounds, in accordance with the goals set for Science of Synthesis. The phosphorus and arsenic containing heterocycles are the most sensitive class of compounds treated in this volume. It is obvious, alone from the size of the chapters treating the different classes of heterocycles, that the knowledge and the number of synthetic procedures vary widely. Some of the heterocyclic rings were first synthesized almost 150 years ago like the imidazole ring (H. Debus 1858). The structures of the parent five-membered heterocycles were proven 120 years ago (imidazole: B. Radziszewski 1882, F. R. Japp 1886, and W. Marckwald 1889; pyrazole: L. Knorr 1887). In contrast to these compound classes, which have a rich history, the first member of the diprophospholes was first reported just over 20 years ago (Issleib 1981) and the newest member of this family, the 1,2-diprophosphole, only appeared in 1996 (Schmidpeter). Since the chemistry of imidazopyridines, pyrazolopyridines, imidazole, benzimidazole, pyrazole, and indazole has been worked on for the longest time, the chapters dedicated to these heterenes are by far the largest ones in this volume.

The synthesis of the pyrazoles and indazoles and the synthesis of imidazoles and benzimidazoles were discussed in the excellent chapters which have appeared in Houben–Weyl Vol. E 8b and in Houben–Weyl Vol. E 8c, respectively. The goal of the authoritative contributions in Houben–Weyl has been to present a comprehensive review of a chosen field. The current authors of Science of Synthesis referred to these chapters while preparing the new contributions. However, the chapters written for Science of Synthesis could not be just an update of the former contributions, but had to be rewritten according to the new rules. Obviously, the authors have been asked to include the latest developments in the product classes treated in Volume 12. The important difference between Science of Synthesis and its predecessor Houben–Weyl is that the authors have been asked to evaluate the information critically. Many of the classical methods, which have been already been treated in Houben–Weyl, were included in the chapters of Science of Synthesis in order to give the reader a clear picture of the state of the art.

The new edition of Science of Synthesis, Houben–Weyl Methods of Molecular Transformations takes into account, that an electronic version will also be published. To give the full picture of a field the worked-out, representative synthetic procedures had to be included in the printed as well as in the electronic versions. It has not been an
easy task for the authors, to make a judicious choice from the huge number of reported synthetic procedures in the literature. Thieme and its editorial board have relaunched the Houben-Weyl series with the goal to achieve very high standards indeed. Science of Synthesis, Houben-Weyl Methods of Molecular Transformations is designed and written to stimulate new discoveries and developments both in industry and in academia. To accomplish this goal the chapters in Science of Synthesis have to give expert guidance to scientists’ synthesis problems. It has not been a trivial undertaking for the authors to write contributions, which meet these high standards. As Volume 12 belongs to the early volumes of this series, the authors had to develop the rules and many formal aspects of the presentation in close collaboration with the editorial office of Thieme. Not only the organizational scheme, but also the guidelines have been refined during this collaboration. Many fruitful contacts between the authors, the volume editor, the responsible member of the editorial board, and the editorial office have been necessary to advance our common goal. I am heavily indebted to all the authors for having been ready to invest their scientific expertise in writing their chapters. Their impressive enthusiasm and willingness to accept suggestions for modifications even at the last minute, have contributed considerably to the quality of this volume. It has been a pleasure to work with them and to be able to count on their knowledge and understanding.

Without the steady help and the excellent advice of Professor Daniel Bellus, it would have been impossible to solve many of the problems en route. It has been an extraordinary chance to collaborate on this project with Professor Bellus, as responsible member of the editorial board. The collaboration with Thieme has always been smooth. The discussions with the members of the editorial office in Stuttgart were characterized by the high standards typical for Thieme and by their willingness to help settle problems. I am especially indebted to Dr. Guido F. Herrmann, who helped to solve the difficulties encountered at the beginning of the project. I am deeply indebted to Dr. M. Fiona Shortt for her efficiency and for her help at all stages of the project. Finally, Lindsey A. Sturdy as a member of the editorial team and Dr. Joe P. Richmond as a freelance member of the editorial team have also made major contributions.

Volume Editor

Reinhard Neier

Neuchâtel, February 2002
Volume 12:
Five-Membered Hetarenes with Two Nitrogen or Phosphorus Atoms

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