Volume Editor’s Preface

This volume covers the synthesis of three- and four-membered heterocycles with maximum unsaturation and of five-membered heteroarenes with one oxygen, sulfur, selenium, tellurium, nitrogen, or phosphorus atom. Maximum unsaturation means that the ring doesn’t contain either a sp³-hybridized carbon atom or a heteroatom incapable of π-conjugation. Some compounds which are derivatives of such ring systems but no longer feature maximum unsaturation are also included, namely thiirene 1,1-dioxides, thiophene 1,1-dioxides, and λ3-phosphirenes or η1-metal complexes of λ3-phosphirenes.

This volume deviates from the common principle of the series to treat benzo-annulated systems directly after the monocyclic ring systems. While this rule is observed where relevant for the three- and four-membered ring systems, annulated systems such as benzofurans, benzothiophenes, benzopyrroles (indoles) etc. are covered separately in Volume 10 (Fused Five-Membered Hetarenes with One Heteroatom). This was done because the three- and four-membered ring systems alone would not have filled one volume, and the material for monocyclic and benzo-annulated five-membered hetarenes is much too abundant for one volume.

The ring systems covered in this volume occupy a wide range of stabilities and reactivities. They can have a fleeting existence such as the antiaromatic three-membered rings of oxirene, thiirene, selenirene, and 1H-azirine, be highly reactive such as the kinetically stabilized, formally antiaromatic tri-tert-butylazete, or represent basic chemicals in their parent form, such as furan, pyrrole, and thiophene, which are tolerant to a broad range of reaction conditions during their synthesis and selective transformation. Also, the various ring systems described in this volume were introduced to the field of chemical science at well-spaced intervals over the last 200 years. While furans (2-furoic acid discovered by C. W. Scheele in 1780, correct ring structure proposed by A. von Baeyer in 1877), pyrroles (first detected by F. F. Runge in 1833, isolated purely in 1857, correct ring structure proposed in 1870), and thiophenes (discovered in 1882 by V. Meyer) have a rich history of well over one hundred years, the phospholes, congeners of the former, did not appear before 1959. Thiirenes, oxirenes, and 1H-azirines were closely studied as reactive intermediates and, in some cases, as matrix-isolated species mainly in the 1970s, azacyclobutadienes (azetes) appeared in 1973 and were a hot research topic in the 1980s, and many of the phosphorus-containing three- and four-membered heterocycles mentioned in this volume were reported over the last twenty years. Since the chemistry of the five-membered hetarenes furan, pyrrole, and thiophene had the longest time to mature, it is clear that the chapters on these three classes of ring systems are by far the largest ones in this volume.

The syntheses of furans, pyrroles, and thiophenes were discussed in Houben–Weyl, Vol. E 6. Since only six years have elapsed between the appearance of this publication and the present volume, the current authors were able to profit from the comprehensive and authoritative reviews in this Houben–Weyl volume and could critically evaluate the information given there and refer to it in Science of Synthesis (Volume 9). This Science of Synthesis volume is of course updated with the latest developments in the synthesis of these three important classes of hetarenes. It was certainly not easy for the authors of these three chapters to develop their own style of presenting the facts in light of the excellent contributions produced by the Houben–Weyl authors previously. Readers who notice that in some cases, the same experimental procedures have been selected in both the Houben–Weyl and Science of Synthesis volumes are assured that this was done deliberately with the explicit approval of the publishing house: It is self-evident that a specific method to construct a target molecule should be illustrated by a representative, well
worked-out synthetic procedure, and no reason was seen to challenge the expertise of the former authors in the selection of suitable procedures.

This volume is only the second one in the new series Science of Synthesis. Since not only the concept but also the organizational scheme is different in some aspects from the former Houben–Weyl, the authors of the present volume did not have a model to follow in the formal presentation of their contributions. Furthermore, in the exactly three years between the start of this project and the publication, the organizational scheme for the volumes on hetarenes as well as the guidelines for authors have been refined constantly, not at least due to the continuous feedback between authors, volume editor, and editorial office. I am very grateful to all authors for their active participation in the development of our common project. I appreciate also their willingness to accept suggestions for changes that were given by me or the editorial office.

It is my great pleasure to thank the publishing house and the staff of the editorial office in Stuttgart for the smooth cooperation in this project. My particular thanks go to Dr. M. Fiona Shortt and to Lindsey Sturdy who were always open for discussions, ready to settle problems, and determined to move the project ahead.

Volume Editor

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Gerhard Maas