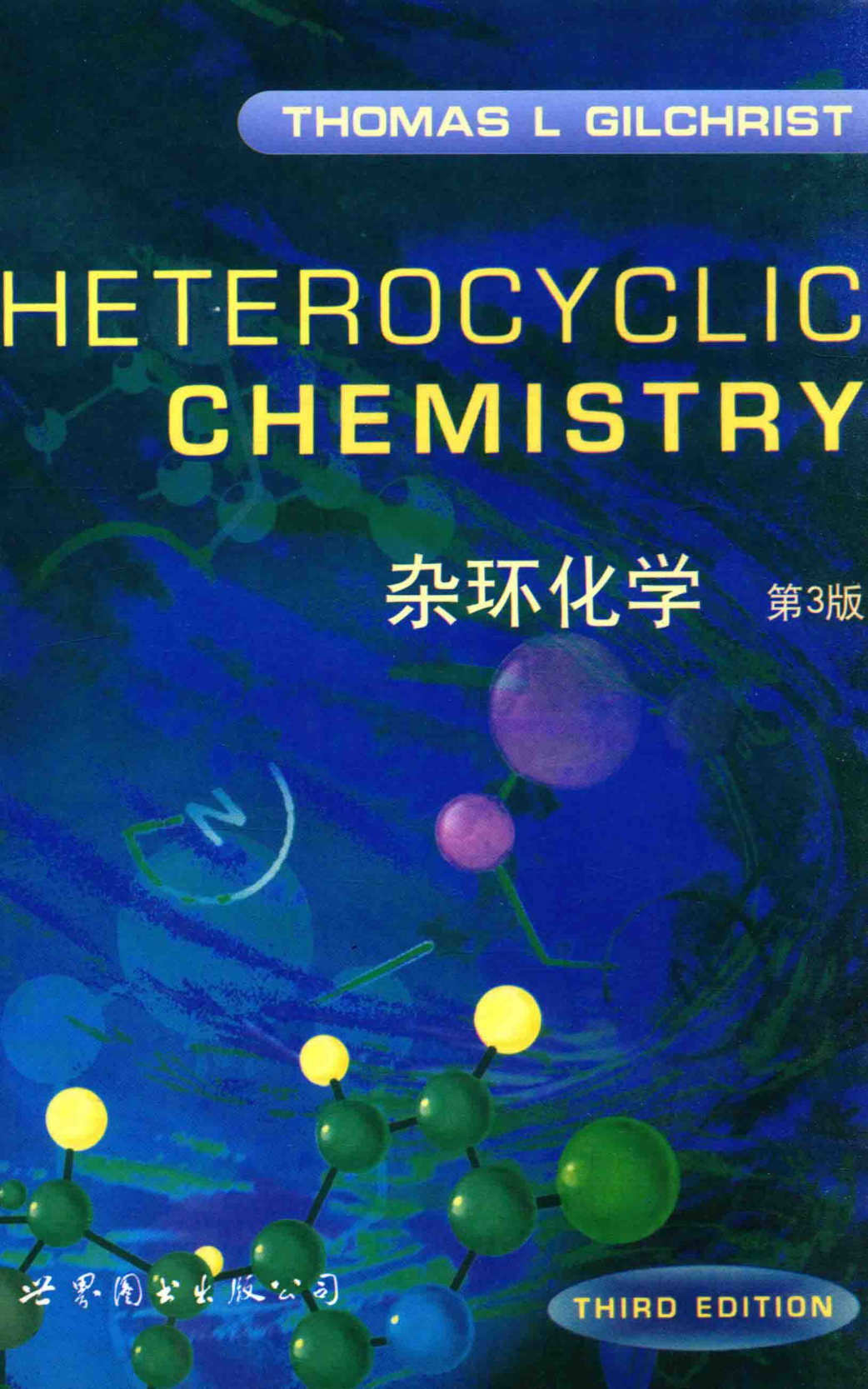
THOMAS L GILCHRIST

HETEROCYCLIC CHEMISTRY

杂环化学 第3版



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THIRD EDITION

Heterocyclic Chemistry

Third Edition

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Preface to the third edition

The material of the second edition has been revised with two principal aims in mind. The first is to bring the contents up to date. To this end, Chapter 1 and several parts of other chapters have been rewritten, the references have been updated (with more emphasis given to recent review articles) and several new reaction schemes have been introduced. These new schemes are intended to illustrate aspects of heterocyclic chemistry that are becoming more important. Organopalladium and other organometallic species are increasingly used in ring synthesis and in substitution reactions; some of the new schemes provide examples. New applications of heterocyclic compounds as pharmaceuticals, as intermediates in organic synthesis and as ligands are also illustrated.

The second aim has been to make the text more 'user friendly'. The text and structure drawings have been completely reset and the layout redesigned. I am indebted to Alexandra Seabrook, Shuet-Kei Cheung and their colleagues at Addison Wesley Longman for making this possible. Some of the obscurities in the text have been removed and captions have been added to all the reaction schemes. Worked examples have been introduced into most chapters, both to illustrate mechanistic points and to extend the chemistry. There are also some new problems at the end of several chapters.

I am grateful to Professor Hans Neunhoeffer and Dr Ian O'Neil for very helpful suggestions for improving the text and to Dr Eric Scriven for advice on the manufacture and uses of pyridines. As always I have relied greatly on my wife, Lorraine, who has patiently worked with me to produce and check the manuscript.

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Preface to the second edition

I have received several very helpful comments and criticisms of the first edition and I have tried to take these into account in producing a second edition. I have also taken the opportunity to update some of the original material. The most substantial additions have been made to the chapter on the synthesis of heterocycles (Chapter 4). There have been important advances in the use of 1,3-dipolar cycloaddition and Diels–Alder cycloaddition in heterocyclic synthesis; the sections covering these topics have therefore been enlarged and reorganized. Other general methods that have gained increased prominence, such as radical cyclization, are also discussed more fully. The introductory chapter and that on the properties of aromatic heterocycles (Chapter 2) have also been substantially revised. Elsewhere new material has been added to reflect the increasing importance of topics such as the use of organolithium reagents in heterocyclic chemistry and the value of heterocycles as intermediates in synthesis. Several new problems have also been added.

Another major change is a cosmetic one: the order of the later chapters has been altered. This has been done because the simpler six- and five-membered aromatic heterocycles seem to be taught first in most courses on heterocyclic chemistry. The chapters on the various classes of ring system (Chapters 5 to 10) are, however, largely self-contained and the material can be presented in any sequence.

There is rarely time to cover all the material presented here in a course on heterocyclic chemistry. The book is therefore intended also to serve as a reference source and as a guide to the enormous literature of heterocyclic chemistry. The reference list has been updated, mainly to include recent review articles. In doing this I have adopted the policy of making little specific reference to review chapters in *Comprehensive Heterocyclic Chemistry* (ed. A. R. Katritzky and C. W. Rees, Pergamon Press, Oxford, 1984). This work is nevertheless the best place to start a search for more detailed information on heterocyclic chemistry and its literature. The periodic guides to the literature provided in *Advances in Heterocyclic Chemistry* (ed. A. R. Katritzky, Academic Press, San Diego) are also invaluable: the latest of these, by L. I. Belen'kii and N. D. Kruchkovskaya, is in Volume 55 (1992).

I am most grateful to those who have made suggestions for changes to the original edition. In particular, I should like to thank Professor Wilhelm Flitsch, Professor Charles Rees, Dr John Boulton, and Dr Derek Hurst, who provided detailed written comments. If their suggestions have not all been incorporated it is because I have had to restrict the length of the book. I am also grateful to Dr Dick Storr, who read part of the new material, to Dr Frank King for his help with Chapter 1, to Dr Michael Rodgers for commissioning a second edition, and to the staff of Longman Higher Education and Reference for their expert guidance.

Preface to the first edition

In this book I have aimed to presend a description of the preparation and properties of heterocyclic compounds which can be used by anyone with a good background knowledge of organic chemistry. The number of different heterocyclic systems and their structural diversity make it difficult to gain a good understanding of the subject by studying individual ring systems in isolation. I have therefore tried to identify and emphasize general features of the properties of heterocyclic compounds throughout the book.

The concept of aromaticity has long proved useful in rationalizing the chemistry of many unsaturated heterocycles. The meaning of the term aromaticity, as applied to heterocyclic compounds, is discussed in Chapter 2. This is intended to provide a firm basis for understanding the chemistry of particular ring systems described later in the book. The chemistry of nonaromatic heterocycles is often regarded as a simple extrapolation of aliphatic and alicyclic chemistry. Although this undoubtedly has some justification there are some important special features of the properties of nonaromatic heterocycles which are discussed in Chapter 3. Chapter 4 is intended to provide a framework for rationalizing the vast literature on heterocyclic synthesis. The approach I have taken is to identify the reactions involved in the ring-forming processes and to classify the synthetic methods accordingly. There are many examples in this chapter, presented in tabular form, which are given to emphasize the common features involved in the synthesis of different ring systems. Many of these examples are referred to in later chapters.

Descriptive accounts of the more important ring systems are presented in Chapters 5 to 10. The ring systems are described in order of increasing ring size and complexity, but the material in this part of the book need not be read in the order in which it is presented. For example, the reader may prefer to study the chemistry of pyridines (Chapter 8) before that of pyrroles (Chapter 6). Imidazole and the other azoles have an interesting and diverse chemistry which is sometimes given little attention in textbooks. I have felt justified in describing these ring systems in more detail (Chapter 7) because of their apparently increasing importance as pharmaceuticals. In all of the chapters covering particular ring systems examples of currently important derivatives are given, and the diverse roles of the

heterocycles as synthetic intermediates in organic chemistry are illustrated. A guide to the various nomenclature systems for heterocycles is presented in Chapter 11.

Each chapter is followed by a summary, listing the main points in the text, and by a set of problems. Most of these problems are taken from the literature, and a list of references to the original papers is given at the end of the book. Literature citations are also given throughout the text. These can be ignored by the reader who simply wants an introduction to the topics being discussed, but they are provided to allow access to the original work on much of the factual material. Where this is not possible, for reasons of space, references are given to reviews. Heterocyclic chemistry is well served by specialized reviews, notably those in the series *The Chemistry of Heterocyclic Compounds*, edited by A. Weissberger and E. C. Taylor, and in the *Advances in Heterocyclic Chemistry* series edited by A. R. Katritzky and A. J. Boulton. An important additional source of specialized information, which has become available since this text was written, is *Comprehensive Heterocyclic Chemistry*, edited by A. R. Katritzky and C. W. Rees.

In writing the book I have been fortunate to have the expert guidance of the staff of Pitman Publishing Ltd. I should like to thank them, and particularly Mr Navin Sullivan, for their help. I am also indebted to the referees who read parts of the manuscript and made invaluable suggestions for its improvement, and to my colleagues at Liverpool who have read and commented upon parts of the text. My wife Lorraine typed most of the manuscript and was a constant source of advice, encouragement and practical assistance during its preparation.

T. L. Gilchrist. September 1984
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Acknowledgements

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