The Inorganic Heterocyclic Chemistry of Sulfur, Nitrogen and Phosphorus

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Preface

Some excellent works on inorganic heterocyclics have appeared in recent years, and I must first make my excuses for writing another book on this branch of chemistry. It happened in the following way.

During the last decade, knowledge of the inorganic heterocyclics has grown so fast that the only fully comprehensive work on them is now seriously out of date; the production of an updated version would be a large undertaking and is not expected in the near future. At the same time, it has become clear that the concept of inorganic heterocyclics, embracing as it does such diverse substances as mineral silicates, carboranes, phosphazenes, and chelate complexes of metals, is, in its fullest sense, too broad to be really useful. The subject simply must be broken down into more manageable chunks, and so it usually is. Some of these, such as the borane derivatives and the silicones, are familiar to many chemists and often figure in reviews or new books. Others, such as the covalent heterocycles of arsenic or selenium, interest few people and account for only a small volume of publication. Still others are more commonly and more appropriately dealt with in other contexts, such as coordination chemistry or mineralogy. However, when all these topics have been eliminated, there remains a solid core of material which lies right outside the experience and training of most industrial and academic chemists, and which many of them now feel a need to know about. This material comprises mainly the covalent ring compounds based on various combinations of the elements nitrogen, sulfur, and phosphorus, and the related non-cyclic chemistry. No previous book has covered precisely this range of topics, and the treatments of parts of the field to be found in previous books and reviews are mostly not recent enough to include some very important and interesting new work. A compact, comprehensive and up-to-date survey is clearly needed, and this book is an attempt to provide it. The impulse to write came from two sources: from the publishers, and from my friend Dr. Henri Garcia-Fernandez who unfortunately had to withdraw from collaboration at an early stage. I am particularly grateful to Academic Press and their referees for their advice on the scope of the book, which was not easily decided upon.

The book is intended as a reference text rather than a monograph. The *Chemical Abstracts* have been scanned up to early 1979, and in addition a few unpublished results, furnished through the kindness of individuals, are mentioned. In order to keep down size and cost, I have not included all literature references but have tried to give enough of the more recent ones so that the user will quickly be led, through them and their bibliographies, to all available information on the subject. Where good reviews exist, or good review sections of research papers, these have been freely cited instead of the primary publications. I apologize to the authors of the latter for my use of this space-saving device, which most certainly was not intended as a slight but may occasionally look like one. Facts are given pretty fully when only otherwise available through a long literature search; where, however, large numbers of facts have been well compiled elsewhere, I have made a selection to illustrate classes of compounds or points of principle, and given references to the compilations.

Although myself engaged in research on sulfur–nitrogen heterocyclics, I am conscious of the small importance of my contributions compared with those of some other workers frequently named in the bibliographies, and I would not want to equate my judgment with theirs. Nevertheless, a mere recital of facts and of the uncoordinated opinions of others makes dull reading, so I have often taken the liberty of giving my own views and suggestions for future work. Some of these will no doubt seem naive to specialists in the particular fields. Inevitably, too, there will be mistakes and omissions, for which I apologize in advance. My hope for the book is simply that it will be found useful.

Writing a book strengthens one's appreciation of other books, and I want to record my debt to several which have made the task easier. These include Haiduc's *Chemistry of Inorganic Ring Systems*, Garcia-Fernandez's *Heterocycles en Chimie Minerale* and *Química Heterocíclica Inorgánica*, Armitage's *Inorganic Rings and Cages*, and Allcock's *Heteroatom Ring Systems and Polymers*. Special mention must be made of Goehring's *Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen*. This, published in 1957, was a pioneering work in the field, and it introduced me to a subject on which I was to research for many years. Though dated now, it still makes interesting reading, and some of the "problems" discussed in it are still worth looking at. It was continually consulted in our laboratory, where it came to be known as "the Black Book". Well thumbed and with the binding falling apart, it still stands on my shelf.

It is a pleasure to make the following acknowledgments: to my employers, the Queen's University of Belfast, for time and facilities; to the University of Southampton (where the book was begun on a study leave) for hospitality and facilities; to my friend Dr. Arthur Banister for criticism of the manuscript; to the researchers who have sent me results in advance of publication and extended hospitality on visits, including Dr. Banister, Dr. H. Garcia-Fernandez, Prof. Dr. O. Glemser, Prof. Dr. H. W. Roesky, and the late Dr. F. P. Olsen; to Mr. J. A. Beckman of the Firestone Tire and Rubber Company for technical literature; and to Academic Press for patience and encouragement.

The person who deserves the heartiest thanks of all is my wife Joan, who spent many, many hours at the typewriter, coping with my exasperating handwriting and continual amendments, and striving to bring consistency into my disorderly typography.

Henry G. Heal

May 1980

The Organization of this Book

The following notes are intended to help the reader to find particular compounds, ring systems, or subject areas in this book.

The book deals *only* with purely inorganic rings and cages, that is, containing no carbon atoms in the ring or cage skeleton. However, inorganic rings and cages with organic *ligands* are covered.

For a user not familiar with the book, the quickest way to find a particular ring system or cage is probably to look it up in the Index of Rings at the back.

For more frequent users, here is a brief explanation of how the subject matter is arranged. Sulfur–nitrogen rings come first (Chapters 2–9), followed by phosphorus–sulfur rings (Chapter 10) and then by phosphorus–nitrogen rings (Chapters 11–13). Rings containing all three elements are dealt with in appropriate chapters on *sulfur*–nitrogen rings, not under phosphorus–nitrogen rings. (S–N–P rings are too diverse to be logically treated in a chapter by themselves; the arrangement just described is at least consistent, though not ideal in all respects.) Within each broad category of rings (S–N, P–S, or P–N) saturated rings precede unsaturated ones, and among saturated S–N, P–S, or P–N rings the lower oxidation states of S or P precede the higher.

Contents

1
Status, nomenclature, and methods of synthesis

I. Introduction

A. Inorganic heterocycles: a modern perspective

Many knowledgeable and experienced chemists are hardly aware of the existence of a subject "inorganic heterocycles". Texts on it rarely meet the eye, even on the shelves of large libraries, and there must be few undergraduate university courses in which it plays more than an insignificant part. To some chemists with well ordered, conventional schemes of ideas, it seems awkward to classify and embarrassing to think about; like fluorocarbon chemistry, it does not fall neatly into any recognized major branch of chemistry, and so tends to be ignored by the practitioners of all. This came home to me in 1965, when my contribution at the Prague IUPAC Polymer Symposium on some derivatives of cyclic sulfur imides was classified in the organic section, though none of the compounds mentioned in it contained any carbon! Inorganic heterocycles have made less of a theoretical splash than borane chemistry or coordination chemistry, and they have not, until recently, formed the subject of any research fashion or bandwagon based upon possible commercial or military applications. Yet, scarcely noticed by the chemical world at large, they have grown into a substantial branch of knowledge with thousands of publications, which now clamors for attention, and which more and more chemists feel a need to learn about.

The first inorganic heterocycle, $(NPCl_2)_3$, was described by Liebig and Wöhler in 1834, and the second, S_4N_4, in 1835 by Gregory; but decades were to pass before Butlerov (1860) first recognized the importance of molecular structures in chemistry, and it was over a century before the structures of these two compounds were actually determined. Inorganic heterocyclic chemistry developed slowly during the nineteenth century. Notable periods were the 1880s (Demarçay's work on sulfur–nitrogen compounds) and the 1890s (Stokes's work on the phosphazenes). Kekulé's theory of the cyclic structure of benzene (1865) must have set inorganic researchers thinking about rings;

ring formulas were suggested, for example, by Stokes for the phosphazenes (1896) and by Hantzsch for sulfimide trimer (1901). Schenck, writing in Abegg's *Handbuch der anorganischen Chemie* (1907), thought that Stokes's ring formulas had "no claim to special probability". Though consistent with elemental compositions and molecular weights, they could not at that date be so reliably established as that of benzene, which was supported by the chemical evidence of isomeric substitution products. However, by 1930 the ring formulas of Stokes and Hantzsch were generally accepted. The early decades of the present century otherwise saw little progress on inorganic heterocycles; this was a period dominated by complexes and the Werner coordination theory. Our subject really came into its own shortly before the Second World War, when X-ray and electron diffraction began to be widely applied to structure determination. As more and more molecular structures were solved over the following decades, it became vastly easier to interpret reactions and plan syntheses in the field of inorganic heterocycles. After the war, too, there were great improvements in laboratory methods which revolutionized the practical study of these often difficult substances: inert-atmosphere and high-vacuum techniques became standard, recording infrared and n.m.r. spectrometers appeared, and chromatography was greatly improved. New reagents such as metal alkyls became readily available; indeed, specialist firms such as Alfa Inorganics began to supply a wide range of useful organometallics and other research intermediates. Thus new reactions can be tried out after much less preliminary work than formerly, and their products characterized with a speed, completeness, and precision not dreamed of a few years ago. The pace of discovery has consequently quickened, though most branches of inorganic heterocyclic chemistry still demand special skills and experience which are confined to a few laboratories.

The first book to deal largely with inorganic heterocycles seems to have been Goehring's little classic *Ergebnisse und Probleme der Chemie der Schwefelstickstoffverbindungen* (1957), still interesting reading. Of the several texts that have appeared subsequently, it seems right to mention specially Haiduc's comprehensive two-volume *Chemistry of Inorganic Ring Systems* (1970). Since 1970 the subject has advanced so fast that Haiduc's intended second edition was by 1978 proving difficult as a publishing venture. Meanwhile, the First International Conference on Inorganic Ring Systems was held at Besançon in 1975, and the second, in which 88 papers were presented, at Göttingen in 1978. Future international conferences are expected at least triennially.

Research on inorganic heterocycles is going on in many countries, including most of the larger industrially advanced ones, and key contributions have come from many places. As shown by the chapter bibliographies in this book, and by the lists of participants at conferences, German chemists are playing a major part in the development of the subject.

B. The importance of inorganic heterocyclics

Industrially the cyclosiloxanes have been important since the 1940s as intermediates in the manufacture of silicone products, and the cage compound tetraphosphorus trisulfide has been used in the manufacture of matches since 1898. For several decades there has been a continuous trickle of patents connected with various inorganic heterocyclics, but an actual new application has only very recently arisen, with the marketing of a phosphazene elastomer by the Firestone Tire and Rubber Company. Very recently, too, there has been intense technical interest in the metallic polymer $(SN)_x$. Both of these unusual substances are made from heterocyclic precursors. It remains true, however, that interest in inorganic heterocycles still centers largely on their fundamental chemistry.

Why are chemists attracted to the compounds discussed in this book as subjects for fundamental research? Everyone who works in the field has his own reasons for liking it, but it does seem reasonable to single out the following explanations for its appeal.

One of the major groups of compounds to be described here is the chlorophosphazenes and their derivatives. These constitute (along with the cyclosiloxanes) the best examples known of inorganic homologous series, with many members (in principle an unlimited number) capable of being isolated and individually studied. This is the most organic-like department of inorganic heterocyclic chemistry. The P–N ring skeletons are very stable and persist through many substitution reactions, like carbon skeletons. The course of these reactions can be interpreted by reasoning broadly similar to that used by organic chemists, but the problems are more complicated and more challenging than those of carbon or siloxane chemistry because of the more flexible stereochemistry and bonding possibilities of the phosphorus atom. There is an intriguing suspicion of aromaticity in these P–N rings. In total contrast are the S–N rings. Some of these are unsaturated in a formal sense, but their chemistry has little in common with that of the carbon–carbon double bond. They do not form homologous series, and the reasons why some unsaturated S–N rings exist, and others (apparently) do not, are decidedly mysterious and tantalizing to the theoretician. Compared with the cyclophosphazenes, these S–N rings are quite labile and can be transformed into each other under mild conditions in unexpected and puzzling reactions. Indeed, the reaction chemistry of these substances deserves to rank with that of the boranes for novelty and interest. A third topic which is full of interest and potential for development is saturated cage compounds, found among the phosphazanes (P–N cages) and phosphorus sulfides (P–S cages). The serious study of these is only just starting, but it is already clear that the isomeric transformations of the cages, and their formation and dismemberment, open up fascinating possibilities for experimental and theoretical study. These are some of the highlights