THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

THE HETEROCYCLIC DERIVATIVES OF PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH, AND SILICON

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THE CHEMISTRY OF HETEROCYCLIC COMPOUNDS

A SERIES OF MONOGRAPHS

ARNOLD WEISSBERGER, *Consulting Editor*

The Heterocyclic Derivatives of PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH, and SILICON

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INTRODUCTION TO THE SERIES

The Chemistry of Heterocyclic Compounds

The chemistry of heterocyclic compounds is one of the most complex branches of organic chemistry. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds.

A field of such importance and intrinsic difficulty should be made as readily accessible as possible, and the lack of a modern detailed and comprehensive presentation of heterocyclic chemistry is therefore keenly felt. It is the intention of the present series to fill this gap by expert presentations of the various branches of heterocyclic chemistry. The subdivisions have been designed to cover the field in its entirety, by monographs which reflect the importance and the interrelations of the various compounds, and accommodate the specific interests of the authors.

Research Laboratories
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ARNOLD WEISSBERGER

Contents

Foreword

The object of this book is to give a systematic account of the heterocyclic organic derivatives of phosphorus, arsenic, antimony, and bismuth, that is to say, of those derivatives which contain these elements and carbon (with or without other elements) in the ring system. Compounds in which the ring is purely inorganic, *i.e.*, carbon-free, are not considered.

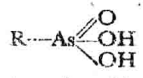
A glance at the Table of Contents will show the order in which the various ring systems are discussed. We may take the arsenic compounds as an example, since they are the most numerous. The first types to be discussed are those in which the ring consists solely of carbon atoms and one arsenic atom, the types being taken in order of increasing size of the ring. Therefore the cyclotetramethylenearsines come first, as five-membered ring compounds, followed by all those derivatives such as the arsindoles and isoarsindolines which contain the same ring system, that is to say, the ring with the same constituent atoms irrespective of its degree of hydrogenation. Then come the cyclopentamethylenearsines as six-membered ring compounds, followed by their derivatives (tetrahydroarsinolines, arsacridines, etc.) which contain the same ring. Next come the smallest ring systems which contain carbon, arsenic, and one other element. All the five-membered ring systems are dealt with, in order of increasing atomic weight of the third element. Hence the carbon–arsenic–nitrogen ring systems come first, then the carbon–arsenic–oxygen systems, etc. The six-membered ring systems are then dealt with similarly: for this purpose and for orderly classification a second arsenic atom in the ring has been counted as a third element.

The nomenclature of the cyclic compounds is often simple, but certain difficult problems arise. If we again take the arsenic compounds as examples, the names of the simpler noncyclic derivatives give no trouble. The main types may be exemplified as follows:

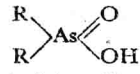
$C_6H_5AsCl_2$	Phenyldichloroarsine
$(C_6H_5)_2AsCl$	Diphenylmonochloroarsine
$(C_6H_5)_3As$	Triphenylarsine
$(C_6H_5)_3AsCl_2$	Triphenylarsine dichloride
$(C_6H_5)_3AsO(S)$	Triphenylarsine oxide (or sulfide)
C_6H_5AsO	Phenylarsenoxide
$C_6H_5AsO(OH)_2$	Phenylarsonic acid
$(C_6H_5)_2AsO(OH)$	Diphenylarsinic acid

The names of the compounds used in synthesizing the cyclic compounds and of many of the cyclic compounds themselves usually follow very simply from those of the above main types.

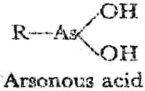
It should be noted, however, that a recent change in the British nomenclature of the acids derived from the Group V elements has created an unfortunate discrepancy between the American nomenclature (as used in *Chemical Abstracts*) and the British nomenclature (as used in *British Abstracts*). This is shown in the following table, in which the American name [*cf. Chemical Abstracts*, **39**, 5939 (1945)] is given immediately below each compound, and the British name in parenthesis beneath; in the formulas the symbol R represents an alkyl, aryl, or halogen group.



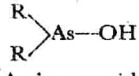
Arsonic acid
(Arsonic acid)



Arsinic acid
(Arsonous acid)



Arsonous acid
(Arsinic acid)



Arsinous acid
(Arsinous acid)

The analogous phosphorus and antimony acids are similarly named; thus, in place of an arsonic acid, one has a phosphonic or stibonic acid, and in place of an arsinous acid one has a phosphinous or stibinous acid.

The American nomenclature has been adopted throughout this book. In the author's opinion it is more logical than the British system, inasmuch as it ensures that the names of the two types of organic acid in which the Group V element has its higher valency have the suffix *ic*, and their salts the suffix *ate*, and those of the two types in which the element has its lower valency have the suffix *ous*, and their salts the suffix *ite*: the names thus fall in line with the long-established names of the purely inorganic acids, for example, phosphoric acid, $OP(OH)_3$, and the phosphates, and phosphorous acid, $P(OH)_3$, and the phosphites. It should be noted, however, that this discrepancy must introduce different names for certain compounds according to the system of nomenclature used. For example, the compound (I) is regarded in the American system as being an ester of pyrocatechol and chlorophosphonous acid and hence is termed *o*-phenylenechlorophosphonite; in the British system this becomes *o*-phenylene-chlorophosphinate.

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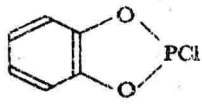


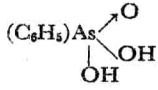
(I)

Another difficulty occasionally arises in the name to be applied to the parent compound of a given heterocyclic system, of which all members will be regarded as derivatives. Some of the names used in the past, such as *o,o'*-diphenylylenearsines and xenylene-2,2'-stibines are too unsatisfactory to be perpetuated. In seeking more suitable names, an attempt has been made to maintain a reasonable balance between a strictly logical system on the one hand and practical convenience on the other. For example, the term "arsa-carbazole" has been applied in the past to compounds in which the nitrogen atom of carbazole could be regarded as having been replaced by arsenic, but logically this term means carbazole in which one =CH— group has been replaced by the =As— group. It is hoped that the term 9-arsafluorene, although possibly strange to many chemists, will not be unacceptable to them. Here, the prefixed number 9 makes it clear that the term *arsa* implies that the $—CH_2—$ group has been replaced by the —AsH— group. In certain cases I have retained a well-established term because it has the merit of great convenience, even if logically, or systematically, it is inaccurate. For example, the term *arsacridine* is used in place of the more logical *10-arsa-anthracene* (p. 49), partly because it has become reasonably well established and partly because it allows a convenient term such as *arsacridinic acid* to be applied to the corresponding cyclic arsinic acid, for which the 10-arsa-anthracene nomenclature gives no such simple name. It is clear, however, that it would be of immense help if the chemists of the English-speaking nations would come to unanimous agreement concerning the nomenclature of these heterocyclic systems before confusion in this rapidly expanding field becomes greater.

With regard to the numbering of the heterocyclic systems, that adopted in *Chemical Abstracts* has been adhered to in most cases as representing standard American practice. In certain cases, however this numbering differs strikingly for strictly analogous types of compounds—a fact that becomes more obvious in a monograph of this type than in the vast indexes of *Chemical Abstracts*—and moreover is often at variance with that advocated in the *Ring Index*. When the numbering ultimately adopted here differs

from that in *Chemical Abstracts*, the two systems have been indicated clearly, so that transference from one to the other (if desired) is quite simple.

One point concerning the use of symbols requires brief discussion. In a compound such as trimethylamine oxide the electronic content of the nitrogen atom demands a coordinate link between the nitrogen and the oxygen, and the formula is written $(CH_3)_3N\rightarrow O$ or $(CH_3)_3\overset{+}{N}\!-\!\overset{-}{O}$. The oxides and sulfides of the tertiary phosphines, arsines, and stibines have until recently been depicted similarly, for example, $(C_6H_5)_3P\rightarrow O$, $(C_6H_5)_2As\rightarrow S$, and phosphonic and arsonic acids have also been depicted as having coordinate links, as



Recent measurements of the interatomic distances between phosphorus and oxygen atoms in phosphorus oxychloride, Cl_3PO, and other analogous compounds show, however, that this distance is too small to be linked by one covalent bond, and that, therefore, the link probably has some double bond character. The exact nature of the bond in these compounds remains uncertain at present, but it is probably a resonance hybrid between a coordinate link and a double bond, with the proportion of double bond character increasing from phosphorus through to antimony. Chemists have no symbol for such a hybrid bond, and for such compounds, therefore, a double bond has been used throughout (for printing convenience). It will be understood that in all such cases this symbol refers to this ill-defined hybrid bond and not to the classical double bond. In the few compounds mentioned in which arsenic is coordinated to a heavy metal such as palladium, however, the coordinate link symbol has been retained because in such compounds there is at present no evidence against the existence of this link.

A glance through this book will show that the heterocyclic derivatives of arsenic are considerably greater—both in variety of types and in actual numbers of compounds—than those of phosphorus, antimony, or bismuth. Of course, this statement is true of organic derivatives of these elements in general, whether cyclic or otherwise. It is not difficult to find the reasons for this predominance of the arsenic compounds. First, there has been for many years an insistent demand for organic arsenic compounds, arising originally from their application as drugs and later (from the days of

World War I), from their potential value as offensive agents in warfare. Second, the synthesis of organic arsenic compounds is facilitated immensely by certain valuable reactions which have only a limited application—or often no application at all—in the synthesis of analogous phosphorus, antimony, and bismuth derivatives.

Two reactions stand out prominently in this respect. In the aliphatic field, the reaction initiated by Meyer in Germany and widely developed by Dehn in America must be noted. If, for example, arsenic trichloride and methyl iodide are added to aqueous sodium hydroxide and the solution is boiled, sodium methyl arsonate results:

$$AsCl_3 + CH_3I + NaOH \longrightarrow CH_3AsO(ONa)_2$$

If the sodium salt is now added to concentrated hydrochloric acid containing a trace of potassium iodide and sulfur dioxide is passed through the mixture, reduction to methyldichloroarsine, CH_3AsCl_2, occurs readily. The Meyer reaction may now be repeated with this dichloroarsine, which when similarly boiled with methyl iodide and aqueous sodium hydroxide gives the sodium salt of dimethylarsinic acid:

$$CH_3AsCl_2 + CH_3I + NaOH \longrightarrow (CH_3)_2AsO(ONa)$$

The latter can be reduced in turn, under the previous conditions, to dimethylmonochloroarsine, $(CH_3)_2AsCl$, and this compound can be subjected to a final Meyer reaction to give trimethylarsine oxide:

$$(CH_3)_2AsCl + CH_3I + NaOH \longrightarrow (CH_3)_3AsO$$

Tertiary arsine oxides usually undergo very ready reduction (usually in chloroform solution) by sulfur dioxide in the presence of a trace of potassium iodide, even at room temperature, to give the tertiary arsine. The Meyer reaction is thus particularly valuable for the preparation of arsines containing different alkyl groups. This reaction, it should be emphasized, cannot be applied to the analogous phosphorus compounds, and in any case there is no ready method by which the exceedingly stable tertiary phosphine oxides can be reduced to the tertiary phosphines themslves. Furthermore, the Meyer reaction cannot be applied satisfactorily to the synthesis of antimony compounds.

In the aromatic field, the Bart reaction is of great value for the synthe-

sis of arsonic acids and the many derivatives that can be prepared from them. In this reaction an aromatic amine is diazotized and the solution made alkaline and then treated with sodium arsenite. Nitrogen is evolved, with the formation of the corresponding arsonic acid as the sodium salt. Aniline, for example, will thus furnish the sodium salt of phenylarsonic acid:

$$C_6H_5N_2ONa + NaAsO_2 \longrightarrow C_6H_5AsO(ONa)_2 + N_2$$

If phenyl arsenoxide, C_6H_5AsO, is used in place of the sodium arsenite, the sodium salt of the corresponding diaryl arsinic acid is obtained:

$$C_6H_5N_2ONa + C_6H_5AsO \longrightarrow (C_6H_5)_2AsO(ONa) + N_2$$

Since the arsonic acid can be reduced readily to the dichloroarsine, $C_6H_5AsCl_2$, for example, and the arsinic acid to the monochloroarsine, $(C_6H_5)_2AsCl$, by the reduction outlined above, the wide value and scope of this reduction will be obvious. The Bart (or Bart-Schmidt) reaction can be applied similarly to the preparation of the corresponding stibonic and stibinic acids, but the yields are usually much lower. It cannot be applied to the preparation of the corresponding phosphorus derivatives.

Many examples of the Meyer and Bart reactions occur in this book, and the vast role they have played in the development of the chemistry of organic derivatives of arsenic must be obvious.

To the practical chemist at the bench the organic derivatives of arsenic must always be very attractive because many separate so readily in such beautifully crystalline condition. After a long and often wearisome synthesis, this factor satisfies not only the chemist's esthetic appreciation of beauty, but also his sense of ultimate justice! Unfortunately this property of ready and decisive crystallization is much rarer in the organic derivatives of phosphorus, antimony, and bismuth.

These heterocyclic derivatives of the Group VB elements also make a strong appeal to the stereochemist, for they have provided solutions for several problems that might never have been solved by the use of noncyclic derivatives alone.

A cursory glance through this monograph will indicate how little is known of the heterocyclic derivatives of phosphorus, arsenic, antimony, and bismuth compared with our vast knowledge of the similar derivatives of nitrogen. However, this glance should also indicate to the reader

the wide and fruitful field of investigation that the heterocyclic derivatives of these four elements still offer to the chemist.

A short account of heterocyclic derivatives of silicon has been included because in some respects (particularly their synthesis) they bear a strong resemblance to the corresponding derivatives of the Group VB elements.

This monograph was started while I held a visiting Senior Professorship at the University of Hawaii, and completed on my return to Cambridge. I would like to take this opportunity to thank the authorities of the University of Hawaii most sincerely for the many facilities they so generously placed at my disposal.

Comments and criticisms concerning the contents of this book would be warmly welcomed by the author.

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