

## Volume Editor's Preface

Of the four metalloid elements, arsenic, antimony, bismuth, and silicon, covered in this volume, the space given to silicon (856 pages out of 972) might seem to be disproportionately large. There is little doubt, however, that in the current practice of organic synthesis, silicon-containing compounds play a much larger part than those of arsenic, antimony, and bismuth. Furthermore, the chemistry of the three group 15 elements was well covered in **Houben-Weyl**, with 429 pages for arsenic, 146 for antimony, and 36 for bismuth, and has not made significant advances since those volumes were written. In contrast, the chemistry of silicon-containing compounds, which rated a respectable 423 pages in **Houben-Weyl** in 1980, has surged even further ahead. Furthermore, the emphasis in that 1980 volume was very different from that used here. Silicon can now be found attached to hydrogen, nitrogen, oxygen, one of the halogens, and especially to carbon, in thousands of papers published every year, and in many functional arrangements, each of which has its uses in organic synthesis. If my own card index is anything to go by, I had 2000 cards in 1980, and have over 12 000 now.

In this volume, there are single chapters devoted to each of the three group 15 elements, and then 42 chapters for the various kinds of silicon-containing compounds used in organic synthesis. The chapters are organized by the functionality attached to the element, and appear in an order determined by the rules used for the whole series of **Science of Synthesis**, with the space given to each determined both by the range of chemistry that needs to be described and by the importance of the functional arrangement in synthesis. Since this order of presentation does not have much logic for anyone trying to gain a general understanding of the organic chemistry of these elements, especially of the wide variety of ways in which functional groups attached to silicon can be manipulated, there is an introduction to the chemistry of all these elements, with special emphasis on organic silicon chemistry, in the Introduction.

The emphasis in all the chapters in this volume, as in other volumes in the series, is on the *synthesis* of the compounds in question. In this volume, as in several of those devoted to organometallic chemistry, there are also substantial sections in most chapters on the *uses* in synthesis of each of the different subclasses of compounds, since in most cases the arsenic-, antimony-, bismuth-, and silicon-containing compounds are rarely an end in themselves. Because this volume was planned at an early stage in the development of the series, a standard way of dealing with this requirement had not emerged when the first invitations to contribute were sent out. As a result, some chapters have the section on applications in synthesis as part of an enlarged introduction, while others, the majority, have it as a section at the end of the chapter, or sometimes at the end of a section within the chapter, sometimes labeled as one or more *Methods*, and called *Applications of [the Subclass] in Organic Synthesis*. A departure from the conventions used in the rest of the series is that, whereas TMS, TBDMS, and other abbreviations have been used elsewhere as a convenient way of representing these common silicon-containing groups, the abbreviations have only been used occasionally in this volume when the silicon atom is attached to the electronegative heteroatoms nitrogen, oxygen, sulfur, and the halogens. The group is written out in full, as Me<sub>3</sub>Si etc., to emphasize the presence of the silicon atom, when it is bound to hydrogen, a metal, and especially to carbon.

For all the space allotted to it here, the organic chemistry of silicon is still not fully covered. All the chapters commissioned arrived, but a few topics are missing by design. For example, there is no discussion of the synthesis of unfunctionalized silanes such as tetramethylsilane, on the grounds that these have few applications in synthesis, and the methods by which they are made are well known. Missing too, except sometimes for a

fleeting reference, are a number of functional arrangements such as thioacylsilanes, cyclopropylmethylsilanes, silylmethylphosphine oxides, silylmethylsulfones, and vinylous versions of the functional groups that are here, all of which, and many more, have well-developed chemistry, but for which there was no easy way to ensure their incorporation into the most relevant chapter. It is hoped that the general principles to be found in the Introduction and in all the chapters that are here, will make it easy enough to understand and to find the chemistry of these more recondite functional groups. A more difficult decision was not to have sections on compounds in which a silyl group, or a silicon-containing alkyl group, is a ligand on a transition metal. This too is a large area, but the focus in most of it is either on the transition metal or on the reactions that it catalyzes. To include all these compounds here ran the risk of squeezing out much useful organic chemistry, and there is the hope that they will be mentioned when they are used to make compounds that appear in other volumes of the series. Perhaps more seriously, there is virtually no discussion of silica, silanols, silane diols, silicones, sesquisiloxanes, other oligomeric siloxanes, silatranes, heterocyclic silicon compounds, or polymeric silanes. The excuse is that they play little part in organic synthesis, and so the choice was to have no entry at all, rather than have a token entry, merely to acknowledge that many of these compounds do have a vast chemistry. Organosilicon chemistry, defined in a broader sense than that used here, is a large subject, in which the focus of interest is often the events taking place at the silicon atom itself. In this volume the focus is on the chemistry of the carbon-based structures to which the silicon is attached, either directly or through an electronegative heteroatom. A line had to be drawn somewhere, and this seemed to be the closest to the general spirit in which **Science of Synthesis** was conceived.

I should like to thank Fiona Shortt and her team at Georg Thieme for their endless patience with my questions and deficiencies, and especially for solving the problems inherent in having placed a highly organized structure into the hands of someone as deeply unsympathetic to the rigors of nomenclature as me.

**Volume Editor**

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Ian Fleming