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Introduction: Silicon Chemistry

Silicon and carbon—are they kissing cousins? They are alike in so many ways, and yet, they are so different! This dichotomy was behind a good portion of the interest in silicon chemistry in the 20th century. Other sources of fascination with this element were the endless variety of natural silicates in minerals and clays and the remarkable properties of synthetic silicones. In recent decades, silicon has thoroughly penetrated areas as diverse as organic synthesis and microelectronics, and the 18 articles collected in this thematic issue survey many of the currently most exciting aspects of its chemistry.

Although ionic species do not dominate the mechanistic chemistry of silicon to anywhere near the degree that they dominate that of carbon, their exploration has presented both great challenges and great opportunities. Damrauer and Hankin survey the gas-phase chemistry of silicon-based anions. Bock and Solouki discuss radical cations, both in the gas phase (photoelectron spectroscopy) and in the condensed phase (electron paramagnetic resonance), while Lambert, Kania, and Zhang address a currently rather controversial issue: to what degree have closed-shell silylium cations actually been approached in condensed phase?

Gaseous silyl, silanediyl, and related radicals play an essential role in chemical vapor deposition (CVD) processes, and their direct kinetic studies are discussed by Jasinski, Becerra, and Walsh. The chemistry of silicon-based radicals in solution, which underlies some of the use of silicon radical chain reagents in organic synthesis, is reviewed by Chatgilialoglu. The utility of silicon in organic synthesis is not limited to radical chain reactions. Silicon-tethered syntheses are surveyed by Bols and Skrydstrup; regio- and stereoselective applications of silylallyl anions, by Chan and Wang; and diastereoselective reactions of allyl and allenyl silanes with carbonyl and related groups, by Masse and Panek. Palladium-catalyzed reactions, such as insertions of organic moieties into silicon–silicon bonds, cross-coupling, and hydrosilylation, are treated by Horn, and a different perspective on the activation of silicon–silicon bonds by a variety of transition metals is offered by Sharma and Pannell. The use of silicon-containing reagents in the synthesis of products occurring in animate nature is covered by Langkopf and Schinzer. The art of synthesizing the two- or three-dimensional polymeric mineral structures that are known from inanimate nature, many of which contain silicon attached to four oxygen atoms (silicates), is not nearly as well developed. However, man has done quite well with artificial polymeric products (silicones) in which only three (silsesquioxanes) or two (silicones proper) oxygen atoms are attached to each silicon atom. The great current interest in silsesquioxanes is documented by the article written by Baney, Itoh, Sakakibara, and Suzuki. A special class of these materials, bridged polysilsesquioxanes, merits a separate treatment, and this has been provided by Loy and Shea. Another practically important field of silicon chemistry in which great advances have been made lately is that of preceramic materials, and these are treated by Birot, Pillot, and Dunoguès.

Isocyclic silicon ring compounds are reviewed in two articles in this issue. Weidenbruch writes about three-membered rings, and the larger ring sizes are covered by Hengge and Janoschek.

Excited-state chemistry of organosilicon compounds is handled by Steinmetz, and last but not least, the vast area of silicon surface chemistry is surveyed by Neergaard Waltenburg and Yates. This subject is shared among chemists, physicists, material scientists, and engineers. To make it manageable, the body of the article deals with work that has been deemed most relevant from the point of view of a chemist, and a more complete list of references with article titles is provided in an appendix for completeness.

I am grateful to the authors for the immense effort that they have invested in the 18 articles and hope that they will be enjoyed by many readers for years to come.

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Editor

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