Science of Synthesis, Volume 23: Three Carbon–Heteroatom Bonds: Ketenes and Derivatives; edited by R. Danheiser; Georg Thieme Verlag: Stuttgart, **2006**, hardcover, 1054 pp, € 2200 ISBN 3-13-118741-7 (RoW)/ US$ 2600, ISBN 1-58890-200-5 (US)

This volume of Science of Synthesis, edited by Rick L. Danheiser, is organised in typical Houben–Weyl manner on the basis of a central functional group – the ketene moiety – and various substituent groups as well as the aza-, thio-, seleno-, and telluro-analogues. Thus, the material is divided up in chapters on ketene itself ('product class 1'), silylketenes, halogen-substituted ketenes, oxygen-substituted ketenes, sulfur- and selenium-substituted ketenes, nitrogen- and phosphorus-substituted ketenes, alkylideneketenes ($R_2C=C=C=O$ and C_3O_2 in a very brief 14-page chapter), cyanoketenes, acylketenes, imidoylketenes, alkynylketenes, aryl- and hetarylketenes, alkenylketenes, alkyl- and cycloalkylketenes, bisketenes, sulfur, selenium, and tellurium analogues of ketenes, and ketenimines, all written by experts in the field. This division according to substituent group hinders any overriding discussion of similarities and differences in reactivities of different types, and the mechanistic foundations of ketene chemistry are treated in a very rudimentary and fragmented, and sometimes erroneous manner; for example, the sequence of events in the [2+2] cycloaddition of bis(trifluoromethyl)ketene with ethyl vinyl ether is presented wrongly (p. 669–670).

Among the numerous uses of ketenes in synthesis, one of the most notable is the [2+2]-cycloaddition reactions leading to cyclobutanones, beta-lactones and beta-lactams (the Staudinger reaction). [2+4] cycloadditions with enones or heterodienes lead to six-membered-ring carbonyl compounds. [2+4] cycloadditions of vinylketenes, e.g. vinyl(silyl)ketenes, can be very useful for constructing six-membered rings, including phenols on reaction with acetylenes, and [4+1] cycloadditions with carbenes or carbenoids produce cyclopentenones. Acylketenes are unique in their aptitude for [4+2] cycloaddition with double and triple bond systems to produce six-membered heterocyclic carbonyl compounds.

Although there are differences in reactivity and stability (silylketenes being particularly stable, and electronegatively substituted ketenes particularly unstable), and not all classes of ketenes have been investigated in the same amount of detail, broadly, the same reactions are encountered again and again in all the chapters, especially the ubiquitous [2+2] cycloadditions. Likewise, the methods of synthesis of ketenes are described in detail for each individual class. There is no comparison of reactivities of different classes of ketenes.

The book is useful for finding out which reactions can be expected of a particular class of ketene, and thereby to answer the question whether such a ketene might be a useful synthon in one's preparative scheme. However, the methods of synthesis of the ketenes come first; their applications in synthesis come second in all the chapters. Most chapters do include a fair coverage of the uses in synthesis; an obvious reason for this is the fact that most ketenes are unstable and not normally isolable at ordinary laboratory temperatures. Therefore, they are generated in situ, and the evidence for their formation often lies exclusively in the nature of the products derived from them. Ketenimines are often, but by no means always, isolable at room temperature. Chapter 23 presents an excellent and highly detailed treatise on the syntheses and chemistry of ketenimines.

The majority of chemists looking into this volume are probably not very interested in the chemistry of ketenes or ketenimines per se. They want to see how ketenes can be used synthetically. Some unified discussion rather than the fragmented presentation could have been useful.

Curt Wentrup, The University of Queensland, Australia

SYNTHESIS 2007, No. 23, pp 3758–3758
Advanced online publication: 26.11.2007
Art ID: B12307SS
© Georg Thieme Verlag Stuttgart · New York

This document was downloaded for personal use only. Unauthorized distribution is strictly prohibited.