

Book Reviews

Stereoselective Synthesis. Houben-Weyl, *Methods of Organic Chemistry*, Volume E21d. Edited by G. Helmchen, R. W. Hoffmann, J. Mulzer, E. Schaumann. Thieme: Stuttgart, 1995, 1195 pp., hardback. DM 2770 (Subscription price DM 2493). ISBN 3-13-100114-3.

This is the fourth volume of the extensive survey on synthetic methods for stereoselective control in organic chemistry. The excellent presentation by the contributing authors continues to reinforce this reviewer's opinion that this will be the first source researchers will go to when investigating this area. This volume continues where volume E21c left off, namely a survey of pericyclic reactions. The excellent overview of [3,3], [2,3], and [1,2] sigmatropic rearrangements which opens this volume is covered in over 500 pages and almost 1200 references, some as late as 1994. All aspects of these important reactions are considered, from olefin geometry to effects of stereocenters, charge and electronic effects, heteroatoms, catalysts, and molecular architecture. Many examples and tables on the scope and limitations are presented so the reader acquires a good feeling for the immense power of these processes. Inter- and intramolecular transfers of stereocenters are clearly and extensively highlighted.

This reviewer, however, was disappointed in the misuse of the term chirality when stereogenic centers are created and destroyed within a molecule. The author described (pp. 3364-3365) a "1,3 chirality transfer process" which, in fact, is **not a transfer of chirality but a conservation of chirality with only a change in stereo (or stereogenic) centers. Chirality can only be transferred between two molecules, but not intramolecularly. Thus, an intermolecular self immolative process may exhibit transfer of chirality.** To be fair to the author, he correctly uses "conservation of chirality" in reference to self-immolative reactions on page 3629, but there should be a substitute for the erroneous term **1,3-chirality transfer** used extensively in this discussion. Why not just say "1,3-stereotransfer"?

The [3,3] rearrangements as well as the tandem [3,3]-[3,3], [2,3]-[3,3], and [1,3]-[3,3] versions cover all variations of the Claisen-Cope process and should provide the reader with much of what is required to delve deeper into this area.

The section on [2,3]-rearrangements, mainly of the Wittig type, is adequately discussed (120 references) with all the heteroatom ylides (O, N, S) and stereochemical characters brought into play. The pericyclic section of this volume ends with an abbreviated look at [1,2] alkyl shifts by concerted, dissociative, or cationic mediated (Wagner-Meerwein) routes and a discussion of electrocyclic 4π and 6π reactions.

The remaining portion of this volume is dedicated to stereochemical aspects when forming C-H bonds (ca 600 pages). All aspects of carbanions that are stereospecifically protonated and the structural properties and environments that are crucial to the successful implementation of this event are covered in detail. Extensive tables and examples are presented covering a wide variety of chiral carbanionic substrates (enolates, hetero-, aryl-, cyclopropyl-stabilized, etc.). Also presented are the chiral proton sources utilized. As usual, experimental procedures accompany these discussions.

A section on radical H-atom transfer from chiral substrates to carbon, both for an intra- and intermolecular process, provides some lesser known examples which are certain to be important in the future. References as late as 1994 are included.

The coverage of stereochemical C-H bond forming reactions by reduction of olefins and carbonyls is extensively laid out to show all the controls now available with variable ring sizes, neighboring hetero atoms, various mediators and metals. Discussions are included on a wide variety of reducing agents, chiral ligands, and enzymes. Other unsaturated systems and experiments to reproduce them are also included in this detailed survey of one of the most basic of organic transformations. The most recent efforts to reduce prochiral unsaturated linkages under a large choice of conditions and reagents is clearly and most adequately presented to the reader. In addition to the heterogeneous and homogeneous catalytic routes, there are clear and detailed descriptions on stoichiometric reducing techniques (e.g., hydroboration, modified hydrides, etc.).

The formation of a stereoselective C-H bond by a concerted [1,n]-sigmatropic hydrogen migration is a recent area of interest and is discussed with future potential. These rearrangements lead to C-H bonds with high levels of stereoselectivity and this section is an important addition to the subject.

This volume terminates with 25 pages on routes to stereochemical introduction of halogen to form C-

Hal bonds. Methods to form C–Hal bonds from other functional groups with retention or inversion are discussed as well as the more recent fluorination techniques that are important in medicinal chemistry.

In summary, the areas covered by this volume dealing with C–C, C–H, and C–Hal bonds and the stereochemical aspects accompanying them will be a welcome source of details, particularly from the most recent literature.

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Organic Reactions, Volume 46. Edited by L. Paquette. Wiley: New York, 1995, 393 pp, hardback. £ 69. ISBN 0-471-08619-3.

Volume 46 of *Organic Reactions*, published in 1994, contains three articles: "Tin(II) Enolates in the Aldol, Michael and Related Reactions" (Teruaki Mukaiyama and Shu Kobayashi) "The [2,3]-Wittig Reaction" (Takeshi Nakai and Koichi Mikami) and "Reductions with Samarium(II) Iodide" (Gary A. Molander). These reviews total 368 printed pages; however, according to the tradition of *Organic Reactions* each article contains several pages of selected Experimental Procedures and in particular a total of more than 150 pages with detailed Tabular Surveys. Thus the amount of purely textual information totals only about 130 pages. In view of the price of (for example) 148 D-Marks (about \$ 105) it seems to this reviewer that the policy of including a Tabular Survey with each article should be reconsidered in these days of computerised literature searches in all their forms.

This criticism does not in any way reflect on the authors of the articles, who have (as one has come to expect from *Organic Reactions*) done a thorough job in each case.

However, the reviews are not as up-to-date as one could have wished: for example, that by Mukaiyama and Kobayashi only covers the literature to the middle of 1991(!). While organotin compounds certainly dominate as reagents for organic synthesis, tin(II) enolates were introduced about 15 years ago by Mukaiyama and have since found increasing use in the reactions discussed in the present article. They have the great advantage over lithium enolates that they can be formed under mild rather than

strongly basic conditions. The review covers the following topics: preparative methods, simple diastereoselective reactions and asymmetric reactions; it ends with a very useful section in which tin(II) enolates are compared with other enolates such as those derived from lithium, tin(IV) and boron.

The review by Nakai and Mikami can be considered as an "update" to those which they published in 1986 and 1991. There is no literature reference later than 1992, so that this article was also somewhat out of date at publication. The authors begin by pointing out the alternatives to the [2,3] reaction pathway, i.e. [1,2] and [1,4] shifts. The section on Scope and Limitations includes a useful discussion of the Ziegler convention applied when cyclic systems are involved. Considerable emphasis is of course placed on stereochemical control. The review ends with a discussion of sigmatropic sequences which have been developed; however, because of the outdatedness of the article no mention is made of tandem processes such as the [2,3]-Wittig/anionic oxy-Cope sequence first reported by Grievies and Vines in 1994.

Molander has also written earlier on the uses of samarium(II) iodide, a reagent which has been used on a very wide scale in organic synthesis in recent years. He has covered the literature up to the end of 1992, so that his article is the least "outdated". Molander starts with a discussion of mechanism and stereochemistry and follows this with a section on scope and limitations and one in which the use of samarium(II) iodide is compared with that of other reagents. A short section on experimental conditions precedes the experimental procedures. Though this appears logical at first sight, it might in fact be more useful for the chemist who wishes to inform himself of the advantages of samarium(II) iodide if he were *first* to be provided with details on the necessary experimental conditions.

While in the opinion of this reviewer the articles under discussion are of a relatively high standard, the delays in publication caused by the present editorial policy of *Organic Reactions* are unconscionably long; a "rethink" of the editorial policy of this series is certainly overdue.

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