

Book Reviews

Advances in the Use of Synthons in Organic Chemistry, Vol. 1. Edited by A. Dondoni. JAI Press: Greenwich, 1993, XII + 227 pp., hardback £ 53. ISBN 1-55938-183-3.

This book series aims to cover the development of the "synthon" concept, the already known and the newly introduced synthetic equivalents, and their methodology. The first volume has now appeared and deals, as the editor announces in the preface, with four totally different themes.

I. Based on the above guidelines, A. Dondoni and L. Colombo report in the first chapter on the developments in the field of formyl anion and formyl cation synthons. All synthetic equivalents for the formyl anion (nucleophilic formylation agents) known up until 1986 are presented in a scheme at the beginning of the chapter with the newer ones listed at the end together with the masked formyl cations. The chapter on formyl anion equivalents is very clearly structured into sulfur-, oxygen- and nitrogen-containing reagents, whereas the acyl cation synthons are predominantly obtained from dithioacetal and orthoformic acid derivatives. Asymmetric formylation with chiral sulfur-containing formyl anions and chiral formyl cation synthons, obtained from ortho esters, is presented in detail.

II. The many aspects of the chemistry of trimethylsilyldiazomethane are presented in the second part by T. Shiori and T. Aoyama. This non-poisonous, easily produced and distillable diazo compound is often used as a substitute for the poisonous and explosive parent compound that can only be prepared in solution. The reactivities of both compounds are similar in many cases, but can also be used differently, e.g., it is very easy to prepare the corresponding lithium derivative from the former, thus it receives a naturally higher nucleophilicity than the nonmetallized counterpart. The authors have listed the use of trimethylsilyldiazomethane and its lithium derivatives as the source for a C-1 unit and a CNN-part in a very detailed way. Especially interesting are the homologization reactions and the formation of epoxides, acetylenes, other silyldiazoalkanes (and the thereof resulting acyl- and vinylsilanes) and many *N*-heterocycles. All of the reactions of the two mentioned species are clearly presented in four schemes at the end.

III. R. W. Saalfrank and R. Burak first present the synthesis and some transformations of push-pull- and (mainly) tetrasubstituted allenes, based on the formal considerations of donor-acceptor-substituted carbenes and synthetic equivalents of 1,1- and 1,3-dianions of malonic esters, malonamides and 1,3-dicarbonyl compounds generally. In the following chapters, as well as the transformations of keto enolates, the reactions of silyl enol ethers and simple enolates of 1,3-dicarbonyl compounds with malonyl dichloride and oxalyl chloride are presented. Acylation at the center C-atom and at one of the oxygen atoms of the dicarbonyl compound (1,3-dianion reactivity), with formation of 2,4-dioxopyrans or 2,3-dioxofurans, takes place preferentially (isomerization and tautomerization behavior of these compounds is described in detail). A specific reaction is the treatment of malonic esters with methyllithium,

metal(II) chlorides and oxalyl chloride in a ratio of 1:1:0.25. Via "spontaneous self-organization", the adamantoid four-nuclear metal chelate complexes are obtained, where the six bridged bidentate ligands consist of two malonic ester molecules, each interconnected by an oxalyl group. The deprotonation to a dianion proceeds gradually.

IV. In the fourth chapter, B. Danieli et al describe the asymmetrization of *meso*-dicarboxylic acid derivatives and *meso*-diols with enzymes and the application of the enantioselectively or enantiospecifically formed compounds in some detailed synthesis of natural products and biologically active compounds. Whereas the latter part is of interest to specialists or participants in a seminar on natural products, the enzymatic preparation of optically active compounds from easily obtainable *meso*-derivatives is of general interest and represents textbook knowledge. Very clear tables display which acyclic, monocyclic and bicyclic *meso*-diesters or diacyclic *meso*-diols are monosaponified with which enzyme with chemical yields and enantiomeric excesses reported. On the other hand it becomes obvious which *meso*-diol derivatives were enantioselectively monoacylated or "mono"-oxidized to the lactone. The enzymes used are introduced. Whereas in the case of the hydrolases, different enzyme systems with varying degrees of success were used (see Tables and the following discussions), only one oxidoreductase, namely HLADH (horse liver alcohol dehydrogenase), is available until now for successful asymmetric oxidation of *meso*-diols. Following the tables, detailed comparisons of the results are presented with relationships between the individual tables shown. The reader learns, e.g., that one of the two enantiomers of *cis*-1-acetyloxy-4-hydroxy-2-cyclopentene can be obtained more or less in enantiomeric pure form by monosaponification of the diacetate, while the other enantiomer is prepared by monoacetylation of the diol.

In spite of the heterogeneity of the volume, it was a great pleasure for the reviewer to read Volume 1 of "Advances in the Use of Synthons in Organic Chemistry", as each of the four chapters contains vast amounts of preparatively interesting material (for research and teaching). Presentation of such a diverse area of research is probably only possible by using such an abstract term as synthon. This prerequisite given, it's less disturbing when the synthon concept is left out completely in some passages (for being superfluous) and exaggerated in others, more disturbing is the mix up of the terms synthon and synthetic equivalent even though the editor hints in the preface at the extension of Corey's abstract term of synthon. While Dondoni himself uses the terms only in their original sense and Saalfrank also only speaks of 1,1- or 1,3-dianion equivalents, trimethylsilyldiazomethane and the asymmetric *meso*-compounds are termed in the title as synthons and not as synthetic equivalents for any kind of synthon.

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