



Molecular Crystals and Liquid Crystals

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BOOK REVIEW

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BOOK REVIEW

Solvent-free Organic Synthesis by Koichi Tanaka, Wiley-VCH. Weinheim, 2003; ISBN 3-527-30612-9; ix + 433 pages; \$135.00.

From the author's preface, this book is about a "green chemistry" approach to organic synthesis. "The best solvent is no solvent" is a fundamental tenet of green chemistry. The book is a compilation of 537 synthetic procedures presented in 14 chapters. The chapters are titled Reduction, Oxidation, Carbon-Carbon Bond Formation, Carbon-Nitrogen Bond Formation, Carbon-Oxygen Bond Formation, Carbon-Sulfur Bond Formation, Carbon-Phosphorus Bond Formation, Carbon-Halogen Bond Formation, Nitrogen-Nitrogen Bond Formation, Rearrangement, Elimination, Hydrolysis, Protection, and Deprotection. There is also a two page foreword by Gerd Kaupp, a key contributor to the topic of solventless reactions.

The book is not a comprehensive summary of the subject. Rather it is primarily a presentation of examples from 1980 to the present from a list of 45 journals. In a number of places throughout the text there are references to earlier work. The examples chosen involve numerous procedures using microwave irradiation and ultraviolet irradiation. These two statements invite the remark that examples using ionizing radiation are largely ignored. Coverage of the journal *Radiation Chemistry and Physics* would have provided additional examples in this area. Solventless reactions were well known before 1980. Indeed, solid-state polymerizations and cinnamic acid photodimerizations go back many years.

The strength of the book comes from the numerous procedures that illustrate that most traditional and new reactions of interest in organic chemistry can be carried out without use of solvent. In fact, even Grignard reactions can be performed in this manner! The information may well motivate others to attempt solventless processes. Only time will tell if this approach to green chemistry will have lasting value. There is very little mechanistic discussion as to how the solventless processes work. What transpires in the course of a gas-solid reaction that allows a product to form in high yield?

While green chemistry is a topic of considerable current interest, to focus a monograph on post-1980 solvent-free reactions almost exclusively on this subject is short-sighted. The cinnamic acid photodimerization has

long been the method-of-choice for many cyclobutane derivatives. The text gives numerous solid-state reactions that are accompanied by crystallographic data in the original paper, and the original paper discusses the reaction with reference to the structural data, as is the usual practice since the 1964 publication of the topochemical principle by the late G.M.J. Schmidt and coworkers. However, the present text only rarely makes use of such data.

The author is also short-sighted in giving only discussions of the procedures cited without material that explains various principles involved in solvent-free synthesis. Readers, especially students, would benefit from a discussion of the use of microwave irradiation, ultraviolet light sources, and solid supports.

The book is not without mistakes. On p. 304, the structure given is that of 2,3,5,6-tetracyanobenzoquinone, not DDQ. On p. 403, the second reaction with alumina does not depict a desilylation, the subject of the paper.

In summary, the authors has produced a useful text on solvent-free reactions, especially in relation to green chemistry, but with additional effort a far more valuable monograph could have been obtained.

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