

Book Review

Organic Synthesis in Water. By P. A. Grieco. Thomson Science, 1997; £79. ISBN 075140101.

Although water is almost the exclusive solvent used in biochemical processes, the synthetic chemist has only recently rediscovered chemistry in aqueous media. This book, the second published in the last two years covering this field, confirms the increasing interest in this non conventional solvent. The international panel of authors makes use of their own experience to review, in eight chapters, seven major areas of synthetic chemistry: Diels-Alder reactions, Claisen rearrangements, transition metal catalysis, oxidation and reduction and organometallic chemistry.

Chapters 1 and 2 cover Diels-Alder reactions. The authors highlight the recent development of the use of water in (hetero)cycloadditions and the related cycloreversion processes. Particular emphasis is given to the causes of rate enhancements and diastereofacial selectivity in aqueous media. The attention of the reader is also drawn to the chemistry of iminium ions, oxo-Diels-Alder reactions and the use of glycoorganic substrates, when water is used as solvent. The synthetic utility of these cycloadditions is illustrated with total syntheses including those of terpenes, steroids and alkaloids.

The third chapter begins with a brief historical review and definition of the Claisen rearrangement. In this reaction, evidence for rate accelerations in aqueous media are shown, even if the exact role of water is still controversial. Examples of successes and failures in the use of water are collected in this section. An important discussion about solvent effects in Claisen rearrangement as well as a multiparameter correlation-factor analysis is also included.

Chapter four deals with carbonyl additions, including Barbier-type reactions, 1,4-conjugate addition, cross-aldol reactions and organometallic pinacol couplings. In the first part, tin, zinc, indium or bismuth catalysed allylation, allenylation and propargylation of numerous carbonyl compounds including sugars are presented. In most of these examples water is used as a cosolvent. Michael additions, cross-aldol, Reformatsky as well as pinacol coupling reactions are depicted in some examples which also show dramatic effects when water is used instead of organic solvents. The second part of this chapter points out the possible uses of metallic catalyst and in some cases ultrasonic irradiation in aqueous media.

In chapter five, the authors outline the dual role played by water as reagent and solvent. Even if the use of water, "looks like a shocking revelation to the majority of the or-

ganometallic community", in some cases, there is evidence for the major role it plays in transition metal catalysis.

The authors first describe the preparation of different water soluble sulfonates, carboxylates or ammonium phosphine ligands. Secondly, they extensively review palladium catalysed cross-coupling reactions in aqueous media such as the Suzuki, Stille or Heck reactions with various examples including well described mechanisms. Furthermore, the use of rhodium and ruthenium based catalysts is shown in hydroformylation and hydrogenation reactions, which use water as solvent.

Chapter six deals with oxidations and reductions. The authors illustrate, using recent examples, two of the oldest reactions known in aqueous media. The first part presents preparation and ring opening reactions of epoxides. The exact conditions for each reaction are strictly reported. The oxidations of other groups such as carbonyl, nitrile, amine and sulfide are also presented and interesting examples of regioselectivities obtained using strict pH control are described. In the second part, selective reductions of different functional groups in water or aqueous media, including reductive coupling and the use of inclusion complexes, are shown.

In my opinion chapters 4 and 7 should have been collected together, as they both deal with carbonyl chemistry. The authors present six different types of reactions, illustrated with some examples. The possible use of additives such as surfactants and hydrotropes is emphasised.

The last part of this book concerns water soluble rare earth Lewis acids. One advantage highlighted is the possible recovery and reuse of the catalyst. Different reactions such as aldol, allylation, Mannich or (hetero)Diels-Alder are reviewed in aqueous or organic media. Furthermore, the properties of several lanthanide triflates are also compared.

In summary, as the book does not attempt to cover all aspects of chemistry in aqueous media but only selected major topics, it is pleasant to read and the important chemistry is thoroughly illustrated. Theoretical and mechanistic considerations are a welcome complement to the synthetic details.

In this volume P. A. Grieco and his colleagues promote the unique properties of water consulting some 750 references. This book convinces the reader of the progress of chemistry in water over the last decade, the advantages and the broad applications of this non conventional solvent.

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