



Aqueous Microwave Assisted Chemistry

Nowadays, there is a tremendous pressure to make chemistry “green” and “sustainable”. This implies that the majority of (industrial) processes must be rethought from scratch to avoid further pollution of the environment.

The use of volatile and highly flammable solvents is the foremost source of ecological pollution. Water appears to be an excellent alternative. However, most organic reagents are insoluble in water. The application of microwave irradiation can tackle this problem efficiently, as water has a good ability to absorb microwaves, allowing rapid heating of reaction mixtures. Moreover, water at higher temperatures behaves as a pseudo-organic solvent, as the dielectric constant is substantially reduced. It appears that combining microwave irradiation with the use of water as solvent can offer an extraordinary synergistic effect.

This book gives a succinct literature overview of the various processes that have been developed using microwave irradiation in aqueous media. The editors appropriately divided the book into seven chapters, each written by different experts in the field, covering most of the microwave-assisted aqueous reactions in depth and in a really multi-disciplinary way. Interestingly, each chapter contains some representative experimental procedures, allowing the reader to quickly replicate some of the experiments and thereby acquire valuable hands-on experience.

After a general introduction by the editors in Chapter 1, the second chapter is devoted to metal-catalyzed reactions (excluding Pd). The example of the hydration of alkynes nicely illustrates that water becomes more acidic as the temperature increases to near-critical conditions (200–300 °C), so that it is able to promote reactions without the aid of an acid catalyst. Regarding cyclization reactions, probably the most important contribution of microwave irradiation has been in the field of “click reactions”, although in nearly all cases a co-solvent in addition to water was needed, to overcome solubility problems and for other reasons.

Chapter 3 focuses on palladium-catalyzed coupling reactions, and is mainly devoted to the Suzuki reaction. For this process, remarkable progress on the activation of the relatively inert aryl bromides and chlorides has been reported. Also worth mentioning is the synergistic effect of the combination of ultrasound with microwave irradiation, resulting in a significantly higher yield, although only three examples have been demonstrated. Of particular interest are the examples of the coupling

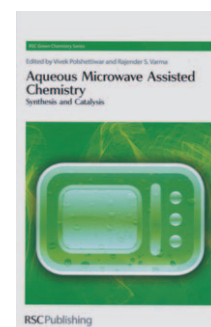
of electron-rich aryl bromides with the electron-poor and sterically hindered compound (2-formyl-phenyl)boronic acid, where the proto-deboronation of the latter was avoided by using an aqueous microwave-assisted method. Finally, the chapter describes some interesting carbonylation reactions in which solid $[\text{Mo}(\text{CO})_6]$ is employed instead of the toxic gaseous reagent carbon monoxide.

Chapter 4 presents a potpourri of aqueous microwave-assisted heterocyclic chemistry, embracing a wide variety of heterocyclic compounds of nitrogen (predominating), oxygen, and sulfur. Although the chosen manner of presentation is understandable in view of the diversity of heterocyclic frameworks, a bit more subdivision in this chapter would have enhanced the readability. Some particularly interesting examples highlight a further advantage of using water as the sole solvent, as in some cases, on completion of the reaction, a phase separation of the desired compound from the aqueous medium occurred, facilitating the isolation of the crude product.

Then a rather short Chapter 5 follows, reviewing how microwave irradiation in aqueous solutions affects enzyme activity and can be used to improve it. It is questionable whether it is useful to cite so many publications from the 1970s and 1980s, as obviously all those experiments were performed in domestic ovens, hampering the possibility to perform experiments under fully controlled conditions. The authors also describe applications of microwave irradiation to enzymatic protein digestion and to reactions performed in aqueous solutions of organic solvents, reviewing the more recent literature. Although interesting, the part about microwave-assisted enzymatic reactions in ionic liquids does not really fit well into this book.

As polymer synthesis under microwave irradiation conditions is a relatively new emerging field, research on the application of aqueous media in this context is still at an early stage. Chapter 6 surveys recent developments in this field. Applications to free-radical and step-growth polymerization are reviewed in detail. An interesting example concerns the synthesis of monodisperse polystyrene microspheres by dispersion polymerization, where substantially smaller and more stable particles were obtained under microwave irradiation compared to conventional heating. Another interesting part highlights the post-modification of polymers by Suzuki coupling and click chemistry, or by other methods.

Lastly, Chapter 7 deals with the synthesis of nanomaterials. After a very instructive introduction for the novice in this field, the chapter discusses the applications of aqueous microwave-assisted chemistry to the synthesis of metal, metal oxide, and other nanoparticles. The advantages include rapid heating, faster kinetics, phase purity, higher



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yields, and better reliability and reproducibility. The use of nanoparticles as catalysts is also discussed. This chapter is nicely illustrated with several photographs and instructive schemes.

Nearly all the examples cited in this book are commented on in depth, giving sufficient details so that the reader gains a good impression about the research that has been performed. This book is an excellent source of information on aqueous microwave-assisted chemistry, both for the novice and for the more experienced researcher. Although in several of the procedures that are cited a domestic microwave oven was used, with the consequent limitations, these examples are still instructive and

useful as starting points for further optimization. The table of contents and the excellent index make it easy to find information about individual topics.

I have read this book with pleasure and I recommend it to all scientists working or getting started in this fascinating field.

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