

Preface

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“The two most common elements in the universe are Hydrogen and stupidity”
Harlan Ellison (Science Fiction writer) [1].

This book is concerned with one of the most common elements in the universe: Hydrogen. The organic chemistry of the hydrogen transfer process dates back to the mid-nineteenth and the early twentieth centuries, and it arises from the investigations of core organic scientists, such as Cannizzaro (1853), Tishchenko (1908), Guerbet (1909), Meerwein (1925), Ponndorf (1926), Verley (1925), and Oppenauer (1937), amongst others. Due to its long history, it could be assumed that no further development can be done in this field. However, the hydrogen transfer process is a very active research field, open currently to new discoveries, and constantly growing. The processes, being sustainable and both environmentally benign and non-hazardous, compared to other alternative processes, foreshadow a promising future. The authors of the different chapters are active researchers in the field, allowing the reader to be introduced easily and quickly into a specific area. Similarly, their experience teaches us about mature areas as well as those areas that are in their early development or in aspects that have not yet been resolved, and unapproachable issues.

In this volume, we aim to give insights for different aspects of the hydrogen transfer processes. Each chapter provides a short overview of the context and subsequent developments of their respective transformations.

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Prof. Požgan and Štefane describe the metal-catalyzed transfer hydrogenation of ketones, introducing the classic, while also assessing the newest ones, capable of performing this enantioselective reduction with high efficiency. Meanwhile, Prof. Wills did the corresponding transfer of hydrogen to imines, pointing up the industrial synthesis of several drugs. Prof. Herrera ends this initial series devoted to different aspects of the Meerwein-Ponndorf-Verley reaction, with a chapter dedicated to organocatalytic versions of this process. Although this last approach has not yet achieved the versatility and wide scope reached by metal-catalyzed versions, they are complementary and in some cases, at the industrial level, can become competitive.

Prof. Knowles et al. describe the unconventional redox process in which both proton and electron are exchanged, usually in a concerted elementary step. The proton-coupled electron transfer is presented not as central biological catalytic processes but as the organic transformation possibilities. The hydrogen transfer processes are not only used in functional redox processes. Prof. Xiao et al. present the [1,n]-hydrogen transfer/cyclization as a powerful tool in the construction of five- and six-membered hetero- and carbocycles, in which the formation of a carbon-carbon bond is fundamental. The role of the heteroatom, as well as the minimum requirements for the success of the processes is highlighted throughout.

The last chapters of this book deals with the *hydrogen autotransfer* processes, also called borrowing hydrogen or a self-supplying system for active hydrogen. In these reactions, the catalyst must transform one starting material, usually an alcohol or amine, into the real electrophilic reagent by abstraction of hydrogen (*mono-activation*). Prof. Ojima describes the utilization of this strategy for the alkylation of carbon-nucleophiles, such as ketones, esters, amides, nitriles, alcohols, and heterocycles. Meanwhile, Prof. Xu et al. present a similar process involving nitrogen-nucleophiles, such as ammonia, amines, and amides. Lastly, Prof. Krische et al. assess a new version of the hydrogen autotransfer in which not only the abstraction of hydrogen takes place but also the in situ formed hydride catalyst must react with another starting material to form the real nucleophilic reagent (*di-activation*), paying special attention to ruthenium catalysts.

Just taking a quick look at the different chapters, one can realize which areas of each field are mature and which can evolve immediately. Although it is very difficult to venture a general trend for the whole area, we could emphasize that there is not a truly enantioselective version for the mono-activated hydrogen autotransfer reaction. The use of first-row transition metals is almost an unexplored “Blue Ocean”, in all aspects. Furthermore, the possible impact of green neoteric solvents, including deep eutectic mixtures, supercritical fluids, and bio-based solvents, on the hydrogen transfer process is definitely unknown.

Finally, as editors, we would like to thank all the contributors, as well as the reviewers, for their participation in this project and for their patience throughout the entire process.

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Reference

1. Balachandran M (2009) Quotations for all occasions. Emerald Publisher, Egmore, p 115