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Abstract

This introductory chapter underlines the essence of the subject. It offers an overview of the topics covered in the present book.

Keywords

electrochemistry; electrocatalysis; organic synthesis; green and sustainable chemistry; how to read

1

Electrochemical Strategies in Organic Synthesis: An Introduction

1.1 Introduction

"*Organic synthesis*" refers to the art and science of constructing complex organic molecules from simpler ones through systematically designed synthetic strategies by means of controlled chemical reactions, with objectives that may include operational simplicity, efficiency, yield maximization, cost-effectiveness, eco-friendliness, and sustainability. These well-developed synthetic strategies/protocols have been playing pivotal roles in the chemical industry for hundreds of years, producing a plethora of organic compounds with diverse structural architectures, with immense applications as fine chemicals, medicinal and pharmaceutical agents, dyes and pigments, polymeric substances, food additives, cosmetics, petrochemicals, agrochemicals, and many more.[1–21] Over the past two centuries, synthetic organic chemistry has seen tremendous growth across the board, and functionalized synthetic organic molecules, in a true sense, are integral to advancements in materials science, pharmaceuticals, energy, and environmental sustainability, driving innovation and addressing societal challenges. Their continued study and application promise a more sustainable and technologically advanced future.

However, with the advent of the *green chemistry concept* proposed by Anastas and Warner,[22] a synthetic organic chemist is now concerned with a "*complete rethinking*" or a "*new look*" in designing a particular synthetic strategy that not only considers the desired product in optimum yield but also gives pertinent emphasis on the greenness and sustainability of the process. Practicing green chemistry by the chemical fraternity thus lies at the forefront of chemical research. The fundamental challenge for green chemistry is to develop practical, sustainable processes for chemical enterprises that minimize environmental impacts, are operationally simple, and are cost-effective.[23–41]

For green chemistry practitioners, the tenets of green chemistry principles[22] serve as guidelines for assessing the greenness and sustainability of developed processes. All these guidelines help a beginner to orient in designing a process that can be capable of meeting eco-friendliness as well as the practicality of a chemical transformation, keeping in view several aspects, such as the toxicity of reacting substances, solvents, catalysts, energy uses, pollution prevention, various green metrics, and, most importantly, the consideration of renewable vs nonrenewable feedstocks. This remarkable field has drawn the attention of chemists from all domains, who have been taking up these challenges for almost the past three decades, as a result of which "*green chemistry*" has made considerable advances.[42–77] Among various techniques and strategies used in practicing "*green and sustainable chemistry*," notable advancements are the development of solvent-free synthesis, organic reactions under aqueous conditions, room-temperature organic synthesis, development of recoverable catalytic systems and also catalyst-free synthesis, and application of energy-efficient green tools involving the use of ultrasonication, microwave irradiation, ball-milling, visible lights, and electrosynthetic techniques, which address the most challenging concern relating to energy consumption in chemical manufacturing. The present book aims to offer a comprehensive overview of recent cutting-edge advances in the development of organic synthetic protocols using electrochemistry as a green tool.

1.2 Electrochemistry-Driven Organic Synthesis – A Step Forward

As mentioned, the primary objective of synthetic organic chemists has been the development of environmentally friendly, practical, and cost-effective long-term technologies for accessing application-oriented organic compounds. As part of these endeavors, electro-organic synthesis has emerged in recent years as a powerful tool in modern synthetic organic chemistry for accessing diverse organic scaffolds, owing to its inherent green, sustainable chemical properties. Its use often hinges on its ability to achieve unique bond constructions that are not possible with established traditional protocols, as well as on the exploration of new chemistries. The technique has been shown to be a highly effective and versatile platform for performing a wide range of nonclassical bond disconnections by generating radical intermediates under mild reaction conditions. As a result, a resurgence of interest in organic electrochemistry has led to a boom in new synthetic methodologies and their mechanistic understandings.

In the electrochemical technique, electrons serve as a "*traceless*" reagent, reducing the risk and expense of synthetic protocols and waste production – electrochemistry thus serves as a benign, environmentally friendly, and atom-efficient means of achieving functional complexity. It uses electricity to catalyze redox reactions. Applying an external potential allows reactions to be driven away from thermodynamic equilibrium, thereby opening reaction pathways and providing access to chemical intermediates that would be challenging to use under other conditions. Despite the potential need for stoichiometric electrolyte levels, this approach can still offer significant selectivity benefits over conventional chemical techniques. Moderate reaction conditions in electrochemical strategies, hence, open the door to scalability, supporting the commercial synthesis of bulk compounds. Technological developments, such as in-line analytical equipment and flow and batch reactors, have also significantly contributed to the uptake of electrosynthesis. However, understanding the tools and techniques, such as the impacts of power supply, the nature and composition of electrodes and their designs, and the solvents and electrolytes used to implement electrochemical transformations, is crucial for maximizing their benefits in academic and industrial applications. The field of electro-organic conversions surely presents a broad outlook for future developments, as more and more organic chemists become aware of its advantages.[78–109]

1.3 Overview of the Book

The book presents recent cutting-edge investigations into electrochemical strategies in organic synthesis in a single comprehensive volume. It provides information on rigorously selected reaction schemes and on new reactions and methods in electrocatalysis. It lists more than 120 important synthetic strategies/methodologies, with particular emphasis on useful reactions for organic synthesis under mild reaction conditions reported in recent times, involving carbon–carbon and carbon–heteroatom bond-forming reactions, resulting in a broad spectrum of chemical compounds, providing an outstanding source of information on industrial applications. There are six technical chapters (Chapters 2–6) in this book, each covering contemporary developments in the electrochemical synthetic strategies in different compound classes. ***Chapter 2***: Electrochemistry-driven synthesis of functionalized heterocyclic compounds; ***Chapter 3***: Electrochemistry-driven synthesis of functionalized aliphatic and aromatic compounds; ***Chapter 4***: Electrochemistry-driven synthesis of functionalized organofluorine compounds; ***Chapter 5***: Electrochemistry-driven synthesis of functionalized organophosphorus compounds, and ***Chapter 6***: Electrochemistry-driven synthesis of functionalized organochalcogenated compounds.

1.4 How to Read

As mentioned earlier, this distinct volume incorporates more than 120 sincerely screened electrochemistry-driven organic synthetic protocols for the generation of carbon–carbon and carbon–heteroatom bonds, resulting in a broad spectrum of chemical compounds – functionalized heterocycles, aliphatics and aromatics, organofluorines, organophosphorus, and organochalcogenides. The synthetic strategies for these diverse organic compounds are described in six dedicated chapters (Chapters 2–6). Clearly structured for easy access to the information, each selected reaction is discussed very compactly, pointwise, covering reaction type, reaction conditions, reaction strategy, keywords, general reaction scheme, representative examples, mechanistic aspects, critical views, and literature. Literature references are continuously numbered and presented at the end of each chapter. Reaction scheme, plausible mechanism, and illustrative examples relating to a particular reaction are given under that reaction and are self-explanatory. Each electrochemical procedure is critically analyzed in the subsection "*Critical*

Views," with particular emphasis on its greenness, key benefits, and advantages over previously reported methods.

1.5 Concluding Remarks

Ongoing developments in greener, more efficient methodologies for synthesizing organic compounds of interest are vital to making chemical processes more sustainable, operationally simple, and cost-effective. Among various techniques and strategies developed in this direction, the application of electrochemistry as a safe, mild, and environmentally friendly tool that uses low-energy electricity to catalyze redox reactions has emerged as a unique and promising avenue in organic synthesis in recent years. The application of electrochemistry as a green tool bears the potential not only to address the most challenging concern relating to energy consumption in chemical manufacturing but also to implement a plethora of organic transformations that could not be feasible under traditional processes, along with the exploration of new chemistries. The book successfully integrates cutting-edge advances in electrochemistry-driven reaction design for useful organic transformations, with a comprehensive range of examples and chemistries that illustrate the significant strides made in this research area over the past few years. This research area is growing progressively; researchers will undoubtedly disclose further developments in more innovative, cost-efficient, and sustainable strategies in the coming days. Under this purview, the present book is an endeavor to boost ongoing green chemistry research and to motivate young minds to this truly dynamic field of chemistry!

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