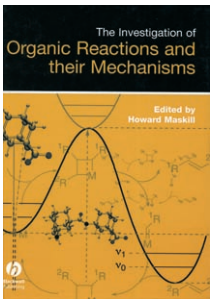
The Investigation of Organic Reactions and their Mechanisms



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The spectacular progress of organic and organometallic syntheses in recent decades would not have been possible without the understanding of chemical reactivity that was developed by the mechanistic investigations in the middle of the 20th century. Today we regard it as a matter of course that modern textbooks generally adopt a mechanistic approach to organic chemistry. In spite of that, the determination of reaction mechanisms plays only a subordinate role in the curricula of many universities, and some graduates feel lost when trying to elucidate the mechanism of a reaction. This book aims to provide a remedy for that, as the editor, Howard Maskill, explains in the preface (Chapter 1): "*This book is to help chemists who do not have a strong background in physical/mechanistic organic chemistry but who want to characterize an organic chemical reaction and investigate its mechanism. They may be in the chemical or pharmaceutical manufacturing industry and need reaction data to help identify reaction conditions for an improved yield or a shorter reaction time, or to devise safer reaction conditions. Another potential user could be a synthetic chemist who wants to investigate the mechanism of a newly discovered reaction in order, for example, to optimize reaction conditions and avoid troublesome side reactions.*"

Maskill, who is the author of the highly esteemed monograph *The Physical Basis of Organic Chemistry* (1985), has succeeded in assembling a team of very competent authors for the present book, and in the chapters that I feel competent to evaluate I found no significant mistakes. The text includes numerous interesting and timely references, and reading this book stimulated me to offer a class on the determination of reaction mechanisms, which I intend to base on this text.

However, I find the structure of this 12-chapter book incomprehensible. The main text begins with three chapters that can be summarized as "methods for determining reaction mechanisms". These are: T. W. Bentley's Chapter 2 on "Investigation of Reaction Mechanisms by Product Studies" and Chapters 3, "Experimental Methods for Investigating Kinetics", and 4, "The Relationship Between Mechanism and Rate Law", which are both co-authored by H. Maskill, M. Canle, and J. A. Santaballa. These chapters are intimately related to C. I. F. Watt's contribution, "The Detection and Characterization of Intermediates in Chemical Reactions", which follows much later (Chapter 9). All these chapters are interesting and worthwhile reading for somebody who is already familiar with the topic and does not get confused when the lines of arguments are interrupted with references to other chapters. However, for the readers mentioned in the preface it would have been helpful if a coordinating editor had structured these four chapters in such a way as to provide a manual for the systematic determination of reaction mechanisms. In that way, the numerous instances of overlapping between these chapters could have been avoided.

Whereas Chapters 2, 3, 4, and 9 teach about the general tools, other chapters deal with more special aspects. In Chapter 5, "Reaction Kinetics in Multiphase Systems", J. H. Atherton describes the problems encountered in multiphase systems, which are of particular importance in industrial processes. In the following chapter, "Electrochemical Methods of Investigating Reaction Mechanisms", O. Hammerich meets the needs of readers who are not familiar with electrochemical methods and gives many practical hints. Chapter 7, by P. R. Schreiner, on "Computational Chemistry and the Elucidation of Mechanism", provides a concise overview of the capabilities of the most commonly used theoretical methods, and discusses the rotational barriers of ethane and the structure of the norbornyl cation. In the following chapter, "Calorimetric Methods of Investigating Organic Reactions", U. Fischer and K. Hungerbühler describe the fundamentals of reaction calorimetry and its applications to the determination of reaction kinetics, as well as IR–ATR spectroscopy and its coupling with calorimetry. It is hard to understand why computational chemistry was squeezed in between electrochemistry and calorimetry.

Chapters 10–12 demonstrate how the tools introduced in Chapters 2–4 and 9 can be used to investigate the mechanisms of certain types of reactions and to identify their intermediates. F. Aldabbagh, W. R. Bowman, and J. M. D. Storey report on the "Investigation of Reactions Involving Radical Intermediates" (Chapter 10). In Chapter 11, "Investigation of Catalysis by Acids, Bases, Other Small Molecules and Enzymes", A. Williams successfully bridges the gap between classical organic chemistry and biology. In the final chapter, "Catalysis by Organometallic Compounds", G. C. Lloyd-Jones discusses recent mechanistic investigations of rhodium-catalyzed additions of organoboronic acids to enones, palladium-catalyzed cycloisomerizations of dienes, and olefin metatheses; he comments that many "mechanisms" of organometallic chemistry should be considered as "working models" rather than established knowledge.

Conclusion: Even though it is often difficult to find the thread through this book, the excellent expertise of the individual contributions, as well as the treatment of recent methodological developments and of topics of current interest, make it a valuable contribution to contemporary chemical literature.

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