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REVISED EDITION

Reaction Mechanism in Organic Chemistry

S. M. Mukherji
S. P. Singh

REVISED BY

S.P. SINGH
OM PRAKASH

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This book is dedicated
to
Our grand children

Poorva, Uday, Adi, and Veer
—S.P. Singh

Khushi, Avi, Aadya, and Aarna
—Om Prakash

Contents

Preface to the Revised Edition

Understanding the mechanisms of reactions constitutes the core of the study of organic chemistry. We made an effort to meet this objective by writing a book in 1976 which was the first book on this topic published from India. It is gratifying to know that the book was used by hundreds of thousands students and researchers in the last four decades hopefully to their benefit.

However, it was felt that the book written in 1970s on such a vibrant and dynamic topic needs to be thoroughly reworked, updated and enlarged to reflect new facts and advances in different areas. This became particularly relevant when the UGC Committee on Curriculum Development in Chemistry-with one of the authors (SPS) being the Convener- recommended a thorough revision of this topic in particular. Hence we have undertaken the exercise of the complete rewriting of the book with lot of addition and deletion taking into account the new developments. Some of the key features of the revised edition are:

We have incorporated two chapters on stereochemistry. While the first chapter deals with the basic concepts of chirality, the second chapter describes stereoheterotopic ligands and faces, stereoselective and stereospecific reactions, asymmetric synthesis, effect of conformation on reactivity and finally conformational analysis of monosaccharides. The objective is to understand reaction mechanisms with particular focus on spatial relationship among the reacting atoms which is one of the important factors in determining how fast a reaction goes and what product it yields.

As the concept of the carbocation has served to relate reactions of many different kinds, chemistry of this important reactive intermediate has received special attention. Neighbouring group participation of a lone pair, a double bond and a phenyl group along with a discussion of sigma bond participation and nonclassical cations have been introduced. Topics such as photochemistry of aromatic compounds, cheletropic reactions, hydrogenation of unsaturated systems, ambident nucleophiles, Hammette and Taft equations are incorporated in appropriate chapters. A large number of energy profile diagrams have been sketched in many chapters to illustrate different processes, and many synthetically important reactions and rearrangements have been added in chapters dealing with aromatic electrophilic and nucleophilic substitutions. Units for expressing energies are given in IUPAC mandated joules as well as in calories which are still being used by many organic chemists.

We feel confident that this reorganization and revision along with a large number of problems will assist the students to develop a knowledge and appreciation of structure and mechanisms of reactions in organic chemistry. Besides helping a large number of post-graduate students (Chemistry and pharmacy), this revised edition will cater to the needs of those students who are preparing for NET and other competitive examinations.

We will appreciate all those who read and use this revised edition to contact us directly with their comments, and point out errors for rectification in the next reprint. Our email addresses are: shivpsingh@rediffmail.com; dromprakash50@rediffmail.com

We thank Ms. Loveena Arora, who had worked as Technical Assistant in the project, for her assistance in the preparation of the manuscript. Without her support, this work would not have been completed in time. We thank our former students, Prof. Devinder Kumar (GJU, Hisar) and Dr. Vinod Kumar (MMU, Mullana) for their help in revising the chapter on Pericyclic Reactions. We take this opportunity to acknowledge the contributions of all our former students and colleagues who had helped us in the development of this text. We especially thank Prof. Ranjana Aggarwal, Prof. Pawan K. Sharma, Prof. Neera Raghav and Dr. Rashmi Pundeer of our Department and Dr. Ravi Kumar of D. S. College, Karnal for their help at one stage or the other.

Finally, the authors gratefully acknowledge that the book was revised under a project catalyzed and supported by the Department of Science and Technology, Govt. of India under its Utilization of Scientific Expertise of Retired Scientists (USERS) Scheme.

Kurukshetra,
June, 2014

S.P. SINGH
OM PRAKASH

Preface to the Previous Edition

In the course of teaching post-graduate classes, we have constantly been feeling the need of a concise volume that gives outlines of most of the important organic reactions, together with a critical examination of the evidence leading to the accepted mechanisms. The students have often expressed their difficulty caused by the absence of such a book. Our present effort is to meet this long-felt need and is designed primarily for the students who had a basic course in organic chemistry at the undergraduate level. It is an attempt to bridge the gap between an elementary treatment and the more masterly treatises on the subject.

The book opens with a chapter on the Chemical Bond which apart from describing the different types of chemical bonds, highlights the importance of the concepts of the electronegativity and effect of the state of hybridization of the bonding orbitals on the physical properties of the molecules. In addition to Hückel's treatment of aromaticity, a new outlook for determining aromaticity and resonance energy has been introduced based on the Perturbational Molecular Orbital (PMO) method developed by M. J. S. Dewar. This chapter coupled with the second and third chapters- which deal with the reaction intermediates, reagents, energies, stereochemical terms and methods for determining reaction mechanisms- form the background materials for the subsequent chapters.

In dealing with the conventional topics such as substitution reactions, addition and elimination reactions, reactions of carbonyl group, free radicals, etc., we have tried to project current developments, wherever possible. The purpose of giving specific examples in these chapters is to illustrate principles rather than giving a review-type coverage. We had to be selective rather than comprehensive because of our anxiety to limit the book to a reasonable size and price.

The last two chapters, namely, Organic Photochemistry and Pericyclic Reactions, have been included due to our conviction that these topics should form an integral part of the course on reaction mechanism in recognition of their growing importance. These topics should also be helpful to those research students whose training in these fascinating areas of organic chemistry was not up to the current standard. In addition to Woodward Hoffmann's orbital correlation method based on the principles of molecular orbital symmetry, and the frontier orbital method, we have discussed in reasonable detail the PMO method for the analysis of pericyclic reactions. This latter method should be particularly welcome to the readers as it offers simple mnemonics of selection rules for prediction of the stereochemical courses of this class of reactions.

An effort to guide the readers to relevant review articles and books has also been made for further consultation. It is hoped that this book would be useful and effective in helping the students of chemistry develop an insight into the mechanistic aspects of organic chemistry as

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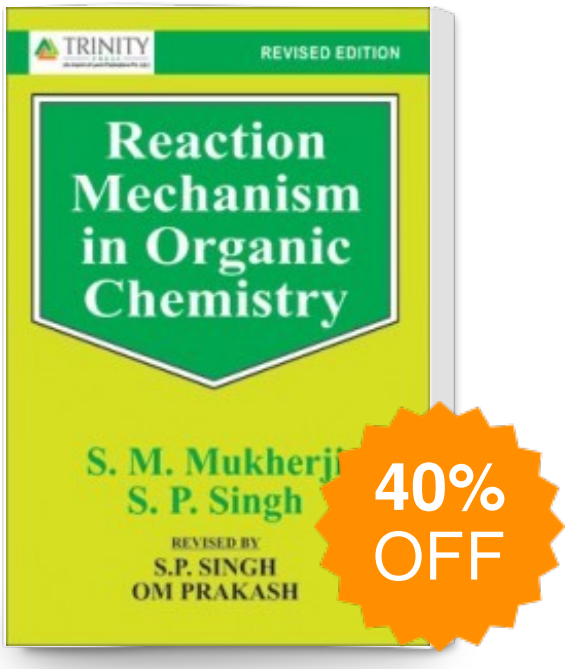

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