Preface

The aim of this book is to offer a decent understanding of the principles of steric and stereoelectronic effects in organic chemistry and their consequences on product selectivity and reaction rates. This book differs from most other books of the same level. In this book, strong emphasis is placed on logical evolution of the subject in a streamlined manner to aid structured comprehension of the intricacies. This book is intended for the honors undergraduate and graduate students, and the teachers.

The discussion is spread over seven chapters. Chapter 1 lays the stress on the important aspects of steric and stereoelectronic effects and their control on the conformational profile and reactivity features of the molecules. Chapter 2 describes the geometrical requirements for reactions at saturated and unsaturated carbons, and the resultant stereochemical features. Application of the said geometrical requirements to intramolecular instances results in remarkable control on diastereoselectivity. Chapter 3 deals with the facial selectivity of nucleophilic additions to acyclic and cyclic carbonyl compounds, and it explains how the steric and stereoelectronic effects control the same through elaborate discussions. The selectivity profile is explained using models such as Cram’s model, Anh–Felkin modification of Cram’s model, Houk’s transition structure and electrostatic models, Cieplak’s $\sigma \rightarrow \sigma^*#$ model, and cation coordination model. Chapter 4 comments on allylic strain and its effect on the conformational profile and related stereochemical outcomes of reactions. The high diastereoselectivity observed in the reactions of Evans enolatesis solely on account of allylic strain. The conservation of orbital symmetry rules is presented in Chap. 5. After defining the bonding and antibonding orbitals of different types, reactions such as $\pi^2 + \pi^2$, $\pi^4 + \pi^2$, and electrocyclic processes have been used to demonstrate the application of the rules. Chapter 6 is an amalgamation of the conservation of orbital symmetry rules and orbital overlap effect, which serves as a very powerful tool to reliably predict the stereochemical course of pericyclic reactions. It is demonstrated by examples how the orbital overlap factor allows one of the otherwise two symmetry-controlled pathways to predominate. Chapter 7 is a must read to understand some of those control elements that did not find mention in the earlier chapters. The prominent among these elements are
spiroconjugation, periselectivity, torquoselectivity, $\alpha$-effect, Hammett constants, Hammond postulate, and Curtin–Hammett principle. A set of questions are provided at the end to challenge the reader by allowing an evaluation of the comprehension level.

The book is based mainly on the lecture notes prepared for the classes at IIT Kanpur. I am grateful to the authors of many books that I have used in preparing the notes. Important among these books are: (a) Stereoelectronic Effects in Organic Chemistry by Pierre Deslongchamps, (b) Molecular Orbitals and Organic Chemical Reactions by Ian Fleming, (c) Modern Physical Organic Chemistry by Eric V. Anslyn and Dennis A. Dougherty, (d) Mechanism and Theory in Organic Chemistry by Thomas H. Lowry and Kathleen S. Richardson, and (e) The Physical Basis of Organic Chemistry by Howard Maskill. I thank Prof. J.N. Moorthy for reading the chapters critically and suggesting changes to improve the quality of presentation. I thank Prof. M.L.N. Rao for his pleasant company and stimulating discussions over numerous coffee sessions. Last but not least, I thank Dr. Arpita Yadav, my better half, and Dhananjay and Dhruv, our sons, for bearing with me while I have been busy with drawing the structures and also for their never-ending enthusiasm and support.

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