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Diastereoselection: Introduction

An important quality which the Editors of *Chemical Reviews* have always successfully pursued is that of comprehensiveness: each paper should carefully inform the reader what area of chemistry is being reviewed and what period is being covered and all the literature on the subject during that time should be included. A second important quality in reviews is that they be critical and not just compilations of all the individual contributions on the topic in that interval.

In recent years, *Chemical Reviews* has occasionally published thematic issues in which a substantial number of closely related topics are presented. Such issues have the advantages that those who are interested in the general area can gain access to many or all aspects of that area in a single volume and that newcomers, seeing that viewpoints in an important segment of chemistry differ, may be enticed into the field. The drawback is that each of the contributing authors may find it more difficult to decide how comprehensive to be and how critical! Where does one draw the lines between related articles? Without care, repetitive overlap may occur, but on the other hand, contrary opinions may be presented side by side as established doctrine! The resulting danger is that the issue begins to resemble a series of individual accounts rather than one of impartial reviews. The task of a Guest Editor is to help ensure that both the selection of contributors and topics strike a reasonable balance between risk and reward.

The field of diastereoselection seemed a fine choice for such an issue. It is very large and multifaceted, and it would essentially be impossible for a single person or even a group to write a coherent and comprehensive review of it. One of the two main factors leading to diastereoselection, namely, the steric one, has a long history and is basically noncontroversial, even as it remains under steady and lively development. The other, known as the electronic one, has only more recently begun to draw attention. While its role is now generally acknowledged, few chemists seem to agree about the cause(s) of it, and some choose to ignore it when they consider the reasons for selectivity in any given case.

Our selection is a reflection of these facts. The first five papers are primarily based on the literature dealing with the practical question of how to obtain important chiral organic compounds with high ee. Kobayashi and Ishitani review the generation of chiral nitrogen-containing biomolecules via catalytic reduction and alkylation of imines, as well as via several other standard carbon−carbon bond-forming reactions. Similarly, the review by Mahrwald is a detailed survey of diastereoselective aldol additions of silyl enol ethers to aldehydes as well as of related transformations, with emphasis on the stereochemical aspects of the reaction and on enantioselective approaches with a variety of chiral Lewis acids. Reetz not only summarizes presently known methods for the preparation of various optically pure *N*,*N*-dibenzylamino carbonyl compounds from amino acids, but also illustrates the power of protective-group tuning in a wide variety of diastereoselective reactions of these chiral building blocks. Klunder, Zhu and Zwanenburg describe new stereoselective routes to functionalized cyclopentanoids and -hexanoids as well as to heterocyclic five-membered ring compounds. These papers precede one by Mengel and Reiser, who examine addition processes with molecules containing a chiral center adjacent to or more remote from a doubly bound carbon atom, on the basis of Cram's rule and its recent extensions.

The next five papers discuss theoretical aspects of diastereoselection and the stereoelectronics producing it. Dannenberg and Tomoda each describe the use of frontier molecular orbital theory to arrive at predictions of product ratios. Cieplak's survey concludes that stereoselectivity often depends not just on the inductive effect but on the resonance effect as well and also that nonlinear Hammett and Taft relationships suggest a dependence of the magnitude of stereoelectronic control of π face selection on transition-state location along the reaction coordinate. Ohwada discusses the effects of desymmetrization of orbitals by remote substituents, while Gung examines the role that geometric distortions of molecular structure might play.

The last four papers review stereoselectivities experimentally observed in reactions of sterically unbiased substrates and their possible explanations. Kaselj, Chung, and le Noble are partisans for transition-state hyperconjugation, based on that group's results with a wide variety of chemistry with ada-

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mantanes incorprating a trigonal center and carrying a remote substituent. Adcock and Trout describe model system studies utilizing carbon-13 and fluorine-19 NMR chemical shifts as electronic probes to delineate modes of transmission of polar effects in saturated systems and the extrapolation of these ideas to an understanding of the nature of the electronic factor governing diastereoselectivity. Mehta and Chandrasekhar show the advantage of combining experimental studies of substrates carefully designed to have their reaction centers in an isosteric environment with computational modeling to unravel the various electronic contributions to facial selection induced by remote substituents. The final review by Wipf and Jung considers that electrostatic effects best explain the selectivity observed in 1,2-additions to 4,4-disubstituted cyclohexadienones—yet another group of sterically unbiased models well-suited for the critical analysis of the various theoretical models for stereoelectronic control in carbonyl addition.

Readers of these pages may well conclude that sterically controlled selectivities are very often predictable and continue to provide the basis for steady progress in asymmetric synthesis, but they are also very likely to be left with the impression that the causes of nonsteric diastereoselection are far from settled. That is all to the good! Controversy has often sparked new proposals and research, and if we have provided food for thought for our colleagues in organic chemistry, we will have succeeded in our aims.

It remains for us to express our thanks to John Gladysz and Josef Michl for accepting our proposal of a special issue dealing with the topic of diastereoselection. We are also grateful to Ms. Karie McGarvey for her cheerful and capable handling of the variety of problems that arise when 14 people at locations scattered all over the world decide to do something together by an agreed-upon date!

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