

Organic reactions and orbital symmetry

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Organic reactions and orbital symmetry

SECOND EDITION

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Preface to the first edition

The application of the concept of orbital symmetry to organic chemistry by R. B. Woodward and R. Hoffmann has proved to be a major theoretical advance, in that it has succeeded in bringing together and rationalising diverse areas of the subject. In particular it has provided the basis for a unified mechanistic approach to cycloadditions and molecular rearrangements; partly as a result of the stimulus of the new theory, the importance of such reactions is now rightly recognised. For historical reasons these reactions have not usually been treated as fully as their importance warrants in student texts. Now that the concept of orbital symmetry control is well established it seems appropriate to present an account of these reactions within a modern mechanistic framework.

The major part of this book (chapters 3 to 7) is devoted to a descriptive account of rearrangements and cycloadditions. The aim has been to illustrate the scope and synthetic utility of the reactions as well as to discuss their mechanisms. Chapter 1 gives an introduction to the types of mechanisms by which such reactions can occur, and to the experimental methods available for establishing the mechanisms. In particular, the important distinction between stepwise and concerted processes is emphasised. The treatment in chapter 1 is elementary and descriptive, the aim being to provide a brief revision of certain terms and concepts which are used throughout the rest of the book. Chapter 2 is a comparative account of the various approaches to the theory of concerted reactions. In a brief final chapter (chapter 8) we have speculated on possible extensions of the theory to other types of concerted processes. Throughout the book, thermally induced reactions are given more detailed treatment than photochemical and catalysed reactions, for which the applications of the theory are, as yet, less firmly established. References are given at the end of each chapter to relevant reviews, and also to important original papers and to work which has appeared since the publication of the reviews.

We are indebted to our colleagues Dr D. Bethell and Dr M. J. P. Harger, and to the Series Editor, Dr K. Schofield, for their constructive criticisms. We are



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also grateful to Professor C. W. Rees, who not only made helpful criticisms of the text, but also was a source of advice and encouragement during its preparation.

August 1971

T. L. GILCHRIST R. C. STORR



Preface to the second edition

This edition follows much the same pattern as the previous one, with the emphasis remaining on the descriptive aspects of pericyclic reactions. We have greatly expanded the treatment of frontier orbital theory, which has recently proved to be particularly useful in explaining the rates and selectivities of pericyclic processes. The chapters on cycloadditions and sigmatropic reactions have been expanded to cover this and other recent work. We have deleted the chapter on non-pericyclic reactions.

We are grateful to Professor K. Schofield for his helpful and constructive comments, and to our colleagues at Liverpool who have read parts of the manuscript.

April 1978

T. L. GILCHRIST R. C. STORR