

Book review

Stereochemistry and reactivity of systems containing π electrons. Ed.: William H. Watson. Verlag Chemie International, Deerfield Beach, FL, 1983 (Volume 3 of Methods In Stereochemical Analysis)

This book is the proceedings of the symposium *Stereochemistry and Reactivity in Pi Systems* held May 19–22, 1982, in recognition of the contributions of Professor Paul D. Bartlett. There are 12 separate papers, clustered mainly around the theme of π -bond distortions and the π -facial stereoselectivity which derives therefrom. Perhaps the principal scientific purpose of the symposium was to bring together several workers who were concerned about the enhanced reactivity of unsymmetrical π bonds, such as that of norbornene, as well as their pronounced stereochemical selectivities (e.g. in cycloadditions), the reasons for which were controversial. While there has been further work, both theoretical and experimental, published in the ~ 5 years since the symposium, the issues addressed remain topical, and the summaries are worthwhile. It should be added, however, that the scope of the coverage is naturally somewhat restricted by the choice of speakers, and the non-comprehensive nature of papers given at a conference.

For readers of this journal who are primarily interested in theoretical developments, this book will prove minimally useful. There are really only two papers which are theoretical in nature: one by Professor Kendall Houk, and another by Professor Rolf Gleiter. Houk's paper primarily deals with calculations (both *ab initio* at the minimal and split valence basis set levels, and force field) aimed at understanding the high reactivity and exo selectivity of the double bond of norbornene. Houk makes the case that all unsymmetrical π bonds are pyramidalized to some extent, and that this factor, enhanced in reaction transition states, is responsible for the observed chemical effects in norbornene. Houk argues for a torsional origin of the pyramidalization, rather than a hyperconjugative origin (a subject of debate at the conference). Houk also points out that *s*, *p*-mixing (rehybridization) is minimal in *cis*-pyramidalized alkenes such as norbornene.

Professor Gleiter deals mainly with stereoselectivities observed in unsymmetrical dienes (in Diels-Alder reactions), the experimental side of which is covered in three separate papers by Professor L. Paquette, P. Bartlett, and P. Vogel. Gleiter treats what are generally known as "secondary orbital interactions" via a perturbational extension of frontier MO theory. However, his applications to specific cases are made in very qualitative terms, with occasional quantitative orbital diagrams. With reference to unsymmetrical dienes such as isodicyclopentadiene, Gleiter attributes the observed endo facial selectivity to closed-shell repulsions which occur between the symmetrical filled diene MO and the π MO of the exo-oriented incoming dienophile. This interpretation, which depends upon the π -facial distortion induced by σ – π interaction, is not universally accepted.

The other subjects covered in this volume include two papers on bridgehead alkenes, three papers on π -bond photochemistry, and two papers on electrophilic reactions of π bonds. Overall, the book might be useful to the theoretician who wants to become acquainted with some of the important aspects of the chemistry of π bonds; there are certainly theoretical contributions to be made in this broad area. However, given the publication date, and the relative paucity of theoretical material, it would be difficult to make a strong "buy recommendation" to most readers of this journal.