

# Chemical Reviews

---

Volume 91, Number 3

May 1991

## Reactive Intermediates: Introduction

The study of reactive intermediates currently permeates all branches of chemistry and there is hardly an issue of *Chemical Reviews* in which the subject does not appear in one way or another. The present collection contains several contributions illustrating three of the forms that the investigation of reactive intermediates takes nowadays: (i) the generation of these species and the characterization of their chemical reactivity, (ii) their spectroscopic characterization, and (iii) the study of the dynamics of the chemical processes in which they participate. The contributions thus run the whole gamut of physical, organic, and inorganic chemistry, from aspects interesting to synthetic chemists to those exciting to mechanistically oriented chemists and those of primary interest to physical chemists, particularly spectroscopists and kineticists.

(i) Four articles relate to carbenes or their analogues and are primarily of organic or inorganic interest. Padwa and Hornbuckle provide a general review of the chemistry of ylides formed by the addition of carbenes or carbenoids to the lone pairs of heteroatoms. Neumann discusses the generation and reactions of the heavy relatives of carbenes: germylenes and stannylenes. Bunnelle covers carbonyl oxides, which can be viewed as the adducts of another carbene analogue, singlet atomic oxygen, to the lone pair of a carbonyl. Finally, Wentrup and Kambouris treat three types of *N*-sulfides, a series of compounds derived formally from singlet atomic sulfur by addition to a lone pair of a triply bonded nitrogen.

(ii) Two articles address spectroscopy. Saunders and Jiménez-Vázquez emphasize nuclear magnetic resonance in their review of the recent developments in the field of carbocations. Optical spectroscopy is the focus of the article by Engelking, who examines the contribution provided by supersonic jets, a powerful new tool in the direct observation of reactive intermediates.

(iii) If the understanding of chemical transformations is the ultimate objective of chemistry, it is only appropriate to include an article that illustrates how modern experimental tools probe the detailed behavior of a reactive intermediate. In his review of the photoisomerization dynamics of stilbene, Waldeck does this on an example of a most elusive reactive intermediate, excited twisted stilbene.

It is striking how much reference is made to chemical theory in all of these articles, and how different this situation is relative to the not so distant past.

We are grateful to the authors of the seven articles for the many hours of work that they invested into the preparation of these reviews and hope that the readers will enjoy them as much as we did.

Josef Michl, Editor

John A. Gladysz, Associate Editor