

Nitrenes and Nitrenium Ions

Having a longstanding interest in reactive intermediates that has recently turned more toward nitrenes, I was looking forward to the publication of this volume of the Wiley series on nitrenes and nitrenium ions, edited by Falvey and Gudmundsdottir. As the editors note in the Introduction, the last monograph on nitrenes was in the mid-80s, before we had convenient access to theoretical methods capable of describing their electronic structures accurately, and studies of nitrenium ions were just getting started. There have been various reviews written over the intervening years, but this volume brings together a diverse array of topics, covering aspects of nitrenes that will appeal mostly to the physical organic chemist who encounters nitrenes as reactive intermediates.

Although the technical content is strong as far as it goes, one challenge I found in reading the book is the lack of chapter organization. It starts smartly enough with a chapter on time-resolved spectroscopy studies of nitrenes and nitrenium ions by Platz and co-workers. This is appropriate as the time-resolved studies, with Platz as an undisputed leader, have historically driven the advances in the understanding of reactivity and structure of aromatic nitrenes. The chapter focuses on more recent work involving ultrafast time-resolved spectroscopy, which provides a very detailed picture of the mechanisms of nitrene reactivity, including the role of excited electronic states. The second chapter by Hadad and co-workers involves a theoretical description of nitrenes and the excited-state precursors, which provides a means for understanding the results in the first chapter. After that, however, the topics jump all over. The third chapter is the first dedicated to nitrenium ions, and focuses on their application as photoaffinity labels, while Falvey's overview of the electronic properties of nitrenium ions, which would seem to be a good starting point, isn't until chapter 6. Subsequent chapters on nitrenes, scattered throughout, cover topics such as alkyl, acyl and hetero- and fluorinated aromatic nitrenes. Chapter 9 by Grote and Sander describes matrix isolation studies of nitrene

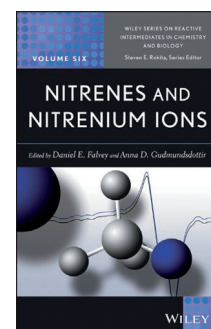
radicals, which are aromatic radicals that include a nitrene moiety. The electronic properties of these (nominally) triradical species result from interaction between the nitrene center and the aromatic radical, and depend on the regiochemical relationship. While fairly exotic even as reactive intermediates go, the fact that they are known is a good illustration of how much we are capable of learning with modern experimental methods. In addition to the photoaffinity labeling applications described in Chapter 3, nitrenium ion topics include time-resolved Raman spectroscopy studies of their reactivity and synthetic applications.

It is always going to be the case in a collection such as this that there are topics left out, either because of space limitations, or as a reflection of the editors' interests. In this volume, there are some topics that could have been included but were not, particularly for the nitrenes. For example, whereas there is a chapter on synthetic applications of nitrenium ions, there is no corresponding chapter for nitrenes. Although nitrenes are notorious for being poor synthetic reagents, there are known synthetic methods where they are utilized effectively (such as the Cadogan reaction). Also not included are nitrene surrogates such as organometallic imido complexes, which undergo reactions expected for nitrenes, as in the aziridination of alkenes. However, for the topics that are covered, the information is generally up-to-date, and reflects the current state of knowledge of the field.

Overall, this volume is probably best viewed as a collection of modern reviews on the selected topics, and in that capacity, the organizational issues are not a concern. With the balance of state-of-the-art content and background provided, it is a useful resource for a fundamental understanding of nitrene/nitrenium ion structure and reactivity. As a physical organic chemist interested in reactive intermediates, it is a great addition to my shelf of important literature reviews. On the other hand, for those who might encounter a putative nitrene or nitrenium ion more generally, such in an application, the library copy would probably suffice.

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