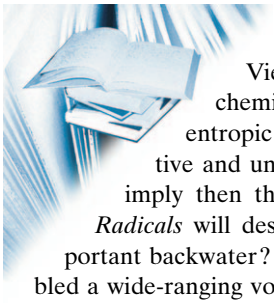

Stable Radicals

Viewed from afar radical chemistry impresses as an entropic domain of highly reactive and unstable species. Does this imply then that a book called *Stable Radicals* will describe a calm and unimportant backwater? Robin Hicks has assembled a wide-ranging volume of seventeen chapters which quickly dispels any such expectation and demonstrates the reverse is true. The book is the first attempt to provide a unified coverage of neutral stable radicals in the four decades since the publication of Forrester, Hay, and Thomson's *Organic Chemistry of Stable Free Radicals*.

In fact it is remarkable how many of the really significant discoveries and developments in chemistry owe something of their genesis to stable free radicals. Gomberg's discovery of triphenylmethyl led chemistry away from sterile fixed valency terrain into the realm of reactive intermediates. Chapters of this book update the flourishing triarylmethyl story and show how extended versions of these species have given rise to new functional materials. Polychlorotriphenylmethyls (PTMs) have lifetimes of decades thus enabling high spin molecules linking several PTM units with organic and/or inorganic coordination spacers to be assembled. New materials with unusual magnetic and optical properties, including redox-switchable systems, thus became accessible.

Another important development showcased in several chapters has been the discovery and exploitation of the persistent radical effect (PRE). In a system where transient radicals are generated in the presence of persistent radicals the concentration of the latter rapidly builds up so that the product from cross-coupling of the persistent radical with the transient radical is selectively formed. The phenomenon has been observed with many persistent radicals and put to use in synthetic organic chemistry. However, it is with persistent nitroxide radicals that the effectiveness of the technique is being realized. In particular, several types of living free radical polymerizations owe their success to the PRE. The propagating polymer chain radicals are transient so that, in the presence in a nitroxide, the PRE ensures that the termination step is dominated by cross-coupling of the nitroxide with polymer radicals. By employing designer nitroxides, the cross-termination step can be made reversible, thus enabling a degree of control to be gained over polymer molecular weight and molecular weight distribution.

Nitroxide radical chemistry is shown to be amazingly rich and varied. In addition to their involvement in PRE-mediated processes and as spin traps, the redox behaviour of nitroxides has been put to use in various preparative oxidations which are reviewed in a chapter by Christian Brückner. One-electron transfer processes of nitroxides are remarkably rapid and reversible and are accompanied by relatively small structural changes. Chapter 14 by Takeo Suga and Hiroyuki Nishide describes how these characteristics enabled rechargeable batteries, including totally organic batteries, to be developed around nitroxide-containing polymers.

Their simple but informative EPR spectra have ensured that nitroxides enjoy a large and varied range of applications as spin labels. Nitroxide labels have been used to address problems of the structure and function of polymers and dendrimers, but Chapter 15 by Lawrence Berliner gives a modern perspective on their employment with proteins, polynucleotides and other biopolymers. Site-specific mutation methodology became available for proteins in the 1980s and site-directed spin labeling (SDSL) blossomed thereafter. Two nitroxide labels can be attached to proteins at specific positions via cysteine units thus enabling distances in the range 8–25 Å to be determined from the dipole–dipole interaction as recorded by EPR spectroscopy. Berliner outlines how the structures and dynamics of proteins that are neither soluble nor crystallizable have been investigated and mentions many exciting new advances. In Chapter 16 Valery Khramtsov and Jay Zweier explain how nitroxides and trityl radicals are used in vivo as oximetry probes, as redox-sensitive probes, for monitoring pH at the molecular level, and in EPR imaging.

The book also contains informative chapters summarizing the chemistry of stable radicals from across the Periodic Table including phenalenyls, nitrogen oxides, verdazyls, thiazyls, stable radicals from the heavy p-block elements, and metal-coordinated species. In a short cameo chapter Keith Ingold recounts the discovery, synthesis and major reactions of di-*tert*-alkyliminoxyls; the only stable sigma radicals.

Although some variation in the style of writing is inevitable in a collection of essays such as this, the overall presentation and formatting is pleasing to both the eye and mind. This is a worthwhile and insightful anthology and leaves the reader with the impression that novel prospects and discoveries could surface at any moment from junctions on the stable radical chemical topology.

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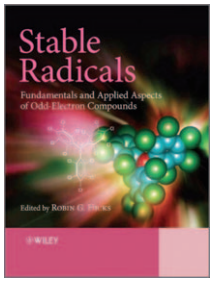
DOI: 10.1002/anie.201007666



Stable Radicals
Fundamentals and Applied Aspects of Odd-Electron Compounds. Edited by Robin G. Hicks. John Wiley & Sons, Chichester 2010. 606 pp., hardcover, € 162.00.—ISBN 978-0470770832