

# This Week's Citation Classic®

**Pryor W A. *Free radicals*. New York: McGraw-Hill, 1966. 354 p.**  
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This book, the first textbook in the field, was published when the organic chemistry of free radicals was beginning to attract increased attention. The book provided an easily understood and accessible guide to the mechanisms of free radical reactions to a generation of students. It was widely adopted and used at many universities and by research workers. As the reviewer for the *Journal of the American Chemical Society* stated, this book "...is clearly written and the coverage is both thorough and up-to-date...." [The SCI® indicates that this book has been cited in more than 290 publications.]

## Mechanisms of Free Radical Reactions

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I received a PhD in chemistry at the University of California, Berkeley, where, at that time, few faculty members had an interest in radicals. I had done a thesis on the mechanism of the aldol condensation (nary a radical in sight!) and was a babe in the radical woods. At that time, the study of ionic reaction mechanisms seemed to be dominated by talented researchers, and I wanted to find another pond into which to stick my oar. Thus, I started my career at the California Research Corporation doing fundamental research on vinyl polymerization and sulfur oxidations, both of which are radical-mediated processes. Cheves Walling, whose groundbreaking monograph<sup>1</sup> had recently been published, was a consultant there.

Thus, my free radical education began. I started by devising mechanistic schemes for the labyrinth of radical reactions through which both elemental sulfur and sulfur compounds wend their way.<sup>2</sup> When I moved to academia in 1960, I began research on the mechanism of the displacement reaction by both polymeric and monomeric free radicals, using disulfides as a model for the study of the Walden inversion reaction by free radicals on carbon compounds.<sup>3</sup>

As I began teaching and directing graduate students in free radical chemistry, the need for a textbook in the field became painfully clear. Walling's monograph had used an organization in which vinyl polymerization was considered first. Since, at that time, most free radical chemists (including myself) began life as polymer chemists, that was quite natural. However, polymer chemistry was a *terra even more incognita* to most students than was free radical chemistry. Therefore, I decided to organize organic radical reactions with less dependence on polymer kinetics and in a way that would be both lucid and reasonably comprehensive.

The book became popular and was translated into a number of languages, including Russian and Japanese. The reviewer for the *Journal of the American Chemical Society* commented that many workers found it useful to "...routinely recommend the book to research students as the best place to begin."<sup>4</sup>

In retrospect, I attribute the success of the book to three factors: the burgeoning popularity of the study of organic free radical reactions, a style that was meant to be transparent and immediately accessible to readers, and a surprising absence of competing texts. The absence of an updated text for current students in this field is, unfortunately, true again today.

Many free radicals have flowed under the bridge in the years since this book was published. Today the study of radicals is more popular than ever. Radical reactions play a useful, important, and acknowledged role in organic syntheses. Radicals are formed by electron transfer even in reactions formerly thought to be nonradical processes (such as the Grignard reaction). Since the discovery of superoxide dismutase in 1968,<sup>5</sup> I and many other workers have concentrated on the vital role free radicals play in biological systems. In view of the demonstrated usefulness and importance of radical reactions in these fields, it remains disappointing to me that most sophomore organic texts continue to offer a dated and incomplete treatment of radicals, which are presented as arcane and exotic (e.g., a special way to add HBr to olefins or to derivatize methane!).

1. Walling C. *Free radicals in solution*. New York: Wiley, 1957. 631 p. (Cited 580 times.)
2. Pryor W A. *Mechanisms of sulfur reactions*. New York: McGraw-Hill, 1962. 241 p. (Cited 120 times.)
3. Pryor W A & Guard H. Reactions of radicals. Part 8. Walden inversion by radicals. *J. Amer. Chem. Soc.* 86:1150-2, 1964. (Cited 55 times.)
4. Kampmeier J A. W.A. Pryor—free radicals. *J. Amer. Chem. Soc.* 89:5996, 1967.
5. Pryor W A & Davies K J A, eds. Special issue: twentieth anniversary of the discovery of superoxide dismutase. (Whole issue.) *Free Radical Biol. Med.* 5(5/6), 1988. 163 p.