

## **Molecular Crystals and Liquid Crystals**



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## A Review of "Reactive Intermediates in Organic Chemistry"

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## **Book Review**

"Reactive Intermediates in Organic Chemistry" by Maya Shankar Singh, Wiley-VCH, 2014, Weinheim; ISBN 978-3-527-33594-7; x +283 pp.; \$80.00 (paperback).

As noted by the author in the preface, the modern exercise of organic synthesis, whether for new materials or new drugs, is largely driven by mechanistic reasoning. The author has produced a book dealing with the major species of mechanistic discussion and consisting of seven chapters: Introduction; Carbocations; Carbanions; Radicals; Carbenes; Nitrenes; and Miscellaneous Intermediates. The latter include arynes, ketenes and cumulenes, *ortho*-quinone methides, zwitterions and dipoles, antiaromatic systems, tetrahedral intermediates, acetals and hemiacetals, and Weinreb amides. Each chapter typically has a discussion of the structure of the intermediate, methods of generation, reactions, and mechanisms as well as a summary, references for further reading, and problems. The book's intended audience is undergraduates and beginning graduate students, and on the whole, this audience will be well-served by Singh's book.

Are there topics not covered that would have been useful? Discussions of metathesis chemistry and oxidative addition chemistry would have been beneficial. The discussion of cation-radicals in Section 2.9 would have been strengthened by the inclusion of stable long-lived systems. Anion-radicals are not discussed at all.

There are occasional statements and figures throughout the text that require further comment. On p. 15, UV-Visible spectroscopy does not tell us about conjugation in a molecule. It tells us about the energy difference between filled levels and empty levels, and through the molar extinction coefficient, whether the electronic excitation is allowed or forbidden. In Scheme 2.10 on p. 30, the second reaction is not the product expected from Markovnikov's Rule. On p. 52, "anchimeric assistance" is not defined or explained. In Scheme 3.4 on p. 70, the structures from loss of a proton from acetonitrile are not correct. The discussion of the mechanism of keto-enol interconversion in Section 3.8.1 is oversimplified. The position of the equilibrium can be very solvent dependent. (See C. K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd ed., Cornell University Press, 1969, Chap. 11.) The EPR spectrum in Fig. 4.4 on p. 105 is that of the ethyl radical, not the methyl radical. In Scheme 4.28 on p. 124, the final product has two extra hydrogen atoms. In Scheme 4.33 on p. 125, the data are not relative rates, but thermodynamic. The list of Further Reading after Chap. 5 does not include the recent reviews of R.A. Moss. Scheme 7.22 on p. 238 shows the wrong isomer of *ortho*-benzyne. The first reaction in Scheme 7.26 involves furan, not tetrahydrofuran. The last reaction in Scheme 7.27 on p. 241 does not involve loss of CO.

All in all, the author's intended audiences will find this a useful book.

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