

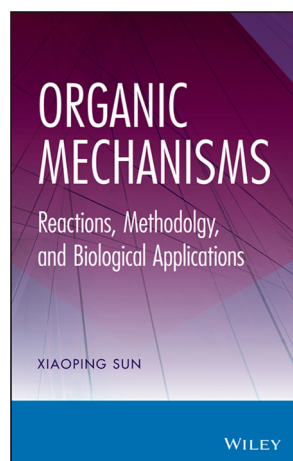
## Review of *Organic Mechanisms: Reactions, Methodology, and Biological Applications*

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**Organic Mechanisms: Reactions, Methodology, and Biological Applications**, by Xiaoping Sun. John Wiley & Sons, Inc.: Hoboken, New Jersey, 2013. 418 pp. ISBN: 9781118065648 (hardcover). \$92.95.

The author states clearly in his introduction: "While the book emphasizes mechanistic aspects of organic reactions, it is a practical textbook presenting the synthetic perspective about organic reaction mechanisms appealing to **senior undergraduate-level and graduate-level students.**" [Emphasis mine.] Thus, it is clear from the beginning of *Organic Mechanisms: Reactions, Methodology, and Biological Applications* that a basic understanding of organic chemistry and biology is presupposed.



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The outside back cover states "[The author's] research focuses on studying the mechanisms of chemical reactions." With such a claim, it would be expected that better attention to known reaction detail would have been included in this work.

It should also be said at the outset that this book could have benefitted from more editing efforts, based on the number of typographical and grammatical errors present in the published version. Furthermore, fewer than 50% of the citations provided throughout the book are from the primary literature; the balance of the citations are from other published textbooks. While it is true that the authors of these books may have utilized the primary literature in their writing, a book which reviews other textbooks appears to be overkill.

The table of contents shows 10 chapters, most organized around a particular functionalization or process. The progression is logical, and the chapters do build on one another.

The author begins in Chapter 1, Fundamental Principles, with a simple (and slightly erroneous) review of  $S_N1$  and  $S_N2$  reactions and what the reaction coordinate would look like for each. (It is in the  $S_N1$  diagram and description where the error occurs: after forming the carbocation, the reaction is given as the addition of water, directly yielding the alcohol product plus a hydrogen halide in Figure 1.1.) After this slight gaff, he moves on through other fundamentals such as thermodynamics, kinetics, and molecular orbital theory.

The next four chapters concern themselves with functionalization of various bond-types: aliphatic C–H bonds, carbon–carbon double bonds and aromatic C–H bonds. Nucleophilic substitutions and eliminations come next (two chapters), followed by carbonyl compound chemistry (two chapters.) He concludes with a chapter on rearrangements.

On the positive side: in all the chapters, the author introduces the basic ideas and then presents a mechanistic review of the materials traditionally taught in a sophomore organic chemistry class. Most chapters conclude with more advanced topics related to the overall chapter scheme but somewhat beyond the usual sophomore organic chemistry course. All the author's mechanistic arrows are well drawn and clearly show both the origin of the moving electrons and the atom within the molecule that they are attacking. His evidence for the mechanisms he presents are well documented and provided this physical organic chemist with some interesting "mind-candy" as he thought through the expected (and proposed) arrow formalisms.

On the negative side, the author sometimes oversimplifies (in this reviewer's estimation) some mechanistic details to drive home a point. If this book is meant for the advanced undergraduate or graduate student, such oversimplifications are unnecessary. Some of these are discussed below.

Objections may be raised at the author's classification of certain electrophilic aromatic substitution (EAS) reactions as following either an  $S_N1$  or  $S_N2$  mechanism. While the intermediacy of carbocations in EAS reactions is accepted as valid, it seems that attempting to couch EAS reactions under the familiar nucleophilic substitution reaction ( $S_N1$ ) rubric is a bit far-fetched. The reader may well be cautioned to read this section with a large grain of salt. However, the EAS reaction described as following an  $S_N2$ -like pathway seems undeniable, as inversion of stereochemistry is observed. Likewise an isomerization pathway was presented, which shows a "free" methyl cation having been lost from an arenium ion. A methyl cation may grate on some chemist's nerves but the product presented seems to allow for no other, more reasonable

pathway. Perhaps a better way to present this pathway would be to draw the intermediate as methyl chloride complexed to aluminum trichloride, providing a good methyl-cation equivalent without the free methyl cation. (This is important because on p 219 the author states that  $\text{CH}_3^+$  cannot be formed owing to instability.)

The discussion in Section 6.3 of good and poor nucleophiles reads a bit confusingly. The author argues, correctly, that as anions get larger, the interaction with a small proton would be less good; however, his examples of “larger” anion as  $\text{I}^-$  and  $\text{HS}^-$  being less basic appears to stand in stark contrast with the  $\text{p}K_a$  values for the corresponding acids presented in Table 6.1 (−10 and +7, respectively). The concepts, once understood, are correct, but the reader should be cautioned to take this section slowly and to think carefully at each stage.

One serious objection this physical organic chemist had was to Figure 6.11b. The author shows the three 2p orbitals of carbon as being of different energy levels merely because under symmetry  $C_{3v}$  they belong to different symmetry designations ( $a_1$  and e). The symmetry designations are certainly correct, but this difference in symmetry, as far as I know, does not imply that they are of different energies. (This error is also repeated in the citation the author gives for the diagram, which is one of his papers.) While there is no debate that the interaction of the carbon-centered orbitals with the LGOs of  $\text{H}_4$  would lead to a splitting, in the free atom, this splitting does not occur.

In the author’s discussion of the orbital underpinnings of the  $\alpha$ -elimination in chloroform to yield dichlorocarbene, he claims the HOMO of the base,  $\text{B}^-$ , overlaps with the  $2a_1^*$  orbital in chloroform to lead to the trichloromethyl anion. While the hydrogen atom is part of this  $2a_1^*$  orbital, it might be better said that the  $2a_1^*$  orbital is where the electrons that were bonding the hydrogen atom end up after the base removes that hydrogen. To write that it overlaps seems to suggest more of an  $\text{S}_{\text{N}}2$ -like mechanism than an acid–base, hydrogen cation abstraction.

In Chapter 9 (Reactivity of the  $\alpha$ -Hydrogens to Carbonyl Groups), in focusing on the carbon–carbon bond forming reactions, he leaves out (or appears to do so) the reactions that occur from the oxanionic form of the enolate, such as those with silyl compounds, to yield enol silyl ethers. Not a terrible omission, but one that could lead the reader to think that the only reactions undergone by enolate anions were carbon–carbon bond forming reactions.

In Chapter 10, he states that most carbenes have a singlet ground state, with the  $\text{sp}^2$ -hybrid orbital doubly occupied, and the p-orbital vacant. As an old carbene chemist, this reviewer would have liked to see a few citations of carbenes in which the triplet is the ground state, whether for steric reasons (as in bis(1-adamantyl)carbene) or electronic. Again, the reader is cautioned to read this section with a grain of salt.

In summary, *Organic Mechanisms: Reactions, Methodology, and Biological Applications*, while perhaps a good collection of what is out there in textbooks, reads mostly like a summary book or a review of the published books in the field. Worse, it is full of errors that span the gamut from spelling errors to serious mechanistic ones. It would be difficult to recommend this book as anything other than a good source of interesting mechanistic questions for inclusion.

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### Notes

The authors declare no competing financial interest.