Highlights of Organic Chemistry

an advanced textbook

William J. le Noble

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（内部交流）

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EDITOR'S FOREWORD

The concept behind the Studies in Organic Chemistry series was to provide, for the chemical community, a group of books which could be used at the advanced undergraduate level and at the graduate level as texts in special topics courses. At the same time, I felt that it was desirable that the members of this series be prepared in a thorough and rigorous fashion, so that they would also prove to be of high value to the practicing organic chemist who might require an authoritative treatise on a given subject. Although I did not originally envision the inclusion of a general advanced organic chemistry text in this series, I am delighted to be able to do so with this publication of Professor le Noble's Highlights of Organic Chemistry.

Highlights of Organic Chemistry provides an advanced conceptual treatment of the basic principles of organic chemistry which is both classically based and impressively modern. The approach is unlike that of any advanced text known to me. The coverage is far broader than that found in many of the "Physical-Organic" texts commonly associated with first-year graduate level courses in organic chemistry. At the same time, basic concepts of modern organic chemistry are dealt with in far more detail and are treated far more rigorously by Professor le Noble's text than by most other "Advanced Organic" texts. In short, I feel that Bill le Noble's Highlights of Organic Chemistry provides a unique work, which should find wide use among advanced students of organic chemistry.

Paul G. Gassman
Columbus, Ohio

PREFACE

This book has grown out of my lecture notes collected over the past ten years for two courses taught in the Chemistry Department at Stony Brook. One of the courses, entitled "Structural Organic Chemistry", is required of those new graduate students interested in Organic Chemistry who haven't had the equivalent elsewhere, but it is also taken by graduate students in the other chemical disciplines and by some of the more ambitious undergraduate students. The other course, called "Reactive Intermediates", is a Special Topics course taught perhaps every fourth year or so; its clientele consists primarily of students and post-doctoral fellows interested in the mechanisms of organic reactions. As these notes grew more voluminous and the reprints on which they were based ran to several thousand, the temptation arose to abstract, combine and edit all this material into some orderly form, and when I was granted a sabbatical leave in 1972-73, I yielded to it.

Most of the writing was done during my stay in Leiden. Many of my colleagues in the United States who have visited that famous, old University commented favorably on the intellectual atmosphere there, and since I speak the native language I thought it would be a good place to do this work. Professor E. Havinga kindly consented to be my host.

Some features of this writing are perhaps somewhat unusual. Thus, I have included a chapter on nomenclature and literature. It has been my experience that only the most elementary nomenclature is introduced in undergraduate work (perhaps

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appropriately), and that the topic is thereafter neglected to the point that many students are hampered by this hiatus in their knowledge even while screening the titles of papers in organic journals. Consequently good papers that might have aroused their interest are passed over like so much Greek. Similarly, I have been surprised to find on numerous occasions how many students are lost in the library if they are unable to locate a piece of information in Chemical Abstracts. For these reasons I decided to include some remarks on both of these topics.

Organic chemistry has had its share of controversies, and our students should know that even the best minds at work in their field do not always agree on the interpretation of all experiments. Since many of the topics presented are still in a state of active development, not every discussion leads to a clear-cut and inescapable conclusion. By the same token, there are numerous instances in this book in which I have quoted work that was shown to be wrong in later publications. These examples include errors in judgment, errors in experimental work, errors in interpretation, errors sometimes due to haste to get a tantalizing new development in print, errors due to prejudice, and so on. To err is human, it is said, and organic chemistry is a human enterprise. I feel that an element of dullness is introduced if these errors are swept under the rug and only the finished package is presented. Those who come after us should have a chance to learn from our mistakes, and this requires their exposure. I may not have endeared myself this way with the chemists whose misfortune it was to be so human; may it be of solace to them that the author has made his share of missteps, and that perhaps this writing will come to stand in testimony to that fact.

In view of the nature of this book, with an unusually full description of some topics which have attracted much attention in recent years, and perhaps neglect of others, the usual titles such as "Organic Chemistry", "Advanced Organic Chemistry", "Physical-Organic Chemistry", *etc. did not seem appropriate. Engaging* in one of favorite pastimes one day, the reading of the monthly feature called "Highlights from Current Literature" in Chemistry and Industry, it occurred to me that "Highlights of Organic Chemistry" would be a descriptive title, and I hope it is. *This book is primarily meant for graduate students whose interests are strongly* research-oriented, but it may also be of use to those who have been unable to keep abreast of the recent literature, and who would like a general overview of what has happened in Organic Chemistry in the past decade.

Unfortunately some very pertinent recent references could not be included in this text. It is hard to describe the sinking feeling one experiences right after putting the finishing touches on a chapter, when the next journal to cross one's desk contains papers describing indisputable evidence pointing to contrary conclusions.

I am deeply indebted to Dr. F. Goudriaan, who taught me the basics of organic chemistry many years ago, and whose encouragement and advice have continued ever since. I owe many thanks to Professor E. Havinga, who gave generously of his time to help in more ways than I can recount. Professor L. Oosterhoff gave me the benefit of his comments on several points bearing on theoretical problems. Mrs. S. Overgaauw was extremely helpful in getting us settled in the initial stages of our visit. Mr. M. Pison provided me with many expert suggestions and

comments regarding the drawing of the structures, and to boot, in his own time drew those in the first three chapters as examples. Some of the best students at Leiden critically read parts of the raw manuscript: Mr. S. Eisma read Chapter 7, Mr. H. de Leeuw read Chapter 2, Mr. T. Mulder read Chapter 8, and Mr. F. Wiegerink read Chapter 10. Their comments have a great deal to do with whatever merit this writing may have. Professor P. Gassman read the entire manuscript; he found and corrected innumerable small errors, and a few more serious ones as well. I owe many thanks to Mrs. P. Holmes, who transformed a badly mangled, handwritten manuscript into a faultlessly typed version. After I had once again cut this into pieces, annotated it and taped it back together, Mrs. L. Lawrence transformed it into the camera-ready copy in an incredible eight weeks.

In conclusion, I wish to express the hope that readers will call to my attention any errors they may observe.

W. le Noble
Stony Brook, N.Y.

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Chapter 1

ELEMENTARY CONCEPTS IN CHEMISTRY

1-1. THE SCHRÖDINGER EQUATION

The Schrödinger equation [1] is the key to much of our present understanding of organic chemistry. It is true that the organic chemist had by 1925 acquired an impressive amount of physical and chemical information about the numerous compounds of carbon found in nature and many others synthesized in the laboratory. Undeniably, he had succeeded in constructing a comprehensive framework - the structural theory - to account for the number of structural isomers, and he had deduced the spatial relationships of the atoms within a molecule so as to account for stereoisomerism as well. Indeed, each time that new facts came to light that did not fit the theories of the structural theory and the tetravalent, tetrahedral carbon atom, small extensions of these ideas such as the chemical incompatibility of groups, steric hindrance, tautomerism, and so on sufficed to save the ball-and-stick view of his science. However, the development of quantum mechanics after 1925 led to so many new compounds and their interconversions that it is fair to say

1. A bibliography of classic papers and books useful to organic chemistry students of quantum chemistry has been given by F. L. Pilar, J. Chem. Educ., 37, 587 (1960).

that organic chemistry owes its decisive new directions to the small group of people, among them Schrödinger, who were at that time rewriting the basic laws of physics.

The Schrödinger equation is a differential equation written as follows:

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{\partial^2\Psi}{\partial y^2} + \frac{\partial^2\Psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E_{tot} - E_{pot})\Psi = 0$$

Here Ψ is the square root of the probability of finding a given particle of mass m at a location x, y, z. The equation is the result of a radical departure from classical mechanics, which would attempt to seek definite information about the precise location of the particle. The derivation and background of the equation need not concern us [2]; suffice it here to say that the solution (i.e., integration) of the differential equation in any particular case is a set of one or more ordinary equations giving Ψ as a function of x, y, z, m, and E. The equations then portray a family of surfaces about the origin where Ψ and Ψ^2 have certain values.

1-2. THE PARTICLE IN A BOX

As a simple if hypothetical example of how one might proceed to solve the Schrödinger equation, let us consider the case of an uncharged particle (so that $E_{pot} = 0$ and $E_{tot} = E_{kin}$) of mass m in a one-dimensional box of length a; that is to say, the energy of the particle is set at infinity at any location other than y = 0, z = 0, and $0 < x < a$ (see Fig. 1-1). The equation then reduces to

$$\frac{\partial^2\Psi}{\partial x^2} + \frac{8\pi^2 m}{h^2} E_{tot}\Psi = 0$$

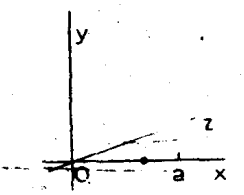

Fig. 1-1. The particle in a box.

2. Students interested in this aspect of our discussion are referred to (a) L. Pauling and E. B. Wilson, "Introduction to Quantum Mechanics", McGraw-Hill, New York, 1935; (b) H. Eyring, J. Walter, and G. E. Kimball, "Quantum Chemistry", Wiley, New York, 1944.

The general techniques used in the solution of differential equations cannot be reviewed here [3]; however, it can readily be verified by substitution that the solution of this equation is

$$\Psi = R \sin\left\{\frac{8\pi^2 m E_t}{h^2}\right\}^{1/2} x + S \cos\left\{\frac{8\pi^2 m E_t}{h^2}\right\}^{1/2} x$$

where R and S are integration constants. To evaluate these constants, we apply the boundary conditions, first of all that Ψ and $\Psi^2 = 0$ when $x = 0$:

$$\begin{aligned} 0 &= R \times \sin 0 + S \times \cos 0 \\ &= R \times 0 + S \times 1 \end{aligned}$$

Evidently, S equals zero, and our equation reduces to:

$$\Psi = R \sin\left\{\frac{8\pi^2 m E_t}{h^2}\right\}^{1/2} x$$

Then we apply: $\Psi = 0$ when $x = a$:

$$0 = R \sin\left\{\frac{8\pi^2 m E_t}{h^2}\right\}^{1/2} a$$

R cannot be 0, since then Ψ is 0 everywhere, even within the box. Alternatively then, the sine function must be 0. This is true when the following condition is fulfilled:

$$\left\{\frac{8\pi^2 m E_t}{h^2}\right\}^{1/2} a = n\pi$$

where n is an integer called a quantum number; it may not have the value 0 since then again Ψ becomes 0 everywhere. We can rewrite the result as follows:

$$E_{tot} = \frac{n^2 h^2}{8ma^2}$$

3. An excellent text for self-study of this topic is L. Kells, "Elementary Differential Equations", McGraw-Hill, New York, 1954.

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