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In the Classroom

Progress in Practice: Organic Chemistry in the Introductory Course

II. The Advantages of Physical Organic Chemistry

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The lasting legacy of the physical organic era is the ways in which we understand reactive intermediates and mechanistic pathways.

The application of physical chemistry to problems in understanding the reactivity of organic substances is one of the significant events in the development of main group molecular chemistry. Over the last 50 years, the contemporary mechanistic model for structure-reactivity relationships has emerged from the seemingly endless and encyclopedic inventory of these ideas into introductory instruction has been embraced but not necessarily melded. In this article, the argument is made that the existing richness of physical organic chemistry provides an overlooked

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Individuals involved in curriculum design often introduce new, modified, or applied ideas about instruction that span from classroom methods to philosophies of education. In this series, we examine progress in chemical education that is related to actual practices, and where many recommendations have originated from areas in higher education that exist alongside of and overlap with chemistry. Rather than an exhaustive review, we will select examples, background, and vocabulary that may either invite interested newcomers to explore a different area in their teaching, or provide language and precedent for individuals who wish to contextualize ideas they have developed independently.

—Brian P. Coppola, Series Editor

strategy for blending introductory instruction in chemistry to be more representative of a more contemporary view than traditional introductory programs are capable of providing.

A. historical context for “Organic Chemistry in the Introductory Course” was described in the previous *Progress in Practice* [1]. The subject matter of organic chemistry is a mature body of knowledge where the state-of-the-art is nonetheless accessible to introductory instruction. Wherever it is located in the chemistry curriculum, the descriptive, pictorial, and narrative nature of this subject represents an instructional advantage compared with subject areas where an understanding of postcalculus mathematics is crucial to teaching a contemporary perspective. The subject matter of modern organic chemistry provides a chance to demonstrate how to construct understanding and operate within a truly hierarchical structure of knowledge; this is not the case with typical survey courses.

Traditionally, introductory organic chemistry has been presented from the perspective of synthetic transformations. A representative sampling of early 20th century textbooks [2–6] indicates a course where the laboratory played a prominent role, and where issues of separation, isolation, and identification by qualitative chemical testing schemes were integrated throughout the presentation. The functional group organization, first introduced by Conant [7] in 1928, was an effort to bring introductory organic chemistry instruction into line with the contemporary practice. Interestingly, although the functional group approach was well-established in research by 1928, Conant is almost apologetic in the preface for the changes he introduced to instructors:

> The formal classification of compounds which is so valuable to the specialist may be barren to the uninitiated....The author’s experience...has led him to believe that the alcohols have certain advantages over the hydrocarbons as a point of departure...

Conant helped move introductory organic chemistry instruction out of the 19th century just as the development of mechanistic organic chemistry began to advance rapidly. The notion of chemical structure was dramatically affected by the coupling of a general acceptance of the electronic structure of matter and the corresponding understanding of bonding [8]. The first quarter of the 20th century brought together progress in creating useful models for chemical bonding with a deeper structural

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understanding of the compounds of main group elements and their transformations. In the second quarter of this century, the application of physical chemistry to problems of organic reactivity created a remarkably comprehensive and unifying conceptual framework. Understanding what had gone before improved, the reliability of predicting new outcomes increased, and rational synthetic design emerged. Organic chemistry moved from an encyclopedic inventory of “named reactions” and empirical functional group relationships to a set of principles related to structural relationships with transformations mediated by kinetic and thermodynamic phenomena.

Gortler [9, 10] and more recently Roberts [11, 12] have outlined a history of the early era of physical organic chemistry in the United States. Roughly between 1925 and 1940, a small community of chemists at four to six institutions were the primary caretakers of the early development of this emerging field. The electronic theory of organic reactions was reasonably mature by the mid-1930s, including the development of the now-familiar “curved-arrow” formalism presented by Robinson [13] and elaborated by Ingold [14]. The lasting legacy of the physical organic era is the ways in which we understand reactive intermediates and mechanistic pathways. For example, in 1939, the first speculative structure (Figure 1A) [15] of what would become known as a “nonclassical carbonium ion” was published. In his 1965 collection of papers, *Nonclassical Ions*, Bartlett elected not to reproduce this nearly unrecognizable representation in favor of the more contemporary version (Figure 1B) [16], a dramatic reminder of how visualizations and their representations were (and are) tied to the development of understanding [8, 17]. By the mid-1940s, the nonclassical cation problem had attracted the interest of the still-growing physical organic chemistry community [9, 11, 18], and the whole area of research blossomed. Alternatively, and perhaps more accurately, the growing flux of creative physical organic chemistry was itself so stunning that it drew the attention of experimentalists and theorists alike.

Authors of introductory organic chemistry textbooks, whose work provides a reflection of organic chemistry instruction, have never adopted “physical organic chemistry” as an easily identifiable organizational principle for the organic chemistry course in comparison with the prevalent “functional group approach.” On the other hand, an integrated treatment of bonding (including stereochemistry), kinetics, and thermodynamics is characteristic of introductory organic chemistry in the United States and Canada (a limited observation by this author, perhaps, but nonetheless based on reviewing credentials presented by students from outside these countries

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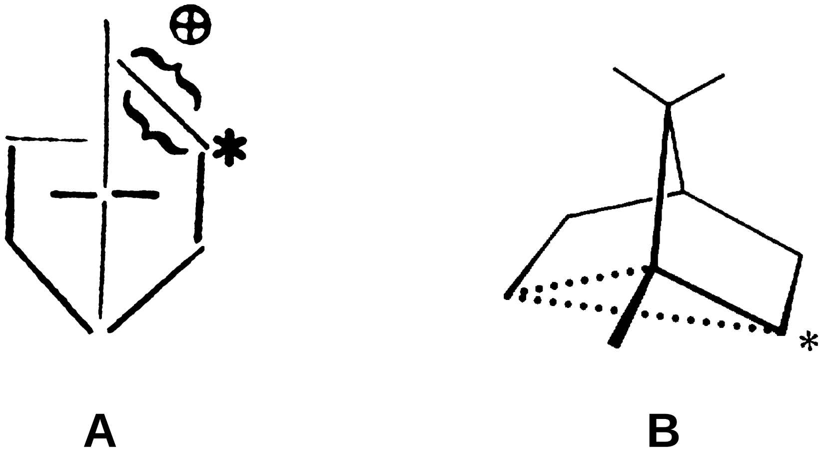

FIGURE 1. TWO DIFFERENT REPRESENTATIONS FOR THE ISOBORNYL CATION: (A) AS FIRST REPORTED IN 1939 AND (B) AS REDRAWN IN 1965. PERMISSION TO REPRINT (A) GRANTED BY THE ROYAL SOCIETY OF CHEMISTRY, CAMBRIDGE CB4 4WF, UK; PERMISSION TO REPRINT (B) GRACIOUSLY GRANTED BY THE PUBLISHER [16].

[seeking transfer credit at the author's institution] in which physical organic topics do not appear to have been emphasized). In the preface to the 1959 text by Morrison and Boyd [19], R. T. Arnold cogently laid out the instructional problem that these authors recognized as well as its solution:

> The application of these new physico-chemical concepts to the systematic study of the general transformations...really ushered in the era of modern organic chemistry. Attempts to modernize classical descriptive textbooks, by inserting newer concepts in a piecemeal fashion, have not been successful. (The authors) have written a unified book...and shown how these concepts can be used to "explain" the chemistry.

Physical organic chemists contributed to the shape of organic chemistry instruction through their involvement as textbook authors, often as coauthors with synthetic chemists. In 1959, Cram and Hammond [20] highlighted general structural chemistry by including spectroscopic methods as the introduction to the subject. In 1964, Roberts and Caserio [21] not only used qualitative results from physical organic chemistry, but also devoted 48 pages to introducing the quantitative linear free energy relationships that provided one of the historically important entry points for practicing organic chemists. This text also brought modern spectroscopic methods into the first chapters. Physical organic chemistry has since provided the canvas on which the first part of organic chemistry courses are painted. In 1975, Gutsche and Pasto [22] were among

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the last authors to include an extensive formal treatment of linear free energy relationships in an introductory text as well as an early and integrated approach to spectroscopic methods. The qualitative structure–reactivity relationships between substituted benzoic and anilinium acids, phenols, and their respective pK_a values, however, have survived as a staple of the modern texts. The first edition of Streitwieser and Heathcock in 1976 [23] increased the visible presence of strictly physical chemical phenomena. In 1984, Seyhan N. Ege, my colleague at the University of Michigan, introduced the first comprehensive and early use of pK_a values and the corresponding structure–reactivity relationships as a primary metaphor for all chemical transformations [24]. She also turned the use of the “curved arrow convention” into a powerful organizing principle in the text. In the 1987 5th-edition rewrite of the Cram and Hammond text [25], Stanley H. Pine, like Conant in 1928, argues for synchronizing instruction with practice. Contemporary organic chemistry uses a mechanistic organization of a few types of bonding changes, regardless of the functional group, as a framework for functional group reactivity [26]. Not every author has used a physical organic context to introduce the subject. For example, Kemp and Vellaccio (1980) [27] began their text with the structural principle of homology. Molecular orbital theory provides an even higher level of organization to the approach of using bonding changes as a basis for instruction. A comprehensive view of frontier molecular orbital (FMO) theory was advocated by Fleming in 1976 [28]. A first example of using FMO theory as a recurring thematic element can be found in the 1997 text by Maitland Jones [29]. The movement towards more contemporary work in courses can be seen in the introductory laboratory, where fewer and fewer organic and general chemistry texts rely on the kind of qualitative analysis schemes that have not been representative of the work of chemistry for over 30 years.

So-called “blended” courses in general and organic chemistry are being developed under the rubrics of both individual and systemic change efforts [30]. In fact, except for its explicit acknowledgment or, perhaps, its exploitation by instructors, organic courses are already “blended” by virtue of the natural integration of physical organic chemistry with synthetic chemistry over the last 40 years. With very little effort, there are already a remarkable number of places in the existing course framework where explicit attention to the consequences of physical chemistry in an organic chemistry context could be advantageous to both subject areas. As Bodner convincingly demonstrated 7 years ago [31], the consequential understanding of physical chemical

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ideas can be the single weakest deficiency in beginning chemistry graduate students. Recognizing the distinction between generating a numerical value (“ΔS = 3 eu”) and any corresponding conceptual understanding has driven a large number of important efforts to change examination (and instructional) practices [32–36].

Many topics could be used as entry points for increasing explicit attention to integrating (re-integrating, actually) the quantitative basis of organic chemistry with its rich qualitative models. Linear free energy relationships (LFERs) are still a standard way of examining appropriate systems [37, 38]. Hammett’s original creation of a quantitatively valid scale of substituent effects is simply elegant. An understanding of LFERs is accessible to students who have been introduced to structure-reactivity relationships through Hammett’s work. Acid–base chemistry also provides many opportunities to examine the descriptive interpretation of enthalpic arguments on differences in pK_a values as well as the need to re-examine those models in the light of carefully obtained quantitative ΔH and ΔS information. Since 1977, Carey and Sundberg [39] have included two superb examples of how early enthalpy-based rationalizations for inductive effects need to be modified in the light of quantitative thermodynamic data. The putative inductive explanations for the difference in pK_a between acetic and propanoic acids, in addition to differences in the chloroacetic acids, are inadequate. Acid–base chemistry, in general, is already visited from many perspectives in the majority of chemistry courses; simple articulation is needed within the course of study in order to rediscover the connections that already exist. Stoichiometry, too, emerges in many courses, and practically so in laboratories where students need to address the issues of relative amounts, limiting reagents, and so on. Heats of hydrogenation, which are typically used for assessing resonance energies and aromaticity, provide a structurally based use of a Hess’s law relationship that could be examined in other examples. The original literature contains many quantitative data about organic reactions that provide useful interpretive descriptions for discussing physical chemical principles. As is the case in research, experimental values should be the beginning, not the end, of a discussion of chemical properties. If carefully selected, presented, and then articulated to upper level courses, rate data and the results from isotopic substitutions could be used to set up elaborated discussions of these familiar systems in other parts of the undergraduate program. Computational chemistry, too, can be a topic that is visited in different ways through a sequence of courses.

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The undergraduate chemistry curriculum is at a familiar juncture in science instruction: when the maturity and complexity of a science begin to substantially increase the distance between contemporary activity in the field and its introduction to students. Introductory physics and biology courses are quite static and uniform across the country, as are the topics in many general chemistry courses. The most common strategy being used to reform general chemistry programs, as posited earlier [1], is to overlay a static group of topics with a new context (such as materials or environmental sciences). Are atomic structure, stoichiometry, electrochemistry, nuclear decay, the gas laws, and significant figures to define the introduction to chemistry the way Newtonian mechanics defines introductory physics? Is chemistry like calculus: a defined set of skills that simply needs to be learned in order for a student to go on to other courses? Or, as also argued earlier, are the reasons for the current look of general chemistry strongly attached to the needs of the engineering disciplines that emerged at the turn of the century? If so, then what of the needs of the biological science clientele who can often be a large fraction of introductory chemistry students in the 1990s, and whose literacy in molecular structural systems and their transformations can only come from courses offered in chemistry departments? For a provocatively new perspective on the organization of chemical sciences that could be used to inform a direction for new curricula, faculty are directed to two outstanding books written by Williams and Fraústo de Silva [40, 41]. The movement towards beginning with main group chemistry, either as the basis for the entire introductory course or as a contribution to blended programs, is indicative of giving molecular (and even supramolecular) topics their deserved place in the chemistry education of all students.

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