# Deeper Beneath the Surface of the Chemical Article

Richard G. Lawton and the Norbornyl Cation Problem

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This article is dedicated to the memory of Paul D. Bartlett.

Richard Lawton at the University of California at Berkeley in the 1950s. n his 1988 article [1] and 1995 book [2], Roald Hoffmann looked "Under the Surface of the Chemical Article." In these, Hoffmann examines the workings of chemistry that are not evident on the surface of a printed page or a luminescent screen. He provides an important semiotic analysis of how we represent and communicate scientific ideas and the impact of these on scientific practice. As a case in point related to

molecular architecture and its understanding, he describes the link between mental imagery in the case of bridged bicyclic molecules and the opportunity for intellectual progress that accompanied research in that area of chemistry.

Hoffmann's perspective is not limited to journal articles. Anyone who has done re-

search for the Ph.D. degree would readily agree that there are important aspects to scientific practice represented, for example, in the difference between the day-to-day workings of your research project and the written thesis you ultimately present. Scientific priority is strongly linked with publication, and its attribution plays an important role in a range of personal and professional practices. We all use noteworthy negative examples of practice, such as the press conference announcing

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cold fusion or an exposed case of misconduct, as exceptions that reaffirm our faith in the traditional customs. This confidence is warranted, but the operations of science are nonetheless painted in shades of gray rather than the clear contrast of black ink on a white page.

### **Beginnings of a Life in Science**

In this essay, I will look under the surface of a

chemical article at a story involving one of my colleagues at the University of Michigan, Richard G. Lawton. The biographical aspects of Professor Lawton's story are an interesting glimpse into one individual's pathway into science, and they also provide a crucial lens through which the development of ideas and actions should be viewed

in order to understand the picture "beneath the surface" and how it impacts scientific practice. In 1943, as an 8-year-old boy in Berkeley, California, "Richie" Lawton asked Santa for a chemistry set, specifying "a chamistre set...a five dollar one and don't forget it" [5] (Fig. 1). By the time he was in junior high school, he had been taken under the wing of Professor William Dauben at the University of California at Berkeley. As a high school senior, Lawton received an Honorable Mention

Pergetta School Veralta School Mec. 13 To Santa Cluc Mis is what & want for Amas a chamistre set and a look on codesand segnate il wast a magicuset. & med some stockings. Chuld you make that chametre Fec. 15 set a five dollar one an don't Richie Lautor

Fig. 1. A request to do chemistry in 1943. (Courtesy of Professor Lawton.) Fig. 2. The need to prepare intermediate VI, used in a biogenetically patterned synthesis in the strychninecurare alkaloid series, also contributed to the norbornyl cation problem. (Reprinted with kind permission from Elsevier Science Ltd., copyright 1996, The Boulevard, Langford Lane, Kidlington OX5 1GB, U.K.) in the 1952 Westinghouse Science Talent Search. Between 1952 and 1956, Richard G. Lawton attended UC-Berkeley as an undergraduate, and his 1956 undergraduate thesis, with Elliot Bergman, was titled "Migratory Aptitude of the Trifluoromethyl Group." Instead of immediately enrolling in a graduate program, Lawton worked at the Merck Company (Rahway, New Jersey) for one year prior to a call from the U.S. Draft Board in 1957. From 1957 to 1959, after basic training, he worked as a chemist at the Walter Reed Army Institute of Research.

In September 1959, Lawton enrolled in the graduate program at the University of Wisconsin at Madison, where he earned a Ph.D. in 1962. One of his first projects in Professor Eugene E. van Tamelen's laboratory was the biogenetically patterned synthesis of the strychnine system via the intermediates shown in Fig. 2 (as presented in the original publication) [4].

## **First Digression**

Gortler [5] and, more recently, Roberts in The Chemical Intelligencer [6] have outlined a history of the early physical organic chemistry era in the United States. Between roughly 1925 and 1940, a small community of chemists at 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, as evidenced by the development of the now-familiar "curved-arrow" formalism. Devising ways of understanding reactive intermediates and mechanistic pathways is a lasting legacy of the physical organic era. In 1939, the first speculative structure (Fig. 3A) [7] 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 un-

recognizable representation in favor of the more contemporary version (Fig. 3B) [8]. In his preface, Bartlett notes that he protested "for years against the inappropriate name 'nonclassical ions,' [but that he was] overruled by general usage and [has employed] the term because of its extreme familiarity." By the mid-1940s, the nonclassical ion problem had attracted the interest of the still-growing physical organic chemistry community [5, 6, 9]. Perhaps more accurately, the growing flux of creative physical organic chemistry was so stunning that it drew the attention of experimentalists and theorists alike. The experiments designed to examine these solvolysis problems still stand as some of the most intellectually rigorous investigations of the last 50 years.

## Making Connections

In 1960, during the beginning of Lawton's second year of graduate school, Saul Winstein gave a seminar at Madison about the nonclassical ion problem [10]. The rate of loss of chirality in the solvolysis of a norbornyl system (via an achiral intermediate) was part of the evidence used to support the nonclassical ion structure. Winstein noted the formation of the two enantiometric products as the only possible outcomes (Fig. 4) [11] in the solvolysis of norbornyl systems. Ed Kosower, an assistant professor at Madison at the time, asked why the cation could not be intercepted to form any other products. Winstein replied that there were simply no other realistic possibilities beyond the two enantiomers, an answer reflecting the wealth of experimental evidence that only the racemic mixture was ever observed.

Questioning the assumptions in a statement the way that novices often do, Lawton imagined an alternative: the nucleophilic attack at the primary carbon that would release the cyclopentenylethyl derivative (Fig. 5). Of course, others had considered this possibility and its implication: that the cyclopentenylethyl derivative might



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Fig. 3. Two different representations for the isobornyl cation: (A) as first reported in 1939 and (B) as recast in 1965. [Permission to reprint (A) granted by The Royal Society of Chemistry, Cambridge CB4 4Wf, U.K.; permission to reprint (B) graciously granted by the publisher.]

Fig. 4. The structure of the bicyclo[2.2.1]2-heptyl (norbornyl) carbonium ion, as represented by Winstein and Trifan in 1949. (Reprinted with permission. Copyright 1996 American Chemical Society.)

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solvolyze to the norbornyl cation. But secondyear graduate students from another area of research would not be inclined to know that Winstein had drawn the cyclopentenylethyl cation in 1951 (Fig. 6) [12], nor the fact that Paul D. Bartlett's group, at Harvard, had begun working on the synthesis of the required cyclopentenylethyl precursor in late 1960 [13]. The third volume of Olah and Schleyer's Carbonium Ions series [14] is an excellent resource on the early history of  $\pi$ -participation in nonclassical carbocation chemistry, including Sargent's [14, p 1101] important discussion of the evolution of representations used by Winstein for the norbornyl cation structure. Bartlett's masterful selection of papers for the beginning of Nonclassical Ions also summarizes the significant intellectual and historical connection between early  $\pi$ -bridged (homoallyl) carbocations and other neighboring-group-assisted structures such as the bromonium ion. However, the formal conceptual use of the term " $\pi$ -route" was not codified by Winstein until 1961 [15].

Not only did Lawton see the cyclopentenylethyl pathway alternative, he already knew how to prepare the precursor. During the course of work on the strychnine problem, the alkylation of ethyl ethylcyanoacetate with 3-cyclopentenyl tosylate was used to prepare the intermediate labeled VI in Fig. 7. Lawton performed the alkylation reaction with the parent nucleophile, ethyl cyanoacetate, as a "bootleg" project during the first part of 1961 (Fig. 7). By the end of a three-week period, Lawton had prepared multigram quantities of the cyclopentenylethyl alcohol that was a derivatization away from the solvolysis experiment (Fig. 7). About this time, Lawton informed van Tamelen about his activities on this project, and van Tamelen gave him "encouragement and permission to pursue the experimentation independently, as the sole investigator" [16]. Eugene van Tamelen also wagered with Lawton, in the amount of one dollar, that the molecule would not close to the norbornyl structure. Both the p-bromobenzenesulfonate (brosylate) and p-toluenesulfonate (tosylate) derivatives were oils, hence difficult to purify. Preliminary solvolysis experiments were performed by dissolving the brosylate in acetic acid and letting the solution stand at room temperature. Later on, rate experiments, which are best done with highly purified materials, were performed with the crystalline p-nitrobenzenesulfonate (nosylate) derivative (see "R" in Fig. 7).

Van Tamelen was away from Madison when Lawton performed the solvolysis experiments. In fact, he was at UCLA as part of their seminar series. Before he gave his presentation, he received a phone call from Carlton Placeway, the graduate student on whose work he was reporting. Placeway had been directed by van Tamelen to call if the synthesis he was working on was completed so that the results could be included in the seminar. During the phone call, Placeway also informed van Tamelen that Lawton had performed some preliminary solvolyses and that the cyclopentenylethyl p-nitrobenzenesulfonate had, in hot aqueous acetic acid, completely closed to racemic norbornyl acetate. Although these solvolysis experiments were not part of van Tamelen's original plan for his presentation at UCLA, he did include them in his discussions with the faculty, and especially with Saul Winstein. In addition to paying off his bet when he returned to Madison, van Tamelen advised Lawton to obtain refined data by learning how to do more precise solvolysis rate experiments because they were, indeed, important. Acetolysis studies using the cyclopentenylethyl p-nitrobenzenesulfonate were run in Harlan Goering's laboratories in Madison, where Lawton learned the appropriate experimental techniques.

According to Lawton, the three-dimensional orbital representation used by Streitwieser (Fig. 8) [17] was in his mind as he listened to the exchange between Kosower and Winstein. Streitwieser's model was not the only orbital picture in the literature, either. Roberts, with the assistance of M.J.S. Dewar, formulated a "nortricyclonium ion" representation in 1954 (Fig. 9) [18].

## Second Digression

Paul D. Bartlett's group was, of course, trying to make a cyclopentenylethyl compound in order to test the same idea. The cyclopentenyl skeleton had already been incorporated into a more elaborate architecture by Winstein [19], where



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Fig. 5. Proposed capture of the Norbornyl cation to give the cyclopentenylethyl derivative, as visualized by Lawton during Winistein's 1960 seminar. Fig. 6. As early as 1951, Winstein introduced the third dashed line into the norbornyl cation to account for the contribution from the cyclopentenylethyl cation form. (Reprinted with permission. Copyright 1996 Société Française de Chimie.)



transannular participation was confirmed, but the intellectual and aesthetic significance of actually closing a monocyclic precursor to the archetypal norbornyl system was compelling. At about the time that Lawton transformed a substantial portion of the alcohol to the crystalline nosylate, Shelton Bank, then a postdoctoral student in Bartlett's group, was completing his preparation of the cyclopentenylethyl alcohol and its tosylate derivative [13].

## **First Convergence**

When van Tamelen returned from UCLA, he carried a request from Winstein to Lawton: could he (Winstein) present the results from Lawton's solvolysis experiments at the upcoming American Chemical Society (ACS) meeting? On March 18, 1961, Lawton wrote to Winstein (Fig. 10) [20], giving him permission to discuss his results. Lawton describes the initial solvolysis of the brosylate and his "[to] be completed soon" rate studies on the alcohol and other sulfonates.

The abstract for Bartlett's invited presentation ("Factors Affecting the Behavior of Carbonium Ions") at the meeting is a single sentence and unrevealing, which is not surprising given the lead time required for printing and the dynamically changing face of the carbonium ion landscape during this period: "Factors affecting the behavior of carbonium ions will be discussed" [21]. Bartlett spoke in the second of two sessions organized and presided over by Harold Hart (Michigan State University). Hart's main intention was "to have the main protagonists (antagonists?) in the non-classical ion controversy, Herb Brown and Saul Winstein, appear on the same platform, each state his case before a live audience and in the presence of other distinguished scientists, especially Paul Bartlett, who might help to resolve the differences" [22]. According to Hart and his colleague, G.J. Karabatsos, Bartlett not only presented Shelton Bank's results from solvolyzing cyclopentenylethyl tosylate to the norbornyl products but also presented rate-enhancement data from methyl substitution on the double bond. Karabatsos "was sitting next to Ned Arnett who, at that moment, leaned over and whispered 'and still the champ'." These experiments certainly did not settle the active discourse on the nonclassical ion question, or the norbornyl system specifically. The actual rate accelerations found by Lawton and Bartlett and Bank were quite modest. It was only appreciated later through Schleyer's research that  $\pi$ -participation had to compete with rather large solvent participation [23].

No one from the 1961 St. Louis ACS Meeting, which ended on Thursday, March 30, carried the information about Bartlett's results back to Madison. On April 3, 1961, Lawton submitted his manuscript [24] as a communication to the *Journal of the American Chemical Society* [20], which was received and accepted on April 6, 1961 (Fig. 11).

Sometime between April 3 and April 9, 1961, part of the news of the events at the ACS meeting reached Madison. On April 10, 1961, Lawton wrote to Bartlett to inform him that he had performed this reaction independently (Fig. 12) [20]. Whether or not this was the first time that Bartlett became aware of Lawton's results is unknownthere is unfortunately no account of how or when Winstein elected to speak of Lawton's results, although he (Winstein) was a member of Hart's morning session during the daylong symposium. Bartlett's reply to Lawton, sent from Cambridge on April 18, 1961, indicates that a future communication is planned, as are additional experiments (Fig. 13) [20]. As will become even more apparent later, the Lawton-Bartlett correspondence points to the (expected!) differences that can arise between the historical record (as presented in published works, which rely on submission dates, public communication, and the interpretation by writers) and the events that occurred, exemplified wonderfully in this case, by the simultaneous and independent work of scientists in different locations. In particular, Lawton, for whom the news of Bartlett's work came



Fig. 7. Reaction pathway used in the original synthesis of a strychnine intermediate (VI in Fig. 2) and the "bootleg" project resulting in cyclopentenylethyl alcohol. Fig. 8. Streitwieser's 1956 orbital representation for the norbornyl cation. (Reprinted with permission. Copyright 1996 American Chemical Society.)



after the submission of his communication, validates the general historical priority that the scientific community affords to accepted publications in peer-reviewed journals. Bartlett, from whose perspective Lawton's results follow the work done by his group at Harvard, refers to Lawton's results as "a decided improvement in elegance," a way that he, arguably tacitly and certainly without malice, advances the *empirical priority* of his own group's work.

On April 27, 1961, Lawton was sent a note from Assistant Editor to the Journal Marshall Gates in which Gates informed Lawton that "we have just had a manuscript covering closely related work from Dr. Paul D. Bartlett who asks that his paper be published simultaneously with yours...Unless you object, we intend to arrange for simultaneous publication ... " [20]. Although on April 27, according to Gates' letter, there was time to publish the communications simultaneously, this did not occur. There are no authoritative accounts for why these manuscripts did not end up published together, but the most straightforward scenario, suggested by Hart [22], "is that Lawton's manuscript had already been sent to the printers (Easton, PA)." In the May 20, 1961, issue of the Journal, Lawton's paper appears unaccompanied. The communication from Bartlett and Bank appears in the next issue of the Journal, dated June 5, with the notation that the manuscript was received on April 24, 1961 [25]. The last paragraph in Bartlett's published communication begins with the following sentence: "The present ring closure has been investigated independently by R.G. Lawton of the University of Wisconsin," along with a reference to the communication that had appeared in the previous issue. Fittingly, one of the first reprint requests to Lawton came from Saul Winstein (Fig. 14).

## Second Convergence

In 1961, Satoru Masamune, a postdoctoral student in the van Tamelen group, and Lawton speculated on the proposal that the bicyclo[3.2.1]octyl system [26] that was being studied by their colleague, Harlan L. Goering, should be accessible via closure of the cycloheptenylmethyl brosylate in a way analogous to the cyclopentenylethyl closure to the norbornyl acetate (Fig. 15) [27]. Masamune knew, because he was aware of Gilbert Stork's synthesis of cycloheptenylcarboxylic acid [28], how to prepare the alcohol precursor. Together, he and Lawton synthesized the corresponding brosylate, performed acetolysis reactions, and measured rates for the closure relative to the solvolysis of the saturated cycloheptylmethyl analogue. The first-order titrimetric rate of the brosylate in 0.02 M aqueous acetic acid containing sodium acetate (0.022 M) was  $k = 0.645 \times 10^{-4} \text{ s}^{-1}$  at 61 °C, which was 101 times faster than that of the saturated compound. However, their Communication to the Journal was rejected on the basis of the fact that this closure had already been performed and published in 1960! Almost incredibly, neither Lawton's nor Bartlett and Bank's solvolysis reaction of their respective cyclopentenylethyl com-





TOP: Richard Lawton in Wisconsin in 1960. RIGHT: Richard Lawton (center) about 1961. Fig 9. The 1954 "nortricyclonium ion" formulated by Roberts and Dewar. (Reprinted with permission. Copyright 1996 American Chemical Society.) pounds is the first published example of a simple transannular  $\pi$ -participation closure of a monocyclic to a bicyclic system, although none of these scientists knew, in early 1961, of the previous work.

## **Third Digression**

Geneviève Le Ny, one of Hugh Felkin's first D.Sc. students, had already published the closure of the cycloheptenylmethyl compound to the bicyclo[3.2.1]octane (Fig. 16) in *Comptes Rendus* in late 1960 [29]. Le Ny's thesis (C.N.R.S., 1964) was primarily concerned with the reactivity of cycloalkylmethyl compounds (reaction rates, ring expansions, etc.).

Felkin writes [30]:

The larger cycloalkylmethyl compounds were made via the corresponding cycloalkenyl carboxylic acids (incidentally, we at first had some difficulty in making these acids in reasonable yields, but this difficulty was overcome when Gilbert Stork came to our lab in the 1950's and was kind enough to show us how to do it). Since we had these unsaturated acids, I told Mme. Le Ny it would be a good idea, as a side line, to look at the corresponding unsaturated brosylates to see if they would lead to bicyclic compounds via double bond participation. So she did, and they did, and I wrote the paper (including the misnaming of the compound in the title).

At the time, French D.Sc. theses were considered to be better, and more acceptable, if only the candidate's name appeared on any preliminary publications. Moreover, I then considered that only the names of those who had actually physically done the work should appear on the resulting paper (later, friends and colleagues convinced me that this attitude was irresponsible, since it made it look as though I was not prepared to take responsibility for the results; consequently, only about 30 papers from my lab do not bear my name).

Interestingly, the similarity between Lawton's and Le Ny's work is not limited to the chemical results: both results were the product of "side" projects, and both publications appeared with the student as the sole author. Given the fact that the Le Ny paper appears in *Comptes Rendus*, it is conceivable that the French publication would not be noticed immediately by scientists in the United States. The first published reference to Le Ny's work appears to be in a 1961 paper by Winstein and Carter [51] (received September 5, 1961) that had been presented at a meeting in early August.

Regardless of the empirical or presentational



priority, interpretation of the publication record (publication priority) constitutes the way in which scientists ultimately chronicled the events of simple  $\pi$ -participation. In Nonclassical Ions, Bartlett codifies history through the ordering of papers and in the informal commentary he provides [32]: "Lawton extended the method of Le Ny and Winstein into more familiar ground: he [a few weeks ahead of Bartlett and Bank] generated the norbornyl cation by the solvolysis of..." In 1972, Felkin, Le Ny, and coauthors [33] began a full report of the earlier solvolysis work done by citing papers by Winstein [19] and Le Ny [29] as



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March 18, 1961

Dr. Saul Winstein Separtment of Chemistry University of California Los Angeles 24, California

#### Dear Dr. Winstein,

Dr. van Tamelen suggested I write you concerning my resent finding that (3-syclepentenyl)ethanel bresylate upon solvolysis predness exe-nerbornyl acetate. Ragarding your request te speak about my work publieky, I feel that it would be quite appropriate for you te discuss this in any manner you wish.

Also, I should correct some data that you received. In his telephone conversation, Dr. van Tamelen did not talk to me, but heard about the results second hand. This resulted in the misinformation. The solvolysis was not carried out in sodium acetateacetic soid but acetic acid alsos. In the initial trial the bresylate in acetic acid was allowed to stand four days at room temperature, then heated to reflux for one hour. The product (85-90% yield) has an infrared spectrum identical with your published spectrum of nerbernyl bresylate acetolysis product. Comparison with the infrared spectrum of (3-sylopentenyl) ethanol acetate seemed to indicate there was none of this compound present, however, gas chromatographic analysis shows about 3%. Rate studies on both 3-eyelopentenglethanol and cyclopentane ethanol sulfonates should be completed scon.

I intend to publish this work as a communication, but until that time feel free to write me if you have any questions about the details of the work.

Sincerely,

#### Richard G. Lawton

Fig. 10. The March 18, 1961 letter from Lawton to Winstein. Fig. 11. Postcard of acceptance sent to Lawton from the Journal of the American Chemical Society. RIGHT: Fig. 12. The April 10, 1961 letter from Lawton to Bartlett. the basis on which the  $\pi$ -participation reaction was extensively studied: "Afterwards, this reaction was studied extensively and is now well known." The two notable exceptions to this interpretation are in Bartlett's original paper (as described earlier) [25] and in Winstein and Carter's paper [15] in which Le Ny was first cited. Winstein had a clear knowledge of the independence of Le Ny, Lawton, and Bartlett and Bank's works, and he does not order the events for us, nor imply an order, based on the publication or submission dates.

#### **Fourth Digression**

The appearance of science, as presented publicly and in retrospect, has always been distinct from the generally nonlinear operations of science. I have introduced terms such as *presentation priority, empirical priority*, and *publication priority* to help label some authentic distinctions in the way scientists think about how scientific results are communicated and credited. As we enter the twenty-first century, access to the Internet enables any individual to conveniently present work to the world without any intermediate arbitration. In many ways, this will have an impact on our understanding of the history of scientific discoveries in the future. Peer-reviewed venues will continue to serve to codify the chronology, regardless of the medium, but the distinctions between what appears on and under the surface of that medium will become more complex now that individual scientists have access to nearly instantaneous and worldwide presentation. The question of whether this access is a right or a privilege is also significant.

#### Last Digression

A handful of exceptional stories of remarkable discoveries typically constitute the understanding of scientific culture shared among scientists. In the 1990s, for instance, tales of the discovery of fullerenes pervade our collective conscious. Lawton's paper reporting the cyclopentenylethyl closure is barely a page long and contains approximately 550 words. The paper has been appropriately cited over the years, and Lawton's work is more integrated into the fabric of chemistry than are many other discoveries. Indeed, a portion of the story is sometimes told during the physical organic chemistry course at Madison [34]. The fact that there is an extensive and interesting background story is not unusual. The fact that this story is not widely known today is not unusual either. The fact that so few of these stories are known, however, is unfortunate. Stories beneath the surface of science need to be toldeven when the account is not, to borrow a mild criticism from a referee of this essay, about a "key development" and the individual is not a "major player on the scientific stage." Over the years, the fundamental narrative nature of our science has become less and less familiar to us except in our own efforts to suppress it. How many of these stories do you know? How many have you told to your students? The emeritus and near-emeritus faculty in my department tell stories about a community of science that often sound like the recollections you might hear at a family reunion. Their stories are fundamentally different from the stories my younger colleagues tell, which are more often like yellow journalism



#### April 10, 1961

Da. Paul D. Bartlett Cenverse Memorial Lateratory of Bavard University Cambridge 38, Massachusetts

Dear Dr. Bartlett,

The Editor of the Journal of the American Chemical Society has recently informed me of the acceptance of my article "1,5 Participation in the Solvelysis of  $\frac{A}{A}(\vec{S}-\text{Cyclopentenyl})$  othyl <u>p-Nitrobensene-</u> sulferate" for publication as a communication sometime in May. I understand you have already disclosed your similar findings at the recent A.C.S. meeting. I am sorry to hear our ideas have everlapped, but I feel that the works are sufficiently different so as not to detract from one another.

Yew will probably be interested in some of the details of my experimental work. Alkylation of ethyl symmometete with  $\Delta^3$ -cyckopentenyl tecylate was accomplished by potassium t-butoxide in t-butanel. A one mole excess of ethyl symmemetate was used to prevent bis-alkylation. The solid tosylate was added to the potassium salt of the symme ester, and reflux with stirring for several hours completed the reaction. Average yields have been 60-70%. Hydrelysis of the resulting symme ester was carried out with petassium hydrelide to give  $\beta^3$ -cyclepentenyl malonic acid which was desarbexylated in refluxing pyridine to give  $\beta^3$ -cyclepentenyl acetic acid. Lithium aluminum hydride reduced this to the alcohol. Yields on all these steps were quite high (70%).

I found that the tosylate and the brosylate of (<sup>3</sup>-syclepentenyl)ethanel were both liquids at room temperature, but the g-mitrobensenesulfounte was a highly crystalline solid, m.p. 65-67°. This was used in most of my work. All my rates were run in glacial acetic acid and product studies on small amounts of materials were accompliabed with a Gelay column. A large product study was carried out on eight grams of mitrobensenesulfounts (90% yield of exe-morbornyl acetate).

- 2 -

I do not plankary further work on these compounds in the immediate future, especially since my research problem under Dr. wan Tamelen is of a synthetic mature.

Sincerely,

Richard G. Lawton

or one of those late-night television "magazines," dominated by tales of who did what to whom, and for how much. Although I can dismiss some of this difference as being due to misty-eyed, rose-colored nostalgia on the one hand, I cannot ignore the general illiteracy (and even disdain) of the broader issues of scientific culture that I have observed firsthand in so many individuals.

Herschbach has maintained that we do research according to paradigms but that we teach by parables [35]. Although he was specifically referring to undergraduate instruction, Herschbach's comment is equally correct for graduate and faculty communities. Tribal knowledge and the fundamental metaphors of any culture have historically relied on oral rather than written histories. But it only takes one generation to forget or neglect them, and then oral histories are gone. In chemistry instruction, and in science instruction in general, even the most widely accessible historical anecdotes have decayed to the point of becoming off-to-the-side comments in introductory textbooks, generally located in easy-to-ignore sidebars or shaded boxes.

All disciplines wrestle with the issue of the difference between what is ultimately presented to the world, in writing or otherwise, and the depth beneath the surface of that representation. In fact, appreciating the distinction between "information" and "meaning" is a characteristic of learning anything. Our colleagues in music departments care deeply about the life behind the notes and directions that comprise a musical composition; our colleagues in language departments have the custom of exposing young writers to more experienced ones in order to specifically examine the process of developing an idea, through drafts, to a publishable literary piece. In chemistry, depending on the custom in one's research group, we do a reasonably good job of bringing graduate students (and sometimes undergraduates) into the current culture of professional writing. On the other hand, we tend to restrict ourselves to trial and error as the sole method, and we have, as argued earlier and elsewhere [36], systematically disintegrated much of the historical, philosophical, and otherwise sociological dimensions of what we do from how we educate.

How do we reintegrate history, philosophy, linguistics, and sociology of science into the education of undergraduates? Textbook sidebars and other lessons that are isolated from the science are, at the least, naive strategies. On the other hand, intergenerational transfer of the operations of science is a reality. There are other responsibilities beyond the operational ones that we do not even realize we have, ones involving the other oral and written traditions, precisely because it

# HARVARD UNIVERSITY

DEPARTMENT OF CHEMISTRY

23 Oxford Strees Combridge 38, Manachusene, U.S.A

April 18, 1961

Mr. Richard G. Lawton Department of Chemistry University of Wisconsin Madison 6, Wisconsin

Dear Mr. Lawton:

Thank you for your letter and account of your work on the ring closure of  $\triangle$  <sup>2</sup>-cyclopentenylethyl p-nitrobenzenesulfomate. Your work and ours are quite parallel, but your use of a solid ester is a decided imporvement in elegance.

We are submitting a Communication also, and are continuing with some of the many experiments indicated by the first results.

With best wishes,

Sincerely your Paul D. Bartlett (per 44)

PDB:bb

Fig. 13. The April 18, 1961 letter from Bartlett to Lawton. Fig. 14. Reprint requests from Winstein to Lawton (postmarked June 26, 1961).

takes only one generation to lose them. Recently, a group of colleagues at the University of Michigan chemistry department has been learning to reveal the depth beneath the chemical article to a relatively large number of undergraduates. As part of a structured study group program for firstyear students, the 1961 Communication by Richard G. Lawton was handed out in early November to be read and discussed under the supervision of upper-level undergraduate leaders [37]. The ultimate objective was for each group of 15-20 students to develop and refine a set of questions as though they were going to meet with the author, which, of course, they did. On an afternoon in early December, 80 of 120 first-term, first-year students were able to meet with Professor Lawton for two hours and ask their questions. They heard about the strychnine, the delayed publication, and the dollar. They heard it as nostalgia and as the way people can be motivated by the science. They wanted to know even more than they had prepared for. With equal fervor, they wanted to know if Lawton still had the dollar he won (he does) and whether a triple bond could  $\pi$ -participate with two different electrophiles in the same way that a double bond can participate with one. They wanted to know what the " $\Delta$ " meant. Since Lawton reported the five-membered ring case and Le Ny reported the sevenmembered ring case, they also wanted to know what the results from the six-membered case were. A group of 80 first-year, first-term chemistry students *wanted to know*.

How many of these stories do you know? How many have you told to your students?

What else lies beneath the surface of these contemporary parables?

Another story for another day...

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## **REFERENCES AND NOTES**

1. Hoffmann, R. Angew. Chem. **1988**, 100, 1653; Angew. Chem. Int. Ed. Engl. **1988**, 27, 1593.

2. Hoffmann, R. *The Same and Not the Same*; Columbia University Press: New York, 1995.

 Taken from the actual note that had been saved by "Richie" Lawton's second-grade teacher at Perlata Elementary School, Ruth Smith, in 1943.

4. van Tamelen, E. E.; Dolby, L. J.; Lawton, R. G. *Tetrahedron Lett.* **1960**, 30.

5. (a) Gortler, L. "The Development of a Scientific Community: Physical Organic Chemistry in the United States, 1925–1950." In *Essays on the History of Organic Chemistry*, Traynham, J. G., Ed.; Louisiana State University Press: Baton Rouge, 1987; pp 95–113; (b) Gortler, L. *J. Chem. Educ.* **1985**, *62*, 753.

6. Roberts, J. D. The Chemical Intelligencer 1996, 2(3), 29.

7. Nevell, T. P.; de Salas, E.; Wilson, C. L. J. Chem. Soc. **1939**, 1188 (as described by Bartlett in Ref. 8, p 27).

8. Bartlett, P. D. Nonclassical lons; Benjamin: New York, 1965. In the







ABOVE: Richard Lawton around 1988. Fig. 15. Figures taken from an unpublished manuscript by S. Masamune and R.G. Lawton, "Acetolysis of  $\Delta^{-}$ -Cycloheptenylmethyl p-Bromobenzenesulfonate." Fig. 16. Figures used to describe the solvolysis of the cycloheptenylmethyl brosylate reported by G. Le Ny. (Reprinted with permission. Copyright 1996 Académie des Sciences.) citation to the Nevell paper on p 27, Bartlett writes that "their formula is here projected in the manner common elsewhere in this book."

9. Tarbell, D. S.; Tarbell, A. T. *Essays on the History of Organic Chemistry in the United States, 1875–1955*; Folio: Nashville, TN, 1986; pp 393–410.

10. Unless otherwise indicated, anecdotal recollections are from R. G. Lawton, University of Michigan, as told to the author.

11. Winstein, S.; Trifan, D. S. *J. Am. Chem. Soc.* **1949**, *71*, 2953. 12. Winstein, S. *Bull. Soc. Chim. Fr.* **1951**, *18*, C55.

13. As reported by two sources: Shelton Bank, State University of New York at Albany, to the author in a private communication, and William Dean "Bill" Closson to R. G. Lawton. After obtaining his Ph.D. with Harlan L. Goering (Madison) in 1960, Closson joined the Bartlett group at Harvard, where he learned much of the history he later reported to Lawton. 14. *Carbonium Ions*, Vol. III; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley: New York; 1972.

15. Winstein, S.; Carter, P. J. Am. Chem. Soc. 1961, 83, 4485.

16. As reported to the author in a letter from Eugene van Tamelen, March 26, 1996.

17. Streitwieser, A., Jr. Chem. Rev. 1956, 56, 571.

18. Roberts, J. D.; Lee, C. C.; Saunders, W. H., Jr. *J. Am. Chem. Soc.* **1954**, *76*, 4501.

19. Bruck, P.; Thompson, D.; Winstein, S. *Chern. Ind. (London)* **1960**, 590. 20. Copies of R. G. Lawton's original correspondence, either received from others or in the form of a carbon copy of a typewritten letter, were generously provided by Richard G. Lawton.

21. Bartlett, P. D. *Abstracts of Papers*, 139th Meeting of the American Chemical Society, St. Louis, MO, March 21–30, 1961, Division of Organic Chemistry Abstract No. 19, p 10–0.

22. As reported to the author in a letter from Harold Hart, March 28,

1996.

23. Schreiner, P. R.; Severance, D. L.; Jorgensen, W. L.; Schleyer, P. v. R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1995**, *117*, 2663.

24. Lawton, R. G. J. Am. Chem. Soc. 1961, 83, 2399.

25. Bartlett, P. D.; Bank, S. J. Am. Chem. Soc. 1961, 83, 2591.

(a) Goering, H. L.; Greiner, R. W.; Sloan, M. F. J. Am. Chem. Soc.
**1961**, *83*, 1391: (b) Goering, H. L.; Sloan, M. F. J. Am. Chem. Soc.
**1961**, *83*, 1397; (c) Goering, H. L.; Sloan, M. F. J. Am. Chem. Soc.
**1961**, *83*, 1992; (d) Goering, H. L.; Closson, W. D. J. Am. Chem. Soc.
**1961**, *83*, 3511.

27. Masamune, S.; Lawton, R. G. Unpublished results from the University of Wisconsin (courtesy of Professor R. G. Lawton).

Stork, G.; Landesman, H. K. J. Am. Chem. Soc. **1956**, 78, 5129.
Le Ny, G. Comptes Rend. **1960**, 251, 1526.

30. As reported to the author in a letter from Hugh Felkin, May 1, 1996. 31. Reference 15. The paper was received September 5, 1961, and is listed in a footnote as having been presented at the Symposium on "Dynamic Stereochemistry" (*Abstracts of Scientific Papers*, XVIII International Congress of Pure and Applied Chemistry, Montreal, Canada; University of Toronto Press: Toronto, 1961.)

32. Reference 8, p 368.

33. Chuit, C.; Felkin, H.; Le Ny, G.; Lion, C.; Prunier, L. *Tetrahedron* **1972**, *28*, 4787.

34. As reported to the author by Mr. Matthew Cohen, November 8, 1996.

35. Herschbach, D. R. J. Chem. Educ. 1993, 70, 391.

36. Coppola, B. P.; Daniels, D. S. "Mea Culpa: Formal Education and the Dis-Integrated World." *Science and Education* (in press).

37. Coppola, B. P.; Daniels, D. S. *Chem. Educator* **1996**, *1*(2), S 1430-4171(96)02018-3. Avail. URL: http://journals.springer-ny.com/chedr.



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