

PAUL D. BARTLETT'S CHEM 17a: A PIONEER COURSE IN PHYSICAL ORGANIC CHEMISTRY

Leon B. Gortler, *Brooklyn College of the City University of New York*
and Martin D. Saltzman, *Providence College*

In the decade of the 1930's, *physical organic chemistry* developed to the point where it had become a recognizable and discernable hybrid discipline. The term *physical organic* was first used in print in 1940 by Louis Hammett as the title of his monograph (1). However, several books and monographs covering some of this work by the British chemists Robert Robinson (1933) (2), Christopher K. Ingold (1934) (3), Thomas Martin Lowry and William Alexander Waters (1935, 1937) (4), and Herbert Benn Watson (1937, 1941) (5) had already appeared.

Watson, in the preface to the first edition of his book, summarized the developments that had occurred up to this point (5):

Professor G.N. Lewis's conception of the sharing of one or more electron pairs by two atoms gave a new and illuminating picture of the bonds which link carbon atoms into chains and rings, and set organic chemists the task of interpreting the reactions of carbon compounds of various types in terms of the electronic

structures of the molecules. The problem was attacked ten to fifteen years ago, mainly by Professors Lapworth, Robinson, and Ingold. Considerations of the chemical evidence in the light of the electronic theory of valence led to results of great value, and it now became possible to express many

of the earlier ideas in more definite and elegant language. Then followed the very fruitful alliance of organic chemistry with physics and mathematics, and a much clearer view of the principles underlying the behaviour of organic compounds has been opened up by the aid of modern physical methods of investigation, and of Planck's Quantum Theory and Schrödinger's Wave Mechanics.

A major question is how these new ideas were being disseminated to students in other countries, particularly in the United States. In this article we present a glimpse of this process of transmission of knowledge by examining the content of Chem 17a, "Theoretical Organic Chemistry," given in 1938 at Harvard University by one of the future



P. D. Bartlett, courtesy of G. M. Bartlett

American masters of physical organic chemistry, Paul D. Bartlett (1907-1997). Dr. Ralph Thompson (6) audited the course and his class notes have been deposited in the archives of the Chemical Heritage Foundation in Philadelphia (7). The notes are 177 pages long and cover 27 lectures presented from February 7, 1938 to May 4, 1938.

Chem 17a was the first half of a two-semester course for graduate students. The second half, Chem 17b, dealt with natural products chemistry and both were taught for many years by J.B. Conant (8,9). As Conant successively became department chair and then president of Harvard, his courses were taken over by new faculty members. Given Bartlett's theoretical orientation and the fact that he had been a Conant graduate student, it was only logical that he would teach Chem 17a.

George Miller Bartlett, Paul Bartlett's father, was a mathematically inclined mechanical engineer who had attended Amherst College and taught at Case School of Applied Science and then in the Engineering Department at the University of Michigan. In 1910 the Bartlett family moved to Indianapolis, where Bartlett's father went to work for the Diamond Chain Company. When Paul Bartlett was in college, his father became a professor in the School of Engineering at Purdue.

George Bartlett was a major influence in Paul's life, taking a formal role in his instruction whenever he considered what Paul obtained in school was not satisfactory. In talking about his father, Bartlett said, "He used to read to me quite a lot. We read things like Jules Verne and science fiction and other kinds of things he and I were both more interested in than any [other] people around (10)."

After finishing high school in Indianapolis, Paul Bartlett entered Amherst College, his father's alma mater, to study chemistry. There he was influenced by Ralph Beebe, a young physical chemist familiar with the latest developments in this subject, and Howard W. Doughty, an organic chemist with a Johns Hopkins Ph.D. under Remsen. Bartlett was interested in organic chemistry, but he also took a fair amount of mathematics while at Amherst. Recognizing his physico-mathematical slant, his instructors directed him to Harvard and James B. Conant.

At Harvard Bartlett worked with Conant (9) but was strongly influenced by Elmer Peter Kohler (11). This was a particularly fortunate combination: Conant, the strategist and big thinker, and Kohler, the superb researcher and technician. Bartlett's paper with Conant based on his doctoral dissertation reflects the methodi-

cal analytical approach that was to characterize his later research (12).

After Harvard, Bartlett spent a year with P.A. Levene at Rockefeller Institute working on stereochemical problems. Nights and weekends he did research in a laboratory at Columbia University, finishing up some details from his thesis research (13). From 1932 to 1934 he was an instructor at the University of Minnesota, where he quickly established a research program and published several papers on reaction mechanisms and stereochemistry (14).

After two years at Minnesota, Bartlett was called back to Harvard, where Conant had become president of the university and Kohler was chair of the Chemistry Department. In retrospect, it appears as if they were choosing Conant's successor, his heir apparent, to the deanship of American physical organic chemistry. Within a few years, Bartlett's reputation had spread; soon almost every physical organic chemist to end up in a large research-oriented university had passed through his laboratory as a graduate student or postdoctoral fellow.

The course, Chem 17a, can be summarized as an introduction to the use of physical methods and mathematics to understand organic structure and reactions. The course begins with the structure of organic compounds, later considers the chemical bond, and then takes up the mechanisms of a variety of reactions. Reference to very recent works of leading investigators in the field are made in almost every lecture, thus attesting to the contemporary nature of the course. This reflects Bartlett's familiarity with the current literature and, in a number of instances, his own research interests. It may also reflect the influence of Kohler who, it is said, destroyed his lecture notes for his advanced organic course at the end of each year and began again from the literature the following year.

In an interview with Bartlett conducted by Leon Gortler, Bartlett commented on Kohler's influence on his research and on his teaching (10):

BARTLETT: Certainly the most influential teaching that I encountered in my first year at Harvard was (Elmer P.) Kohler's Chemistry 5.The course that he gave, I think, never left anyone uninfluenced. He centered it around the really important questions and problems, and how these things were solved, and who had done what about them and so on. It was just a great course. Kohler, of course, had been Conant's research professor, and he was one of the people held in highest respect in the university as a whole.

GORTLER: Did you consciously try to pattern your Chem 5 course after his course? [Chem 5, The Car-

bon Compounds, the second course in organic chemistry, had been taught by Kohler until his death in 1938.]

BARTLETT: Not consciously, but actually I was not aware of any other way to teach organic chemistry, except basing it on what are the important problems. If there are lots of people who don't do this, why, it probably means that Kohler was very influential on my teaching. It seemed to me that it was pretty axiomatic that this was the right way to go at it.

Bartlett's choice of topics, then, reveals his views on what were the important problems at the time.

Bartlett's lifelong interest in physical organic chemistry was the result of his interaction with many people: his father, his instructors at Amherst in chemistry and mathematics, Kohler and, of course, Conant. In a letter to William M. Tuttle in 1977, Bartlett gave a retrospective assessment of Conant's research(15):

Conant was an organic chemist interested on the research level in two branches of organic chemistry. The first was so-called physical organic chemistry, which was an uncommon preoccupation in those days in which the mathematical and physical relationships governing reactions or organic compounds were worked out and used as a framework for understanding what was going on at the molecular level. His other field was the chemistry of natural products, notably including chlorophyll. I never knew which of these branches of research he considered more fun, but it was quite clear that he considered natural products the more important. Organic chemistry originally arose in the attempt to understand more about living things, and he felt that chemistry must get back to this objective as fast as it could work through the enormous complexities involved.

During the years of Bartlett's graduate work, 1928 to 1931, Conant became increasingly more interested in biochemistry and natural products. Bartlett, however, throughout his career, never showed an interest in biochemical problems even though he spent a post-doctoral year with P.A. Levene at the Rockefeller Institute.

Bartlett was aware of this intriguing anomaly, and he comments on it on a number of occasions. In the 1978 interview he was asked why he went to work for Levene. He replied (10):

Well, there were two components of that. Conant always felt that you must go on to more important things than you were on and he felt that clearly an end use of organic chemistry on any level was to get into the biochemical side.

Bartlett then comments on the effect of the Rockefeller year on his career:

I don't feel that that was in the direct line of my career at all. If I'd been a different kind of person, I might have picked up all sorts of stuff by osmosis at the Rockefeller Institute, but I didn't. I mean, I just never evolved into an even peripheral biochemist, and I think this was probably a disappointment to Conant, because by his way of analyzing these things, I think it marked me as someone who had reached my high point and wasn't going anywhere from then on.

In 1973, Bartlett wrote to Conant on the occasion of Conant's 80th birthday and expressed somewhat the same concern. After talking about the ways in which he was influenced by Conant he wrote (16):

And yet I realize that I am not a good example of a real Conant disciple, for I never moved into either of those main streams where you correctly predicted that the action be — physics and biochemistry — nor would I, I think, if I had it to do again. I have continued to be fascinated by organic reaction mechanisms, and the field has been anything but static. This fascination, too, I owe in good part to you.

Bartlett was obviously ambivalent about his career. He continued his work in physical organic chemistry because it gave him great pleasure and great satisfaction, and yet he always felt that he was, in some way, a disappointment to his mentor Conant.

Summaries of the Chem 17a lectures can be found in the appendix to this paper. Almost all the lectures included references to the material being discussed, and many included tables of data (meticulously copied by Thompson) and/or mathematical analyses of the problems being discussed. The first several lectures deal with the structure of organic molecules and various physical methods—ultraviolet spectroscopy, electron diffraction, and, especially, X-ray analysis—used for the determination of structure. The data for what appear to be ambiguous bond lengths as well as the unreactivity of vinyl halides are rationalized by the use of resonance theory. At the end of this section he talks briefly about steric factors and their effect on the chemistry of organic molecules. He mentions the failure to synthesize *tri-tert*-butylcarbinol but suggests that it might be synthesized by "some highly refined method." Bartlett was sufficiently intrigued by the problem to attempt the synthesis of this bulky alcohol, and in 1945 he reported the success of this work (17). Inasmuch as the work had been initiated before the war, it is clear that Bartlett had more than an academic interest in the problem when he mentioned it in 1938.

Bartlett then begins a discussion of what Thompson titles "The Nature of the Chemical Bond." He spends several lectures discussing polarizability and dipole moments, bond energies derived from heats of combustion and heats of formation, and then makes a brief shift to a discussion of thermodynamics and its application to organic chemistry. Some of this material has now made its way into many undergraduate textbooks.

Bartlett's interest in physical methods and in thermodynamics reveals something of his approach to research. He was always seeking ways to achieve the quantitative measure of a chemical change. By lecturing on these methods, he was in fact learning by teaching. This approach to research was certainly influenced by Conant. In the 1978 interview Bartlett talked about Conant's approach to research (10):

I remember that fairly early on in the game, Conant said, "Anyone can identify a good research problem. The real work of it is to find something that you can do that works. If you want to measure something, find something that you can measure that works."

In the final fifteen lectures, Bartlett turns his attention to a variety of organic mechanisms. First he takes up free radicals, methods for trapping them and measuring their rates of formation, and the effects of steric bulk and resonance on their formation. Free radicals would eventually be a subject for one of Bartlett's major research programs. He then proceeds to a discussion of acids and bases and the measurement of acid and base strength in aqueous and nonaqueous systems. Acid-base catalysis in ionic reactions was then discussed, followed by a lengthy review of studies of the mechanism of the mutarotation of glucose to illustrate this type of catalysis.

The next several lectures deal with the work of Ingold, Hughes, Hammett, and others on nucleophilic substitution— S_N1 versus S_N2 . In this discussion Bartlett considers kinetics, stereochemistry, and the effects of solvent. At one point he mentions the α -lactone as a possible explanation for the retention of configuration in the reaction of β -chloropropionic acid with dilute base. Thompson writes, "This α -lactone formation looks fishy." It is impossible to tell whether this is the conclusion of Bartlett or Thompson.

Bartlett then takes up molecular rearrangements, where he discusses the work of Whitmore, Meerwein, as well as some of his own results with Pöckel. He completes the course with a discussion of ionic and free radical additions to double bonds. He cites his own recent work with Tarbell as well as the work of Lucas, Conant, Taylor, Ziegler, and Kharasch, but he does not mention

the bromonium ion proposal published by Roberts and Kimball in 1937. To a contemporary observer this course, given in 1938, would still be a very good introduction to physical organic chemistry. This is the best possible tribute to Paul D. Bartlett, one of the outstanding pioneers in American physical organic chemistry.

APPENDIX

CHEM 17a - Theoretical Organic Chemistry, February 7, 1938 - May 4, 1938

Lecture 1 (100)*

Structural considerations; importance of Lewis theory in structure; assignment of number of electrons for stable form of an element. X-ray studies to determine bond lengths; advances in application to less oriented states than crystals.

Lecture 2 (102)

X-ray diffraction discussed in detail. Discussion of normal covalent radii and comparison of bond distances with radius sum.

References to work of Bragg & Bragg, Debye, Compton, DeBroglie, Thomson, Randall, Pauling, Brockway, Sutton.

Lecture 3 (109)

Discussion of C-C bond distances as well as C-X bonds in various aliphatic and aromatic molecules. Other types of bonds discussed based upon X-ray data. Correlation between X-ray data and resonance theory. References to work of Brockway, Sidgwick, Pauling, Lucas.

Lecture 4 (115)

Resonance theory and further explanation of bond lengths discussed with respect to specific examples: vinyl halides; nitro compounds; diazo compounds. Reference made to Robinson's "Outline of an Electrochemical Theory" and Ingold's, 1934 *Chem. Rev.* article.

Lecture 5 ((121)

Further discussion of X-ray results with respect to carbon chains; use of electron diffraction and ultraviolet methods to determine radii. Steric factors governing radii. References to work of Pauling & Brockway, Stuart, Carothers, Heitler, London, Wilson, Dushman, Slater & Frank (*Introduction to Theoretical Physics*).

Lecture 6 (127)

Steric factors in certain molecules, e.g., tri-*tert*-butyl carbinol, biphenyls with restricted rotation. The nature of the chemical bond: derivation of relationships involving dielectric constant and polarization.

Lecture 7 (133)

Discussion of molar refractivity, polarizability, and dipole moments. References to work of Hückel, Debye, Smyth, Sutton.

Lecture 8 (139)

Dipole moments of aliphatic and aromatic compounds, correlation with structure, vector analysis of dipole moments. References to work of Lefevre, Kistiakowsky, Pauling, Kharasch.

Lecture 9 (145)

Calculation of dipole moments and relationship to structure, e.g., conformations in cyclohexane. Bond strengths: Definition of and problem with ionic organic reactions. References to work of Williams, Sutton, Sidgwick, Weissberger.

Lecture 10 (153)

Thermochemical data: Heats of combustion and formation. Bond energies: Methods of measurement and difficulties in interpretation. Resonance energy from heats of formation and combustion. Heats of hydrogenation and their interpretation. References to work of Pauling, Kistiakowsky, Giauque, Pitzer, Kossel, Teller.

Lecture 11 (157)

Thermodynamics: entropy calculations; free energy; equilibrium constants; barriers to rotation.

Lecture 12 (163)

Free energy and solubility; free energy and temperature; introduction to the study of mechanisms; free radical reactions in the gas phase. References to the work of Eyring, Polanyi, London, Gomberg, Walden, Ziegler, Rice & Rice (*The Aliphatic Free Radicals*).

Lecture 13 (169)

Activated complexes; Arrhenius equation; dissociation of bonds to form radicals and methods of measurement; magnetic properties of radicals.

Lecture 14 (175)

Free radicals: Examples involving dissociation of hexaphenylethane and dixanthyls, hydroquinone oxida-

tion. Rates of dissociation and methods of measurement using I_2 , O_2 , and NO. References to Werner, Schlenk & Mark, Marvel, Conant, Ziegler, Michaelis.

Lecture 15 (181)

Effect of aliphatic groups on the dissociation of dixanthyls; resonance effects in dixanthyls and radicals in general; steric effects in radical dissociation. References to the work of Hückel, Pauling & Wheland, Ziegler & Ewald, Bent.

Lecture 16 (187)

Mechanism of the reaction of triphenylmethyl radicals and oxygen. Organic acids and bases; methods of measurement of pK_a and pK_b . References to the work of Conant, Hammett, Hildebrand, Bjerrum, Wheland, Kolthoff.

Lecture 17 (195)

Further discussion of acids and bases; solvent effects; problems of measurement of strength of highly ionized acids in water; experimental methods to determine acidities and basicities in non-aqueous solvents. References to work of Conant, Hammett, Watson's *Modern Theories of Organic Chemistry* (5).

Lecture 18 (201)

Acid and base catalysis in ionic reactions; strength of acids: substituent effects, dipole moments; mutarotation of glucose. References to the work of Brnsted & Guggenheim, Lowry, Dawson, Ingold, Polanyi, Pedersen.

Lecture 19 (207)

Further discussion of the mechanism of the mutarotation of glucose involving acid and/or base catalysis. References to Reaction Kinetics Symposia in *Trans. Faraday Soc.* (1937), *Chem. Rev.* (1932), and work of LeMer.

Lecture 20 (217)

Medium effects in ionic reactions; problems with measurement of parameters that affect reaction — viscosity, dielectric constant, electrolytes. References to the work of Conant, Polanyi, Meisenheimer, Olson.

Lecture 21 (225)

Discussion of rates of reactions: alkyl chlorides with KI in acetone; alkyl bromides with pyridine; enolization versus racemization; kinetics of racemization versus

tautomerization; Discussion of reactions which do not clearly involve ions. References to the work of Olson, Hughes, Ward, Dawson, Cowdrey.

Lecture 22 (231)

Kinetics of decomposition of trialkyl sulfonium compounds; Walden inversion mechanism; various experiments proving inversion of configuration discussed; S_N1 and S_N2 reactions of halides. References to the work of Conant, Hammett, Hughes, Ingold, Polanyi.

Lecture 23 (239)

Problem of the mechanism of the substitution reactions of secondary halides; evidence for the formation of carbocations in organic compounds; structure of carbocations. References to the work of Whitmore, Ingold, Hughes, Ward, Polanyi.

Lecture 24 (245)

Solvolysis reaction mechanisms. Wagner-Meerwein rearrangements; kinetics of rate of rearrangement of camphene hydrochloride.

References to the work of Hammett, Taylor, Whitmore, Meerwein, Bachmann, Bartlett, Young, Winstein, Johnson, Burton, Ingold, Meisenheimer.

Lecture 25 (253)

Carbocations and molecular rearrangements; migration aptitudes; further discussion of the pinacol and the isobornyl chloride rearrangements, including role of catalysts. References to work of Ingold, Bartlett & Pöckel, Meerwein, Whitmore.

Lecture 26 (261)

Mechanism of addition of bromine to double bonds: Role of free radicals; evidence for radical as well as ionic mechanism; Kharasch's mechanism of addition of HBr. References to the work of Price, Pfeuffer, Ingold.

Lecture 27 (269)

Mechanism of ionic addition of bromine to alkenes: Experiments and interpretation. References to the work of Lucas, Francis, Conant, Bartlett & Tarbell, Taylor, Robinson, Ingold.

* Page in notes

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4. W.A. Waters, *Physical Aspects of Organic Chemistry*, G. Routledge & Sons, Ltd., London, 1935; 2nd ed., D. Van Nostrand Co., New York, 1937. Waters is listed as the only author, but Lowry was influential in the preparation of the book and is credited with the introduction to both the first and second editions.
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6. Ralph Thompson entered Harvard in 1934 after receiving his B.Ed. from Southern Illinois Normal University. He did his doctoral work principally with E.P. Kohler but also worked with George Kistiakowsky. Dr. Thompson completed his Ph.D. in 1938 and after one year of post-doctoral work with J.B. Conant went to work for Union Oil Products Company in Chicago. In 1961 he moved to Nalco Chemical Company and retired in 1968 to become a self-employed consultant.
7. Archives of the Chemical Heritage Foundation, 315 Chestnut Street, Philadelphia, PA 19106. The archives also contain a collection of the papers of P. D. Bartlett which he donated to the Foundation.
8. We have located Bartlett's own notes for Chem 17a taught by J.B. Conant in 1930 in the Bartlett collection at the Chemical Heritage Foundation. This will be the subject of a separate report.
9. For further information on Conant see: P. D. Bartlett, "James Bryant Conant," *Biogr. Mem. Nat. Acad. Sci. USA*, **1983**, *54*, 91-124.
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ABOUT THE AUTHORS

Leon B. Gortler is Professor Emeritus of Chemistry, Brooklyn College, Brooklyn, NY 11210-2889, who earned his Ph.D. at Harvard under the tutelage of P. D. Bartlett. Martin D. Saltzman is Professor of Natural Science at Providence College, Providence, RI 02918. Both authors are past chairs of HIST.

NOTE: Professor Bartlett died in Lexington, MA on October 11, 1997; see *Chem. Eng. News*, **1997**, Nov. 10, 45.

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