Howard E. Zimmerman (1926–2012)

H E. Zimmerman

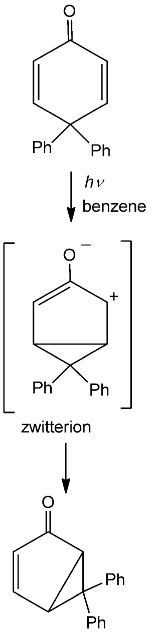
Howard E. Zimmerman, Professor of Chemistry at the University of Wisconsin, Madison, since 1960, died on February 12, 2012 as a result of a fall. Since 1990, Zimmerman was the Hilldale and A. C. Cope Professor of Chemistry at UW. He was the recipient of many prestigious awards over the course of a very long and productive career, including the American Chemical Society James Flack Norris Award in Physical Organic Chemistry (1976), the Halpern Award of the New York Academy of Sciences (1980), the American Institutes of Chemists Pioneering Award (1985), the ACS Arthur C. Cope Scholar Award (1991), and the IUPAC Porter Medal for Photochemical Research (2006). He was elected to the National Academy of Sciences in 1980, and received a Senior Alexander von Humboldt Award in 1988. He organized the 1972 IUPAC Photochemistry Symposium in Baden-Baden, Germany, and five Pacifichem Symposia on Photochemistry, the latest in 2010.

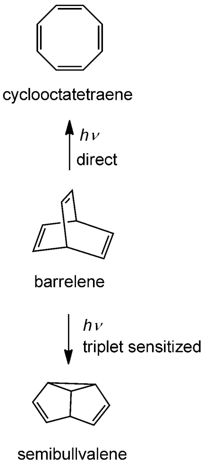
Howard Zimmerman was born in New York City on July 5, 1926, and grew up in Stamford, Connecticut. He served in World War II as a tank gunner in the U. S. Army, and enjoyed showing visitors his photograph as a teenager peering out of a large tank. He obtained a B.S. in Chemistry in 1950 and a Ph.D. in Organic Chemistry in 1953, both from Yale University. He was a postdoctoral fellow in synthetic organic chemistry with R. B. Woodward at Harvard from 1953 to 1954, and then went to Northwestern University as Assistant Professor. In 1960, he moved to the University of Wisconsin in Madison as Associate Professor, and was advanced to Full Professor in 1961. He officially retired in 2010 after a remarkable 56-year career, but continued to be active in research. At a symposium in his honor in Madison last September, he appeared to be in good spirits and good health. His sudden death was a great shock. He is survived by his third wife Peggy, three sons (Robert, Steven, and James) from his marriage to his first wife Jane, along with numerous stepchildren, grandchildren and step-grandchildren. His son Steven C. Zimmerman is Roger Adams Professor of Chemistry and Head of the Department of Chemistry at the University of Illinois.

Zimmerman (Z, as he was known to his circle of friends and students) is most well-known for his pioneering work in the field of mechanistic organic photochemistry. Together with George S. Hammond at the California Institute of Technology, Zimmerman helped to establish organic photochemistry as an exciting field of research in the early 1960s. A large number of graduate students and postdoctoral fellows were introduced to photochemistry by Hammond and Zimmerman and then went on to significant research careers in academia in this field. While there were other organic and physical chemists who participated in the remarkable photochemistry outburst in the late 1950s and early 1960s, Zimmerman and Hammond had the greatest impact. They gave back-to-back presentations of their seminal mechanistic concepts in organic photochemistry at the National Organic Symposium in Bloomington, Indiana, in June 1961, and caused a sensation. Soon, graduate and postdoctoral students were flocking to Pasadena and Madison to join their groups.

Their approaches were fundamentally different, and fed off each other. Hammond was concerned with identifying the electronic excited states responsible for a given reaction, and determining the kinetics of the fundamental processes utilizing newly developed sensitization and quenching techniques along with luminescence data. Zimmerman approached photochemistry from an entirely different perspective. As he noted, implicit in the literature of the 1950s was the suggestion that photochemical reactions were essentially random events, not subject to mechanistic analysis, as the large excitation energies were sufficient to break most carbon–carbon bonds. He also was aware of the remarkable finding of Havinga that *p*-nitrophenyl phosphates hydrolyzed more rapidly in the dark than the corresponding *meta* isomers, while on UV irradiation the opposite was true. Z had the rather controversial idea (for that time) that photochemical processes in organic molecules are in fact highly selective, and that it should be possible to understand the reactivity of excited states if one only knew the electronic structures of the reactive excited states, coupled with “organic intuition”, derived from the huge recent advances in understanding of organic reaction mechanisms.

Z invented a controversial “circle, dot, y” notation to represent electronic excited states of organic molecules, which he used to write explicit mechanisms for key photochemical processes. The triumph of mechanistic reasoning was the postulation of a step-by-step mechanism for the previously inexplicable photorearrangements of α-santonin, a tricyclic 2,5-cyclohexadienone. Z’s mechanism could account for all the observed reaction products as well as their stereochemistry. As a newly arrived postdoctoral fellow in September 1960, I was asked to tackle the dienone photochemistry problem using a model system, 4,4-diphenyl-2,5-cyclohexadienone. We quickly found that this compound underwent photorearrangements analogous to those observed for α-santonin. Our *JACS* Communication on this work in 1961, Z’s first photochemistry paper, and the subsequent full *JACS* paper in 1962, drew a lot of attention. Our proposed mechanism accounted for all the photorearrangement products in the model system as





well as in α-santonin in various media. Using simple molecular orbital theory, Z could predict which carbon–carbon bonds would be most likely to form and/or break following photoexcitation, and then specified which processes ensued on the excited state potential surface, and which occurred after decay to the ground-state surface. For the cyclohexadienones, Z postulated formation of ground state zwitterion intermediates, and their subsequent rearrangements analogous to those observed in carbocation chemistry. He found that the same zwitterions could be generated in the dark using a Favorskii reaction, while other later showed they could be chemically trapped. This success encouraged Z to undertake extensive photochemical investigations of a large variety of systems, in hopes of discovering new types of photochemical processes and to confirm his basic premise "that one could correlate excited-state structure with reactivity in a fashion characteristic of ground state organic chemistry".

A turning point in his research involved the multistep synthesis in 1960 of barrelene, bicyclo[2.2.2]octa-2,5,7-triene. The name derives from its obvious resemblance to a barrel, with the staves being three ethylene units attached to two methine groups. The compound is the formal Diels–Alder adduct of benzene and acetylene. Like benzene, barrelene has a set of six overlapping p orbitals, but these are not coplanar. Because it is not possible to avoid destabilizing overlap of opposite-sign lobes, the structure represents Möbius-type aromaticity, which was of special interest to Zimmerman and organic theorists in general.

Subsequently, Zimmerman and Grunewald discovered the triplet-sensitized rearrangement of barrelene to a tricyclic isomer, which they (controversially) called semibullvalene. This was the prototype of what became to be known as di-π-methane or Zimmerman rearrangements, which quickly became the focus of his research. Again, he proposed a rational step-by-step mechanism for the reaction, and predicted that some systems underwent reaction via triplet excited states, while others occurred via singlet excited states. This led in turn to studies of "bicycle rearrangements", in which a divalent carbon with two substituents "walks" around the π surface of a molecular fragment. In the 1980s, he became increasingly interested in the theoretical aspects of excited state decay as a determinant of the outcome of photochemical reactions. He proposed, along with others, that the nature of the products is determined by the details of the electronic relaxation process, that is, the contour of the excited and ground state hypersurfaces at the crossing point. In his later years, his attention was directed to host–guest and crystal lattice photochemistry.

Throughout his career, Zimmerman was interested in the interplay of theory and reactivity in organic chemistry. When not in the laboratory talking with students, he would be in his office doing computations of one sort of another. He authored a textbook entitled *Quantum Mechanics for Organic Chemists* in 1975, and gave American Chemical Society short courses on organic quantum mechanics and molecular orbital theory. He developed "MO Following—a Qualitative MO Counterpart of Electron Pushing". Perhaps his most important theoretical contribution was the development of the Möbius–Hückel concept for concerted pericyclic reactions (ring-opening, ring-closure, and cycloadditions) as an alternative to the Woodward and Hoffmann approach (*JACS*, 1965). The latter involved correlation of orbital symmetries of starting materials and final products and the construction of orbital correlation diagrams which indicated whether such processes are energetically allowed or forbidden. As applied to photochemical reactions, the Woodward–Hoffmann theory was fundamentally flawed, as correlations were drawn between MOs of the electronic excited states of reactants and products, even though product excited states are never formed. Furthermore, Woodward–Hoffmann theory could not be directly applied to processes in which elements of symmetry are absent.

Zimmerman's approach to this problem involved determination of whether transition states of pericyclic processes corresponded to Möbius (M) or Hückel (H) p-orbital arrays; that is, cyclic p-orbital arrays with either zero or an even number of sign inversions in pairwise orbital interactions (H), or arrays with one or an odd number of sign inversions (M). An H array is predicted to be stable with $(4n+2)$ electrons while an M array is predicted to be stable with $4n$ electrons. Z was annoyed that the organic community largely ignored his way of analyzing these reactions. Many academicians now prefer the Zimmerman M–H approach in teaching pericyclic reactions, since students more readily grasp it and can use it easily in solving problems. It also has the virtue of not invoking electronic excited states of reaction products in photochemical processes.

Zimmerman made important contributions in other areas of organic chemistry, including the mechanism of the Birch reduction, 1,2-carbanion rearrangements, the stereochemistry of ketonization of enols and enolates, and the synthesis of barrelene mentioned earlier. It is ironic that his most cited paper is not in photochemistry or organic theory, but rather is a paper published in *JACS* in 1957 on the Ivanov and Reformatsky reactions, based on research done at Northwestern with undergraduate student Marjorie Traxler. They focused on the mechanisms and control of stereochemistry in these reactions. Their premise was that the cation of the nucleophilic species, such as the enolate, would ultimately need to pair with the oxygen atom of the carbonyl reactant. They developed a six-membered-ring transition-state model whose preference for a chair conformation explained the stereochemical outcome of the reaction. This model has been applied broadly to aldol and related reactions and has come to be known as the Zimmerman–Traxler transition state.

As a research mentor, Z was demanding. He was attentive to what was going on in the lab, and had exacting standards for laboratory work. He would visit each person in the lab at least once a day to find out what was new. He worked long hours and most weekends, and expected the same from his studenten. He worked tenaciously to find good jobs for his students and postdocs, and remained intensely interested in their progress. He was proud that so many of his people obtained good academic positions. When visitors would meet with Z in his office, he would proudly show them a large map of the United States with over 80 stickpins indicating where his former research associates currently held academic positions. His annual Christmas newsletter to the Z group summarized what he had accomplished in the past year and the problems he was experiencing with the bureaucracy at UW and with funding. At times when difficulties arose in obtaining outside grant support for his research from the usual federal agencies, he would take the unusual step of using his own funds to support ongoing operations in his laboratory.

He also took an interest in the careers of other Wisconsin students whom he had come to know, and strongly supported many of his colleagues at Wisconsin in receiving national recognition, American Chemical Society awards, and particularly in gaining admission to the National Academy of Sciences.

Howard Zimmerman was an exceptional scientist, a great teacher, and a unique character. He was not interested in frivolous pursuits or small talk; he did not enjoy traveling, except to meetings, and rarely took a vacation. His commitment to science was all-consuming. He often felt that he didn't get enough credit and respect for what he had done, and sometimes even mentioned this in his lectures, to the discomfort of people in the audience. In fact, he was greatly respected, even if he didn't always believe it. The originality and high quality of his work spoke for itself and did not need external verification. He had enormous impact on the development of mechanistic organic photochemistry; it is hard to imagine this field without his seminal contributions. We honor Howard Zimmerman for what he taught us and for his personal example of courage, commitment and intellectual rigor.

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