

Howard Elliott Zimmerman



Courtesy of the University of Wisconsin–Madison

Howard Elliott Zimmerman was born July 5, 1926, in New York City to Charles and May (Cohen) Zimmerman, who moved with him shortly after his birth to Connecticut. He was the grandson of German Jewish immigrants from Austria. Following his graduation from high school, he enlisted in the Army and served in a gunnery division in the European theater of World War II. Howard loved to tell the story of how Rolf Huisgen introduced him at a seminar as a young professor on his “first” visit to Munich, initially unaware that his true first visit was in an American tank. Upon honorable discharge from the army, he entered Yale University and remained after his baccalaureate degree to work with James English for his Ph.D. in organic chemistry. His thesis was on the reverse Prins reaction, an indication of his early interest in stereochemical consequences of transition states. After his Ph.D. was conferred in 1953, he moved to Harvard University to spend one year on the synthesis of terramycin with R. B. Woodward. In 1950, he married the former Jane Kirschenheiter, with whom he had three sons, Robert, Steven, and James. Steve Zimmerman became an eminent organic chemist in his own right.

Upon beginning his first academic appointment at Northwestern University in 1954, Zimmerman’s early work was a continuation of his interest in stereochemistry. Most controversial was his early hypothesis that the ketonization of enols would involve initial formation of the contrathermodynamic (cis) products, even though most reactions involving reprotonation of enols and enolates appeared to yield the thermodynamic products. He recognized that these thermodynamic products were the result of equilibration of the initially formed less stable products. In subsequent work, he showed

that the transition state of the aldol concentration invoked similar stereochemical constraints, leading to the adoption of what is now quoted as the “Zimmerman–Traxler transition state”. In a related area, he, along with Erling Grovenstein, discovered what is now known as the Grovenstein–Zimmerman rearrangement, a reaction of carbanions similar to that of the Wagner–Meerwein rearrangement but with different theoretical foundations.

Zimmerman accepted a position on the faculty at the University of Wisconsin–Madison in 1960. Although not primarily known as a synthetic chemist, Zimmerman continued to contribute to significant advances in synthetic methodology, and the thesis work of his average Ph.D. student was more consumed with organic synthesis than with any other activity. His was the first synthesis of the $(\text{CH})_8$ hydrocarbons barrelene and semibullvalene. Subsequent syntheses of “rod” molecules, i.e., those with energy or electron donor/acceptor groups separated by bicyclo[2.2.2]octane moieties, added to the availability of molecular “Tinkertoys” for studying distance dependence of energy and electron transfer, preceding the work of Michl in the [1.1.1] series.

One of Zimmerman’s two major contributions to the field of physical organic chemistry lies in the area of topological control of organic reactions. Although Woodward and Hoffmann are properly given credit for symmetry correlation of molecular orbitals in reactions with cyclic transition states, Zimmerman’s early work paralleled Woodward and Hoffmann’s. His development of the Möbius–Hückel concept provided a more general topological basis for studying transition states and provided pedagogically more useful analogies to aromatic and antiaromatic transition states. It is a combination of the Woodward–Hoffmann rules and the Möbius–Hückel treatment which is now taught in modern undergraduate texts. That Woodward and Hoffmann’s work received early recognition, and ultimately a Nobel prize, is one of the common ironies of modern science.

After his move to Madison, Zimmerman developed and became known for his unique mechanistic approach to organic photochemistry. The current high degree of instrumental and theoretical sophistication which a photochemist can bring to bear on a mechanistic question belies the early crude “atomization and recombination” mechanisms characteristic of the field when Zimmerman began his work. Zimmerman was one of the first to suggest, and was the first to demonstrate, that relatively straightforward concepts such as bond order and electrophilicity, together with the organic chemist’s “arrow-pushing” tools, could be used to rationalize deep-seated photorearrangements and to make useful predictions. Underpinning this approach was the notion that, despite considerable photon energies, the fraction of excitation energy as a proportion of total bond energy in a molecule was relatively small. Thus, normal concepts of bond order and a smooth approach to a potential minimum within an excited state manifold still controlled reactivity. Zimmerman’s role in placing photochemistry on a rationalistic basis cannot be overestimated.

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The body of Zimmerman's work in photochemistry was extremely varied and included the photochemistry of carbonyl, nitro, cyano, and imino compounds as well as photorearrangements of a variety of hydrocarbon classes, including the teasingly named "bicycle rearrangement". Within these studies he embraced a breathtaking range of techniques, including new synthetic methodology, time-resolved fluorescence, new quantum yield techniques ("electronic actinometry"), molecular orbital calculations at all levels, crystal lattice effects, and even polymer immobilization! He will always be associated most firmly, however, with the photorearrangement he (unfortunately) named the "di- π -methane rearrangement". I say "unfortunately" because the ready acceptance of this appellation has discouraged more widespread use of the more appropriate "Zimmerman rearrangement". The Zimmerman reaction is probably the only photoreaction to be studied in such detail that it can really be considered to be "understood". It was to Zimmerman, perhaps, what vitamin B₁₂ was to Woodward: the ultimate achievement in the art of organic chemistry.

In his later career, Zimmerman developed a number of theoretical and calculational tools, e.g., the "delta density matrix" and an analysis of spin-orbit coupling, which are of great benefit in understanding photochemical reactivity. However, his most outstanding achievement in his last years was to experimental chemistry and the underlying theory of solid-state photoreactions, i.e., "molecules in a cage". As a result of his always careful experiments, we learned a great deal about how the crystal lattice controls photochemical pathways in the solid state. Unquestionably, these experiments were among the best he ever did, and these set the stage for much modern work in crystal chemistry.

Zimmerman's contributions were recognized by the conferment of many awards over the course of his career, including the James Flack Norris Award of the American Chemical Society, the Porter Medal, a Cope Scholar Award, American Institute of Chemists Pioneer Award, an Alexander von Humboldt Senior Scientist Award, and of course, election to the National Academy of Sciences.

Notwithstanding his numerous awards, Howard Zimmerman was most proud of and dedicated to the promotion of his numerous students. Almost 100 of them ended up in tenure-track academic positions, a fact he never failed to recite, and he was loyal and supportive of the success of all his students. Always determined to remain active, he lived to see many of his students retire. All of them viewed him with a mixture of awe, respect, and wonder. He was one of a kind.

Laren M. Tolbert

Georgia Institute of Technology

The articles in this issue of *The Journal of Organic Chemistry* are dedicated to the memory of Howard E. Zimmerman, who died on February 12, 2012. The Editors are grateful to Howard's students, colleagues, and friends for their diverse contributions to this special issue. The substance and quality of the research stand as a fitting tribute to Howard.

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Notes

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