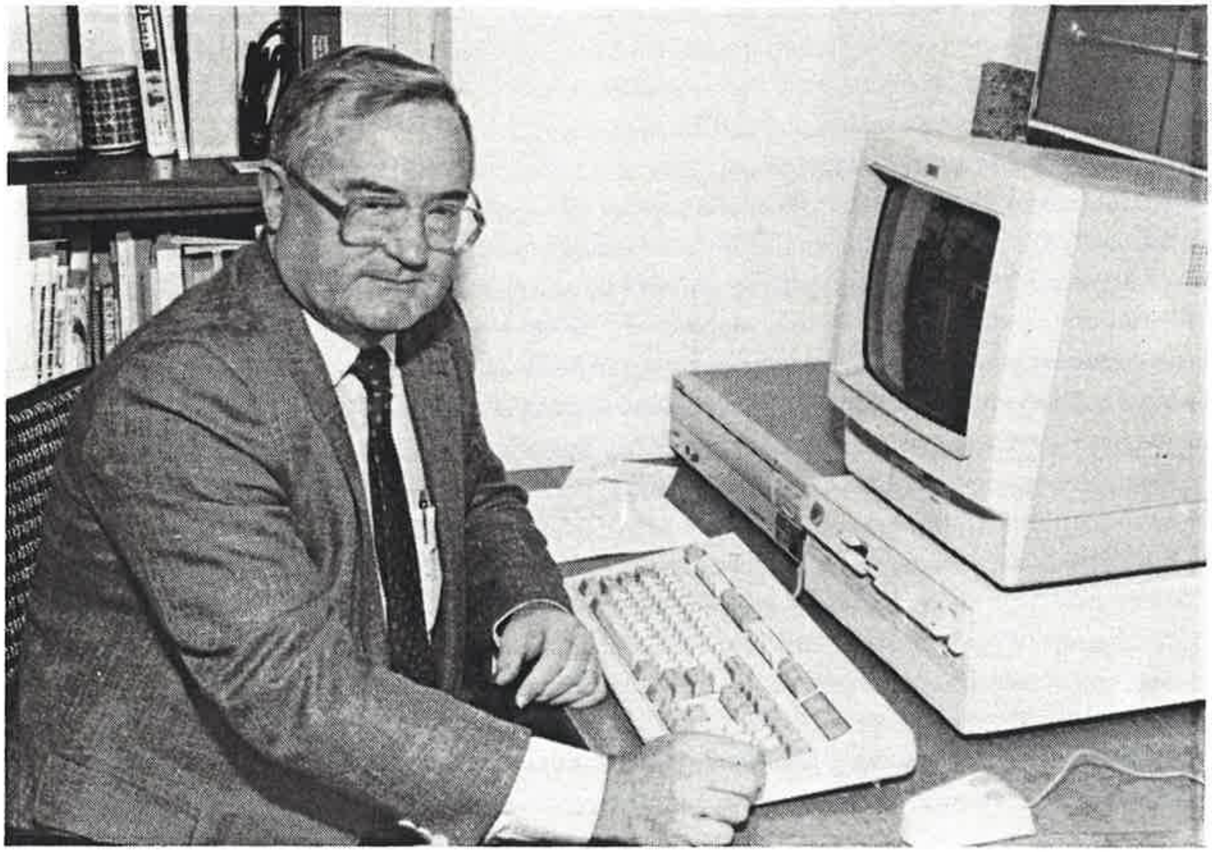
Orville L. Chapman Celebrates 60th Birthday



Intense creativity is perhaps the dominant characteristic that distinguishes all of the contributions that Orville Chapman has made to organic chemistry. His career has been marked by a series of imaginative and original approaches to a wide variety of chemical problems. Complementing this creativity has been his sure sense of what it is that constitutes a good, important, and most of all interesting problem. Never settling for the mundane, he has always concentrated on discoveries of maximal impact. Orville has also always had a keen interest in education at all levels. This dedication has been manifested not only in his formal teaching, but also in his publications. There, one can always find a desire to educate the reader, and to distill questions down to their essence.

Orville L. Chapman was born in New London, Connecticut on June 26, 1932. After receiving his B. S. from Virginia Polytechnic Institute in 1954, he carried out graduate work in natural product chemistry at Cornell under the direction of Jerry Meinwald. His Ph.D., awarded in 1957, dealt with mechanistic studies on the conversion of scopinone to *m*-hydroxybenzaldehyde. That same year he joined the faculty at Iowa

State University as an instructor, and rapidly moved up the ranks to full professor in 1964. In 1974, he assumed his present position as Professor of Chemistry at the University of California, Los Angeles. It is interesting to note that along with a number of graduate students and postdocs, Orville's scientific legacy includes his son Kevin, who is now a Ph.D. organic chemist at Merck.

Orville has authored 153 research publications, 5 patents, 4 educational programs and 1 book, and was editor of the first 3 volumes of Organic Photochemistry. He has spoken at most major organic chemistry meetings. In addition, he served as director of the Gordon Research Conference on Organic Photochemisty in 1965 and chairman of the IUPAC Commission of Photochemistry over the years 1972-1976. Most noteworthy among the long list of his awards are the following: Alfred P. Sloan Foundation Fellowship, 1962; ACS Pure Chemistry Award, 1968; elected to National Academy of Sciences, 1974; first recipient of the Texas Instrument Foundation Founders Prize, 1974; ACS Arthur C. Cope Medal, 1978; and elected a Fellow of the American Association for the Advancement of Science, 1980.

Orville was one of the key players in the renaissance of organic photochemistry that began in the later 1950s. He clearly saw this new field as an opportunity to apply his interests in mechanistic chemistry and spectroscopic structure elucidation. His initial ventures in this area concentrated on products and mechanisms in the photochemistry of conjugated cyclic ketones. This prolific beginning was aided by the able assistance of his first graduate student, Daniel J. Pasto (presently at Notre Dame). In early work on tropolone photochemistry, Chapman began to capitalize on the relatively new technique of proton magnetic resonance to elucidate the structures of his complicated photoproducts. His penchant for spectroscopic innovation was demonstrated early when he uncovered new correlation between cycloalkene ring size and vinylic coupling constants[1], and developed a new technique for distinguishing primary, secondary, and tertiary alcohols based on coupled hydroxy proton spectra in DMSO solvent[2]. For his scientific accomplishments during this early part of his career, he was accorded the ACS Award in Pure Chemistry in 1968.

In the late 1960s, Orville ventured down a research path that would influence the rest of his career. He and his coworkers found that irradiations of various organic molecules cooled to 77K gave reactive intermediates that could be directly detected by IR spectroscopy. In this fashion, they reported characterization of ketene[3], strained olefin[4], and cyclopropanone[5] intermediates in low- temperature photolyses of cyclic carbonyl compounds. A major breakthrough came, however, when Chapman enticed a recent physical chemistry Ph.D., Jake Pacansky (presently at IBM in San Jose), to join his group as a postdoc. Pacansky brought with him expertise in the inert gas matrix isolation technique, which had thus far been primarily the province of spectroscopists. In short order, he had the Chapman group set up to take advantage of this more powerful tool.

Their first dramatic application of the matrix isolation method came in 1973, with the publication of the direct characterization of cyclobutadiene by IR spectroscopy[6]. Besides the novelty of this observation, these results (and similar ones published simultaneously by Krantz) were striking in that they seemed to suggest that the geometry of this fundamental reactive intermediate was square, or D_4h. Quantum theory, which was also rapidly becoming more sophisticated during this same time period, predicted a D_2h structure. Chapman soon reported elegant deuterium labeling experiments that were also consistent with the square structure[7]. These results initiated a flurry of theoretical activity directed toward cyclobutadiene, seeking compatibility between theory and experiment. This storm of controversy was only quieted several years later when work of others, with use of newer and more sensitive FT-IR spectroscopy, showed the presence of additional weak vibrational absorption's signaling a D_2h structure.

In this same year, Chapman reported the photochemical generation and spectroscopic characterization of another archetypical reactive intermediate, benzyne[8]. Over the next several years, there came a number of other novel matrix isolated molecules from the Chapman group, including twist-boat cyclohexane[9], benzocyclobutadiene[10], 9,10-didehydroanthracene[11], and 1,1,2-trimethylsilaethylene[12].

In the later 1970s, the matrix isolation work in the Chapman group took on a more mechanistic tone, with a focus on carbenes and nitrenes. In 1978, with J. P. LeRoux, Chapman reported that irradiation of argon matrix isolated phenyl azide gave 1-aza-1,2,4,6-cycloheptatetraene[13]. Until this time, there had been considerable speculation in the literature about the source of unusual products found in photochemistry of aryl azides. Chapman's landmark observation of the ring-expanded ketenimine photoproduct dissipated much of the confusion, and opened the door to a profusion of subsequent activity in his group and in others'. For the first time, photochemical, and in some cases thermal, rearrangements of various carbenes and nitrenes could be directly observed. Adding ESR capabilities to their arsenal of spectroscopic techniques led to additional intriguing results. Chapman and his coworkers found that photochemical interconversions between arylnitrenes and isomeric carbenes could be directly observed[14], as could rearrangements between regioisomeric tolylmethylenes[15]. Strong parallels could be found between the photochemical interconversions and those previously observed in gas phase pyrolyses. This work culminated in the characterization of the parent cyclohepta-1,2,4,6-tetraene[16], and confirmed its central role in rearrangements on the phenylmethylene energy surface. In a similar vein, their elegant spectroscopic studies of matrix isolated triplet ketocarbenes dramatically clarified the mechanism of the photochemical Wolff rearrangement[17].

Synthetic innovation has always also played a central role in Chapman's chemistry. Much of this originality can be seen in novel approaches to photochemical precursors. He has in addition carried out an active synthesis based program aimed at an elucidation of insect pheromone perception. His ultimate synthetic achievement, however, was the construction of the natural product carpinone[18]. Borrowing from experience his group accumulated on quinonoid compounds generated from photochemical extrusion reactions, Orville devised and accomplished a remarkably simple but elegant synthesis of this complicated molecule, where five contiguous stereocenters were correctly established in one cyclization step.

Although he has always had a strong interest in chemical education, in the last several years Orville has assumed a more active role in teaching methodology. This is exemplified by his recent post at UCLA as Associate Dean for Education Innovation. His contributions to this area include several novel computer programs that teach symmetry in science and effective scientific writing. His most monumental undertaking in this area, however, represents a particularly apt combination of his interests in education and spectroscopic methods. He has produced an extensive and powerful laser videodisc interactive program on solving FT-NMR problems, in collaboration with Arlene A. Russell.

Finally, I would like to offer a personal anecdote which illustrates Orville's enthusiasm for grand gestures. I was fortunate to be an undergraduate member of his research group at Iowa State University in the early '70s. To celebrate the publication of the cyclobutadiene manuscript in 1973, Orville threw an all-out New England style clam bake for his research group. Live clams and lobsters were imported from the east coast for the event. This was a major undertaking, since there were about 20 people present including group members and their partners. Being a sheltered midwesterner , I was just getting over the culture shock of my first experience with steamers and whole lobsters by the time that the feast seemed to be winding down. Suddenly, Chapman entered with a slight grin, said "Who's ready for seconds?", and began plopping *another* lobster down on each plate.

Happy 60th birthday Orville! Your friends in the photochemical community applaud your distinguished career and thank you for all the interesting chemistry you have given us. We wish you continued success as an innovator and an educator.

Selected References

1. Chapman, O. L. *J. Am. Chem. Soc.* **1963**, *85*, 2014.
2. Chapman, O. L.; King, R. W. *J. Am. Chem. Soc.* **1964**, *86*, 1256.
3. Chapman, O. L.; Lassila, J. D. *J. Am. Chem. Soc.* **1968**, *90*, 2449.
4. Barber, L. L.; Chapman, O. L.; Lassila, J. D. J. *Am. Chem. Soc.* **1969**, *91*, 531.
5. Barber, L. L.; Chapman, O. L.; Lassila, J. D. *J. Am. Chem. Soc.*, **1969**, *91*, 3664.
6. Chapman, O. L.; McIntosh, C. L.; Pancansky, J. *J. Am. Chem. Soc.*, **1973**, *95*, 614.
7. Chapman, O. L.; De La Cruz, D.; Roth, R.; Pacansky, J. *J. Am. Chem. Soc.*, **1973**, *95*, 1337.
8. Chapman, O. L.; Mattes, K.; McIntosh, C. L.; Pacansky, J.; Calder, G. V.; Orr, G. *J. Am.. Chem. Soc.*, **1973**, *95*, 6134.
9. Squillacote, M. E.; Sheridan, R. S.; Chapman, O. L.; Anet F. A. L. *J. Am. Chem. Soc.*, **1975**, *97*, 3244.
10. Chapman, O. L.; Chang, C. C.; Rosenquist, N. R. *J. Am. Chem. Soc.*, **1976**, *98*, 261.
11. Chapman, O. L.; Chang, C. C.; Kolc, J. *J. Am. Chem. Soc.*, **1976**, *98*, 5703.
12. Chapman, O. L.; Chang, C. C.; Kolc, J.; Jung, M. E.; Lowe, J. A.; Barton, T. J.; Tumey, M. L. *J. Am. Chem. Soc.*, **1976**, *98*, 7844.
13. Chapman, O. L.; LeRoux, J. P. *J. Am. Chem. Soc.*, **1978**, *100*, 282.
14. Chapman, O. L.; Sheridan, R. S.; LeRoux, J. P. *J. Am. Chem. Soc.*, **1978**, *100*, 6245.
15. Chapman, O. L.; Johnson, J. W. ; McMahon, R. J.; West P. R. *J. Am. Chem. Soc.*, **1988**, *110*, 501
16. McMahon, R. J.; Abelt, C. J.; Chapman, O. L.; Johnson, J. W.; Kreil, C. L.; LeRoux, J. P.; Mooring, A. M.; West, P. R. *J. Am. Chem. Soc.*, **1987**, *109*, 2456.
17. McMahon, R. J.; Chapman, O. L.; Hayes, R. A.; Hess, T. C.; Krimmer, H. P. *J. Am. Chem. Soc.*, **1985**, *107*, 7597.
18. Chapman, O. L.; Engel, M. R.; Springer, J. P.; Clardy, J. C. *J. Am. Chem. Soc.*, **1971**, *93*, 6696.

R. S. Sheridan
Department of Chemistry
University of Neveda
Reno, Neveda.