

Reflections on the Development of Mechanistic and Exploratory Organic Photochemistry From One Perspective

Howard E. Zimmerman

Department of Chemistry

University of Wisconsin

It was in the mid-1950's when the author's interests became heavily focused on organic photochemistry. This interest was a consequence of his growing involvement with the theoretical aspects of his experimental chemistry and the realization that excited state chemistry of organic molecules was a virtually unexplored field.

In addition, the literature of the 1950's had the implicit suggestion that photochemical reactions were random and a mere consequence of the rather large excitation energies imparted to the reactants. This was a complete contrast with ground state mechanistic organic chemistry in which selectivity was the ordinary and in which one could write reasonable reaction mechanisms.

One paper which provided a particular stimulus was by Egbert Havinga (E. Havinga, R. O. de Jongh and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956)). In this publication it was reported that, as expected, in the dark, p-nitrophenyl phosphates hydrolyzed much more rapidly than the meta isomers. Yet on photolysis, the reactivity was reversed with the meta-nitrophenyl isomers being much more reactive. The Leiden group noted that this behavior could not be explained with qualitative valence bond reasoning.

In view of the present author's increasing interest in molecular orbital theory, he wondered if it were not possible to understand the seemingly bizarre behavior of excited states on the same basis as ground state reactions if he only had available excited state structures. At this time a postdoctoral

student, S. Somaskhara, was joining his research group. It was found that a series of meta- and para-substituted phenyl triphenylmethyl ethers exhibited the same phenomenon as the Leiden group's phosphates. The meta-nitrophenyl ethers were found to solvolyze photochemically more efficiently than the para-isomers, and the same was found true for cyano-substitution. This clearly signified meta-electron transmission in the excited state which contrasted with ground state ortho-para electron withdrawal (Zimmerman and Somasekhara, *JACS*, **85**, 922 (1963)).

This led us to the quantum mechanical calculations in these two papers which revealed that meta electron transmission in the excited states had a theoretical basis. The calculations at the time were necessarily of the Hückel level. This was part of the basis for the author beginning to believe that one might predict, or at least understand, excited state reactions if he had good electronically excited state structures as a basis for prediction.

This work had been done at Northwestern prior to 1960 when the author moved to Wisconsin. It was during those days that there was intense thinking in the author's group about the factors controlling organic photochemistry and the question of whether calculations and also "organic intuition" could be used to understand excited state behavior.

Another publication which provided a challenge to the thinking of the present author was an elegant publication by Derek Barton (D. H. R. Barton, J. McGhie, and M. Rosenberger, *J. Chem. Soc.*,

1215, (1961)), in which the rearrangement of Santonin to Lumisantonin was described. This profound rearrangement with known stereochemistry provided a provocative challenge to the present author's mechanistic reasoning. The rearrangement seemed most likely to arise from the $n-\pi^*$ triplet with its electron-rich π -system, yet the molecular details of the process seemed most characteristic of an electron deficient reaction. It was in 1960 that the present author was invited by the ACS Organic Division to address the National Organic Symposium in 1961 at Bloomington, Indiana. Also speaking on the same subject was George Hammond who had also been thinking heavily about the factors controlling organic photochemistry. Interestingly, the Cal Tech and Wisconsin groups approached organic photochemistry from two different and distinct directions. It was like two armored columns advancing on the same target but with different strategies. The Hammond group concentrated on kinetic behavior, energy transfer and the involvement of triplets in photochemistry. The Wisconsin viewpoint as presented (Abstracts of the 19th National Organic Symposium, June 1961, Bloomington, Indiana) showed how one might proceed from an excited state structure to the photochemical product by mechanistic processes which were reminiscent of ground state transformations. The Organic Symposium provided an opportunity to present these two new approaches to organic photochemistry deriving from Cal Tech and Wisconsin. A number of examples of the present author's approach to mechanistic organic photochemistry were presented and detailed in the Symposium Abstracts. In the Symposium Abstract it was stated that there was a reason for lack of sophistication in photochemical research at the time. The main reason was paucity of information about the reactant excited state structure and the question of whether the same principles which apply to ground state processes apply to the excited state. It was noted that for a ground state reaction to succeed, there must be a continuous, preferably low energy

electron redistribution process available. In 1961 the suggestion by the present author that this might be true of photochemical reactions was received with uncertainty. The view presented argued that excited state species do not react indiscriminately but select low energy pathways. The point was made that the high, electronic energy is "locked in" and unavailable for random bond breaking as had often been assumed, since that energy is needed to remain on the excited hypersurface.

The presentation proceeded to note that two types of excitation were of special importance, $n-\pi^*$ and $\pi-\pi^*$, and showed how Wheland's representations of the former could be used in three dimensions. A "circle, dot, y" representation was employed to permit one to write a three dimensional excited state in two dimensions while still thinking in three and then applied to a number of photochemical processes.

Once an organic chemist writes such a Lewis structure for an $n-\pi^*$ excited state, he quickly sees a number of possible reactions, and this was the case with the present author in the late 1950's and early 1960's. As noted, this approach was not really accepted quickly at the time. The approach nevertheless was presented at that 1961 Symposium and in the meeting Abstracts in detail. It was applied to a number of $n-\pi^*$ and $\pi-\pi^*$ reactions. Interestingly, the basic mechanistic reasoning is not only accepted today but is considered obvious. One example was the Norrish Type I fission in which the disengagement of acyl and alkyl radicals was attributed three dimensionally to overlap of the coplanar and singly occupied p_y (i.e. "n") orbital. Another reaction was the hydrogen abstraction by the singly occupied p_y orbital; the Norrish Type II and the Yang Reaction were given as examples. Similarly, it was noted that carbonyl compounds with α -substituents capable of leaving as a radical species or anionically would do so because of the radical-anion character of the π -system. Of several examples given, one was the reaction of α,β -epoxyketones in which the α -carbon to oxygen bond

is broken with subsequent migration of a β -substituent to the α -carbon.

Also presented at the 1961 Organic Symposium was our first report of the "meta transmission phenomenon" in aromatic compounds.

At this point I should mention that a very bright and enthusiastic young postdoctoral student from Cal Tech joined my group. This was Dave Schuster who had done his PhD work with Jack Roberts. He had been urged by George Hammond and Jack Roberts to come to Wisconsin. At the time I believed I had a mechanism for the complex rearrangement of the 2,5-cyclohexadienone, Santonin to Lumisantonin. Rather than work on the natural product, Dave and I employed as a model, 4,4-diphenyl-2,5-cyclohexadienone. This rearranged rather prettily in what we termed a "Type A" (lumi) process. This result, too, was reported in that 1961 Organic Symposium. The mechanism involved four steps which were common to a number of organic photochemistry reactions, $n-\pi^*$ excitation, a change in molecular bonding in the excited state, radiationless decay to ground state (we termed it "electron demotion") and then some reaction of the ground state species. In the dienone case the ground state species was zwitterionic. The mechanism was only gradually accepted as evidence accumulated. Now the intermediate is often called the "Zimmerman-Schuster Zwitterion" and the mechanism is considered established.

The main thrust of these ideas was that excited state behavior was understandable on the basis of the structure of the excited state. While I cannot establish that this was the nucleation of acceptance of the concept, it is true that people began to be less concerned about devising photochemical mechanisms. Another point should be noted, namely that organic chemists had an advantage in the field, because they were accustomed to thinking in "electron pushing" terms. Given any reactant's structure and reaction conditions, an organic chemist was trained to predict, partially intuitively, what reactions might ensue. It just wasn't considered

reasonable at the time to apply this ability to organic photochemistry.

To be fair, at the time the present author's ideas were being developed and presented, there were others who had contributions. Mike Kasha had noted the propensity of the p_y orbital of the $n-\pi^*$ excited state to hydrogen abstract. Orville Chapman had in mind that there was a "dipolar state" responsible for enone rearrangements. Mike Kasha was at a disadvantage in approaching the field from a physical chemist's viewpoint and not having at his disposal the framework developed in ground state organic chemistry. Without a doubt he, too, would have come to the same broad conclusions of the present author.

Returning to the Cal Tech group's efforts, these were "orthogonal" to those of the Wisconsin group in emphasizing the kinetics of excited state processes, looking at energy transfer, and firmly establishing the idea, earlier noted by Sandros, that triplets were responsible for such reactions as the benzophenone - benzhydrol reaction. This was just one example thoroughly examined by the Cal Tech Group.

A pleasant and informal rivalry developed between the Cal Tech and Wisconsin groups; and, this continued for a rather long time. Both George Hammond and I recognized that our efforts emphasized different aspects of organic photochemistry and were not inconsistent. However, it wasn't clear that some graduate students and postdocs didn't take the rivalry more seriously.

Continuing efforts from our Wisconsin group proceeded onward to search out and evaluate mechanisms of a variety of new photochemical reactions with an emphasis on unimolecular processes. Our reasoning was two-fold. On one hand we hoped to find new types of photochemical processes; and, secondly, the reactions studied were selected to cast light on our original premise that one could correlate excited state structure with reactivity in a fashion so characteristic of ground state organic chemistry.

Our cyclohexadienone "Type A" lumi rearrangement was formally published in 1961 (with Dave Schuster, *J. Amer. Chem. Soc.*, 1961, 83, 4486-4487) and in 1962 in a full paper (also with Dave, *J. Amer. Chem. Soc.*, 1962, 84, 4527-4540). In the full paper we showed how the Type A mechanism accounted not only the unusual structural details of the Santonin to Lumisantonin rearrangement but also the stereochemistry. Also, the diversion of the reaction to Isophotosantonin Lactone in acidic medium was mechanistically described. The paper included a formal discussion of the electronic details of the Norrish Type I and Type II reactions as well as the Yang reaction forming cyclobutanols.

"Type B" rearrangements of bicyclo[3.1.0]cyclohex-3-en-2-ones, which were the photoproducts of the 2,5-cyclohexadienones, also were described in the 1962 paper with Dave Schuster. In this rearrangement a 6-ring zwitterion arises by fission of the internal three-ring bond and radiationless decay. This zwitterion then gave rise to 2,3-diphenyl- and 3,4-diphenyl-phenols in the case studied.

Summaries also appeared in reviews by the present author (*Tetrahedron*, 1963, Suppl. 2, 19, 393-401 and "Advances in Photochemistry" Interscience, Vol. 1, 183-208, 1963).

Somewhat earlier a number of exceptionally bright graduate students joined our group, being intrigued by the prospect of correlating photochemical reactivity with excited state electronic structure. This group included Joe Wilson (now of the Univ. of Kentucky), Al Padwa (Emory), Harry Morrison (Purdue), Stuart Staley (Carnegie-Mellon), Reuben Rieke (Nebraska), John ("Jerry") Scheffer (U.B.C.), and John Swenton (Ohio State).

In a 1964 publication, a molecular orbital treatment of the Type A rearrangement was presented in which further evidence was presented for the $n-\pi^*$ triplet being the reactive species and advancing a molecular orbital treatment showing that the $\beta-\beta$ bond order of the $n-\pi^*$ excited state was augmented

more than with $\pi-\pi^*$ excitation. At the same time it was noted that, while the β -carbons of such conjugated ketones are electron-rich, the $\beta-\beta$ bonding and subsequent radiationless decay to a zwitterion is able to deal with the paradox of an electron rich π -system giving a cationic rearrangement.

However, there were skeptics who suggested that the second double bond of the cyclohexadienone might not be playing a role. It was with this challenge that Joe Wilson and Ken Hancock studied 4,4-diphenylcyclohexenone to see if the second π -bond really was a necessity. These studies led to the finding that without the second π -bond a totally different reaction occurred in which a γ -phenyl group migrated to the β -carbon of the excited cyclohexenone with subsequent $\alpha-\gamma$ -bonding to afford 5,6-phenylbicyclo[3.1.0]-hexanone (Wilson, *J. Amer. Chem. Soc.*, 1964, 86, 4036-4042). Also in this paper evidence was presented that cooling of vibrationally excited ground state reactant is more rapid than the rate of rearrangement, thus noting that the cyclohexenones (lacking the second π -bond) not rearranging, rate measurements showed the enone triplets to rearrange orders of magnitude more slowly than the dienones (K. G. Hancock, *J. Amer. Chem. Soc.*, 1968, 90, 3749-3760).

In 1964 the first IUPAC Symposium on Organic Photochemistry was held in Strasbough. George Hammond had organized the Symposium and a number of us were invited as plenary speakers; this included Oskar Jeger, Bill Dauben, Dick Cookson, N. C. Yang, Klaus Gollnick, Paul DeMayo, Gerhard Quinkert, George Porter, and Orvill Chapman. It would be impossible to outline here all the chemistry presented. Orville Chapman described some intriguing new reactions of nitro compounds. Oskar Jeger reported on further results obtained with Kurt Schaffner and other coworkers on the epoxyketone rearrangement to β -diketones originally described in 1961 by the present author and slightly after by the ETH group. Gerhard Quinkert spoke about the photochemistry of unconjugated ketones in solution. Orville Chapman, Gerhard Quinkert

and Dick Cookson described molecular details of their photochemistry. George Porter reviewed transitions between different energy states.

I hope the reader will realize that in presenting the present author's perspective, he is forced by space limitations to emphasize his own efforts and viewpoint.

Still, in this year of 1964 there was a reluctance to deal with the electronic details of molecular structure of the excited states along the reaction coordinate. By this I mean details which go beyond naming of the initial excited state configuration.

At that 1964 symposium the present author discussed the detailed mechanism of the Type A rearrangement and presented evidence that the β -carbons of 2,5-cyclohexadienone triplets were electron rich and the β,β -order was enhanced in the triplet. The former came from the blue shift of the 0-0 triplet emission band of a series of dienones as the γ -substituents became more electronegative. The latter came from primitive Hückel level calculations possible at that time (with R. W. Binkley, J. J. McCullough, G. A. Zimmerman, *J. Amer. Chem. Soc.*, 1967, 89, 6589-6596). Also, an aryl rearrangement of a benzo derivative of a 2,5-cyclohexadienone was reported in which it was shown that p-cyanophenyl migrated to the β -carbon more rapidly than did a phenyl group (with R. C. Hahn, H. Morrison and M. C. Wani, *J. Amer. Chem. Soc.*, 1965, 87, 1138-1140) to afford 3-p-cyano-4-phenyl-1-naphthol.

One interesting turning point in the author's mechanistic organic photochemistry came as a result of our looking at the sensitized photochemistry of barrelene which we had earlier synthesized. A C₈H₈ isomer resulted and was assigned the name and structure of semibullvalene; the referees objected to both names as being flamboyant and unnecessary since in their view no further barrelenes or semibullvalens would be studied in future years. The reaction of barrelene to semibullvalene was described in the first JACS issue of 1966 (with G. L. Grunewald, *J. Amer. Chem. Soc.*, 1966, 88,

183-184). Yet, near the end of that year, the rearrangement of dibenzobarrelene to dibenzosemibullvalene was reported by Ed Ciganek of Du Pont (*J. Amer. Chem. Soc.*, 1966, 88, 2882) and in years to follow the number was ever increasing.

Up to this point, only one mechanism had been suggested, this by the present author; and, this mechanism was incorrect. Extended Hückel calculations on the excited state hypersurface revealed an impossible energy barrier, and deuterium labeling experiments on the barrelene to semibullvalene conversion demonstrated the actual mechanism. In a publication (with R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, 1967, 89, 3932-3933) it was noted that the rearrangement, despite its superficial complexity, proceeded by a mechanism which was general. This was said to be a mechanism in which two π groups needed to be bonded to an sp³ hybridized carbon in the reactant; we renamed this the Di- π -Methane Rearrangement once we realized that π -groups other than vinyl were sufficient for the reaction.

At this juncture it needs to be noted that one of the diradical species written in the Di- π -Methane Rearrangement has been controversial. Clear evidence had been presented for the second triplet diradical of the mechanism while we stated that the first might be an energy minimum in some cases but not necessarily in all. Our philosophy was that any species for which one can write a good Lewis structure and for which one can provide evidence, should be included in writing a mechanism.

It was 1964 when Edgar Heilbronner published his idea that someday Möbius cyclic polyenes would be synthesized. Edgar's theory concluded that Möbius annulenes would be as stable, but never more stable, compared with the corresponding Hückel one, when there were 4N electrons. But the theory included a twisted ring only for the Möbius systems. This prompted the present author to suggest that one did not need to await the synthesis of Möbius annulenes and that one already had such systems in many transition states. We also argued

that it was more fair to compare Möbius and Hückel systems of comparable twisting. The Möbius systems were found to be lower in energy with 4N reverse was true. The Möbius generalized systems were defined as having an odd number of plus-minus sign inversion in going around a cyclic array of localized basis orbitals while the Hückel ones had an even number. A Möbius circle mnemonic, a counterpart of the well-known "Frost-Musulin" one was presented. This theory permitted one to write correlation diagrams without the use of presence of symmetry, by noting that where degeneracies occurred along the reaction coordinate, two MO's would cross (*J. Amer. Chem. Soc.*, 1966, 88, 1564-1565). This followed publication in 1965 of the well-known Woodward-Hoffmann and Longuet-Higgins - Abrahamson approach based on symmetry. Also, later in 1966 Mike Dewar proposed a method, based on his very pretty non-bonding MO theory, which he noted came to the same conclusion as our Möbius-Hückel one. All of these approaches really arrived at the same conclusion; in 1971 Woodward and Hoffmann provided generalized selection rules which included our method of counting the even or odd number of antisymmetry components.

By 1966 we had been writing discrete species along the various reaction coordinates for some years and yet did not feel that photochemists were as at ease with such structures as with symbolic energy level diagrams. This difference in approach probably arises from the present author having had his roots in structural and mechanistic ground state chemistry where one demands description of all species along a reaction coordinate. One example of our approach came in the "Type B" rearrangement of 6,6-disubstituted-bicyclo[3.1.0]-hex-3-en-2-ones to afford 2,3-diaryl and 3,4-diaryl phenols. In efforts with several now well known students (J. Nasielski, R. Keese, J. S. Swenton, *J. Amer. Chem. Soc.*, 1966, 88, 4895-4903) it was shown that the internal 3-ring bond was broken in the excited state, followed by radiationless decay to a ground state zwitterion,

which elected to have one of its two 3-aryl groups migrate to C-2 or C-4 depending on whether the zwitterion was protonated or not. A 1966 Science article (*Science*, 1966, 153, 837-844) reviewed this and a variety of mechanisms with discrete steps. One mechanism included was a very pretty set of steroid rearrangements, studied by Oskar Jeger and coworkers (*Helv. Chim. Acta*, 57, 2757, 1964), which were shown to be explicable on the basis of an alternating set of Type A and Type B rearrangements.

Our approach often involved the synthesis of molecules designed to test some hypothesis followed by the photochemical study. One such example was our picture of the $n-\pi^*$ excited state of cyclohexenones. Thus we found that in 4,4-diarylcyclohexenones p-cyanophenyl migrated in preference to phenyl (work by Reuben Rieke) and that p-methoxyphenyl also migrated more rapidly than phenyl (by Jerry Scheffer); (with R. D. Rieke, and J. R. Scheffer, *J. Amer. Chem. Soc.*, 1967, 89, 2033-2047). This suggested an excited state which was primarily odd-electron in character, since the rearrangements, taken together, were neither explicable on a cationic nor an anionic basis.

Also in 1966 we were successful in generating the "Type-A Zwitterion" without light, from a α -bromo-6,6-diphenylbicyclo[3.1.0]hexane-3-one, and observed the usual photoproduct (with D. Döpp, and P. S. Huyffer, *J. Amer. Chem. Soc.*, 1966, 88, 5352-5353; also *idem, ibid*, 1969, 91, 434-445).

A rearrangement of dibenzoyl ethylenes to phenoxyketenes, by migration of one benzoyl phenyl group to the vicinal benzoyl oxygen, had been uncovered in 1962 (with H. G. Dürr, R. G. Lewis and S. Bram, *J. Amer. Chem. Soc.*, 1962, 84, 4149-4150) and also found by Gary Griffin at that time. This was later shown to proceed via the singlet while reduction of the triplet arose only when a hydroxybenzhydryl radical could deliver a hydrogen atom (with R. S. Givens, and R. G. Lewis, *J. Amer. Chem. Soc.*, 1967, 89, 1863-

1874; V. J. Hull, *J. Amer. Chem. Soc.*, 1970, 92, 6515-6520).

We also made use of stereochemistry in many of our studies. For example, it was shown that the out-of-plane 3-ring bond is preferentially broken in the triplet interconversion of cis and trans 5,6-diphenylbicyclo[3.1.0]hexan-2-ones (with G. Hancock, and G. Licke, *J. Amer. Chem. Soc.*, 1968, 90, 4892-4911). In this study evidence was advanced that the excited state of reactant went directly to ground state of product rather than adiabatically to excited product.

Over the years we continued our efforts to study all aspects of the Di- π -Methane Rearrangement. Benzobarrelene (with R. S. Givens and R. Pagni, *J. Amer. Chem. Soc.*, 1968, 90, 6096-6108), α - and β -Naphthobarrelene (with C. O. Bender, *J. Amer. Chem. Soc.*, 1970, 92, 3474-3476), Benzonaphtho-barrelene (with M-L.Viriot-Billaume, *J. Amer. Chem. Soc.*, 1973, 95, 1274-1280) and further barrelenes-- all were shown to proceed via triplet mechanisms and with preferential vinyl-vinyl bridging where possible, but aryl-vinyl bridging where not. By use of azo-precursors we were able to generate the first diradical species of the rearrangement (with R. J. Boettcher, N. E. Buehler, G. E. Keck and M. G. Steinmetz, *J. Amer. Chem. Soc.*, 1976, 98, 7680-7689) and to establish that this contrasted with the ground state singlet and also S_1 in affording the corresponding semibullvalenes.

The chemistry of acyclic Di- π -Methane rearrangements was shown to most often derive from singlets, and the reaction was shown to be stereospecific at the three sites of interest (with A. C. Pratt, *J. Amer. Chem. Soc.*, 1970, 92, 6267-6271; J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Org. Chem.*, 1979, 44, 1982-1989). The "methane" carbon was shown to be inverted in the rearrangement and the cis vs trans stereochemistry was demonstrated to be retained at the remaining two centers.

One further interesting result from this work; this was the idea of "free-rotor" excited state decay

(with A. C. Pratt, *J. Amer. Chem. Soc.*, 1970, 92, 6267-6271) wherein excited states, particularly triplets with flexible π -bonds were susceptible to a facile radiationless decay mode involving an MO degeneracy and an excited state - ground state approach, giving rise to a vibrationally excited ground state. Interestingly, this idea was misconstrued by a number of people. Jack Saltiel still continues to ask me if I mean that the triplet itself begins to rotate madly until it loses its energy.

At this point I think that I have covered much of the early years of photochemistry at Wisconsin. At Wisconsin we continued with the same approach. The "bicycle rearrangement", in which a divalent carbon with two substituents "walks" over the π -surface of a molecule from one end to another (with J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, 1971, 93, 3662-3674; T. P. Cutler, *J. Org. Chem.*, 1978, 43, 3283-3303; R. E. Factor, *J. Amer. Chem. Soc.*, 1980, 102, 3538-3548 and *Tetrahedron*, 1981, 37, Suppl. 1, 125-141; HEZ, *Chimia*, 1982, 36, 423-428) was pretty thoroughly investigated. In this work the 1966 idea of degeneracies playing a role in species on an excited state surface getting in S_0 was presented in terms of states as providing "bifunnels"; Joe Michl had also noted the role of such points in the hypersurfaces. In our own work we developed a number of hypersurfaces for reactions such as these and presented the idea of canted bifunnels. One interesting point dealing with diradical species was the generalization that S_0 1,4-diradicals undergo a 1,4-(2,3)-fission to afford two ethylenic units. This came out of our SCF-CI computations as well as our earlier MO considerations. Thus our research made use of theoretical chemistry as much as the larger systems of interest permitted.

We certainly recognized the utility of measurement of kinetics clearly expounded in the early Cal Tech efforts. For example, in 1973 we developed some new algorithms and apparatus for convenient single photon counting measurement of very rapid singlet reactions (with D. P.

Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **1973**, *95*, 5094-5095; D. P. Werthemann, and K. S. Kamm, *J. Amer. Chem. Soc.*, **1974**, *96*, 439-449; with C. Carpenter and J. Penn, *Proc. Natl. Acad. Sci. USA*, **1983**, *79*, 2128-2132). A method based on the temperature dependence of singlet rates led to our "magic multiplier" and permitted measurements approaching the picosecond range. Thus we were able to determine the rate of rearrangement of the 2,2-(diphenylvinyl)-propane (we called it the "Mariano Compound" since it was Pat Mariano who had elucidated the Di- π -Methane rearrangement of this compound (P. S. Mariano, *J. Amer. Chem. Soc.*, **1969**, *91*, 1718-1727).

The last decade added much new chemistry: excitation passing rapidly through organic rods composed of bicyclo[2.2.2]octane units, more on the stereochemistry and regiochemistry of the Type A rearrangement, examples of the reverse Di- π -Methane Rearrangement, reactivity of low energy excited states, some new photochemical rearrangements such as the conversion of cyclohexenones to vinylcyclobutanones, solid state unimolecular rearrangements which we term "photochemistry in a box" (*i.e.* the unit cell of the crystal; the referees didn't like this title either), the lowered efficiency of sensitized triplet reactions by attachment of a remote quenching chromophore to the molecule, and the chemistry of 1,3-diradicals, photochemistry without light by molecules with internal dioxetane groups, and many other items.

In summarizing the trend of organic photochemistry, as I see it, over these decades -- I'd argue that photochemistry began with a search for new reactions and was really not separate from organic chemistry as a field; it was primarily practiced by organic chemists. With the realization that excited states were understandable, there was a period in which the more hardy of organic chemists applied physical-organic methodology to the reactions they uncovered. However, this brand of organic photochemistry required familiarity with organic synthesis, theoretical chemistry and physical chemical methods. The number of people utilizing this combination rose to a peak somewhere between 1960 and the present and then diminished. The tendency these days has been to look at the photophysics of known and relatively uncomplex reactions. Whether this trend is good or bad, I'll leave to individual judgments. I think the trend results from physical chemists not liking organic methodology and organic chemists not always being willing to become theoreticians and kineticists. Another factor is the uncertainty of funding agencies, outside of NSF, to see the eventual utility of such abstract and arduous research. Yet one sees certain research groups on the international scene still working to add to this base of scientific knowledge, and I hope this will continue.

In conclusion, any contributions made by this author derive from the remarkable, amazingly dedicated, brilliant and capable students he has had.