More Photochemical Reflections

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I was much interested to read the articles by Howard Zimmerman and N. C. Yang in the May issue of the *Newsletter*. It is indeed intriguing, for a number of reasons, to look at a part of science which has undergone significant change and development during a period of time covered by our own personal memories. For example, we can ponder whether or not the change in the science shows any correlation with changes and development in ourselves, other than the fact that both we and the science have grown older. It is also worth asking whether or not change in science may have followed some vector which might have been apparent at some earlier time as contrasted to development being stimulated primarily by the stochastic appearance of new observations and their report in the literature. How much of the change has been a consequence of influences external to the science, such as economic, political and even philosophical factors in the society which supports the science?

I do not propose to supply definitive answers to any such profound questions, but will provide an anecdotal account of my own experience in photochemistry with occasional thought concerning factors involved in the building of a history.

When I entered Harvard as a graduate student in late 1943 I was fortunate to discover Paul Bartlett and to be accepted by him as a graduate student. I really had little notion as to the meaning of the term "physical organic chemistry" but my very meager exposure to courses in both physical and organic chemistry as an undergraduate student at Bates College had impressed me with the notion that both were probably rather interesting subjects. I had also worked most of a year at Rohm and Haas in the lab then run by the late Herman Bruson, an organic chemist of some distinction. Bruson sometimes speculated about reaction mechanisms and that seemed like an interesting intellectual activity. The fact that some of his speculation proved to be rather far off base was of no concern to me because I was in no position to make a critical evaluation. However, I did learn that part of Bartlett's work involved the study of mechanisms. Finally, some of the interesting graduate students whom I met, especially Ted Lewis, worked with Bartlett and spoke well of him.

Bartlett set me to work on a problem in vinyl polymerization initiated by free radical sources. The concepts of chemistry of transient free radicals were not new at the time, but were in a rather juvenile state. That was a great stage for a young scientist to get into a field; a lot was happening. New facts drawn from clever experiments were stimulating rapid growth and change of the ideas of chemists about free radicals. New ideas were presented, subjected to discussion by everyone, even graduate students. Those ideas lived, died or under went modification at an astounding rate. I learned that the pronouncements of even the wisest scientists in the field were only intellectual forays, not immutable statements of truth. Even the very finest could be dead wrong! One of the great highlights of my Harvard experience and later as a postdoc at UCLA was association with a lot of people who were very bright and blessed with such sturdy egos that they did not need to continually strive to prove themselves "right". They thought about alternatives, modified their views when presented with significant new information or new logical perspectives and occasionally stopped shouting to listen in even the most heated scientific discussion.

Photochemistry began to penetrate my conceptual world through polymer science. I discovered that photochemists knew some interesting things about radicals. I was in a continuing mess trying to sort out the fundamental radical chemistry involved in the thermal decomposition of benzoyl peroxide, the initiator which I used in most of my polymerization experiments. To this date, I still know of no one who can give a complete account of the timing of appearance of phenyl and benzoyloxy radicals, the exact extent of cage recombination of geminate radical pairs or, in most cases the extent and nature of induced decomposition of the peroxide.

I read the Noyes and Leighton classic "Photochemistry of Gases" and admired what I then perceived as the certainty with which they knew just what radicals were produced in photolytic experiments.

In 1946 Burnett and Melville published a study of time intermittency (the rotating sector method) in photo initiated polymerization to determine the absolute values of the propagation and termination rate constants. The results were of limited quantitative significance because of assumptions made about the mechanism of photodecomposition of the initiator, benzoyl peroxide. Some of the problems were rectified in later work by Bartlett and his coworkers, but the fact remained that high precision study of photopolymerization was marred by ignorance of the primary photolytic chemistry. I began incubating the idea that a properly designed photo initiation system could clean up the whole business.

In 1947 I went to UCLA to postdoc with Saul Winstein, a remarkably fortunate choice. Saul was inspirational in his indefatigable desire to discuss all open questions in chemistry. Saul certainly wanted to be "right", as illustrated by his later ongoing involvement in the never ending semantic squabble known as "the great non classical ion controversy"; however, the great issues to him in 1947-1948 were, "How does chemistry work?". We did not settle any large number of those questions, but discussing them was incredibly enjoyable and planted the seeds of many ideas, some of which came to fruition of sorts in later years.

There were two other parts of my year's experience at UCLA which had enormous effect on the rest of my scientific life. Three of us - Ted Lewis, Don Cram and I - went from Harvard to UCLA as postdocs that year. My interaction with Ted continued and was great; but even more important was my increasing interaction with Don Cram. He was beginning to elucidate the mechanistic significance of the stereochemical consequences of solvolytic reactions of 3-aryl-2-butyl X compounds. We talked a lot about that chemistry and about many other things. Included was our belief that we should write a text book organized on the basis of classes of reactions rather than structural compound classes. When we later wrote the book it did attract attention and have an impact on the teaching of organic chemistry, although it never attained the dominant position in the text book field to which we had aspired.

The last of the great influences of the UCLA community derived from the presence of Francis Blacet and his group of photochemists. That was a small, but wonderful, group - Jim Pitts, Jack Calvert, Bob Brinton and Bob Crane. They were a perfect answer to my desire to learn more about photochemistry. I spent a great deal of time with them and determined that when it became possible I would start doing photochemistry. The Blacet work was concerned largely with photochemistry of ketones in the vapor phase, a then very fashionable preoccupation with many of the world's leading photochemists - W. A. Noyes, Jr., E. W. R. Steacie, Milton Burton and others. Nearly all of the quantitative work in the field was done by people who called themselves "physical chemists" and most of them preferred to work in the vapor phase in order to simplify studies designed to elucidate the fundamental chemical actions of excited states.

In retrospect, it is not entirely clear that the ultimate in simplification was actually obtained. Molecular photoexcitation in solution is nearly always followed by very rapid vibrational relaxation of the electronically excited molecule to thermally equilibrated vibrational condition which, at commonly encountered temperatures, means population of relatively small numbers of low levels of most molecular vibrational modes. This rapid vibrational relaxation tends to wipe out many of the wavelength effects observed when gases at medium to low pressures are irradiated, thereby simplifying interpretation of results.

At any rate, discussion with the Blacet group was stimulating and led to establishment of long time friendships. It also introduced me to the photochemical fraternity. At that time North American photochemists tried to meet informally once a year. In 1948 the meeting took place at UCLA. Because of my growing interest in the field I was invited to participate. It was a great honor and a thrill. I don't remember all who attended and the meeting was rather small. I got to meet Albert Noyes for the first time and I believe that Burton came, and also believe that Steacie was unable to. The discussion was interesting and I was pleased to realize that I understood most of what was said, largely as a consequence of my many bull sessions with Pitts and Clavert.

In 1948 I went to Iowa State College (now University) to set up my own research program. I started doing free radical chemistry, some aromatic substitution studies and solvolysis, then probably the single most popular subject among the breed known as physical organic chemists. However, I still harbored thoughts about photochemistry and was delighted when William P. Baker, III, showed up in my office, having been sent to me by my friend Harlan Goering of Wisconsin. It seemed that Bill Baker was a first class graduate student in physical and organic chemistry who had, however, developed a strong allergic reaction to doctoral exams in inorganic. It was even said that when the same question appeared on both the physical and inorganic exams he managed it perfectly on the former but made a mess of it under the label "inorganic".

In any event, I was glad to take Bill into my group, largely because he had been doing photochemistry with John Willard and was eager to do more of the same, and did not mind at all moving into part of the field about which neither of us really knew anything. Fortunately, Bill insisted on setting up an optical bench, rather than employing some of my simpler sounding, but half baked, ideas for getting quantitative results.

Our initial foray was an attempt to use the photolysis of benzophenone as a means of generating and studying "authentic" phenyl radicals. The fact that E. J. Bowen had reported several years previously that benzophenone does not undergo photocleavage escaped our attention and Bill spent some time rediscovering the non reaction. However, the optical bench was there and Baker had developed a fondness for benzophenone so we simply switched the solvent from benzene to toluene and gathered a good deal of quantitative data from the photoreduction of benzophenone by both toluene and cumene.

Baker was succeeded by Bill Moore who switched to benzhydrol as the photoreductant so that hydrogen abstraction by the ketone would generate a pair of identical radicals. We measured quantum yields under various conditions, with the most important being in the presence of paramagnetic metal chelates which were powerful quenchers of the reactive excited state of the ketone. Analysis of the quenching data showed that the reactive state of the ketone must have enormously longer lifetime than that predicted for the S_1 state by applying the Einstein relationship to the integrated intensity of the first absorption band. We concluded that all of the excited singlets must undergo intersystem crossing to triplets at some enormously rapid rate (now known to be a few pico seconds).

Having worked out the rather simple radical chemistry fairly well and come to the conclusion that ketone triplets were the chemically responsible excited states, we decided to publish the accumulated work of Baker, Moore and Bob Foss. We sent the papers to *JACS* and the editor, Albert Noyes, sent them back with one external review which did not say much and Albert's personal review, eminently justified because of his preeminent stature as a photochemist, which raised troublesome questions. He was unconvinced of our case for the involvement of triplet states, largely because we had not used any of the methods that he and his group had been employing to characterize triplets in experiments with acetone and other aliphatic ketones. I rewrote the paper trying to clarify the exposition and in a few weeks received a letter of acceptance from Noyes in which he said that he had turned the paper over to his research group and that their verdict was that we had developed a nice new piece of methodology and were almost surely right in our conclusions. I do not know just who were the people in the Noyes group at that time but believe that they included R. Srinivasan, Peter Ausloos and perhaps Jim McNesby, all of who became good friends in later years. Furthermore, Albert Noyes became one of my best friends and most respected colleagues.

It was during this period that I moved from Iowa State to Caltech. some of my students, such as Bill Moore and Jim Waters, moved with me so there was no real break in the continuity of the Iowa State and Caltech programs. However, a discontinuity occurred because of the actions of Peter Leermakers, a student who joined the group after we moved. There occurred a long discussion between Bill Moore and Peter about Moore's work. Peter charged into my office and announced that he wanted to drop his crummy problem in metal chelate chemistry and do some photochemistry. That seemed fine to me. Peter showed that 2-acetonaphthone does not undergo facile photoreduction like benzophenone and acetophenone; it could be reduced by tributyltin hydride, presumably because of the weakness of the Sn-H bond. The experience led us to learn a little more spectroscopy and it became clear that the lowest triplet state of naphthyl ketones probably have, $\pi\pi^*$ rather than $n\pi^*$ configurations and that the electron deficiency at the oxygen atom of n, π^* triplets had a lot to do with the avidity with which the oxygen atoms of the excited ketones abstracted hydrogen from well known hydrogen atom donors.

Our work was not carried in a vacuum. The decade of the 60's was a boom time for photochemistry. Work in condensed media - liquid solutions, matrices held at cryogenic temperatures and the solid state - became the order of the day, although some people stayed with the vapor phase but worked with increasingly complex mixtures. The advance in the physical tools of the trade was almost miraculous. Flash kinetic studies became routine, laser light sources began to be laboratory tools rather than exotic new developments (although lasers only became omnipresent in photochemical labs in the 70's). New, rugged machines for accurate measurement of emission spectra and emission lifetimes became readily available, vastly improved gas chromatographs with modest price tags speeded up the work of many of us; some of us even chose research projects to be compatible with GC analysis. Perhaps most important was the tremendous overlap between spectroscopy and condensed phase photochemistry. People even forgot which of the two fields they belonged to in their pursuit of excited states and their remarkable chemical capabilities.

Photo reactions of all kinds were subject to study but the most popular probably were molecular rearrangements and cyclo additions induced by light. Cyclo dimerization of compounds such as anthracenes and the cinnamic acids and related compounds had been known for years but interest in them was revived by curiosity about their scope and mechanisms. This mind set led somewhat indirectly to what I regard as the most significant development which we contributed to photochemical science.

Bowen had adduced by an interesting, but not entirely compelling, argument that dimerization of anthracene involved the addition of an excited S_1 molecule to another molecule in its ground state. Discussions of the mechanism overlapped with discussions of the mechanism(s) of Diels-Alder reactions, thermal cycloadditions. Recall that I am speaking of a time before the Woodward-Hoffmann rules had been formulated to give a great deal of new insight into the mechanistic details of cycloadditions in general; in fact it was only beginning to be realized that in some cases thermal and photochemical cycloadditions between the same pairs of molecules gave different results.

At that time I gave myself one delightful self indulgence. Once a week I went to the local barbershop and was shaved by a barber. My rationalization for this extravagance was that it was: (1) very relaxing, a condition conducive to free floating thought, and (2) the fact that the barber was continually doing something to my face kept me from falling asleep. The latter was important, to me, in generation of any useful thoughts. (Unlike Kekule, my dreams about chemistry have, when I have been able to reconstruct them, always turned out to be abject triviality.) I did set myself chemical questions to ponder while I was being shaved. On one occasion I decided to cogitate concerning the mechanism of photocycloadditions which had been discussed in a seminar the previous evening. It suddenly occurred to me that the question of excited state involvement could be settled, at least in some cases, in an absurdly simple fashion. All we had to do was to make the excited triplet state of the photoreactant by energy transfer, as Terenin and Ermolaev had done when they sensitized phosphorescence of napthalene by irradiating with light absorbed by benzophenone in a low temperature glass containing both solutes. When I returned to the lab the first person I met was Leermakers. We decided to settle the question by running a familiar Diels-Alder reaction, the addition of maleic anhydride to piperylene, photochemically. The reaction was chosen because the thermal reaction is very slow at room temperature and because we concocted a line of reasoning which convinced us that the excited states of maleic anhydride would lie below those of benzophenone which we would use as a sensitizer. Leermakers put the system together and fired up the lamp. A half hour later he was in my office tearing his hair out. Vapor chromatography showed the appearance of no new high molecular weight product, but the peak attributed to piperylene was splitting into two!

A logical explanation was that we were seeing the photosensitized cis-trans isomerization of piperylene. However, the label on the bottle which Leersmakers had taken from the storeroom indicated that the material was a mixture containing cis and trans isomers in 45:55 ratio, the common commercial mixture. Under the circumstances we cannot be severely faulted for having assumed that our GC column did not separate the isomers; but we did encounter difficulty in deciding what other isomer was appearing. (To recount some of the hypotheses which were considered would not enhance the scientific value of this report.) To make a long story a little shorter, Leermakers traced the history of the sample which he had used. It had been returned to the stock room by Grover Farrar, a grad student who had finished his work for the PhD some years before. Perusal of Farrar's notebooks indicated that he had purified *cis*-piperylene by removing the trans isomer by reaction with maleic anhydride! Apparently when he finished his work and settle accounts with the stock room he had put the pure cis isomer into the commercial bottle and returned it. Soon thereafter we published the report of the sensitized cis-trans isomerization and pointed out that the result confirmed the enormous splitting between the S_1 and T_1 states in conjugated dienes, as had been reported by Evans who had courageously run spectra of highly explosive mixtures of organic compounds under very high pressures of oxygen.

Those experiments which were conceptually sound, but badly flawed in their detailed planning, were seminal to our development of triplet-sensitized reactions. The methodology has now become "old hat" as a procedure for differentiation of singlet and triplet reaction mechanisms. It has also proved to be useful in guiding the choice of photochemical procedures to bias experiments toward production of desired results, although the number of examples that can now be cited is smaller than we would like.

At the present time one of the most active and fruitful aspects of photochemistry is photo-induced electron transfer. That is a part of the science which we unwisely ignored in our work for a long time. Our preoccupation with transfer of electronic excitation energy led us to force every bimolecular excited state process into that mode. For example, we began to find a number of triplet sensitized reactions for which energy transfer was not a straightforward rationalization because of strong spectroscopic evidence that the acceptor molecules did not have triplet states at energies lying below those of the sensitizer. In our best known example Jack Saltiel carried out a comprehensive study of the isomerization of the stilbenes. We found that many triplet sensitizers which do not have sufficient excitation energy to promote the stilbenes to their Franck-Condon excited triplet states still sensitize isomerization albeit with reduced rates. We suggested that energy is transferred with concomitant change in the geometry of the acceptor to bring it closer to the configuration of the relaxed, probably perpendicular, form of the excited triplet. We coined the term "nonvertical energy transfer" to describe the process. A number of detailed descriptions of the microphysics of the process have been suggested and the basic assumption still appears to merit some credibility.

Weller first suggested that in some cases sensitization attributed to nonvertical excitation of the acceptor (e.g. sensitized reversion of quadricyclane to norbornadiene) actually involved electron transfer to produce transient ion radicals as intermediates. At this time I find his suggestion far more palatable than when I first read it. There are no unequivocal ways to distinguish between the ostensibly different mechanisms for energetically disfavored olefin isomerization at the present time, although the search for key transients by flash kinetic studies will probably resolve the issue in many cases, as has been done in countless other photoredox reactions. It may even be a mistake to insist on the view that sensitization by electron transfer and by electronic energy transfer are always discrete and separable mechanisms with partial electron transfer proving to be a part of the process which effects energy transfer by nonvertical excitation.

A similar problem arises in interpretation of quenching of fluorescence of organic molecules by metal ions, or complexes thereof. If the inorganic species is easily reducible or oxidizable by single electron transfer it is tempting to postulate that excited molecule is quenched by electron transfer to or from the excited molecule and the inorganic quenched. A number of studies of limited series of compounds demonstrate linear free energy relationships between quenching rates and calculated potential energies of full electron transfer. The reasoning is tempting, but not entirely compelling. Is it not reasonable to believe that electron exchange without the appearance of spectroscopically observable products of full electron transfer?

The uncertainties concerning the "completeness" of electron transfer in the decay of electronically excited states is of special importance in conjunction with the age old problem of chemical storage of solar energy in which irreversible transfer of electrons is a critical step. The process is carried out remarkably well by chloroplasts in green plants. Many laboratories have tested candidate and prototypes designed to accomplish the desired photochemistry with no results more successful than "tantalizing". The chemical storage of solar energy by man-contrived, commercially feasible schemes seems almost within reach, a situation which has existed for 25 years. I am impatient for the successful system to appear but confess, with humility, that I cannot now see how to put it together. I only hope that during my lifetime some one will show me how to do it.

I have only scratched the surface of the action of photochemistry during my scientific lifetime. I have said nothing about the potential for control of photochemistry by carrying out the processes in reorganized media, a subject in which I have recently become very interested. We are learning things which may be put to work during the coming months and years. We are surely following many false trails but I believe that we will find some things which will be worthy of note in reviews, such as this, when they are written 30 years hence. It is a great game and is far from over.

My personal involvement in the development of photochemistry over the past four decades has been major source of pleasure in my life. I have seen the unfolding of a fascinating field and have been privileged to take an active part in the process. I have had the great pleasure to work with many scientists who are also fine people. These include not only the people who have worked in my laboratories but also many colleagues from all over the world. I cannot possibly name them all but I must name a few to whom I have enormous debt.

I have mentioned the coworkers who really got me "on the map" - Bill Baker, Bill Moore, Bob Foss, Nick Turro, Pete Leermakers. Others who contributed enormously during those first years were Jack Saltiel, Bill Herstroeter, Bob Liu, Angelo Lamola, Ron Cole, Bill Stephenson, Dave Whitten, Frank Quina, Felix Carrol, Peter Wagner, Dick Caldwell, Dwaine Cowan, Dick Wiess, Tom McCall, Tom Penner, Don McGregor, Jim Meyer, Amitava Gupta, Atom Yee, Mark Wrighton, Peter Gaspar and dozens of others. I also owe a great deal to other colleagues such as Pitts and Clavert, Ted Bowen, Bill Dauben, Albert Noyes, Howard Zimmerman, Wilse Robinson, Josef Michl, Frank Mallory and many, many others.

In addition I must mention the contributions to my chemical life which have derived from my work as a consultant. I have learned an incredible amount from those with whom I have consulted. My greatest ongoing consulting experience did not involve much photochemistry, but I report it anyway. For 19 years I consulted with the Rohm and Haas Redstone Division in Huntsville, Alabama. People such as Bill Emmons, Bob Ross and Jerry Freeman shared their forays into nitroalkane chemistry with me. I watched as Fred Hawthorne began his truly brilliant career in borane chemistry in the Huntsville laboratory. I saw the genesis of the Rohm and Haas program in N-F chemistry, really created conceptually by Warren Niederhouser but persued wonderfully well by Charlie Colburn and others: it also contributed to offshoots like the work of Rick Merritt and Travis Stevens with other new fluorine chemistry. There were even occasions when we squeezed a little photochemistry into the programs.

During the first 22 years that I consulted with Du Pont I learned a lot of polymer chemistry and physics and was a fascinated observer of the evolution of new photopolymer systems designed as the basis of new photoimaging applications. I saw this work carried out in three different Du Pont departments and I learned a lot from those chemists and physicists - too many to mention but they included Rolf Dessauer, Peter Walker, Catherine Chang, Charlie Baylor, Abe Cohen, Dave Eaton (one of the many former students who came from Wesleyen University to work in my laboratory at Caltech) and my current co-author, V. Ramamurthy.

My experience as a full-time industrial employee also included a substantial amount of photochemistry, along with a number of other things. Part of the experience was working for three different corporations (Allied Chemical, Allied Corporation and Allied Signal), reporting to three different bosses and issuing five different business cards while sitting in the same office with the same secretary for 9.5 years.

I interacted strongly with the strange and highly talented group that Mike Berry had assembled to form the Photon Chemistry Department, the well known "laser group", and with the successor Photochemistry Group put together by Jim Yardley. My own intrusion into the laser activities was to work with K. V. Reddy and David Lishan to do what we believed to be a critical test for "mode specific" photochemistry, reactions consequent to exciting molecules to specific and very pure high vibrational states by resonant absorption in overtone bands. We concluded that mode specific photochemistry was too small a phenomenon to have practical significance. I watched while Yardley and his people did things like making new electrostatic printing plates and new photoresists sensitive to light of 260 nm or shorter wavelengths. (To photoimaging people this is the "deep" UV, although I have always felt that nothing above 200 nm is very deep.

At this time my role in photochemical science is not much more than that of an involved spectator. However, my association with the research groups presided over by Dick Weiss at Georgetown and Doug Neckers at Bowling Green is something for which I am grateful. In both cases I not only keep my hand in (in a <u>very</u> figurative sense) but I continue learning new things. It is fascinating to watch Neckers and his group use their ever expanding arsenal of reactions to produce radicals by photo induced electron transfer, create new polymers and turn them into 3D models. While working with the Weiss group I have come to understand more than ever before about the significance of phase diagrams and have also learned that the phase relationships in delicately organized organic stems (liquid crystal and other mesophases) are quite different from those of metallic alloys which I have seen in textbooks. I also wish to express my gratitude to Fred Menger who has allowed me to dabble in his ever changing research program, even to the extent of introducing a bit of photochemistry into it.

As I review what I have written above I realize that it includes many names but not nearly enough. I have not mentioned a quarter of those who have helped me substantially to live and relish my life in science. In fact, I am tempted to go back and remove all the names to avoid, by omission, hurting those whom I have not mentioned, people who worked in the laboratories along side of those named avove and contributed to their work as well as to mine. The casualness with which I have alluded to <u>examples</u> of the hundreds of collegues who have been important to me is illustrated that I have failed to mention, untill now, two who were among my finest collegues and who remain among dearest friends–Harry Gray and Chin-Hua Wu! I humbly applogize for failure to mention everyone who contributed to my slice of science. If I were to try to do so, this paper would grow to a size greater than even Ramamurthy could find spacefor–and I would still forget someone important. Science has a beauty in its own right, but it can only be enjoyed properly when done with other people.

Not everything that I have done in life, in science or even photochemistry has been either well or succeeded for serendipitous reasons. When I was at the University of California at Santa Cruz I decided, along with a group of Colleagues to establish a Center for Photochemical Science. The others were Roger Anderson, Earl Eveleth, David Klinger and Eve Menger. We formulated a comprehensive plan to create a research center which would then have been unique in the United States, although an excellent center of somewhat similar character did exist in Canada at the University of Western Ontario. I still believe that the plan was eminently reasonable and well developed; but it "came a cropper" for reasons largely external to the science itself. It was not accepted by some of the faculty at Santa Cruz, including some of the most respected chemists. That tells me that our presentation was not adequate to accomplish the task for which it was intended. We prepared a proposal for the NSF program for Research Initiation and Support (RIAS) but, partly because of the mixed reaction of our faculty in science, the Dean of Natural Science decided to submit another proposal instead of ours as the sole submission from the campus, in conformance with the rules of the NSF program. The other proposal had significant merit but did not win in the competition. In the second year of the program (1975) our proposal was submitted by the University. It was subject to two rounds of reviews. The first round won gratifyingly high marks; the response in the second round was less enthusiastic. The negative reactions appeared to be largely stimulated by guidelines from the Foundation which stressed the fact that RIAS programs should not establish new graduate programs or lead to expansion of existing programs. At that time the scientific community still reflected the down turn in the job market which occurred in the early 70's and many scientists feared that the society was saturated with PhDs. The plans of the Santa Cruz Center were certainly contrary to that philosophy.

A few years later Doug Neckers led the establishment of the Center for Photochemical Sciences at Bowling Green and it has been wonderfully successful. What made the difference? I will not attempt a detailed analysis, but it is clear that the time was different, the milieu was different and so on. However, one indisputable fact stands out, Neckers was more successful in the local politics at Bowling Green than I had been at Santa Cruz. I admire his success and mention the fact that care in presentation is exceedingly important in promoting novel initiatives.

I certainly do not regret the abortive effort to create a photochemical center. Not only was it interesting and instructive in its own right, but the fact that Eve Menger agreed to marry me makes the period one of the most personally gratifying in my life.

I return briefly to the more general. Photochemistry has moved a pace during the past half century and the movement has been due to the efforts of many people and the fact that they have usually worked in concert rather than in conflict. As I have said previously, I derived great benefit from discussions with Jim Pitts and Jack Calvert; this interaction continued into the time when they were writing their classical treatise, Photochemistry. I was privileged to read and make input to the manuscript as it developed. It was an education and a gratifying intellectual and personal experience. In 1964 Noyes, Pitts and I agreed with the chemistry editors (Bob Polhemus and Bill Grimshaw) of John Wiley & Sons Publishing Company to edit a series to be known as "Advances in Photochemistry". It was not designed to become a review journal but was intended to get people doing creative photochemistry to comment on a part of their field as they saw it. The editors have read chapters and tried to tread a fine line between making purely editorial suggestions concerning rhetoric, style and clarity and suggesting reconsideration of conclusions which do not seem consistent with the facts as presented, or known from other published literature. We have always encouraged authors to present their considered views irrespective of whether or not the editors growth and maturation of science depends heavily on freedom of information, even though that information may not be rigorously derived from what anyone knows. It is through that freedom to advance views not yet rigorously defensible that science can grow faster than if we always waited until opinions can be based on unequivocal evidence. (I have never seen any evidence which has seemed to me to absolutely unequivocal about any subject.) Reading, and in some cases editing, the input from our "Advances" authors has taught me a lot about my science and seems to me to illustrate cooperative growth of science.

The "cooperative" growth of the field was illustrated by an occurrence at the first IUPAC Symposium on Photochemistry which Jacques Levisalle and I organized. Two of our speakers were Howard Zimmerman and Roald Hoffmann. Both addressed the problem of interpreting the results which Zimmerman had been observing in the photorearrangements of 2,5-cyclohexadienones. Zimmerman's model was extracted directly from formalism developed from decades of study or organic reaction mechanisms. Hoffmann found the Zimmerman model not only naive, but deceptive. He pointed out that

Zimmerman ignored virtually everything that spectroscopists and theoreticians had been saying about the nature of electronically excited states. The discussion had the character of a debate without any stated question for debate. The Zimmerman model used Lewis electronic structures to represent excited states to rationalize the dynamic changes which generated rearrangement products. The Hoffmann formulation gave, what seemed to me, to be a more comprehensible description of the excited states of dienones but was not particularly informative about the details of the crossing between the excited dienones and some isoenergetic species which would be expected to decay to observed reaction products, or to intermediates which could lead to them by more or less familiar reaction paths. In short, I could see virtues in both approaches but also saw both as rather primitive forays into the evolution of viable theory of excited state photochemical dynamics. (I also saw, at that time, little usable overlap between the virtues of the two approaches.) Since then there has been great development of theory of photochemical reactivity and the input to it has come from both people known as physical chemists and those known as organikers. A notable example is the output from a summer which Nick Turro, Bill Dauben and Lionel Salem spent together explaining the intricacies of topicity for those of us who were not there.

The structures of excited states can now be described in great detail and one can now have considerable confidence in the validity of calculated potential energy surfaces for even rather complex molecules. The best calculations of the pathways of adiabatic reactions now deserve considerable confidence, although not all published pathway calculations are of equal quality. However, I am not familiar with any theory which gives highly accurate description of the microdynamics of crossing between states. (Since I have not evaluated, or even seen, all extant theory, I cannot guarantee that no highly useful description of state crossing exists.)

One of the great needs of modern chemical dynamics is modeling of complex reaction systems, including photochemical systems. It is interesting that one of the first complex systems to be given serious attention was a photochemical system, the sunlight induced ripening of polluted atmospheres to produce smog. Serious modeling of atmospheric photochemistry continues and some systems have been widely accepted as valuable guides in environmental planning even though the models are still far from finished. Photopolymerization in complicated mixtures, such as those encountered in various photoimaging processes, is another example of a system for which serious modeling attempts have been made. However, the whole field is in its infancy. Because most useful reaction systems are complex, a lot remains to be done. There may be advantages in using photochemical reactions as linchpins in development of the theory since control of irradiation conditions gives one at least one handle for systematic control of the experimental part of the work.

Because I can see huge gaps in our understanding of excited states and their chemical behavior, many of which I do not even see how to address effectively, I have a good deal of confidence that the science will maintain its vitality long after my own has become a memory.