

The Photochemists of 1938

Editor's Note: The winter and spring issues of *The Spectrum* will feature the six photochemists born in 1938, who were honored at the ACS national meeting in Boston last August. Research overviews from three of the six will be featured in each issue. We wish a very happy birthday to Bob Liu, D. C. Neckers, Jack Saltiel, Nick Turro, Peter Wagner, and Dave Whitten. It is a great pleasure to honor such distinguished scientists who individually and collectively have contributed so prodigiously to the evolution of photochemical sciences.

George Hammond's recollections, reflections and observations about the six from the forward of the *Journal of Physical Chemistry* follows and sets a marvelous tone.

Foreword*

George S. Hammond

This special issue commemorates a special event. It provides opportunity and motivation to reflect on the changes that have occurred in photochemical science during the lifetimes of many of us. It is appropriate that we use the occasion to especially honor six people who have made enormous contributions to evolution of the field as we now know it. We need not go back to the year they were born, which was also the year that I graduated from high school, to appreciate the magnitude of the change during recent decades. That sense is well conveyed by returning to 1959, the year that Nick Turro entered Caltech as a graduate student.

At that time we were considered pioneers, real frontiersmen, because a few years earlier we, meaning Bill Baker, Bill Moore, and I, had started measuring quantum yields of photochemical reactions in solution, had thought a little about the results, and published some of our ideas. Of course, we did not discover the triplet states of organic molecules. That had been done by Mike Kasha in his graduate work with G. N. Lewis at Berkeley. A generation of physical chemists—Noyes, Steacle, Leighton, and Burton to name a few—had recognized and exploited the fact that the slow emission, called phosphorescence, of simple ketones in the vapor phase comes from triplet states. George Porter had just begun to identify some of the long-lived transients which he saw in flash photolysis of solutions as triplets.

Our working equipment was, by today's standards, incredibly primitive. However, we were one of the few (perhaps the only) "organic" laboratories in the world to have an optical bench with light-collimating lenses, solution filters, and a calibrated thermopile.

A number of labs, including ours, went to work studying the scope and mechanisms of photo-reactions in solution. It was exciting to be able to speak with some confidence of the reactions of excited singlet and triplet states, what they might and might not do, and something of the kinetics of reactions and various decay paths. We could talk sagely about various quenching processes, energy transfers, $n\pi^*$ and $\pi\pi^*$ states, etc. We now know that some of our assumptions and conclusions were imperfect, but we made great progress. Those of us working with organic molecules

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From the Executive Director

D. C. Neckers, Executive Director, Center for Photochemical Sciences, Bowling Green State University

You've all heard this one I'm sure, but I was complaining the other day about turning 60 and my daughter had the typical rebuttal, "Consider yourself lucky; it's better than the alternative".

It's interesting to occasionally think about things that weren't here when one was born. In our case, penicillin and most other common antibiotics, birth control pills, jet planes, airports called O'Hare, J. F. Kennedy, Charles DeGaulle, ball point pens, stereos, VCRs, Walkmans, computers, televisions, interstate highways, automatic transmissions, National Public Radio, CNN, long distance by direct dial, touch-tone telephones, Nick Turro and I had four original Achilles tendons between us, and now we have but two, AIDS, the NBA, NSF, NIH, NASA, space travel, and atomic bombs.

Hardware stores sold hammers, saws and wrenches. Software, if it existed, was found in the lingerie department. Women wore cotton stockings or silk. Nylon didn't become commercial until the mid-1940s. Coke was a drink sold in returnable, green glass bottles, or by soda jerks at soda fountains. There were no quick-open cans, PET bottles, or vending machines. Neither Pepsi nor Seven-Up existed. Beer wasn't sold in Kansas and only in private clubs in Texas.

The border between Germany and France was closed to all but a few venturesome travelers. There was no Benelux or NATO. The Common Market, Iron Curtain, Berlin Wall, North and South Korea were still in the future. The world hadn't heard of Mao Tse-tung, Lenin was a hero, Stalin's purges were going forward, full-throttle in the Soviet Union. Chamberlain was still to bring England peace in our times, Hitler to take the Sudetan land, invade Poland, and start World War II. Pearl Harbor was an obscure US Navy base somewhere in the Pacific. Roosevelt was busy packing the Supreme Court and the world was trying to escape the Depression. Most Americans had never traveled to Europe or Asia; most Europeans and Asians never traveled to the US or Canada.

A diagnosis of Hodgkin's disease meant death. Hospitals had no X-ray machines or CT scanners. Ether was the anesthetic. Bacterial infections meant death unless you were lucky. School students wrote with lead pencils or pens dipped in inkwells. Carbon paper was sold by the ream. Manual typewriters were pounded on by secretaries and a lot of common business transactions were confirmed in handwritten documents. Plastic was limited to Bakelite. There was no Teflon, styrofoam, PET, PVC, or synthetic rubber. The world had never seen "Gone with the Wind". Music lovers who didn't live in a city with a symphony orchestra had likely not heard Beethoven's 5th, Brahms Double Concerto, or Mendelsohn's Midsummer Night's Dream.

Chemists worked with test tubes, double-pan balances, Gooch crucibles, Erlenmeyer flasks and dumped their waste down the drain. Block and Purcell hadn't thought about NMR. There were no commercial infrared spectrometers. UV and visible spectra were taken point by point. There were no gas chromatographs, liquid chromatographs or commercial mass spectrometers. Organic chemists tasted the fruits of their synthetic labs and washed their hands in benzene, chloroform and carbon tet. There was no OSHA or EPA. Research laboratories existed in very few universities.

Teachers taught; students learned. For assessment the teacher gave a test, the students answered the questions, and the teacher gave a grade. Misbehavior by a schoolboy meant the rod, paddle or switch. Classrooms had no overhead projectors, slide projectors, lantern projectors, or movie projectors. Teachers wrote on blackboards with chalk. Learning long distance meant sitting in the back of the room. Girl students still got pregnant but married the boy that got them that way. Nice girls didn't smoke cigarettes, and even the not nice ones that did, did not smoke on the street. Real men chewed Mail Pouch, smoked big cigars, Lucky Strikes or Camels. Most everyone over the age of 20 knew how to saddle and bridle a horse, hook up a buggy, and milk a cow.

In the good old days central heating wasn't common; schools, homes and churches had outhouses. A university education was reserved for a small percentage of the population most of whom were white and male. Trains in the south had Jim Crow cars, stations had separate waiting rooms for blacks and whites, separate drinking fountains, separate lunch rooms, and separate bathrooms.

In many ways, humanity has benefited untold gains in the last 60 years. We've also managed to develop unheard of ways to kill one another and horrible new approaches to war. But, and I hope this isn't too idealistic, we've learned to live a little more with each other. To respect one another's differences; to be a kinder, gentler humankind. Perhaps, and I hope this isn't naïve, we are more a world that celebrates peace and abhors war in 1998 than we were in 1938.

One of our brightest graduates at Bowling Green looked strangely at me on the graduation platform a few years ago when I said, "Tom; you are so incredibly lucky. The world is going to be so exciting during your lifetime and professional career. The discoveries of your colleagues and yourself will be literally amazing." I suppose it takes the retrospective of age but that's the way I feel. The next decades, if they are half as exciting as the last 60 years, are going to be downright awesome.

Correction

The following figures were published incorrectly in "Directional Photoinduced Charge Transfer in Thin Polymeric Porphyrin Films" by Dr. Carl Wamser in the Fall 1998 issue. Our apologies to Dr. Wamser.

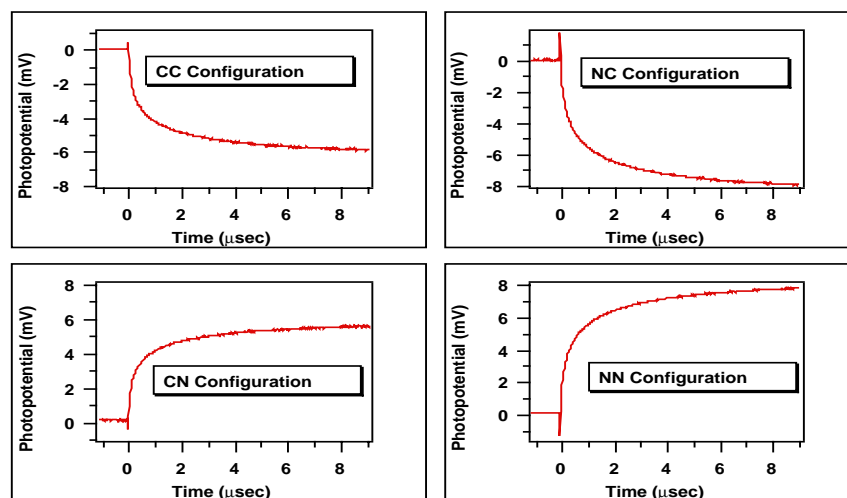


Figure 2. Photopotentials arising from pulsed laser irradiation of porphyrin polyamide films.

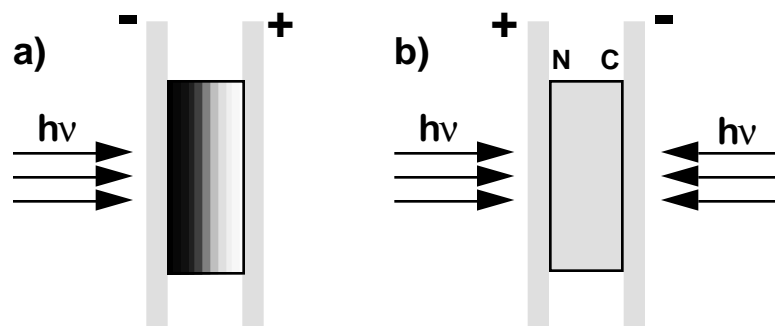


Figure 3. a) Irradiation leads to a gradient of excited states favoring electron injection at the nearer electrode regardless of film orientation; this effect predominates in optically thick films. b) In optically thin films, electron transfer is favored from the N side towards the C side regardless of the direction of the irradiation.

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began to realize that the voluminous work that had been accumulated by scientists developing silver halide photography contained concepts, especially photoinduced electron transfers, and had considerable relevance to our work. [Unfortunately, the suggestions which Gerald Oster had been making concerning photoinduced electron transfer had been largely ignored.]

We made tremendous progress in the 1960s, but we left many questions, some of which we had not even thought of asking, unanswered. This is not a historical piece. However, comparison of where we were then with where the science is now shows that a good deal of ground has been traversed. The many papers in this symposium give a picture of where we are today. Photochemistry is spread over the entire map of physical science. The field of life science, especially medicine, is permeated with photochemical science. The same is true of materials science.

Our capability to do things has been marvelously enhanced. Lasers had not even been invented in the early 1960s. At that time we were pleased to monitor transients produced by light absorption on the millisecond time scale. Today, a number of laboratories are working in the femtosecond domain. It is interesting that in at least some of the labs where lifetimes are routinely measured in picoseconds or less, there is no longer any equipment with which one can do millisecond kinetics. Similar evidence of change was brought to my attention a few years ago when I was working with Dick Weiss and his group at Georgetown University. We wanted to do experiments for which a nitrogen laser would have been an ideal light source. Fifteen years earlier the giant nitrogen laser was a workhouse in many laboratories doing research in spectroscopy and photochemistry. However, I could not locate one by calling all of the labs that I could think of within a 50 mile radius of Washington, DC. I suddenly realized that time and photochemistry were marching on.

I have looked especially at what the crop of *young* people turning sixty this year are doing at this time. They have traversed the ground from then to now and in doing so have been among the leaders who have moved photochemical science. After beginning at rather similar places, they have spread in different ways. There are those who have expanded themselves broadly and those who have penetrated ever more deeply in one direction. Superficial observers might see the latter as stuck in muddy ruts, yet they keep coming up with gold in the form of new science.

Peter Wagner and Jack Saltiel are two who have studied basically similar systems throughout their careers to probe ever more deeply the microphysical behavior of excited states. Wagner has used ketone photochemistry to establish time scales for intramolecular action ranging from times required for conformational adjustment of molecules to establishment of internal charge transfer interactions. He, along with Yang and Scaiano, has taught us a great deal by study of the biradicals produced by ketone undergoing the Yang (or Norrish Type II) reaction.

Saltiel began his photochemical career studying photoisomerization of the stilbenes and has never stopped. He has mapped the excited state energy surfaces for stilbenes and related compounds, and the times required to explore them, in remarkable detail by using photochemistry, spectroscopy, and shrewdly chosen structural changes. For example, his study of *cis*-1-(2-anthryl)-2-phenylethylene has allowed him to document (1) adiabatic isomerization, (2) conformer control of intramolecular electronic interactions, and (3) quantum chain processes. In a related study of the 1,6-diphenyl-1,3,5-hexatrienes, he also found a quantum chain process similar to those recently reported by Arai and Tokumaru.

Two who have chosen paths rather different from those of their photochemical peers are Liu and Neckers. Liu has worked primarily with the photochemistry of the retinoids and carotenoids, conjugated polyunsaturated, natural substances which play crucial roles in human physiological action. The materials, especially the retinoids, because of their role in vision, have been studied extensively by flash kinetic spectroscopy. Liu has chosen a unique role to amplifying our knowledge of their photochemistry. He and his co-workers have synthesized many of the geometric isomers of the natural materials and studied their spectra and photochemistry. The results have provided insight into the excited state processes in the compounds which could not have been gained by study only of the natural compounds or their readily available chemical relatives. A crowning jewel of this work is their discovery of a new class of compounds, the spiralenenes, in which suitably placed, sterically demanding substituents force a lower homologue of β -carotene in spiral configuration. In this configuration C=C bonds are held in a configuration appropriate for excitonic interaction giving rise to what Liu calls "secondary orbital" interactions. (Whitten might call the interactions "excitonic").

Neckers did not begin his research in photochemistry by studying spectra and measuring quantum yields. He looked for ways to use in polymer science what the rest of us were doing and has done so with remarkable success. He

first made and used polymeric photosensitizers and then went on to develop photoinduced polymerization. His stock in trade has become use of photoinduced electron transfer to initiate acrylate polymerization. His group has learned more than some people thought they ever wanted to know about the excited states of dyes as electron donors or acceptors, and gone on to use that knowledge to produce remarkable new polymer science. They have pushed the wavelength for photoinitiation into the near-infrared region of the spectrum and have discovered simple fluorescence probes to monitor the state of cure of cross-linked polymers. Neckers has also participated in development of commercial applications of his chemistry, most spectacularly in employing computerized data from CAT scans to create three-dimensional models of internal structures in the human body. If you want a replica of your skull or heart, see Neckers.

Turro and Whitten have cast their nets broadly and both continue to come up with bumper catches of new science. It is noteworthy that both have in recent years come to work extensively with aggregates. It is significant that leaders in photochemistry are taking steps on the path from chemists' traditional province of molecular science to the supramolecular domain of materials science.

Whitten began his postdoctoral research by using comparison with photochemistry to adduce molecular mechanisms of reactions initiated in solutions by γ -rays. However, at the same time he and Bill Stephenson discovered and investigated the quenching of fluorescence of aromatic hydrocarbons by conjugated dienes. That process cannot be attributed simply to electronic energy transfer, the process which had then come to be our first recourse in accounting for quenching of excited states. Much of Whitten's research since that time has, in one way or another, related to excited states interactions in bimolecular or polymolecular systems.

He was one of the first to thoroughly document the fact that many quenching processes involved electron transfer which often escaped detection because rapid reverse transfer to generate molecules in their ground states occurred at rates faster than diffusive separation of the reaction partners. One such example was quenching of the emission from the ruthenium tris(bipyridyl) cation by trinitrobenzene. Flash spectroscopy showed the transient appearance of the TNB anion radical. In that case the products of the transfer were a negative ion and a triply charged cation so there was a substantial electrostatic barrier to separation.

Whitten was one of the first to understand the complexity of photoluminescence quenching. Energy transfer and electron transfer are two, now obvious, mechanisms but there are other ways in which quencher and quenchee can form hybrid excited states which undergo rapid nonradiative decay. David Whitten has probably contributed more than anybody else to documentation of the complexities. He has employed a remarkable arsenal of tools in the work; in a recent publication he cites the use of "micro-calorimetry, dynamic light scattering, cryo-transmission electron microscopy, and reagent entrapment." He has also made use of photochemistry and classical spectroscopy.

Much of his work has involved assembling systems for study in configurations which they are unlikely to find in bimolecular encounter in isotropic solutions. Langmuir—Blodgett films and vesicles formed by fatty acids and amphiphilic phospholipids have been most frequently used. Experimental methods have been absorption and emission spectroscopy in both classic and flash kinetic modes. Most recently, the group has used experience with simpler systems to diagnose structures of dimers and higher aggregates. For example, amphiphilic monosquaraines and bis(squaraines) form a number of structures having very spectra and excited state lifetimes. Since in most cases symmetry precludes permanent electrical polarization of the ground states, binding energies in aggregates are attributed to exciton coupling. The results shed important light on the nature of such forces which are responsible for long-known phenomena such as the stacking of dyes in solution.

One of Whitten's major contributions was organization of the Center for Photoinduced Electron Transfer at the University of Rochester, one of the most successful of the Science and Technology Centers sponsored by the National Science Foundation in recent years.

Turro's first work in photochemistry was made in my laboratory at Caltech. He and the late Peter Leemakers carried out the first *designed* photosensitized reactions based on intermolecular transfer of triplet excitation energy. During a two-week period they discovered both photolysis of ethyl pyruvate and isomerization of conjugated dienes sensitized by benzophenone. Turro has never slackened his pace after that rapid beginning; nor has he ceased to seek genuinely new knowledge. In the modest space appropriately allowable for a Foreword it is not possible to even skim the cream from the flood of new science in his 600+ papers. He discovered the chemiluminescence of 1,2-dioxetanes which are so energy rich that their thermal decomposition produces excited states of ketones. A number of applications for the process have been found, including use to provide the readout in highly successful new clinical assays. He has made the interpreted telling observations about many of the processes by which excited molecules seek to

divest their excess energy—radiative and nonradiative decay, chemical reactions, classical and nonclassical energy transfer, etc. Some of the most brilliant of these studies describe *and put to use* the effects of magnetic fields, both external and provided by nuclei, the reactive molecules on photoreactions. An example acceleration of the triplet \rightarrow singlet process in radical pairs by ^{13}C nuclei. Perhaps the most comprehensive work has involved photochemistry and spectroscopy of molecules in environments which in some way restrict their motion. Included are silica surfaces, crystalline zeolites, and cavities of cyclodextrin complexes and, most recently, the molecular tentacles of starburst dendrimers.


One of the reasons for Turro's productivity is the ease with which he works with others. In a quick count I found 28 senior scientists with whom he has co-authored articles, and there are probably more. I am one who believes that active collaboration does more than fervid competition to advance the science. The two editions of Turro's *Molecular Photochemistry* were obviously written to inform, rather than impress, and are still another way in which he has enriched the science.

These six scientists have taken rather different paths and, because they have done so, have done far more to enrich the science than if they had become enmeshed in fervid competition in which all did essentially the same things. I am both proud and humble because of my own close association with each of them. Three (Turro, Liu, and Saltiel) were students in my group at CalTech. Two (Wagner and Whitten) spent time with me as postdoctoral fellows. The sixth, Doug Neckers, was never a member of a group which I directed, but for the past ten years it has been my good fortune to be a regular visitor in his laboratory at Bowling Green. I have not only enjoyed the associations but I have also learned more than they will ever know from each of them.

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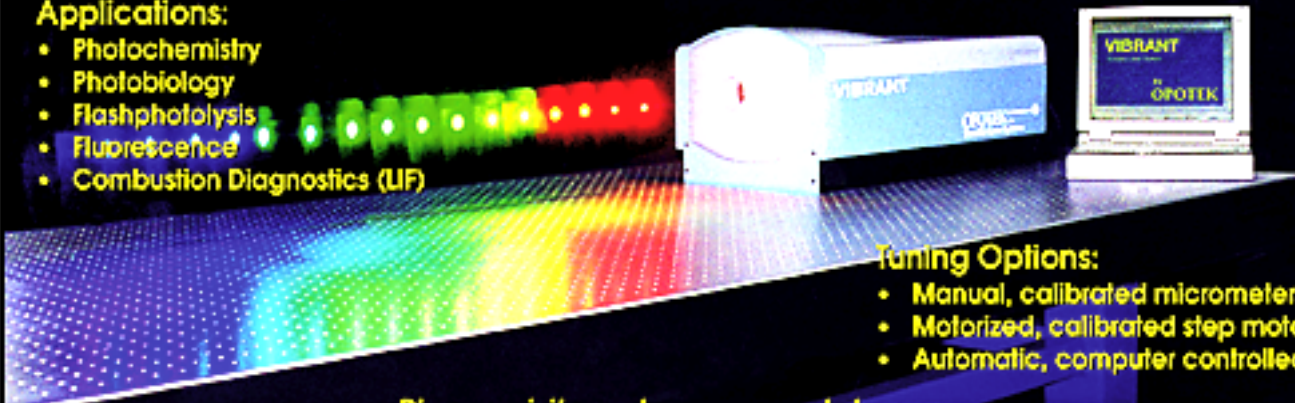
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Looking Back to My Research Effort (1962-1998)

Robert S. H. Liu, Department of Chemistry, University of Hawaii

I still vividly remember the morning when George Hammond showed up in my lab with a smile on his face and proceeded to explain to me his new concept of **isomeric triplets of conjugated dienes** based on the isoprene dimer data I gave him the week before. That was only near the end of my first year as a graduate student at Caltech. I could not follow all his reasoning. But his enthusiasm made me very happy and more importantly for the first time I had the feeling that I might be allowed to stay at Caltech.

Of course, that experience turned out to be more than keeping myself alive. Rather, by staying with George and the closely knit group under him, I finally learned part of the art of independent thinking and deductive reasoning. Subsequently, I also benefited from working under Howard Simmons at duPont and the sabbatical leaves in the laboratories of George Wald and George Porter.

In starting my own research career, whether because of the situations I was in (first in an industrial lab at duPont and then as a new faculty member in the relatively isolated State of Hawaii) or for some other reasons, I never considered myself very good at competing against others in popular research areas. Instead, I was quite lucky in picking projects in less popular fields, stumbling onto some photochemical results that violated rules of the accepted norm. Findings of this nature usually help to turn a few sympathetic ears, much needed when later I went out to look for money or other favors.

I guess I was the right person at the right time when the **second triplet state** project was launched at duPont. It started at a time (mid-sixties) when the “non-vertical” excitation process was in vogue. And, the group of chemists at the old Radiation Laboratory (R. Kellogg, P. McCartin and R. Bennett) had just spectroscopically located the position of second triplet states of anthracenes. It was logical for me to carry out the series of triplet-triplet energy transfer experiments using T_2 -donors. At that time such “violations” of Kasha’s Rule were rare. We were fortunate not only to be the first to identify such a process but also were one step ahead of the spectroscopists in reporting the lifetime of an upper excited state (via chemical kinetics). The program continued through the early-seventies when more sensitive emission and double-laser equipment became available that allowed direct examination of such states as carried out elegantly by E. Lim, T. Scaiano and others.

Strangely, terpenes kept on popping up as startup systems for new projects of mine. I mentioned the role of isoprene dimers in the discovery of isomeric triplets. Myrcene helped me start a program to investigate modes of **inter-nal photocycloaddition**. And, alloocimene opened the door to **photoisomerization of polyenes**.

The program for preparation of **new stereoisomers of vitamin A** started with the discovery of **one-way triplet sensitized isomerization** to produce the hindered 7-cis isomer of precursors of vitamin A. It was only after successful characterization of the hindered 7-cis geometry and well on our way to prepare new isomers of vitamin A, that we discovered an early paper by L. Pauling stating that such hindered 7-cis isomers were supposed to be too unstable for isolation. (The slightly less crowded 11-cis isomer was also considered unstable but was already characterized to be the chromophore in visual pigments.) But, of course Pauling’s conclusions are still valid if they are limited to comparing relative thermodynamic stability of the isomers rather than predicting their kinetic stability at room temperature. The program later led to all previously unknown isomers of vitamin A and A_2 . The collection of new stereoisomers allowed us to probe for the **stereospecificity of the binding site of opsin** on a broader basis. The finding cast doubt on the notion of a rigid, specific (lock and key interaction) binding site (also suggested by analog studies by P. Blatz, K. Nakanishi and others). The flexible binding site argued for possible inclusion of substituted vitamin A as the chromophore. Subsequently, many **fluorinated and alkylated retinal** analogs were prepared. Such substituents were useful reporters for information on specific protein-substrate interactions. More recently, we finally took up the courage to tackle pigments containing the larger and more sensitive **fluorinated carotenoids**.

A few years ago, Al Asato in my group prepared a series of compounds that we called “**Mini-carotenes**”. Tomas Gillbro of Umea turned them into a wonderful set of compounds that systematically violated the Kasha’s Rule,

again—by emitting from the second singlet state with varying intensity. (This work followed that of R. Christensen of other chain shortened carotenoids.) The best known compound that violates the Kasha's Rule is of course the azulene. Al Asato was able to attach to this chromophore polyenal side chains. Such highly colored retinal analogs eventually led to the first **NIR absorbing analogs of bacteriorhodopsin and other polarized polyenes**. (Nakanishi's group first reported an azulenic bR analog.)

In considering conditions for **regioselective** (especially cases of **regiospecific**) **isomerization of polyenes** including the visual chromophore, we came up with the "Hula-twist" model of isomerization—simultaneous twisting of a pair of adjacent double and single bonds, a process that violates the NEER principle. We thought it could only be a high energy process taking place in a confined medium. For a while it did look like an unlikely high energy process because there were no new experimental evidence supporting this idea. It was a surprise to me that a decade later, high level calculations showed that the trajectory of deactivation of an excited singlet polyene traced a low energy pathway, via conical intersection, to such a two-bond twisted product (M. Olivucci *et al.*). And, photoisomerization of vitamin D compounds was shown to follow the "Hula-twist" process (W. Fuss) and isomerization data of exocyclic dienes suggested simultaneous two-bond twist (W. Leigh). When taken together with the early low temperature photochemical work on 1,3-butadiene and 1,3,5,7-octatetraene (M. Squillacote and B. Kohler), there appears to be room again for this conceptually simple process (although admittedly I was guilty being excessively optimistic in presenting the model).

In looking back, I can honestly say that at the outset I never envisioned the type of complex systems that we were later involved in. The program simply evolved with the help of many capable associates. The polyene photochemical program was initiated by Yondani Butt and V. Ramamurthy. The observation by the latter of one-way sensitized isomerization of β -ionol literally ushered in our retinoid program. Synthetic value of this observation was subsequently realized through the effort of my long term associate, Al Asato, joined by Aravinda Kini, Dennis Mead, Achla Trehan, Rong-Liang Chen, Jin Liu and Rajeev Muthyala along the way. Hiro Matsumoto brought biochemical expertise into the group. Marlene Denny provided reliable analytical and photochemical work, Tara Mirzadegan in computer graphics, Letty Colmenares in her all around effort of synthesis, protein NMR and F-shift interpretation, S. Ganapathy and Bao-Wen Zhang in quantitative retinal photochemistry and Xiao-Yuan Li and Yun Zhu in spectroscopic and analog studies. I am also fortunate to have had interactions with many wonderful people around the world who either showed us new tricks (e.g., Wim deGrip on visual proteins, Allen Kropf on hplc, Bill Ripka on molecular modeling and recently George Britton on crustacyanin) or collaborated with us fruitfully (with Toru Yoshizawa and Yoshinori Shichida on biophysical studies and Reid Kellogg, Tomas Gillbro and Randy Larsen on molecular spectroscopy). It has been fun to learn with these people, and to share the fruit of their efforts including the occasional reward of the dawning of simple explanations out of the initial, seemingly chaotic sets of data. To them I am most grateful.

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It Sure Helps To Understand Free Radical Behavior If You Want To Be a Photochemist

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As a follow-up to the very gratifying Boston photochemical symposium in honor of the 1938 six, I was asked to write an overview of my research over the years. A wickedly witty fellow photochemist once introduced me as someone who studied everything from ketones to acylbenzenes. Now that might have been partially sufficient if I were being evaluated for my contributions to materials science (perish the thought!), but it disregarded the reasons why so many of us have studied the photochemistry of carbonyl compounds. The simple answer is that the high reactivity and the strong localization of excitation that characterize excited carbonyls combine to allow their photoreactions to provide answers to both specific and general fundamental questions about excited state reactivity as well as a variety of ways to generate biradicals and radical pairs for study. In my case early interest in the mechanisms of several ketone photoreactions spread into more general questions about conformational effects on intramolecular reactions of both excited states and biradicals, development of proper equations for analyzing reactivity when two or more excited states are involved,¹ and various studies on energy transfer.

I should start at the beginning, which would be my Ph.D. work with Cheves Walling at Columbia. I was lucky enough to discover a rare solvent effect on the behavior of radicals: polar solvents increase β -cleavage relative to hydrogen abstraction by alkoxy radicals.² We attributed this effect to preferential solvation of the transition state for cleavage, which generates a significant increase in dipole moment as the carbonyl is formed. I was delighted to see major research groups in Ottawa and Inchon revisit this work in 1994 and yet another group in Novosibirsk do so just last month. Amazingly, everyone agrees with our transition state solvation but disagree over the importance of alkoxy radical solvation.

My postdoctoral work with George Hammond at Caltech resulted in another lucky finding. Quenching studies intended to show that intramolecular hydrogen abstraction is much slower for triplet 2-pentanone than for triplet 2-hexanone did just that but also showed that they each undergo unquenchable singlet state reaction as well.³ I extended such quenching studies of the Norrish type II reaction to phenyl ketones, which react only from their triplets, but in surprisingly low quantum yields.⁴

I then moved to my present address, entranced by the radical-like behavior of triplet ketones and puzzled by their low quantum yields of product formation. Prevailing thinking assigned low quantum yields entirely to radiationless decay of excited states. In the late 60s several of my first students studied the α -cleavage of cycloalkanones,⁵ the photodimerizations of thymine⁶ and of 2-cycloalkenones,⁷ and more type II reactions.⁸ In all cases there was no correlation between excited state kinetics and quantum yields. This fact, combined with consideration of the often observed rearrangement of starting materials, added up to what is now a general principle: triplets react to give intermediates that revert to ground state reactant as well as form photoproducts. Yang's early suggestion of biradical intermediates provided an explanation for product structures. We expanded its role to the reversion process as just another radical-radical reaction: cyclization, β -cleavage, and disproportionation, respectively, for the three reaction types listed.

We devoted the most attention to the type II reaction of aryl ketones, in particular exploring every possible facet of its mechanism. Thus we trapped the biradical intermediate with thiols,⁹ demonstrated racemization at the γ -carbon,¹⁰ and found products that could result only from monoradical rearrangements of the biradicals.¹¹ We discovered that product quantum yields are enhanced, often to 100%, by Lewis base additives to which the biradical's hydroxy group can hydrogen bond and thus suppress reversion to ketone.¹² Our careful study of concentration and conversion effects on valerophenone¹³ has made it a widely used actinometer, even though it is not included in the official IUPAC listing. We measured how rate constants for γ -hydrogen abstraction varied with substitution at the γ - and more remote carbons,¹⁴ providing the first firm evidence that the reactivity of triplet ketones almost exactly parallels that of alkoxy radicals in terms of both C-H bond strength and inductive effects. (Earlier suggestions were based on relative

quantum yields, which need not parallel excited state rate constants.) We also studied how substituents on the benzoyl group affect triplet reactivity, a very hot topic around 1970 because of spectroscopic evidence for the proximity of n,π^* and π,π^* triplets in phenyl ketones. Prevailing sentiment suggested that the reactivity of those ketones with π,π^* lowest triplets arose from mixing with the n,π^* state. We provided evidence *au contraire*, that simple thermal equilibrium between the two states populates the n,π^* sufficiently to promote reactivity.¹⁵ Later flash kinetics studies by Steel's and Scaiano's groups provided conclusive evidence for this equilibrium picture, which is widely accepted by physical and inorganic photochemists but often is ignored by organic photochemists. (I hope I am allowed one pet peeve!)

Over the years we accidentally uncovered several important facets of the photoenolization of *o*-alkylphenyl ketones to *o*-xylylenols. In the mid-70s we found that the *syn* and *anti* rotamers of such ketones form two kinetically distinct triplets, with the rate-determining step for decay of the *anti* triplet being rotation to the *syn*, which rapidly abstracts a γ -hydrogen from the ortho-alkyl group.¹⁶ Cyclic systems such as 8-methyltetralone produce a single *syn* triplet with a sub-nsec lifetime. In collaboration with Jacob Wirz we then found that acyclic ketones produce two photoenols, a very short-lived Z isomer with the OH in and a long-lived E isomer with the OH out, while the tetralone forms only the former.¹⁷ This finding settled the puzzle regarding why Diels-Alder adducts are formed only from the E isomer. In 1991 we discovered that a wide variety of such ketones form benzocyclobutenol photoproducts that are stable below 50°, with stereoselectivity indicative of conrotatory cyclization of a single E-enol isomer.¹⁸ Our most recent efforts were actually planned and confirmed our idea that product stereoselectivity in the reactions of the photogenerated *o*-xylylenols is controlled by the most stable 90° twisted geometry of the 1,4-biradical triplet *o*-xylylenol.¹⁹

Given its high γ -regioselectivity and its highly variable rate constants for hydrogen abstraction, the type II reaction is very useful for monitoring rates of other competing reactions, either of the same carbonyl, of another functional group in the molecule, or of another molecule with the excited carbonyl. In our early work we allowed γ -hydrogen abstraction to compete with α -cleavage,²⁰ and with intramolecular quenching by amines,²¹ azides,²² β -phenyls, and β -vinyls.²³ This work led to later focus on how conformational kinetics affect photoreactivity.²⁴

A large part of my interest in the type II reaction involved its usefulness in determining relative hydrogen abstraction rate constants. Bimolecular hydrogen abstraction by triplet ketones as first reported by Hammond's group is what got me interested in photochemistry. I am especially pleased with the work my students did in determining the extent to which charge transfer influences rate constants for hydrogen abstraction by triplet ketones from various alkylbenzenes.²⁵ We were able to measure that extent by looking at the primary/tertiary radical ratios produced from *p*-cymene²⁶ and by the size of any deuterium isotope effect at the benzylic carbon being attacked.²⁷ Our papers of a decade ago are a low-tech version of the recent Farid and Gould spectroscopic results: the extent of charge transfer in exciplexes is related to thermodynamic redox potentials, as are the kinetics of hydrogen transfer.

We also studied interactions of other electron donors with excited ketones. Our work with amines emphasized the charge transfer nature of the process, especially the lack of electron transfer in 4-benzoylpiperidines²⁸ and the difference in the behavior of *p*-(ω -dimethylaminoalkoxy)acylbenzenes depending on whether the lowest triplet is n,π^* or π,π^* .²⁹ Both results indicate the necessity for close overlap of the nitrogen lone pair with the half-filled orbitals of the ketone. Our CIDNP studies of the reactions of strong electron donors with triplet ketones provided the first evidence for the triplet mechanism of CIDNP.³⁰

Our early evidence for charge transfer reactions of olefins with triplet ketones³¹ led us to study some *p*-(3-buten-1-oxy)acylbenzenes and we again found that those with π,π^* but not n,π^* triplets undergo fast internal quenching.³² However, the quenching is chemical, leading to [2+2] cycloadditions followed by an intriguing array of thermal and photochemical pericyclic reactions,³³ all of which show amazingly high regio-³⁴ and stereoselectivities.³⁵

In the 80s Mike Meador talked me into basing his thesis on ketone systems that undergo δ -hydrogen abstraction. These systems taught us a lot about conformational effects, both kinetic and thermodynamic, on photoreactivity and reminded us that stereochemistry is the essence of organic chemistry.³⁶ Conformational equilibrium of the triplets was found to greatly affect triplet reactivity³⁷ whereas no strong C-H-O orientation requirements were found.³⁸ The 1,5-biradicals formed as intermediates provided new insight into how conformational preferences affect product selectivity³⁹ and how triplet biradicals form singlet products. This all led us to some of our most recent work involving temperature effects on the stereoselectivity of biradical cyclization.⁴⁰

Since quenching studies were key to early kinetics measurements and remain key in distinguishing between singlet and triplet reactions, I gave energy transfer a lot of attention. Accurate values of rate constants are essential for

Stern-Volmer quenching analyses of triplet lifetimes, so we tested the conventional wisdom that all exothermic bimolecular energy transfer occurred with diffusion-controlled rate constants. We found that such is the case only in solvents more viscous than those normally used for solution studies, with rate constants in solvents such as benzene, acetonitrile, and the shorter alkanes being only partially, not completely, diffusion controlled.⁴¹ We also found that energy transfer to rare earth ions is slower than diffusion in protic solvents,⁴² despite assumptions to the contrary, a reality now well established as due to strong solvation of the cations preventing close approach of excited donor. These measurements were all performed with phenyl ketone donors and their type II reactions as the monitoring clock; their validity has since been verified by direct flash kinetics studies.

Biphenyl quenches triplet ketones with rate constants considerably lower than diffusion control. This apparent anomaly, given biphenyl's 65 kcal/mole 0-0 phosphorescence energy, led me to scrutinize biphenyl. EPR studies indicated a planar triplet compared to a twisted ground state.⁴³ The large difference in geometry produces a large Stokes shift between S→T absorption and T→S emission.⁴⁴ Rate studies as a function of donor concentration revealed the reversibility of energy transfer between benzophenone and biphenyl and indicated that **during energy transfer** biphenyl has an effective triplet energy slightly higher than benzophenone's 68.5 kcal/mole.⁴⁵ Thus biphenyl's behavior completed the picture of "nonvertical energy transfer", with rate constants higher than predicted by its S→T absorption and lower than predicted by its T→S emission. Balzani very astutely noted that the effect of this geometry change on kinetics is an example of the reorganizational energy so well known to inorganic chemists; and so began the blending of organic and inorganic thinking about photochemistry.

Intramolecular energy transfer has received much attention. One of my favorite uses of the type II reaction was putting acylpyridine ligands on Ru(II) complexes to estimate the rates for internal conversion of ligand-localized excitation to MLCT states⁴⁶ and for internal energy transfer to bipy ligands.⁴⁷ More recently we have provided several examples of how triplet energy transfer in ω -substituted alkanophenones occurs through space due to coiling of the polymethylene chain connecting the carbonyl with a remote energy acceptor.⁴⁸

One of my most recent interests involves homolytic cleavage reactions of triplet ketones, with the leaving radical connected somewhere other than to the carbonyl. One of my favorite early uses of the type II reaction was our measurements of relative rates of radical cleavage by groups originally at the δ -position of valerophenone, which are β to the γ -radical site of the 1,4-biradical.⁴⁹ Our recent studies of acyl-iodobenzenes and -bromobenzenes have demonstrated how electronic configuration of the triplet affects the interconversion of nonreactive n,π^* and π,π^* states with dissociative excited states.⁵⁰

Of course all of the work, except for my first few years at MSU, was done by a wonderful group of hard-working and highly motivated graduate students and post-docs. I hope my efforts on their behalf repaid them sufficiently for their efforts on my behalf.

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Reversible Association of Free Radicals with Benzene. The Seed of an Idea*

Jack Saltiel, Department of Chemistry, Florida State University

I take this offer to reminisce as an opportunity to tell a story that might not otherwise be told. It has to do with an irritating side reaction that led us to the study of the photooxidation of benzil and from there to the photolysis of benzoyl peroxide in the presence of oxygen. Serendipity pulled me back to the project George Hammond assigned me when I joined his research group. The demonstration that benzoyloxy radicals add reversibly to benzene brought a kind of closure to that initial free radical quest. But let me place the story into context.

Not too long ago, in my first article to this newsletter, I described how, in 1960, I started work in George Hammond's laboratory seeking evidence for reversible formation of π -complexes between free radicals and aromatics.¹ It was George's idea and he, no doubt, could describe my project better. It concerned the thermal decomposition of benzoyl peroxide in toluene with the goal of determining quantitatively the dependence of the methylbiphenyl and bibenzyl products on the concentration of benzoyl peroxide. The formation of the methylbiphenyl would be first order in radicals if phenyl addition to toluene were irreversible, but second order in radicals if the addition were reversible and the rate determining step required a second radical to abstract a hydrogen atom from a phenyl radical/toluene complex. Bibenzyl formation, on the other hand, had to be second order in radicals, and its relative yield would increase at low radical concentrations if the phenyl radical/toluene association were freely reversible. Much data had been gathered by two graduate students and a postdoctoral fellow who had preceded me on this project. My part, the determination of the yield of bibenzyl as a function of benzoyl peroxide concentration, was soon completed, but interest in the interpretation of the data had subsided. Measurements of deuterium isotope effects by Ernest Eliel and coworkers had made a strong case for essentially irreversible addition of aryl radicals to benzene.^{2,3}

How serendipity led me to the study of the isomerization of stilbene triplets and of the mechanism of stilbene photoisomerization, generally, I have already described.¹ That became my Ph.D. thesis topic during a very exciting time in George Hammond's laboratory. The paper that George wrote on this work remains one of the cornerstones of the area of cis-trans photoisomerization.⁴ Though much had been learned, I was not satisfied. As I was about to leave Caltech, I asked George whether it would be alright for me to continue working on stilbene. I knew that he was of the opinion that continuing work on one's thesis topic was not a good way to start an independent career. I was surprised, therefore, when he told me that while normally his advice would be not to do it, my case was an exception. He encouraged me to continue.

One nagging question had to do with the azulene effect on stilbene trans/cis photostationary ratios. These ratios increased with increasing azulene concentration under both triplet sensitized and direct excitation conditions and this qualitative agreement had been taken as evidence supporting common triplet intermediates in both reactions. I fear we were swayed by the then wide spread acceptance of the Förster mechanism for direct cis-trans photoisomerization.⁵ The problem was that, since azulene had a shot at quenching both singlet and triplet trans excited states, its effect should have been larger on the direct than on the sensitized photoisomerization. The opposite was very much the case.

At Florida State University I assigned the problem to my first graduate student, E. Dennis Megarity. Denny's work soon established that my misgivings were justified. Without a fluorimeter, we devised a method for using a scintillation counter to evaluate the quenching of *trans*-stilbene fluorescence by azulene.⁶ The results, later confirmed by a fluorimetric study,⁷ showed that the azulene effect on the direct isomerization of the stilbenes was accounted for quantitatively by singlet quenching. No triplets were involved. Later, differential viscosity effects on the influence of azulene under direct and sensitized excitation conditions were more nails in the coffin of the triplet mechanism for stilbene photoisomerization.⁸ The Lewis "loose-bolt" mechanism in which photoisomerization occurred following $S_1 \leftarrow S_0$ internal conversion as a hot ground state reaction again seemed possible,⁹ although it had been criticized soundly on the basis of the Kassel-Rice theory.¹⁰ Proponents of the triplet mechanism did not give it up easily and it suffered a slow demise.^{11,12} One exchange in this connection that I remember vividly to this day, occurred when I first

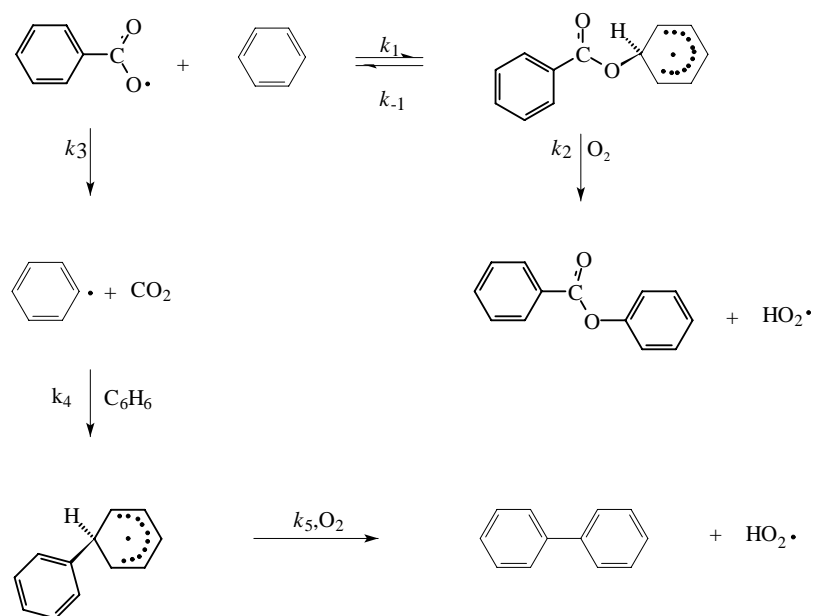
met David Whitten. I was visiting Caltech in late 1965 and David was a postdoctoral fellow in George Hammond's laboratory studying the mechanism of reactions initiated in solution by γ -rays. In front of a board in George's laboratory I was subjected to David's probing, tough questions concerning the interpretation of our scintillation counting results. David, to his credit, was one of the earliest converts to our singlet mechanism for the photoisomerization. Others waited until transient spectroscopic measurements provided direct confirmation of our conclusions.^{13,14}

The Lewis mechanism deposits all the electronic energy into ground state vibrational modes and should be subject to large deuterium isotope effects so I set out to synthesize perdeuteriostilbene. The perhydrostilbene was deuterium exchanged in D_2O over platinum at 200 °C. Since exchange of the olefinic hydrogens of the trans isomer is very slow,¹⁵ *cis*-stilbene was employed as the starting material. The exchange is accompanied by *cis* \rightarrow *trans* isomerization and, as the process had to be repeated several times, the partially deuterated *trans*-stilbene was separated from side products by chromatography and converted to a *cis*-rich photostationary state using triplet sensitization.¹⁶ Benzil seemed to be the sensitizer of choice as it gives photostationary states in excess of 90% *cis*-stilbene. However, for irradiations carried out in benzene under a constant stream of nitrogen bubbles, the *cis*-stilbene obtained was contaminated with a small amount of biphenyl. Pyrene, which gives a photostationary state of about 90% *cis*-stilbene, was used instead. With perdeuteriostilbene in hand, the dramatic deuterium isotope effects on the direct photoisomerization of the stilbenes that were expected for the Lewis hot ground state "loose bolt" mechanism were shown to be absent.¹⁶ Torsional relaxation to a common twisted singlet excited state seemed the only viable alternative and the stilbene phantom singlet was born.¹⁶

In 1966 I assigned the problem of identifying the source of the biphenyl in the benzil irradiations to Howell C. Curtis, my third graduate student. Howell had experience in photochemical research as an undergraduate in Harry Morrison's laboratory. Photolysis of benzil in degassed benzene, $\lambda_{exc} \geq 330$ nm, gave a complex product mixture in which biphenyl and benzophenone were present in trace amounts, $\sim 1\%$ each.¹⁷ Irradiation in benzene- C^{14} and isotopic dilution also showed that for a reaction taken to $\sim 50\%$ benzil loss, recovered benzil has $\sim 1\%$ activity incorporated. Since under nitrogen in the presence of stilbene most of the benzil survives the irradiation, biphenyl formed directly from benzil photolysis was insufficient to account for the contamination of *cis*-stilbene noted above. The source of the biphenyl in the presence of stilbene was traced to oxygen contamination of the nitrogen used in the outgassing procedure. Our attention turned to the study of the photooxidation of benzil. In the presence of air or pure oxygen the photooxidation of benzil in benzene gave biphenyl, phenyl benzoate, benzoic acid and benzoyl peroxide as major products.¹⁸ Benzoyloxy radicals seemed likely intermediates, and a comparative study of the photolysis of benzoyl peroxide in the presence of oxygen was undertaken.

The key observation in the photolyses of benzil and benzoyl peroxide in benzene at 30 °C in the presence of oxygen was a similar strong dependence of the phenyl benzoate to biphenyl product ratio on the oxygen concentration.¹⁹⁻²⁰ As the oxygen concentration is increased the yield of phenyl benzoate increases at the expense of the yield of biphenyl. While our work was in progress a paper appeared by Tokumaru and co-workers on the photolysis of benzoyl peroxide which similarly found that the yield of phenyl benzoate increases with increasing oxygen concentration.¹⁹ The two sets of results differed in that, in the Tokumaru study, the increase in the yield of phenyl benzoate appeared to come at the expense of benzoic acid.¹⁹ This was the same Katsumi Tokumaru whom I came to know and admire through our mutual interest in the mechanisms of *cis-trans* photoisomerization of arylethenes.

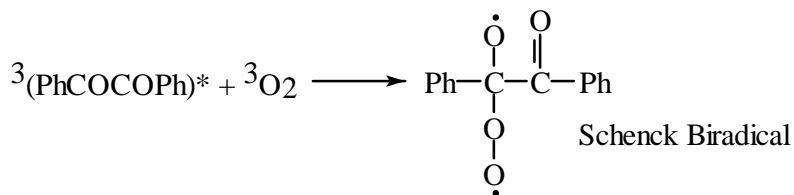
The conclusion seemed inescapable. Reversible addition of benzoyloxy radicals to benzene gives an adduct radical that reacts with oxygen to give phenyl benzoate.¹⁹⁻²⁰ At low oxygen concentrations, inefficient trapping of this σ -adduct increases the importance of its dissociation and subsequent decarboxylation to phenyl radicals whose irreversible addition to benzene led to an increase in the yield of biphenyl. The mechanism is summarized in Scheme I. The reversible addition of a free radical to benzene that had eluded me in Hammond's laboratory was now established. Moreover, it was found, albeit for a different radical, in essentially the same system I had investigated as a graduate student. That it was probably a σ - rather than a π -adduct seemed of little consequence. Guided by Eliel's work we carried out the benzoyl peroxide photolyses in $\sim 1:1$ mixtures of benzene- d_0 and benzene- d_6 .²⁰ The isotopic composition of the biphenyl product gave $k_4^H/k_4^D = 1.2_1 \pm 0.0_6$ at 30 °C, independent of $[O_2]$ and in reasonable agreement with $k_4^H/k_4^D = 1.06$ obtained at a higher temperature for phenyl radicals generated from the thermal decomposition of phenylazotriphenylmethane in benzene.³ Hydrogen abstraction from the phenylcyclohexadienyl radical by the triphenylmethyl radical gives biphenyl in the latter case.³ In the benzoyl peroxide reaction, in the absence of O_2 , an important pathway to biphenyl is the disproportionation of phenylcyclohexadienyl radicals²¹ which is subject to a



Scheme I. The Fate of Benzoyloxy Radicals in Benzene

“why so many $\text{ArCOOC}\cdot$ radicals should wait around for step 4 to occur so that they can then participate in” the hydrogen abstraction step.² The reversibly formed benzoyloxycyclohexadienyl radical provides an answer to this dilemma.

Reversible addition of benzoyloxy radicals to benzene furnished analogy in free-radical chemistry for deactivation pathways of the triplet states of carbonyl compounds, such as benzophenone, via reversible addition to benzene²²⁻²⁵ and to alkenes.^{26,27} The latter addition is the first step in Schenck’s mechanism for sensitized *cis-trans* photoisomerization,²⁸ a mechanism which probably applies when triplet excitation transfer to the alkene is highly exothermic.²⁷ Interestingly, our results on the photooxidation of benzil also led to the conclusion that formation of a Schenck biradical is the initial step.¹⁸ This, despite the fact that excitation transfer in this case would be exothermic.



large deuterium isotope effect.² Trapping of the phenylcyclohexadienyl radicals by O_2 in our system eliminated this complication.

Cage recombination of phenyl and benzoyloxy radicals obtained from the fraction of excited benzoyl peroxide that decomposes by two bond cleavage gives phenyl benzoate in ~11% yield.¹⁹ Upon correction of phenyl- d_0 benzoate yields for the cage product, d_0/d_5 ratios for phenyl benzoate formed from free benzoyloxy radicals are 2.3 and 3.0 for O_2 - and air-saturated benzene, respectively. This requires substantial C-H bond breaking in the rate-determining step for phenyl benzoate formation confirming expectations based on Scheme I. The reason for the relatively high yields of benzoic acid was a puzzle.² Abstraction of hydrogen from phenylcyclohexadienyl radicals by benzoyloxy radicals was a possible source of this product, but there was the predicament of explaining

With Hammond’s discovery of the crucial role of triplet excitation transfer in many photochemical reactions, many of us tended to discount Schenck biradicals as viable intermediates. Finding two systems^{18,27} in which Schenck biradical formation is the dominant pathway made a considerable impression on me. What appeared to be incorrect ideas for many systems could be correct for the right reactants. A

few years later I met G. O. Schenck while visiting the Max Planck Institute in Mülheim. He told me that he was seriously ill in the hospital when my paper on alkene photoisomerization²⁷ appeared. His son had brought a copy to his hospital bed and this vindication of his mechanism had so cheered him up that he made a miraculous recovery.

Experience upon experience has taught me not to categorically reject ideas just because they fail to account for observations in specific systems. Schenck biradicals do not provide the universal mechanism for triplet sensitization envisioned by Schenck, but they can be the right intermediates in certain cases. The Förster mechanism does not correctly describe the photoisomerization of the stilbenes, but it is correct for other olefins, for instance, *p*-nitro-¹³ and *m*-bromostilbenes²⁹ and certain thioindigos.^{30,31} Lewis et al. could not find evidence for Olson’s mechanism³² of adiabatic *cis-trans* isomerization in S_1 because they searched for it in stilbene⁹ where it occurs as a minor pathway.³³ Yet Olson’s mechanism was resurrected nearly half a century later by Sandros, Becker and co-workers.³⁴ In our recent work, we have shown that the adiabatic photoisomerization pathway in S_1 can be highly conformer specific and that its contribution increases with the size of the aryl group in *cis*- ArCH=CHPh .³⁵ The adiabatic conversion of *cis*-stilbene

triplets to *trans*-stilbene triplets⁴ is consistent with Olson's mechanism, although it was several years after his proposal that the existence of triplet states in molecules was accepted. Important examples of adiabatic cis-trans isomerizations on an electronically excited potential energy surface are Tokumaru's one way photoisomerizations in the triplet state.³⁶ Above, I described how the reversible association of radicals with aromatics that could not be demonstrated for phenyl radicals, was demonstrated for benzoyloxy radicals. Who knows, somewhere the system may lie in wait for which Lewis' hot ground state photoisomerization mechanism will still be found.

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