Creation and Detection of Reactive Intermediates
A Reflection

Anthony M. Trozzolo
Department of Chemistry and Biochemistry
University of Notre Dame
Notre Dame, Indiana 46556

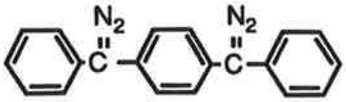
Preamble

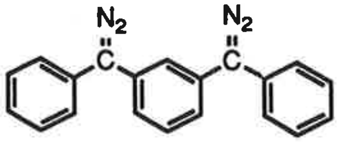
When I was invited to write this article by the Editor of this Newsletter, Dr. Ramamurthy, I was of course struck by the fact that this is a somewhat unique opportunity to comment on an area of science which has been at the core of my scientific career. It also was a challenge to prevent the commentary from becoming merely an apologia pro vita sua. I, therefore, have attempted to integrate the personal aspects into the historical development both of our work as well as the subject of photochemistry. One of the pleasant though humbling consequences of such an exercise is the realization that much of what has been accomplished is largely due to luck, an excellent research environment, superb colleagues and collaborators, and attendance at meetings and conferences. What follows is an account of that exercise.

My interest in photochemistry actually began as an interest in the spectroscopy of charge-transfer complexes during the three years (1953-56) that I spent at Armour Research Foundation (now IIT Research Institute) working on a variety of contract research projects. I had always had a fascination for generating colors by chemical reactions and the mere mixing of trinitrobenzene and anthracene in solution to generate an orange color provided an excellent example worthy of explanation. The classic Mulliken papers (1) had just appeared and stimulated many studies in this particular area of research. My interest in solid-state organic chemistry also began during this period under the tutelage of Walter McCrone, who was already at that time a microscopist of international repute.

When I returned to the University of Chicago in 1956 to pursue my doctoral research with Professor Wilbert H. Urry, my studies initially concentrated on the photochemical decomposition of diazomethane in polyhalomethanes (a reaction which has had very interesting mechanistic aspects(2,3)), but ultimately became concerned with bimolecular initiation of free-radical reactions. It was near the end of this period (1958) that I became aware that Bell Laboratories was going to add a few organic chemists to its technical staff in Murray Hill. I was fortunate enough to be one of the five additions in 1959 to join Ed Wasserman (who had arrived a few years earlier from Harvard) in the department headed by Field H. Winslow. The next few years were to be scientifically rewarding for each of the six (Ed Chandross, Gerry Smolinsky, Dick (Paul) Story, Bob Murray, Ed Wasserman and I) as we launched our individual careers in physical organic chemistry, and in particular, the creation, detection, and characterization of reactive intermediates, such as carbenes, carbocations, and nitrenes. In many of these studies, the photochemical decomposition of a suitable precursor was the preferred method for generating the reactive intermediate. At this point, I would be remiss if I did not acknowledge the encouragement of the Bell Labs administration, particularly that of our department head, Field "Stretch" Winslow, who was to become, and still is, the Editor of **Macromolecules.**

In the Summer of 1960, I attended my first Gordon Research Conference (Organic Reactions and Processes) and heard Phil Skell talk about the differences in reactivity of the singlet and triplet states of diphenylmethylene (4). At a blackboard at Bell Labs shortly after my return, Bob Murray and I were discussing how interesting it would be to make a molecule with two diazo groups and what multiplicity might one expect from the dicarbenes.





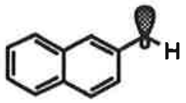
Since we had no technical assistants, Bob and I became each other's postdoc and we synthesized the diazo compounds and showed that their decompositions did give products that could be explained on the basis of dicarbene intermediates (5). These diazo compounds crystallized as lozenge-shaped crystals which were very strongly dichroic, being colorless or of a reddish hue, depending on the orientation of the crystals with respect to the plane of polarization of the microscope illumination. We thus performed our first anisotropic photo-decompositions which were made visible by placing a thin film of Nujol over the crystals thus trapping the nitrogen bubbles so that they could be seen (6).

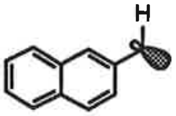
Another event took place in 1961 which further increased our interest in photochemistry and its implications in mechanistic organic chemistry. The 19th Organic Chemistry Symposium took place at Indiana University and two of the speakers, Howard Zimmerman and George Hammond, presented their respective studies and interpretations for a variety of organic phototransformations (7). It was evident that mechanistic organic photochemistry was becoming more rational and excited-state descriptions (largely obtained from the detailed studies of spectroscopists) could be used along with the concept of energy transfer (from photosensitization studies) to explain many photochemical reactions.

Although Bob Murray and I had *chemical* evidence that dicarbenes were being formed from the photodecomposition of bis-diazocompounds, we thought it would be worthwhile to test the more simple diphenyldiazomethane in an epr experiment where the diazocompound would be decomposed *thermally* (We didn't have a cavity set up for irradiation yet). Bill Yager, who was a pioneer in epr spectroscopy (He was the first to determine a g-factor for an organic compound (DPPH)), had some misgivings about the experiment, but his kind nature came to the fore, and we blew up his cavity. The consequence of this is that we were not allowed back into his lab for some time. In the meantime, Ed Wasserman and Bill Yager had discovered that it was possible to detect $\Delta m = 1$ lines in the epr spectrum of phosphorescent (triplet) naphthalene in low temperature *glasses*(8). Previously these lines had only been seen in single crystal studies which required a much more elaborate sample preparation and experimental set-up (9). This discovery made possible the characterization of not only phosphorescent triplets, but also of ground-state triplet molecules. Diphenylmethylene was the first carbene to be detected by epr spectroscopy (10), and a variety of other aryl methylenes (11) as well as aryl nitrenes (12) followed quickly. The epr spectrum not only established the triplet ground state of the methylene but also provided quantitative measure (as reflected in the zero-field splitting parameters, D and E) of the spin-spin interaction of the two unpaired electrons in the divalent carbon species. Similar experiments on diphenylmethylene in a benzophenone host were also being carried by Brandon, Closs, and Hutchison (13).

An example of serendipity in research was the discovery of the chemiluminescent reaction of diphenylmethylene with oxygen to produce the phosphorescence of benzophenone (11a). It occurred in the late afternoon of a summer day when a thunderstorm was approaching the Murray Hill labs and Richard Cramer, who ran the epr spectrometer in Bill Yager's lab, realized that he had left the windows open on his car in the parking lot. An epr experiment involving diphenylmethylene in an organic glass at 77 K had just been completed, and Cramer left me to rescue the sample tube from the spectrometer cavity as he rushed from the lab and turned off the room lights. It was fairly dark in the room because of the approaching storm, and one couldn't help but notice the glow from the sample tube as it warmed. One wonders how many chemiluminescent reactions remain undetected because we keep the room lights on.

A study of the environmental effects of various hosts (both glassy and crystalline) on the line widths of the epr spectrum of diphenylmethylene (14) paved the way to obtaining lines narrow enough to detect and measure C^{13} splittings of these lines obtained from the photodecomposition of diazocompounds labelled with C^{13} at the diazo site. This allowed even greater structural detail to be elucidated such as the bond angle at the divalent carbon (15). Further developments involved the discovery of geometric isomers (or rotamers, if you will) in the naphthylmethylenes (16) such as those shown and the detection of quintet states (17).



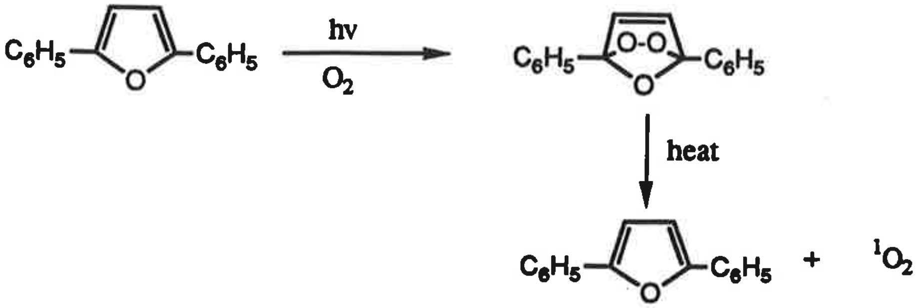


All of this work on the methylenes was done in collaboration with Ed Wasserman, Bill Yager and Bob Murray and, although we were often referred to as the "Bell Labs Group" by some academicians (who would hate to be referred to as the "________ University Group"), we did maintain a commitment to each other and to the work, and that period still epitomizes for me what we mean by scientific collaboration.

In 1962, Professor W. George Parks, the Director of the Gordon Research Conferences, published a notice in **Science** soliciting proposals for new Gordon Conferences. I sent in a proposal citing the fact there was no conference being held on a continuing basis on organic photochemistry and that the subject was developing at a very rapid rate. Although the proposal was not acted upon in 1962, a chance meeting at a luncheon (1963 Metro Regional Meeting in Newark) with Cecil L. Brown, who was on the Board of Trustees of the Gordon Conferences, gave me the opportunity to reinforce the case for a conference, and the Gordon Conference on Organic Photochemistry was approved to be held for the first time in 1964 at Tilton School in New Hampshire. Coincidentally, an International Conference on Photochemistry (honoring W. A. Noyes) was held in Rochester in March, 1963 and I had the opportunity to meet many of the leading photochemists, such as Norrish, Porter, Weller, Havinga, Schenck and others. Attendance at this meeting proved invaluable in contacting prospective speakers for the Gordon Conference. In 1963, photochemistry studies were largely focussed on the use of energy transfer in controlling the excited-state chemistry although charge-transfer quenching was being studied by Weller and others. The program of the first Gordon Research Conference was arranged to show this progression. The first speakers (Porter and Yang) stressed energy transfer and differences in reactivity of singlet and triplet excited states while the Friday speakers (McGlynn and Weller) concentrated on charge-transfer processes. One of the first persons that I invited to lecture at that first Gordon Conference was George Hammond. However, just shortly before that time, George had suffered a fainting spell at the fall ACS meeting in New York and for health reasons did not feel that he could accept. However, he did like the idea of a conference on photochemistry, and having an international perspective, became the organizer of the first IUPAC symposium on Photochemistry which was held in Strasbourg. These two series of conferences, along with the International Conference on Photochemistry (organized mainly by physical chemists) and, more recently, the IAPS Winter Conferences, have provided the main forums for the photochemist. For those interested in photobiology and photo-induced electron transfer, there are several series of conferences available on an international as well as a local level. By looking at the programs of these conferences over a period of time one can glean some of the history of the subject of photochemistry that has occurred since 1961 (7).

One of the interesting features about a molecule with a triplet ground state, such as diphenylmethylene, is the triplet-singlet energy gap. We thought that by looking for the luminescence processes of this species, it might be possible to derive a Jablonski diagram similar to that involving molecules with singlet ground state. With William (Willie) A. Gibbons, who arrived at Bell as a postdoc after completing his doctoral work with George Porter, we were able to characterize the fluorescence of diphenylmethylene and its excitation spectrum, and assign the excited triplet as a π-π^* state (18). However, we also found that no intersystem crossing occurred to the singlet probably because of a large T_1->S_1 energy gap. Later, at Notre Dame with Kam Wu (19), we were able to show that the excitation energy could be transferred to a molecule, fluorescein, that fluoresces from its excited singlet state.

One of the more practical aspects of the research in our Department at Bell Labs was that involving the environmental degradation and stabilization of polymers. Although a substantial amount of effort had gone into this work led by F. H. Winslow and W. L. Hawkins, there were clearly differences between the mechanisms of the thermal autooxidations (thought to proceed via a free-radical chain process) and the oxidative photodegradations. In 1964, a number of papers appeared by Foote and Corey which implicated a new intermediate, singlet molecular oxygen, in a variety of sensitized photooxidations, although the mechanism then in vogue was supported by the vast volume of work in this area of G. O. Schenck. We began a series of studies with Susan Fahrenholtz and Field Winslow to ascertain if there was a role for singlet molecular oxygen in the photodegradation of polymers. This culminated in a series of papers (20) which suggested that there might be a role for $^1O_2$ in the photodegradations. At about the same time, Bob Murray, who had been studying the mechanism of ozonolysis of alkenes with Paul Story, discovered that triphenyl phosphite reacted with ozone to form a relatively stable adduct, which on thermal decomposition appeared to release singlet molecular oxygen as a product, and that the $^1O_2$ could be trapped with a number of typical $^1O_2$ acceptors (21). It was also at this time that I became a member of the Committee on Conferences of the New York Academy of Sciences. The function of this committee was to approve proposals for conferences sponsored by the New York Academy of Sciences. One of my first impressions as a member of the committee was the large preponderence of bio-medical conferences which were being approved and the paucity of chemical conferences, and I was determined to increase the number of chemical conferences. Bob Murray and I had both discussed the rapid development of singlet molecular oxygen chemistry in a variety of areas and we decided to propose an International Symposium on Singlet Molecular Oxygen. The proposal was accepted and the conference was held in New York City in October, 1969 (22). The paper which Susan Fahrenholtz and I presented at this meeting involved an attempt to look for a Schenck Sens-O_2 adduct.

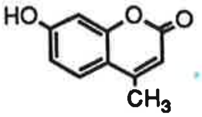


By looking at the kinetics of decomposition of the ozonide obtained from 2,5-diphenylfuran, we were able to show that the decomposition is first-order and that the rate is not affected by the presence or absence of $^1O_2$-acceptors such as cyclohexa-1,3-diene or 2,3-dimethyl butene-2 (23). Bell Labs was also developing a group in biophysics headed by Robert Shulman. One of the leading members of that group was Angelo Lamola who had a variety of interests in photochemical and photobiological problems and one of these involved a genetic disorder known as erythropoietic protoporphyria (EPP). This disorder resulted in an excess of protoporphyrin in the blood and persons affected with this malady suffered severe skin photosensitivity resulting in lesions and wounds. Previous work had suggested that the photodamage was a result of photohemolysis brought about by photodynamic action involving the protoporphyrin as sensitizer. The mechanism that we had proposed for the oxidative photodegradation of polyethylene involving $^1O_2$ (20a) seemed like a simple model on which to base an analogous mechanism for the EPP process. A series of collaborative studies in this area resulted in several publications which suggested that cholesterol and its hydroperoxides might have a significant role in the photohemolysis (24) and that α-tocopherol was an efficient quencher of $^1O_2$ (25). More recently, we focussed our attention on the mechanism on the energy-transfer steps by which $^1O_2$ is formed and, in work done at Notre Dame with Kam Wu (26), found that with sensitizers whose S_1-T_1 energy gap is greater than 22.5 kcal mol^{-1}, the quantum yield of $^1O_2$ can be more than unity indicating that energy transfer can occur from both S_1 and T_1.

In April 1966, the Chicago ACS Section held a one-day Symposium on Photochemistry and Gary Griffin and I were among the speakers. He described some interesting studies involving the photolysis of oxiranes which appeared to involve carbene intermediates (27). Since our studies described earlier had characterized diphenylmethylene by its epr and luminescence spectra, I embarked on a collaborative effort with Gary Griffin and Thap DoMinh (who had just arrived at Bell Labs after a postdoctoral stint with Gunning and Strausz at Alberta following his Ph. D. work with N. C. Yang) which ultimately showed that the photolysis of tetraphenyloxirane (28) is wavelength-dependent with irradiation below 300 nm giving rise to a two-bond cleavage and formation of a carbene and a carbonyl compound (later studies at Notre Dame with Thomas M. Leslie showed (29) that this is an *adiabatic* cleavage resulting in production of the *phosphorescence* of the carbonyl compound), whereas irradiation above 300 nm results in a one-bond cleavage and formation of a carbonyl ylide (30).

As a result of our work on carbonyl ylides, we became interested in photochromic systems, and after a visit to Bucknell University to learn of Harold Heine's intriguing aziridines whose crystals changed color in sunlight, we were convinced that the colorations were due to formation of azomethine ylides. However, the photochemistry of Heine's aziridines in solution turned out to more complex than a simple ring opening to form the ylide, and studies with Thap DoMinh (31) showed that the photochemistry of these bicyclic aziridines *in solution* was a series of consecutive electrocyclic reactions involving *two* ylides. In addition, by using laser-flash-time-resolved spectroscopy, Tom Leslie at Notre Dame was able to show that the two ylides have very different lifetimes, and that the first to be formed cannot be trapped efficiently by the usual dipolarophiles (32). Thus, the criterion of using dipolar cycloaddition trapping product stereochemistry for establishing modes of ring-openings must be viewed with some caution. The solid-state photchromism of these systems has been reviewed (33) and offers excellent opportunities for lecture demonstrations and photomicrographs illustrating anisotropic photodecompositons and the phenomenon of dichroism.

The late 1960s was a period which saw the emergence at Bell Labs of a number of research areas related to photochemistry. With growing interests in (a) photobiology and the related photophysics, (b) photoresist and imaging technology, (c) photodegradation of polymers, (d) lasers and their uses, and (e) photo-creation of reactive intermediates, it was decided to hold a biweekly seminar series entitled "Photosensitive Materials" which was intended to bring together interested staff members from the Holmdel laboratories as well as those from Murray Hill. In the group that regularly attended from Holmdel were Andrew Dienes and Charles V. Shank, both recent Ph. D.graduates from Berkeley (Dienes is now a professor at the University of California, Davis and Shank is the Director of the Lawrence Berkeley Laboratory). Their interest in late 1969 was to make tunable dye lasers. They had noticed a solvent effect in the tunability of a dye laser using 4-methylumbelliferone



as the dye and wondered if one could offer an explanation for it. After we looked up the "real" chemical name (7-hydroxy-4-methylcoumarin) and did a few experiments, we were able to devise a dye laser that, in a slightly acidified solution, could be tuned over half the visible range (34). The tunability was due to the fact that several excited-state species are generated (by proton transfers), each of which is capable of lasing, with no change in the absorption spectrum. We labelled this type of laser an "exciplex" laser, and further studies time-resolved the stimulated emission from the various excited-state species to obtain a time-profile of the excited-state proton transfers (35). Other proton-transfer lasers employing an *intramolecular proton transfer* have been developed recently (36).

For the physical organic chemists the 1960s provided an abundance of new physical techniques for studying mechanisms and detecting and characterizing reactive intermediates. A technique which was particularly suited for studying free radical intermediates in photochemical reactions was chemically induced dynamic nuclear polarization (CIDNP). Our interest in this technique came about somewhat accidently. Michael Cocivera and I had planned to study the electron distribution of excited triplets by attempting to achieve a steady-state population of T_1 in equilibrium with S_0 and measuring the various paramagnetic shifts in the nmr spectrum. However, Mike found nuclear polarization instead (37). We then began to study the photochemistry of benzaldehyde and benzoin and found that the respective polarized nmr spectra were essentially identical. Since the Closs-Kaptein-Oosterhoff (CKO) theory of CIDNP was being developed, we realized that the same radical pair must be formed in each of the two photolyses (38). Later, Gerhard Closs and Donald Paulson were able, in a series of elegant experiments, to delineate some of the more subtle features of the polarization mechanism in these photolyses (39). One of the consequences of the CKO theory was that, all other factors being equal, triplet and singlet radical pairs should exhibit opposite polarizations in the nmr spectrum. Susan Fahrenholtz was able to demonstrate that the photosensitized decomposition of benzoyl peroxide gave polarized nmr spectra of benzene and phenyl benzoate in accordance with the CKO theory (40). The study also helped clarify the sensitization mechanism, since earlier it had been assumed to proceed via triplet sensitization and the CIDNP results clearly implicated the possibility of a singlet mechanism if the triplet energy of the sensitizer is too low for efficient transfer to the peroxide.

In 1971, Nick Turro invited Angelo Lamola and me to give his photochemistry course at Columbia since he was going to be on leave (as it turned out, although he was on leave, he stayed at Columbia during this period). It was my first teaching experience since my undergraduate days at Illinois Tech (I had been an AEC and NSF Fellow at Chicago, and these fellowships carried no teaching responsibilities) and I enjoyed it very much except on two occasions. The first exception was when I had to lecture on carbonyl photochemistry with Nick Turro in the front row (he came to all the lectures) and the second was when I had to give a magic show with Koji Nakanishi in the audience. Talk about carrying coals to Newcastle! In the following year, I was invited to give a series of Peter C. Reilly Lectures at the University of Notre Dame. The title of the series was "Creation and Detection of Excited-State Intermediates" and the lectures dealt with the topics that have already been discussed. Although I had been raised in nearby Chicago and did not leave until the completion of my doctoral research, and had been a life-long Notre Dame football fan, I had never visited the University before my lectures in October 1972. That visit made a lasting impression on me and three years later in 1975, I joined the Department of Chemistry and became a member of the Radiation Research Laboratory as well. It was not easy to leave Bell Labs' superb research environment and my colleagues there, many of whom had international reputations as outstanding researchers, but in retrospect, it was the right thing to do at that time. My career then began to take on additional facets, involving more administrative functions, such as the Associate Editorship of the **Journal of the American Chemical Society** and the Editorship of **Chemical Reviews** (One can point out that the last three Editors of Chemical Reviews, Harold Hart, myself, and the current Editor, Josef Michl, have all had photochemical research interests) and many committee and Board assignments both in the ACS and in the Gordon Research Conferences. Also, being the early occupant of an endowed chair at Notre Dame made me vulnerable to frequent assignments on various committees such as search committees for additional chair positions which were then being established. However, the presence of many congenial colleagues, both in the Department and throughout the University, has made the last seventeen years quite intellectually satisfying and five Notre Dame degrees for my children (a sixth one, hopefully next spring) attest to the nonscientific gratification enjoyed during this period.

As one looks back on the last thirty-five years in photochemistry, one cannot help but notice the impact of new and more sophisticated instrumentation, which allows us to obtain the kind of data on photochemical reactions that we merely fantasized about three decades ago. Another major transition has been that the whole concept of bimolecular interactions in the excited state now is a continuum encompassing energy transfer, "simple" quenching, exciplex formation and electron transfer and that the elucidation of mechanistic details of photochemical reactions is becoming more complex. One also has seen a greater appreciation for the anisotropic and micro-environmental effects on photochemical reactions and the driving force of applied photochemistry toward miniaturizing the photochemical reactor (such as in photography, photoresist technology, and molecular models for photosynthesis). In addition, the materials research aspect of photochemistry has greatly expanded the need for interdisciplinary approaches for solving problems, and this challenge continues to provide a stimulus for ever-expanding one's own intellectual horizons (I always felt that being a photochemist required one to be interested in, and, if possible, master a wide spectrum of physical, chemical and even biochemical data and techniques). From a pedagogical standpoint, training involving photochemical research provides the student with a broad armamentarium with which to attack a wide spectrum of problems in physical organic chemistry or related topics in materials science research.

Where will we go from here? Attend a photochemistry meeting and you will get a glimpse of the future. The interaction of light with matter is so multi-faceted that I believe we will continue to see new types of photochemical transformations and new physical techniques that will allow us to probe the more subtle features of mechanisms and structures, and the advent of microphotochemical reactors approaching the molecular scale and new non-linear optical materials will permit the fabrication of optical devices challenging the electronic ones currently in commercial use.

Earlier I commented on the important role of meetings in the development of photochemistry. Another sign of "growing up" is the recent establishment of awards and prizes to honor those who have made significant contributions to the subject. The Porter Medal and the IAPS Award, as well as the Halpern Award in Photochemistry of the New York Academy of Sciences (awarded 1977-1984), all remind us of the human aspects of research, and that, although individuals are honored, the communal aspects of collaboration need to be recognized. Therefore, I would like to end this account by recognizing the tremendous impact that my students at Notre Dame and my colleagues at Bell Labs, Notre Dame and my collaborators throughout the photochemistry community have had on me. It has been much like that of the reactive intermediates that spring to life as a result of a photochemical process. Their motto can be seen on one of my poster demonstrations of photochromism: "Photochemistry gives meaning to my transient existence", where the saying appears as a photochromic aziridine is irradiated. If you add "collaboration" to the subject of that saying, it's our motto, too. Finally, I must acknowledge the most important people in my life, namely, my wife, Dolly, whose patience and support have constantly bolstered me during the course of my career, from the sacrifices in graduate school down to the present time, and our family of six children (now increased by in-laws and grandchildren), who continue to be a source of gratification to both of us.

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