JOC The Journal of Organic Chemistry

Perspective

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Reflections on a Fifty-Year Career in Organic Photochemistry: A Personal Perspective

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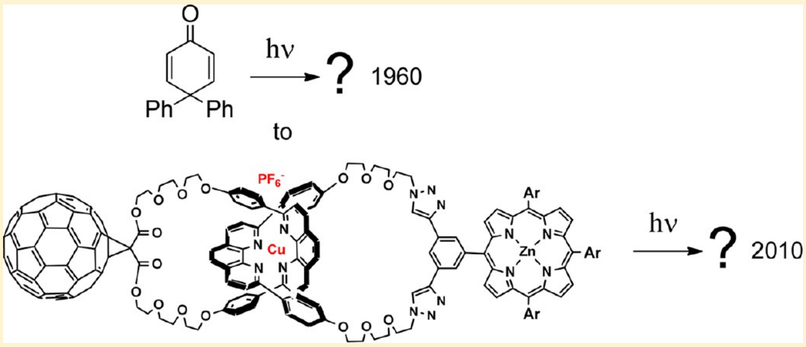


ABSTRACT: This Perspective traces the career of the author in the area of mechanistic organic photochemistry from the primitive state of this field in the late 1950s and early 1960s until its maturity as a highly sophisticated discipline at the present time. The paper focuses on early studies carried out by the author and his associates to delineate mechanisms of basic types of photochemical reactions of small organic molecules to studies in recent years involving photoinduced electron-transfer processes occurring in nanoscale artificial photosynthetic systems in ultrashort time domains. The important role that serendipitous events played in directing key career decisions and events is emphasized. The important ways that developments in instrumentation influenced the choices, possibilities, and accomplishments of performing research in photochemistry between 1960 and the present time are emphasized. Acknowledgment is given by the author to the many people who contributed directly and indirectly to the course that his career has taken over more than half a century.

INTRODUCTION

The occasion of my receiving a 2012 ACS Senior Arthur C. Cope Scholar Award, coinciding with the closing of my research laboratory at New York University (NYU) after 51 years, prompts me to reflect on my long career in organic chemistry with particular emphasis on organic photochemistry. This Perspective outlines the course of my career and the choices that were made along the way and pays tribute to the people who played significant roles in my personal and my professional life. As will be seen, serendipity played a very significant role in charting this course. I will present some highlights but obviously cannot include the research contributions of all the undergraduate research students, graduate students, and postdoctoral fellows, numbering over 200, who played key roles in my career at NYU. My career trajectory, as will be seen, is closely allied with the huge scientific advances in instrumentation that occurred during this period.

HIGH SCHOOL INFLUENCES

I was born in Brooklyn, New York, in 1935, during the depression. For reasons which I frankly have never completely understood, my parent decided in 1940 to move away from their parents and siblings in Brooklyn to remote Far Rockaway, on the extreme eastern end of the borough of Queens. Life in Far Rockaway, which is situated between the Atlantic Ocean and Jamaica Bay, was idyllic, even during the Second World War, when there was constant concern about German submarines just off the beach (they were indeed out there). Although technically part of New York City, Far Rockaway was more like “the country”, uncrowded, safe, and peaceful. It was a great place to grow up. (This area has recently been devastated by Hurricane Sandy, including loss of the beautiful boardwalk along the ocean.) My elementary school and high school were within walking distance of our house. Far Rockaway High School (February 1949 to June 1952) was a very fine school at that time, with excellent faculty in Mathematics, Science, and the Humanities (an earlier attendee at the same high school a decade before was Richard Feynman, who worked at Los Alamos and Caltech and won a Nobel Prize in Physics; an infamous attendee a few years after me was the notorious swindler Bernie Madoff). The seeds of my interest in Chemistry were planted by Mr. Rassiga, my Chemistry teacher, who made the subject fascinating to me. Physics was too abstract for my tastes. In my last year of high school I met Carlotta Lief, who was my date for the senior prom in June 1952. Little did we guess that we would be married ten years later.

Received: April 15, 2013
Published: May 28, 2013

dx.doi.org/10.1021/jo4007078 | *J. Org. Chem.* 2013, 78, 6811−6841

COLUMBIA COLLEGE 1952−1956

As high school class valedictorian, I applied to most of the fine colleges on the East Coast and was accepted to all of them except Harvard. I would like to believe it was because they had a quota for Jewish students, which was an issue at that time. I decided to stay in the city at Columbia, where I had a Regents Scholarship, which enabled me to live on campus in Hartley Hall. My extracurricular activities centered on the Columbia Band, where I played percussion as I had done in high school. During football season I carried and played the big bass drum at all home and away football games. Despite our terrible team, the band played enthusiastically. My favorite recollection goes back to the fall of 1952 when General Dwight Eisenhower, then President of Columbia, was running for the United States Presidency. The Army−Columbia game was held that year at Baker Field at the northern tip of Manhattan, and Eisenhower was present, spending half his time on the Columbia side of the field and the other half on the Army side. At the start of the game he trotted with his guards through a phalanx of the two bands. As he passed me, I impetuously gave a thunderous series of bangs on the big bass drum. Eisenhower turned to me and shouted "Keep beating it, boy"! The game was a draw, which for Columbia was a triumph.

I was stunned to learn very quickly that the writing skills which were good enough to get me through high school with flying colors were not good enough by Columbia standards. I had to learn a much more sophisticated style of writing, which eventually stood me in good stead. Columbia's undergraduate curriculum emphasized the "Whole Man" and included two years of required courses in the Humanities and the Social Sciences. These courses were a critical part of my education and had a great influence on me personally, although at the time they were often tedious. I had to read a book a week in the Humanities "Great Books" course, where I had two outstanding teachers, Martin Ostwald and Moses Hadas, both from Classics. I was shocked to find out later that most other colleges did not place nearly as much emphasis on these areas as did Columbia. I placed out of the Humanities Music course due to my extensive knowledge of classical music, derived from piano studies since the age of 7 and regular attendance at New York Philharmonic concerts since 1950. However, I had to take the Fine Arts course given by the great Howard Davis, a superb teacher. This course was the basis of my great love of paintings, sculpture, and architecture. The fact that art, music, and literature have played an enduring role in my life stems directly from my courses at Columbia.

Of course I chose to do my major in Chemistry. I enjoyed my Freshman Chemistry course with Larkin Farinholt, but I hated Qualitative Analysis and Quantitative Analysis in my sophomore year, with their onerous and boring laboratory components. In my junior year I took Organic Chemistry with Charles Dawson (see Figure 1, left), and I was hooked. I found the subject fascinating, and it all made sense to me, which was not the case for many of my premed classmates. I held pre-exam review sessions for them, where I found that I could convey the basic ideas and concepts of the subject in ways that helped them to markedly improve their understanding of the subject. At that time, 1954−55, Organic Chemistry was a descriptive course with only a minimal mechanistic underpinning. Our textbook by Noller was organized on the basis of functional group reactions; mechanistic considerations were merely footnotes. This remained true until the pioneering book by Morrison and Boyd (of NYU) appeared several years later with its emphasis on structure and mechanism, which radically changed the way Organic Chemistry was taught. I loved organic chemistry and knew right away that I wanted to pursue this subject in graduate school. Physical Chemistry, which I took at the same time, was taught by an aging Louis Hammett, a great scholar but a boring lecturer. Hammett's dry manner of presentation was the antithesis of Dawson's exciting lecture style. I did well in PChem, as I did in Physics which I also took concurrently, but these subjects did not turn me on nearly as much as did Organic Chemistry.

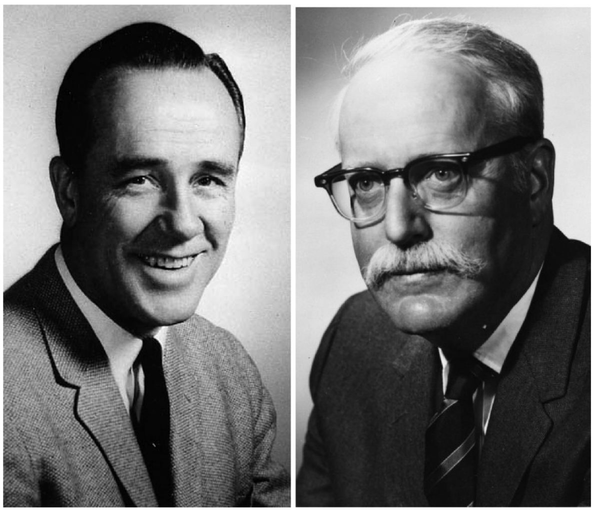


Figure 1. (Left) Charles Dawson. (Right) Cheves Walling (Columbia). Dawson photo reprinted courtesy of University Archives, Columbia University in the City of New York. Walling photo taken by Fabian Bachrach Studio, reprinted with permission.

In my senior year (1955−56), in addition to a number of Humanities electives, I took two graduate courses with Cheves Walling (Figure 1, right), Physical Organic Chemistry (POC) and Free Radicals, which was Walling's area of research. They were both terrific! Walling would put the pertinent literature references on the upper left section of the blackboard and then would meticulously present the subject material. There was no textbook for either course. I was fascinated about what was going on in POC, which introduced me to the work of the leading people who were changing the course of organic chemistry: Frank Westheimer (Chicago and Harvard), Paul Bartlett (Harvard), Saul Winstein (UCLA), Gardner Swain (MIT), Bill Doering (Yale, formerly Columbia), and John D. Roberts (Caltech). I knew immediately that this was the area in which I wanted to work. When I applied to graduate school that fall, I was really applying to these guys, although of course the overall reputation of their departments was a consideration. I also applied for a National Science Foundation Predoctoral Fellowship, of which a large number were awarded, including one to me. MIT accepted me with a fellowhip offer very early, and the other schools quickly followed suit, all except Harvard. The acceptance letter from Harvard arrived only after I won an NSF fellowship, and I tore it up in anger. Along with another chem major at Columbia, Howard Taylor, who later became a very successful theoretical chemist at the University of Southern California, I visited MIT and Harvard to talk with the people there about graduate study. MIT greeted us warmly, but Harvard made no efforts on our behalf. I managed to get an interview with Frank Westheimer, who was very welcoming and who gave me a copy of his latest manuscript to read (before the age of photocopying!). After weighing the pros and cons of all the alternatives, I decided to accept the Caltech offer in order to work with Jack Roberts (Figure 2), whose work on benzyne and carbonium ion chemistry I found particularly fascinating.

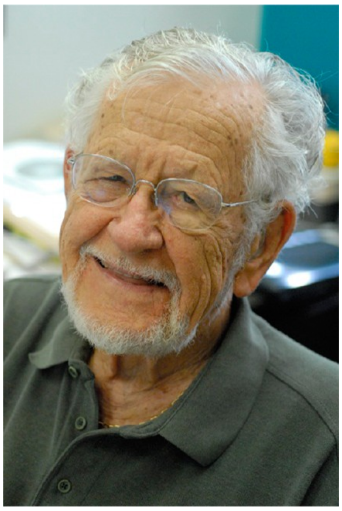


Figure 2. John D. Roberts, California Institute of Technology, with permission.

This meant uprooting myself from my family, my friends, and cultural life in New York (by that time I had become a habitué of the Metropolitan Opera as well as the Philharmonic) to pursue a completely different lifestyle in California. It was like moving to a foreign country! For a somewhat insecure young man of 21 this was a major life change; I was by no means sure it was the right choice.

I arrived at Caltech without any prior research experience, which was not unusual at that time. In my senior year, I took a seminar at Columbia with physical chemist Ralph Halford, who introduced me to infrared spectroscopy, which was a revelation. I was fascinated that one could get so much information about a compound simply by taking its infrared spectrum! I also served in my senior year as a laboratory teaching assistant in the Honors section of Freshman Chemistry, where my best student was a brilliant young guy by the name of Roald Hoffmann. This reinforced my attraction to teaching, and I was resolved at that point to make my career in academia. To put things in perspective, Ronald Breslow joined the Columbia Chemistry Department just after I left in 1956; Gilbert Stork was already there, but he had no contact at all with undergraduates. We did not know he existed.

■ CALTECH (1956–1960)

Following my graduation from Columbia, I went to Europe on a wonderful student tour lasting ten weeks that covered a large part of western Europe, along with some Columbia pals including Howard Taylor, who would start at Berkeley in the fall. We traveled back and forth on the Greek Line, which used reconverted German ships. The crossing was very slow, leaving plenty of time for rest, bridge, and partying. Knowing I had to prepare for a series of qualifying exams at Caltech, I instructed my parents to put a bunch of my books on the ship for the return trip. I passed all the qualifiers, and so, according to Caltech rules, I did not have to take any graduate courses in Chemistry. I thought this was bizarre, so I signed up for an advanced PChem course with Harden McConnell, who had just arrived at Caltech, but not for any organic chemistry courses, which in retrospect was a mistake. McConnell's course focused on contemporary aspects of Physical Chemistry, including the new field of magnetic resonance. He seemed very surprised that a lowly organic chemist could master this material. I later sat in on a course on statistical mechanics with the brilliant Werner Schomaker. In order to satisfy my minor in Physics, I had to take a very difficult full year advanced course in mechanics, taught by Nobel Prize winner Carl Anderson, and also one in Modern Physics the following year, taught by Thomas Lauritsen. Accordingly, my Caltech diploma reads Ph.D. in Chemistry and Physics. As part of my final oral examination, I had a one-on-one meeting with Lauritsen who asked me to explain Hückel molecular orbital theory to him. This turned out to be fun; he had never heard of it.

At Caltech, the first order of business as a graduate student was to select a research adviser. Although I knew I wanted to work with Roberts, he insisted that I meet with other people in the department before I committed myself. I was one of the few first years who met with Linus Pauling, then Division Head, which was a fascinating experience. The only other organic chemistry faculty members at that time were Carl Niemann, an excellent bioorganic chemist whose work centered on the mechanism of action of chymotrypsin, Edwin Buchman, a nontenured Research Scientist who specialized in small ring chemistry, Laszlo Zechmeister, an elderly heterocyclic chemist, and Jack Richards, who had just joined the department. I naturally chose Roberts. He asked me to talk to people in the lab about what they were doing and then come back to him with an idea for a research project. At that time, several people were working on "nonclassical" carbonium ions and, in particular, on bicyclobutonium ions derived from cyclopropylcarbinyl, cyclobutyl, and allylcarbinyl precursors. With my background on free radicals derived from Walling's course, I suggested to Roberts that perhaps we should take a look at the behavior of analogous free radicals. I suggested that we generate these free radicals by radical-initiated decarbonylation of corresponding aldehydes. And so I set out on what turned out to be a lengthy journey to synthesize cyclopropylacetaldehye, which at that time was not a known compound, and some other small ring aldehydes. I tried many ways to make these aldehydes from the rather limited set of starting materials available from Eastman Kodak, the chief supplier of fine organic chemicals in those days. After a lot of hard work, I eventually succeeded and was able to demonstrate that cyclopropylcarbinyl radicals underwent ring-opening to give allylcarbinyl radicals; according to trapping studies, the two radicals were in equilibrium. Thus, unlike the analogous electronically delocalized carbocations, these radicals were discrete species, which it turns out is entirely consistent with molecular orbital theory; if we had only bothered to do some Hückel-level MO calculations we would have known this years earlier. Nonetheless, Roberts remained unconvinced about my findings, and so my work was never written up for publication, although he did publish work on analogous phenyl-substituted systems a few years later. The only reference to my thesis study is in Walling's *Free Radicals in Solution* in a chapter on Free Radical Rearrangements,[1] based on discussions we had on one of my periodic trips to New York. Roberts and I published one paper on free radical decarbonylation of cyclopropane- and cyclobutanecarboxaldehyde, which gave expected and rather unexciting results.[2]

Perhaps the most significant development in organic chemistry in the last four decades of the 20th century was the advent of nuclear magnetic resonance (NMR), in which Jack Roberts played a critical role. It is hard to imagine that there was a time when research in chemistry was done without the help of NMR, which has become indispensable to research in many fields, but especially in organic chemistry. NMR was discovered by physicists Purcell and Pound in the 1940s, who won the Nobel Prize; at that time, no one imagined its potential as an analytical technique in chemistry. As described in his recent Perspective,[3] Roberts had been introduced to NMR at du Pont during his frequent consulting trips there and immediately recognized the potential of this technique in organic chemistry. However, it took some time and much cajoling before Jack was able to convince Linus Pauling, the Chair of the Chemistry and Chemical Engineering Division, to purchase an instrument from Varian, the only supplier at that time. For a while in the late 1950s we possessed the only NMR spectrometer in an organic chemistry university laboratory in the entire United States! Our 40 MHz NMR spectrometer was a very temperamental instrument, hard to tune and impossible to keep in tune. Taking a spectrum on that instrument was physical labor, involving cranking the magnets into position while simultaneously monitoring the ringing pattern of the methyne proton of acetaldehyde. There was no time averaging; you got one shot at a spectrum and sensitivity was low, so one needed substantial amounts of material to get a spectrum. Spectra were taken using concentric tubes containing water and a solution of the sample in an organic solvent (this was before the days of tetramethysilane and deuterochloroform). Nearly every time we took a spectrum it was the first ever for that compound. Sometimes the spectra made sense, but often they did not; we were just learning the rules. Roberts published a little book laying out the ground rules for interpretation of NMR spectra.[4] We also recorded spectra on samples sent to us from organic chemists around the country, so that by the late 1950s the organic community came to realize the enormous value of NMR for structure determination. It was truly a revolutionary development, and Jack Roberts was the guy leading the charge. Just as in the use of ^{14}C-labeling in elucidating organic reaction mechanisms and in applications of Hückel molecular orbital theory in organic chemistry, Roberts was way ahead of the rest of the field. He also pioneered ^{19}F, ^{15}N, and ^{13}C NMR techniques. Before long, Varian A-60 NMR spectrometers became workhorse instruments in laboratories everywhere. It is hard for contemporary students (who work daily with 400, 500, and 600 MHz spectrometers) to realize that there was a time, within living memory, when NMR data were not routinely available. Structure determination of complex natural products had to be carried out by laborious chemical degradation to known compounds, which had to be identified by melting and boiling points and other physical properties without the use of any spectroscopic techniques. Later infrared and ultraviolet−visible absorption spectroscopy proved to be of some use, but were rarely definitive.

During my junior year at Caltech, 1958−59, I was asked to serve as a teaching assistant in organic chemistry. As I became more informed about undergraduate education at Caltech, I was shocked to discover that these guys (all male at that time) were required to take only one course in the Humanities during their entire college experience! The Humanities department consisted of only a handful of teachers (only two at that time, to the best of my recollection). Caltech students were woefully deficient with respect to Literature, Art and Music, as well as the Social Sciences. The "Whole Man" educational approach at Columbia was the antithesis of the Caltech undergraduate experience. Sometime during 1958 I was lamenting this situation at home to one of my housemates, Fred Anson, then an Assistant Professor of Chemistry in Analytical and Inorganic Chemistry. Fred suggested that I do something concrete about this rather than just ranting and raging. I contacted Hunter Meade in the Humanities Department, an amateur musician, and proposed giving a series of weekly evening seminars on music, tracing the symphony as an art form from the 18th century to the present time. My idea was to provide illustrations on the piano (imitating what Leonard Bernstein was doing at that time on television with huge success) supplemented by recordings. To the surprise of everyone, (including me) over 200 people, mostly students, showed up at the first seminar. I examined symphonic form as developed by Mozart and Haydn, and then showed how Beethoven expanded the forms he inherited, incorporating romantic ideas into his music to make it more dramatic. In succeeding weeks, I examined symphonic form in Germany and Austria through Gustav Mahler, and then went back and traced symphonic traditions in France and Russia, and finally in this country. While the attendance fell off somewhat over 15 weeks, there were never less than 50−60 people at each presentation. While I put a lot of effort into this project, I still devoted most of my time to my research. JDR did not appear to be terribly upset with me, or at least that is what I believed. The success of these seminars showed that students at Caltech were receptive to learning about music and the arts, and indeed in succeeding years the Humanities program at Caltech was greatly expanded.

While I was not compensated financially for my efforts, Dr. Meade arranged through friends for me to attend the stereorecording sessions being held in Hollywood by Bruno Walter (Figure 3) with the Columbia Symphony Orchestra, a pick-up orchestra of movie studio musicians and principals of the Los Angeles Philharmonic. Walter, one of the greatest conductors of the twentieth century, was my idol from many NY Philharmonic concerts. Through him I was first introduced to the amazing music of Gustav Mahler. I attended nearly all of these recording sessions, accompanied by orchestral scores and

Figure 3. Dr. Bruno Walter, famed orchestra conductor. Photo by Fred Fehl, courtesy of Gabriel Pinski, source New York Philharmonic Archives. Published with permission.

Caltech friends. At the first session I attended Walter, then 82, was recording the Adagio from Beethoven's Ninth Symphony, the final piece of his Beethoven cycle. Walter went on to make memorable stereo recordings of works of Schubert, Schumann, Brahms, Dvorak, Wagner, Bruckner and Mahler, recordings which are still currently available on compact discs. The old man usually sent a warm welcoming nod in my direction upon his arrival on the podium.

My passion for music made me wonder whether or not I was making a mistake pursuing an advanced degree in Chemistry, or whether I should pursue a career in music as a conductor. I decided to seek advice from Walter himself. I arranged to meet with him on a Sunday morning at his home on Bedford Drive in Beverly Hills. He looked much older than he did at the recording sessions, when the years flew away as soon as he was absorbed in the music. I told him about my experiences hearing him conduct in New York, particularly my introduction through him to the music of Mahler. Walter inquired about my work and my interests. I told him that I was torn between my passion for science and for music, and he then said something to me which I remember vividly to this day: "Remember that you can have science as a vocation and music as an avocation, but not the other way around". That message was critical for the course my life would take. I chose to follow an academic career in science, knowing that music would always be there for comfort and inspiration. I left Dr. Walter that morning knowing what I had to do. Chemistry has been the central theme of my professional life, but music has always been there for sustenance and inspiration. In 1980 at the age of 45 I made the commitment to return to serious study of the piano, initially with the famous piano pedagogue Alexander Lipsky, and after Lipsky's death with other fine teachers. I still take a weekly lesson with Michael Cannon, a Juillard graduate and occasional concert pianist. Since 1985 I have given occasional solo piano recitals, as well as performances at scientific gatherings, usually with musically gifted chemistry colleagues. The most recent event was an all-Chopin solo piano recital in 2010 to mark the composer's 200th birthday.

■ THE WINSTEIN SEMINARS, JERRY BERSON, AND GEORGE HAMMOND

Shortly after I started in the Roberts lab, I learned that a number of people in the lab went regularly on Thursday nights to UCLA to attend the seminars hosted by Saul Winstein (Figure 4a) where presentations were frequently made by distinguished visitors. Roberts himself was often in attendance. These seminars were famous for the discussions, dominated by Winstein, who probably had the sharpest mind in physical organic chemistry. He would ask very probing questions, often as soon as the speaker opened his mouth, creating a very tense and electric atmosphere. Everyone who was anyone in physical organic chemistry in the LA area would be there, including of course members of the Roberts group. I probably learned more about organic reaction mechanisms at the Winstein Seminars than in any course I took at Caltech.

One of the people who attended the Winstein Seminars regularly was Jerry Berson (Figure 4b), who at the time was Assistant Professor at the University of Southern California. I first met Jerry in late 1956, and was immediately aware that he was an exceptionally brilliant young physical organic chemist and a hell of a nice guy. He was interested at that time in free radical rearrangements, which was of course my chief interest. We met regularly at his office at USC where we had intense discussions on this and other subjects. A warm relationship developed which has lasted to the present day, through Jerry's subsequent moves to Wisconsin (Madison) and finally to Yale. Jerry was my host when I spent a sabbatical leave at Yale in 1975–76.

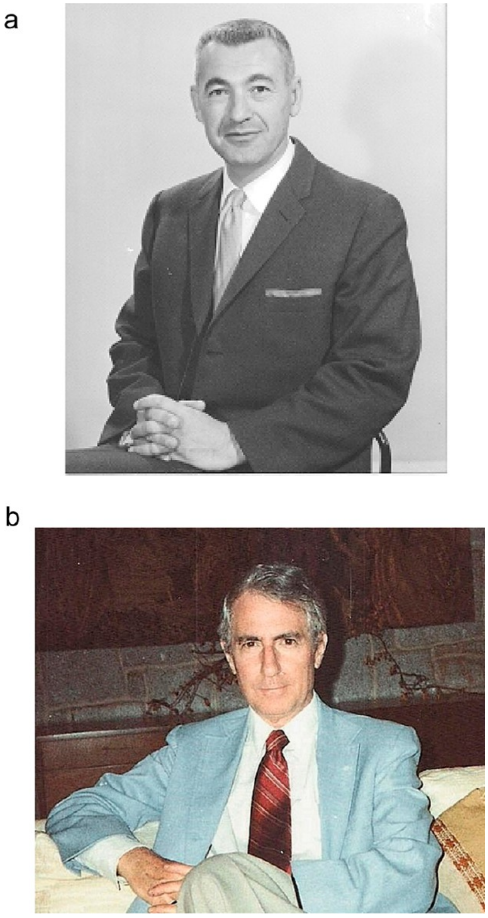


Figure 4. (a) Saul Winstein, University of California Los Angeles, taken by ASUCLA Photography, reprinted with permission from UCLA Archives. (b) Jerome A. Berson (USC, Wisconsin, Yale). Photo courtesy of Professor Berson.

The other young organic chemist who made a particularly strong impression on me at the Winstein Seminars was George Hammond, then at Iowa State University (see Figure 5). During a sabbatical year at UCLA in 1957–58 George gave a series of presentations at the Winstein Seminars on his work in free radical chemistry and his new ventures into organic photochemistry. George's free-wheeling style provided an excellent foil to Winstein. George moved to Caltech later in 1958, where he established an outstanding research program in organic photochemistry, which was then enjoying a renaissance. While physical chemists had worked for many years repeatedly on the photochemistry of acetone or formaldehyde in the vapor phase, a number of important organic chemists were beginning to make forays on solution-phase organic photochemistry, including Georg Büchi at MIT, Derek Barton at Imperial College in London, Oskar Jeger at the ETH in Zürich, and a few others. I frequently went to George's office one floor down from the Roberts lab late in the evening to find out what was new concerning the photoreduction of benzophenone and other projects. I found the subject interesting, and George's enthusiasm for his work was infectious. I often talked about this

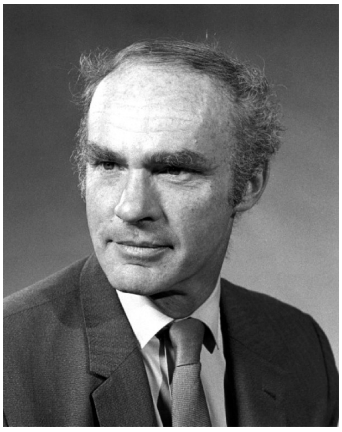


Figure 5. George S. Hammond, Caltech. Photo courtesy of Institute Archives, California Institute of Technology.

new line of research with Bill Moore, Pete Leermakers, my housemate Jim Clovis, and others in the Hammond lab.

After defending my Ph.D. thesis during the summer of 1960 I had hoped to go to Switzerland on an NSF postdoctoral fellowship to work with Cyril Grob at Basel. Grob had visited Caltech in 1959, and I was very taken with his work and his personality. I thought he would be a terrific mentor, and I looked forward to living in Europe following my first trip there four years earlier. After having held NSF predoctoral fellowships for 4 years, I was stunned when I was turned down for a postdoctoral fellowship. The fact that I had no publications was undoubtedly a factor, but Roberts may have had some misgivings about my seriousness as a research scientist, perhaps because of the seminars on music. In any event, I suddenly had no plans or prospects for what to do after leaving Pasadena. I was beginning to think that I should go into physical chemistry, where I felt comfortable, and indeed I applied for positions with several people, including Sam Weissman at Washington University in St. Louis, who was doing fine work in electron spin resonance. I also considered applying to Bill Doering at Yale, whose work on organic reaction mechanisms was brilliant and whose writing style was the most elegant in the field, but Roberts thought this was a bad idea; he said "that I would push Doering over the brink!" By April of 1960 I was still undecided what to do next, when Hammond returned from a visit to Northwestern where he met Howard Zimmerman (Z), then an Assistant Professor (see Figure 6). I was aware of Z's work on the mechanism and stereochemistry of ketonization of enols, which I found intensely boring. George was very excited about Z's new plans for research in mechanistic organic photochemistry after his upcoming move to the University of Wisconsin, Madison, and that he was looking for good postdocs. George felt that this would be an excellent career move for me, given my interest in photochemistry, and strongly recommended me to Z. Some telephone calls were made, and a few days later JDR walked into the lab and loudly said, in his usual drawl, "Schuster, do you wanna work for Zimmerman?" I said "OK" and that was that; this is typical of how important career transactions were made in those days. This was the first of a number of entirely serendipitous events which determined the trajectory of my career in chemistry. If not for this chance meeting between Hammond and Zimmerman at Northwestern in Spring 1960, I would have followed an entirely different career path, possibly in physical chemistry, and almost surely not in New York City. My life would have been entirely different.

Figure 6. Howard E. Zimmerman, University of Wisconsin. Reprinted with permission from Howard Zimmerman Memorial Issue, *J. Org. Chem.* **2013**, *78*, 1707. Copyright 2013 American Chemical Society.

POSTDOCTORAL YEAR AT WISCONSIN WITH HOWARD ZIMMERMAN, 1960–61

I arrived in Madison, Wisconsin, in early September 1960, ready to throw myself into postdoctoral research in mechanistic organic photochemistry with Zimmerman. He had a moderate-sized research group, including three other postdocs with very different backgrounds and some hard-working graduate students. He ran a very tight ship, quite different from Roberts' more casual mentoring style. Z came into the lab at least once a day to check with everyone and find out what was up. While I appreciated his keen interest, and the technical advice that he provided, I was uncomfortable with such close supervision of every minute detail of my work. As my project progressed, I asked him not to hover over me so much, telling him that he would be the first to know as soon as I had significant results. Since he was pleased with my progress, he agreed to let me proceed essentially on my own with minimal direction from him, supplemented by discussions of my project at weekly group meetings. And that was how my work in Madison proceeded until I departed in August 1961.

Howard presented me with a great project, at the core of his new photochemistry program, concerning the photorearrangements of 2,5-cyclohexadienones. The tricyclic sesquiterpene derivative α-santonin, a natural product used at one time for treatment of parasitic worm infections, was known through the work of Barton and others to undergo a number of astounding transformations on irradiation with ultraviolet (UV) light, as illustrated in Figure 7.[5] These photorearrangements had defied mechanistic rationalization for many years. Z had developed a mechanistic proposal for these photochemical reactions, based on a general concept which at that time was revolutionary, namely that mechanisms could be written for photochemical transformations of organic molecules using the same principles as had been successfully applied during the preceding decade to mechanisms of a huge variety of ground state organic reactions by Roberts, Winstein, Bartlett, and others. The key was to come

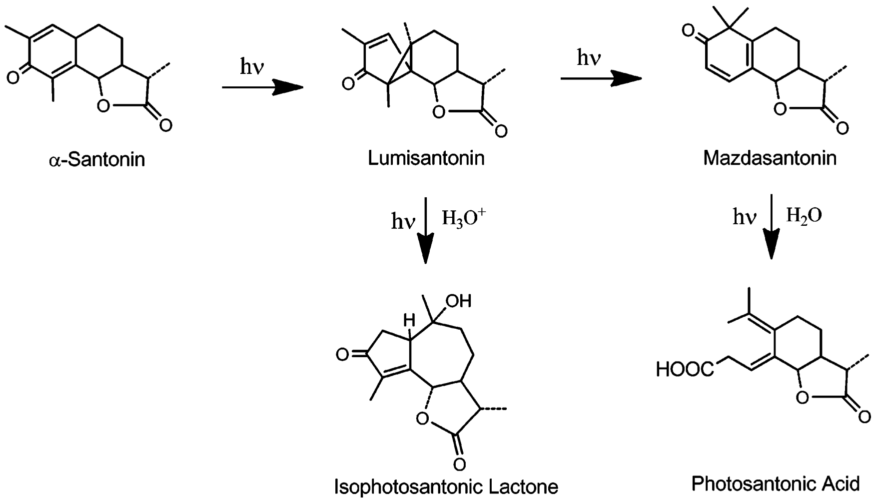
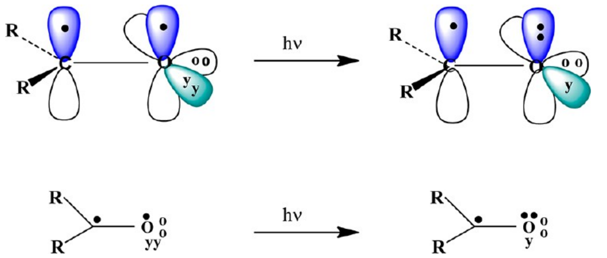


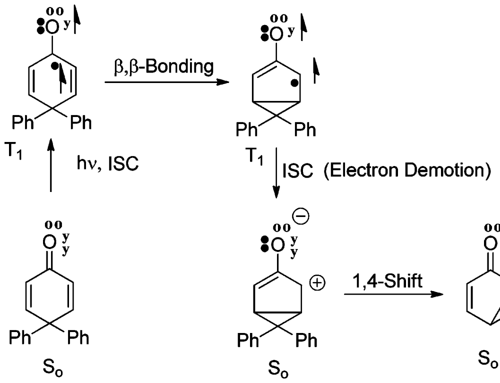
Figure 7. Photorearrangements of α-santonin.

up with a structural representation of the electronic excited state of the molecule in question, and then to proceed from that point using the mechanistic principles which had been so successful in describing ground state transformations, assisted by simple molecular orbital (MO) theory. Z invented a "circle-dot-y" notation to describe the lowest energy n,π* excited states of aldehydes and ketones, where the circles represented electrons in low energy nonbonding orbitals on the oxygen, dots represented electrons in the π-system of the molecule, and "y" represented electrons in the p_y-orbitals on oxygen.[6] Thus, n→π* excitation of a simple carbonyl compound could be represented as shown in Scheme 1. In this representation, one of the resonance forms for the n,π* excited state has a reverse dipole, with positive charge on oxygen and negative charge on carbon, consistent with the discovery by physical chemists that dipole moments of electronic excited states of ketones and aldehydes were significantly lower than those of the corresponding ground state molecules. Z extended this mechanistic concept to the photorearrangement of 2,5-cyclohexadienones to bicyclic [3.1.0]hexenones ("lumiketones"), the so-called Type A photorearrangement, as exemplified by santonin (the product in the case of α-santonin shown in Figure 7 had been named lumisantonin many years earlier).[5] I discovered that the same rearrangement occurred with 4,4-diphenyl-2,5-cyclohexadienone, our model system. On the basis of MO analysis, Z reasoned that the most likely process that the dienone excited state would undergo is formation of a σ bond between C_3 and C_5 to give a bicyclic intermediate in which the odd electron in the allylic π-system is in an MO which is orthogonal to the oxygen p_y orbital, which possesses only one electron. At this point, an "electron demotion" was proposed (corresponding to radiationless decay to the ground state potential surface) in which the extra electron in the allylic π-system returns to oxygen, giving a ground state oxyallyl zwitterion intermediate (see Scheme 2).

Scheme 1. Zimmerman's Pictorial Description of n→ π* Excitation of Ketones



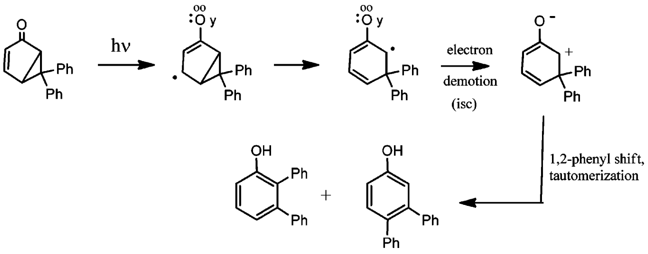
Scheme 2. Zimmerman–Schuster Mechanism for Photorearrangement of 4,4-Diphenylcyclohexadienone



This zwitterion is proposed to then undergo a Roberts-type cyclopropylcarbinyl cationic rearrangement[7] on the ground state potential surface to give the lumiketone. This is an example of a ground state 1,4-sigmatropic shift, a class of reactions named and described a few years later by Woodward and Hoffmann.[8] WH theory predicts that this sigmatropic rearrangement should occur with inversion of configuration at the migrating carbon atom, which we later verified experimentally.[9]

Just as lumisantonin undergoes a number of further photorearrangements as shown in Figure 7, the lumiketone derived from 4,4-diphenylcyclohexadienone also undergoes further photorearrangements, to 2,3- and 3,4-diphenylphenol. These rearrangements could also be readily rationalized by application of similar mechanistic reasoning, involving electronic excitation, structural changes on the excited state potential surface, electron demotion to a zwitterion, and ground state rearrangement, in this case 1,2-phenyl shifts, to give the final isolated products (see Scheme 3). For the first time, the structure as well as the stereochemistry of the products derived from photoexcitation of lumisantonin,

Scheme 3. Mechanism of Lumiketone Photorearrangement



including the effects of solvent polarity, could be rationalized mechanistically. Our JACS communication on these photorearrangements in JACS in 1961,[10] which was Z's first photochemistry paper, featuring the so-called Zimmerman–Schuster mechanism, caused a great deal of excitement in the organic chemistry community. Our full paper on cyclohexadienones appeared in JACS the following year.[10] Howard presented this work, along with results of other ongoing investigations in the lab, in a lecture at the National Organic Symposium (NOS) in June 1961 in Bloomington, IN, to great critical acclaim. The preceding lecture by George Hammond was also a sensitization, centering on his recent studies at Caltech on the mechanism of photoreduction of benzophenone in solution and other reactions in which triplet excited states were invoked as reactive intermediates. The idea that one could determine experimentally whether photochemical reactions proceeded via singlet as opposed to triplet electronic excited states was a completely new concept at that time. As Hammond showed, it was even possible to determine rate constants for these very fast reactions using triplet quenching techniques. While Zimmerman and I believed that the cyclohexadienone rearrangements most likely proceeded via triplet excited states, we had no direct evidence for this in 1961. Experimental evidence that these reactions indeed occurred via very short-lived triplet excited states was obtained several few years later.[11]

One cannot ovestate the impact that these two 1961 NOS presentations had on the organic chemistry community. Suddenly, a whole new generation of graduate students and postdocs flocked to Pasadena and Madison to do research in organic photochemistry with George and Howard, respectively. Many of these people pursued independent careers in this field, resulting in a flood of publications in photochemistry in the 1960s and 1970s. Other organic chemists who had been independently working on photochemistry in the early 1960s (including Jeger and Schaffner at the ETH in Zürich, Büchi at MIT, Barton in London, Orville Chapman at Iowa State, Bill Dauben at Berkeley, and N. C. Yang at Chicago) now had a solid mechanistic framework on which to discuss their findings. This led in the 1960s to a series of highly exciting conferences where people presented their latest findings, often provoking vigorous, sometimes rancorous, discussions. The first Gordon Conference in Organic Photochemistry organized by Tony Trozzolo from Bell Laboratories was held in 1964, and the first IUPAC Conference on Photochemistry organized by Hammond was held in Strasbourg, France, also in 1964. The very popular biannual Gordon Conference subsequently shifted to odd years and the IUPAC conferences remained in even years, where they both remain to the present day. I religiously attended these and other photochemistry conferences for decades. It was an exciting time in this field, and lifelong friendships between conference participants were established at these meetings, over scientific discussions, drinks, tennis matches, and late night poker games. Photochemistry was where the action was, and I was thrilled to be included and accepted in this wonderful community, which included esteemed established senior investigators such as Egbert Havinga from The Netherlands, Theodor Förster, Albert Weller and Gunther Otto Schenk from Germany, and George Porter from the UK. The first volume of Advances in Photochemistry (Wiley), edited by Albert Noyes, Hammond and Jim Pitts, came out in 1963 (with chapters by Zimmerman, Chapman, Srinivasan and other major players),[12] and the first volume of *Organic Photochemistry* (Dekker), edited by Chapman, appeared in 1967.[13] The late Nick Turro's book *Molecular Photochemistry* (Benjamin, 1967)[14] appeared shortly after he started his highly productive research career at Columbia; *Photochemistry* by Calvert and Pitts (Wiley, 1966),[15] provided a more general view of photochemistry. All these books served to popularize the field. Turro's later textbooks, *Modern Molecular Photochemistry* (Benjamin/Cummings, 1978)[16] and his recent update *Modern Molecular Photochemistry of Organic Molecules* with Tito Scaiano and V. Ramamurthy (University Science Books, 2010),[17] contain comprehensive and sophisticated discussions of what has become, after 50 years of intense multifaceted research, a very mature field.

■ ENTER KURT MISLOW

Late in 1960 or early in 1961, Kurt Mislow from New York University (NYU) came to Madison to give a talk (see Figure 8). I was aware of Mislow's work on optically active biphenyls which frankly I did not find very interesting. However, I was transfixed by his talk on this subject and finally understood what it was all about. This lecture was one of the most brilliant presentations I had ever experienced. Kurt found time during that day to talk with me about my work and my prospects. We hit it off from the beginning, on both a personal and professional level. NYU had a lousy reputation at that time, especially in comparison with my alma mater Columbia (although the medical school, law school, Courant Institute of Mathematics and Art History Department at NYU always enjoyed excellent reputations). Columbia chemists in that era tended to look down their noses at NYU. Kurt asked if I might be interested in a faculty position at NYU, as two positions were open—one at the University Heights campus in the Bronx where Kurt was located and the other at Washington Square in Greenwich Village. At that time, I had no plans to return to New York and had applied for faculty positions at several universities around the country. I told Kurt that I would be

Figure 8. Kurt Mislow (NYU, Princeton). Photo courtesy of Professor Mislow.

happy to visit NYU. I found myself in New York in February 1961 in the midst of an enormous snowstorm, the kind that completely shuts down transportation in the city for several days. I met the Chemistry faculty at both campuses (at that time, the two colleges were independent entities, but the graduate program was unified, with duplication of basic graduate courses at the two campuses), and I felt confident that I had made a good impression. The guys at the Heights were a particularly congenial group, were very receptive to the work I was doing with Z, and were taken with my enthusiasm about the project and organic photochemistry in general. The faculty at Washington Square were in general more reserved. They included Bob Morrison and Bob Boyd, who had just published the first edition of their revolutionary organic chemistry textbook in which the subject was organized and presented for the first time from a mechanistic perspective,[18] and some smart and interesting physical chemists. Except for Mislow, I had never heard of any of these guys, although several had good reputations in their respective fields. Overall, The NYU department was not very impressive compared to the chemistry departments I knew well at Columbia, Caltech, and Wisconsin. Walling was very excited about the research I was doing at Wisconsin. Within two weeks of my return to Madison I had a letter from NYU offering me a position as Assistant Professor at the Heights campus beginning in September 1961 at the magnanimous salary of $6,500 for 9 months, with the possibility of earning additional summer salary from teaching or research grants. There was no setup money; that was not an issue in those days. I had no competing offers, and the opportunity of becoming a colleague of Kurt Mislow was too tempting to turn down, so I accepted. So through an entirely serendipitous series of events involving Zimmerman and Mislow, I joined the NYU faculty at the tender age of 26 and resumed my life in New York City. The job at Washington Square was taken by the late Bob Shapiro, a biochemist who had done his Ph.D. at Harvard with Woodward and postdoctoral work with Lord Todd in England. Bob and I became the Young Turks of the department, both of us hard working, eager, and ambitious.

■ EARLY YEARS AT NYU: 1961–1968

Aside from knowing that I wanted to do research in organic photochemistry, I had no clear idea where to start. In those days, new faculty were not offered setups to get their program started. I was told that I could order a gas chromatograph, and the chemistry department at the Heights was about to get a Varian A-60 Varian NMR spectrometer, which was to be under my supervision, based on my experience at Caltech. The lab space assigned to me was pathetic; I occupied a long narrow laboratory with my office at the end, near the window, with space near the door where a few students could work using the one fume hood available. Mislow had several larger laboratories directly across the hall, while another organic colleague, Carlton Dickerman, had laboratories on the next floor. I was assigned to teach one section of the basic undergraduate organic chemistry course for the coming year, and I was completely focused on making a good impression on my students and my colleagues. The textbook of course was the first edition of Morrison and Boyd.[18] I prepared my lectures meticulously; in many instances, I was learning the material for the first time! Overall, the course went well, and I had good reports from the students and my senior colleagues. During the following summer, I earned additional money by teaching at Washington Square.

What I did then, and in ensuing years, was to identify the best undergraduate students in my classes, and invite them to meet privately with me to discuss the course and their career aspirations. My hope was to find a few top students who might be interested in doing some research, even if they were planning to go to medical school, which was usually the case. I also was able to find a few first year grad students who could be seduced into working on a Master's level research project with me. In the 1960s, graduate students in Chemistry were admitted to Ph.D. candidacy based on their grades in a series of required first year graduate courses. At that time, we had many part time graduate students who were working full time in industry, mostly for pharmaceutical companies in New Jersey or Westchester, and then took graduate courses at night. These guys had family responsibilities along with full-time jobs; many of them did not perform well in our courses and were dismissed from the program. The best of them arranged with their companies to work full time for two years to do their graduate research after being admitted to Ph.D. candidacy. There were also some younger full-time grad students. In the early 1960s most of the organic Ph.D. candidates chose to work with either Mislow or Dickerman, who had established research programs, space, and money. I was the new kid on the block trying to find my way, still an unknown quantity. Nonetheless, I was able to lure a few grad students who had been restricted to candidacy for the M.S. degree to work with me, along with a handful of undergraduates. Thus, by the end of my first year, I was able to initiate some projects in ketone photochemistry.

During my first year at NYU, I lived in the Riverdale section of the Bronx, with a view of the Hudson River from my 14th floor studio apartment. Through high school friends I managed to reconnect with my former girlfriend Carlotta whom I had not seen in 8 years. Last I knew, she was pursuing a career as an actress, and had had some success at Barnard and in summer stock. In the interim, she decided to go into medicine, the "family business". Her father and mother as well as most of her family were doctors. She did postbac premed studies at Sophie Newcomb College in New Orleans and was now in her second year at NYU Medical School, where her parents had met 30 years earlier. We began seeing each other in December 1961, became engaged the following spring, and were married on Labor Day weekend in 1962. We had a one-bedroom apartment in a new building on the Upper East Side of Manhattan, between the Heights campus and the med school. The rent was $212/month! Two days after our wedding she started her third-year rotation in obstetrics while I went off to a Mechanisms Conference at Brookhaven, notorious for an incendiary confrontation over nonclassical carbonium ions between Saul Winstein and Herb Brown. Because of our long working hours and conflicting schedules Carlotta and I did not spend nearly as much time together as we would have liked. We had a belated honeymoon trip to Europe in the summer of 1963 and returned there as often as we could manage, often in connection with IUPAC conferences. By the time she finished her residency in psychiatry at St. Luke's Hospital in 1968, I had been promoted to Associate Professor with tenure.

My initial forays into organic photochemistry at NYU were limited by the equipment available to me: a Hanovia photoreactor, several types of immersion lamps and filters, an F&M gas chromatograph, and an A-60 Varian NMR spectrometer, as well as IR and UV–vis spectrophotometers. Looking back at the work I did in 1961–1963 and my first papers, I am struck now by the naiveté and lack of sophistication of these studies. Not surprisingly, I focused my attention on various types of photorearrangements. Mislow had published several papers with Carl Djerassi on inherently dissymmetric chromophores, a prime example of which was norbornenone (or dehydronorcamphor, as we called it).[19] Ultraviolet spectroscopy as well as optical rotatory dispersion and circular dichorism data indicated that there was strong ground state electronic interaction between the homoconjugated carbonyl and alkenyl moieties in this molecule. I was curious about the photochemical consequences of this electronic interaction, which over time developed into a series of investigations on the photochemistry of acyclic and cyclic β,γ-unsaturated ketones. Two new grad students, Joe Auerbach and Michael Axelrod, soon demonstrated that norbornenone **1** underwent rearrangement upon UV irradiation in the absence of oxygen to the bicyclic ketone **2**, which upon further irradiation fragmented to give 1,3-cyclopentadiene and ketene (see Figure 9); the latter could be trapped by maleic anhydride and aniline.[20] A completely different reaction to give a tricyclic ketone occurs upon triplet sensitization. The photorearrangement of **1** to **2** had precedent in the recently reported photochemical interconversion of bicyclic ketones **4** and **5**, derived from eucarvone (Figure 10).[21] These are the first examples of what we and others termed a 1,3-sigmatropic acyl shift (1,3-SAS) using Woodward−Hoffmann terminology, a general photoreaction of β,γ-unsaturated ketones. The reaction involves homolytic cleavage of the bond between the carbonyl group and the bridgehead carbon, and recombination at the other end of the incipient allyl radical. We were shocked in early 1963 to see a paper from the lab of the eminent German photochemist G. O. Schenk claiming that irradiation of **1** led directly to ketene and cyclopentadiene, including observation of an isosbestic point,[21] which we knew was not correct. We immediately published our findings on **1** as a communication in the new journal *Tetrahedron Letters*,[20] which was my first independent publication (a full paper on this work was never published, for reasons which escape me in hindsight). Although we did not know it at that time, the 1,3-SAS reaction proceeds exclusively from the lowest singlet excited states of enones **1** and **4**, since a totally different reaction occurs upon triplet sensitization, namely a 1,2-SAS to give the tricyclic ketones **3** and **6**, respectively. Our second paper[22] dealt with eucarvone **7**, which gives a host of photorearrangement products, as shown in Figure 10, some of which had been reported by others.[23] We were the first to isolate products **8** and **9**. Using triplet sensitization and quenching techniques, à la Hammond, we showed that the photocyclization of **7** to **4** occurs from both singlet and triplet excited states of eucarvone, one of the few mechanistic studies of this type of process ever reported.[22] The obvious mechanism is a symmetry-allowed photochemical disrotatory cyclization, but a more interesting mechanistic alternative for the triplet state process involves photoinduced rotation around the C4−C5 bond of **7** to give the *E,Z* isomer (analogous to triplet sensitized photoisomerization of *cis*-2-cycloheptenone to *trans*-2-cycloheptenone, discovered by Corey and Eaton)[23] followed by a ground state conrotatory cyclization. We rationalized the rearrangement of **7** to **8** in acidic media in terms of photocyclization of protonated eucarvone, followed by a Wagner−Meerwein rearrangement. While we could envisage a path to dehydrocamphor **9**, the actual mechanism for this curious photorearrangement was never established. By this time (1964), I had succeeded in getting a research grant from the U.S. Army Research Office (Durham, NC), which was a strong supporter of research in photochemistry under the leadership of George Wyman. Support from AROD was very welcome at this early stage of my career.

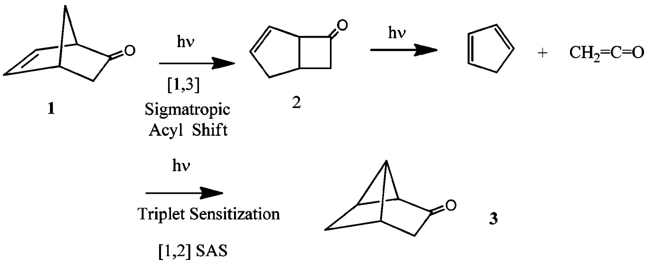


Figure 9. Photorearrangements of norbornenone **1**.

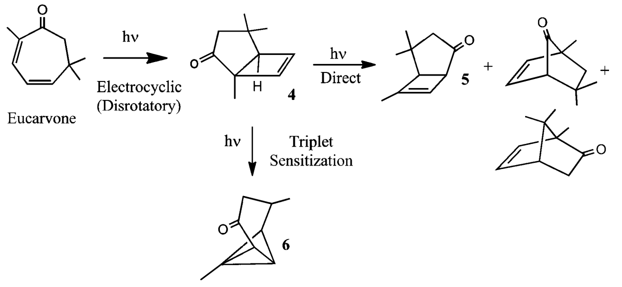
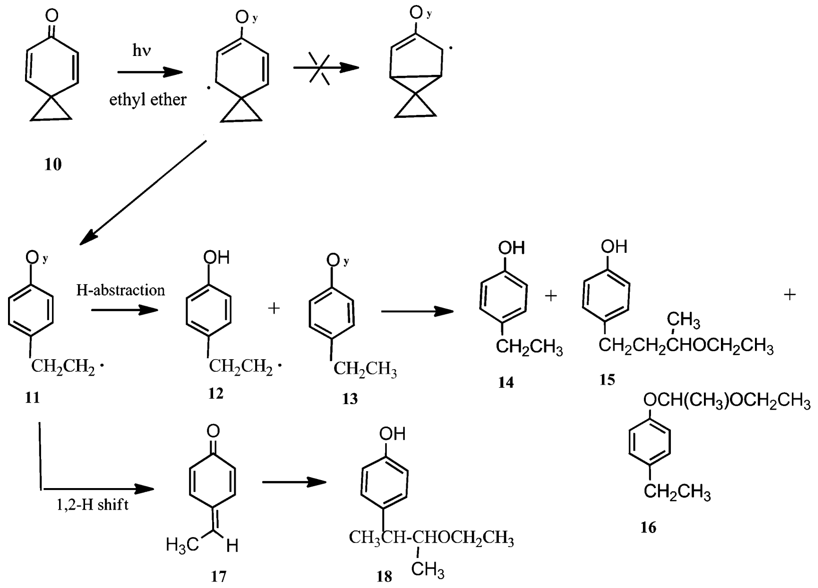


Figure 10. Photorearrangements of eucarvone 7.

A very important development was getting my first Ph.D. student, Carl Polowczyk, who started working with me in September 1962. I was delighted that Carl, who was one of the best grad students in the department, chose to work with me rather than with Mislow. Carl was considerably older than me (35 vs 27) and had considerable prior experience as a laboratory technician. Since he was married with three kids, he was strongly motivated to complete his research in the minimum possible time. He succeeded in obtaining an NIH predoctoral fellowship, so he could devote all his time to research and did not have to teach; the fellowship even provided some much-needed money for supplies. Carl's research was completed in just over two years, with a thesis defense in May 1965. My excellent experience with him personally and professionally set the pattern for how I would interact with Ph.D. students over the coming decades.

Carl's research project was related to my earlier work on 2,5-cyclohexadienones.[10] I was looking for experimental validation of various aspects of the Zimmerman-Schuster mechanism for the photorearrangements of 2,5-cyclohexadienones, shown in Scheme 1. In this mechanism, although the first-formed n,π^* excited state of 2,5-cyclohexadienones was pictured as a diradical-like species, all the phototransformations reported to date were rationalized as proceeding via a zwitterionic intermediate derived from the n,π^* excited state.[6,10] I was looking for a cyclohexadienone which would undergo free radical-type photoreactions directly from the excited state, prior to formation of the proposed zwitterion. A good candidate was the spiro 2,5-cyclohexadienone **10**, which had been recently reported by Baird and Winstein.[26] I reasoned that the n,π^* excited state of **10**, which incorporated a cyclopropylcarbinyl radical moiety (the subject of my Ph.D. research with Jack Roberts!),[27] should undergo ring-opening to give the aromatic

Scheme 4. Photorearrangements of Spirocyclohexadienone 10



diradical **11** rather than forming a highly strained 3,5-bridged structure. Carl soon found that spirodienone **10** behaved exactly as predicted upon UV irradiation in diethyl ether, giving *p*-ethylphenol **13** and the other products shown in Scheme 4, which *required* the postulation of free radical intermediates.[28] Thus, abstraction of an H- atom from the solvent by the ring-opened diradical **11** would give radicals **12** and **13** which by subsequent H-abstraction and radical−radical reactions would give p-ethylphenol **14** and ether adducts **15** and **16** (whose structures were proven by independent synthesis). Rearrangement of diradical **11** by a 1,2-H shift would generate quinone methide **17**, the precursor of adduct **18**. This suggestion was validated a few years later by graduate student Ira Krull using deuterium-labeled **10**.[29]

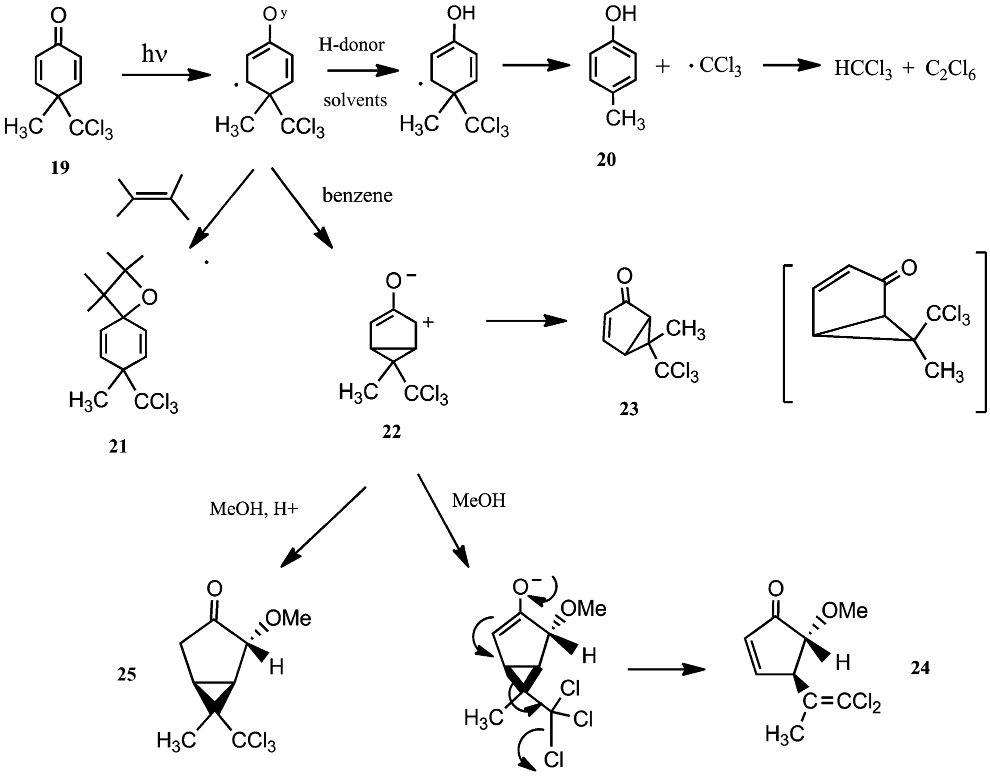
Thus, the photochemistry of **10** provided strong evidence that an excited state with diradical character was indeed a precursor of the bridged zwitterion intermediate on photoexcitation of cyclohexadienones. Our communication in JACS in 1964[28] was my first independent paper in what became my favorite journal for publication of my work; a full JACS paper followed in 1966.[30] The latter paper has an interesting history. After it was reviewed, revised and finally accepted for publication, the editor of JACS, Marshall Gates, personally edited this paper in order to show me how it could be substantially cut and reorganized so as to vastly improve the presentation, a lesson in scientific writing that I never forgot.

Kurt Mislow left NYU for Princeton in summer 1964. I was devastated at losing my close friend and mentor. I chatted with him every day, and he gave me invaluable advice about my career and my life. I learned more from him than from any of my mentors. The up side of Kurt's departure was that his ample research space was passed on to me and now the best organic Ph.D. students at the Heights campus tended to work with me (two new organic chemists, Yorke Rhodes and Graham Underwood, who joined the Heights department in the mid-1960s soon provided serious competition). Nonetheless, I was able to build an energetic and productive research group that always included some talented undergraduates. We were publishing several papers every year and made presentations regularly at Gordon Research Conferences, ACS meetings, IUPAC photochemistry conferences, and special symposia. On the strength of my accomplishments in research and my teaching performance, I was promoted to Associate Professor with tenure in 1965. AROD continued to provide research support, and I finally landed a small NSF grant in 1967; I also benefitted from institutional grants from NSF and NIH. I was awarded an Alfred P. Sloan Research Fellowship in 1967, which enabled me to hire my first postdoctoral research associates (from England) and provided support during my forthcoming sabbatical leave in England in 1968−69 (see below).

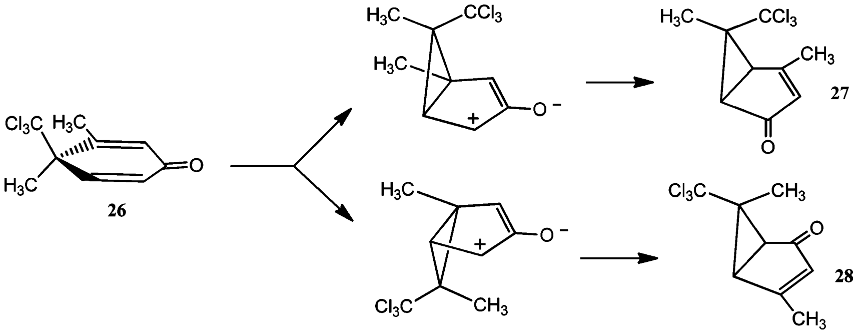
The research in our group in the mid- to late 1960s focused on various aspects of ketone photochemistry,[31] including studies which probed the effect of structure on photochemical behavior of cyclohexadienones[32] ring-fused cyclohexenones,[33] and other systems. We used Hammond's techniques more and more to determine which photochemical reactions involved singlet excited states and which involved triplet excited states.[24,34] Using triplet counting techniques based on precisely executed quenching studies, we were finally able to demonstrate convincingly that the rearrangements of α-santonin and other 2,5-cyclohexadienones occur via short-lived triplet excited states with lifetimes in the nanosecond time domain.[11]

An unanticipated major breakthrough in the mechanistic understanding of cyclohexadienone photorearrangements came from studies of 4-methyl-4- trichloromethyl-2,5-cyclohexadienone **19**. We wanted to confirm the generality of the radical fragmentation reaction seen by Carl Polowczyk with spirodienone **10** but in a dienone system where ring strain was not a factor. I anticipated that excitation of dienone **19** should lead to loss of the stabilized CCl_3 radical to give *p*-cresol. I vividly recall discussing this project on a Friday afternoon in early 1965 with Dinshaw Patel, a new graduate student who had recently arrived at NYU from Caltech where he had worked with Jack Roberts. By Monday morning Dinshaw had synthesized **19** and had shown that irradiation of **19** in diethyl ether gave high yields of *p*-cresol **20** and chloroform, products clearly derived from a radical fragmentation process. He later isolated hexachloroethane, proving definitively that CCl_3 radicals were generated from photoexcitation of **19**.[35] This

Scheme 5. Photochemistry of 4-Methyl-4-trichloromethyl-2,5-cyclohexadienone 19



Scheme 6. Stereochemistry of Photorearrangement of Chiral Cyclohexadienone 26



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observation clearly contradicted Chapman's popular "polar state hypothesis" used to depict the excited state and to rationalize the course of photoreactions of cyclohexadienones.[36] But this was only the beginning. When **19** was irradiated in benzene, a solvent in which H-abstraction is not likely, lumiketone **23** was formed instead of *p*-cresol, indicating that a competitive reaction pathway involving zwitterion **22** was now in play. This demonstrated that the triplet n,π^* state of **19** could be trapped by good H-donors to give *p*-cresol and CCl_3 radicals, or by olefins (to give oxetanes **21**), in competition with radiationless decay to zwitterion **22** which is the precursor of lumiketone **23.** Interestingly, only one diastereomer of **19** was formed, ultimately shown by Vasanth Prabhu to be the one depicted in Scheme 5 with an endo CCl_3 moiety.[37] These reactions could be sensitized by benzophenone and quenched by piperylene (1,3-pentadiene), a standard triplet quencher, showing they are all derived from a triplet excited state, identified as the diradical-like ^{3}n,π^* state.[38] The quenching data provided estimates of the rate constants for all the excited state processes. A still greater surprise arose from irradiation of **19** in methanol, which led not to **23** but to methanol adduct **24,** produced by an ionic fragmentation pathway initiated by stereospecific attack of methanol at the electrophilic α-carbon of zwitterion **22** followed by Grob-like ionic fragmentation of the resulting oxyanion.[39] If the methanol is saturated with dry HCl, a different methanol adduct **25** is formed in which the structure of the zwitterion is preserved intact. Methanol adduct **25** arises by trapping of zwitterion **22** by protonation on oxygen, blocking the ionic fragmentation pathway leading to **24**, followed by stereospecific nucleophilic attack of methanol at the adjacent cationic center.[40] The entire mechanistic scenario is depicted in Scheme 5. There could no longer be any doubt thati (a) that zwitterion **22** is produced from a diradical-like ^{3}n,π^* excited state, (b) that **22** is the precursor of lumiketone **23**, and (c) that the intermediate zwitterions, at least in this case, can be trapped by nucleophiles in a process which inhibits lumiketone formation but does not directly perturb the triplet excited state of **19.**[41] The variety of processes that evolve from photoexcitation of dienone **19** is unique in the photochemistry literature.

Further aspects of this mechanism came from studies a few years later by doctoral students Vasanth Prabhu and Kou-chang Liu. By using the chiral cyclohexadienone **26** with an added methyl group on the ring, Prabhu was able to relate the absolute configurations of the starting dienone and the diastereomeric lumiketones **27** and **28**, proving that the [1,4]-sigmatropic shift to give the these lumiketones from their diastereomeric zwitterionic precursors proceeded with inversion of configuration at the migrating carbon,[9] consistent with predictions of Woodward−Hoffmann theory (see Scheme 6).[38] Prabhu and postdoc Stuart Adcock showed that the stereoselectivity in lumiketone formation (i.e., whether the 4-substituent on the dienone ends up exo or endo on the lumiketone) arises from a subtle interplay of steric and electronic factors in the disrotatory ring closure which generates the diastereomeric zwitterions in the first place.[37] Liu also showed that nucleophilic trapping (e.g., by chloride ions) of the intermediate zwitterions, which quenches lumiketone formation but not formation of *p*-cresol, is a general phenomenon.[42]

The unusually complete and diverse mechanistic picture derived from our studies of cyclohexadienone **19** and its analogues is rare and possibly unique in the photochemistry literature.[43,44] It derives from a rather fortuitous choice of substrate, which showed a much wider range of photoreactivity than we could possibly have anticipated, and the excellent work of some superb and diligent graduate students. This project, which kept on giving, remains one of the most satisfying in my long career in organic photochemistry.

■ LONDON, 1968−69: THE ROYAL INSTITUTION AND GEORGE PORTER

With my promotion to Associate Professor with tenure, the award of an Alfred P. Sloan fellowship, and the completion of my wife's residency in psychiatry at St. Luke's Hospital (where she was the first female Chief Resident in the history of the institution), 1968−69 was the perfect year to take a sabbatical leave. I decided to go to London to work with George Porter (Figure 11), who had shared in the Nobel Prize in 1967 for his work on flash photolysis. I was intrigued by this new technique which could give insight into the nature and dynamic behavior of short-lived intermediates implicated in the photochemistry of organic compounds in solution, including free radicals and triplet excited states.[44] At that time Porter was Director of the Royal Institution (RI) in London, the first place in England where scientific research was carried out in an institutional setting, beginning with Sir Humphrey Davy in 1799. Other notable directors of the RI included Michael Faraday, James Dewar, Sir William Bragg, and Sir Thomas Bragg. This venerable institution, in which Faraday's lab and equipment is preserved intact, is located in the heart of London on Albemarle Street near Piccadilly. We found a place to live on Curzon Street in the heart of Mayfair, in the charming area known as Shepherd Market, not far from the RI. Besides being a fashionable red light district, there were superb pubs, a wonderful bakery, food markets, an excellent wine shop, and even a cinema. We were totally free and made the most of it. We went out frequently to the theater, opera, concerts and ballet, and dined at the best restaurants, as the dollar was quite strong at that time. We traveled outside of London by car after I summoned the courage to drive on the "wrong" side of the road. It was a glorious time for us. We came to know London much better than most Londoners. And I got some serious work done in collaboration with the young scientists in Porter's lab at the RI.

I arranged to give lectures at most if not all of the institutions in England where research in organic photochemistry was ongoing, including Imperial College, London (Derek Barton and Peter Sammes), Reading (Alan Gilbert and David Bryce-Smith), King's College, London (John Perkins), Oxford (John Barltrop and Gordon Whitham), Bristol (Kevin Mackenzie), Southampton (Richard Cookson), and Leicester (Stephen Davidson). I particularly loved my visits to the older universities with their venerable traditions and great architecture. We went to Zürich in March 1969 to visit the renowned ETH where I talked with Oskar Jeger and Kurt Schaffner who were doing groundbreaking research on photochemistry of cyclohexadienones and other organic systems of interest to me. This was the beginning of a very close personal and professional relationship with Schaffner that exists to the present day (see Figure 12). After Zürich, we went to Salzburg for the famous (and very expensive) Easter Festival directed by Herbert von Karajan, for memorable performances of Wagner's "Das Rheingold" and "Siegfried" and concerts by the Berlin Philharmonic, followed by several wonderful days in Vienna, including a memorable performance of Richard Strauss' "Der

Figure 11. George Porter, Royal Institution of Great Britain. Photo courtesy of Professor David Phillips, Imperial College, London.

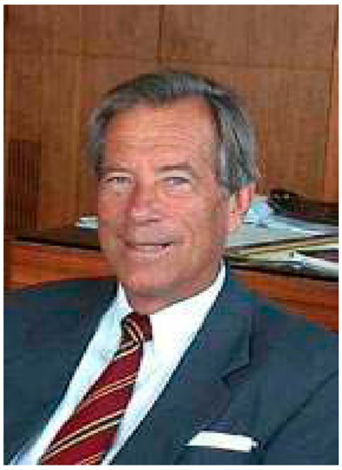


Figure 12. Kurt Schaffner, Max-Planck-Institute für Strahlenchemie, Mülheim. Photo courtesy of Max-Planck-Institute for Chemical Energy Conversion, Mülheim.

Rosenkavalier" at the Vienna Opera. We ate very well in both Salzburg and Vienna. This pattern of coupling science with music and fine dining during trips to Europe has been a persistent theme of my career until the present time.

At the RI, I learned how to use the microsecond flash photolysis apparatus with the help of Paul Suppan, a staff postdoc from Switzerland who soon became my best friend, and several graduate students, including John Kelly and Michael Ledger. The apparatus was relatively crude, with several large capacitors that went off with a loud bang to provide the initial excitation pulse. The interrogation pulse was triggered at a fixed delay after the excitation pulse, at a wavelength controlled by a monochromator. The apparatus was connected to an oscilloscope to which a Polaroid camera was attached, which provided pictures of the growth and decay of transient absorption appearing on the oscilloscope screen. The trickiest part was to synchronize (by hand) the excitation and interrogation pulses and operation of the camera. With practice, I was able to get the apparatus to work properly, but there were many misfires early on. The decay curves were then copied on to graph paper and analyzed manually to obtain the rates of growth and decay of the intermediates generated in the experiment. Absorption spectra of the intermediates could be constructed by measurement of optical densities at various interrogation wavelengths on a modified apparatus equipped with photographic plates. The experiments carried out using this early pre-electronic technology were very tedious and the apparatus was very temperamental. Nowadays such experiments are carried out routinely on electronically controlled instruments incorporating nanosecond, picosecond, and even femtosecond laser pulse excitation, electronic control of delay times for interrogation pulses, digital readouts, and instant analysis. Nonetheless, it was exciting for me way back then to actually generate and kinetically analyze the various reaction intermediates that were previously just mechanistic suggestions on a piece of paper.

I first looked at excitation of benzophenone in ethanol and 2-propanol, a much-studied reaction system that generates Ph_2COH (ketyl) radicals by a hydrogen-abstraction mechanism.[45] The spectrum of this radical and its rate of decay had been measured many times in Porter's lab, and I was able to reproduce these data without difficulty. I then focused on several ketones that we had investigated at NYU, including dienone **19**. No transient intermediates showing absorption between 390 and 600 nm were observable for any of our systems using both the classic microsecond flash apparatus as well as the new nanosecond flash apparatus with ruby laser excitation at 347 nm built by Michael Topp to study singlet state decay processes.[46]

Experiments were carried out on benzophenone in a variety of solvents using both flash setups. Benzophenone had achieved paradigm status in organic photochemistry,[14−16] and was the logical candidate for fundamental studies of triplet excited state behavior using the new nanosecond flash technique. I was curious as to why benzophenone triplets were much shorter lived in benzene, a solvent in which H-abstraction was not an option, than in inert perhalogenated solvents, such as perfluoromethylcyclohexane and CCl_2FCF_2Cl, where benzophenone phosphorescence could be observed even at ambient temperatures. The triplet lifetime of benzophenone in benzene had been reported to be ∼10 μs in a classic microsecond flash photolysis study by Bell and Linschitz,[47] a value that was at the limit of detection of that apparatus. The lifetime of benzophenone triplets in hydrogen-donor solvents such as ethanol, 2-propanol and toluene was estimated to be in the nanosecond time domain, according to triplet quenching studies,[48] making this ideal for direct measurement using the new nanosecond flash technique. A table of our kinetic data on benzophenone triplet states was included in Topp and Porter's classic 1970 paper on nanosecond flash photolysis which otherwise was focused on singlet excited state decay kinetics which could be studied directly for the first time.[49] After leaving the RI Michael joined Bell Laboratories, where we continued to collaborate and eventually published our nanosecond flash data on benzophenone triplet states.[50]

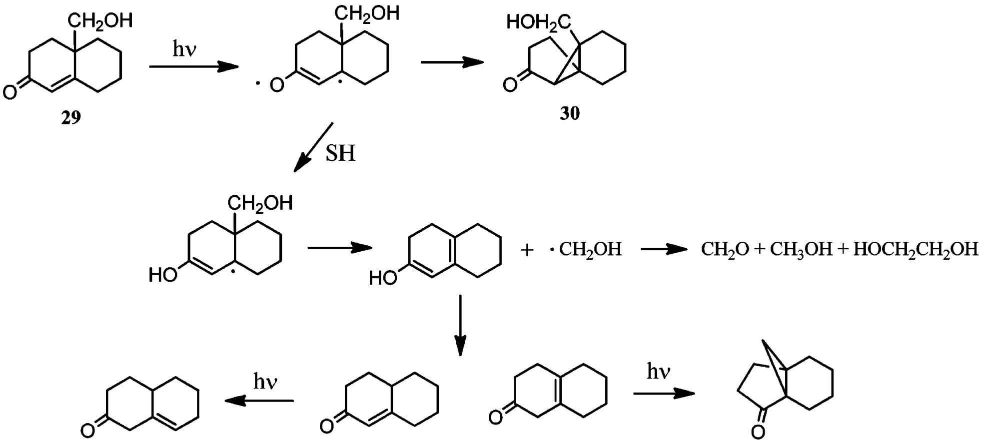
We indeed found that the decay of Ph_2CO triplets in H-donor solvents occurred on the nanosecond time scale, from which second order rate constants for H-abstraction were directly obtained for the first time; these were in very good agreement with those estimated from Hammond's triplet quenching studies,[48] validating the basic assumptions of that technique. Second, the Ph_2CO triplet decay rate in highly purified degassed benzene was close to 10 μs, within experimental error the same value reported by Bell and Linschitz;[47] significantly the Ph_2CO triplet decay rate in C_6D_6 was slightly faster, proving that H-abstraction is not taking place. In fact the Ph_2CO triplet decay rate in C_6F_6 was even an order of magnitude faster![50] These data suggested to me that the accelerated triplet decay rates of Ph_2CO in benzene is best accommodated by a mechanism involving addition of the ketone triplets to the aromatic ring to give a triplet diradical intermediate, which then slowly reverts to Ph_2CO ground state after a spin flip; i.e., benzene essentially catalyzes radiationless decay of benzophenone n,π* triplet states in solution.

After leaving London in June 1969 we embarked on a three-week gastronomic tour of France with close friends, involving visits to many highly regarded restaurants. We started in Paris and then proceeded to the Champagne area, Burgundy, Provence, the Dordogne district, the Loire valley, and finally Normandy. This was a memorable trip, which would be unthinkable now considering cost and age-related dining limitations. The greatest meal we had during this gastronomic odyssey was a lunch at La Pyramide in Vienne, a town in the Rhone valley just south of Lyon. Pyramide was a Michelin three-star temple of gastronomy made famous by the great chef Fernand Point, mentor to Paul Bocuse and many other great chefs of the next generation. Our meal there (I still have the menu!) was unforgettable and inexpensive Other dining experiences were only slightly less memorable. We returned on the S. S. France, which had an outstanding first class dining room, which the food critic Craig Claibourne claimed was the finest restaurant in the world!

■ NYU 1969−74

Returning to ordinary life and work in New York after our amazing time in Europe was difficult. I had to rebuild my research group at NYU after graduation of most of my former grad students in 1968. Vasanth Prabhu and Kou-chang Liu, who joined my group just before I left for England, put the finishing touches on our cyclohexadienone work with the stereochemical and kinetic studies discussed earlier. Tom Weil, a new student from Brazil, took on the benzophenone/benzene project and embarked on extensive kinetic studies using steady state photolysis (quantum yields, emission spectroscopy, quenching experiments), flash photolysis (using a microsecond flash system acquired from Northern Precision in London, affiliated

Scheme 7. Photochemistry of 10-Hydroxymethyloctalone 29

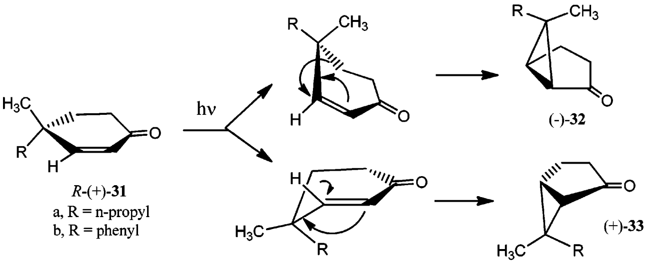


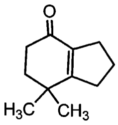
with the RI), and single photon counting (in collaboration with my young colleague Arthur Halpern).[51] The latter investigation was the first time this new technique was used for studying dynamics of short-lived triplet states. Tom's kinetic studies represented a turning point in our research with increased emphasis on photophysical techniques. These studies, together with those by Marc Goldstein on Michler's ketone, provided evidence of the importance of triplet−triplet annihilation processes and triplet excimer formation in these well-studied systems.[51,52]

Around this time, we began a series of investigations of the photochemistry of 4,4-disubstituted cyclohexenones, which were also known to undergo Type A photorearrangement to lumiketones.[53] Orville Chapman had attempted to mechanistically link the Type A photorearrangements of cyclohexenones and cyclohexadienones in terms of a "polar state hypothesis".[36,54] We had successfully shot down that concept with our cyclohexadienone work, and now Don Brizzolara undertook a study of the bicyclic enone **29** to specifically test Chapman's hypothesis on cyclohexenone systems. Based on a diradical description of the excited state of enones, we anticipated that the triplet state of **29** would undergo radical fragmentation with the release of hydroxymethyl radicals in competition with formation of lumiketone **30**. As shown in Scheme 7 this is indeed the case. The nature of the products that were formed indicated that the reactive triplet excited state was best described as a diradical-like rather than dipolar-like molecular species.[33] This in turn led us to wonder about the mechanism of lumiketone formation from 4,4-disubstituted cyclohexenones, since these lack the second double bond that plays such a key role in the cyclohexadienone systems.[43] Bridged zwitterions cannot be invoked as intermediates in the cyclohexenone photorearrangements. Formally, the Type A photorearrangement of cyclohexenones involves cleavage of the σ bond between C-4 and C-5 and formation of new sigma bonds between C-5 and C-3 and between C-4 and C-2. The question was whether or not these were stepwise or concerted processes, since triplet excited states were known to be reaction intermediates. Another issue was the possibility that *trans*-cyclohexenones played a role in these reactions, at least in monocyclic systems. By this time strong evidence had been presented in the literature for formation of short-lived *trans*-[2]cycloheptenone,[25] *trans*-1-phenylcyclohexene[55] and *trans*-1-acetylcyclohexene[56] upon irradiation of the corresponding *cis*-isomers.

In order to gain mechanistic insight into these systems, we studied photorearrangements of structurally unbiased chiral cyclohexenones. Graduate student Bruce Resnick undertook the task of preparing optically active enone **31a**, determining its optical purity and absolute configuration, and relating these to the optical properties of the diastereomeric lumiketones **32a** and **33a** and other photoproducts derived from **31a**.[57] He showed that the Type A photorearrangement of **31a** proceeded stereospecifically without loss of optical purity, a [$_\sigma 2_a + _\pi 2_a$] cycloaddition process involving antarafacial addition of the C4−C5 σ-bond to the C2−C3 π-bond with inversion of configuration at C-4, consistent with orbital symmetry considerations (see Scheme 8). From a structural perspective, this process requires twisting around the π-bond of the triplet π,π^* state of the enone with concomitant pyramidization at C-3, followed by concerted electronic reorganization; intermediates capable of racemization are definitely not formed at any stage of the reaction.[57,58] Robert Brown obtained identical results with optically active enone **31b** and also observed stereospecific phenyl-migration processes.[58] Meanwhile, Saadat Hussain showed that the rigid enone **34**, which is structurally constrained from twisting around the C=C bond, did not undergo the Type A photorearrangement,[59] supporting our hypothesis that such twisting is a necessary feature of this process. These studies turned out to be crucial in gaining insight into how the shapes of the potential surfaces of the T_1 and S_0 states of reactants and products control the quantum efficiency and course of photochemical reactions of enones.[53]

Scheme 8. Stereospecific Photorearrangements of Chiral Cyclohexenones 31





34

CLOSING OF THE HEIGHTS CAMPUS AND THE MOVE TO WASHINGTON SQUARE

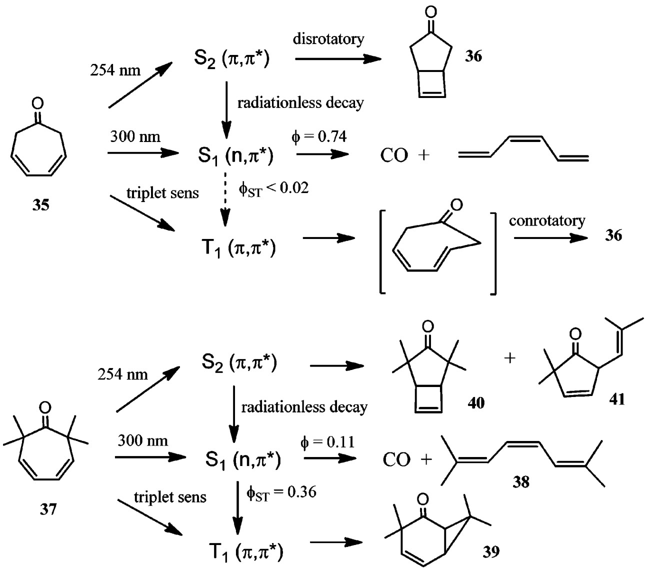
A major financial crisis hit NYU in the early 1970s. With the construction of the expensive new Philip Johnson-designed Bobst Library at Washington Square, major deficits in the School of Engineering at the Heights campus, and decline of the area surrounding the Bronx campus, NYU decided it could no longer enjoy the luxury of two Arts and Science colleges. Accordingly, the difficult decision was made to close operations in the Bronx, to merge University Heights College and Washington Square College and to close the School of Engineering. The problem was particularly grave as far as the Chemistry Department was concerned. We were told that of the 33 faculty members in the combined department before the merger, only 22 would be retained after the merger, and it was up to us to figure out how to accomplish this. Under the leadership of Alvin Kosak, our Department Head, we came up with a plan involving negotiated retirements of senior faculty and termination of most nontenured faculty. There were three tenured organic chemists from the Heights for whom research space had to be found or created at Washington Square: Yorke Rhodes, Graham Underwood and myself. The architecturally distinguished Heights campus (including buildings designed by McKim, Meade, and White, the most distinguished architectural firm in New York in the late 19th—early 20th centuries) became the home of Bronx Community College, under a deal worked out between NYU and the Board of Regents of the State of New York. The Chairman of the Chemistry Department at BCC, my former Ph.D. student Carl Polowczyk, arranged for Graham and me to continue to operate in our research laboratories until our new laboratories were ready at Washington Square in the old Brown Building, site of the notorious Triangle Fire in 1911. For several months we and our grad students had to travel back and forth between the Bronx and Washington Square in lower Manhattan to fulfill our teaching responsibilities.

Our new laboratories were finally ready in late February 1974. The move had to take place quickly, as a team of experts (including Harold Hart and Jerry Berson) was coming to evaluate our Ph.D. program as part of a mandated review of all the doctoral programs in New York State. Chemistry was first on the list. My group (Bruce Resnick, Atma Gupta, Marc Goldstein, and Dr. M. Santhanam) packed up all our stuff (glassware, samples, reagents, solvents, papers, books, etc.) and then unpacked at the other end. We had two days to get our new lab organized before arrival of the visiting committee, to show that we were hard at work in our new space. In the end, the department passed muster with flying colors, I ended up with some of the best lab space in the department, and my group was happy. It was like moving to a new university and marked the beginning of the second phase of my career at NYU. The drawback was that I now had a major commute from my home in Wilton, CT, to Washington Square, nearly two hours in each direction. I frequently stayed overnight in the city with students, friends, or my mother-in-law when schedules or weather was an issue. Commuting remained a major issue until 1995 when my wife started working in Addiction Psychiatry at NYU Medical School and we rented a conveniently located *pied a terre* for weekdays.

PHOTOCHEMICAL STUDIES, 1974–93

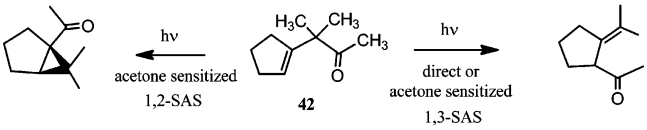
The move to Washington Square saw further development of our photochemistry program with the inclusion of ever more sophisticated experimental and computational techniques, involving collaborations both inside and outside the university. The addition of Jens Eriksen to my group in 1974 was a major development. Jens came to NYU from Denmark at the invitation of my colleague Mark Ratner, planning to spend a year or two in New York. After taking my photochemistry course Jens decided to stay and work in my lab (Mark subsequently moved to Northwestern where he has had a very distinguished career in theoretical chemistry). Once again serendipity played a role! I had become increasingly interested in the photochemistry of β,γ-unsaturated ketones (β,γ-UKs) where fascinating questions regarding reactivity patterns had emerged.[53] There were many reports that completely different photochemical reactions occurred in β,γ-UKs as a function of substitution patterns and reaction conditions. Jens measured quantum yields for reactions of many β,γ-UKs, as well as fluorescence lifetimes and quantum yields, and correlated these data with results of theoretical calculations done in association with Ratner and Karsten Krogh-Jespersen, another Danish student.[61,62] The β,γ-UKs, twenty in all, were obtained from group members and from Paul Engel at Rice, while others were synthesized by Jens. These data were organized in terms of a comprehensive mechanistic framework in Jens' very fine Ph.D. thesis and a series of publications. He is sole author of a definitive paper on the fluorescence properties of β,γ-UKs, an experimental and computational study carried out with minimum input from me, the only solo student publication from my lab during my entire career.[64] Jens discovered that there were fundamental differences in the reaction pathways evolving from singlet and triplet excited states of β,γ-UKs, as we had suggested many years earlier,[20,24,34] and that these were exquisitely sensitive to substitution patterns. We had reported as early as 1968 that singlet and triplet excited states of 3,5-cycloheptadienones underwent different reactions.[65] Ten years later, with the benefit of new photochemical and photophysical data and theoretical calculations, Jens developed a mechanistic framework to explain the behavior of these puzzling systems, including wavelength effects which at that time were rarely invoked in organic photochemistry.[63,66] For example, direct irradiation of 3,5-cycloheptadienone **35** at 300 nm results exclusively in decarbonylation to give 1,3,5-hexatriene (φ = 0.74) from the S_1 state (τ_s = 1.05 ns), while irradiation at 254 nm into S_2 gives **36**, the product of disrotatory ring closure; the T_1 state of **35**, accessible in this case only by triplet sensitization, also gives **36** by a different mechanism, probably involving formation of an intermediate ground state *Z,E*-dienone which then undergoes conrotatory ring closure (see Scheme 9). The tetramethyl analogue **37** behaves quite differently. In this system, 300 nm excitation gives only a small amount of decarbonylation (φ = 0.11) to triene **38** from a much shorter lived S_1 state (τ_s= 0.11 ns), accompanied by formation of ketone **39** by a 1,2-sigmatropic acyl shift (1,2-SAS) originating from the T_1 state. In the case of **37** T_1 is populated by intersystem crossing from S_1 (φ_{ST} = 0.36) competitive with decarbonylation, a process which is not observed with **35**. Meanwhile excitation of **37** into S_2 at 254 nm causes disrotatory ring closure to give **40** along with formation

Scheme 9. Photochemical Reaction Pathways of 3,5-Cycloheptadienones



of **41** by a 1,3-SAS process (see Scheme 9).[66] Thus, unusually rich photochemical reactivity patterns are seen with these compounds upon careful investigation, accompanied by wavelength dependence and exquisite structural sensitivity of excited state behavior. Such state-selective reactivity patterns are not common in organic photochemistry but are characteristic of *β*,*γ*-UKs, as demonstrated only a few years later by Tessie Calcaterra in her very careful study of enone **42**.[67] Again wavelength effects are observed, and one is forced to invoke different reaction pathways for S_2, S_1, T_2 and T_1 states (see Scheme 10). Interestingly, a rare heavy atom effect on photochemical reaction pathways was observed by Tessie when irradiations of **42** were carried out in a Xenon atmosphere.

Scheme 10. Photochemistry of *β*,*γ*-Enone 42

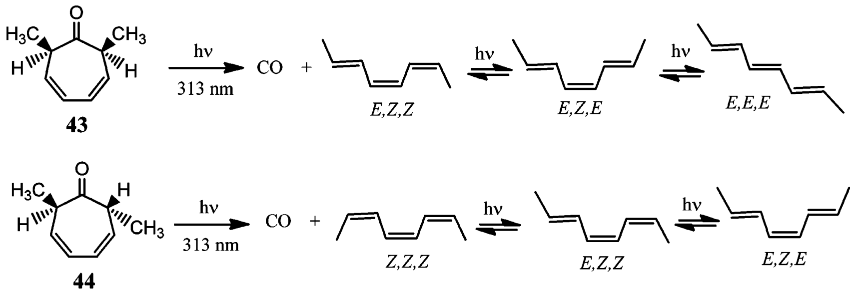


I was curious to know whether the cheletropic fragmentation of 3,5-cycloheptadienones **35** and **37** was a concerted or stepwise process and whether it followed the path predicted by Woodward–Hoffmann theory for such reactions.[8b] Jens and I had predicted that, if concerted, loss of CO upon irradiation of **35** and **37** would proceed by an axisymmetric pathway from C_2-symmetric conformations of these dienones.[66] Graduate student Li Wang set out to solve this very tricky problem by studying the reaction of *cis*- and *trans*-2,7-dimethyl-3,5-cycloheptadienones **43** and **44**. The stereochemical assignments to **43** and **44** came from X-ray crystal structures of their Diels–Alder adducts with PTAD (4-phenyl-1,2,4-triazoline-3,5-dione) in association with Jim van der Veen at Stevens Institute of Technology. Li synthesized the three trienes that could possibly be formed by decarbonylation, namely (*Z*,*Z*,*Z*)-, (*E*,*Z*,*Z*), and (*E*,*Z*,*E*)-2,4,6-octatriene, and studied their photochemical behavior, since photoisomerization of the trienes was likely to occur under the reaction conditions. He showed that the initial product of photodecarbonylation of *cis*-dienone **43** was the *E*,*Z*,*Z*-triene, while the *E*,*Z*,*E*-triene was initially formed from the *trans*-dienone **44** (see Scheme 11).[68] The mechanistic interpretation of these findings was complicated by conformational issues of **43** and **44**, and whether these are linear (disrotatory) or nonlinear (conrotatory) concerted photochemical processes. The discovery by Li that the primary process involves conrotation is consistent with the nonlinear pathway, but it is also compatible with least motion considerations. In any case, there is no doubt that loss of CO is a concerted light-induced cheletropic reaction.[68]

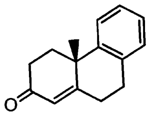
Eriksen went on to do postdoctoral research with Chris Foote at UCLA on photoinduced electron transfer (ET) processes, studies that are classic.[69] We also became interested in photochemical ET processes in the 1980s, and embarked on investigations of quenching of 9,10-dicyanoanthracene (DCA, an electron acceptor) and 9,10-dimethoxyanthracene (DMA, an electron donor) by several types of ketones.[70] Among the reactions investigated was DCA-sensitized photooxygenation of 3,5-cycloheptadienones and related compounds.[71] We obtained some interesting results, but efforts in that direction were discontinued since many other people were active in the ET field at that time besides Foote. As will be seen, photoinduced ET processes did indeed become the major focus of our research in the last phase of my career.

During the early 1980s, our attention was increasingly focused on the photochemistry of cyclohexenones, including fused-ring structures such as phenanthrone **45** as well as monocyclic systems. Although the stereospecific lumiketone-type photoearrangement of **45** had been reported earlier, there was still debate as to the nature of the triplet excited state responsible for this reaction, i.e., $^3n,\pi^*$ or $^3\pi,\pi^*$. Using quenching techniques, Alex Chan showed that two distinct triplet states of **45** were involved in reactions in 2-propanol, a higher energy $^3n,\pi^*$ state which was the precursor of a pinacol,

Scheme 11. Stereospecific Photodecarbonylation of 3,5-Cycloheptadienones 43 and 44



an allylic alcohol and a *trans*-fused hexahydrophenanthrone photoreduction product, and a lower energy $^3\pi,\pi^*$ state which was the precursor of the lumiketone and a *cis*-fused hexahydrophenanthrone.[60,72] The same pattern of reactivity was observed for an analogous bicyclic enone lacking the aromatic ring.



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Proof that the triplet state precursor to lumiketones had to be the $^3\pi,\pi^*$ state came from the observation that alkenes quenched lumiketone formation from UV irradiation of 4,4-dimethylcyclohexenone by undergoing [2 + 2] photocycloaddition to the enone, a reaction known to involve enone $^3\pi,\pi^*$ states.[73] Since this very well-known reaction gives both *cis*- and *trans*-fused [2 + 2] cycloadducts, we were led to the conclusion that a twisted enone triplet state had to be the precursor of both the bicyclic lumiketone and the [2 + 2] cycloadducts.[53,60,73] This proposal was strengthened by the fact that conformationally rigid enone **34** does not undergo photorearrangement; only photoreduction of **34** was observed.[59] While we succeeded in chemically trapping a *trans*-cyclohexenone in one particular case,[74] we never succeeded in obtaining evidence for formation of ground state *trans*-2-cyclohexenones as discrete reaction intermediates using nanosecond laser flash techniques at ambient temperatures (see below) as well as infrared studies in matrices at low temperatures, in collaboration with Mike Squillacote in Providence.

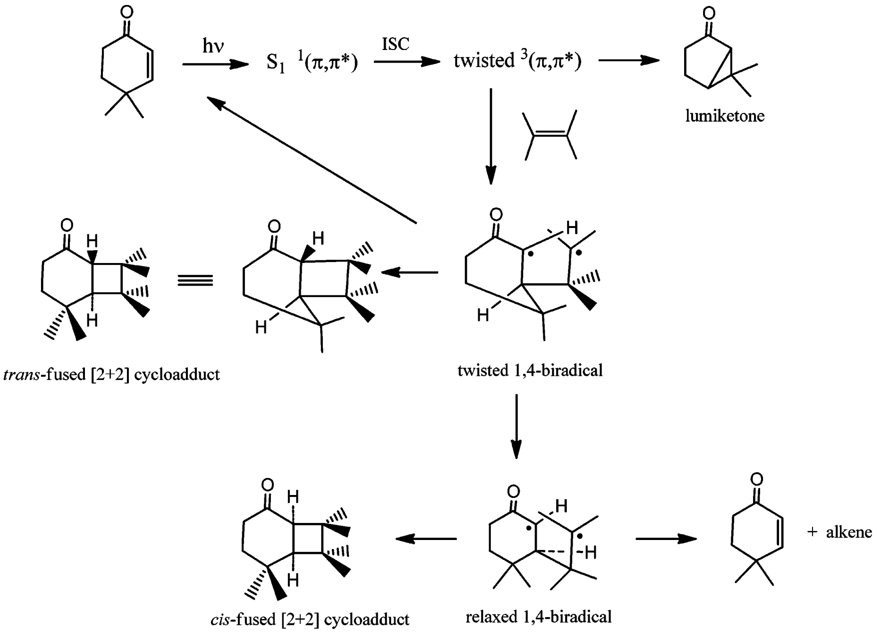
These investigations led inexorably to the next important phase of our studies in enone photochemistry, namely studies of the dynamics of enone triplet states by nanosecond flash photolysis (NFP), a collaboration between Roland Bonneau at Bordeaux and NYU graduate student David Dunn, sponsored by a NATO grant. In the early 1980s Bonneau had determined lifetimes of triplet excited states of several types of enones using NFP techniques, and showed that enones that could undergo some degree of twisting around the C═C bond invariably had triplet state lifetimes that were shorter than those of enones that were structurally constrained from twisting.[75] Thus, the triplet lifetime of testosterone in deaerated cyclohexane was 440 ns while cyclohexenone itself had a triplet lifetime under identical conditions of only 25 ns. Dunn traveled to Bordeaux on three occasions to carry out studies on a wide variety of enones using Bonneau's nanosecond flash apparatus. On two of these occasions, I participated in the experiments and in discussions with the group of distinguished photochemists in the department at Bordeaux at that time, led by the late Jacques Joussot-Dubien. David and I also took the opportunity to visit some of the excellent vineyards in the immediate vicinity of the university, including the famous Chateau Haut Brion which one could see from the windows of the lab; these vineyard visits invariably improved the quality of the experiments done later in the day. The triplet state lifetimes in solution of eighteen enones which possessed large structural diversity were inversely related to the conformational flexibility of the enone chromophores.[76,77] We determined rate constants for quenching of enone triplets by naphthalene, conjugated dienes, oxygen, nitroxyl radicals, alkenes, and amines.[77,78] From the variations in the rate constants for quenching of the enone triplets by naphthalene, we concluded that the triplet state energies of structurally rigid enones were up to 10 kcal/mol higher than those of simple cyclohexenones, consistent with conformational relaxation of enone triplet states. In accord with this hypothesis, the triplet lifetimes were more than an order of magnitude higher for conformationally rigid vs conformationally flexible enones.[77,78] There was no longer any doubt that cyclohexenones triplet states underwent relaxation by twisting around the C═C bond, as had been observed much earlier for 2-cycloheptenone and acetylcyclohexene.[56,75]

We were deeply gratified by the excellent correlation between the triplet state energies and lifetimes of enones determined at Bordeaux with data obtained for a group of enones using time-resolved photoacoustic calorimetry (PAC) by George Heibel working in collaboration with Dick Caldwell at the University of Texas at Dallas.[77,79] The latter technique involves measurement of the incremental heat loss after photoexcitation as a function of time. These photochemical and photophysical studies of cyclic enones represent one of the most extensive investigations of its kind in ketone photochemistry.[53,60,77]

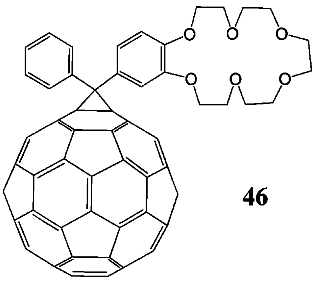
A very pleasant outcome of our Bordeaux collaboration was that David Dunn was invited to present a second Ph. D. thesis defense at Bordeaux in May 1985, followed by a gala celebration, in which I participated. A report of these events and the very productive Bordeaux-NYU research collaboration appeared in the Newsletter of the European Photochemical Association.

The final period of our research efforts in the area of small molecule mechanistic organic photochemistry in the late 1980s and early 1990s focused on the mechanistic details of the [2 + 2] photocycloaddition of alkenes to cyclic conjugated enones. Earlier mechanistic suggestions about the fundamentals of this reaction by Corey and de Mayo[80] were simply not compatible with the rate constants that we had obtained for quenching of enone triplets by alkenes using both TAS and PAC techniques.[77] There was absolutely no correlation between the kinetics of triplet quenching and the quantum yields for formation of cycloadducts; i.e., the fastest reactions were usually not the most efficient. For example, rate constants for quenching of enone triplets by electron deficient alkenes (such as acrylonitrile and fumaronitrile) were significantly higher than those for quenching by electron rich alkenes (such as 1,1-dimethoxyethylene and cyclopentene), yet the latter processes were much more efficient in affording cycloadducts. Quantum efficiencies for trapping of enone triplets by alkenes calculated from the quenching rate constants were invariably much less than the quantum yields for adduct formation. Thus, a mechanism was required involving formation of intermediates which are able to revert back to starting materials in competition with product formation. These intermediates had to be triplet 1,4-biradicals.[81] The generally accepted reaction mechanism at that time invoking "polar state exciplexes"[80] as reaction intermediates was simply not in accord our kinetic data. Using PAC techniques we were able to determine the energies as well as the lifetimes of the proposed triplet 1,4-biradical intermediates,[82] parameters that cannot be obtained using optical techniques. Using a variety of enones and alkenes, Nick Kaprinidis and George Lem, in collaboration with NYU faculty member Scott Courtney, found that while the triplet 1,4-biradical energies varied over a narrow range, there was a huge spread in triplet biradical lifetimes, ranging from 15 to 900 ns. From these data, and results of biradical quenching

Scheme 12. Mechanism of [2 + 2] Photocycloaddition of Alkenes to Cyclohexenones



experiments done concurrently by Alan Weedon at the University of Western Ontario, we proposed a comprehensive mechanistic description of enone-alkene [2 + 2] photocycloadditions, as illustrated in Scheme 12. Our mechanism is able to account for all aspects of this process, including the efficiency, regiochemistry, and stereochemistry of these reactions.[60,83] It should be noted that this reaction is perhaps the most synthetically useful reaction in all of organic photochemistry.[84]


46

■ STUDIES IN FULLERENE SCIENCE, 1993–2012

A rather innocent question from my NYU colleague Steve Wilson in early 1993 serendipitously led to a major change in the focus of our research from small molecule mechanistic organic photochemistry to the new field of fullerene science. Based on our expertise in [2 + 2] photocycloaddition chemistry, Steve asked me if I thought cyclohexenones would undergo [2 + 2[photocycloaddition to the newly discovered buckminsterfullerene, C_{60}, just as it did to ordinary alkenes. I was aware that Chris Foote and his colleagues at UCLA had recently discovered that C_{60} triplet states were generated in ∼100% yield on direct excitation, based on the quantum yield for singlet oxygen formation on quenching by dioxygen.[85] They determined that the triplet energy of C_{60} was unusually low, only 38 kcal/mol above the ground state. Consequently, I told Steve that photocycloaddition of cyclohexenone to C_{60} would probably not take place, since the high energy enone triplet states[77] should undergo triplet–triplet energy transfer to C_{60}, leading to unreactive C_{60} triplets. Fortunately, Nick Kaprinidis in my group and Yunhui Wu in Wilson's group were not impressed by my argument and tried the reaction anyway, using the C_{60} derivative **46** with an appended 18-crown-6 moiety which Wilson and Wu had synthesized for electrospray ionization mass spectrometry (ESI-MS) studies.[86] In a matter of hours, they discovered using ESI-MS that UV irradiation of a mixture of 3-methyl-2-cyclohexenone (3MCH) and **46** in benzene led to addition of up to seven enone units to the fullerene sphere in a matter of hours![87] We soon discovered that this reaction was completely general, as a variety of cyclohexenones, including testosterone acetate, also underwent photoaddition to C_{60}.[88,89] No adducts were formed upon irradiation of the enone–C_{60} mixture at 532 nm where the only light absorbing material is the fullerene. I was amazed and delighted by these discoveries. Using untagged C_{60} and 3-MCH or CH, and adjusting the reaction conditions, they were able to isolate and characterize the *cis*- and *trans*-fused [2 + 2] monoadducts, which were formed in ∼1:1 ratio on the basis of HPLC analysis on a "Buckyclutcher" column.[90] Adduct structures were established by NMR and IR spectra, and by the conversion of the highly strained *trans*-fused adduct to the more stable *cis*-fused adduct by treatment with acid or base.[88] The racemic adducts could be separated into their enantiomers using a chiral HPLC column.[90] We also carried out the reaction using ^{3}He@C_{60} in which a ^{3}He atom is incorporated inside the fullerene sphere, a material recently prepared at Yale by Martin Saunders, Jim Cross, and their associates for analysis of C_{60} reactions using ^{3}He NMR.[91] Using ^{3}He NMR we showed that two monoadducts of both 3MCH and CH were indeed formed, the ratio of which could be directly determined from their peak heights in the ^{3}He spectrum of the crude reaction mixture.[88,89] Higher adducts showed ^{3}He resonances well upfield of the monoadducts.

Before discussing the directions in which these initial studies led us, it is worth asking why my initial prediction about the course of photoadditions of enones to C_{60} proved to be erroneous. As mentioned, triplet–triplet energy transfer from cyclohexenones to C_{60} is extremely exergonic, by at least 25 kcal/mol, depending on the particular enone donor. It is precisely this large exergonicity which is the heart of the problem. Triplet energy transfer is known to occur by the Dexter electron exchange mechanism, in which an electron in the LUMO of the donor is transferred to the LUMO of the acceptor while an electron in the HOMO of the acceptor is transferred to the HOMO of the donor (see schematic Figure 13).[92] The kinetics of such a process are governed by the Marcus theory of electron transfer (ET), according to which the ET rate k_{ET} increases as the free energy for ET ($-\Delta G_{ET}°$) becomes increasingly large. The maximum value of k_{ET} is reached when $-\Delta G_{ET}°$ corresponds to the reorganization energy for the process, but then decreases as $-\Delta G_{ET}°$ increases; i.e., there is a parabolic relationship between k_{ET} and $-\Delta G_{ET}°$.[93] The internal reorganization energy λ is governed by the ability of donor and acceptor molecules to accommodate charge, while the external component of λ is associated with solvent reorganization during the ET event. Both components of λ are small for C_{60} because of its high symmetry (I_h) and poor solvation; consequently, highly exergonic ET processes involving C_{60} are generally in the inverted region of the Marcus curve and are relatively slow.[94] As a result, the rate of triplet energy transfer from the enone triplets to C_{60} is not competitive with the rate of addition of the enone triplets to the fullerene. Highly exergonic triplet−triplet energy transfer processes in general should be strongly inhibited, a phenomenon which has not been well investigated, to the best of my knowledge.

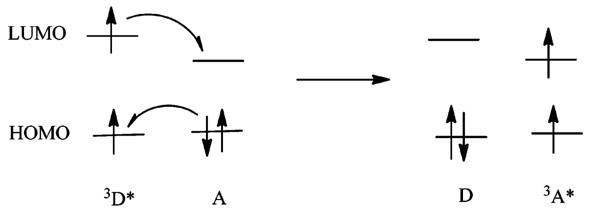


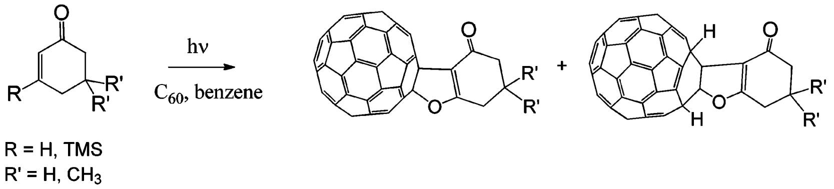
Figure 13. Schematic description of triplet−triplet energy transfer by the Dexter mechanism.

These photocycloaddition studies led to a major concentration on fullerene chemistry in my group in the 1990s. Postdoctoral fellow Anton Jensen investigated De Mayo-type photocycloadditions of 1,3-diketones to C_{60}. It was well established that the enol form of 1,3-diketones undergoes [2 + 2] photocycloaddition to alkenes ultimately giving 1,5-cyclooctadiones.[95] Jensen found that a quite different process occurred on photoaddition of dimedone, 1,3-cyclooctadione and their corresponding enol ethers to C_{60}. As shown in Scheme 13, the isolated products were fused furanylfullerenes.[96] The proposed multistep reaction mechanism involves initial formation of [2 + 2] cycloadducts, which then undergo oxidation by singlet oxygen ($^1O_2$), generated from fullerene triplets, followed by free radical hydrogen atom abstraction, cleavage and cyclization processes.[96]

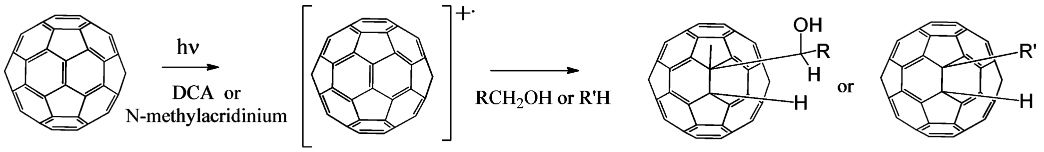
A quite different type of reaction was seen on photosensitized addition of alcohols and hydrocarbons to C_{60}, studied by George Lem. This investigation was stimulated by Foote's report that C_{60} radical cations ($C_{60}^{\bullet+}$) could be generated by photoinduced electron transfer (ET) from C_{60} to *N*-methylacridinium hexafluorophosphate (NMA) in the presence of biphenyl (BP).[97] In this reaction, initial ET from BP to NMA generates $BP^{\bullet+}$, followed by a second ET process from C_{60} to $BP^{\bullet+}$. The growth and decay of the intermediate $C_{60}^{\bullet+}$ could be followed spectroscopically. We were interested in whether $C_{60}^{\bullet+}$ would show chemistry analogous to that of other types of alkene radical cations generated by photosensitized ET.[98] Using 9,10-dicyanoanthracene as the photosensitizer, the crown-ether tagged fullerene **46** as the substrate and methanol as the addend, ESI mass spec analysis showed that methanol-C_{60} adducts were indeed formed. Similar results were obtained with other alcohols when *N*-methylacridinium salts (NMA) were used as the photosensitizer. To our surprise, ^{1}H NMR spectra indicated that these alcohol-C_{60} adducts did not arise from nucleophilic addition of the alcohol with formation of a C−O bond,[98] but rather involved C−C bond formation indicative of free radical reactions, as illustrated in Scheme 14.[99] Hydrogen abstraction by $C_{60}^{\cdot+}$ leads to the highly delocalized fullerenyl carbocation $C_{60}H^+$; back electron transfer from $DCA^{\bullet+}$ and radical−radical coupling would then give the observed products.[99] We also observed photosensitized addition of hydrocarbons including toluene, cyclohexane, and cyclohexene to C_{60}. Nanosecond flash photolysis studies, in which we could follow the growth and decay of $C_{60}^{\bullet+}$ at 980 nm, confirmed the mechanism.

We made extensive use of ^{3}He NMR techniques to analyze products of reactions with $^3He@C_{60}$ in collaboration with the Yale group led by Martin Saunders and Jim Cross. One of the key problems associated with all types of additions to C_{60} and higher fullerenes is the generation of *bis* and higher adducts, since fullerene monoadducts are usually chemically more reactive than the parent fullerene.[100] The situation gets even more complicated when the addend is unsymmetrical or if two different addends are involved. Differentiation of *bis*-adduct isomers, which often can be separated chromatographically, is possible using ^{13}C NMR in combination with UV−vis spectroscopy, as shown by Hirsch.[100] We were interested to see if ^{3}He NMR might be a valuable and simpler analytical tool in this connection. Accordingly, we used $^3He@C_{60}$ as the substrate in the Bingel−Hirsch reaction (reaction of malonates and a base to give methanofullerene derivatives) and the Prato reaction (generation and addition of azomethine ylides to C_{60} to give *N*-methylfulleropyrrolidines). We showed that the crude reaction mixtures indeed showed well resolved ^{3}He resonances for the eight possible bis-adducts.[101] These isomeric bis-adducts were then separated chromatographically, their structures were

Scheme 13. Photocycloaddition of 1,3-Diones to C_{60}



Scheme 14. Sensitized Addition of Alcohols and Hydrocarbons to C_{60}



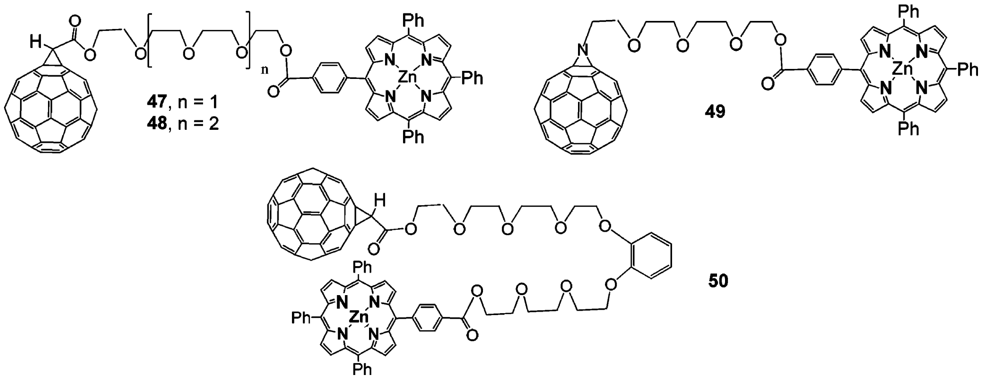


Figure 14. First-generation porphyrin−fullerene dyads.

assigned following literature procedures,[100] and the ^{3}He resonances were then assigned to each individual isomer. We discovered that bis-adducts with addends attached on opposite hemispheres of the fullerene sphere tend to have ^{3}He resonances downfield of those bis-adducts with addends attached in the same hemisphere. Clearly the magnetic field felt by the ^{3}He atom inside the fullerene sphere due to the ring currents in the residual π-system is exquisitely sensitive to the pattern of ligation on the surface of the sphere.[101] Although it is clear from our joint studies and those of the group at Yale that ^{3}He NMR is very useful in determining the number and ratio of adducts formed in all kinds of reactions of C_{60} as well as C_{70},[91,101,102] this research program at Yale has been terminated and no one else has picked it up, to the best of my knowledge. Thus, the full potential of the ^{3}He NMR technique in fullerene science remains unrealized.

■ PHOTOINDUCED ELECTRON TRANSFER IN FULLERENE PORPHYRIN DYADS AND RELATED SYSTEMS

A seminal paper by Devens Gust, Tom Moore, and Ana Moore at Arizona State University appeared in 1994 on the synthesis and photophysical properties of a hybrid molecule (a so-called dyad) in which an electron donating porphyrin moiety is covalently linked to C_{60}.[103] They reported that photoinduced electron transfer (PET) took place to produce a relatively long-lived charge separated state with oxidized porphyrin ($P^{\bullet+}$) and reduced C_{60} ($C_{60}{}^{\bullet-}$) moieties, detected spectroscopically, and suggested that such systems might prove to be useful in solar energy storage and photovoltaic devices. This report triggered a worldwide effort in the synthesis and photophysical studies of fullerene-based dyads, triads and increasingly complex electron donor−acceptor (DA) hybrid systems.[104] Players who have continued to make important contributions in this field include Hiroshi Imahori and Shinuchi Fukuzumi in Japan, Dirk Guldi and Andreas Hirsch in Germany, Nazario Martin and Tomas Torres in Spain, Nicola Armaroli, Maurizio Prato, and Michele Maggini in Italy, François Diederich in Switzerland, and Jean-Francois Nierengarten in France, while in the United States significant contributions have come from the Arizona State group, Francis D'Souza at the University of Texas, and our group at NYU.

Our interest in this field was as usual based upon basic principles of physical organic chemistry. We were interested in how the rates of intramolecular energy transfer (EnT) and electron transfer (ET) processes in porphyrin-fullerene hybrid systems were governed by the nature and size of the linker between the C_{60} moiety and the electron donor group. In our early studies the electron donor was invariably a porphyrin, either the free base or a Zn(II)porphyrin. With no prior experience in porphyrin chemistry, we soon learned that the synthesis and purification of porphyrins was a very tricky business. Our first forays into this field were made by Phil Baran, then a young, eager, enthusiastic, talented, and tireless NYU undergraduate. As a teenager Phil already showed the attributes that have made him a dominant figure in synthetic organic chemistry in recent years. The first porphyrin−fullerene hybrid he synthesized was compound **47**, in which a methanofullerenecarboxylic acid (for which we had developed a high-yield preparation)[105] was joined to tetraphenylporphyrincarboxylic acid by a polyether bridge.[106] Phil succeeded in preparing the porphyrin over a weekend working nonstop and was able to present me with a pure sample of the material along with its NMR spectrum on Monday morning. The rest of the synthesis to give dyads **47** and **48**, differing only in linker lengths, proceeded without difficulty.[106] He also made azafullerene-linked dyad **49** and an analogue **50** with an appended benzo group on the linker, working together with Igor Safonov, another bright undergraduate (see Figure 14).[107]

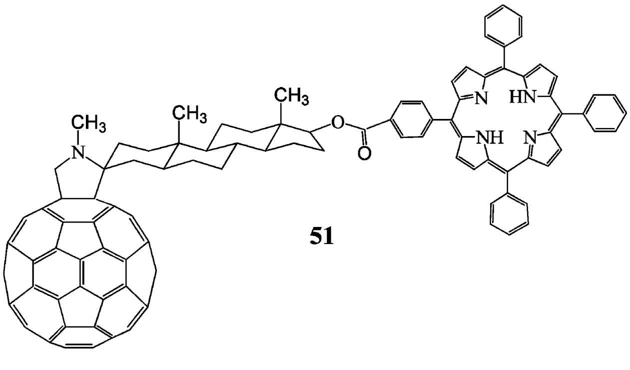
At that time, we had no collaborative arrangements in place for photophysical studies of these dyads using fast laser flash photolysis techniques and were limited at NYU to fluorescence studies and determination of quantum yields for photosensitized formation of singlet oxygen ($^1O_2$), in collaboration with Ahsan Khan, a pioneer in this field.[108,109] Phil found that the porphyrin fluorescence in his dyads was strongly quenched relative to that of a 1:1 mixture of an amphiphilic C_{60} derivative and the porphyrin methyl ester, showing that the porphyrin moiety in his dyads was talking to the fullerene intramolecularly, but we did not know at that time if this involved ET or EnT processes.[106] Recognizing that the polyether linker in his dyads with six oxygens resembled 18-crown-6, Phil studied the effects of potassium salts on the spectroscopic properties of his dyads. Indeed, in the presence of excess KSCN, UV−vis spectra of dyad **47** and **48** are red-shifted, along with pronounced changes in ^{1}H NMR chemical shifts and splitting patterns, all indicative of complexation of the dyad with K^+.[106] No such changes were noted on addition of NaSCN. Computational studies with Dr. Regina Monaco suggested a change in conformation of the dyad in the K^+ complex, as the porphyrin twists so as to approach the C_{60} moiety; indeed quenching of porphyrin fluorescence in the K^+ complex increased dramatically compared to that in the free dyad. Finally, the quantum yield for sensitized formation of $^1O_2$ by the K^+ complex was significantly attenuated relative to that of a model porphyrin, indicating that electronic interaction between C_{60} and the singlet excited state of the porphyrin moiety ($^1P^*$) is competitive with quenching of $^1P^*$ by dioxygen.[106]

Phil presented his work in May 1997 at the Electrochemical Society Meeting in Montreal in a symposium of the Fullerene Division.[107] The ECS remains to this day the most important forum for presentation of new research in fullerene science, now expanded to include carbon nanotubes and other nanoscale carbon systems. Phil's brilliant presentation caused quite a stir and led directly to the initiation of a very productive collaboration with Dirk Guldi on photophysical studies, first at Notre Dame and currently at the University of Erlangen in Germany (see Figure 15). These involve time-dependent fluorescence and transient absorption measurements in picosecond and nanosecond time domains. In association with Guldi, Shaun MacMahon subsequently demonstrated that ether-linked dyads analogous to Phil's systems undergo both energy transfer (EnT) and electron transfer (ET) processes upon photoexcitation, the extent of which varies with the polarity of the solvent. EnT leading to $^3C_{60}{}^*$ dominates in nonpolar solvents such as toluene while ET to give charge separated states dominates in more polar organic solvents such as tetrahydrofuran (THF) and benzonitrile (PhCN).[110,111] The various transient species could be easily and definitively detected using transient absorption spectroscopy.

Figure 15. Dirk Guldi (Notre Dame, Erlangen-Nürnberg). Photo courtesy of Professor Guldi.

Phil also carried out studies on the mechanism of formation of $C_{60}O$ on photoexcitation of C_{60} in the presence of oxygen.[112] Since no fullerene oxides were formed on thermolysis of the endoperoxide of 1,4-dimethylnaphthalene (which is known to give $^1O_2$) in the presence of C_{60} and C_{70}, we concluded that the mechanism of formation of $C_{60}O$ had to involve reaction of $^1O_2$ with long-lived C_{60} triplet excited states and not with ground state C_{60}, contrary to pronouncements in the literature.[112]

Phil's success inspired us to undertake studies of a number of other P−C_{60} dyads. Our data along with those in the literature on and those accumulating in the literature on related dyad systems were strongly suggestive of through-space electronic interactions between porphyrin excited states and C_{60}.[104a] Consequently, we became interested in seeing what would happen when porphyrin and fullerene moieties were forced by structural constraints to be far apart. Robert Fong, another bright undergraduate, synthesized a series of dyads with steroid spacers, including **51**, in which the porphyrin is attached to a hydroxyl group on ring D while C_{60} is attached to the carbonyl group at C-3 on ring A through a Prato reaction.[111,113,114] Absorption spectra indicated no ground state interactions between the two chromophores in these steroid-linked dyads, as expected. However, fluorescence studies, carried out at high dilution (20 μM) to prevent intermolecular interactions, showed that the porphyrin fluorescence in **51** and related steroidal dyads was quenched by 50−70% in benzene relative to model systems, and to a slightly higher extent in chloroform, suggesting that intramolecular ET processes are occurring. No intermolecular fluorescence quenching was seen in a mixture of model porphyrin- and C_{60}-linked steroids, also in dilute solution. Thus, the electronically excited porphyrin and ground state C_{60} moieties in **51** and other rigid steroid-linked dyads manage to communicate through the rigid steroid framework, even at a distance of ∼12 Å.[111,113]



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By the late 1990s, it was clear from the work by several groups that strong attractive interactions exist between the π-systems of porphyrins and fullerenes that bring these moieties into close proximity in conformationally flexible dyads, so that intramolecular energy and electron transfer occurs through space rather than through bonds.[103,104a,106] Such π−stacking interactions were clearly evident in X-ray studies of mixed crystals formed from C_{60} and a variety of both free base and metalloporphyrins.[115] We[116] and others[117] set out to synthesize conformationally constrained doubly linked P−C_{60} dyads in which the porphyrin and C_{60} moieties are forced into close proximity. In our lab, this involved the challenging synthesis by

Peng Cheng of the parachute-shaped dyad **52** by the Bingel–Hirsch reaction between strapped porphyrin malonate **53** and C_{60}.[116] The UV–vis spectrum of **52** is superimposable on that of a mixture of C_{60} and **53** indicating no appreciable ground state electronic interactions exist between the two neighboring π–systems. However, the porphyrin fluorescence in free base **52** and its Zn(II) analogue **52**–Zn is quenched by 3 orders of magnitude relative to **53** and **53**–Zn, respectively.[118] The fluorescence lifetimes of **52** and **52**–Zn in benzene and THF are extremely short, in the short picosecond time domain, 3 orders of magnitude less than for **53** and **53**–Zn. Picosecond flash excitation of **52** and **52**–Zn at 532 nm (excitation mainly of the porphyrin moiety) in nonpolar as well as polar solvents led within 20–40 ps to the formation of porphyrin radical cations $P^{\bullet+}$ and $ZnP^{\bullet+}$ (characteristic absorption centered at 670 nm). In these experiments, the fullerene radical anions $C_{60}{}^{\bullet+}$ ($\lambda_{max} \sim$ 1040 nm) were not directly detected due to experimental problems. Thus, the rate constant for photoinduced electron transfer (ET) in these systems is extremely fast, $\sim 10^{11}$/s, consistent with a process occurring through space, not through bonds. The rate constants determined for charge recombination (back ET) are once again orders of magnitude slower than for charge separation. These lifetimes for the charge-separated states were inversely related to the polarity of the six solvents investigated, indicative of back ET in the inverted Marcus region. From a plot of the rate constants for forward and back ET vs the thermodynamic driving force for ET, shown in Figure 16, values of the reorganization energy λ of 0.80 ev and the electronic coupling matrix element V of 9.9 cm^{-1}can be derived.[119] These are very similar to parameters found for other types of P–C_{60} and ZnP-C_{60} dyads.[120] The fact that our parachute dyads undergo photoinduced ET even in a nonpolar solvent such as toluene is consistent with the close proximity of the porphyrin and C_{60} moieties.

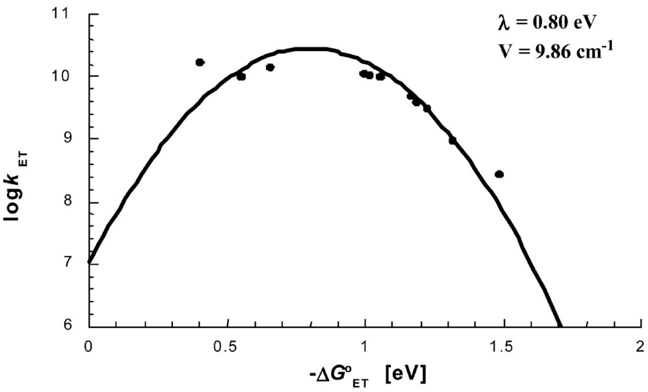
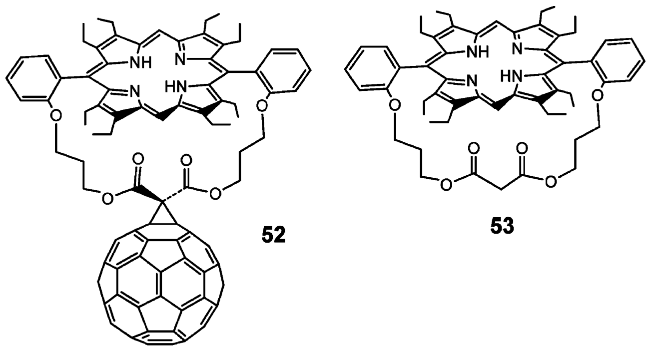


Figure 16. Marcus plot of forward- and back-electron-transfer rate constants for parachute dyad **52**.

We were approached in 1999 by Haim Levanon at Hebrew University in Jerusalem to collaborate with his group on studies of spin dynamics in ZnP–C_{60} systems at low temperatures using time-resolved electron paramagnetic resonance (TREPR), starting with parachute dyad **52-Zn**. This venture represented a unique opportunity for extending our investigations of electron transfer in porphyrin/fullerene hybrid systems in solution using standard optical techniques. In particular, TREPR studies in isotropic solvents and anisotropic liquid crystals (LCs) at low temperature provide data about intermediate triplet charge separated radical pair (CSRP) and triplet excited states which aid in delineation of ET pathways, information that is not directly obtainable using optical techniques. From TREPR studies of **52-Zn** we were able to conclude that the CSRP state in frozen toluene lies energetically between those of ZnP–$^{1}*C_{60}$ and ^{3}ZnP*–C_{60} and that the CSRP state is generated from ^{1}ZnP*–C_{60}. The CSRP state decays by back-electron-transfer (BET) to give the lower-lying porphyrin triplet state (^{3}*ZnP–C_{60}) and ultimately the fullerene triplet (ZnP–$^{3}*C_{60}$). As in the optical studies, direct decay to the ground state is relatively slow since it is in the Marcus inverted region. In more polar media where the CSRP state lies energetically below both ^{3}ZnP* and $^{3}C_{60}$*, the polarization of the EPR signals indicates that the long-lived CSRP state is generated mainly from ^{3}*ZnP-C_{60}.[121]



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Parachute dyad 52 and its porphyrin-malonate precursor 53

In our studies of parachute dyads **52** and **52**–Zn we were concerned about the actual conformation of these as well as other hybrid molecules that we had studied in solution and at low temperatures. In order to gain further insight we turned to computational techniques. Computations at various levels of theory by undergraduate Peter Jarowski pointed to lowest energy conformations of conformationally flexible systems in which the porphyrin and fullerene moieties were close to each other due to attractive interactions.[122] For the parachute dyads, we had assumed that the system was axi-symmetric with the porphyrin plane situated above the fullerene sphere. However, the computations indicated that the energetically preferred conformation of **52** is in fact the one shown on the left in Figure 17, in which the porphyrin moiety lies to the side of the sphere, minimizing the interchromophoric distance and maximizing the attractive forces.[119,122] In order to account for the average symmetry of the system indicated by ^{1}H NMR spectra, we suggested that the porphyrin moiety swings from one side of the C_{60} to the other, like a windshield wiper. The TREPR data is also consistent with a tilted relationship

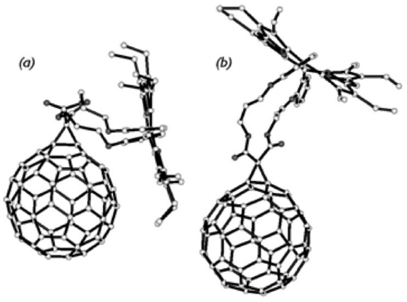

Figure 17. Low energy (a) and high energy (b) conformations of parachute dyad **52**.

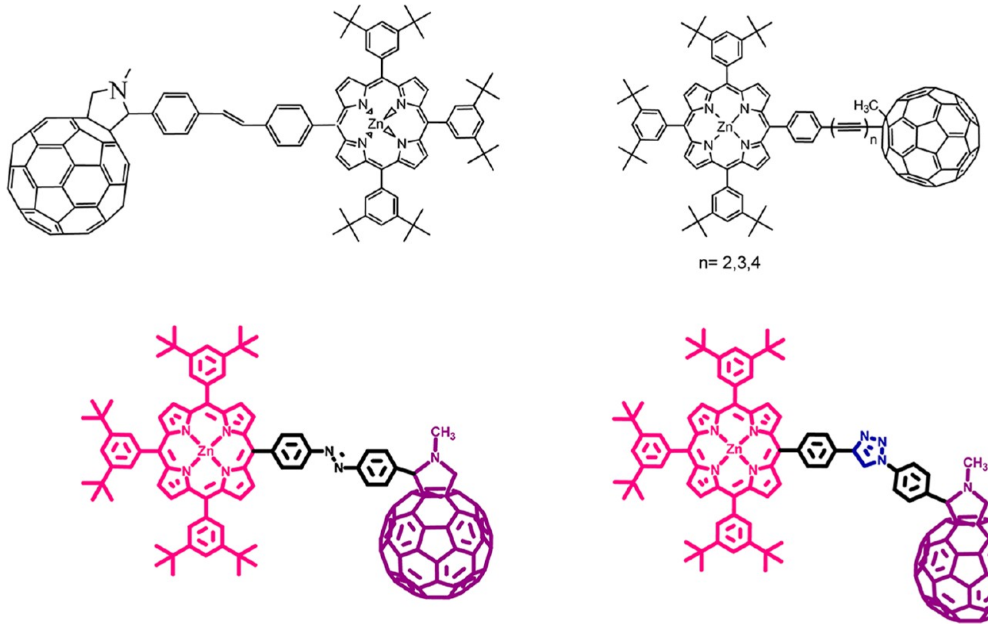

Figure 18. Miscellaneous porphyrin/C_{60} dyads.

between the frames of reference of the ZnP and C_{60} moieties in this dyad and not with a structure with C_{2v} symmetry.[121] If so, the NMR spectra of these dyads should be temperature dependent, depending on the activation barrier for the windshield-wiper motion. To test this idea, graduate student Mike Fazio later prepared a doubly linked parachute dyad bearing substituents to provide improved solubility at low temperatures, and obtained temperature dependent NMR data that were consistent with the proposed conformational interconversion but were not absolutely definitive.[123] Obviously, an X-ray structure of this material would be highly informative, but none of our hybrid compounds have afforded crystals to date, with the unique exception of an axially symmetric π-complex between an *N*-pyridylfulleropyrrolidine and Zn(II)tetraphenyl-porphyrin,[124] for which TREPR data indicated that ET occurs on excitation in fluid media while EnT occurs in frozen media at low temperatures.[125]

Pursuing physical organic chemistry structure−activity relationships in these systems, a variety of covalently linked porphyrin/C_{60} dyads were synthesized in which the kinetics of photoinduced ET and EnT processes were studied as a function of the nature and size of the linker. These included systems with styrene,[126] alkyne,[127] azobenzene,[128] and triazole[129] linkers, some examples of which are shown in Figure 18. As before, a wide variety of steady-state and time-resolved techniques were used to probe photoinduced events in these systems. In all cases very fast photoinduced charge separation was observed, usually on the picosecond time scale, while charge recombination (back electron transfer) was much slower, usually by ~3 orders of magnitude, attributable to the low reorganization energy associated with the fullerene moiety. As a result, many of these nanoscale dyads possess CSRP lifetimes approaching microseconds, and represent materials for strong consideration as components of solar energy storage devices and photovoltaic cells.[130]

The direction of our research on photoinduced ET processes in electron donor/fullerene hybrid systems took a dramatic turn as the result of a lecture I attended in July 2000 at the International Conference on Porphyrins and Phthalocyanines in Dijon, France. Jean-Pierre Sauvage from Strasbourg (see Figure 19) presented his elegant pioneering work on the synthesis and properties of interlocked electron donor−acceptor systems incorporating Zn(II)−porphyrins as electron donors and Au(III)−porphyrins as electron acceptors. He and his group developed a metal template technique to assemble large interlocked systems in good yields, including rotaxanes (in which a chain with porphyrin end groups is threaded through a large porphyrin-linked macrocyclic ring) and catenanes (possessing two interlocked rings, both attached to porphyrin moieties).[131] The self-assembly involved coordination of 1,10-phenanthroline (phen) moieties in carefully designed subunits with Cu(I) to give a tetrahedral complex, followed by ring closure to generate catenanes, or addition of end groups to give rotaxanes. Very rapid intramolecular ET processes take place in these interlocked systems upon photoexcitation, involving formation and decay of relatively short-lived charge-separated states. While listening to Sauvage's superb lecture in Dijon, it occurred to me that analogous interlocked systems with much

Figure 19. Jean-Pierre Sauvage (Strasbourg). Photo courtesy of Professor Sauvage.

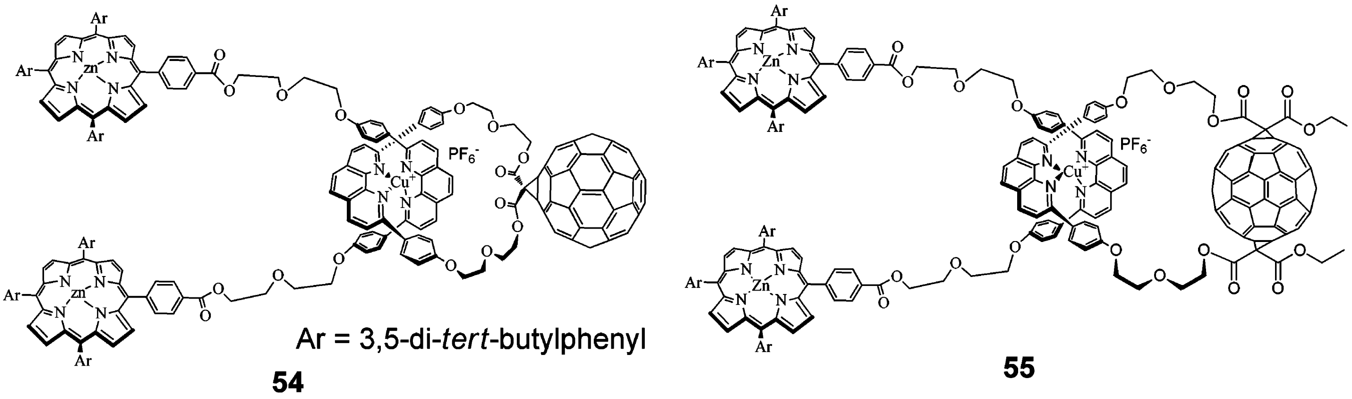

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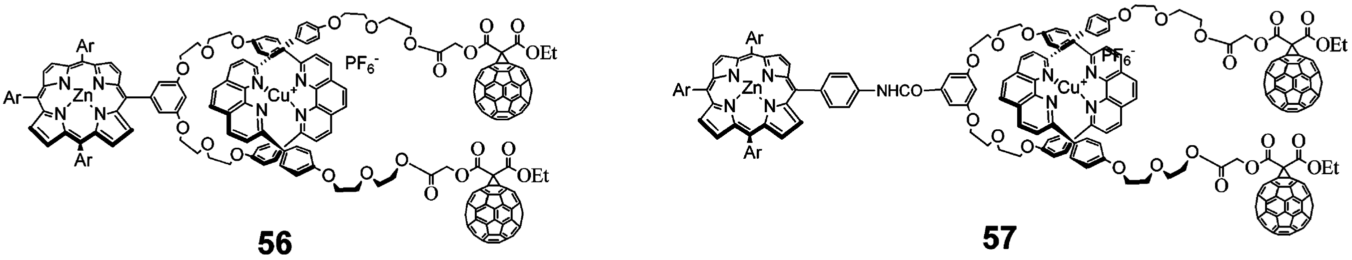
Figure 20. First-generation ZnP/C_{60} rotaxanes.



56

57

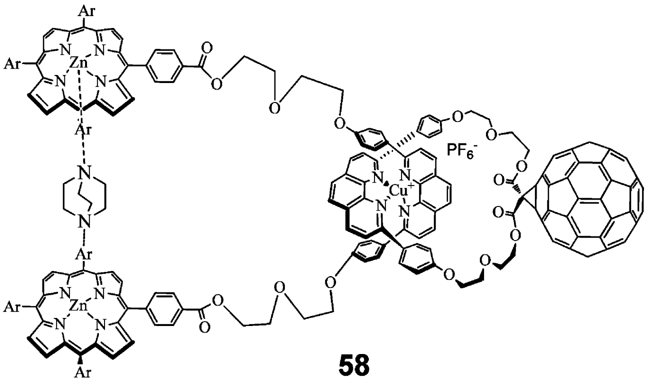
Figure 21. ZnP−$(C_{60})_2$ rotaxanes **56** and **57**.

longer CSRP lifetimes could be constructed using fullerenes as the electron acceptor in place of a metalloporphyrin. I envisaged synthesis of new materials incorporating mechanically linked porphyrin and C_{60} moieties whose electrochemical and photophysical properties would then be studied in collaboration with Luis Echegoyen (then at Clemson) and Dirk Guldi (at Erlangen), respectively. I anticipated that the CSRP states of systems in which the electron donor and C_{60} moieties are not covalently linked would be quite long. The synthesis of such systems, the major hurdle in this project, was delegated to Ke Li, a very talented graduate student who had just joined my group.

The plan was to adapt Sauvage's successful synthetic approach to purely porphyrinic interlocked DA systems[131] to our desired materials containing C_{60}. This required synthesis first of symmetrical macrocyclic compounds with a central phen moiety possessing functional groups to which C_{60} could be attached. Our first choice was a malonate group through which C_{60} could be attached using a Bingel−Hirsch reaction. Alternatively, terminal malonate groups on a chain with a central phen moiety could be used to form bis-methanofullerene adducts in a double Bingel−Hirsch reaction.[132] An alternative was a Prato reaction on macrocyclic precursors with a central benzaldehyde moiety.[132] A chain possessing a central phen moiety and a Zn(II)−porphyrin end group could then be threaded these C_{60}-based macrocycles in the presence of $Cu(CH_3CN)_4^+$ PF_6^- to give a pseudorotaxane, which could then be capped by a second Zn(II)−porphyrin moiety. In this way Ke synthesized the first generation ZnP−C_{60} [2]rotaxanes **54** and **55** shown in Figure 20, as well as model rotaxanes lacking C_{60}.[133] Photophysical studies by Guldi showed that the ZnP fluorescence in **54**, **55**, and model $(ZnP)_2$ rotaxanes lacking C_{60} is quenched to the same extent, indicating that the ZnP singlet excited state is talking to the Cu(I)−$(phen)_2^+$ complex and not to C_{60}. However, the luminescence lifetime of the copper complex is much shorter in rotaxanes bearing C_{60} indicating that electronic interaction is taking place between the Cu(I)−$(phen)_2^+$ and C_{60} moieties. Transient absorption spectra of **54** and **55** on the nanosecond time scale showed characteristic features for oxidized ZnP ($ZnP^{+\cdot}$) and reduced C_{60} ($C_{60}^{\bullet+}$) moieties, confirming the formation of the charge-separated radical-pair (CSRP) state $(ZnP)_2^{\bullet+}$-$Cu(phen)_2^+$-$C_{60}^{\cdot-}$.[133,134] We concluded that this CSRP state is produced following ZnP photoexcitation by a multistep process: (1) energy transfer (EnT) from $^1ZnP^*$ to $Cu(phen)_2^+$; (2) electron transfer (ET) from the MLCT state of $Cu(phen)_2^+$ to C_{60}; (3) ET from ZnP to the oxidized $Cu(phen)_2^{2+}$ moiety. Finally, (4) the rotaxane ground state is regenerated by slow back electron transfer (BET) through the Cu(I) complex.[134] Decay of the CSRP states in N_2-saturated dichloromethane was cleanly unimolecular, corresponding to lifetimes of 0.49 and 1.17 μs for **54** and **55**, respectively. These lifetimes are much longer than those observed by Sauvage in his purely porphyrinic systems[131,135] and by us[103,119,126−129] and others[104] in covalently linked P/C_{60} dyads; nonetheless they were shorter than we had expected for such mechanically linked systems. These long CSRP lifetimes indicate that BET over nanoscale distances is once again occurring in the Marcus inverted region, almost surely by a superexchange mechanism.[93,94,136] A full study of solvent effects on the dynamics of EnT and ET processes in these would have been informative but was not possible given the small amounts of material available.

Modification of the synthetic strategy afforded fullerene-stoppered porphyrinorotaxanes **56** and **57** (Figure 21) in which ZnP is appended to the macrocycle and C_{60} moieties function as stoppers on the thread.[134,137] Upon photoexcitation, these materials again formed $ZnP^{\bullet+}$−$Cu(phen)_2^+$−$(C_{60})_2^{\bullet-}$ long distance CSRP states. The most significant finding is that the CSRP state of **57** is extremely long, 29 μs in DCM and 32 μs in THF, the longest we have measured for any donor−C_{60} hybrid system. We attribute this elongation to the unique topology of **57**, and the possibility that stabilization of the CSRP state is enhanced by shuttling of an electron between the neighboring C_{60} moieties.

A change in topology from rotaxane to catenane could be induced by complexation of the ZnP moieties in bis-porphyrinic rotaxanes **54** and **55** with DABCO (1,4-diazabicyclo[2.2.2]octane) or 4,4′-bipyridyl.[138] Evolution of the bidentate complex **58** could be easily monitored by changes in UV–vis and fluorescence spectra as a function of DABCO concentration. Analysis of these data gave association constants K_a of ~10^5 M^{-1}. The photophysical changes resulting from this topological change were minimal in that the same EnT and ET processes occurred in the catenanes as in the rotaxane precursors and at similar rates.[134,138] Since the CSRP lifetimes of catenane **58** and rotaxane **54** are quite similar, we conclude that the ZnP groups are arranged in space similarly in both molecular architectures.



58

The laborious synthesis of these interlocked materials, which nonetheless could be reproduced by undergraduates, led us to look for more efficient and higher yield synthetic approaches to ZnP/C_{60} interlocked systems. This was achieved spectacularly by Jackson Megiatto, a postdoc from Brazil via Bordeaux, using click chemistry (1,3-dipolar cycloaddition of azides to alkynes to give 1,2,3-triazoles) in conjunction with Sauvage metal-templated self-assembly protocols. Accordingly, alkyne or azide functional groups were introduced at the termini of a symmetrical phen-containing chain, which in the presence of Cu(I) could be threaded through a C_{60}-linked phen-containing macrocycle to give pseudorotaxanes. Reaction with either *p*-azidophenyl- or *p*-alkynylphenylporphyrins then gave triazole-linked [2]rotaxanes, such as **59**, while reaction with 3,5-bis-azidophenyl or 3,5-bis-alkynylphenylporphyrins gave triazole-linked [2]catenanes, such as **60** (see Figure 22).[139,140] The problem was that the "click" reactions had to be done at room temperature to prevent unthreading of the pseudorotaxanes. To accomplish this, Jackson developed a magic "click soup" containing CuI, sodium ascorbate, sulfonated bathophenanthroline, and 1,8-diazabicyclo[5.4.0]undecene (DBU) in oxygen-free 1:1 ethanol/water, which allowed a one-pot synthesis at room temperature of the desired [2]rotaxanes and [2]catenanes in yields on the order of 60–80%.[139−141] The synthetic methodology proved to be completely general, allowing for the synthesis of [2]catenanes with a variety of peripheral functional groups which are suitable for other possible applications.[142] It also proved possible to synthesize [3]catenanes such as **61** by linking pseudorotaxanes with terminal azide groups to pseudorotaxanes with terminal alkyne groups.[141] Related rotaxanes bearing ferrocenyl (Fc), Mg(II)-porphyrin, and phthalocyanines as electron donor groups (in place of ZnP) with C_{60} as the acceptor moiety were also prepared.[143,144]

The amounts of these materials have allowed more extensive photophysical investigations than were possible with Ke Li's first generation rotaxanes and catenanes. Photophysical studies in the Guldi lab on the triazole-linked ZnP/C_{60} [2]rotaxanes and [2]catenanes as well as Fc-linked materials have been completed. In the case of the [2]-catenane system, photophysical studies were carried out on **60** as well as model systems containing (a) only C_{60}, (b) only ZnP, and (c) neither chromophore.[145] We established that the ^{1}ZnP* state generated upon irradiation of **60** transfers energy to the $(\text{phen})_2$-Cu(I) core, that electron transfer then occurs from the MLCT state of the Cu(I) core to C_{60}, and that a final electron transfer from ZnP to the oxidized metal complex generates the long distance CSRP state $\text{ZnP}^{\bullet+}-[\text{Cu(phen)}_2]^+-C_{60}^{\bullet-}$ detected by transient absorption techniques. This state has a lifetime of 1.1 μs in benzonitrile (BzCN) and 1.5 μs in THF, in the range expected. The sequence of events and the rate constants for all processes for catenate **20** in BzCN are shown in Figure 23.[145] As before,

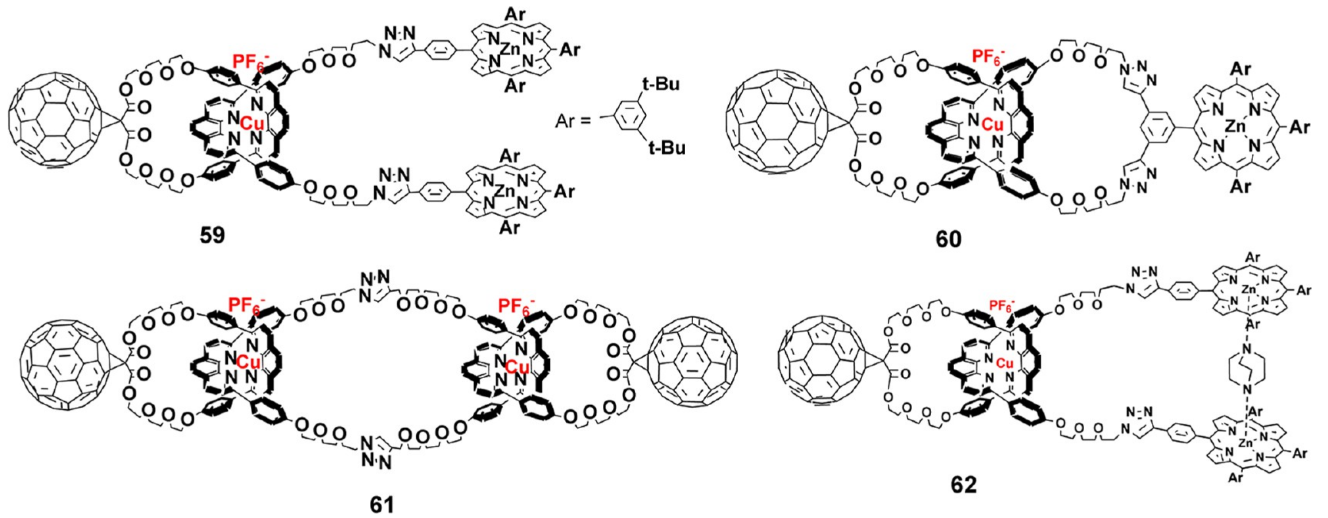


Figure 22. Representative rotaxanes and catenanes synthesized by combining Sauvage self-assembly and click protocols.

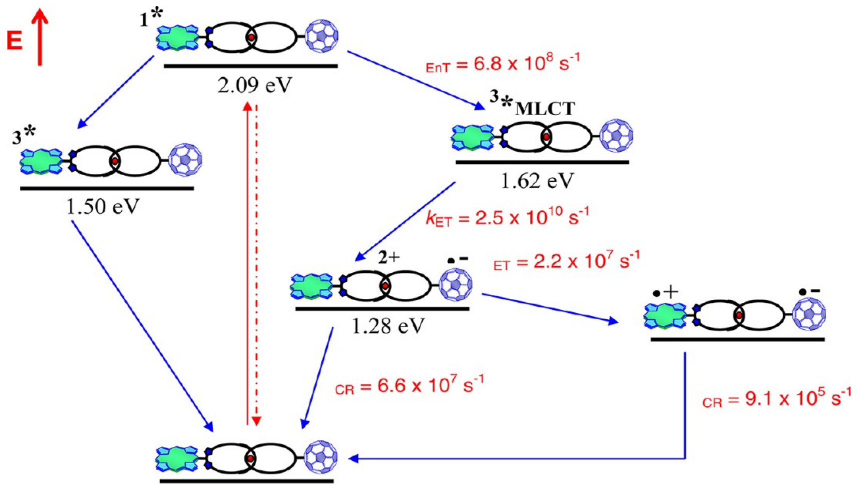


Figure 23. Dynamics of events following photoexcitation of [2]catenate **60**.

BET is occurring in the Marcus inverted region, but now over a distance of nearly 3 nm.

A similar study of the related [2]rotaxane **59** along with appropriate model systems[146] revealed complexity, since the rotaxane structure possesses conformational flexibility not present in the catenane systems. Spectroscopic and computational data indicate that two extreme conformations seem to play a role, a folded one in which one of the ZnP moieties is close to C_{60} and an extended structure in which both ZnP groups are far from C_{60}. The CSRP lifetime for **59** is 0.24 μs in anisole, indicating that on average the $ZnP^{\bullet+}$ and $C_{60}^{\bullet-}$ moieties are closer than in the corresponding catenane **60**. A change in topology from the tweezer-like rotaxane structure of **59** to the more rigid [2]catenane **62** could again be accomplished using DABCO which links the two ZnP moieties. Photoexcitation of **62** leads to the same series of events as in the parent rotaxane **59**, but the CSRP lifetime of **62** (1.03 μs) is much longer, indicating increased structural rigidity. As anticipated, the change in topology from rotaxane to catenane inhibits charge recombination.[146]

Photoinduced processes in these rotaxanes and catenanes were also studied by the Levanon group in Israel using TREPR.[147] It was found that the routes and rates of ET processes in these materials embedded in various phases of nematic liquid crystals and frozen isotopic solvents at low temperatures were very dependent on their microenvironments. The data support the formation of localized CS states under these conditions rather than the more extended CSRP states implicated in the optical studies at ambient temperatures.

An obvious question is the role played by the central Cu(I)−$(phen)_2$ complex in these long distance ET processes. The standard way to remove Cu(I) from interlocked structures of this type involves reaction with KCN.[131] However, this is problematic in our systems since KCN reacts with C_{60}.[100] Jackson synthesized a $(ZnP)_2$−C_{60} [2]rotaxane lacking Cu(I) by removing Cu(I) using KCN from the intermediate [2]rotaxane prior to attachment of C_{60}. We found that photoexcitation of this demetalated rotaxane afforded only C_{60} and ZnP triplet excited states; i.e., no charge separation was observed, even in polar solvents.[146] Thus, the central Cu(I) complex seems to be essential in facilitating long-range ET processes in nanoscale interlocked porphyrin/C_{60} donor−acceptor systems. Jackson subsequently discovered a general and much milder method for removing Cu(I) from rotaxanes and catenanes containing C_{60} involving treatment with aqueous ammonium hydroxide in acetonitrile.[148] Photophysical studies on demetalated ZnP−C_{60} [2]catenanes have not been carried out to date.

Photophysical studies are still ongoing in Guldi's lab on rotaxanes synthesized by Jackson possessing Mg(II)porphyrin and phthalocyanines as electron donor groups with C_{60} as the acceptor. This is where this project was left when the decision was made in 2012 to close our lab due principally to funding problems.

■ CONCLUDING REMARKS

Over the course of more than fifty years, our research has progressed from fundamental mechanistic investigations of photochemical reactions of small organic molecules using rather rudimentary techniques to investigations of the photophysics of large complex molecules using very sophisticated instrumental methods. This period has seen a huge advance in the ability to gain insight into the behavior of organic materials upon photoexcitation as instrumentation necessary to accomplish this became available. We have sought to take advantage of new spectroscopic techniques at NYU and through collaborations with leading scientists in the United States and in Europe. We have attempted to be as thorough as possible, driven by our motivation to probe ever more deeply into the behavior of electronic excited states of organic molecules. Throughout my career I have been stimulated and influenced by close interactions with many members of the very tight community of organic photochemists, and especially with George Hammond, Howard Zimmerman, Kurt Schaffner, and Nick Turro.

For a while, from 1975 until the early 1990s, we also pursued a research program in the field of neuroscience in an attempt to understand the molecular basis of mental illness, particularly schizophrenia, and the mechanism of action of antipsychotic drugs. This work was carried out in collaboration with Randall Murphy, a brilliant young biochemist then on our faculty. We made extensive use of photochemical techniques in these studies whenever possible and appropriate.[149] The questions we asked were timely and relevant, and some progress was made, but we did not have the resources to compete effectively with large research programs in this field at major medical centers. After Randy left NYU the program was abandoned. It is gratifying that a Nobel Prize was awarded in 2012 to Robert

Lefkowitz at Duke, one of the early pioneers in this area of research, whose early work was very familiar to our group through the literature and attendance at annual meetings of the Society for Neuroscience. All our effort in the last two decades went into organic photochemistry, fullerene science, and eventually the merger of the two fields with focus on the synthesis and properties of artificial photosynthetic systems incorporating fullerenes.

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Notes

The authors declare no competing financial interest.

Biography

David Schuster is currently Professor Emeritus at New York University at Washington Square in lower Manhattan, New York City. He was born in Brooklyn in 1935, graduated from Columbia College *magna cum laude* in 1956, and received his Ph.D. in Chemistry and Physics from Caltech in 1961 where he worked with John D. Roberts. Following a highly successful postdoctoral year doing pioneering studies in mechanistic organic photochemistry with Howard Zimmerman at Wisconsin (Madison), he joined the faculty at the University Heights Bronx campus of NYU in September 1961, moving to Washington Square in 1974. For many years his research continued to focus on mechanisms of photochemical reactions of organic molecules, using increasingly sophisticated experimental techniques. In recent years, his focus changed to fullerene science and studies of photoinduced intramolecular electron transfer processes in a variety of covalently and mechanically linked fullerene−porphyrin artificial photosynthetic systems.

ACKNOWLEDGMENTS

I deeply acknowledge the contributions of the many research collaborators in my group over the course of my long career, including undergraduate students, graduate students, postdoctoral fellows, high school students, and occasional visitors. I am very proud that I have mentored more Ph.D. students (53) than anyone in the history of the NYU Chemistry Department to date, a record that will surely be broken by some of my present colleagues. Whatever our group has accomplished is attributable to the hard work of my co-workers in the lab, their dedication, and their creativity. The best of them took the ideas for research projects that I presented to them in directions that were totally unanticipated, and that often led to new and much more interesting projects. I attempted to make myself available to them as much as possible for direction and advice and to make sure they did not get lost in the thickets of their individual projects. It is a hard thing to abandon a research project when it is not going well, after a substantial investment of time and effort, but occasionally this had to be done. The names of most of these co-workers are given in the individual references. Space limitations do not permit a complete list. The personal side of these student/mentor relationships was something I treasured very much, including but not limited to fierce racquetball and tennis matches, after-work libations, and parties at my home in Connecticut and other locations. Working with these people and watching them develop as mature, independent research scientists has been the most gratifying part of my career. As I have frequently noted publicly, the academic life is unique in that while we professors age, the ages of the people with whom we are intimately involved day-to-day in teaching and research remain the same, which helps to keep us young, at least in our outlook on life. On the occasion of my official retirement from teaching at NYU in June 2005, just prior to my 70th birthday, a full-day symposium was organized in my honor by a group of former co-workers, followed by a large gala reception and dinner, the first event of its kind in the history of the NYU Chemistry Department. A very large number of former members of my research group as well as close professional friends from other institutions spoke at the symposium and at the gala dinner that followed. It was the most wonderful day of my professional life! Pictures from that remarkable event can be seen on my NYU web site http://www.nyu.edu/projects/schuster/.

I thank the various funding agencies that made my work in photochemistry possible. The U.S. Army Research Office (Durham) under the direction of George Wyman was a very important early source of funding of photochemistry research in the 1960s for fledgling research scientists including me. The National Science Foundation came on board a bit later, and I continued to receive funding from NSF (with breaks) until 2010. An award of a Research Fellowship from the Alfred P. Sloan Foundation in 1967 was crucial in allowing me to spend nine months in George Porter's lab at the Royal Institution in London in 1968−69. Occasional grants from the ACS Petroleum Research Fund were also helpful, while in the years following my retirement grants from the Camille and Henry Dreyfus Fund under their Senior Mentor Program allowed the support of undergraduate research in my lab until 2011. NYU provided some funds during periods when outside sources dried up and also directly supported undergraduates in my lab through the Dean's Undergraduate Research Fund. Finally, a fund established at the time of my retirement by some of my former students, spearheaded by Vasanth Prabhu, was very helpful and appreciated. I am grateful to all of these individuals and agencies for allowing me to pursue my scientific curiosity and to follow my dreams. It has been a wonderful ride.

I thank the many people who were instrumental in providing and authenticating the photographs used in this article. This includes archivists at Columbia University, Caltech, UCLA and the New York Philharmonic, John Dawson, Cheves H. and Stella Walling, Jerry Berson, Carolee Winstein, Eve Menger Hammond, Steve Zimmerman, Kurt Mislow, Kurt Schaffner, Dirk Guldi, Jean-Pierre Sauvage, Gabriel Pinski, Robert Bachrach, and David Phillips and Andy Porter at Imperial College, London.

Finally, I thank my wife Carlotta, whom I have known since high school in Far Rockaway, and to whom I have been married since 1962, for providing the love and support I needed to do

my thing. She has been my constant companion at photochemistry meetings worldwide since the 1960s and is admired by my many friends and colleagues in this field, not least for putting up with me over these many years. Special thanks to my colleague Bart Kahr for the design and execution of the inspired cover and to his associate Shane Nichols for technical assistance.

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