

# A Reflection on the Evolution of Organic Photochemistry from the University of Chicago

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by Nien-chu C. Yang  
University of Chicago

*Prologue. This article is a brief historical account of my research on organic photochemistry at the University of Chicago. A few contributions made by other scientists which are directly relevant to my work are cited in this article. This does not mean that I am not aware of the numerous significant and exciting contributions in organic photochemistry made by many scientists whom I personally respect and admire. Their contributions will not be reviewed due to the limited scope of this article.*

Since the days of Ciamician and Silber, photochemical transformations of organic compounds lapsed to sporadic attentions of chemists. Interest in the photochemistry of organic compounds was revived in the mid-1930's by Norrish and his coworkers at Cambridge, and by Noyes and his coworkers at Rochester. They made systematic studies on the photochemistry of simple carbonyl and aromatic compounds, mostly in the gas phase. In the 40's and 50's, Schenk in Germany contributed to the photochemical oxidation of organic compounds, and Havinga in the Netherlands and Dauben in Berkeley contributed to the photochemistry of steroids related to Vitamin D. Modern organic photochemistry was popularized by Hammond, then at Cal Tech, and Zimmerman at Wisconsin in the National Organic Symposium held in Bloomington in 1961. This was followed by the First IUPAC Conference on Photochemistry organized by Hammond in Strasbourg in 1964 and

the first Gordon Conference on Organic Photochemistry organized by Trozzolo at Tilden in the same year. These two conferences, taking place now in alternating years since 1965, play a pivotal role in increasing the awareness of organic photochemistry among the scientific community.

My personal interest in photochemistry was initiated in the laboratories of my PhD mentor, the late Professor Morris S. Kharasch at Chicago, and my first postdoctoral mentor, Professor George H. Buchi at MIT. Following another stimulating stay as a postdoctoral fellow in the laboratory of the late Professor R. B. Woodward working on the chemistry of natural products, I returned to the University of Chicago in 1956 as an assistant professor in the Institute of Organic Chemistry. After a systematic survey in the literature on the photochemistry of simple carbonyl compounds, I was troubled by the low quantum efficiency of the Norrish Type II Process or the  $\beta$ -cleavage. Acetone was known to undergo the Norrish Type I Process or the  $\alpha$ -cleavage in gas phase with unit quantum efficiency, yet it undergoes photoreaction in solution. Carbonyl compounds containing  $\gamma$ -hydrogen do not undergo the Type I Process in the gas phase in spite of the fact that they have a weaker  $\alpha$ -CO-C bond than acetone, yet they undergo the Type II Process in gas phase or in solution with less than unit quantum efficiency. This paradox suggested the existence of a pathway responsible for the deactivation of photoexcited ketones related to the Type II process. Being a junior faculty with no graduate students at the University of Chicago, my

wife, Dr. Ding-Djung Hwang Yang (PhD, MIT, 1955), and I started to examine the photochemistry of 2-octanone. 2-Octanone was chosen because its  $\beta$ -cleavage product would be a pentene which is the lowest boiling alkene above room temperature. If the reaction were to proceed via a radical process, the pentene formed might be a mixture of isomers. On the other hand, if the reaction were to occur via a more or less concerted process, the pentene formed would be 1-pentene. We also wished to examine whether any higher molecular weight products which might be formed in the reaction yet had not been characterized previously. In order to avoid extensive secondary reactions, the photochemical reaction was interrupted after only <20% of 2-octanone was consumed. The reaction mixture was carefully worked up by fractional distillation first through a Podbielniak column rated at 50 plates. After the pentene fraction was isolated, most of the solvent, isooctane, was removed under reduced pressure using the same column. The distillation was then continued through a spinning band column. The unreacted 2-octanone was recovered, and an alcoholic fraction was isolated. Only a trace of high boiling material was left at the end of the distillation. The whole work-up, which was meticulously and capably performed by my wife, took a period of several days and evenings. The fractional distillation was kept under total reflux when we went home late in the evenings. These were the days when gas chromatography and 40 MHz proton NMR were considered to be modern techniques. A phenylurethane of the alcohol fraction was prepared. Since the phenylurethane isolated had a mp of 78°C, which was much lower than the mp of 2-octyl phenylurethane, 114°C. The compound was then analyzed for its elemental composition. It was found that the alcohol product is an isomer rather than the reduction product of 2-octanone. Since it did not react with Br<sub>2</sub>-CCl<sub>4</sub>, the alcoholic product is likely an alicyclic compound. We also analyzed the pentene fraction by gas chromatography and found it to be exclusively 1-pentene. The NMR of

alcoholic fraction, done by Dr. George V. D. Tiers of 3M, suggested that the product was a cyclobutanol or a mixture of isomers. However, we were unable to resolve the fraction by gas chromatography. Since we were concerned that the cyclobutanol fraction formed might be a mixture of isomers and that the phenylurethane isolated may be the less soluble of the two, the reaction was repeated with 2-pentanone. 1-Methyl-1-cyclobutanol isolated from the reaction was characterized by the comparison of an authentic sample synthesized by the addition of methylmagnesium iodide to cyclobutanone. The discovery of cyclobutanol formation was thus the result of a devoted, dedicated and trustworthy coworker with meticulous laboratory techniques (1).

Following my postdoctoral training in the laboratory of Professor R. B. Woodward, it was my personal aim to achieve a synthesis of a worthy natural product. Our next endeavor was an attempt to functionalize the C-18 methyl of 20-keto steroids as an approach to a partial synthesis of aldosterone (2). This work was met with intense competition from the Swiss group headed by Professor O. Jeger. Although neither group achieved a practical synthesis of aldosterone, our research might have catalyzed the interest of Professor D. H. R. Barton to achieve the elegant partial synthesis of this adrenal cortical hormone by the photochemistry of nitrite (3).

After the untimely death of Professor Kharasch in 1957, I made a decision to focus my research away from radical chemistry which was an area of research strongly identified with my late mentor. Our discovery of a photochemical reaction of an organic functional group, in this case a C=O group, with an unactivated C-H bond away from the excited group led to our work on the phototransannular reaction of medium-sized cycloalkanones (4) and photodeconjugation of  $\alpha,\beta$ -unsaturated ketones (5). Because a former teacher and senior colleague at the University of Chicago, Professor Weldon Brown, was interested in the radiation chemistry of aryl

alkyl ketones (6), I decided to forego the photochemistry of these ketones but to study the photochemistry of o-alkylbenzophenones and o-alkylacetophenones instead. o-Benzylbenzophenone was chosen as the initial substrate as a possible precursor to 1,4-diphenyl-2,3-benzocyclobuten-1-ol. Dr. Carlos Rivas found the substrate was quite photostable. Since o-hydroxybenzophenones were known to be light-protecting agents, Dr. Rivas studied the photocatalyzed H-D exchange of o-alkylbenzophenones via the photoenol intermediate, and I succeeded in trapping of the photoenol intermediate by dimethyl acetylene dicarboxylate (7).

In the 1960's, I was promoted first to a tenured position and subsequently to the rank of professor at the University of Chicago in 1963. My wife took a leave from her work to start our family. Only at that time did I begin to have a group of more than five coworkers (never more than ten). I had the privilege of associating with many excellent collaborators, including postdoctoral associates, Dr. Y. Gaoni, Dr. M. Nussim and Dr. A. Shani from Israel, Dr. M. Jorgenson from Harvard, Dr. R. Coulson from Columbia, and Dr. J. Houser from Penn State, as well as graduate students, Dr. E. Feit, Dr. G. R. Lenz, Dr. L. Gorelic and Dr. D-M. Thap. My research activities in photochemistry at that time included the role of singlet state in the  $\alpha$ -cleavage (8) and the mechanistic study of the Paterno-Buchi Reaction (9), a name coined by me in honor of my mentor, Professor George H. Buchi. We also enjoyed some moderate successes in studying the photochemistry of enamides (10) and in synthesizing alkaloid systems using photochemical methods (11).

Beginning in the late 1960's through the early 1970's, Dr. S. Elliot, a graduate student whose interest in photochemistry began as an undergraduate at Cal Tech, assisted by Dr. B. Kim from Mülheim, showed the role of singlet biradicals in the deactivation of  $^1n,\pi^*$  of alkanones containing  $\gamma$ -hydrogens (12). We also made a fruitful collaborative study with Professor Donald S.

McClure on the relationship between the photochemistry of aromatic ketones and their photophysical properties, which was performed mostly by two outstanding graduate students, Dr. S. L. Murov and Dr. Ruth Dusenbery. We established the substituent effect on the nature of low-lying triplet state of aromatic ketones (13) and discovered the dual phosphorescence of aryl alkyl ketones (14).

This period also represents a transition period in my research away from photochemistry of carbonyl compounds to photochemistry of aromatic compounds. This transition was catalyzed by two findings in our laboratory: one was on the effect of ketone concentration on the quantum efficiency of their photochemical reactions (15), and the other was the inactivation of excited singlet states of organic compounds by unsaturated compounds (16). Dr. William Eisenhardt from Professor Al Padwa's laboratory made significant contributions to these studies. The work was further stimulated by the contributions from Hammond's group (17) as well as Weller's group on exciplexes (18). Assisted by the most capable collaboration of Dr. Jacqueline Libman from Israel and Dr. Kim, we began a series of studies on the photoamination of aromatic compounds (20). Mechanistically, we had the generous assistance of Professor Stuart Rice and the excellent experimental work done by three graduate students, Dr. D. Shold, Dr. J. McVey (21) and Dr. M-H. Hui. Additional contributions were made by Dr. Ronald Yates from Washington, Dr. M. Kimura from Tohoku (22) (now at Okayama) and two other graduate students, Dr. W. Chiang and Dr. Kim.

Beginning in the 1970's and extending into recent years, stimulated by the development of Woodward-Hoffmann Rule and coupled with our interest in the photocycloaddition of 1,3-dienes to arenes, we began a program on the synthesis of energy-rich dimers of aromatic hydrocarbons, using photocycloaddition as a key step in constructing the molecular framework, and dewararenes. The work was carried out by a group of most capable graduate students, Dr. R. V. Carr, D. K. Srinivasachar, Dr.

K-T. Mak, Dr. J. Masnovi, Dr. M-J. Chen, Dr. J. King, Dr. M. G. Horner, Dr. X-Q. Yang, Dr. H. Gan, and Dr. T. Noh, a postdoc from Johns Hopkins, Dr. B. J. Hrnjez, and an undergraduate, Dr. Peter Chen. We synthesized, hemidewaranthracene (23), hemidewarnaphthalene (24), a number of mixed dimers of benzene including those of benzene:anthracene (25) and benzene:naphthalene (26), as well as syn-o,o'-di-benzene (27) and a derivative of p,p'- dibenzene (28). In the meantime, we developed an efficient synthesis of anti-o,o'-dibenzene (29) which led to the synthesis of 1,4-benzene endoperoxide (30). In collaboration with Professor Josef Michl, we delineated the rule of conservation of orbital symmetry in adiabatic photochemical reactions, including both photopericyclic reactions (24) and retrophotocycloadditions (25). We also discovered a new pericyclic chemiluminescence (31), and a photon upconversion in the singlet manifold (29).

In conjunction with our interest in arene:amine exciplexes, we extended our research into photo-induced electron transfer (PET) (32). Our work in this area was carried out by Dr. J. Larson from Washington and Dr. D. Johnson from Minnesota, a visiting scientist from China, Professor H. Shou, two graduate students, Dr. David Minsek and Dr. Jacob Petrich, and an undergraduate, Mr. Rex Gerald, III. The physical measurements in these investigations were made possible through collaboration with my colleagues, Professors G. R. Fleming and D. H. Levy and Dr. M. R. Wasielewski of Argonne. We are particularly proud by their recent contributions in the discovery of CT fluorescence from the intramolecular PET in a rigid system (33), found independently and simultaneously from those by Verhoeven and coworkers (34) and intramolecular PET of a bichromophoric molecule in a supersonic jet (35).

I was always fascinated by natural biological molecules such as proteins and nucleic acids. Dr. F-T. Liu and Dr. L. Gorelic, two graduate students in my laboratory, with the assistance of Dr. R.

Okazaki from Tokyo, studied the photochemistry of nucleotides (36). Dr. Liu showed that CdpT undergoes intramolecular photodimerization to form UdpT which, upon photoreactivation, provides a possible pathway for the C U(T) conversion on the mutagenic effect of light on DNA. Beginning in the mid-1980's, in collaboration with Professor Fleming and the assistance of two graduate students, Dr. Mary Chang and Dr. Bruce Locke, we carried out a series of fluorescence studies on lipoproteins (37) and retinol binding proteins (38). The latter work led us to examine the photochemistry of 4-halotryptophans which marks the reentry of my devoted wife into photochemistry (39). We are actively elaborating this process into a new method of photoaffinity labeling in peptides and proteins. Since we recently succeeded in creating a peptide assembly with an annular space (40), one of our current goals is to use deNovo proteins as rigid frameworks for donor and acceptor groups in PET studies.

Epilogue. Looking back into almost four decades of my work since I first plugged the power supply of a low-pressure Hg-lamp into an AC line in the laboratory of Professor Kharasch in an aborted attempt to initiate a photochemical reaction, followed by a fruitful stay with Professor Buchi in studying the photochemistry of ionones, photochemistry has grown and matured into an exciting field of science. Judging from the many new discoveries in photochemistry made recently in photosynthesis, PET, vision, and nonlinear optical material, including those made by my colleagues Professor G. R. Fleming, Professor D. H. Levy, Professor G. L. Closs and Professor L. Butler, I am convinced that photochemistry is not only alive and well, but will reach new and exciting horizons in the future.

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Sciences, and the National Cancer Institute. In addition to the many coworkers acknowledged in this reflection, I also had the privilege of associating with Professor L. C. Lin of the National Taiwan University, Professor J-D. Ni of the Nankai University, Professor D-Y. Wang of the Institute of Photographic Chemistry in Beijing, and Professor Z-H. Lu of the Guangzhou Institute of Chemistry. Professor Lu is currently the Lieutenant Governor of the booming province of Guangdong in China. I wish to apologize to many other fine coworkers whose names were inadvertently neglected from this article. During my scientific career, I also enjoyed my professional association with Professor Nick Turro of Columbia. His enthusiasm always provides a spark to scientists in the field of photochemistry. Above all, I sincerely believe that my work in photochemistry would not have been possible without the love and devotion of my beautiful wife who is known affectionately to many of us as Ding. She provides me with moral and technical support even in my darkest days. I also take pride in that, when she was not in my laboratory, she raised our three wonderful children, Charles, Julia Ann and Morris. She is a loving and devoted mother to them all. She succeeded in teaching Morris, our youngest and autistic child, to read before he uttered his first meaningful word. It was mainly through her inexhaustible patience and ingenuity in his home education that Morris is currently holding his first job in a bank in the near northside of Chicago. His case is one of the three cases cited by Dr. Cheryl Seifert in her book, "Autism", to provide hope and future to relatives and friends of autistic people.

#### Footnotes:

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#### Footnotes:

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