

On Happy Accidents and Random Encounters in Photochemistry

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My career as a photochemist began precisely on that day in October of 1957 when I joined the laboratory of Professor W. Albert Noyes, Jr. at the University of Rochester as a post-doctoral fellow. I had just arrived from India where I had spent a frustrating year trying to be a research scientist at the Indian Atomic Energy Establishment in Bombay. I had joined the AEE full of ambition to be an independent researcher in radiation chemistry and I had been promised all kinds of facilities and help. It took me less than six months to realize that at the pace things happened at the AEE, I would, at best, only be doing catch-up research to what was going on in the Western World. It took another six months for me to gather the funds that I needed to travel to the U.S. with my wife. This interlude at the AEE is worth mentioning because it gave me the negative feedback that I needed to get the thought of going back to India "for good" out of my system.

October of 1957 saw the launching of Sputnik I and marked the eve of the tremendous growth of funding for scientific research in this country. The state of Organic Photochemistry in that year deserves analysis. There were many *physical chemists* who were actively studying photochemical primary processes in organic compounds in the gas phase. There was Professor Norrish at Cambridge who had already formulated his Types I, II and III reactions in carbonyl compounds. The detailed photochemistry of aliphatic carbonyl compounds and cyclic ketones had been and was actively being studied by many groups at Rochester, Harvard, UCLA, Ohio State, Northwestern, Ottawa, Toronto and Alberta. They never even considered studying any of these molecules in the condensed phase - that was left to the "organic chemists". Noyes had the philosophy that one cannot possibly study the photochemical primary processes in a molecule unless its spectroscopy was well-understood. That could be done only in the gas-phase so that the vibrational and rotational structures could be resolved and solvent effects did not perturb the system. He told me that he had persuaded Professor A.B.F. Duncan to move to Rochester so that the electronic spectrum of a molecule could be studied at the same time as its photochemistry. I do not mean to imply that none of the photochemical research that was going on at that time was being carried out by organic chemists. Actually, Professors Barton, Havinga, Schenck, Schönberg, Kharasch and many others were investigating the photochemical reactions of organic molecules in solution. However, their stated interest was the use of photons in synthesis rather than the study of photochemical primary processes.

When I walked into Noyes's lab., I fully expected to be assigned a problem in photochemistry. But at that time Noyes was unbelievably over-extended in his commitments. He was the Dean of the School of Arts and Sciences and therefore fully responsible for the budget for that school. He was the Editor of both JACS and the Journal of Physical Chemistry. While he had assistant editors for both journals, he felt that he should do his

share of the work. He did not teach but he had a research group of 4-5 graduate students and two post-docs. He was an advisor to UNESCO and to the NBS. He had at least one industrial consulting job which took him to NJ and Texas. His contact with his research group was limited to one group meeting a week on Saturday afternoon. He expected his graduate students to get their research guidance from his post-doctoral fellows and his post-doctoral fellows to be independent researchers. This suited me wonderfully. After a year of bumbling, I hit my stride with a study of the photochemistry of the cyclic ketones. What I discovered was that in addition to the photodecarbonylation reaction, there was a photoisomerization to an -enal. The latter reaction had previously been reported by Kharasch and his co-workers but, as I have pointed out already, Noyes paid no attention to results that were reported from photochemical studies in the condensed phase. In retrospect, the significant result that I did obtain was the demonstration that the partitioning of the excited state of the ketone along the various decomposition pathways was controlled by the vibrational energy that it possessed in its excited state.

Since Noyes had not proposed this problem to me, he refused to take credit for it and let me publish the work under my own exclusive authorship. Noyes had a sense of ethics concerning the publishing of papers that I have never encountered again in anyone. He let me publish not only these papers but 15 of the 16 papers that I authored during my four years with him did not have him as a co-author. Since he provided the research money (including my salary) and the space for my research work, I can only think of his generosity as being an impulse to support some one who enjoyed working in the lab. This aspect of him is somewhat at variance with his general outlook regarding education, politics and research in all of which he was extremely conservative. One of the happiest accidents that I mention in the title of this article was certainly landing in Noyes's lab on that October day in 1957.

I conducted a variety of experiments in Rochester of which the major portion concerned the photochemistry of ketones. When it became clear that the photodecarbonylation reactions of cyclic ketones would be promoted in the gas phase, it was a simple extrapolation to the decarbonylation of bicyclo [3.2.0] heptan-3-one to give bicyclo [2.2.0] hexane and norcamphor to bicyclo [2.1.1] hexane. Norcamphor was commercially available but bicyclo [3.2.0] heptan-3-one had to be synthesized from cyclobutane-1,2-dicarboxylic acid. Once again I was lucky enough to make the friendship of Sheldon Cremer, a graduate student with Professor Stan Tarbell. He synthesized the ketone, supposedly "in his spare time". Of course, Tarbell knew what was going on and he did not stop Sheldon from doing this work. Three decades later, I still find it extraordinary that I could walk into a lab as the post-doctoral fellow of one professor and persuade graduate students of other professors to collaborate with me on problems of my suggestion ! I say "students" because I published another paper that was based on experimental work with a graduate student of Professor W.D. Walters.

It was a time when small-ring chemistry attracted attention and the synthesis of bicyclic compounds which incorporated small rings was being pursued in several leading chemistry departments. Photochemistry seemed particularly suited to the synthesis of the hydrocarbons, a fact that I caught on quickly. The photochemical synthesis of the two bicyclohexanes mentioned above constituted the very first syntheses of these

compounds and the one-step formation of bicyclo[2.1.1]hexane scooped a 13-step "conventional" synthesis that was carried out by a well-known organic chemist. Both features brought me a lot of attention from the organic chemists but not the physical chemists. All through my career, I have been quite puzzled and to some degree confused by the rigid barriers that exist in the Chemistry Departments of the academic world among the various subgroups. I spent much of my time at Rochester with the organic chemists from whom I learnt a great deal about techniques. Don Arnold who is now a Professor at Dalhousie University in Halifax, N.S. was then a graduate student with Professor Marshall Gates. Don and I used to have a private coffee session nearly every morning when he would patiently give me advice. I have already mentioned Sheldon Cremer who is now a Professor at Marquette University. An nmr machine had just been installed at Rochester and was essential to decipher the structures of the bicyclic hydrocarbons and the by-products that I was preparing. So I needed a lot of advice and education !

I stayed in Rochester for four years because I had come into the US on an exchange visitor visa. It required that I leave the country for two years before I could come back in as a permanent resident. In those days before J.F. Kennedy revised the immigration laws, the immigration quota for Asian Indians was so small that there was a tremendous waiting list. Since I had no hope of immigrating, I thought I would stay as a post-doctoral fellow for as long as I could and then "retire"! Noyes grumbled when he had to extend my contract to a third year. When he extended my appointment for a fourth year he flatly said that there would be no more extensions. His idea was that I should go back to India and "help research to grow there". It was useless to argue with him. But, once again, a random encounter led to a happy solution to my problem. I had started to look for a job with the companies that were prospecting among the graduating students. I was repeatedly told that I could not get a job unless I had a resident status. The only way to get around the rule about exchange visitors was to get a congressman to pass a bill which said that so-and-so was essential to U.S. interests and should be allowed to stay. I had found a friend among the trustees of the U. of R. who was quite willing to introduce me to the local congressman (actually a congresswoman at that time) but he thought that it would help to get a letter from Noyes to back up my credentials. Noyes refused to have anything to do with it. Although he never explained to me why he would not support my cause, I can guess (knowing his conservatism) that he could not reconcile supporting the petition of a young, third-world scientist to settle in the U.S. while the UNESCO was campaigning against the "brain drain" from the same countries. Fortunately, the congresswoman made some enquiries and determined that there was no need for even a special bill because a case could be made that since I worked on a research project that was supported by ONR, my work must be essential to this country ! So in 1961, I received my green card.

The next happy accident that determined my career occurred at the ACS meeting in New York in the Fall of 1960. As I was wandering around the lobby of one of the hotels where the meeting was being held, I ran into Harold Friedman who had been a faculty member at the University of Southern California when I was a graduate student and who had been on my thesis committee. He had since joined the IBM Corporation which was about to open a new Research Center in Yorktown Heights, NY. Harold had a charter to recruit a small

group of chemists who would do basic research in those aspects of chemistry which would be of long-term interest to the company. I had been one of the good performers in Harold's murderous thermodynamics course and he was aware of the research I had been turning out at Rochester. He encouraged me to apply to IBM for a job. So in the summer of 1961, I started to work at the IBM T.J. Watson Research center.

Since I now had an assurance that I could stay in one place and carry out a sustained program of research, I was able to chart a plan of what I wanted to do. I had studied the photochemistry of 1,3-butadiene in the gas phase while I was at Rochester in the hope that it might isomerize to cyclobutene in the manner of other cyclic, conjugated 1,3-dienes whose isomerization *in solution* had been demonstrated by others. I was disappointed that there was not even a trace of cyclobutene formed in this reaction. I reasoned that just as with the cyclic ketones, the vibrational energy possessed by the electronically excited state of the 1,3-diene that underwent the photoreaction might determine the course of the reaction. The first olefinic system that I studied at IBM was 1,3,5-cycloheptatriene. This certainly showed the same pattern in that in the gas phase it photoisomerized exclusively to toluene whereas in the condensed phase it gave very little or no toluene and yielded the bicyclic cyclobutene instead. Further study showed that the formation of toluene was not strictly a photochemical process but occurred from the vibrationally excited electronic ground state that is formed by internal conversion from the excited singlet state.

The key to studying conjugated dienes in their singlet excited states in the condensed phase was a source of intense light in the mid-ultraviolet. I had put together just the reactor for this purpose in my last year at Rochester. It worked very well for me for a number of years. On a casual visit to Yale University in 1962, I described this lamp and gave the plans for building it to Gary Griffin who promptly set about commercializing it. When the commercial version which was called the "Rayonet" made its debut, I realized that Gary, instead of being my agent had become the co-developer of the lamp !

The photoisomerization of linear, 1,3-dienes led first to cyclobutenes and then in 1964 to the second known synthesis of bicyclo[1.1.0]butane. The stereochemistry of the ring closure in 2,4-hexadienes was established in 1967. Alongside of this work, the internal photocycloaddition of non-conjugated dienes was also investigated. These systems had to be photosensitized with mercury (3P_1) atoms. A process was developed to run the reaction at an atmosphere of pressure at the boiling point of the reactant. The general unifying thought in all of these studies is "Valence Isomerization". I do not know if this terminology is still in vogue but at that time, I seemed to be the only person who was interested in studying photochemical valence isomerization in molecules which were not loaded with chromophores other than the olefinic groups. The high point of my work as far as I was concerned was an invitation to speak at the International Conference on Valence Isomerization that was organized by Professor Criegee in Karlsruhe in 1967. It was a pleasure to be there to listen to Professor Woodward give a five-hour lecture on "Orbital Symmetry" !

If it was my own choice, I would have expanded my research activities to include related areas such as thermal rearrangements and unimolecular reactions. I even tried to branch off into such areas without letting go of the photochemical research. In order to understand why I did not succeed, I should explain how my

activities fitted into the IBM Research Center. While the Research Center was supposed to be for pioneering research work, it did not mean that everyone was free to do whatever he pleased. Most of the activity was somehow or other related to IBM's commercial interest which was the manufacture of nearly everything that went into a high-speed computer. Photochemistry was an appropriate field because the chips and circuits were all made by the use of photoresists. I actually dabbled in the making of photoresists in 1964 and my management was satisfied that should there be a need for one I could be called upon to make it. I was never told in what areas of photochemistry I could work on but the other side of it was that nobody within the company ever paid any attention to what I did publish. There were other short-comings as well. Both space and labor were at a premium which contrasts sharply with the academic world where these two items are plentiful. I know there was a lot of envy among some of my academic colleagues at the autonomy that I seemed to enjoy at IBM. One of them (from one of the top five universities) actually wrote a letter to the Director of Research at IBM to protest the "unfair competition" that I offered to the poor university scientist who did not have the facilities that I had!

The strangest aspect of life at IBM was the cycle of ups and downs that seemed to have a periodicity of 6-8 years. Either because of the business cycles or a change in the management or the growth of sun-spots, there would be a sudden belt-tightening and a re-examination of the priorities. The first of these occurred in 1964-65. It scared me so much that I tried to move to a University. But by the time I had landed a job at Ohio State University in 1966, IBM was on the upswing again. I was persuaded not to resign my position but merely to take a sabbatical leave for a year and try out the academic world. My group at IBM was left intact and I continued to direct it. IBM even made up the difference in the salary between what I was being paid at Ohio State and what I used to earn at IBM !

I did not last at Ohio State. I quickly learnt that (with apologies to Groucho Marx) the universities that would make me an offer are not those that I would like to join while the Universities that I would like to join are not likely to make me an offer !

There was a maturing process in my research outlook that came out of the interlude at Ohio State University. It would have been sensational if I had gained that insight at a stroke. But it happened only over the next decade. I realized slowly that I was foolish to do the kind of organic photochemistry that the academic researchers did without having the same facilities in terms of students and space. On the other hand, it would make sense to move to areas of research - still within organic photochemistry - where the peculiar advantages that the IBM Research Center offered were well-utilized. There was an extremely active group in laser physics at the Research Center and I was actually a part of it in the organization chart. So I decided to take an interest in building lasers and in using lasers for photochemical reactions. My first attempts were in the area of new compounds for dye lasers. While I had some success, I was not satisfied because a good dye for a laser is one that does not undergo any photochemical transformation ! Then in the late seventies I started a study of organic photochemistry in the far-ultraviolet in the condensed phase. The irradiation cells had to be made of the purest quartz which was no problem since there was a superb glass shop at the Center. IBM was in one of its boom phases - its last one as it turned out - and there was an endless supply of analytical equipment. Best of all, the

excimer laser had become commercially available and I was able acquire one for my use. When I started to use it in the far-UV, I stumbled upon the phenomenon of APD or "Ablative Photodecomposition" (*JACS*, 104, 6784 (1982); *Science*, 234, 559 (1986)). This is the interaction of an ultraviolet laser pulse of a few nanoseconds duration and a fluence of $\sim 0.1 \text{ J/cm}^2$ with the surface of an organic solid which causes an explosive decomposition reaction and leads to ablation and etching. This time I had found an area of organic photochemistry that was novel, was of interest to everyone from applied physicists to chemists to material scientists and to surgeons and had great technological potential. The period from 1978 to the present has been the most stimulating and rewarding time to me in every way. I have had the satisfaction of seeing APD used in many high-tech industries. Corneal surgery based on the phenomenon is an accepted procedure in a dozen countries in the world today including Western Europe, Canada, S. America, Australia, Japan and Korea. The field is still crowded with researchers and I am as deeply in it today as I was in the beginning. APD is principally a reaction from the upper electronic excited states of simple organic chromophores such as esters, imides, etc. The intensity of the reaction is a function of the time in which it occurs which, in turn, is determined by the width of the laser pulse. The commercial excimer laser has a pulse width of a few nanoseconds so that the intensity of the laser beam, when it is focused on the surface of a polymer or tissue, is of the order of 10 megawatt/cm^2 or more. This is a new frontier in organic photochemistry. The reactions that occur under these conditions have hardly been probed but there are indications that some very novel and deep-seated rearrangements take place.

I retired from IBM in 1990 but I am continuing to carry out research on the interactions of UV laser radiation with organic polymers. How I manage to do this is another story which I will recount at some future date ! I will merely say that the excitement that I get out of research today is no less than what I experienced thirty-six years ago when I stepped into Noyes's lab in Rochester !

I would like to conclude this article by acknowledging the deep debt I owe to the many collaborators I have had over the years. I have already mentioned those that helped me during the years in Rochester. At IBM, around 1970, a program of visiting fellowships was started. This brought in some talented young faculty as well as some promising new Ph.D.s. Among the former, I should mention Jan Cornelisse who is now a Professor of Organic Chemistry at Leiden, Clemens von Sonntag who is a senior member and a Professor at the Max-Planck-Institute in Mulheim, Angelo Rossi who was a Professor at the U. of Connecticut and who has now joined IBM, Peter Dyer, Professor of Applied Physics at the University of Hull and Francoise Lahmani from CNRS in Orsay. Among the latter I should make special mention of William J. Leigh who is an Associate Professor at McMaster U., Sylvain Lazare from CNRS at the University of Bordeaux, Emile Sutcliffe who is now with Conraves in Berne and Karen Brown who is a Senior Technical Staff Member at IBM and also is my wife. There were many others who did not actually work at IBM but with whom I collaborated actively and to whom I am equally in debt.