

## Memoirs of a Dilettante

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### PREFACE

*One day, almost a fairy tale's long, long ago, a small six-year-old espied what was revealed as a six-penny chemistry set in the window of a toy shop in Willesden High Street in London, England. It must have elicited a significant response since, to his delight, it appeared as part of the following birthday present. On that same day the small boy-me-was taken on a long-promised visit to the Power Station that hummed incessantly at the bottom of our garden. The purpose behind the large, whirring wheels was explained to me, or at least I assume so, but aside from being frightened by a lack of conviction on my part that the whirring monsters were indeed firmly fixed to the floor, the only thing that remained with me was that, if the whirring were to cease, we would have no electricity-the stuff that made the light come on. Physics lost a student to chemistry.*

*Two other points deserve comment. It is difficult to discuss one's accomplishments without producing a list. I have tried to avoid this, but the reader will see that I failed. Also, the reader may be disconcerted by this rather personal presentation. I make no apology but point the finger at Dr. Ramamurthy (Murthy), who required this of me. In addition, if the reader sometimes gets the feeling that all is not quite as it seems, he may be right....*

It is hard to recall, now, why the aforementioned chemistry set was so enticing. In appearance it was modest: it consisted of several shallow cylindrical cardboard containers, deep blue with yellow printed labels, which contained a small amount of various powders, some litmus paper, two test tubes, and a wire thing to hold one with, a piece of rubber tubing, a short piece of glass tubing, a filter funnel, and a few discs of filter paper. Possibly there were other things-but they made little impression. And there was a very small booklet with experiments....

The containers provided, as I recall, Flowers of Sulphur, Calcium Carbonate (later revealed to be merely common chalk), Iron Powder, Logwood Chips, Iron Sulphate, and Potassium Permanganate (this name only sank in gradually). There was also, a solid acid: it may have been Tannic. With these, one was directed to make a gas, carbon dioxide, ink, turn litmus paper the appropriate colour with the acid and the carbonate. By far the most striking was the permanganate, which gave such a beautiful solution in water. Sulphur, despite its encouraging

yellow colour did not. Flowers, indeed! In fact, sulphur didn't seem to do anything much, and it remained a source of frustration until it was found to burn with an obnoxious smell. In any event the small boy was hooked, and thereafter all presents were required to be in the form that could be transformed into chemical supplies. At first this simplified the problems of birthday presents for those concerned with their purchase, but such relief was misguided. At some stage it was discovered that other, more spectacular, experiments were possible than were described in

the little booklet. And so I followed in the steps of the Chinese. Earnest discussions with a sympathetic (but ill-advised) pharmacist produced the missing ingredient....

My mother suffered patiently through this period when diverse experiments produced the partial dehairing of her son, the hyperventilation of an otherwise useful pair of trousers, and an almost controlled experiment demonstrating the oxidizing powers of permanganate, and the cheerful purple that was freely spread about.

Popular sentiment curtailed further researches which had just resulted in the preparation of nitrogen triiodide and the liquid hydrogen di- and trisulphides, fortunately, in time to terminate prospective researches on the preparation of mercury fulminate, the successful accomplishment of which would most probably have greatly abbreviated the present contribution.

At school I was fortunate to come in contact with one stimulating teacher. He, Mr. Flook, bless him!, who was inspired enough to stay after school to make Pharaoh's Serpents, preparation of which I had failed, and the moral was drawn.

College was another matter. There were few lecturers available after the war-teachers were dragged out of retirement who had sadly lost contact with the living science. The furtherance of chemical growth was largely attributable to a physical chemist, Dr. S.J. Gregg, who represented my first introduction to a live practicing scientist. But, alas, he was a physical chemist and for reasons-emotive or rational-now lost in time, I considered myself a potential "Organic" chemist. Ironically, some 40 years later my work, concerned with photochemistry on surfaces, passed close to his.

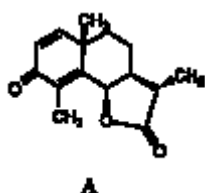
As an organic chemist I was directed into industry by the Ministry of Labour. There I passed two years with each of two companies attempting to learn about steroid and plant hormones. There was also a brief sojourn in the pathology laboratory of University College, and from where the publication obtained exceeded in reprint requests any other publication obtained since .... From the latter, as well as from the industrial laboratory, I was able to work in the evenings at Birkbeck College (M.Sc. 1952) with Dr. W. Rigby. Then, a great wind blew through Birkbeck; a young fire-bird was coming from Imperial College via Harvard. Dr. D.H.R. Barton had arrived.

He obtained a grant for a graduate student. Me. At £240 p.a. Mary, my spouse, was prepared to suffer penury for a little longer. Thankfully, I jumped in (Ph.D. 1954). Amongst Barton's interests at that time, natural products-structural work-figured importantly. This was largely structural determination without the heavy artillery that we have now. This was the Heroic Age of Caryophyllene and the triterpenoids (the amyrins, euphol and lanosterol), and the bitter principles, such as limonin. But Barton was aware that such work must gradually terminate: the

day of the X-ray crystallographer was nigh. In characteristic way he jumped-and landed in another of his fields-and this time I was carried along too. In connection with some triterpenoid work he wished to epimerize a quaternary methyl group, and, by an early steroid analogy, was led to the use of ultraviolet irradiation to induce reaction. Then, as a cheaper model he irradiated the sesquiterpenoid, santonin. A change-not the hoped for one-occurred. By this time we had become aware that a number of irradiation products had been reported from early days and that the proposed structures were improbable on general chemical grounds irrespective of their mode of formation. Further investigation and elucidation of their true structures was accomplished, the groups of Van Tamelen, Buchi, and Cocker also participating. So strange did

the transformations seem, that investigations could not cease. It was the beginning of the Photochemical Renaissance.

The term "Photochemical Renaissance" has a fine ring about it, but the invocation of such a phrase has need of greater justification than that, if it is not to be gathered by Tittivulus [1] and his enthusiastic minions of the Ministry of Verbiage and stacked away into Chaos awaiting the moment when the Word should sweep the land. Certain requirements must be met before this phrase be acceptable in polite society. They can be, and I shall report on the matter at another time, and at another place.



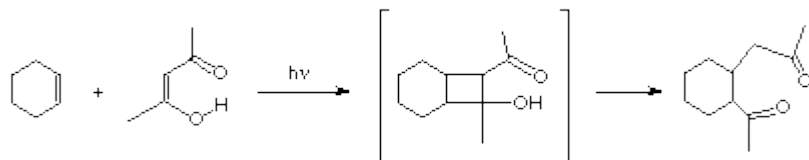
Having decided, on the basis of some molecular acrobatics performed by an exotic sesquiterpenoid, santonin (A), that photochemistry was a Good Thing [2], I determined that, on my migration from Imperial College, via Harvard to London, Ontario in 1959, I would continue its study.

It seemed prudent to try simpler systems first, where understanding might be more easily acquired. So this we did-and demonstrated that serendipity is all very well, but if your mind's eye is closed [3] the resultant darkness can make a fool, and an embarrassed fool at that, of any man.

It was known that irradiation of acetone in the gas phase gave carbon monoxide and methane, where all the energy was being absorbed by the acetone. To achieve the same end in solution required the use of a transparent solvent, and this had been attempted by Bowen in 1913. He used cyclohexane and obtained a product in poor yield, which he did not characterize, but took to be cyclohexyldimethylcarbinol- which, indeed, it was. Excited acetone in solution would abstract hydrogen, and presumably the weaker the C-H bond, the better the hydrogen would be abstracted. So with cyclohexene, the corresponding carbinol was obtained in modest but presentable yield. There were other examples. Heptan-2-one showed that intramolecular abstraction could occur. Hexan-2-one also reacted; the product, which gave a crystalline 3,5-dinitrobenzoate, was presumed to be a pinacol for which there was analogy in the

photochemistry of benzophenone.... Shortly afterwards Yang and Yang revealed that the compound was cyclobutylmethylcarbinol! Ichabod!

The hydrogen abstracting powers of the photo-excited carbonyl were many and various, but did not lead to something breath-taking. How to persuade it to do something else, or if that failed, what could render the H-abstraction product innocuous? We had, as an extension, intended to examine the effect of a second carbonyl in the molecule. With 1,3-diketones, there was already interaction in the ground state-in hydrocarbon solvent it was predominantly enolic .... providing an easily abstracted hydrogen? Did that mean we would just be exercising a new quencher?



But we weren't.

It did not take much effort to identify the product as a 1,5-diketone, revealing itself, and, by cyclization (1962), as a harbinger of its future utility.

This represented the first intermolecular cycloaddition (by a few days!) of a conjugated carbonyl to an isolated ethylenic linkage. If you include esters and anhydrides, the cycloaddition of maleic ester and maleic anhydride was achieved at about this period also, by Barltrop and ourselves.

Some days later Eaton announced the photoaddition of cyclopentenone to cyclopentene (1962). With commendable (1962) insight he remarked... "attention is drawn to the potential synthetic utility of these photoreactions", later to be followed by the further comment: "This prophesy has been amply verified".

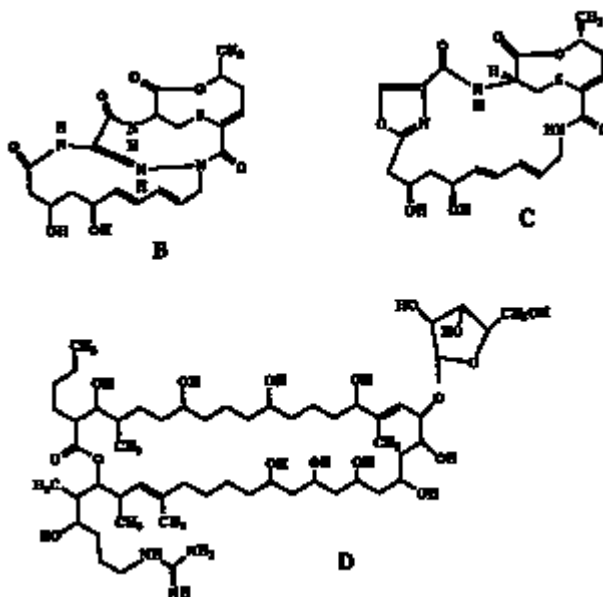
And indeed it has, as indicated by the plethora of reviews-ten in the succeeding 20 years. Of the multitude of syntheses that were reported in the 10 years following the original announcement, i.e. to 1972, and aside from our own contributions: [ $\gamma$ -Tropolone (1964); Stipitonic Acid (1969); b-Himachalene (1969); Methyl Isomarasmate (1970) 1, the following seem to be particularly noteworthy: Caryophyllene (Corey, 1963); -Caryophyllene Alcohol (Corey, 1964); the Cubane system (Eaton, 1964); numerous contributions involving the use of allenes instead of olefins, from the UNB group; Annotinine (1969); Ishwarane (1972).

At about this time Howard Clark, our Leader, a shrewd man, indeed, had the idea that if photochemistry were a Good Thing, it might even be a Very Good Thing, and so suitable for an award from the N.R.C. The University was willing to support the project and to accept the commitments pertaining thereto. We were inspected, interrogated-we being John Brand, just appointed, Patrick Jacobs, Colin Baird, and myself-and generally third-degreed. One of the Committee took me aside and tactfully enquired whether it was true that

I would leave if the funds were not forthcoming. I, to whom the idea had not occurred, equally tactfully, replied that such things were always possible....

We got the award which approximated \$10<sup>6</sup> over three years. Part of the funds were to pay the salaries of the new faculty for three years after which the University would assume responsibility. By this means we were able to attract Bill Ware and Jim Bolton from Minneapolis and Don Arnold from Union Carbide (Tarrytown). Thus was the beginning of the Photochemistry Unit.

Also during the first ten years at Western I indulged my affection, acquired with Derek Barton, for structural work. Carried out with limited spectral data-the game is gone forever-it was an endlessly absorbing pursuit while it lasted. From Helminthosporal, a sesquiterpene which was here when I arrived and the structure of which was determined in collaboration with Elvins Spencer of Agriculture Canada, to Marasmic Acid, to Sativene, to Arctiopicrin, also a C<sub>15</sub>



compound, to Chapparin, a diterpenoid, to Ceanothic and Ceanothenic Acids, and Senegenin, triterpenoids; a predilection for terpenes is obvious. But the two most difficult, Griseoviridin (C) and Primycin (D), the latter with Professor I. Szilagy at Budapest and Professor D.B. MacLean at McMaster University, were not terpenes but mold-produced antibiotics.

But to return to cycloaddition: the first paper on the mechanism, and which contained the germ of much which was to come, was that of Corey. This, modified by our group, has been generally but skeptically accepted up to the present. It would be fair to say that all the workers in the field have reservations about its correctness as a whole, whether, for instance, cyclopentenone and

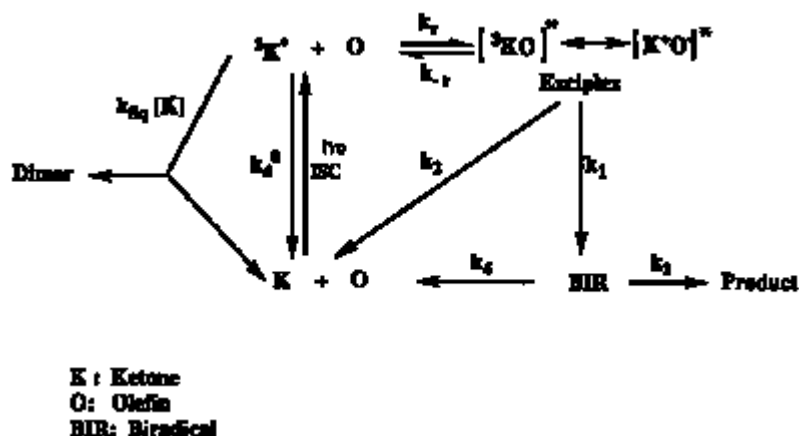
cyclohexenone traverse the same path—we are concerned, essentially, with derivatives of these two enones, because open-chain (if not constrained by hydrogen bonding) and larger than 7-membered cyclic enones decay rapidly by cis-trans isomerization. In the course of time, a number of aspects appear to have been clarified with a fair degree of certainty.

First, it is quite certain that in at least the majority of instances the enone is reacting as the triplet (probably  $^3(n\pi^*)$ ), and that intersystem crossing is efficient with  $\phi = 1$ .

Secondly, it has been shown that cyclopentenone triplets have a sufficiently long lifetime to undergo bimolecular processes of which self-quenching (and dimer formation) are special cases.

Thirdly, there is no doubt that somewhere on the synthetic route there is an inefficiency; in the scheme, this could be  $k_{-1}$ ,  $k_2$  or  $k_4$ , or any combination of these, and reveals itself in a quantum yield of adduct less than unity when extrapolated to infinite concentration of olefin. The presence of a discrete intermediate of some sort we have shown by the obtention, in certain cases, of a negative activation energy of cycloaddition. The intermediacy of a biradical was also,

from the earliest studies, implied by the presence of the concomitantly produced unsaturated products very commonly accompanying the cycloaddition. Where observed, the isomerization in the recovered alkene supported this view.

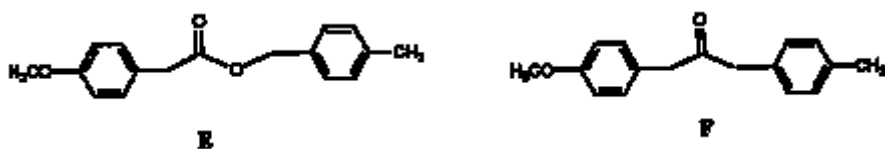


Fourthly, triplet 1,4 biradicals have been observed by photoacoustic calorimetry by Schuster, Caldwell, and their colleagues.

Finally, all ambiguity was resolved, at least as far as simple alkenes and ethyl vinyl ether are concerned when Weedon discovered that  $\text{H}_2\text{Se}$  was an efficient biradical trap in the cyclopentenone system. This has enabled him to show that the rates of alkene attack at the  $\alpha$  and  $\beta$  positions were not significantly different, and, most importantly, the regioselectivity observed was derived not in the selectivity of formation of precursor biradicals, but in the differing extent to which these biradicals revert to starting material as against closure to product.

It occurred to me that the presence of another phase might be useful in directing the stereochemistry in cycloaddition—the main weakness in the synthetic utility of this procedure—in

fact, its effect on photochemistry in general was an interesting question. That photochemistry was possible had already been shown by Leermakers using slurries of silica gel in hydrocarbon medium. With silica gel, at least, the equilibrium between dissolved and adsorbed material we found unsatisfactory, and we had more success with deposition on dry SiO<sub>2</sub>. We were able to show, using the addition of allene and simple alkenes to steroid enones that, as expected, the addition from the more hindered side is favoured. A number of other reactions were found to be accessible when performed on SiO<sub>2</sub>, the first being the Photo-Fries (1978) (where David Avnir rather lost patience with me [4], and on his return to Israel at the Hebrew University, proceeded, via fractals [5], to make a science out of it). He was right: before we had finished our study of the "cage effect" obtained in the photolytic (singlet) decomposition of the ester (E) and the ketone (F) (triplet), Turro published the first of his extensive micellar studies of dibenzyl ketone photolysis. Oh, Well.... Some you win and some you lose....



There was the amide Photo-Fries (1984), and some interesting work on benzoin ether photolysis (1982), and on the movement of cyanopropyl radicals on a silica gel surface correcting some earlier work, and thence to the (belated) generation of radical pairs (1984).

Probably the most interesting work we did in this area was a demonstration that bimolecular processes could be carried out (almost) quantitatively on silica gel. For this we chose the careful study of Cowan on the dimerization of acenaphthylene to give syn and anti isomers. We were able to demonstrate the processes of quenching (energy transfer) and sensitization of this photoaddition, and the dimerization of 9-cyanophenanthrene, the quenching of pyrene fluorescence by 2-halonaphthalenes (part of an extensive study with Bill Ware), and the occurrence of intergranular motion-representative processes from the field of photochemistry. This work represents the opening of the field of organic photochemistry at the solid-liquid interface. In the intervening years surface photochemistry has emerged as a major field in photochemical research: it has already outgrown its infant nappies....

The physical technique of flash thermolysis, sometimes called flash vacuum pyrolysis, has been used for the generation of very reactive molecules. It consists of heating the reactant(s) to a high temperature (600-1000°C) for a short time in nitrogen under reduced pressure. The process being a technique, rather than a specific area of chemistry, has led to a rather scattered distribution of work in the literature. The writer has no rational explanation for entering this field and less for leaving it. It just happened-catalyzed by some work at Union Carbide where, for 10 years, the writer was a consultant to a most exciting group of workers.

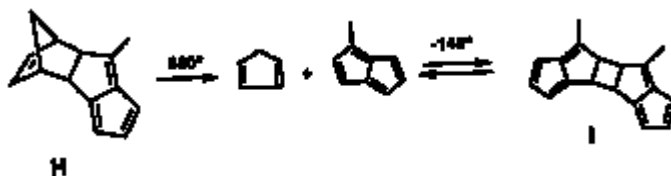
In principle there is nothing new in the technique of flash thermolysis, and indeed, like M. Jourdain in another connection [6], many people have been using it for a long time without knowing it. Not all the work was really exciting but two aspects had attractive points: the synthesis of 1-methylpentalene and the low-temperature isolation and spectroscopy of sulphene in collaboration with James King.

Pentalene (G) was a compound proposed to be aromatic by Sir Robert Robinson



years ago. At the same time, various theoretical approaches were making it clear that the  $8\pi$ -electron system of pentalene should preclude any aromatic stabilization, and that, in fact, it should be anti-aromatic. Under such circumstances ready addition reactions, leading to the more stable fulvene system, were to be expected.

It appeared desirable, therefore, to generate pentalene in the absence of any reactive substrate. The tetracyclic hydrocarbon (H) was synthesized and its

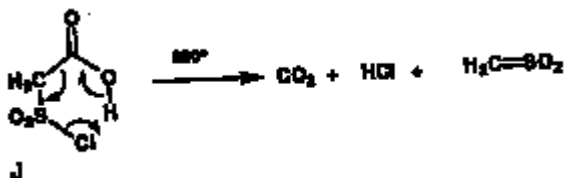


readiness to cleave at the dotted line (reverse Diels-Alder reaction) was signalled by its mass spectrum. This showed its most intense peak at the place expected for 1-methylpentalene, that is (M-66). The product was a mixture of dimers, the main component having the above structure (1) (or geometrical isomer about the cyclobutane ring).

This dimer (1) also could be thermolysed to regenerate the monomer and its spectra could be determined. The product had a greenish colour, but on warming to  $-140^{\circ}\text{C}$  this changed to bright yellow because of the virtually quantitative formation of dimers (all of which contain the fulvene chromophore).

Sulphene,  $\text{CH}_2=\text{SO}_2$ , is the sulphonyl analogue of ketene. Both have long histories as concepts, but whilst the studies on ketene have been very extensive indeed, sulphene was, until comparatively recently, a Cinderella. This was largely, though not entirely, because ketene itself is stable although reactive at room temperature. In the 1960's, interest in sulphene was revived and strong circumstantial evidence was presented which required that sulphene be an intermediate in the making of sulphonic acid derivatives.

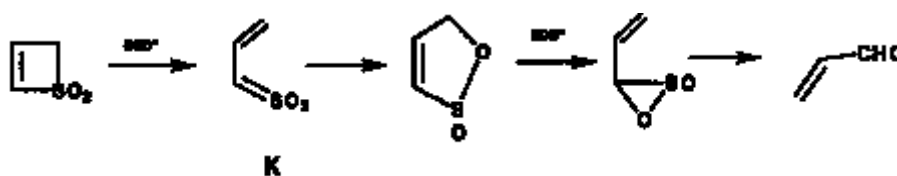
A procedure which could generate sulphene in the gas phase would be free of the complexities arising from the presence of other species in solution. The thermal decomposition of the acid (J) achieved this object.





The sulphene formed showed an appropriate infrared spectrum and, unless otherwise prevented, reacted with the hydrogen chloride generated at the same time to give methanesulphonyl chloride. However, if methanol were introduced after the hot zone then high yields of the ester ( $\text{CH}_3\text{SO}_3\text{Me}$ ) were obtained. More significant, however, was the fact that if deuterium chloride were introduced the acid chloride was again formed, but now largely containing one deuterium atom per molecule. Using the spectroscopic apparatus it was possible to show that sulphene on the plate was transformed, probably to polymer, above  $-120^\circ\text{C}$ .

The pursuit of sulphene led to the discovery of other transformations. It appeared that the generation of sulphene or some derivatives, above  $600^\circ\text{C}$ , resulted in a rearrangement and loss of SO. Generation of vinylsulphene (K) by the electrocyclic reaction shown below gives, at  $600^\circ\text{C}$ , the five-membered sultine.



At  $900^\circ\text{C}$ , the  $\alpha\beta$ -unsaturated aldehyde is obtained, presumably by a similar rearrangement, in high yield.

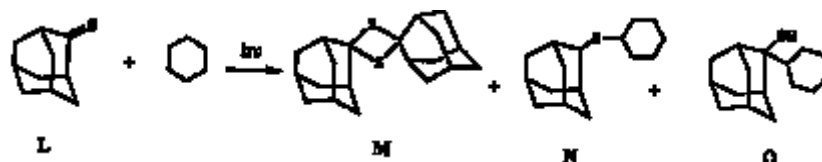
As far as I am aware there was no deep and profound reason for our turning towards thio ketone (thione) photochemistry-or if there were such it blushed modestly and retreated ever deeply into the woolly subconscious. Perhaps it was no more than the desire to work with coloured compounds after a chemical lifetime of colourless compounds. There appeared to be enough clues in the earlier papers (Kaiser and Wulfers, Ohno, Tsuchihashi, Osters, and others) which could, with the clarity of hind-sight, justify the sanctity of the Scientific Method. Since we did not have a systematic approach we ended by accumulating a number of new reactions, some contributions towards mechanism, -and an error in interpretation.

All thiones have bands in the UV/VIS region of  $n,\pi^*$  character, representing contributions from both singlet and triplet transitions. Their importance depends on the temperature, solvent, contributions from  $T_2$  etc. A significant observation, both photochemically and spectroscopically, was the detection of an  $S_1$ - $T_1$  equilibrium. The decay route  $T_1$ - $S_1$ - $S_0$  may be important. At shorter wavelengths there appears in the absorption spectrum a much more intense band termed  $S_2$ . Much of the novel photochemistry and spectroscopy observed upon irradiation of thiones derives from this state (but see below). Irradiation at short wavelength and at longer wavelength may lead to the same or different products by different excitation pathways. Photochemical products derived from the long wavelength  $n,\pi^*$  triplet tend to resemble those derived from the  $n,\pi^*$  state of carbonyl compounds when allowance is made for the differences in

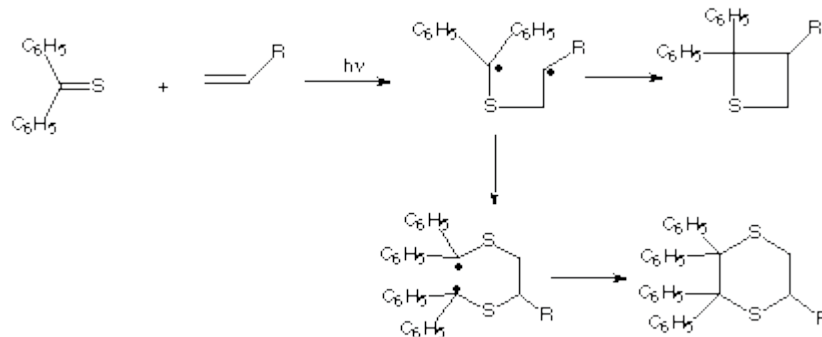
the energy of the states. But when the products are the same, the efficiency of the processes may be very different. Analysis of the thione system is rendered more difficult by the presence, in  $S_2$  processes, of a solvent interaction which enhances radiationless decay, and in the dynamics of

self-quenching reactions from the lowest triplet which, for unhindered triplet thiones, may occur at a diffusion-controlled rate.

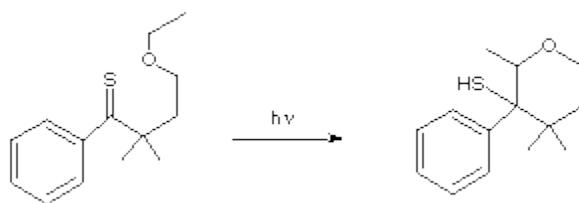
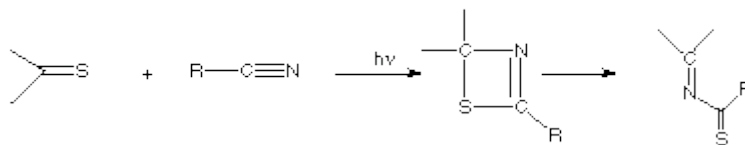
Thus, as an example, when adamantane-1-thione (L) is excited into its strong  $S_0$ - $S_2$  absorption band in hydrocarbon solvent, the 1,3-dithietane dimer (M) is produced together with sulphide (N) and thiol (O). The formation may be rationalized by

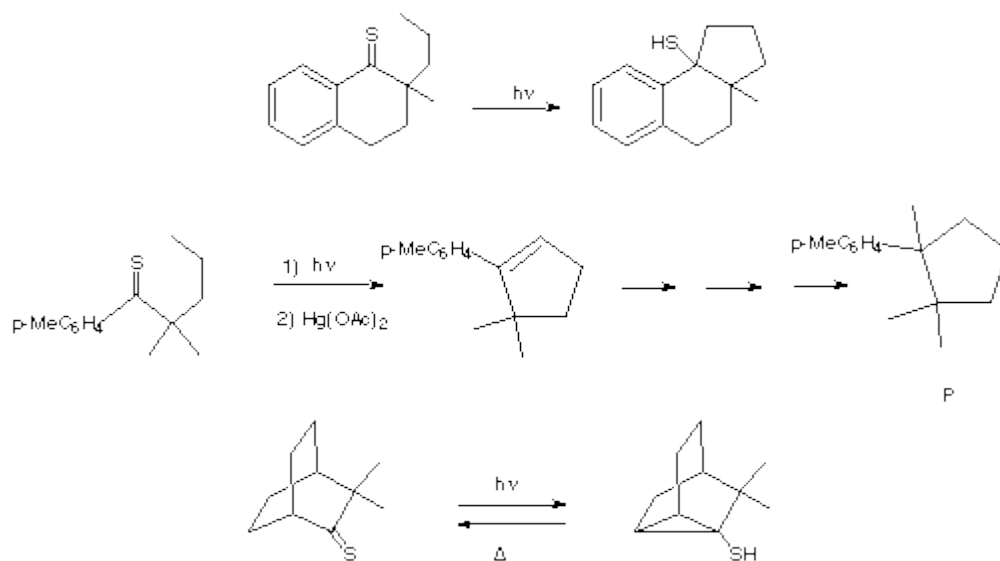


postulating the insertion of the excited thione into the C-H bonds of the solvent. Irradiation at long wavelength (triplet reaction) leads to the formation of the dimer (N) unencumbered by (N) and (O).



Amongst reactions derived from the  $S_2$  state of thiones are those shown below. Included is a short synthesis of the terpenoid  $\pm$  cuparene (P).



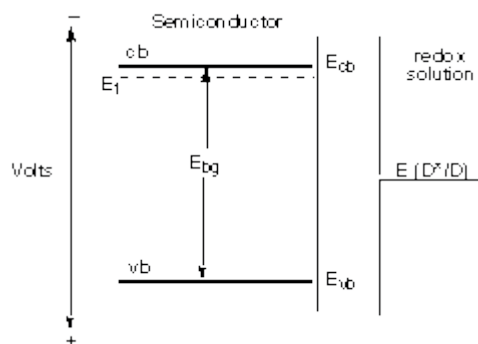


In a kinetic analysis of scavenging of intermediates, such as in  $S_2$ -derived cycloaddition, a species was required with a lifetime of ca. 200 ps which, on this basis, was assigned to the  $S_2$  state of adamantanethione. However, as pointed out by Steer, the  $S_2$ - $S_0$  fluorescence quantum yields are very small even in fluorocarbon solvents. By measuring this, and estimating the radiative decay rate constant, it was shown that the lifetime of the  $S_2$  state was of the order of  $<1$  ps. The mystery of the nature of the 200 ps species is as yet unclear. It may represent, when clarified, the most interesting aspect of thione photochemistry yet observed.

And now to semiconductors, the final stop....

In this pursuit, I was far from the first. But essentially all the earlier work was carried out in homogeneous systems. From work concerned with the adsorption of aromatic molecules on silica and alumina (with Bill Ware), there were instances, e.g., perylene on alumina, where electron transfer occurred, on irradiation, in a heterogeneous system. From there to the use of semiconductors, where the electron transfer is built into the system, was a short step.

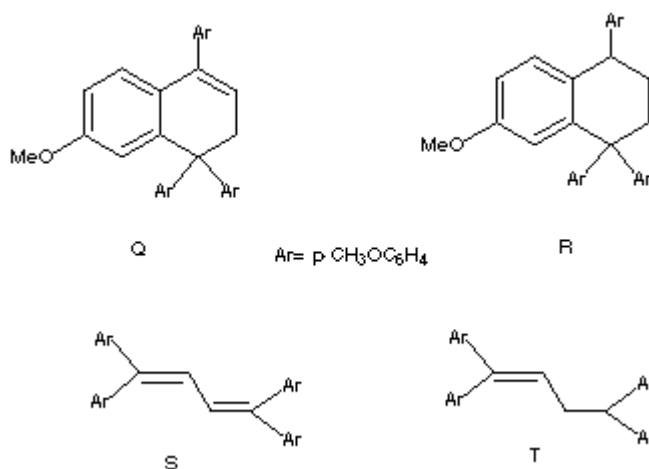
The most commonly-used semiconductors are CdS, ZnO, and  $\text{TiO}_2$ . Their respective valence bands (V vs.SCE) are at 1.6, 2.4, and 2.2; the corresponding conduction bands are at -0.80, -0.80, and -1.20. The "hole" from  $\text{TiO}_2$  the positive center remaining after excitation of the electron from the valence band (bonding orbitals) to the conduction band (anti-bonding orbitals), thus is a powerful oxidant (ca. 3.4 V).



Since we began our investigations, a wide variety of transformations have been reported by us and others. These include geometrical isomerization; the cis-trans isomerization of simple olefins can be induced by hn and CdS or ZnS. The reaction is efficient and the photostationary state is, in most but not all, cases identical with that produced in the thermodynamic equilibrium. Two mechanisms are, at present, available—the route via a radical cation (in which it is believed possible for *inversion* to take place) or isomerization via an adduct of a sulphur radical species and the olefin. The choice may depend on the oxidation potential.

Similarly, the cis-trans isomerization of 1,2-diarylcyclopropanes can also be induced by irradiated CdS. The equilibrium composition of 1,2-di-*p*-anisylcyclopropane is essentially all trans, the composition expected for a thermodynamic equilibrium.

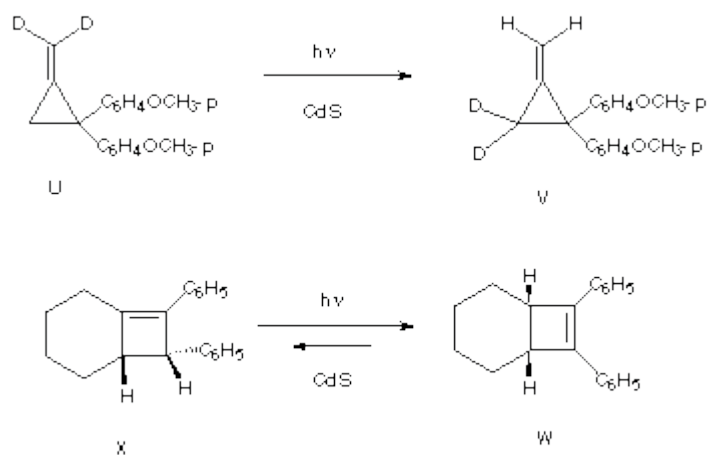
A variety of **v alence isomerizations** have been achieved including those of hexamethyl(Dewar)benzene to hexamethylbenzene and quadricyclane to norbornadiene. In the former, we have descended into the mire of kinetics with dubious results. Examples of **dimerization** include the photoinduced [2+2]cyclodimerization of phenyl vinyl ether to the trans- and cis-cyclobutane with ZnO or CdS. CdS-mediated dimerization of N-vinylcarbazole led exclusively to the trans-isomer. CdS-mediated dimerization of 1,1-di-*p*-anisylethylene gave the [4+2]cyclodimers (Q) and (R) and open-chain dimers (S) and (T) depending on the nature of the CdS sample; the ratio of cyclized to open-chain dimers was 1:3-6. This very interesting observation has not yet been rationalized.



The cycloreversion of dianthracene to anthracene can be induced by CdS. A cation radical mechanism is involved because, for instance, p-dimethoxybenzene ( $E_{1/2} = 1.35$  V vs. SCE) quenches the reaction by electron transfer.

An example of a **sigmatropic rearrangement** is the conversion, in the presence of CdS or TiO<sub>2</sub>, of 2,2-bis(p-methoxyphenyl)-1-dideuteriomethylene cyclopropane (U) to 2,2-bis(p-methoxyphenyl)-3,3-dideuterio-1-methylenecyclopropane (V). The suprafacial [1,3]sigmatropic

hydrogen shift (CdS) we reported for the diphenylcyclobutene (W) took place via a cation radical. This is noteworthy since the suprafacial pathway is symmetry-forbidden in closed-shell systems. The reaction is inefficient, perhaps because of a fast back reaction; the irradiation of (X) affords (W).



Various workers have investigated a wide range of the oxidative and reductive reactions of semiconductors. In particular, TiO<sub>2</sub> has received a great deal of attention because of its indiscriminate oxidizing ability used for the purification of contaminated water and air. (Shall photochemistry redeem the sins of the chemists?...)

#### ENVOI

*There remains for me to thank many colleagues who participated in this endeavour. First, the many collaborators who laboured long and hard and who provided the intellectual stimulus for our work. Their serious efforts to activate a naturally lethargic spirit were almost successful. Secondly, I would like to thank the secretarial assistance at UW, in particular, Sandy McCaw. I would also like to thank the librarians (Diana Edwards and John Lutman) for their strenuous efforts to obtain remotely-accessible exotica. Finally-my gratitude to M.Y., P.M., and A.G. for putting up with my absence.*

*There remain two people of particular importance. First is Dr. V. Ramamurthy, Editor, IAPS Newsletter, Photochemical Society of America, who, as mentioned earlier, suggested that this article be written and stressed the personal aspects [7]. He accepted editorial responsibility well beyond the norm when we were confronted by serious difficulties [8]. Without him, this article would never have been started.*

*Second is Dr. M. Gordon, who provided generous assistance when I was faced with the difficulties referred to above. But for her massive help as secretary, librarian, historian and, most*

*of all, as a fortifying blast, the article certainly would never have been finished. (Needless to say, any errors are my responsibility entirely.)*

*And here I stop. Work initiated some 30 years ago is contained in a single filing cabinet. it is considered polite to ask such bald-headed pates to deliver nourishing morsels of wisdom [9] to the advancing ranks. Alas, I find myself barren of such verbiage.*

*I shall go and sit and watch the trains go by...*

#### **Notes**

[1] M. Ayrton, *Tittivulus or The Verbiage Collector*, Max Reinhardt, London, 1953.

[2] W.C. Sellar and R.J. Yeatman, *1066 and All That*, Methuen, London, 1931.

[3] *Dans les champs de l'observation, l'hasard ne favorise que les esprits*

*préparés. Louis Pasteur*

[4] *He that can have Patience can have what he will. Ben Franklin*

[5] B.B. Mandelbrot, *The Fractal Geometry of Nature*, W.H. Freeman, San Francisco, 1982.

[6] Molière, *Le Bourgeois Gentilhomme*, Acte 11, Scène IV.

[7] *'Tis pleasant, sure, to see one's name in print;*

*A book's a book, although there's nothing in't. George Gordon (Lord) Byron*

[8] *If only I could break my leg, what a lot of scientific work I could do.*

*T.H. Huxley*

[9] *I hate quotations. Tell me what you know. Ralph Waldo Emerson*