DIRADICALS, SURFACES AND MOLECULAR PHOTOCHEMISTRY

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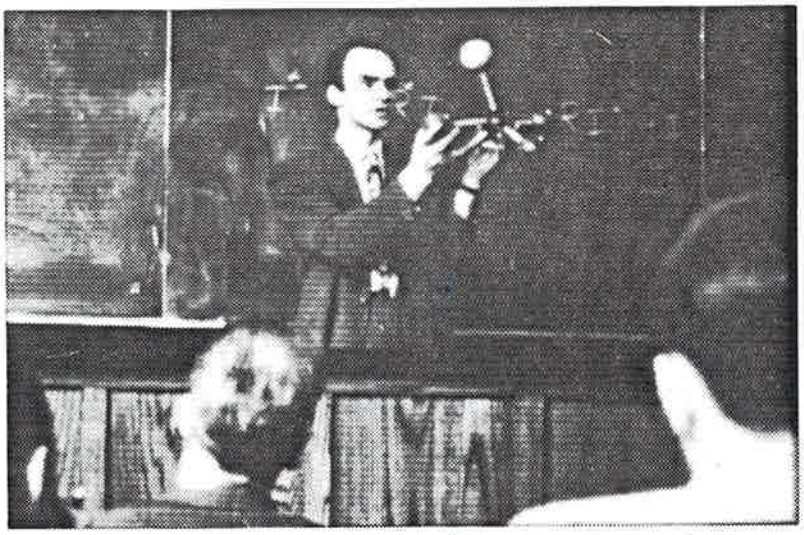
During July 12-18, 1970 the Third IUPAC Symposium on Photochemistry was held at St. Moritz, Switzerland. Although I did not attend that meeting, I learned of an exciting discussion or debate on the question "What is a diradical?" by two of the dominant figures in the field, George Hammond and Lionel Salem. There is a written record of the discussion that is reproduced in this volume. Although I was not present at the Hammond/Salem debate, it turned out to have a major impact on my career and my intellectual perceptions of how photochemical reactions occur. This was the result of my interactions with Lionel Salem and Bill Dauben during the 1970's that resulted from the "Diradical Debate".

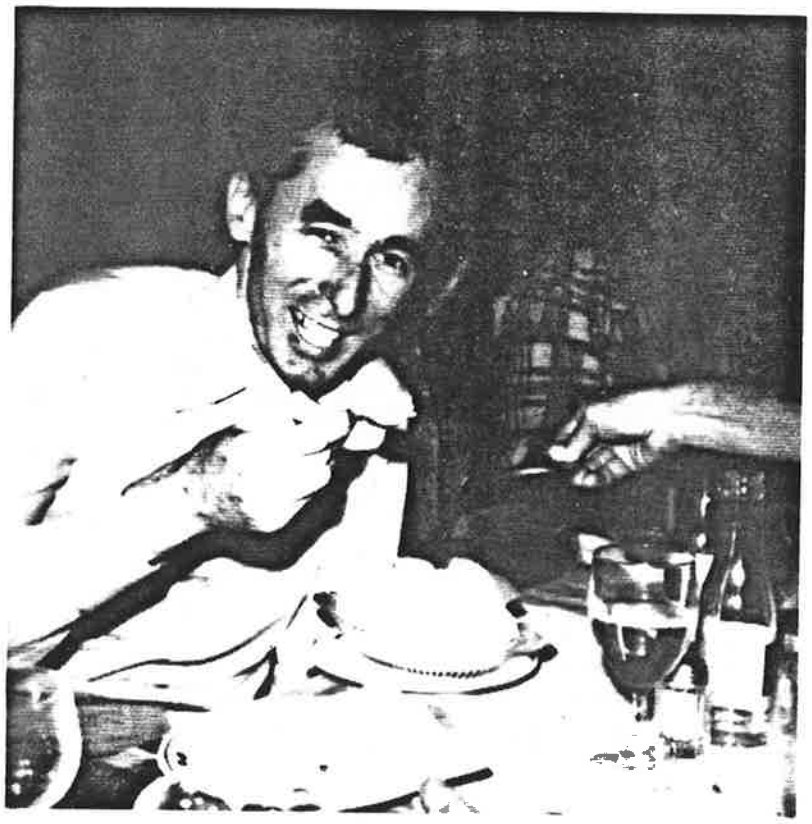


George Hammond lecturing on nucleophilic substitution reaction.

At the Fourth IUPAC Symposium on Photochemistry, held in Baden-Baden, Germany during July 16-22, 1972, the lecture hall was very high tech and the audience sat two to a desk with a shared microphone available for asking questions after each lecture. I sat next to Lionel on a number of occasions and during the "organic lectures", he would needle me about the discipline that existed in the writing of organic photochemistry reaction mechanisms. He felt that "anything goes" was the rule used to explain the seemingly endless variety of reaction products that were being discovered in those early days of many exciting discoveries in organic photochemistry. During the Symposium, Lionel presented an outstanding lecture on diradicals (*Pure Applied Chemistry*, **33**, 313, **1973**). At the very end of the conference, Lionel, Bill Dauben and I had a beer at the hotel as we were waiting for transportation to the airport. Lionel again began needling about the lack of coherence in the mechanisms and theory of organic photochemistry. Bill and I retorted with, "Lionel, you're just the person to do something about this deplorable state of affairs!" Lionel retorted by challenging us to join him in a venture to seek the framework of a coherent theory. German beer, with its ability to produce gemuethlichkeit, had produced the atmosphere for a partnership that was to be exceedingly stimulating and informative for all three of us. The results of these discussions and correspondence led to a short note written by Lionel and entitled "Surface Crossings in Photochemistry" (*J. Chim. Phys.*, 694, **1973**) in which he pointed out the use of a symmetry plane to classify orbitals and to serve as the basis for energy surface diagrams.

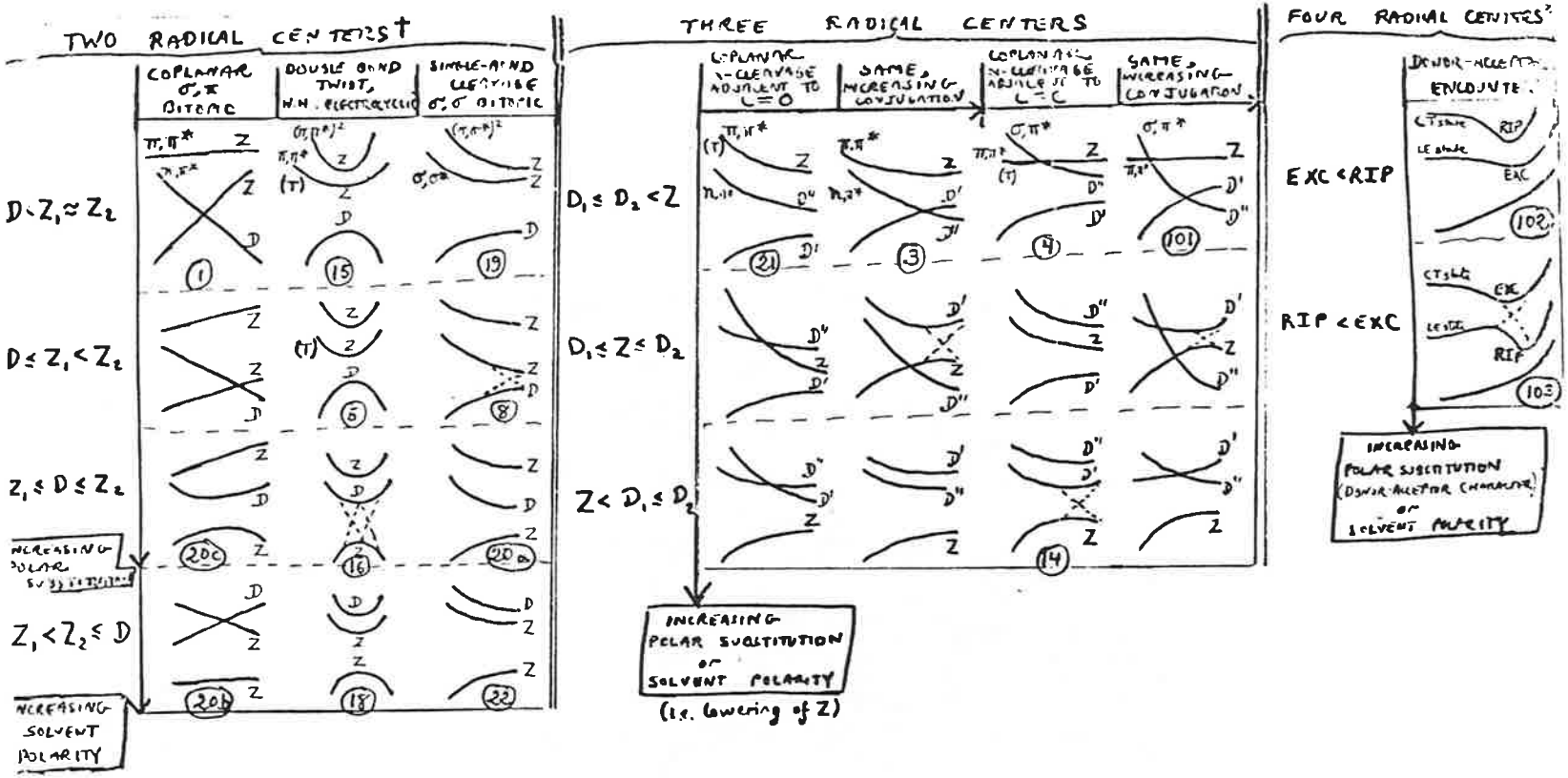
During the week of August 6-10, 1973, at the Gordon Conference on Organic Photochemistry at Tilton, New Hampshire, Lionel Salem presented another outstanding lecture on diradicals emphasizing the possibilities of excited state reactions being either heterolytic or homolytic but in the context of energy surfaces. Lionel and I had an opportunity to follow up on our discussions of the theory of photoreactions, but Bill Dauben was

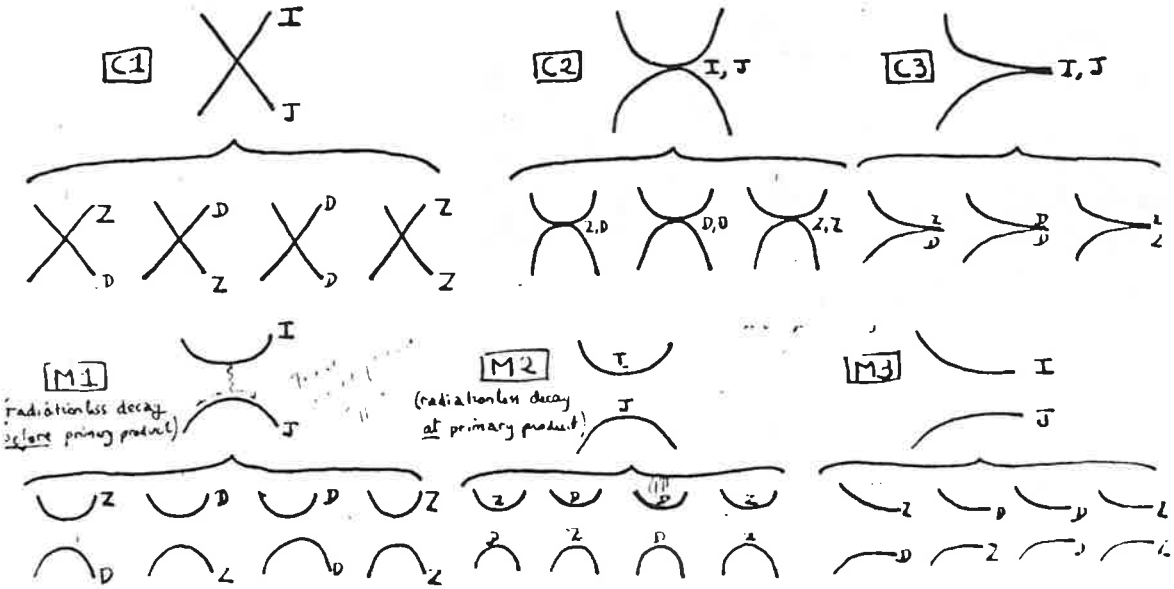
unfortunately not able to make the Conference. Nevertheless, it was determined that the three of us must move forward with the sacred pledge we had made over a beer in Baden-Baden. One afternoon, while he had a strawberry shortcake and I had a hot fudge sundae, at an ice cream shop in greater downtown Tilton, Lionel wondered if some simple rules, employing the ideas of surface correlations, could be used to examine organic photoreactions, especially reactions of the ubiquious n, π^* excited states. This seemed like a very exciting possibility to me. Perhaps in the same way that organic chemists write lines and connections so profitably to describe molecules, an extension of the idea of connections could be created to describe reaction steps. For example, we speculated that there may be a relatively small number of a priori possibilities based on the simple notions of "perfect crossing", "perfect avoiding" and "contact" of energy surfaces. Bill was informed of this progress and it was determined that we would meet with Lionel in Orsay, just before the Vth IUPAC, which was to be held in Enschede, The Netherlands during July 21-27, 1974.



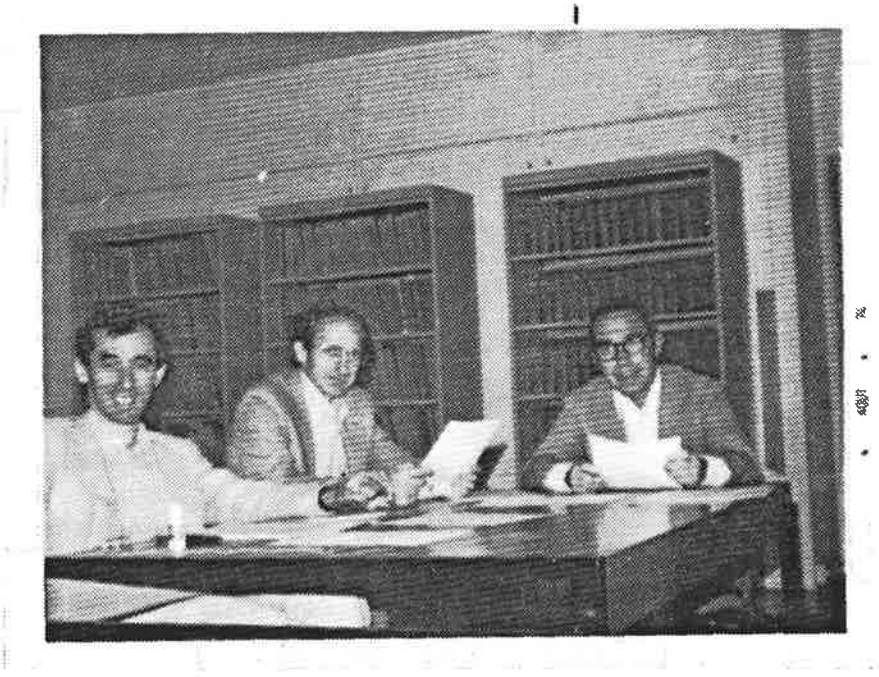
Lionel Salem with strawberry shortcake.

Before that meeting, there would be one opportunity for me to meet with Lionel during the Fall of 1973 and to work with him on the preliminary aspects of the theory. By the time I arrived in Paris, he had already discovered over 20 families of surface types, which depended on the number of radical centers. This was very exciting, but the simplicity I had hoped for was not apparent. We communicated the results to Bill Dauben and then prepared for our meeting in Orsay.


TWO RADICAL CENTERS†
COPLANAR σ,π BITOPIC
DOUBLE BOND TWIST, NN. ELECTROCYCLIC
SINGLE-AND CLEAVAGE σ,σ BITOPIC
D < Z1 ≈ Z2
D ≤ Z1 < Z2
Z1 ≤ D ≤ Z2
Z1 < Z2 ≤ D
INCREASING SOLAR SUBSTITUTION
INCREASING SOLVENT POLARITY
THREE RADICAL CENTERS
COPLANAR σ-CLEAVAGE ADJACENT TO C=O
SAME, INCREASING CONJUGATION
COPLANAR σ-CLEAVAGE ADJACENT TO C=C
SAME, INCREASING CONJUGATION
D1 ≤ D2 < Z
D1 ≤ Z ≤ D2
Z < D1 ≤ D2
INCREASING POLAR SUBSTITUTION OF SOLVENT POLARITY
(i.e. lowering of Z)
FOUR RADICAL CENTERS†
DONOR-ACCEPTOR ENCLOUNTER
EXC < RIP
RIP < EXC
INCREASING POLAR SUBSTITUTION (DONOR-ACCEPTOR CHARACTER) OR SOLVENT POLARITY


C1
C2
C3
I, J
M1
(radiationless decay before primary product)
M2
(radiationless decay at primary product)
M3

When Bill and I met Lionel in Orsay in the summer of 1974, he had prepared a 38 page draft which was to serve as a basis for a manuscript to be submitted to *Accounts of Chemical Research*. The first sentence of the draft was "Classification has been the dream of chemists for centuries." This sentence was one of the few things left unchanged in the final paper. During three weeks of exhilarating daily meetings and brainstorming and some fabulous French meals, we came up with the classification of photochemical reactions that appeared in the Accounts article (*Account Chem. Research*, **1974**).



Lionel Salem, Nick Turro and Bill Dauben in Orsay preparing the Accounts article.

Lionel Salem provided the driving force in the development of this surface theory of photoreactions. We all felt in the end that we had each contributed in some significant manner to an enterprise that was worth the effort because of the pure delight of joining of our imaginations. Both Bill and I were extremely fortunate to be part of a very special intellectual and scientific adventure and collaboration that comes all too infrequently inspite of good intentions.