An Overview of Phenomena and Generalizations Introduced by the Zimmerman Group

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I. Introduction - So often in planning research or in writing completed research I have found that searching for some relevant references has necessitated more effort than should be necessary. Thus I thought it would be useful to list some key references to our own past research. In addition, I thought it would be interesting to look back over the past decades and see what we have accomplished here. This promised to alert me to what was unfinished and to provide guidelines for future efforts.

I've organized this by topic with a brief statement of the type reaction, phenomenon, or generalization and then listed some key references.

II. PHENOMENA, GENERALIZATIONS AND THEORETICAL CONCEPTS

A. n-Orbital vs π-system Reactivity

It was in 1961 that the author first reported that photochemical reactivity of carbonyl compounds fell into two categories. The first arose from the singly occupied p_y (or "n") oxygen orbital hydrogen abstracting or attacking the π system of another molecule. The second derived from the π-system having one extra electron and thus being similar to a radical-anion.

One example of the π-system reactivity we presented was the β-β-bonding of 2,5-cyclohexadienones due to the enhanced β-β bond order in the n-π^* excited state. Both the mechanism and the stereochemistry of the Santonin to Lumisantonin rearrangement were reported as well as the conversion to isophotosantonic lactone in acidic medium. In these papers the 4,4-diphenylcyclohexadienone rearrangement was included, and the rearrangements was given the designation of "Type A". Another example was α-expulsion of anionic and odd-electron species in the same way that the carbonyl radical anion, which also has an antibonding electron, would do this.

For n-π^* p_y orbital reactivity, one example was the Norrish Type I disengagement of an alkyl radical by overlap of the coplanar sigma bond with the electron deficient p_y orbital. Another was hydrogen abstraction of a γ-hydrogen in the Norrish Type II reaction including the Yang cyclobutanol formation. Still another was the mechanism of oxetane formation by an oxygen p_y orbital attack on a double bond. The proclivity of the p_y orbital of the n-π^* state to hydrogen abstract was simultaneously reported by Mike Kasha.

References:

28. "A Mechanistic Approach to Organic Photochemistry," H. E. Zimmerman, Seventeenth National Organic Symposium of the Amer. Chem. Soc., Bloomington, Indiana, 1961, pgs. 31-41.

30. "Mechanistic Organic Photochemistry. IV. Photochemical Rearrangements of 4,4-Diphenylcyclohexadienone," H. E. Zimmerman and D. I. Schuster, *J. Amer. Chem. Soc.*, 1962, 84, 4527-4540.

33. "Mechanistic Organic Photochemistry.," H. E. Zimmerman, *Tetrahedron*, 1963, Suppl. 2, 19, 393-401.

35. "A New Approach to Mechanistic Organic Photochemistry," H. E. Zimmerman, in "Advances in Photochemistry," Editors: A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience, Vol. 1, 183-208, **1963**.

See also Ref. 53 and other reviews listed below.

In 1964 we reported the triplet multiplicity of the Type A rearrangement and also that the triplet rearrangement rate was so rapid that quenching by 0.1 *M* naphthalene did not occur. The n-π nature of the triplet was established by the vibrational structure of the phosphorescence.

38. "Mechanistic Organic Photochemistry. VIII. Identification of the n-π* Triplet in Rearrangement of 4,4-Diphenylcyclohexadienone," H. E. Zimmerman and J. S. Swenton, *J. Amer. Chem. Soc.*, **1964**, *86*, 1436-1437.

In order to more rigorously characterize the n-π* triplet of cyclohexadienones, we compared the phosphorescence emission of a series of dienones with C-4 groups of differing electronegativity. This revealed that with increasingly more effective electron-withdrawing groups near the β-carbon, the triplet energy was lowered. This led to the conclusion that the β-carbons of the dienones are electron rich in the n-π* triplet.

In the same study configuration-interaction calculations revealed that the n-π* triplet of the cyclohexadienones has a markedly enhanced β-β-bond order, in agreement with the experimental bridging observed on photolysis.

64. "Organic Photochemistry. XXVII. Electronically Excited State Structures," H. E. Zimmerman, R. W. Binkley, J. J. McCullough, and G. A. Zimmerman, *J. Amer. Chem. Soc.*, **1967**, *89*, 6589-6595.

See also Ref. 193.

B. Factors Controlling Organic Photochemical Reactivity

The impression one had in 1960 was that photochemical reactions were virtually random, a mere consequence of excitation energy. It was in 1961 and the few years following that the present author suggested that excited state reactions were selective and that electronic excitation energy was not immediately available to indiscriminately break bonds. It was stated that excited state molecules follow energy valleys and avoid energy maxima in a way reminiscent of ground state species. For a goodly fraction of photochemical reactions, including complex rearrangements, this view is still valid. It was noted that in many photochemical reactions, "rebonding" of the excited state occurred first, followed by radiationless decay (it was termed "electron demotion" then), and finally, any subsequent transformation on the ground state surface.

References:

[Refs 28, 30, 33, 35, 53, 193]

The role of excited state bond order was presented as one means of predicting the tendency of an excited state to molecularly rearrange in some fashion. In the case of the Type A Rearrangement this could be easily seen resulting from electron excitation from a p_y (or "n") orbital with no β-β bond order to the first antibonding MO which is β-β bonding. The idea was also presented at the first IUPAC Photochemistry Symposium held in Strassbourg in 1964.

43. "A Report on Recent Photochemical Investigations," H. E. Zimmerman, Pure and Appl. Chem., 1964, 9, 493-498.

Also Ref 38 above.

C. Allowedness - Forbiddeness, Radiationless Decay, and Conical Intersections

In 1961 the first organic correlation diagram was described [Ref 25], for some ground state reactions. In 1966, the year following the Woodward-Hoffmann papers, an alternative method of predicting allowedness-forbiddeness was advanced based on the idea of cyclic orbital arrays having either an even (for Hückel systems) or and odd (for Möbius) number of plus-minus overlaps in the basis set of orbitals. Where there was a HOMO-LUMO degeneracy along the reaction coordinate, it was noted that the reaction would be excited state allowed and that radiationless decay would be optimized at that point due to degeneracy of the excited and ground states. More generally, degeneracies along the reaction coordinate were obtained by a simple Möbius-Hückel mnemonic and shown to correspond to MO crossings.

A discussion of the nature of conical intersections was given in a paper on "MO Following" in 1972. Perhaps the most exciting results arose from the finding that singlet diradicals could give different rearrangements depending on their mode of generation and, more exactly, on their electronic state (S_1 vs S_0). For example, ground state cyclopropyldicarbinyl diradicals undergo a "Grob-like" 1,4-(2,3) fragmentation to give 1,4-pentadienes while the S_1 counterparts undergo a bicycle rearrangement to afford a vinylcyclopropane.

25. "Carbanion Rearrangements. II," H. E. Zimmerman and A. Zweig, J. Amer. Chem. Soc., 1961, 83, 1196-1213.

47. "On Molecular Orbital Correlation Diagrams, the Occurrence of Möbius Systems in Cyclization Reactions, and Factors Controlling Ground and Excited State Reactions. I," H. E. Zimmerman, J. Amer. Chem. Soc., 1966, 88, 1564-1565.

48. "On Molecular Orbital Correlation Diagrams, Möbius Systems, and Factors Controlling Ground and Excited State Reactions. II," H. E. Zimmerman, J. Amer. Chem. Soc., 1966, 88, 1566-1567.

106. "The Möbius-Hückel Concept in Organic Chemistry. Application to Organic Molecules and Reactions," H. E. Zimmerman, Accounts of Chem. Res., 1971, 4, 272-280.

118. "Multiplicity Control of Reaction Pathways. Mechanistic and Exploratory Organic Photochemistry. LXXIII," H. E. Zimmerman and G. A. Epling, J. Amer. Chem. Soc., 1972, 94, 8749-8761.

119. "MO Following. The Molecular Orbital Counterpart of Electron Pushing," H. E. Zimmerman, Accounts of Chem. Res., 1972, 5, 393-401.

177. "The Bicycle Rearrangement: Relationship to the Di-π-Methane Rearrangement and Control by Bifunnel Distortion. Mechanistic and

Exploratory Organic Photochemistry," H. E. Zimmerman and R. E. Factor, J. Amer. Chem. Soc., 1980, 102, 3538-3548.

188. "Topics in Photochemistry," H. E. Zimmerman, Topics in Current Chemistry, 1982, 100, 45-73, Springer-Verlag, Heidelberg-New York.

Note also Refs [43, 193, 197]

190. "Möbius and Hückel Systems in the SCF and CI Approximations," H. E. Zimmerman, Tetrahedron, 1982, 38, 753-758.

208. "A Graph Theoretical Approach to Möbius Systems in Organic Chemistry", Milan Randic and Howard E. Zimmerman, "International Journal of Quantum Chemistry," Symposium No. 20, 1986, 185-201.

D. The Role of the 2nd π-Bond in Type-A Rearrangements

Rearrangements in enones lacking γ-phenyl substitution as well as the second π-bond of dienones, had triplets which rearranged at a rate 10^4 more slowly than the dienones. Thus it was apparent that the Type-A rearrangement of 2,5-cyclohexadienones utilized the second double bond in the rearrangment mechanism.

Ref 49.

E. Singlet and Triplet Energy Transfer Through Organic Rod-like Molecules

Our first report on the energy transfer through rigid, rod-like molecules was in 1971 when we noted that both singlet and triplet energy transfer occurred between π-moieties located at the two bridgeheads of a bicyclo[2.2.2]hexane system. The analysis was based on extended Hückel calculations which suggested a delocalized "electron hole" distributed through the alicyclic portion of the molecule.

Our subsequent 1980 report dealt with determination of the kinetics of singlet energy transfer through rod-like molecules composed of the bicyclooctane units fused bridgehead to bridgehead. With a naphthyl group at one bridgehead and an acetyl or benzoyl at the other, singlet transfer was shown to proceed through the rod with a rate which was a function of the rod length and the exothermicity of the singlet excitation transfer. The quantum mechanics of singlet sigma-bond exciton transfer was treated in a fashion analogous to the Dexter triplet theory. The dependence of the singlet energy transfer on rod length indicated a through-bond rather than through-space mechanism.

102. "Electron and Energy Transfer Between Bicyclo[3.1.0]octane Bridgehead Moieties," H. E. Zimmerman and R. D. McKelvey,, J. Amer. Chem. Soc., 1971, 93, 3638-3645.

180. "Rod-like Organic Molecules; Energy Transfer Studies Using Single Photon Counting," H. E. Zimmerman, T. D. Goldman, T. K. Hirzel and S. P. Schmidt, J. Org. Chem., 1980, 45, 3933-3951.

226. "Molecular Rods; Synthesis and Properties", Zimmerman, H. E.; Meinhardt, M. B. J. Org. Chem., 1992, 57, 5484-5492.

F. The Free Rotor Effect - One Mode of Dissipation of Triplet Excitation with Intersystem Crossing

The "Free Rotor Effect" was described as a general mode of energy dissipation in organic photochemistry. This is the rotational analogue of Eyring's "Loose Bolt Effect." The basic idea was that by π-bond rotation there was an approach or intersection of excited and ground state surfaces which enhanced the probability of internal conversion and intersystem crossing.

Refs [179 above and the following].

89. "Organic Photochemistry. LV. Geometric Control of Multiplicity in the Di-π-Methane Rearrangement," H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **1970**, *92*, 1411-1412.

88. "Organic Photochemistry. LIV. Concertedness, Stereochemistry, and Energy Dissipation in the Di-π-Methane Rearrangement. Source of Singlet-Triplet Reactivity Differences," H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **1970**, *92*, 1409-1411.

97. "Stereochemical Aspects of the Di-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry. LVII," H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **1970**, *92*, 6267-6271.

96. "Unsymmetrical Substition and the Direction of the Di-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry. LVI," H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **1970**, *92*, 6259-6267.

97. "Stereochemical Aspects pf the Di-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry. LVII," H. E. Zimmerman and A. C. Pratt, *J. Amer. Chem. Soc.*, **1970**, *92*, 6267-6271.

141. "A Photochemical Rearrangement Without Light. Dioxetane Effected Photochemistry by Direct Intramolecular Excitation," H. E. Zimmerman and G. E. Keck, *J. Amer. Chem. Soc.*, **1975**, *97*, 3527-3528.

142. "Mechanisms of Electron Demotion. Direct Measurement of Internal Conversion and Intersystem Crossing Rates. Mechanistic Organic Photochemistry," H. E. Zimmerman, K. S. Kamm and D. P. Werthemann, *J. Amer. Chem. Soc.*, **1975**, *97*, 3718-3725.

144. "A New Photochemical Rearrangement. A Cyclopropyl-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and C. J. Samuel, *J. Amer. Chem. Soc.*, **1975**, *97*, 4025-4036.

143. "Multiplicity and Molecular Flexibility in Controlling Molecular Reactivity. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, F. X. Albrecht, and J. J. Haire, *J. Amer. Chem. Soc.*, **1975**, *97*, 3726-3740.

206. "Di-π-Methane Rearrangement of Highly Sterically Congested Molecules; Inhibition of Free Rotor Energy Dissipation. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and D. N. Schissel, *J. Org. Chem.*, **1986**, *51*, 196-207.

G. Fingerprint Identification of Reactive Species

One useful technique for identifying a reactive species was termed the "Fingerprint Method". We suggested that when two reactions afforded the same distribution of photoproducts, one could reasonably assume that the they had an excited state or a reactive intermediate in common.

References: [58,68,71].

66. "The Photochemistry of 4,4,5-Triphenyl-2-cyclohexen-1-one. Mechanistic and Exploratory Organic Photochemistry. XXX," H. E. Zimmerman and R. L. Morse, J. Amer. Chem. Soc., 1968, 90, 954-966.

H. Single-Photon Counting Methodology and Results

Several new single-photon counting methodologies were developed: (a) An algorithm for convenient deconvolution, (b) use of a minicomputer for on-line multichannel data collection followed by deconvolution, and (c) a method of "magic multipliers" which permitted measurement of even more rapid decay rates. The last depended on measurement of the temperature dependence of fluorescence coupled with the assumption of the temperature independence of the rate of radiative decay; one can then obtain the ratio of room temperature to a slower and thus more readily measured low temperature decay.

128. "Superfast Singlet Excited State Di-π-Methane Rearrangement and Decay Rates; Picosecond Range Measurements by Single Photon Counting and Use of Magic Multipliers. Mechanistic Organic Photochemistry. LXXXI," H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, J. Amer. Chem. Soc., 1973, 95, 5094-5095.

131. "Single Photon Counting and Magic Multipliers in Direct Measurement of Singlet Excited State Di-π-Methane Rearrangement Rates in the Picosecond Range. Mechanistic Organic Photochemistry. LXXXIII," H. E. Zimmerman, D. P. Werthemann, and K. S. Kamm, J. Amer. Chem. Soc., 1974, 96, 439-449.

148. "Capabilities in Single Photon Counting with Reiterative Convolution; A Reply," H. E. Zimmerman and T. P. Cutler, J.C.S. Chemical Communications, 1975, 598-599.

189. "Evaluation of Single Photon Counting Measurements of Excited State Lifetimes," H. E. Zimmerman, J. H. Penn and C. W. Carpenter, Proc. Natl. Acad. Sci. USA, 1982, 79, 2128-2132.

Also: [Ref 156]

I. The ΔP Matrix and Location of Excitation Locale

One useful theoretical method involved our "Delta-P Matrix" which was defined as the difference between an excited state bond order matrix or density matrix and the ground state one. Thus, each element of the ΔP matrix gives us the change in the atom and bond electron densities resulting from electronic excitation. The change in bond orders are given by the off-diagonal elements. Most bond order elements are negative, signifying bond weakening and accumulation of the excitation energy in these bonds. A few elements are positive indicating bond strengthening in the excited state compared with ground state. Many bonds, especially those not near a chromophore, are near zero. Thus the method permits assessment of the effect of excitation at various sites in the molecule and provides a guide to the distribution of excitation energy around the molecule. The method is applicable at any computational level but was initially used with PPP-SCF-CI computations.

In reference 171 the ΔP treatment was shown to permit prediction of the mode of molecular relaxation from the vertically excited geometry. The idea was that bonds with negative vertical excitation ΔP values will stretch when vibrationally relaxed while those with positive values will contract.

Refs [166, 167, 168]

171. "A New Theoretical Approach in Photochemistry. Minimization of Excited State-Ground State Surface Separation by Selected Molecular Deformation. Vibrational Dissipation of Local Contributions to Excitation Energies," H. E. Zimmerman and M. G. Steinmetz, *J.C.S. Chemical Communications*, **1978**, 231-232.

197. "Reactivity of Aryl Vinyl Di-π-Methane Systems; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. L. Swafford, *J. Org. Chem.*, **1984**, *48*, 3069-3083.

J. Generation of Di-π-Methane Diradicals by Independent Routes

In the photochemical rearrangements of barrelene, benzobarrelene and 2,3-naphthobarrelene -- an intermediate triplet cyclopropyldicarbinyl diradical had been postulated. For each of these systems an azo precursor was synthesized such that loss of nitrogen would leave the diradical. It was found that thermolysis afforded the corresponding barrelene while triplet sensitization led to the corresponding semibullvalene. While the thermolysis might be pictured as involved an electrocyclic loss of nitrogen, it also can be envisaged as forming an incipient S_0 1,4-diradical. It has been postulated that such ground state diradicals react with fragmentation of the central 2,3-bond, and this accounts for formation of barrelene on thermolysis. The triplet diradicals were formed on sensitization and led to the semibullvalene as expected. In this study it was noted that the evidence favors preferential intersystem crossing to S_0 only as Diradical II of the Di-π-Methane mechanism is reached. At this point excited state and ground state surface approach.

147. "Generation of Photochemical Species on Ground, Excited Singlet, and Triplet Hypersurfaces in Barrelene Photochemistry," H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, and G. E. Keck, *J. Amer. Chem. Soc.*, **1975**, *97*, 5635-5637.

153. "Independent Generation of Cyclopropyldicarbinyl Diradical Species of the Di-π-Methane Rearrangement. Excited Singlet, Triplet and Ground State Hypersurfaces of Barrelene Photochemistry," H. E. Zimmerman, R. J. Boettcher, N. E. Buehler, G. E. Keck and M. G. Steinmetz, *J. Amer. Chem. Soc.*, **1976**, *98*, 7680-7689.

K. Photochemistry Without Light

Generation of Type-A and Type-B zwitterions from the corresponding α-bromoketones might be considered to constitute photochemistry without light since the same oxy-allyl zwitterions utilized in the photochemistry are formed and react to give the photochemical product (note Refs 54,72,77,110,116). Still, these examples involve generation of photochemical species after decay to S_0.

By use of an internal dioxetane moiety capable of undergoing thermal fission to afford 4,4-diphenylcyclohexadienone, a means of specifically generating the dienone n-π^* triplet was available. It was found that for a variety of these compounds, the Type-A product resulting on warming. The second carbonyl compounds released on O-O and C-C fission varied in their triplet energies above and below that of the cyclohexadienone. Nevertheless, the efficiency of dienone triplet formation and rearrangement did not vary. It was suggested that the energy of the n-π^* triplets rather than any lower energy π-π states were controlling.

141. "A Photochemical Rearrangement Without Light. Dioxetane Effected Photochemistry by Direct Intramolecular Excitation," H. E. Zimmerman and G. E. Keck, *J. Amer. Chem. Soc.*, **1975**, *97*, 3527-3528.

152. "Molecular Rearrangements of Excited States Generated by Intramolecular Dioxetane Scission. Photochemistry Without Light. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, G. E. Keck, and J. L. Pflederer, *J. Amer. Chem. Soc.*, **1976**, *98*, 5574-5581.

L. Meta-Transmission in the Aromatic Excited State

In an early publication by Egbert Havinga it was noted that a meta-nitrophenyl phosphate ester hydrolyzed rapidly with light while the para isomer was no more reactive than in the dark. This is the reverse of ground state expectation and Egbert noted that this was not readily understood on a standard resonance basis. This led us to study electron density transmission in excited states having electron withdrawing groups and also electron donating groups. Simple molecular orbital theory, including computations, revealed that in the first excited state *meta-transmission* was preferred over para-transmission. We termed this the "meta effect".

Experimentally, we found that the photolysis of meta methoxylated benzylic esters led to facile formation of the benzylic cation while the para isomers underwent only homolysis. Two meta methoxyl groups gave further enhancement. Thus the prediction of unusually stabilized meta-methoxylated benzylic cations and meta electron transmission was experimentally established.

In the case of withdrawing groups, m-nitrophenyl trityl ethers reacted photochemically with facility while the para isomers were not reactive. Again the "meta effect" was operative.

31. "Mechanistic Organic Photochemistry. II. Solvolytic Photochemical Reactions," H. E. Zimmerman and V. R. Sandel, *J. Amer. Chem. Soc.*, **1963**, *85*, 915-922.

32. "Mechanistic Organic Photochemistry. III. Excited State Solvolyses," H. E. Zimmerman and S. Somasekhara, *J. Amer. Chem. Soc.*, **1963**, *85*, 922-927.

Also Refs [28,35]

M. Exchange Integral Control of Photochemical Reactions

The exchange integral K gives the energy splitting between T_1 and S_1. Since a number of reactions are multiplicity dependent, it was of interest to seek a generalization. Our rule stated that singlet reactions tend to prefer "small K" mechanisms while triplet reactions prefer "large K routes". The exchange integral for an excited state species enroute to photoproduct can be obtained computationally. However, some qualitative generalizations also proved to be possible. Thus, pericyclic reactions are of the "small K" type while homopolar diradical reactions are of the "large K" variety. Having an electronegative group on a diradical center, or having some perturbation making the diradical ionic, results in a "small k" species. The concept is based on the idea that with a small singlet triplet gap for one pathway and a large one for an alternative route, the "large K" triplet will be of lower energy than the "small K" triplet, while the converse will be true for the singlets.

175. "Unusual Organic Photochemistry Effected by Cyano and Methoxy Substitution. Exploratory and Mechanistic Organic Photochemistry," H. E. Zimmerman, D. Armesto, M. G. Amezua, T. P. Gannett, and R. P. Johnson, *J. Amer. Chem. Soc.*, **1979**, *101*, 6367-6383.

183. "Di-π-Methane Hypersurfaces and Reactivity; Multiplicity and Regioselectivity; Relationship Between the Di-π-Methane and Bicycle Rearrangements," H. E. Zimmerman and R. E. Factor, *Tetrahedron*, **1981**, *37*, Supplement 1, 125-141.

185. "New Reactions and Theory in Organic Photochemistry: The 1,3-Vinyl Migration and its Relevance to Exchange Integral Control," H. E. Zimmerman, J. H. Penn and M. R. Johnson, *Proc. Natl. Acad. Sci. USA*, **1981**, *78*, 2021-2025.

Also Ref. [196]

III. NEW REACTIONS

A. The Di-π-Methane Rearrangement

In 1966 we reported the rearrangement of barrelene to semibullvalene, a reaction we initially termed the "divinylmethane rearrangement"; this was the first photochemical rearrangement of a barrelene to a semibullvalene and was the first report of semibullvalene itself.

However, it was the next year before the reaction mechanism was firmly established. Also, the triplet hypersurface was obtained using extended Hückel theory. In this publication, the reaction was noted to be a general one, and this became the first report of the Di-π-Methane Rearrangement as a generality.

46. "The Chemistry of Barrelene. III. A Unique Photoisomerization to Semibullvalene," H. E. Zimmerman and G. L. Grunewald, *J. Amer. Chem. Soc.*, **1966**, *88*, 183-184.

60. "Mechanistic Organic Photochemistry. XXIV. The Mechanism of the Conversion of Barrelene to Semibullvalene. A General Photochemical Process," H. E. Zimmerman, R. W. Binkley, R. S. Givens, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **1967**, *89*, 3932-3933.

Shortly thereafter, the triplet reaction of benzobarrelene was found to occur via vinyl-vinyl bridging rather than the alternative benzovinyl mechanism. The singlet was shown to lead instead to benzocyclooctatetraene via benzo-vinyl bridging.

69. "Control of Photochemical Reactivity by Excited State Multiplicity. Mechanistic and Exploratory Organic Photochemistry. XXXIV," H. E. Zimmerman, R. S. Givens and R. M. Pagni, *J. Amer. Chem. Soc.*, **1968** *90*, 4191-4193.

74. "The Photochemistry of Benzobarrelene. Mechanistic and Exploratory Organic Photochemistry. XXXV," H. E. Zimmerman, R. S. Givens and R. Pagni, *J. Amer. Chem. Soc.*, **1968**, *90*, 6096-6108.

The Di-π-Methane Rearrangement of acyclic dienes was reported to occur via the singlet excited state in contrast to the monocyclics and bicyclics which utilized the triplet. It was proposed that a concerted Möbius array in an allowed reaction was responsible for the singlet process and that π-bond twisting, i.e. a "free-rotor effect, was responsible for triplet energy dissipation for these acyclics.

80. "The Di-π-Methane Rearrangement. Interaction of Electronically Excited Vinyl Chromophores. Mechanistic and Exploratory Organic Photochemistry. XLI," H. E. Zimmerman and P. S. Mariano, *J. Amer. Chem. Soc.*, **1969**, *91*, 1718-1727.

82. "The Barrelene to Semibullvalene Transformation. Correlation of Excited State Potential Energy Surfaces With Reactivity. Mechanistic and Exploratory Organic Photochemistry. XLIV," H. E. Zimmerman, R. W. Binkley, R. S. Givens, G. L.Grunewald, and M. A. Sherwin, *J. Amer. Chem. Soc.*, **1969**, *91*, 3316-3323.

83. "The Di-π-Methane Rearrangement of 1-Methylene-4,4-Diphenyl-2-cyclohexene and Related Photochemical Processes. Mechanistic and Exploratory Organic Photochemistry. XLV," H. E. Zimmerman and G. E. Samuelson, *J. Amer. Chem. Soc.*, **1969**, *91*, 5307-5318.

The Di-π-Methane Rearrangement was found to occur for both α- and -β naphthobarrelenes. The former proceeded by naphtho-vinyl bridging while the latter rearranged by vinyl-vinyl bridging.

86. "Mechanistic and Exploratory Organic Photochemistry. XLIX. Excited State Aromaticity and Energy Localization. The Di-π-Methane Rearrangement of Naphthobarrelenes," H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **1969**, *91*, 7516-7518.

95. "The Di-π-Methane Rearrangement of Naphthobarrelenes. Mechanistic and Exploratory Organic Photochemistry. L." H. E. Zimmerman and C. O. Bender, *J. Amer. Chem. Soc.*, **1970**, *92*, 4366-4376.

The rearrangement of benzo, β,β-naphthobarrelene was found to occur with equal amounts of benzo-vinyl and naphtho-vinyl bridging. In addition, anthracenobarrelene rearranged, again, by vinyl-vinyl bridging; however, in this case only T_2 was reactive.

120. "Competitive Naphtho vs. Benzo Bridging in the Di-π-Methane Rearrangement of Benzo-2,3-naphthobarrelene. Exploratory and Mechanistic Organic Photochemistry. LXXIV," H. E. Zimmerman and M-L Viriot-Villaume, *J. Amer. Chem. Soc.*, **1973**, *95*, 1274-1280.

127. "Photochemical Rearrangement Effected by Triplet Excitation Transmitted Through a High Energy Moiety. Mechanistic and Exploratory Organic Photochemistry. LXXX," H. E. Zimmerman, D. R. Amick and H. Hemetsberger, J. Amer. Chem. Soc., 1973, 95, 4606-4610.

In a study of an isopropenyl Di-π-Methane system, the singlet was found to rearrange nicely while the triplet merely underwent cis-trans isopropenyl isomerization. It was suggested that the "free rotor" effect was responsible for the lack of triplet rearrangement. Also in this work, the singlet rearrangement was noted to involve a Möbius orbital array and thus allowed in a concerted process.

88. "Organic Photochemistry. LIV. Concertedness, Stereochemistry, and Energy Dissipation in the Di-π-Methane Rearrangement. Source of Singlet-Triplet Reactivity Differences," H. E. Zimmerman and A. C. Pratt, J. Amer. Chem. Soc., 1970, 92, 1409-1411.

96. "Unsymmetrical Substitution and the Direction of the Di-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry. LVI," H. E. Zimmerman and A. C. Pratt, J. Amer. Chem. Soc., 1970, 92, 6259-6267.

In these papers and in related publications, the regioselectivity of the Di-π-Methane Rearrangement was shown to be controlled by the mode of "unzipping" of the cyclopropyldicarbinyl diradical species. This occurred such that the more stabilized diradical center was preserved.

87. "Organic Photochemistry. LIII. Directionality of the Singlet Di-π-Methane Rearrangement and Alkyl Migration in a Unique Vinylcyclopropane Transformation," H. E. Zimmerman and A. C. Pratt, J. Amer. Chem. Soc., 1970, 92, 1407-1409.

97. "Stereochemical Aspects of the Di-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry. LVII," H. E. Zimmerman and A. C. Pratt, J. Amer. Chem. Soc., 1970, 92, 6267-6271.

103. "Electron Delocalization as a Controlling Factor in the Di-π-Methane Rearrangement. Exploratory and Mechanistic Organic Photochemistry. LXII, H. E. Zimmerman and A. A. Baum, J. Amer. Chem. Soc., 1971, 93, 3646-3653.

The role of para substitution in aryl groups of the Di-π-Methane Rearrangement was also studied. It was found that in a 1,1,5,5-tetraaryl-1,5-pentadiene having electron donating or withdrawing substituents on one of the diarylvinyl groups, the electron deficient aryl rings were found on the three-ring of photoproduct while electron rich aryl groups were preferred on the residual double bond of product. A further approach was quantum mechanical and correlated the competitive fission of the two three-ring bonds as a function of bond weakening on excitation [note ref. 167].

In addition, electron donating groups were shown to inhibit the rate of π-π bridging while electron withdrawing groups enhanced this rate as measured by single-photon counting techniques.

The Electron Withdrawing Case:

138. "Substituent Effects and the Di-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry," H. E.Zimmerman and B. R. Cotter, *J. Amer. Chem. Soc.*, **1974**, *96*, 7445-7453.

The Electron Donating Case:

163. "Unusual Regioselectivity in the Di-π-Methane Rearrangement. Reaction Inhibition and Control by Electron Donating Substituents. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and W. T. Gruenbaum, *J. Org. Chem.*, **1978**, *43*, 1997-2005.

166. "Differing Substituent Effects on Rates and Regioselectivities in the Di-π-Methane Rearrangement. New Photochemical Theory: Excitation Distribution (the ΔP Matrix), Reaction Inhibition by Vertical Excited State Stabilization, Ground State vs. Excited State Control," H. E. Zimmerman, W. T. Gruenbaum, R. T. Klun, M. G. Steinmetz, and T. R. Welter, *J.C.S. Chemical Communications*, **1978**, 228-230.

167. "Control of Regioselectivity and Excited State Singlet Reaction Rates by Substitution in the Di-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and T. R. Welter, *J. Amer. Chem. Soc.*, **1978**, *100*, 4131-4145.

169. "The Di-π-Methane Rearrangement of Systems With Simple Vinyl Moieties. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. T. Klun, *Tetrahedron*, **1978**, *43*, 1775-1803.

The reaction stereochemistry of 1,4-pentadienes (i.e. acyclic Di-π-Methane systems) was also investigated. There are three points of stereochemistry. Inversion of configuration was shown to occur at the "methane carbon", C-3. At C-1, where the vinyl group remained intact during the rearrangement, the cis vs trans configuration was maintained. Finally, at C-5, the carbon incorporated into the product cyclopropyl ring, the stereochemistry was also delineated. Here a group originally cis on the π-bond which is lost, becomes cis on the photoproduct three-membered ring. Conversely, a group trans on the initial double bond appears as a trans group in the three-ring of product. The stereochemistry of the singlet Di-π-Methane rearrangement was shown to be in accord with the presence of a Möbius cyclic array of basis orbitals, making the reaction excited state allowed with the observed stereochemistry.

113. "The Stereochemistry of the Di-π-Methane Rearrangement; Mechanistic and Exploratory Organic Photochemistry. LXIX," H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **1972**, *94*, 5504-5505.

132. "C-1 Stereochemistry of the Di-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LXXXIV," H. E. Zimmerman, P. Baeckstrom, T. Johnson, and D. W. Kurtz, *J. Amer. Chem. Soc.*, **1974**, *96*, 1459-1465.

133. "Stereochemistry of the Di-π-Methane Rearrangement at the Methane Carbon. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **1974**, *96*, 1974-1976.

136. "Stereochemistry at the Methane Carbon in the Di-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, J. D. Robbins, R. D. McKelvey, C. J. Samuel, and L. R. Sousa, *J. Amer. Chem. Soc.*, **1974**, *96*, 4630-4643.

162. "Stereochemistry in the Di-π-Methane Rearrangement; Aryl Migration. Exploratory and Mechanistic Organic Photochemistry," H. E. Zimmerman, T. P. Gannett and G. E. Keck, *J. Amer. Chem. Soc.*, **1978**, *100*, 323-324.

173. "Stereochemistry of the Aryl-Vinyl Version of the Di-π-Methane Rearrangement," H. E. Zimmerman, T. P. Gannett and G. E. Keck, *J. Org. Chem.*, **1979**, *44*, 1982-1989.

Interestingly, the acyclic Di-π-Methane, 1,1,5,5-tetraphenyl-1,4-pentadiene, lacking central, "methane" substitution was found to rearrange to a photoproduct which superficially appeared to be an ordinary Di-π-Methane product. However, deuterium labeling revealed that the reaction proceeded by an initial central hydrogen 1,2-shift and then three-ring closure.

114. "An Unexpected Sigma Plus Pi Rearrangement of a Di-π-Methane Reactant. Inhibition of the Di-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry. LXX," H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **1972**, *94*, 6208-6209.

123. "Sigma Plus Pi Rearrangements of Di-π-Methane Systems. Central Substitution and Di-π-Methane Reactivity. Mechanistic and Exploratory Organic Photochemistry. LXXVI," H. E. Zimmerman and J. A. Pincock, *J. Amer. Chem. Soc.*, **1973**, *95*, 2957-2963.

In the case of aryl-vinyl methane systems, the singlet reaction rates were determined to be slower than the corresponding divinylmethane rearrangements. Quantum mechanical (SCF-CI) computations were used in several ways. A correlation of the S_1 aryl-vinyl bridging energies with the S_1 rates was found. Also, the excited state 3-ring bond orders accounted for the reaction regioselectivity. Another interesting finding was came from the ΔP method. This showed that initial electronic excitation in the diphenylvinyl moiety of vertical S_1 had migrated to the cyclopropyldicarbinyl group after aryl-vinyl bridging.

168. "The Aryl-Vinyl Methane Version of the Di-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, M. G. Steinmetz and C. L. Kreil, *J. Amer. Chem. Soc.*, **1978**, *100*, 4146-4162.

In the case of aryl-vinyl rearrangements of reactants with aryl groups having especially low singlet energies and unsubstituted vinyl moieties, the rearrangement rate proved to be particularly slow (ca 250 to 6×10^5 s^{-1}).

187. "Reactivity of Low Energy Excited States," H. E. Zimmerman and J. R. Blinn, *Tetrahedron*, **1981**, *19*, 3237-3243.

196. "The Photochemistry of Phenanthrene-substituted Molecules," H. E. Zimmerman and G-S. Wu, *Canadian J. Chem.*, **1983**, *61*, 866-871.

Another interesting facet arose from a suggestion that the Di-π-Methane rearrangement might result from a mechanism not involving π-π-bridging but rather a $\sigma + \pi$ mechanism. This led us to look at analogs lacking one of the two π-bonds. In the case of 1,1,5,5-tetraphenyl-3,3-dimethyl-1-pentene, it was found that the Di-π-Methane rearrangement did not occur; instead a much less efficient, but still interesting, 1,4-phenyl migration took place.

137. "A Novel Photochemical 1,4-Phenyl Migration. The Role of the Second Double Bond in the Di-π-Methane Rearrangement. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. D. Little, J. Amer. Chem. Soc., **1974**, 96, 5143-5152.

209. "A Photochemical Long Range Pinacol Rearrangement; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and John M. Nuss, J. Org. Chem., **1986**, 51, 4604-4617.

The generalization was mentioned above that acyclic Di-π-Methane systems react via the singlet with the triplet dissipating energy via a free-rotor mechanism. It was found that substitution of the methane carbon with electron delocalizing groups - such as phenyl, cyano, carbomethoxyl - leads not only to enhanced singlet efficiency but also to triplet reactivity. This emphasized that free-rotor excited state energy dissipation had to be compared rate-wise with the competitive reaction process.

122. "Accentuation of Di-π-Methane Reactivity by Central Carbon Substitution. Mechanistic and Exploratory Organic Photochemistry. LXXV," H. E. Zimmerman, R. J. Boettcher, and W. Braig, J. Amer. Chem. Soc., **1973**, 95, 2155-2163.

One might wonder whether there is a conformational requirement for the Di-π-Methane rearrangement in which the two double bonds needed to be in a "U-conformation" or in a transoid conformation. It was found by use of reactants with fixed conformations that both conformations are reactive.

146. "Conformation and Di-π-Methane Reactivity. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and L. M. Tolbert, J. Amer. Chem. Soc., **1975**, 97, 5497-5507.

An interesting example involved a cross-conjugated analog of 4,4-diphenylcyclohexadienone in which the carbonyl group was replaced by dicyanovinyl. There was no β-β-bonding and only 4-phenyl migration to afford α,α-dicyano-3,4-diphenyltoluene. β-β-bonding was shown to be excited state forbidden. In contrast, the corresponding 1-diphenylmethylene-4,4-diphenylcyclohexadiene did undergo a singlet Type-A rearrangement by β,β-bridging [Ref 172].

One particularly esoteric example of the Di-π-Methane Rearrangement involved multiplicity control of the regiochemistry. Thus 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene was observed to give the vinylcyclopropane photoproduct with the carbomethoxyls substituted on the three-ring when direct irradiation was employed but the carbomethoxyls on the vinyl group when the reaction was sensitized. This provided an example of the "Small-K Large-K" principle. In this study, reaction MO correlations and state hypersurfaces were obtained.

Ref. [183]

More recently the Di-π-Methane Rearrangement has been studied theoretically and experimentally in the case of the barrelenes. It has been shown that "Diradical I", the initially formed cyclopropyldicarbinyl diradical triplet, is an energy minimum and that the reaction regioselectivity is controlled at this stage of the reaction.

229. "Experimental and Theoretical Exploration of the Detailed Mechanism of the Rearrangment of Barrelenes to Semibullvalenes; Diradical Intermediates and Transition States", Zimmerman, H. E.; Sulzbach, H. M.; Tollefson, M. B. J. Am. Chem. Soc., **1993**, 115, 6548-6556.

B. The Epoxy Ketone Rearrangement

One of the early photochemical reactions to which the new mechanistic theory was applied was the rearrangement of α,β-epoxyketones; the reaction leads to β-diketones with migration of a β-substituent to the α-carbon. The first example, reported in 1961, [Ref. 28 above] revealed unusual migratory aptitudes wherein methyl migrated from the β to the α carbon in preference to phenyl. (The same reaction was independently uncovered by the Schaffner - Jeger group in 1962, and an early (1918) example by S. Bodforss in the Chem. Ber. may proceed by the same mechanism or by an alternative β-hydrogen abstraction.

36. "A General Theory of Photochemical Reactions. VII. Mechanisms of Epoxy Ketone Reactions," H. E. Zimmerman, B. R. Cowley, C-Y. Tseng, and J. W. Wilson, J. Amer. Chem. Soc., **1964**, 86, 947-948.

40. "Photochemical Reactions of 2.3-Epoxy-2-methyl-3-phenylindanone," H. E. Zimmerman and R. D. Simkin, Tetrahedron Lett., **1964**, 1847-1851.

C. Rearrangement of Aryl Groups in 4-Arylcyclohexenones and Cyclopentenones

In 1964 the rearrangement of 4,4-diphenylcyclohexenone was reported. It was Ken Hancock who showed that the rearrangment proceeded via the n-π* triplet; and shortly thereafter in 1965 in a related example, evidence was obtained that the β-carbon was not electron deficient. This derived from an enhanced migration of γ-cyanophenyl relative to phenyl. In the same study the reacting species was shown to be a triplet. Shortly thereafter graduate students Reuben Rieke and "Jerry" (John) Scheffer showed that both p-anisyl and p-cyanophenyl groups migrated in preference to phenyl in simple 4,4-diarylcyclohexenones. This signified that the triplet excited enone β-carbon showed odd-electron character.

42. "Mechanistic and Exploratory Organic Photochemistry, IX. Phenyl Migration in the Irradiation of 4.4-Diphenylcyclohexenone," H. E. Zimmerman and J. W. Wilson, J. Amer. Chem. Soc., **1964**, 86, 4036-4042.

44. "Mechanistic and Exploratory Photochemistry. XII. Characterization of the Reactivity of the β-Carbon in the Triplet Excited State of α,β-Unsaturated Ketones," H. E. Zimmerman, R. C. Hahn, H. Morrison, and M. C. Wani, J. Amer. Chem. Soc., **1965**, 87, 1138-1140.

58. "Photochemical Migratory Aptitudes in Cyclohexenones. Mechanistic and Exploratory Organic Photochemistry. XXIII," H. E. Zimmerman, R. D. Rieke, and J. R. Scheffer, J. Amer. Chem. Soc., **1967**, 89, 2033-2047.

68. "Electronic Details of the Photochemical Phenyl Migration in 4,4-Diphenylcyclohexenone. Mechanistic Organic Photochemistry. XXXI," H. E. Zimmerman and K. G. Hancock, J. Amer. Chem. Soc., **1968**, 90, 3749-3760.

p-Cyano-substitution was shown to markedly increase the rate of rearrangement of the triplet enone when substituted in the migrating aryl group and to a lesser extent when present in the aryl group remaining at C-4 of the enone. This established the formation of the aryl bridged diradical as rate-limiting [Ref 78]. Shortly thereafter, the activation energy for the rearrangement of 4,4-diphenylcyclohexenone was measured and shown to be 10 kcal/mole. Wavelength independence established that the rearranging triplet was thermally equilibrated.

78. "Relative Rates of Aryl Migrations in Excited State Transformations. Mechanistic and Exploratory Organic Photochemistry. XXXIX," H. E. Zimmerman and N. Lewin, J. Amer. Chem. Soc., 1969, 91, 879-886.

79. "Energy Barriers in Photochemical Molecular Rearrangements. Mechanistic and Exploratory Organic Photochemistry. XL. H. E. Zimmerman and W. R. Elser, J. Amer. Chem. Soc., 1969, 91, 887-896.

Interestingly, the analogous rearrangement of 4-phenylcyclopentenones was observed and the intermediate "housone" could be identified at low temperature as well as a ring-opened unsaturated ketene.

112. "Contrasting Cyclopentenone and Cyclohexenone Photochemistry," H. E. Zimmerman and R. D. Little, J.C.S. Chem. Communications, 1972, 689-700.

135. "Photochemical Rearrangement of 4-Aryl-Substituted Cyclopentenones. Low Temperature Photochemistry and Direct Observation of Reaction Intermediates," H. E. Zimmerman and R. D. Little, J. Amer. Chem. Soc., 1974, 96, 4623-4630.

D. The Type-A Cyclohexadienone Rearrangement

Derek Barton had elucidated the structure of Lumisantonin and thus was able to establish the course, including the stereochemistry, of the esoteric rearrangement of Santonin to Lumisantonin. This work was in collaboration with Paul DeMayo. There remained the problem of the reaction mechanism. With Dave Schuster, who was a postdoc at Wisconsin at the time, we demonstrated that precisely the same process occurred in the case of 4,4-phenylcyclohexadienone, and we termed this the "Type-A Rearrangement". The mechanism we advanced involved initial β-β-bonding in the n-π^* excited state, followed by radiationless decay to a ground state zwitterion of the oxyallyl type, followed by an interesting ground state rearrangement. The same mechanism, when applied to the case of Santonin, led to the Lumisantonin structure with the known stereochemistry [Ref 30]. This mechanism accorded precisely with the philosophy that excited state transformations follow low energy pathways with mechanisms which would be acceptable to a ground state chemist, assuming that he had available the structure of the excited state reactant.

However, the reaction multiplicity and the efficiency needed to be established, which was done by Swenton in his Ph.D. thesis

56. "Mechanistic Organic Photochemistry. XXI. Electronic Details of the 2,5-Cyclohexadienone Rearrangement," H. E. Zimmerman and J. S. Swenton, J. Amer. Chem. Soc., 1967, 89, 906-912.

Also, the reality of the proposed "Zimmerman-Schuster" oxy-allyl zwitterionic intermediate was firmly established by Dietrich Döpp in his postdoctoral work by independently generated this species from the appropriate α-bromobicyclic ketone and base in a "Favorski-like" approach. Subsequent to this, by labeling the two aryl groups in the Type-A zwitterion, it was possible to show that the rearrangement proceeded to the bicyclo[3.1.0]hex-3-en-2-one with the endo-aryl group remaining endo and the exo group staying exo. The proposed mechanism involves a Möbius transition state with 4 delocalized electrons.

54. "The Generation of Photochemical Intermediates Without Light. Mechanistic Organic Photochemistry. XX," H. E. Zimmerman, D. Döpp, and P. S. Huyffer, J. Amer. Chem. Soc., 1966, 88, 5352-5353.

72. "Photochemistry Without Light and the Stereochemistry of the Type A Dienone Rearrangement. Organic Photochemistry. XXXVI," H. E. Zimmerman and D. S. Crumrine, J. Amer. Chem. Soc., 1968, 90, 5612-5614.

77. "Photochemistry Without Light and the Stereochemistry of the Type A Dienone Rearrangment; Organic Photochemistry. XXXVIII," H. E. Zimmerman, D. S. Crumrine, D. Döpp, and P. S. Huyffer, J.Amer. Chem. Soc., 1969, 91, 434-445.

With a β-methoxyl or a β-cyano group, the Type-A rearrangement proceeded regioselectively to afford the bicyclo[3.1.0]hex-3-en-2-one with the substituent on the double bond. In the methoxy case, the Type-A zwitterion could be generated without light from the corresponding Favorski approach to give similar selectivity. Theoretical computations were in accord with the slower rate observed for the β-methoxydienone, with the regioselectivity and with the n-π* assignment to the reacting triplet.

181. "Regioselectivity in Cyclohexadienone Photochemistry; the Role of Zwitterions in Type A Photochemical and Dark Rearrangements. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. J. Pasteris, J. Org. Chem., 1980, 45, 4864-4875.

182. "Type A Zwitterions and Cyclohexadienone Photochemical Rearrangements. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. J. Pasteris, J. Org. Chem., 1980, 45, 4876-4891.

A particularly unusual Type-A system was 4,4-dinaphthylcyclohexadienone. In the case of the β-naphthyl dienones, two triplets were identified. T_2 was the usual n-π* triplet with excitation centered in the dienone carbonyl region. The other triplet was the naphthyl-excited T_1. T_2 was a faster reacting triplet and afforded the usual Type-A photoproduct. T_1 gave only naphthyl migration affording 3,4-di-β-naphthylphenol. Sensitization with thioxanthone, which has just enough energy to generate T_1, afforded the 3,4-dinaphthylphenol. Quenching studies showed two slopes. The steep slope, corresponded to the slower reacting T_1 forming the phenol; here the naphthyl centered triplet excitation was being quenched. The smaller slope corresponded to quenching of the carbonyl centered triplet and the Type-A rearrangement. Further evidence came from generation of T_2 specifically by the intramolecular thermal dioxetane route; here excitation was generated in the locale of the carbonyl group. The interpretation was that on direct irradiation, the carbonyl moiety acted as a singlet-triplet switch by virtue of its spin-orbit coupling capability.

204. "Rapidly Rearranging Excited States of Bichromophoric Molecules; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and D. C. Lynch, *J. Amer. Chem. Soc.*, **1985**, *107*, 7745-7756.

E. The Type-B Rearrangement of Bicyclo[3.1.0]hex-3-en-2-ones

We had noted that 6,6-diphenylbicyclo[3.1.0]hex-3-en-2-one, which was a Type A photoproduct resulting from the Type A rearrangement of 4,4-diphenylcyclohexadienone, underwent a rearrangement to afford 2,3-diphenylphenol and 3,4-diphenylphenol. Our generalized mechanistic reasoning proved applicable to this process, except that the antibonding π-electron led to initial three-ring opening as the first excited state process. [Ref 30].

In subsequent studies, John Swenton, Reinhard Keese and Jacques Nasielski showed that the ratio of 2,3- to 3,4-diphenylphenol was depended on the acidity of the photolysis medium. Our reaction mechanism involved fission of the internal three-ring bond in the triplet excited state, followed by radiationless decay to a six-ring oxy-allyl ("Type B") zwitterion, which then underwent phenyl migration either to C-2 or to C-4. In neutral media, migration to C-2 was preferred. Thus protonation of the Type B zwitterion changed the regioselectivity from C-2 to C-4 migration. However, in acidic medium, the phenyl group preferred C-4. Application of the same reasoning to the zwitterion derived from Santonin accounted for the formation of isophoto- santonic lactone under acidic conditions, since here the protonated Zimmerman- Schuster" species no longer was a zwitterion with its negative oxygen; instead an external nucleophile supplied the negative charge.

51. "Mechanistic Organic Photochemistry. XVI. The Photochemistry of 6,6-Diphenylbicyclo[3.1.0]hex-3-en-2-one," H. E. Zimmerman, J. Nasielski, Reinhart Keese and J. S. Swenton, *J. Amer. Chem. Soc.*, **1966**, *88*, 4895-4903.

Evidence for the nature of this six-ring Type-B zwitterion was obtained from the rearrangement of 6-cyanophenyl-6-phenylbicyclo[3.1.0]hex-3-en-2-one [Ref 61] where it was shown that it was the phenyl group which migrated in preference. Had the rearrangement occurred on this excited state hypersurface, cyanophenyl would have migrated in preference.

Equally convincing was the generation of this Type-B zwitterion from 6-bromo-5,5-diphenylcyclohex-2-en-1-one on treatment with base. The zwitterion formed afforded 2,3-diphenylphenol and 3,4-diphenylphenol in the same ratios as in the corresponding photochemical approach from bicyclo[3.1.0]-3-en-2-one in a series of solvents with differing polarities.

61. "Pathways Leading From Excited-State Reactant to Ground-State Products in Dienone Photochemistry. Mechanistic and Exploratory Organic Photochemistry. XXVI," H. E. Zimmerman and J. O. Grunewald, *J. Amer. Chem. Soc.*, **1967**, *89*, 5163-5172.

110. "Entrance Onto Potential Energy Surfaces of Photochemical Reactions Without Light; The Type B Reaction. Mechanistic Organic Photochemistry. LXV," H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **1972**, *94*, 3245-3246.

116. "Generation of Photochemical Intermediates Without Light; the Type B Zwitterion. Mechanistic Organic Photochemistry. LXXI. H. E. Zimmerman and G. A. Epling, *J. Amer. Chem. Soc.*, **1972**, *94*, 7806-7811.

F. Type-A and Other Ring Contractive Rearrangements of Alicyclic Cyclohexenones

Orville Chapman had showed that 4,4-dimethylcyclohexenone undergoes a rearrangement to give, inter alia, a Type-A photoproduct. Then our own group found that the occurrence of Type A skeletal rearrangements occurred cleanly in β-octalone and phenanthrone [ref 49]. By use of isotopic labeling we found that 4,5-diphenylcyclohexenone rearranged to a bicyclo[3.1.0]hexan-2-one by a Type-A ring contraction mechanism rather than the more common aryl migration process [ref 56].

49. "Mechanistic and Exploratory Photochemistry, XV. The Relations of Cyclohexenone to Cyclohexadienone Rearrangements," H. E. Zimmerman, R. G. Lewis, J. J. McCullough, A. Padwa, S. Staley, and M. Semmelhack, *J. Amer. Chem. Soc.*, **1966**, *88*, 1965-1973.

52. "Mechanistic and Exploratory Organic Photochemistry. XVIII. Competing Pathways in the Rearrangements of 4,5-Diphenylcyclohexenone," H. E. Zimmerman and D. J. Sam, *J. Amer. Chem. Soc.*, **1966**, *88*, 4905-4914.

A comparison of the efficiency and rate of rearrangement of the 4,4-diphenylcyclohexenone with the Type A ring rearrangements of non-aryl substituted alicyclic cyclohexenones and cyclohexadienones with the finding that the phenyl migration process was intermediate. The quenching efficiencies of a series of triplet acceptors correlated with the energies of the acceptors [Ref 68].

G. Phenyl Migration in Dibenzoylethylenes

In 1962, simultaneous with Gary Griffin, we found a rearrangement of dibenzoylalkenes in which the phenyl group of one benzoyl group migrates to the n-π^* oxygen orbital of the other benzoyl group to afford a ketene which then undergoes nucleophilic solvent addition to afford an ester. Rich Givens in his Ph.D. thesis showed that the reaction proceeds via the singlet excited state and via the cis-stereoisomers. The triplet sensitized reaction was found to afford reduction to afford dibenzoylethanes, and the superficial conclusion in the literature was that the triplet reacted instead by hydrogen abstraction. In subsequent studies we found a more mundane source, namely delivery of a hydrogen atom by the triplet sensitizer which first formed (e.g.) hydroxybenzhydryl radical which transferred a hydrogen atom to the dibenzoylethylene.

29. "Mechanistic Organic Photochemistry. V. Phenyl Migration in a New Photochemical Reaction," H. E. Zimmerman, H. G. Dürr, R. G. Lewis and S. Bram, *J. Amer. Chem. Soc.*, **1962**, *84*, 4149-4150.

57. "The Photochemistry of Dibenzoylethylenes. Mechanistic and Exploratory Organic Photochemistry. XXII," H. E. Zimmerman, H. G. Dürr, R. S. Givens, and R. G. Lewis, *J. Amer. Chem. Soc.*, **1967**, *89*, 1863-1874.

99. "Singlet-Triplet Differentiation. Mechanistic and Exploratory Organic Photochemistry. LIX," H. E. Zimmerman and V. J. Hull, *J. Amer. Chem. Soc.*, **1970**, *92*, 6515-6520.

H. The Stereoisomerization of Cyclopropyl Ketones

Cis and Trans Bicyclo[3.1.0]hexan-2-ones were found to undergo interconversion via the triplets. It was shown that the reaction was non-adiabatic with excited state reactant affording only ground state product directly without a common point on the excited state hypersurface. Also, it was demonstrated that there was a preference for scission of the out-of-plane three-ring sigma bond with intervention of the the in-plane bond breaking only in the cis to trans conversion. An interesting note was that microscopic reversibility does not apply to such non-adiabatic stereoisomerizations.

71. "The Stereochemistry and Mechanism of the Photochemical Interconversion of cis- and trans-5,6-Diphenylbicyclo[3.1.0]hexan-2-ones. Mechanistic Organic Photochemistry. XXXII," H. E. Zimmerman, K. G. Hancock, and G. Licke, J. Amer. Chem. Soc., **1968**, 90, 4892-4911.

In a series of studies intended to determine the nature of the three-ring scission in cyclopropyl ketones, the stereoisomerization of 1-benzoyl-2-aryl-3-phenylcyclopropanes was investigated with the finding that the preferred diradical resulted from breakage of that α-β bond bearing the cyanophenyl or anisyl substituent. Also single rotations in the triplet diradical about the α-β bond were shown to be preferred over double rotations, and concerted conrotatory or disrotatory rotations could be excluded.

90. "Excited State Bond Weakening in Photochemical Rearrangements of Cyclopropyl Ketones. Exploratory and Mechanistic Organic Photochemistry. XLVIII," H. E. Zimmerman, S. S. Hixson, and E. F. McBride, J. Amer. Chem. Soc., **1970**, 92, 2000-2015.

92. "Excited State Electron Distribution in Cyclopropyl Ketone Rearrangments. Mechanistic and Exploratory Organic Photochemistry. LI," H. E. Zimmerman and C. M. Moore, J. Amer. Chem. Soc., **1970**, 92, 2023-2031.

100. "Excited State Three Ring bond Opening in Cyclopropyl Ketones. Mechanistic Organic Photochemistry. LX," H. E. Zimmerman and T. W. Flechtner, :J. Amer. Chem. Soc., **1970**, 92, 6931-6935.

205. "An Unusual Photochemical Rearrangement; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. W. Binkley, Tetrahedron Letts., 5859-5862, **1985**.

I. The Bicycle Rearrangement

An unusual, remarkably general, rearrangement in which an sp^3 hybridized carbon, bearing two substituents, walked stereospecifically along the surface of a π-system was reported. The reaction was shown to proceed via the singlet excited state. Excited state reaction rates were determined. A series of singlet diradicals were shown to be on the excited state hypersurface. Also, MO and state correlation diagrams were obtained. One interesting facet was the finding that a common diradical structure seemed to be generated from different reactants, but the reactivity differed depending on the mode of diradical formation. The apparent paradox was found to arise from the diradicals having an electronic configuration, S_0 or S_1, depending on it source.

94. "Walk Processes in Photochemical Molecular Rearrangements. A General Photochemical Transformation. Mechanistic and Exploratory Organic Photochemistry. LVIII," H. E. Zimmerman, D.F. Juers, J. M. McCall, and B. Schröder, J. Amer. Chem. Soc., **1970**, 92, 3474-3476.

104. "Competitive Photochemical Pathways in the Di-π-Methane Rearrangement. Exploratory and Mechanistic Organic Photochemistry. LXIII," H. E. Zimmerman, P. Hackett, D. F. Juers, J. M. McCall, and B. Schröder, *J. Amer. Chem. Soc.*, **1971**, *93*, 3653-3662.

165. "Topology of the Photochemical Bicycle Reaction. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and T. P. Cutler, *J.C.S. Chemical Communications*, **1978**, 232-234.

170. "Generality of the Photochemical Bicycle Rearrangement. Exploratory and Mechanistic Organic Photochemistry," H. E. Zimmerman and T. P. Cutler, *J. Org. Chem.*, **1978**, *43*, 3283-3303.

Also Refs [177, 183]

J. Photo-Racemization of Optically Active Biphenyls

It was found that optically active biphenyls photoracemize one-third via intermediate benzvalenes and two-thirds by planarization in the excited state as a consequence of the enhanced π-bond order between the aryl groups.

109. "Duality of Mechanisms in Photoracemization of Optically Active Biphenyls. Mechanistic and Exploratory Organic Photochemistry. LXV," H. E. Zimmerman and D. S. Crumrine, *J. Amer. Chem. Soc.*, **1972**, *94*, 498-506.

K. A 1,3-Vinyl Shift in the Reaction of Acyclic Di-π-Methane Reactant Triplets

Whereas most acyclic Di-π-Methane molecules are unreactive as triplets, two examples are known where the triplet undergoes a 1,3-vinyl migration. For example, 1,1,4-triphenyl-3,3-dimethyl-1,4-pentadiene exhibits a 1,3-shift of the diphenylvinyl group with modest efficiency. 1,1,3,3-Tetraphenyl-5,5-dimethyl-1,4-pentadiene does this in competition with the Di-π-Methane rearrangment.

130. "A Photochemical 1,3-Sigmatropic Vinyl Migration. Mechanistic and Exploratory Organic Photochemistry. LXXXII," H. E. Zimmerman, D. W. Kurtz, and L. M. Tolbert, *J. Amer. Chem. Soc.*, **1973**, *95*, 8210-8212.

See Also Refs. 122 and 185.

L. Excited State Transannular Aryl Migrations

An unusual long-range phenyl migration was encountered in the singlet photochemistry of 1,1,5,5-tetraphenyl-1-pentene. The original purpose of this work was to establish whether a second π-bond was necessary for the Di-π-Methane Rearrangement or if a $\sigma + \pi$ process would lead onwards to product. This reactant, lacking the usual second π-bond, did afford a cyclopropyl product. Rather a C-5 phenyl group migrated to the terminus of the excited diphenylvinyl moiety. The resulting diradical then competitively closed to a 5-ring and also disproportionated.

[Refs 137,209].

M. A Cyclopropyl-π-Methane Rearrangement

It was found that there is a counterpart of the ordinary Di-π-Methane rearrangement in which one π-bond is replaced by a three-ring. In the case of 3-(2,2-diphenylcyclopropyl)-3-methyl-1,1-diphenyl-1-butene the initial bridging between the π-bond and the three-ring leads to a singlet diradical. This affords a cyclobutane photoproduct in analogy to the Di-π-Methane case and also undergoes competitive fragmentation to diphenylethylene and 1,1-diphenyl-4,4-dimethylbutadiene.

Ref [144]

212. "The Aryl Version of the Cyclopropyl-π-Methane Rearrangement; Partitioning of a 1,4-Diradical; Mechanistic and Exploratory Organic Photochemistry," Zimmerman, H. E.; Carpenter, C. W. J. Org. Chem., 1988, 53, 3298-3305.

N. The Vinyl Cyclopropene Rearrangments; Singlet and Triplet

The direct and sensitized reaction of 3-vinylcyclopropenes to afford cyclopentadienes was discovered in 1977. In the case of the singlet reaction, the observation was simultaneous with the work of the Padwa Emory group. The reaction proved to be extraordinarily versatile. For the singlet, two mechanisms were considered by both research groups, one starting with three-ring opening to give a carbene and the other initiated with vinyl-vinyl bridging to give a housane diradical. However, these mechanisms differed only in chronology.

Our own research began to focus on the question of whether the triplet reaction might be proceeding by a fundamentally different mechanism from those considered for the singlet, starting with initial Di-π-Methane bridging. Evidence gradually accumulated for a rather esoteric, third mechanism which accounts for the triplet vinylcyclopropene to cyclopentadiene rearrangement. This involves initial formation of a bicyclobutanyl-carbinyl triplet diradical, central bond fission to afford a cyclobutenyl-carbinyl diradical, and ring expansion to the cyclopentadiene. Perhaps the most convincing evidence was independent generation of the penultimate triplet diradical and finding that its regioselectivity was the same as the original reaction.

155. "The Photochemistry of Vinylcyclopropenes; a New and General Cyclopentadiene Synthesis. Exploratory and Mechanistic Organic Photochemistry," H. E. Zimmerman and S. Aasen, J. Amer. Chem. Soc., 1977, 99, 2342-2344.

164. "Vinylcyclopropene Photochemistry; Photochemistry Applied to Organic Synthesis. Exploratory and Mechanistic Organic Photochemistry," H. E. Zimmerman and S. M. Aasen, J. Org. Chem., 1978, 43, 1493-1506.

174. "Mechanistic and Exploratory Organic Photochemistry. Cyclopropene Studies," H. E. Zimmerman and M. C. Hovey, J. Org. Chem., 1979, 44, 2331-2345.

191. "Photochemical Studies of Cyclopropenes and Cyclopentadienes; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and D. J. Kreil, J. Org. Chem., 1982, 37, 2060-2075.

192. "Cyclopropene Photochemistry. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. A. Bunce, J. Org. Chem., 1982, 47, 3377-3396.

195. "Vinylcyclopropene Triplet Rearrangement Mechanisms; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and S. A. Fleming, *J. Amer. Chem. Soc.*, **1983**, *105*, 622-624.

201. "Diradical Pathways in Vinylcyclopropene Triplet Rearrangements; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and S. Fleming, *J. Org. Chem.* **1985**, *50*, 2539-2551.

N. Photochemistry of Bichromophoric Reactants

A study of enones having C-4 substituents which normally would be considered to be quenching groups, demonstrated that such bichromophoric molecules, if anything, show enhanced reactivity. The low energy triplet moieties prove capable of energy storage. The carbonyl group was noted to be a catalytic center for intersystem crossing by virtue of spin-orbit coupling.

202. "The Photochemistry of a Biphenylyl Substituted Cyclohexenone; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, R. K. King, J-H Xu and C. E Caufield, *J. Amer. Chem. Soc.*, **1985**, *107*, 7724-7732.

203. "Photochemical Rearrangements of Naphthyl-substituted Enones; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, C. E. Caufield and R. K. King, *J. Amer. Chem. Soc.*, **1985**, *107*, 7732-7744.

Ref. [204]

Another phenomenon having to do with bichromophoric reactants concerns the nature of the energy transfer process. Thus it was found that for a bichromophoric system with two bulky acceptor moieties of roughly the same size, the probability of collision and energy transfer to each of the two is about the same.

214. "Photochemical Rearrangements of Molecules Having Quenchers on a Chain; Mechanistic and Exploratory Organic Photochemistry." H. E. Zimmerman and A. M. Weber, *J. Am. Chem. Soc.*, **1989**, *111*, 995-1007.

O. Cyclohexenone Ring Contraction of Cyclohexenones to Vinylcyclobutanones

In those cyclohexenones having a single delocalizing group at carbon-5, [Refs 66, 52] a minor product was a cyclobutanone. When *two* phenyl groups were substituted at C-5, σ-bond-4,5 of 4-methyl-5,5-diphenylcyclohexenone was broken in the n-π^* excited state; this is a vinylous α-expulsion. The triplet diradical thus formed then closed to afford 4,4-diphenyl-2-propenylcyclobutanone. That the diradical was indeed an intermediate was established from the observation of mainly racemized photoproduct starting with optically active reactant.

207. "A Photochemical Reaction Leading from Cyclohexenones to Cyclobutanones; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and R. D. Solomon, *J. Amer. Chem. Soc.*, **1986**, *108*, 6276-6289.

P. 1,2-Alkyl Shifts in Singlet 1,3-Diradicals and a 1,2-Phenyl Shift in a Triplet Diradical

Singlet 1,3-Diradicals may be generated by ring-opening of cyclopropanes. When the central carbon of such diradicals is alkyl-substituted, a 1,2-shift of the alkyl group was noted to occur.

211. "Diradical Rearrangements; An Unusual 1,2-Shift in a Photochemically Generated 1,3-Diradical; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and A. P. Kamath, J. Amer. Chem. Soc., 1988, 110, 900-911.

222. "Rearrangement of 1,3-Diradicals; Arylcyclopropane Photochemistry," Zimmerman, H. E.; Heydinger, J. A. J. Org. Chem., 1991, 56, 1747-1758.

Also See [Ref. 96]

In the case of a triplet 1,3-diradical substituted with a phenyl group on the central carbon, the phenyl group has been observed to migrate to both of the odd-electron centers.

215. "An Assortment of Highly Unusual Rearrangements in the Photochemistry of Vinylcyclopropanes; Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, F. L. Oaks and P. Campos, J. Am. Chem. Soc., 1989, 111, 1007-1018.

Q. Singlet Diradical Behavior with a 1-Electron Center Bonding to the Central Carbon of an Allylic Radical Moiety with 1,3-Allylic Closure

A particularly unusual molecular process has been encountered in several singlet diradical cases. Here an allylic odd-electron moiety was separated from a one-electron center by a single carbon. The one-electron center then bonded to the central carbon of the allylic group while the termini of the allylic group then bonded with formation of a housane. A similar process occurred wherein the odd-electron center transferred a hydrogen atom from an adjacent carbon to the center atom of the allylic system.

Refs [123,124,215]

R. The Reverse Di-π-Methane Rearrangement

S_1 Vinylcyclopropanes with cyano or carbomethoxyl substitution often undergo a "Reverse Di-π-Methane Rearrangement". The reaction begins by "bicycling" of one 3-ring carbon to the adjacent C-C bond to afford a cyclopropyldicarbinyl diradical. Some portion of the cyclopropyldicarbinyl diradical species is formed adiabatically and then rearranges further to afford the isomeric vinylcyclopropane regioisomer while some portion is formed as S_0 and undergoes decay with 1,4-(2,3)-fragmentation to afford Di-π-Methane photoproduct. The formation of regioisomeric vinyl cyclopropane is tantamount to the bicycle rearrangement.

Also Refs [175,183,215]

S. Rearrangement of Type A and Type B (Oxyallyl) Zwitterions

In a variety of systems six-membered ring zwitterions rearrange. The six-membered ring intermediates afford phenols while the bicyclo[3.1.0]hex-

3-en-2-ones undergo a bicycle rearrangement with retention of the original endo-exo stereochemistry. This chemistry is general enough to operate in polycyclic systems.

220. "The Photochemistry of Some Extended π-Systems: Type A and Aryl Migrations of Systems with Extended Conjugation Related to Cyclohexadienones and Cyclohexenones. Mechanistic and Exploratory Organic Photochemistry," Zimmerman, H. E.; Lamers, P. H., J. Org. Chem., **1989**, 54, 5788-5804.

Also Refs [30,54,61,72,77,110,116,182]

T. Photochemical Rearrangement of Acylcyclopropenes to Furans and Acyliminocyclopropenes to Pyrroles

With our finding that vinylcyclopropenes rearrange to cyclopentadienes, we studied the photochemical behavior of acylcyclopropenes and acyliminocyclopropenes. The former rearranged nicely to furans and the latter to pyrroles. The reaction mechanism of the triplets proved different from that of the corresponding vinyl compounds and involved bonding between the three-ring double bond and the carbonyl oxygen or nitrogen.

224. "A New Photochemical Reaction and Its Mechanism: Rearrangement of Acyl and Imino Cyclopropenes", Zimmerman, H. E.; Wright, C. W. J. Am. Chem. Soc., **1992**, 114 363-365.

225. "Novel Rearrangements of Acyl and Imino Cyclopropenes; Multiplicity Dependence and Mechanism", Zimmerman, H. E.; Wright, C. W. J. Am. Chem.Soc., **1992**, 114, 6603-6613.

III. CONFINEMENT CONTROL OF UNIMOLECULAR PHOTOCHEMICAL REARRANGEMENTS

Our group has studied a rather large number of unimolecular photochemical rearrangements in crystalline and polymeric environments. This chemistry has led to different stereochemistry, different regiochemistry, or totally different products than the corresponding solution chemistry. This had literature precedent, especially for bimolecular reactions. However, theoretical and quantitative treatments capable of predicting the reaction course of unimolecular rearrangements had been lacking. Where a rationale had been given, it was an isolated observation for the one case; the tendency was to invoke some specific group-lattice interaction. Thus there was a need for a more general treatment.

We uncovered several modes of predicting the reaction course in confined media. One of these is least motion from reactant to the first reaction intermediate as measured computationally. Another is minimization of overlap of the first reaction intermediate with the crystal lattice determined by X-ray. Again, computational methodology was provided. A third approach [in press] utilized molecular mechanics comparison of relative energies of the reacting species by geometry optimizing the entrapped reacting molecule in a fixed crystal lattice composed of a minimal number of surrounding reactant molecules.

In polymer glasses, designed to wrap reactants and restrict motion, least motion in proceeding from reactant to the first intermediate accounted for the change in reaction course compared with solution.

217. "Confinement Control in Solid State Photochemistry; Photochemistry in a Box", Zimmerman, H. E.; Zuraw, M. J., *J. Am. Chem. Soc.*, **1989**, *111*, 2358-2361.

219. "Photochemistry in a Box; Photochemical Reactions of Molecules Entrapped in Crystal Lattices; Mechanistic and Exploratory Organic Photochemistry", Zimmerman, H. E.; Zuraw, M. J., *J. Am. Chem. Soc.*, **1989**, *111*, 7974-7989.

234. "The Photochemistry of Organic Molecules Entwined in Spiderwebs; the Use of Poly(Methyl Methacrylate) Glass for Restricting Excited State Motion", Zimmerman, H. E.; O'Brien, M. E. *J. Org. Chem.* , **1994**, *59* 1809-1816.

IV. METHODOLOGY

Photolysis Apparatus and Useful Solution Filters

107. "Apparatus for Quantitative and Preparative Photolysis: The Wisconsin Black Box," H. E. Zimmerman, *Mol. Photochem.*, **1971**, *3*, 281-292.

An Electronic Actinometer

161. "An Electronic Actinometer for Quantum Yield Determination," H. E. Zimmerman, T. P. Cutler, V. R. Fitzgerald, and T. J. Weight, *Mol. Photochemistry,* **1977**, *8*, 379-385.

Monitoring Reactions With Absorbing or Quenching Photoproduct

Often a photoproduct competes for light or capture of a triplet sensitizer. An analytical method was provided which permits a linear plot and permits quantum yield determination.

Refs [44,56]

Non-Beer's Law Dependence of Fluorescence on Concentration

In most spectrofluormeters the exit slit is placed halfway along the solution cell. At increasing but low concentrations Beer's Law is followed and the emission intensity increases. As the solute concentration increases, a point is reached where the emission intensity decreases due to absorption in the first half of the cell. A maximum emission is obtained at an optical density of 0.887 and an analytical treatment of the phenomenon was presented in this work.

Refs [146,163]

Detection of Transient Ground State Intermediates by Dynamic Isotopic Mixing

A method of determining if a plausible reaction intermediate is involved depended on running the reaction in the presence of that intermediate isotopicically labeled. Absence of the label in the final product then permits exclusion of involvement of the intermediate. In the later studies, the detailed kinetics were solved in a way permitting quantitative determination of the extent of intervention of the intermediate.

172. "Molecular Control of Excited State Cross-Conjugated Triene Rearrangements. Exploratory and Mechanistic Organic Photochemistry," H. E. Zimmerman and D. R. Diehl, *J. Amer. Chem. Soc.*, **1979**, *101*, 1841-1857.

199. "Dynamic Isotope Dilution as a General Method for Ascertaining Partition of Photochemical Pathways Potentially Utilizing Non-Discernable Intermediates; Application to a New Reaction," H. E. Zimmerman, C. W. Carpenter, A. M. Weber J. Amer. Chem. Soc., 1985, 107, 1073-1075.

See also Ref. [209]

Dissection of Singlet and Triplet Contributions to Reactions; The Bracketing Relationship

196. "The Photochemistry of Phenanthrene-substituted Molecules," H. E. Zimmerman and G-S. Wu, Canadian J. Chem., 1983, 61, 866-871.

Refs for more general cases [51,168,187,192]

V. REVIEWS

35. "A New Approach to Mechanistic Organic Photochemistry," H. E. Zimmerman, in "Advances in Photochemistry," Editors: A. Noyes, Jr., G. S. Hammond and J. N. Pitts, Jr., Interscience, Vol. 1, 183-208, 1963.

43. "A Report on Recent Photochemical Investigations," H. E. Zimmerman, Pure and Appl. Chem., 1964, 9, 493-498.

53. "Interpretation of Some Organic Photochemistry," H. E. Zimmerman, Science, 1966, 153, 837-844.

67. "Molecular Details of Photochemical Transformations," H. E. Zimmerman, Photochem. and Photobiol., 1968, 7, 519-523.

76. "Mechanistic Organic Photochemistry," H. E. Zimmerman, Angewandte Chemie, 1969, 81, 45-55. Internat. Ed., 1969, 8, 1-11.

129. "The Di-π-Methane and Oxa-di-π-Methane Rearrangements," S. S. Hixson, P. S. Mariano, and H. E. Zimmerman, Chem. Revs, 1973, 73, 531-551.

134. "Stereochemistry as a Probe for Photochemical Reaction Mechanisms," H. E. Zimmerman, Tetrahedron, Van't Hoff - Le Bel Memorial Issue, 1974, 30, 1617-1628.

149. "Di-π-Methane Rearrangement," H. E. Zimmerman and D. Döpp, Houben-Weyl, Methods of Organic Chemistry, G. Thieme Verlag, 1975, 413-448.

150. "Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, Science, 1976, 191, 523-528.

156. "Recent Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman, Pure and Appl. Chem., 1977, 49, 389-398.

179. "The Di-π-Methane (Zimmerman) Rearrangement," H. E. Zimmerman in "Rearrangements in Ground and Excited States," Vol. 3, Edited by P. DeMayo, Academic Press, New York, 1980.

188. "Topics in Photochemistry," H. E. Zimmerman, *Topics in Current Chemistry*, **1982**, *100*, 45-73, Springer-Verlag, Heidelberg-New York.

193. "Some Theoretical Aspects of Organic Photochemistry," H. E. Zimmerman, *Accts. of Chem. Research*, **1982**, *10*, 312-317.

194. "The Bicycle Rearrangement. A Review," H. E. Zimmerman, *Chimia*, **1982**, *36*, 423-428.

223. "The Di-π-Methane Rearrangement", H. E. Zimmerman, *Organic Photochemistry 11*, **1991**, Marcel Dekker, Inc., New York, Ed. A. Padwa.