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WISCONSIN UNIV-MADISON DEPT OF CHEMISTRY

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A STUDY OF PHOTOPHYSICAL PROCESSES OF EXCITED STATES IN PHOTOCH--ETC(U)

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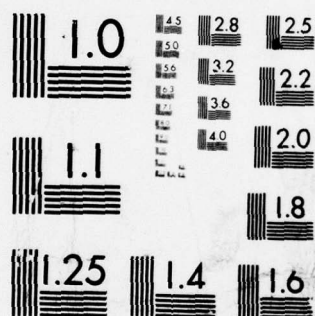
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A STUDY OF PHOTOPHYSICAL PROCESSES OF
EXCITED STATES IN PHOTOCHEMISTRY.

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List of Students Supported During Period 9/1/75-8/31/78

Steven M. Aasen - Now at MMM Company

Donald R. Diehl - Now at Eastman Kodak

Thomas P. Gannett - Presently writing his Ph.D. thesis

Gary E. Keck - Now Asst. Prof. at Univ. of Utah

Robert T. Klun - Now at Dow Chemical Co.

Mark G. Steinmetz - Now Postdoctoral student at Johns Hopkins

Thomas R. Welter - Now at Eastman Kodak Co.

Jeffrey Blood - Graduate student

John Penn - Graduate student

Rhonda Factor - Graduate student

Richard Bunce - Graduate student

Dennis Kreil - Graduate student

Gary Mong - Graduate student

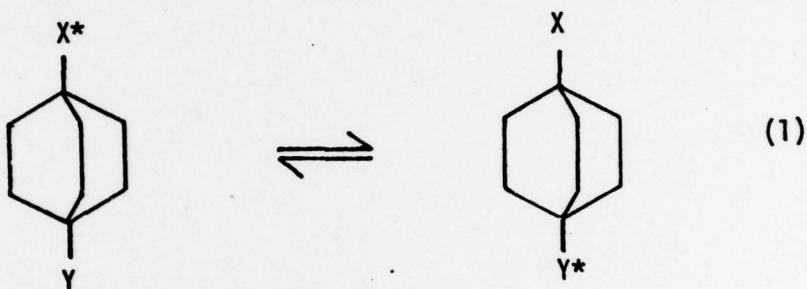
Linus Linder - Graduate student

Robert Pasteris - Graduate student

Jeffrey Moore - Graduate student

Summary of Research Accomplished

1. One interest we have had is the measurement of energy dissipation and transfer in rigid systems. Through our synthetic efforts we have had available "rod-like" compounds consisting of bicyclo[2.2.2]octane units attached bridgehead to bridgehead and with groups X and Y at the terminal bridgeheads. Thus far we have obtained [1]-rods, [2]-rods and have our synthesis of [4]-rods under control. Our work thus far has been heaviest in [1]-rods having α -naphthyl and β -naphthyl groups at one end of the rod (i.e. as group X) and different groups at the other end as group Y. We are interested in transfer of electronic and vibrational excitation from one end of the rod to the other; note equation 1.



Our initial results are summarized in Tables 1 and 2.

TABLE 1. Intramolecular energy exchange rates



Ar	X	SINGLET LIFETIME ^a	λ EMISSION
α -Naphthyl	H	65.1 nsec	335 nm
β -Naphthyl	H	64.2 nsec	332 nm
β -Naphthyl	β -Naphthyl	64.2 nsec	332 nm
α -Naphthyl	Cis-Propenyl	64.7 nsec	335 nm
α -Naphthyl	Acetyl	1.84 nsec	320-335 nm
		4.39 nsec	390-405 nm
β -Naphthyl	Acetyl	0.28* nsec	330 nm
		3.68 nsec	400 nm
α -Naphthyl	Benzoyl	0.23 nsec	331 nm
β -Naphthyl	Benzoyl	0.10 nsec	331 nm

*0.16 nsec when excited at 265 nm; 0.36 nsec when excited at 285 nm.

^aExcitation at 275 nm except where noted.

TABLE 2. Singlet lifetimes with variation of excitation wavelength

Ar	X	EXCITATION	SINGLET LIFETIME
β -Naphthyl	Acetyl	265 nm	0.16 nsec
		275 nm	0.23 nsec
		285 nm	0.36 nsec
α -Naphthyl	Cyclohexane-carbonyl	270 nm	0.56 nsec
		280 nm	0.62 nsec
		290 nm	1.1 nsec

Inspection of the results obtained thus far reveals that having two, equivalent groups at the ends of the rod, does not lead to energy wastage by degenerate energy transfer (i.e. with both ends being naphthyl). Also energy is not transmitted non-vertically from naphthyl to the higher energy propenyl group; no lifetime shortening or cis-trans isomerization was observed. However, dramatically, the lifetime of the naphthyl end is diminished by a low energy acceptor as acetyl or benzoyl at the other end of the [1]-rod. New emission, characteristic of the acetyl group, demonstrated that the diminution of the naphthyl S_1 lifetime was due to energy transfer. Concentration independence showed that the transfer was indeed intramolecular.

A further exciting result was the observation that the lifetime of the S_1 naphthyl end could be diminished by use of decreasing wavelengths of excitation (note Table 2). One rationale is that a vibrationally hot, electronically excited naphthyl group transfers energy before it thermally equilibrates and does so more efficiently when vibrationally hot. Another possibility is that excitation of the L_a band of the naphthyl group allows more efficient dipole-dipole interaction; note conformation B in Figure 1 below. This fits the observation of a shorter lifetime in the β -naphthyl than the α -naphthyl acyl and aroyl derivatives.

We are pursuing these leads and are studying the longer rod systems (i.e. [2]-rods, [4]-rods) as well as looking at the interaction of different types of end groups.

Our preliminary results have been published (ref. 156 in attached full bibliography).

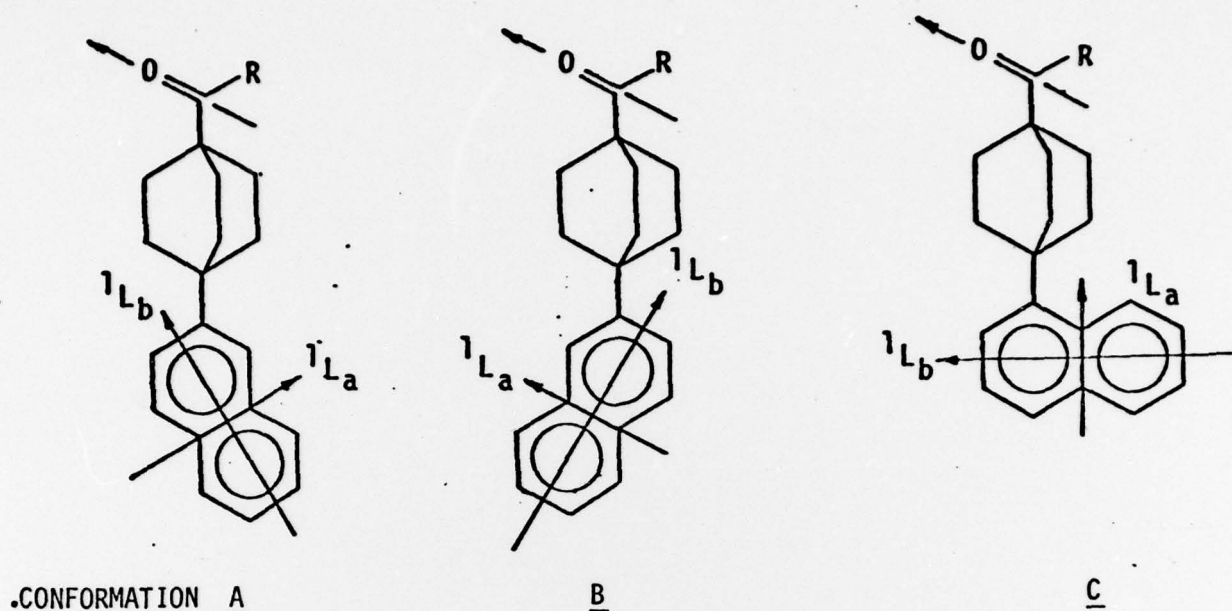
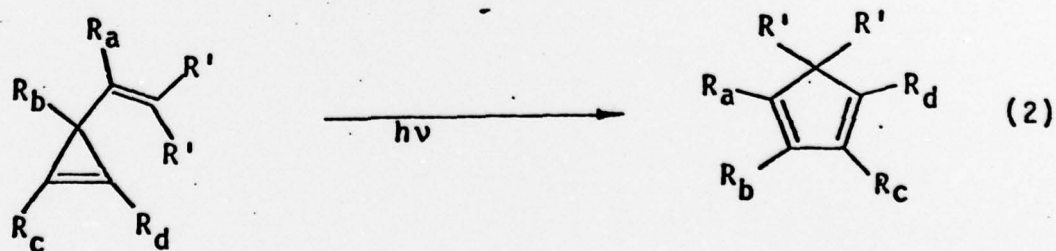


Figure 1. Some possible conformations and relationships between the transition dipoles of naphthyl and acyl groups

2. Another area of interest to us has been the study of excited singlet π - π interactions. Thus, when one of the two π -chromophores is electronically excited it may interact with a second π -system in the molecule.

One intriguing reaction we uncovered involves the direct photolysis of vinyl substituted cyclopropenes. This leads to cyclopentadienes as shown in equation 2.



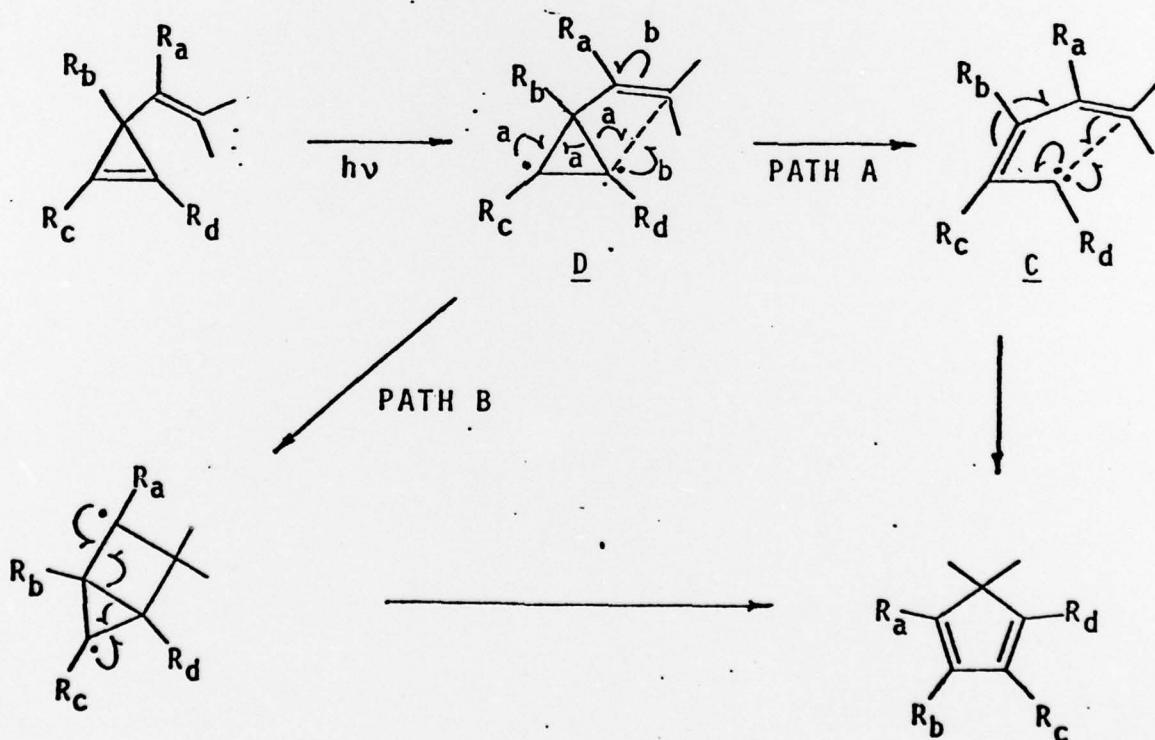
$R_a, R_b, R_c, R_d = \text{Ph}; R' = \text{H}$
 $R_a = \text{H}; R_b, R_c, R_d = \text{Ph}; R' = \text{H}$
 $R_a = \text{H}; R_b, R_c, R_d = \text{Ph}; R' = \text{CH}_3$

$\phi = .049$
 $\phi = .027$
 $\phi = .010$

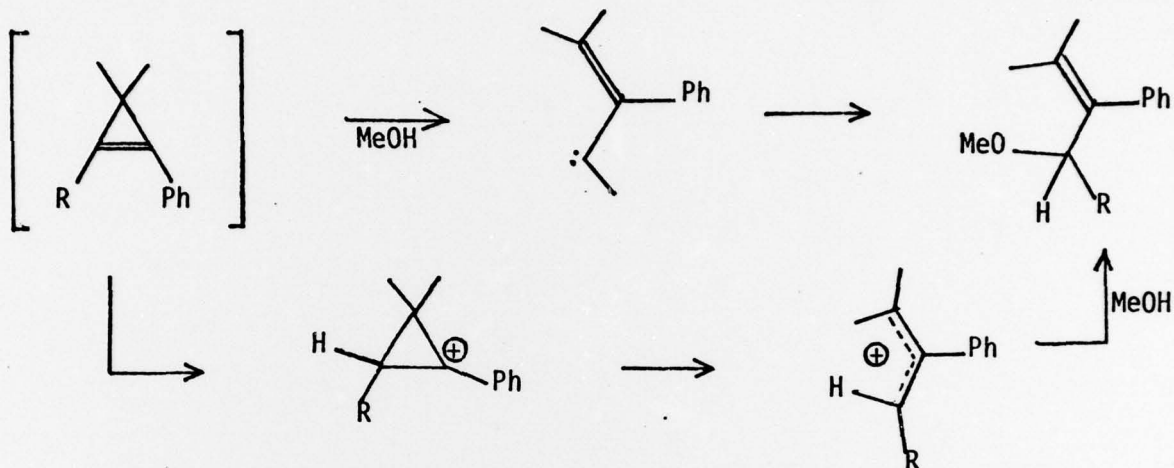
The quantum yields were found to be a function of substitution as shown. Interestingly, the efficiency was increased with phenyl substitution as R_a . Terminal methyl substitution on the vinyl group (i.e. as R') diminished the efficiency.

Two mechanisms are shown in Chart 1. One mechanism involves excited state bridging between the two ethylenic chromophores; this is labeled PATH B. The second mechanism begins with carbene formation followed by five ring formation; this is labeled PATH A. While clear evidence is not yet available to distinguish these mechanisms, the pattern of effects of substitution on efficiency suggests that PATH B is the correct one. Thus, phenyl substitution as R_a would stabilize odd electron density in the bicyclo[2.1.0]biradical formed by bridging. The carbene mechanism does not offer a similar source of this substituent effect. Also the decrease of efficiency with terminal methyl substitution would make sense in MECHANISM B as a steric effect; and a parallel rationale does not derive nicely from MECHANISM A since ring closure would occur only after the high energy carbene intermediate had already been formed. Finally, where $R_c = \text{Ph}$ and $R_d = t\text{-Bu}$, the more stable diradical D is formed in MECHANISM B but the less stable carbene C in MECHANISM A.

CHART 1. Two mechanisms for the cyclopropene to cyclopentadiene rearrangement



The problem is a complex one with evidence pointing towards and against both mechanisms. For example, Padwa has shown that irradiation of cyclopropenes in methanol does give adducts which can be construed as coming from formation and capture of the less stable of two carbenes. On the other hand, the products may come instead from protonation of the cyclopropene styryl bond, in analogy to work of Hixson and Kropp, followed by cyclopropyl cation opening.



Arguing against a simple carbene mechanism is our observation that carbenes generated thermally from the vinylcyclopropenes give cyclopentadienes but with regioselectivity reversed from the photochemical reaction. Furthermore, the selectivity is not temperature dependent. One might be inclined to conclude that if carbenes are generated thermally, they cannot be involved in the photochemical run where different behavior is found. The problem is that more than one electronic configuration of the carbene are possible.

A further finding of considerable interest is the observation that those cyclopropenes having unsubstituted vinyl groups (i.e. $\text{CH}_2=\text{CH}-$) react preferentially by way of the excited singlet and have unreactive triplets while, in contrast, those cyclopropenes having isopropylidene moieties react especially efficiently by way of the triplets (ϕ circa 0.13) while the singlets react with considerably less efficiency ($\phi = .01$ and below).

It is clear that there are many unanswered questions concerning this new reaction, and we are continuing efforts directed towards a solution. (Our preliminary results are published in reference 155 of attached full bibliography.)

3. In another study we have investigated the behavior of cyclopropyl-dicarbonyl diradicals which are involved in a number of photophysical and photochemical processes. For this, we artificially generated these biradicals from azoprecursors.

The three azo compounds shown in Chart 2 were used to generate the corresponding diradicals. These diradicals have been postulated by us as involved in the di- π -methane rearrangement of barrelene derivatives.

Chart 2 describes the behavior of the azo compounds under thermal, direct photolytic and sensitized photolytic conditions. The most important observation is that thermally the azo compounds revert to the barrelene relatives while on irradiation semibullvalenes, observed in barrelene photochemistry, are among the products. From the sensitized runs, the semibullvalene products are major products. This is in agreement with the photochemistry of barrelenes where it is the triplet which rearranges.

Although the azo chemistry may involve nitrogen in the transition state, especially in the case of the ground state process which is most likely a simple electrocyclic reverse Diels-Alder, the diradicals and species (e.g. transition states) incorporating nitrogen are electronically similar and should prove analogous in behavior. Our results on this problem have been published (references 147 and 153).

4. A particularly fruitful area has been correlation of excited singlet reaction rates of di- π -methane rearrangements with some new theory developed.

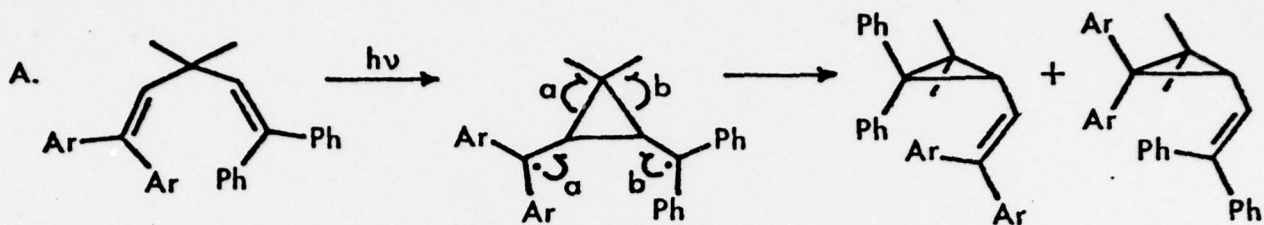
Three types of di- π -methane rearrangements are tabulated in Chart 3. These include two types of vinyl-vinyl methanes and one type of aryl vinyl methane. The rates were determined by single photon counting.

The unusual features are regioselectivity effected by cyano and methoxy substitution and the effect of substituents on the excited singlet reaction rates. Our efforts at understanding the substituent effects led to some new photochemical theory.

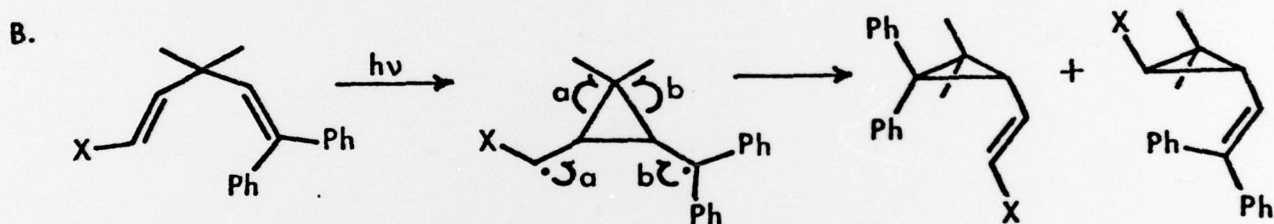
The first striking observation was the regioselectivity. Throughout, cyclopropyldicarbonyl diradical ring opening (path b) retaining cyano or *p*-cyanophenyl stabilization of a diradical center is observed rather than opening to give a diphenyl stabilized diradical center (path a). Similarly, retention of a diphenyl stabilized diradical center (path a) is favored over methoxy or *p*-methoxyphenyl stabilization (path b). Dimethylaminophenyl effected complete regioselectivity in the same direction as *p*-methoxyphenyl. *m*-Methoxyphenyl selectivity was weaker but similar to that of *p*-cyanophenyl. In series A (note Chart 3), the log of the regioselectivity (i.e. $\log R_x$ in Figure 2 and Table 2) proved to be linear with the (ground state!) Hammett sigma constant with a slope of $\rho = -2.07$. The same effect is seen qualitatively to control the regioselectivity of series B while in series C rearomatization dominates.

That there is a correlation with ground state sigma constants is remarkable, since a basic question in photochemistry is when excited state substituent effects will be observed rather than ground state behavior. This is discussed below. Another point is that the negative ρ constant signifies that in the three-ring opening step the carbonyl carbon generating the vinyl group of product becomes very electron deficient compared to the carbonyl carbon becoming part of the product three-ring.

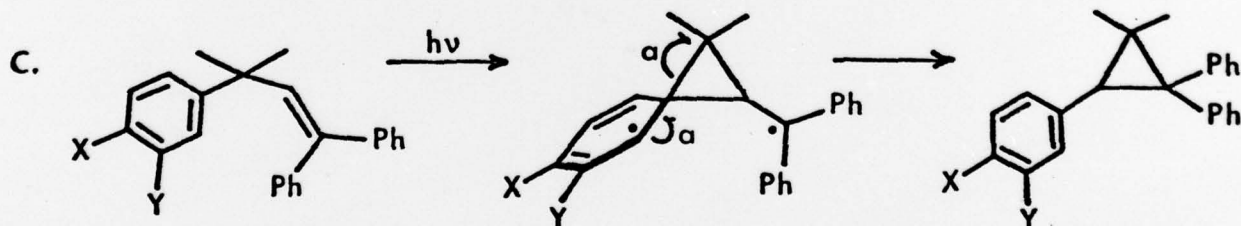
CHART 3. Three types of di- π -methane rearrangement.



	Ar	$^1k_r(\text{sec}^{-1})$	Φ (path a)	Φ (path b)
1	Ph	1.4×10^{11}	0.082	---
2	<i>p</i> -MeOPh	3.4×10^9	0.075	0.022
3	<i>p</i> -Me ₂ NPh	5.4×10^7	0.0027	not observed
4	<i>p</i> -NCPh	2.2×10^{11}	not observed	0.094
5	<i>m</i> -MeOPh	8.8×10^9	0.072	0.086



	X	$^1k_r(\text{sec}^{-1})$	Φ (path a)	Φ (path b)
6	H	4.7×10^8	0.011	not observed
7	OMe	1.9×10^9	0.051	not observed
8	CN	1.5×10^{10}	not observed	0.35



	X	Y	$^1k_r(\text{sec}^{-1})$	Φ
9	H	H	1.8×10^9	0.036
10	OMe	H	9.5×10^9	0.058
11	H	OMe	1.3×10^9	0.024
12	CN	H	2.1×10^9	0.044

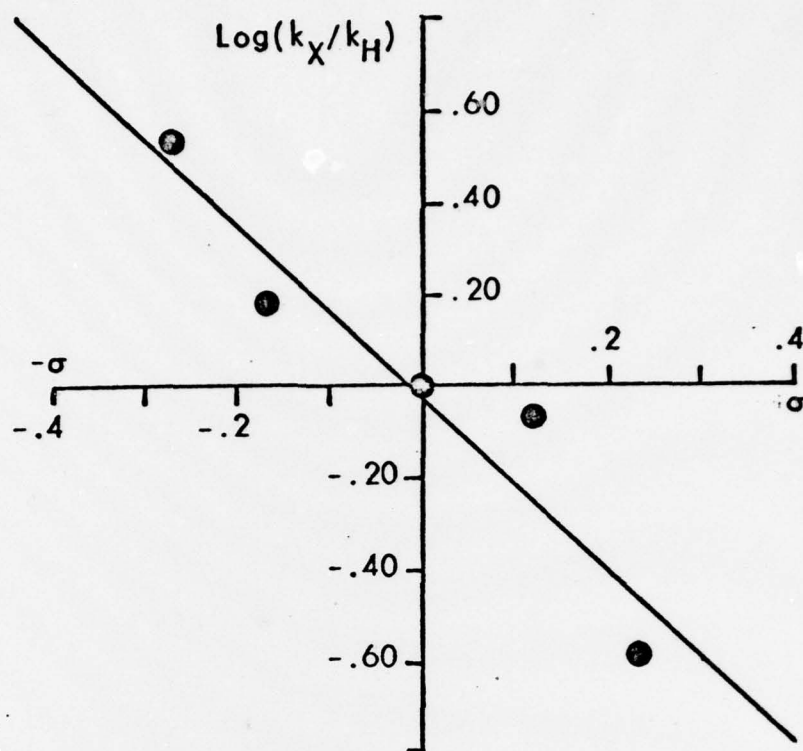


FIGURE 2. Plot of $\text{Log } R_X = \text{Log}(k_X/k_H)$ vs Hammett Sigma, σ . Correl. Coeff. = 0.96

TABLE 2. Regioselectivity and the Hammett Sigma Constant.

Reactant	$R_X = (k_X/k_H)^a$	$\text{Log}(k_X/k_H)$	σ_X
Di- <u>p</u> -methoxy Diene <u>2</u>	3.41	0.532	-0.27
Di- <u>p</u> -methyl Diene <u>13</u>	1.52	0.182	-0.18
Tetraphenyl Diene <u>1</u>	1.00	0.000	0.00
Di- <u>m</u> -methoxy Diene <u>5</u>	0.84	-0.076	0.12
Di- <u>p</u> -chloro Diene <u>14</u>	0.25	-0.595	0.23

a. Ratio obtained from ratio of photoproduct quantum yields.

Turning to the S_1 rates (note Chart 3), we find a dramatic spread ranging from circa 10^7 sec^{-1} for the bis-dimethylaminophenyl compounds of series A to 10^{11} for the bis-*p*-cyanophenyl analogs. Yet the pattern of substituent effects was not the same for the three series. *p*-Dimethoxy accelerated the rate in series C while inhibiting the rate in series A. Cyano substitution led to increases in excited state reactivity in all series.

We performed SCF-CI calculations (up to 100 singly and 5050 doubly excited configurations) on the energy required to lead from the vertically excited state of all reactants to the cyclopropyldicarbonyl diradicals. Comparison of the experimental rates with the calculated bridging energies revealed a linear relation between the log of the S_1 reaction rates and the theoretical ΔE 's (note Figure 3). Each series had its own slope as would be expected if the excited state transition state more closely approximated the diradical in one case (series A).

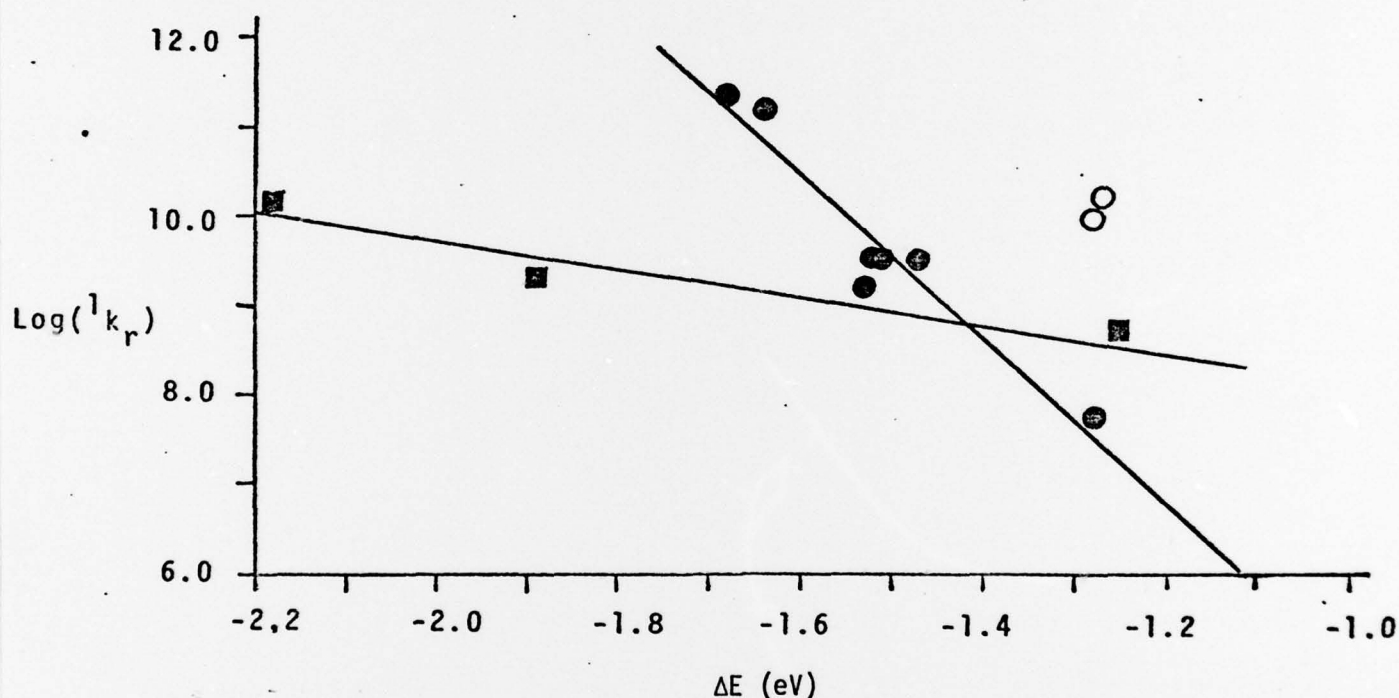


FIGURE 3. Correlation Between $\text{Log}(1/k_r)$ and Bridging Energies for Systems A and B. Correlation Coefficient (excluding meta compounds) = 0.96 for series A and 0.91 for series B.

● Series A (para), ○ Series A (meta), ■ Series B.

From our calculations and the experimental results several new photochemical theoretical concepts were derived. To begin with, we needed a simple way of determining the distribution of electronic excitation in a photochemical reactant and also in the molecule along the reaction hypersurface. Thus, comparison of the excited state and ground state wavefunctions obtained in our calculations revealed that these wavefunctions often did not differ everywhere in the molecule but rather just in portions; but such direct comparison is cumbersome. A simple approach was obtained by subtracting the ground state bond orders from the excited state values. For every pair of

orbitals, r and t , the change in bond order on electronic excitation is then $\Delta P_{rt} = P_{rt}^* - P_{rt}^0$. Where the bond order change is zero, the molecule is inappreciably excited. Where ΔP_{rt} is negative the molecule is excited and becomes more antibonding in the excited state. Where it is positive the molecule has become more bonding, and again there is excitation concentrated.

Applied to the di- π -methane rearrangements studied here, we found that the locus of excitation in the reactants corresponded to the lowest energy (longest wavelength) chromophore in accord with intuition. In the cyclopropyldicarbonyl diradical formed on excited state bridging, the energy of excitation was found concentrated in the cyclopropyldicarbonyl moiety rather than in the aryl groups. The flow of excitation energy is shown for one case in Figure 4 below.

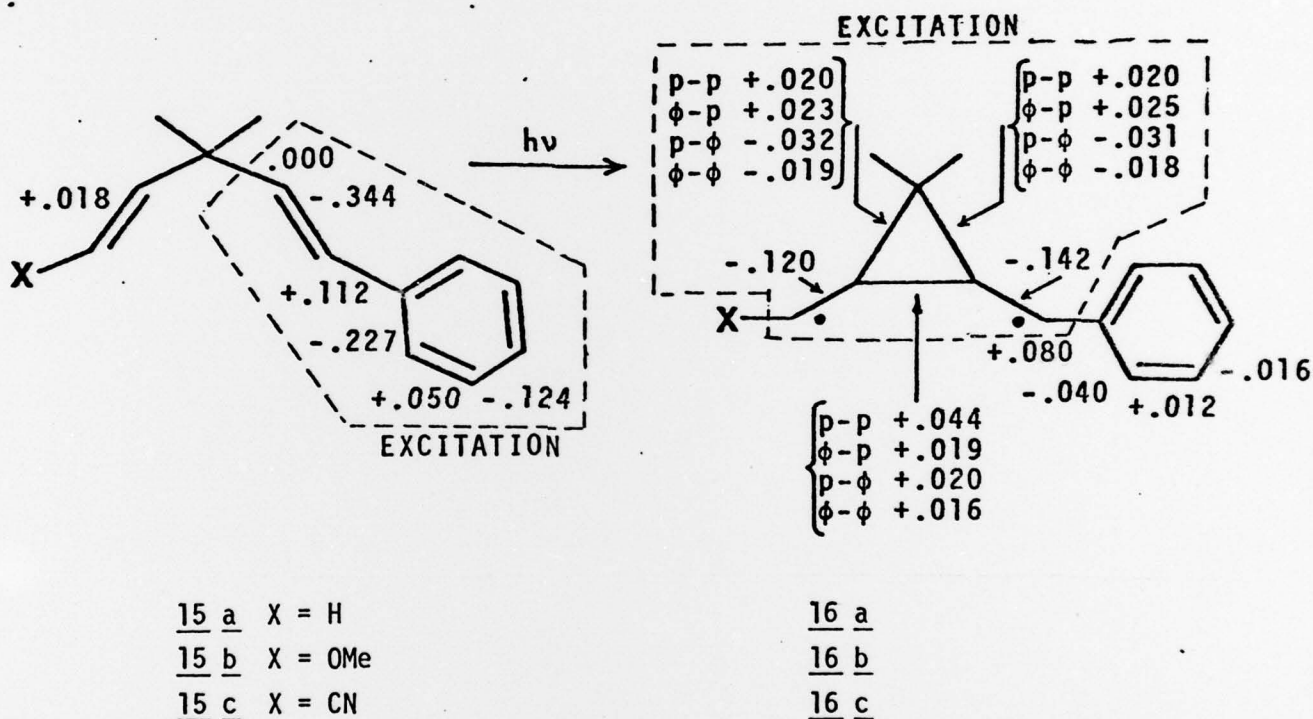


FIGURE 4. ΔP_{rt} 's for the bridging process. The numbers given apply only to 15 a and 16 a but these are similar to those for the remaining two cases. $p-p$, $p-\phi$, $\phi-p$, $\phi-\phi$ refer to overlap between p -orbitals and/or hybrids. In the $p-\phi$ and $\phi-p$ cases, the first symbol refers to the orbital at the methane carbon. Conformation with carbonyl p and walsh three ring p orbitals coplanar. Excitation heaviest in dotted areas.

This flow of excitation from the lowest energy reactant chromophore into the cyclopropyldicarbonyl diradical was used to understand the anomalous excited state inhibition by p -methoxy and p -dimethylamino in series A of Chart 3. This inhibition was found both experimentally and in the calculations; it was necessary only to dissect the source of the effect from the calculations.

Such a dissection revealed that the inhibition (i.e. slow rates) of the reactions in the dimethylamino and p-methoxy examples of series A was due to excessive vertical excited state stabilization by these groups when substituted on the chromophore shown to be perturbed by electronic excitation. This made the ΔE 's of excited state bridging much less favorable. In the case of series B and C, our ΔP treatment showed that the substituents were not on the chromophore having the excitation and did not diminish the rate. Rather the effect was a lowering of the diradical energy after bridging.

This situation is summarized in Figure 5 where the different vertical excited state energies are seen to vary more with substitution than do the cyclopropyldicarbonyl diradical energies.

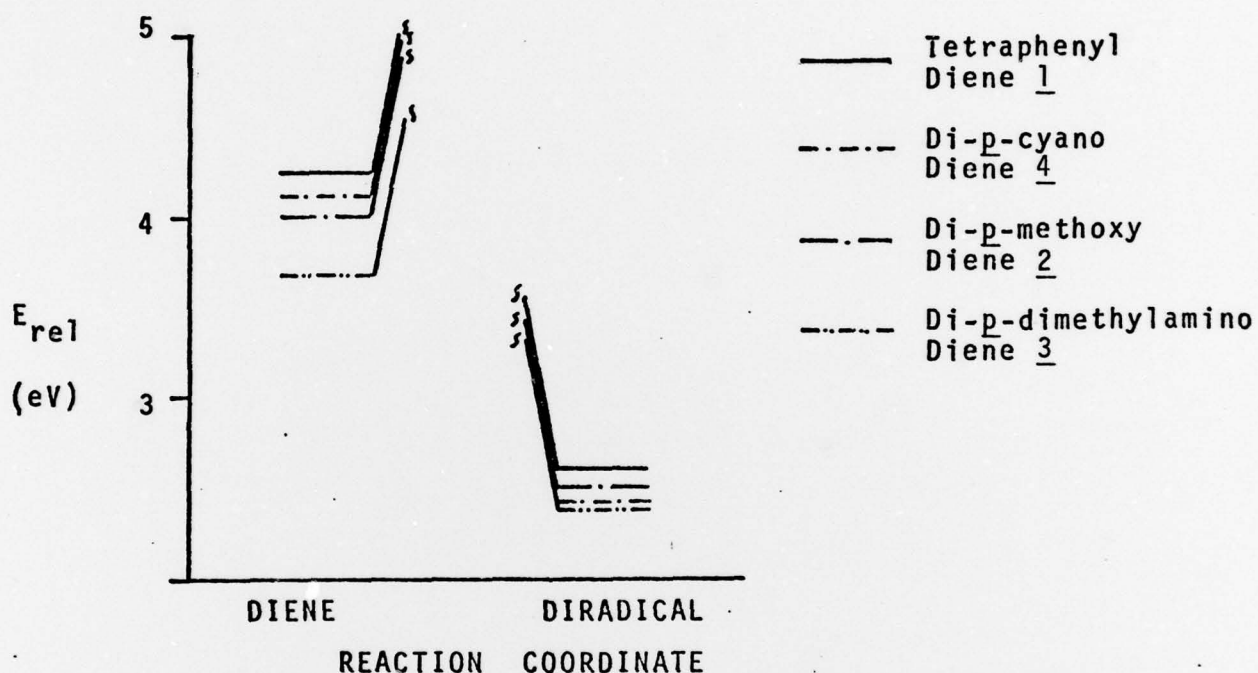


FIGURE 5. Energetics of Bridging

The concept of vertical excited state energy affecting excited state rates is a new one and promises to be generally useful.

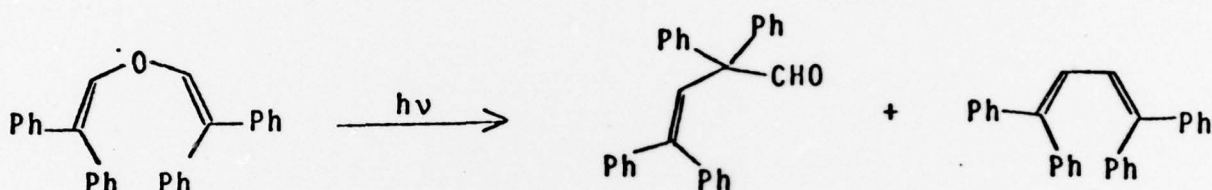
A further point of interest is the observation that throughout, ground state substituent effects are observed. Thus, ground state Hammett sigma constants correlate with regioselectivity. Also, stabilization of the intermediate cyclopropyldicarbonyl diradical centers is better by para than meta substituents. This ground state para-transmission is not always the case in photochemistry; many years ago we noted that meta-transmission is characteristic of excited aromatic rings. However, in the present chemistry our ΔP treatment reveals that these aromatic moieties are no longer excited portions of the molecule at that point along the reaction coordinate where the substituent becomes determining in the regioselectivity or in diradical

stabilization. Hence the ΔP matrix treatment is able to discern the extent to which excited state or instead ground state behavior is anticipated.

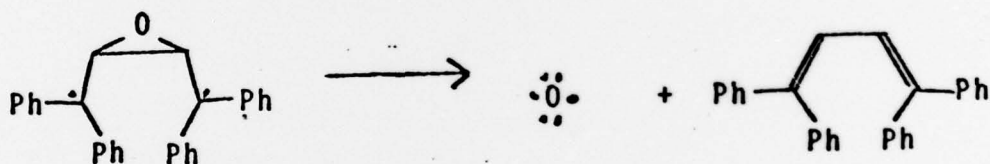
This work is in press (accepted) in Communication form in Chemical Communications and also described in two JACS full papers (accepted).

5. Another area in which we have been working has been on the formation and behavior of oxygen analogs of the cyclopropyldicarbonyl diradical.

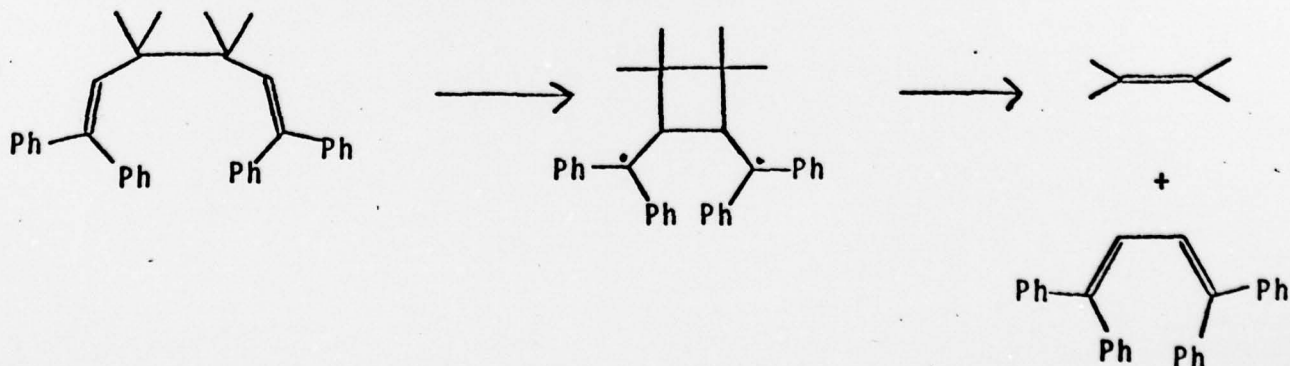
One interesting result is the photolysis of the oxygen analog of 1,1,5,5-tetraphenyl-3,3-dimethyl-1,5-pentadiene which has received so much study. The reaction was found to give two major products: a tetraphenyl aldehyde derived from a 1,3-vinyl migration and tetraphenylbutadiene.



The tetraphenylbutadiene seems to arise from the diradical derived from excited singlet π - π bridging. This involves oxygen atom expulsion, and we are now in the process of proving this point.



6. In an unusual reaction we have found the diene below to give a fragmentation affording tetramethylethylene and tetraphenylbutadiene. This is reminiscent of the oxygen expulsion described above.



The most reasonable mechanism for the process involves the diradical shown.

7. In other research which is in its early stages we have been investigating photochemistry effected by a 1 Megawatt NRG Nitrogen laser. Our intent is to study intensity effects on the course of solution photochemistry with a special interest in two photon absorption. We have developed a flow apparatus allowing the laser beam to be focussed on a very small volume of solution with the aim of maximizing the photon flux. At the present we know only that products not obtained under normal photochemical conditions are obtained, and we are in the process of determining product structures.

8. Also in its very beginning stages is our work on picosecond spectroscopic measurement of ultrarapid excited state events. One aim is to check the validity of our single photon counting measurements. Another is to penetrate to the femtosecond (i.e. 10^{-15} sec) region. Thus far we have been able to synchronously pump a dye laser using a mode-locked Argon-Ion laser. We have developed an optical arrangement allowing us to use our mini-computer facilities to control translation stages and to collect and signal average data. Our resolution has been improving rapidly with experience and our latest measurements indicate that our pulse width is below 10 picoseconds. For determination of ultrarapid pulses we have constructed an autocorrelating interferometer (i.e. autocorrelating the circa 3 mm long "light bullets"). These results are obtained on ultraviolet pulses resulting from frequency doubling. Our efforts on picosecond spectroscopy are being applied in two ways. One is in a study of relaxation phenomena including energy degradation; this is ARO supported. The other is in the investigation of rearrangement mechanisms supported by the NSF.

9. We have initiated some efforts on tri-Pi-methane systems. Thus far we have mainly been involved in the synthetic approaches to the reactants.

10. We have been studying the generation of excited state intermediates by indirect means and have had some success in this direction. We are continuing these efforts.

11. Another area of interest to us has been the photochemistry of systems with bichromophoric groups which can react in the excited state. We have begun some efforts in this direction. This is in its early stages.

Summary. It is to be recognized that the present period covers just three years. Yet, a remarkable number of exciting results have accumulated, and a number of publications have resulted. It is seen that our efforts have been especially productive and exciting.

Research Publications

1. "A Photochemical Rearrangement without Light. Dioxetane Effected Photochemistry by Direct Intramolecular Excitation," H. E. Zimmerman and Gary E. Keck. J. Amer. Chem. Soc., 97, 3527 (1975).
2. "Conformation and Di- π -Methane Reactivity. Mechanistic and Exploratory Organic Photochemistry," H. E. Zimmerman and Laren M. Tolbert. J. Amer. Chem. Soc., 97, 5497 (1975).
3. "Generation of Photochemical Species on Ground, Excited Singlet, and Triplet Hypersurfaces in Barrelene Photochemistry," H. E. Zimmerman, Robert J. Boettcher, Niklaus E. Buehler, and Gary E. Keck. J. Amer. Chem. Soc., 97, 5635 (1975).
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