Scheme XV

65 R' = H,Me   66

67a: 1-OMe, R' = H
67b: 1,3-diOMe, R' = Me
67c: 1-OMe, 2,3-OCH₂O-, R' = Me

Tandem metalation of α- and β-naphthamides leads largely to phthalide products, e.g., **64**, suggesting ineffectiveness of the second metalation step. Nonetheless, the phthalides are useful intermediates for conversion into quinone products by conventional methods.[26a,50]

Ortholithiated benzamides are also useful for the preparation of acridones as illustrated by the formation of **67** (Scheme XV).[53] The copper coupling reaction, based on the work of Yamamoto,[54] is very sensitive to the purity of the cuprous chloride used in the preparation of the copper anilides **65** from the corresponding lithiated species and appears to be more seriously inhibited by steric effects than reactions of ortholithiated benzamides with other electrophiles. Since direct Friedel–Crafts cyclizations of **66** to **67** can be achieved, the overall sequence provides ready access to unusually substituted acridones, including acridone alkaloids, e.g., evoxanthine **67c**.

Concluding Remarks

The tertiary amide, together with secondary amide, thioamide, and oxazoline structures, offer a flexible range of ortho metalation directing groups for appli-

cation in synthetic endeavors. Advantages of the tertiary amide include ease of preparation, priority over other directors with sec-BuLi/TMEDA at −78° in THF, utility in polysubstituted aromatic systems, and resistance to nucleophilic attack. Indeed, its principal disadvantage is resistance to hydrolysis.

The present Account demonstrates the use of the readily available alkoxybenzamides in lithiation–substitution sequences for the regiospecific synthesis of a variety of polysubstituted aromatics. The amide facilitates further manipulation of the introduced electrophiles to allow ortho carbon chain extension and cyclization to carbocyclic and heterocyclic systems including a variety of natural products. The use of ortholithiated tertiary benzamides in tandem metalation sequences is a particularly efficient approach to the synthesis of carbocyclic and heterocyclic benzoquinones.

The development of ortholithiated tertiary amides is part of a generally renewed interest in directed metalations.[15] Promising developments have been forthcoming, and new approaches and applications can be anticipated.[55]

(53) Iwao, M.; Snieckus, V., unpublished results.
(54) Yamamoto, H.; Maruoka, K. *J. Org. Chem.* 1980, 45, 2739.

(55) For recent examples, see lithiations of (arene)chromium tricarbonyl complexes: Semmelhack, M. F.; Bisha, J.; Czarny, M. *J. Am. Chem. Soc.*, 1979, 101, 768. Card, R. J.; Trahanovsky, W. S. *J. Org. Chem.* 1980, 45, 2560. Fukui, M.; Ikeda, T.; Oishi, T. *Tetrahedron Lett.* 1982, 1605. The use of ortholithiated sulfonic acids for the regiospecific synthesis of meta-substituted benzenes: Figuly, G. D.; Martin, J. C. *J. Org. Chem.* 1980, 45, 3728. Lithiation of aminopyridines: Tamura, Y.; Fujita, M.; Chen, L.-C.; Inoue, M.; Kita, Y. *Ibid.* 1981, 46, 3564.

Some Theoretical Aspects of Organic Photochemistry

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Until 1960 organic photochemistry was only an occasionally studied field. This stemmed partly from the feeling that photochemical reactions were random and unpredictable. It was often stated that reactions oc-

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curred by virtue of the high energy imparted to reacting molecules by light photons absorbed. In 1960, the author[1-6] suggested that despite the high energy of excited states, these molecules did not react indiscriminately but, rather, transformed themselves by continuous electron redistribution, seeking out low-energy pathways and avoiding high-energy routes. Controlled by the same forces as ground-state reacting species, the energy

(1) Zimmerman, H. E. Abstracts of the 17th National Organic Symposium, Bloomington, IN, 1961, p 31.
(2) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* 1961, 83, 4486–4487.
(3) Zimmerman, H. E.; Schuster, D. I. *J. Am. Chem. Soc.* 1962, 84, 4527–4540.
(4) Zimmerman, H. E. *Adv. Photochem.* 1963, 1, 183–208.
(5) Zimmerman, H. E. *Tetrahedron Suppl.* 1962, 2, 393–401.
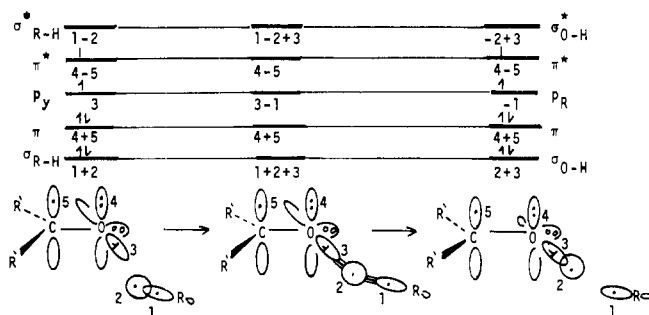(6) Zimmerman, H. E. *Pure Appl. Chem.* 1964, 9, 493–498.

Figure 1. Correlation diagram for hydrogen abstraction.

of excitation of molecules in solution is not directly available for random reaction. Beyond this, it was postulated that, given an excited-state structure, organic chemical intuition (e.g., electron pushing) would suffice to rationalize, if not predict, photochemical reactions. For example, a variety of photochemical reactions of carbonyl group containing molecules was related to simple three-dimensional representations of the excited state.[1-4,6,7] Similarly, the phenomenon of aromatic excited-state meta transmission was derived from simple MO considerations.[1,5,7-10] In the case of bond orders, similar reasoning proved useful and led the author in 1961 to rationalize the ubiquitous photochemical cyclization of butadiene to cyclobutenes,[1] the key step of cyclohexadienone rearrangements,[1,2,6,11-18] and the bridging step of the di-π-methane rearrangement.[19-21] The purpose of this Account is to relate some of our more recent theoretical work that has proven useful in organic photochemistry.

Use of MO and State Correlation Diagrams and Surfaces

The method of MO Following has been described in an earlier Account.[22,23] MO Following is a technique of tracing the change in molecular orbitals as a reaction proceeds; here the change in each MO itself rather than just the energy is monitored. MO Following has proven to be of value in obtaining correlation diagrams and in assessing the change in the MO's as a reaction pro-

(7) This was also presented in detail in a 1959 NSF proposal and numerous lectures by the author.

(8) Zimmerman, H. E.; Somasekhara, S. *J. Am. Chem. Soc.* **1963**, *85*, 922–927.

(9) Zimmerman, H. E.; Sandel, V. R. *J. Am. Chem. Soc.* **1963**, *85*, 915–922.

(10) For a useful review to more recent publications note Havinga, E.; Cornelisse, J. *Pure Appl. Chem.* **1976**, *47*, 1–10.

(11) Zimmerman, H. E. *Science (Washington D.C.)*, **1966**, *153*, 837–844.

(12) Zimmerman, H. E.; Swenton, J. S. *J. Am. Chem. Soc.* **1964**, *86*, 1436–1437.

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(15) Zimmerman, H. E. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 1–11.

(16) (a) Zimmerman, H. E.; Keck, G. E. *J. Am. Chem. Soc.* **1975**, *97*, 3527–3528. (b) Zimmerman, H. E.; Keck, G. E.; Pflederer, J. L. *Ibid.* **1975**, *97*, 5574–5581.

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(21) Zimmerman, H. E. "Rearrangements in Ground and Excited States"; Academic Press: New York, 1981, Vol. 3, pp 131–166.

(22) Zimmerman, H. E. *Acc. Chem. Res.* **1972**, *5*, 393–401.

(23) Zimmerman, H. E. In "Pericyclic Reactions", Marchand, A., and Lehr, R. Eds.; Academic Press: New York, 1977; Vol. 1.
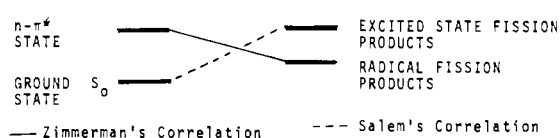
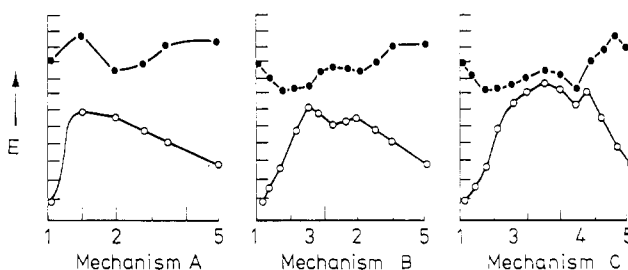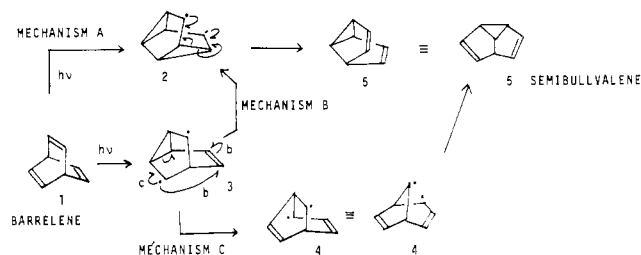**Figure 2.** Direct formation of ground-state product in some n–π* reactions.

Figure 3. Potential energy vs. reaction coordinate for three mechanisms of barrelene to semibullvalene rearrangement.

Scheme I
Three Alternative Mechanisms for the Barrelene Rearrangment

ceeds.[22,23] The method does not require molecular symmetry, nor is a cyclic orbital array needed, as in the Möbius–Hückel method.[24,25] MO Following has been applied chiefly to ground-state processes, and it is of interest to explore its photochemical utility.

One example of interest is the hydrogen abstraction process by the triplet n–π* excited state of a ketone. The correlation diagram is shown in Figure 1. The correlations are made simple once one recognizes that at half reaction the hydrogen donor to hydrogen bond is stretched and that there is a new bond to the hydrogen formed by the p_y oxygen orbital. This forms an allyl-like array of three orbitals in a linear sequence (i.e., 1—2—3; note Figure 1). In such a linear array, the lowest energy MO has the general form 1 + 2 + 3, the second has the form 1 – 3 or 3 – 1, and the highest energy MO has the form 1 – 2 + 3. In addition there are the two carbonyl MO's: π_{45} and its antibonding counterpart π^*_{45}.

It can be seen that, as a result of the allyl nature of the 1—2—3 array, there is no degeneracy along the reaction coordinate. With the excited state of reactant affording the lowest states of the two free-radical primary products, the reaction is allowed.[26]

It is seen with such correlation diagrams that the n–π* excited state in reactions such as hydrogen abstraction, type II fission, etc., proceeds directly to the

(24) Zimmerman, H. E. *J. Am. Chem. Soc.* **1966**, *88*, 1564–1565.

(25) Zimmerman, H. E. *Acc. Chem. Res.* **1971**, *4*, 272–280.

(26) (a) Bigot, B., Devaquet, A.; Turro, N. J. *J. Am. Chem. Soc.* **1981**, *103*, 6–12. (b) The derived diagrams were said to be "natural correlations" showing intended crossings. However, just as MO's 1 and 2 of allyl show no intention of being degenerate, there appears to be no basis for crossing in these reactions. Thus, our diagrams differ from the literature. The difference occurs in a number of similar cases.

ground state of product, as shown by the heavy line in Figure 2, which paraphrases the Zimmerman (1961–1963) n–π* theory[1,3–5] in slightly different language.

A novel addition to this picture was added by Salem in 1974.[27] He noted that the ground state of the starting materials (bottom left in Figure 2) correlates with the excited state of products; this is depicted in Figure 2 with a dashed correlation line. It is not surprising that this reaction does not occur. Also, as noted by Salem,[27] the two correlation surfaces differ in symmetry and do not avoid one another.

The two types of correlations, the first deriving from our work[1,3–5], i.e., the excited reactant state to product ground state, and the second deriving from the hypothetical reactant ground state to product excited state incorporated together, have been termed "Salem diagrams" (e.g., ref 26). The crossing here is quite different from the avoided type we discuss below in that crossing occurs due to differing symmetries. Relevance to photochemical mechanisms is minimal due to this difference (vide infra).

Computer Calculation of Correlation Diagrams and Surfaces

Aside from simple processes such as cis–trans isomerization, the first example of a potential energy surface derived for a photochemical rearrangement or reaction was in 1966. In this work[19,28–31] the hypersurface for the di-π-methane rearrangement of barrelene to semibullvalene was obtained; note Figure 3. The three corresponding mechanisms are given in Scheme I. Although only simple three-dimensional Hückel theory was employed in this early study, the results are qualitatively correct.

Mechanism A is the simplest and was initially favored; however, the vertical excited state is born in an energy well and is unlikely to react. Mechanism B is a variation in which the first two bridging steps are sequential. The vertical excited state may now reach an energy minimum positioned near a ground-state maximum. However, the approach of ground and excited states, a "bifunnel", is not far along the reaction coordinate and is canted, with decay being most facile back to ground-state reactant.

In the third mechanism, C, vertical excitation leads to an excited state born with excess vibrational energy (i.e., on the slope of an energy well). This energy is seen to be enough to allow the molecule to reach the second excited state minimum that corresponds to the penultimate species of the barrelene to semibullvalene rearrangement (an allylic biradical). Close approach of ground- and excited-state surfaces allows radiationless decay, with the preferred pathway on the ground-state surface then leading to product semibullvalene.

One way to generate surfaces is by explicit quantum mechanical SCF-CI calculation of species as they are followed through some mechanism. The philosophy here has been to include as basis orbitals only those

(27) Salem, L. *J. Am. Chem. Soc.* **1974**, *96*, 3486–3501.
(28) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Sherwin, M. A. *J. Am. Chem. Soc.* **1967**, *89*, 3932–3933.
(29) Zimmerman, H. E. *Photochem. Photobiol.* **1968**, *7*, 519–523.
(30) Zimmerman, H. E.; Binkley, R. W.; Givens, R. S.; Grunwald, G. L.; Sherwin, M. A. *J. Am. Chem. Soc.* **1969**, *91*, 3316–3323.
(31) Zimmerman, H. E.; Boettcher, R. J.; Buehler, N.; Keck, G. E.; Steinmetz, M. G. *J. Am. Chem. Soc.* **1976**, *98*, 7680–7689.
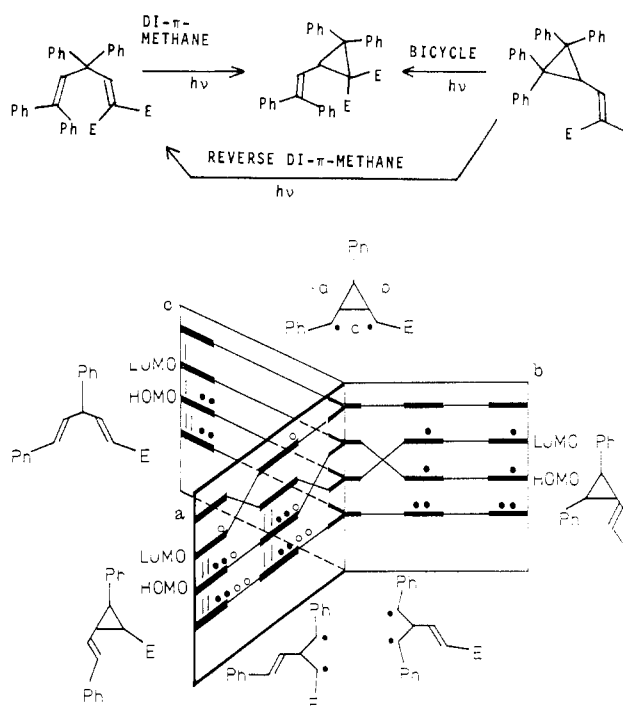
Figure 4. MO triptych for the di-π-methane and acylic bicycle rearrangements of the dicarbomethoxy compounds.

atomic and hybrid orbitals that are part of chromophores or make up bonds that are altered, broken, formed, or modified during the photochemical transformation. Additionally, basis orbitals aimed along the directions of bonds are used, since then the SCF wave functions are linear combinations of recognizable orbitals of bonds rather than arbitrary vertically and horizontally oriented atomic orbitals. Finally, substitution by pairs of phenyl or other (e.g., COOMe) groups is approximated by single substitution where necessary.

This approach has been applied to a number of reactions of interest to the author:[32–37] the di-π-methane rearrangement,[32–37] the bicycle rearrangement,[33–37] and the reverse di-π-methane rearrangement.[32–37] One example[37] of these will suffice. Thus, the photochemical reactions interconverting 1,1-dicarbomethoxy-3,3,5,5-tetraphenyl-1,4-pentadiene, 1,1,2,2-tetraphenyl-3-(2,2-dicarbomethoxyvinyl)cyclopropane, and 1,1-dicarbomethoxy-2,2-diphenyl-3-(2,2-diphenylvinyl)cyclopropane are of interest in several ways. The singlet processes provide an example typifying the treatment of many of the cases referenced above. (Note Scheme II).

It is observed that there are three isomeric compounds that interconvert photochemically and that

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(33) Zimmerman, H. E.; Armesto, D.; Amezua, M. G.; Gannett, T. P.; Johnson, R. P. *J. Am. Chem. Soc.* **1979**, *101*, 6367–6383.
(34) Zimmerman, H. E.; Factor, R. E. *J. Am. Chem. Soc.* **1980**, *102*, 3538–3548.
(35) Zimmerman, H. E.; Cutler, T. P. *J. Chem. Soc., Chem. Commun.* **1978**, 232–234.
(36) Zimmerman, H. E.; Cutler, T. P. *J. Org. Chem.* **1978**, *43*, 3283–3303.
(37) Zimmerman, H. E.; Factor, R. E.; *Tetrahedron Suppl.* **1981**, *1*, 125–141.
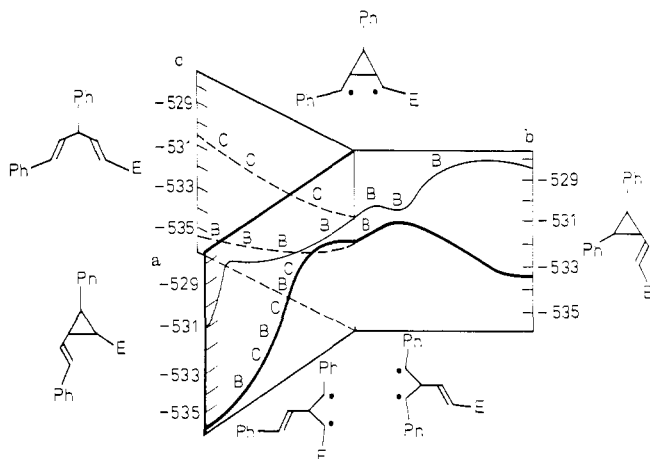
Figure 5. Surfaces derived for the rearrangements of the dicarbomethoxy compounds. B's represent molecules originating in branch b, and C's represent molecules originating in branch c of triptych.

Figure 6. Energetics and canting of a bifunnel.

there is an intermediate cyclopropyldicarbinyl diradical species common to the mechanism involving the three. Hence it is convenient to plot the SCF-derived correlation diagram as a triptych (Figure 4) following the example of our earlier work.[35] In addition to the SCF calculations that afford molecular orbitals, CI was also employed, giving the results in Figure 5. Here surfaces, or states, are obtained rather than MO's.

The triptyches for Scheme II show that the S_1 state of the cyclopropyldicarbinyl diradical is necessarily formed in the di-π-methane approach starting with the diene. This is seen in two ways. In the MO triptych of Figure 4, we see no HOMO–LUMO crossing. In the state triptych of Figure 5, the surfaces then do not approach one another. Hence, there is no mechanism for interconversion to ground state en route to the diradical from the S_1 diene.

Having arrived at the central triptych axis electronically excited, the diradical a priori might select either front branch of the triptych to follow. The MO version of Figure 4 affords no indication of prejudice. However, the SCF-CI triptych of Figure 5 shows a lower energy surface leading off to the left branch, and there an approach of the excited- and ground-state surfaces occurs, thus allowing internal conversion, via this "bifunnel", to ground state. The bifunnel is seen to occur at the point along the reaction coordinate where in the MO triptych a HOMO–LUMO crossing is present. This is in accord with our 1966 reasoning about internal conversions, HOMO–LUMO crossings, and bifunnels.[34,35,37,38]

With similar reasoning we can see that the (diphenylvinyl)cyclopropane is incapable of reaction in accord with observation. Also the reaction of the (dicarbomethoxyvinyl)cyclopropane to give reverse di-π-methane and bicycle products is understandable. The former can be seen to proceed via S_0 and the latter via S_1 of the diradical.

Bifunnels

Avoided crossings and other approaches of excited and ground state sometimes are needed to provide a route for the excited state of reactant to get to the ground state of product. It should be noted that very
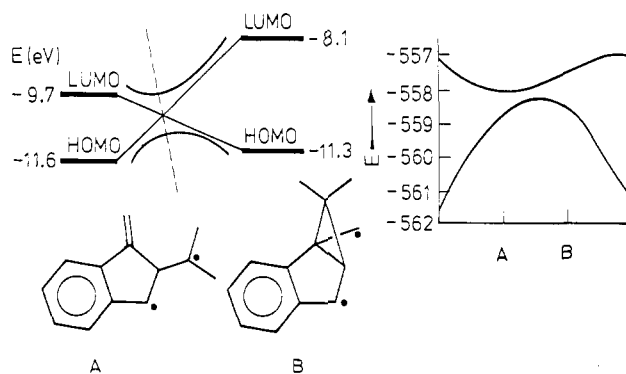
elegant and early discussions of funnels, or bifunnels (i.e., avoided crossings), were presented by Michl.[39] The discussion of Longuet-Higgins and Abrahamson[40] on the surfaces expected to correspond to a HOMO–LUMO crossing are basic to all these discussions. Note also research by the author relating molecular twisting of 1-phenylcycloalkenes to the rates of S_1 and T_1 radiationless decay.[41]

One interesting point is that the bifunnels encountered are not invariably positioned vertically. Thus, the bifunnel may be canted; the expectation then is that decay will preferentially occur to one side of the ground-state maximum. An example of this was found in one study[34] of the bicycle rearrangement. Note Figure 6 where canting derives from a change in the HOMO and LUMO energies prior to and following the crossing with the product MO's both being of higher energies than their counterparts prior to the crossing.

Beyond this factor a momentum effect was originally suggested by Teller.[42] This would not apply to a molecule that had time to equilibrate in the upper funnel.

Additionally, with increased separation between the upper and lower surfaces of the bifunnel, the efficiency of decay to S_0 would decrease with diminution of any momentum effects. Such an effect has been observed[34] in our studies on the bicycle rearrangement. With appreciable surface separation, then, the momentum effect should be inhibited.[34] However the main consequence of an inefficient bifunnel is a diminished tendency toward internal conversion.

Role of S_0-S_2-S_1 Mixing

An important point was made by Oosterhoff[43] concerning the photochemical butadiene to cyclobutene closure. He noted that the state diagrams of the Longuet-Higgins and Abrahamson type reveal an avoided crossing of S_0 and S_2[40] while it is S_1 that is generally of photochemical interest.

Additionally, we note that if we consider only S_0 and S_1, mixing cannot occur as a consequence of Brillouin's theorem. Nevertheless, the situation is not as serious as it appears. In a one-electron MO approximation the S_0 and S_1 configurations do become degenerate where

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(39) Michl, J. *Mol. Photochem.* **1972**, *4*, 243–255.
(40) Longuet-Higgins, H. C.; Abrahamson, E. W. *J. Am. Chem. Soc.* **1965**, *87*, 2045–2046.
(41) Zimmerman, H. E.; Kamm, K. S.; Werthemann, D. P. *J. Am. Chem. Soc.* **1975**, *97*, 3718–3725.
(42) Teller, E. *J. Phys. Chem.* **1937**, *41*, 109–116.
(43) van der Lugt, W. Th. A. M.; Oosterhoff, L. *J. Am. Chem. Soc.* **1969**, *91*, 6042–6046.
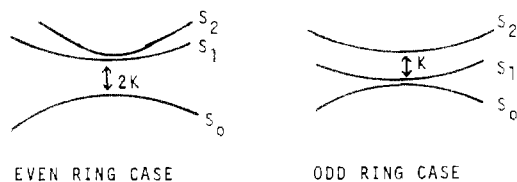
Figure 7. SCF-CI surfaces for even- and odd-membered orbital systems at pericyclic extrema. Note, K is exceedingly small.

Figure 8. α expulsion and ΔP method.

a HOMO–LUMO crossing occurs, and this signifies that where Möbius–Hückel theory[24,25] predicts a degeneracy, surfaces will at least approach one another.

An intriguing point is to be seen. We realize that the Oosterhoff state correlation, in which S_1 did not interact with the S_0 and S_2 configurations, derives not only from Brillouin's theorem precluding interaction of S_1 and S_0 but also from the exact symmetry of the butadiene–cyclobutene reacting system. This imparts different symmetries to the S_1 and S_2 configurations which therefore cannot interact. However, more generally, a reacting system will not have perfect symmetry. Even in the butadiene–cyclobutene case, one can expect molecular deformations to break up symmetry.

In such rearrangements as the bicycle process it has been observed that the $\mathbf{S}_1$ state becomes progressively more heavily weighted in S_0 and S_2 configurations as the bifunnel is approached.[37] Furthermore, an interesting and general analysis is possible. Thus, in the absence of symmetry effects the S_2 configuration will admix with S_0 and S_1 but S_0 and S_1 will not mix. This is analogous to the MO problem of the allyl species in that there are three basis orbitals interacting in a "linear" fashion, except that here the basis orbitals are configurational wave functions rather than atomic orbitals. Also, here the matrix elements leading to admixture are positive (energy raising, deriving from repulsions) whereas in the allyl problem the off-diagonal elements are negative (bonding). The fact that the basis orbitals are of unequal energy in the surface problem is of lesser consequence. Hence, we have a S_0—S_2—S_1 linear array and an "inverted allyl-like" resultant set of configurations (surfaces). The highest energy surface takes S_0, S_2, and S_1 in positive combination. The lowest state, $\mathbf{S}_0$, not to be confused with the configuration S_0 before configuration interaction, should be weighted as $S_0 - S_2 + S_1$. The $\mathbf{S}_1$ state should have a single change in sign along the string of three configurations, with the center configuration vanishing only if the energies were identical, which they are not. $\mathbf{S}_1$ is found to have the form $S_0 + S_2 - S_1$.[37]

The important conclusion is that the $\mathbf{S}_1$ state becomes progressively more heavily weighted in S_0 and S_1 configurations as a bifunnel is approached. Thus Möbius–Hückel considerations are relevant despite the problem noted by Oosterhoff (vide supra).

More can be said about bifunnel surfaces and the mixing of these three configurations. Thus, very recently an analytical SCF and SCF-CI treatment of Möbius and Hückel systems has been reported.[44] This shows that at pericyclic extrema of even-membered rings the energetic situation is as shown on the left in Figure 7 while for odd-sized rings it is as shown on the right in Figure 7. Here K is the exchange integral
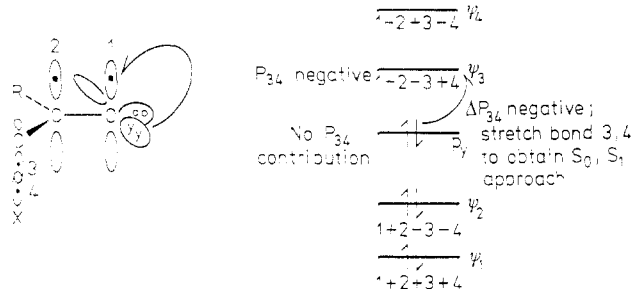
discussed below (note eq 3).

Two Useful MO and QM Methods

A challenging problem is determination of the distribution of electronic excitation energy in a molecule. A priori, one might inspect the excited-state wave function and try to compare it with the ground-state wave function in different portions of the molecule. This is rather tedious and difficult. Easier is the approach we described some years ago.[34,36,37,45–49] This involves obtaining an overlap population matrix or bond order matrix P^* for the excited state of interest; any off-diagonal element P_{rt} gives the bond order between orbitals r and t. Then one subtracts the ground-state matrix, P_0, as in eq 1 to obtain a ΔP matrix.

$$\Delta P = P^* - P_0 \tag{1}$$

Where the bond orders do not really differ in the excited state from those of the ground state, the corresponding ΔP_{rt} element will be near zero. Alkyl substituents included in calculations will tend to contribute small ΔP_{rt} elements, as will other portions of the molecule not appreciably excited. When the ΔP_{rt} term is negative, this overlap has become more antibonding in the excited state than in the ground state; this corresponds to a more energy-rich part of the molecule where excitation energy is concentrated. Such overlaps tend to diminish by stretching of bonds or twisting of π type bonding. Such diminution of antibonding drives the molecule toward a bifunnel by diminishing the S_0—S_1 or S_0—T_1 energy gap. For ΔP elements that are positive, that locale of the molecule is more bonding than in the ground state and is also energy poor. Such overlaps tend to increase with bond compression, also leading the molecule toward a bifunnel.

Where hybrid orbitals are involved it is more precise to use corresponding ΔE_{rt} values as has been noted in these studies; note eq 2. The first two terms represent

$$\Delta E_{(k \to l)} = H_{ll} - H_{kk} + 2\sum_w^{occ} G_{wlwl} - 2\sum_w^{occ} G_{wkwk} +$$
$$\sum_w^{occ} G_{wkkw} - \sum_w^{occ} G_{wllw} + 2G_{kllk} - G_{klkl} \tag{2}$$

one-electron promotion energy, the second two terms represent a change in electron–electron repulsion with

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Scheme III
Multiplicity Control of the Di-π-methane Rearrangement
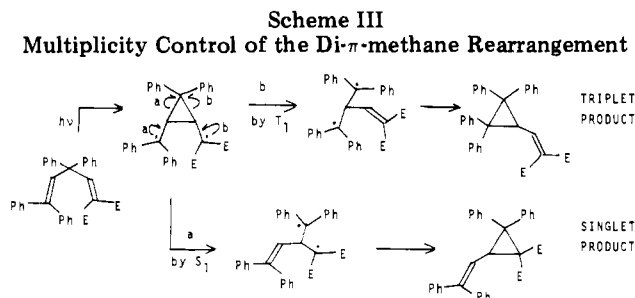
one electron each in the k and l MO's when compared with the ground state, and the remaining terms represent a change in exchange energy stabilization on excitation.

However, more effort is required in using ΔE's rather than just ΔP's. With either variation, the method nicely indicates the fate of excitation energy and helps predict reactivity. Since P matrices are available for all levels of sophistication ranging from simple Hückel calculations to SCF-CI, the method is of broad applicability.

Often qualitative MO's can be used to predict reactivity.[45] Thus, reference to Figure 8 provides one example of the qualitative approach. Here α expulsion is considered. The four-orbital sequence is butadienoid and hence allows writing the wave function for the π system in qualitative form, as shown. The negative ΔP_{34} indicates that this bond will relax by stretching.

Occasionally in photochemistry it is observed that the singlet reacts differently than the triplet. A useful generalization has been developed in our research that deals with this phenomenon.[33,37,50] This is seen most readily in terms of the chemistry of 1,1,3,3-tetraphenyl-5,5-dicarbomethoxy-1,4-pentadiene in Scheme III.

Here, which bond of the cyclopropyldicarbinyl diradical opens, and hence which product is formed, is determined by the spins of the odd electrons. Figure 9 schematically shows the energies of the two alternative pathways available to the diradical (i.e., energies taken from the calculated potential energy surfaces). It is seen that the lower energy singlet pathway is the one designated the "small K" process, and the lower energy triplet pathway is designated the "large K" route. K here is the exchange integral, which before configuration interaction is just half the singlet–triplet (i.e., $S_1 - T_1$) energy splitting.

Then the question is how one determines independently whether a reaction is of the small K or large K type. One can obtain the singlet–triplet splittings from polyelectron calculation as has been done in these cases in order to understand the source of the effect.

Secondly, one can obtain the value of K approximately by use of Hückel or SCF LCAO MO coefficients (eq 3).[51] We note that this involves the summation of

$$K_{kl} = \sum_{r,t} C_{rk}C_{rl}C_{tk}C_{tl}\gamma_{rt} \qquad (3)$$

(50) Zimmerman, H. E.; Penn, J. H. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2021–2025.
(51) Zimmerman, H. E. "Quantum Mechanics for Organic Chemists"; Academic Press: New York, 1975.
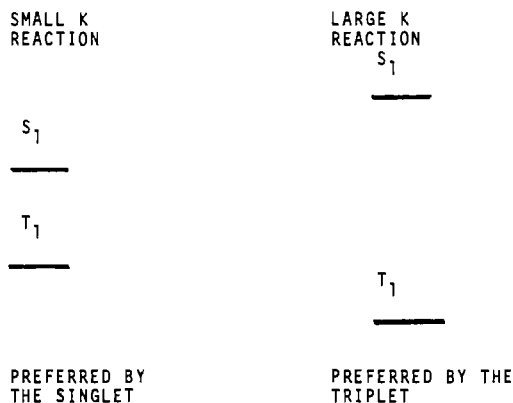
Figure 9. Large K vs. small K processes.

pairs of products of coefficients (as $C_{rk}C_{rl}$), with one Hückel coefficient being taken from HOMO (i.e., MO k) and the other from LUMO (i.e., MO l); but both coefficients are for the same atom r (or t). The summation is over all pairs of atoms or basis orbitals. Thus, where HOMO and LUMO do not appear heavily localized at the same atoms of the molecule, K will be small.

While eq 3 can be used to estimate the relative magnitudes of K for different excited-state transition states or species, a number of generalizations prove more convenient. For example: (1) Pericyclic reactions tend to have small K's (HOMO and LUMO tend not to match). (2) Double bond twisting tends to give a high K. (3) Diradical species with electron-withdrawing groups on diradical centers have diminished K's. (4) Processes extending conjugation in diradicals increase K. And, there are more, obvious, rules.

Concluding Remarks

A final comment is required about our mechanistic approach to organic photochemistry. It is clear that this is bifurcated. On one hand we use MO calculations to obtain predictions and excited-state descriptions. On the other, we write Lewis-type structures to represent excited states and then use arrow notation reminiscent of ground-state chemistry to predict reactivity. The question is whether the latter is too naive. The answer is no! Through our studies we have found that excited-state reactivity follows the guidelines one uses for ground-state behavior except that the structures with which one is dealing are now electronically excited. With reasonable approximations for excited-state structures, organic intuition based on precedent and the requirement for continuous electron redistribution leads one, if not to the actual reaction product, at least to a potential product. The requirement for continuous electron redistribution was one we postulated 21 years ago, and it has proven useful. Electron pushing is rapid and convenient. QM methods such as MO Following, surface calculations, etc., are helpful. The two approaches are complementary, and one makes maximum progress by using both.