analog is air sensitive and must be crystallized from methylene chloride–hexane in an inert atmosphere. In the infrared spectrum (CH_3CN solution) the characteristically sharp A mode is seen at 2008 cm^{-1}. However, the E mode predicted by C_{3v} local symmetry for $Mn(CO)_3$ is split into a broad doublet (1933 and 1919 cm^{-1}). Splitting of the E mode[10] is also observed in the spectrum of $(1,7\text{-}B_9H_9CHPCH_3)Mn(CO)_3^-$. Analytical data for all compounds are given in Table I.

Further studies of phosphaborane chemistry are now in progress and will be reported later.

Acknowledgments. We wish to thank Research Corporation for support, Professor L. J. Todd and Mr. G. M. Bodner of Indiana University for the boron-11 nmr spectra, and Ethyl Corp. for a gift of methyldichlorophosphine.

(10) J. L. Little, P. S. Welcher, N. J. Loy, and L. J. Todd, *Inorg. Chem.*, 9, 63 (1970).

John L. Little,* Andrew C. Wong
Department of Chemistry, The University of Mississippi
University, Mississippi 38677

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Energy Barriers in Photochemical Reactions. A Case for the Relevance of Woodward–Hoffmann-Type Correlations[1]

Sir:

The Woodward–Hoffmann (W–H) rules[2] state that a reaction is photochemically allowed if the lowest excited state of the reactant correlates with the lowest excited state of the product. van der Lugt and Oosterhoff (V–O) have recently suggested[3] that the existence of such a correlation is irrelevant. Instead, they proposed a simple rule, "ground-state forbidden" = "excited-state allowed," based on the general quantum mechanical argument that whenever crossing (or avoided crossing) of potential energy curves leads to a potential energy barrier in the ground state, it will also lead to an excited-state energy minimum through which radiationless deactivation will proceed efficiently.

Decision between the two rules is difficult because they most often give identical predictions. However, we have recently observed[4] that the ground-state-forbidden ring opening I → II does not occur in the first excited singlet (S_1) and triplet (T_1) states, but proceeds from one of the higher triplets (T_x). This clearly shows that the V–O rule is overgeneralized. We have also pointed out[4] that the pattern of triplet reactivities agrees with the W–H rule by symmetry arguments alone, but that it is not immediately obvious that S_1 of I does not correlate with S_1 of II (both are of the same symmetry).

Therefore, we have worked out the correlation diagrams in greater detail using the simple PPP method[5] (Figure 1): energy barriers are imposed both for S_1 and T_1 of I, since both attempt to correlate with very highly excited states of II, while S_1 and T_1 of II originate in highly excited states of I (corresponding to transfer of an electron from the benzene chromophore to the naphthalene chromophore). The course of the state correlations is easily understood in terms of the orbital correlation diagram, also shown in Figure 1:[6] to remove the ground-state forbiddenness of the reaction, one needs to remove an electron from that orbital which becomes antibonding as the reaction proceeds and place it in that empty orbital which becomes bonding during the reaction. The excited state of I formed in this manner is just the above "charge-transfer" state. On the other hand, excitations such as 1 → −1, 1 → −2, 2 → −1, 2 → −2, etc., important in the lowest excited singlets and triplets of I, do not help to remove the energy barrier present in the ground state.

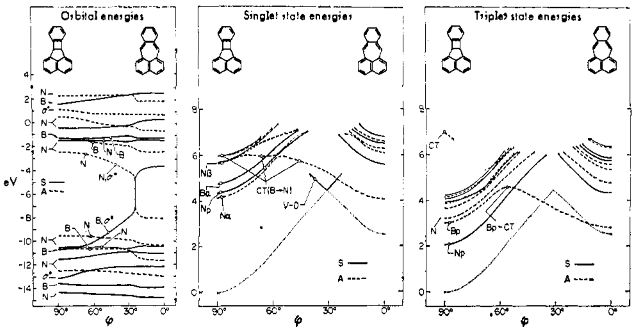
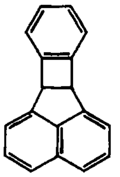


Figure 1. Correlation diagrams for I → II (schematic, based on PPP calculations[5]): φ, angle of (dis) rotation; S and A, symmetric and antisymmetric with respect to the molecular plane of symmetry, respectively; dotted line, ground state; V–O, the van der Lugt–Oosterhoff minimum (the crossing with the ground state is actually avoided when multiply excited configurations are included in the calculation); N, B, σ, states (orbitals) localized mostly on naphthalene, benzene, and the originally single bond, respectively; CT, charge-transfer state; p, α, Clar's notation for excited states. Numerous higher states are not shown.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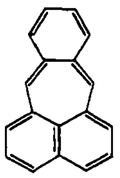
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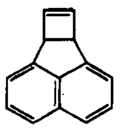
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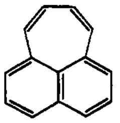
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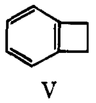
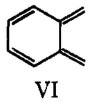

V


VI

We conclude that allowedness in the W–H sense is important if a photochemical reaction is to proceed under usual conditions. Barriers imposed by the course

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(1) Presented at the 3rd IUPAC Symposium on Photochemistry, St. Moritz, Switzerland, July 12–18, 1970.

(2) R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

(3) W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

(4) J. Michl and J. Kolc, *ibid.*, **92**, 4148 (1970).

(5) Pariser–Parr–Pople self-consistent-field calculations (interaction of singly excited configurations), using the parametrization suggested by J. Koutecký, J. Paldus, and R. Zahradník, *J. Chem. Phys.*, **36**, 3129 (1962), which reproduces S → S spectra well but predicts generally too low energies for triplets relative to singlets. To obtain the correlation curves we repeat the calculations for about ten points along the reaction coordinate. The latter is approximated roughly by assuming that 2p orbitals on carbon atoms 6b and 10b in planar I, originally pointing toward each other and forming a localized σ bond, rotate symmetrically in a disrotatory fashion by 90° to give II. The results are insensitive to the details of the assumptions needed to perform the calculations (value of the resonance integral for σ overlap, etc.).

(6) Simple HMO method gives a virtually identical diagram. The value of closed-shell SCF procedure is actually questionable for values of φ near 30°.

of orbital (and state) correlations are just as real in excited states as they are in ground states. Even if the deactivation step leading to products actually proceeds through the V–O minimum,[3] that minimum cannot be reached if such a barrier intervenes, unless sufficient extra energy is available.

We wish to propose that the requirement of "extra energy" in photochemical reactions in dense media may be much more common than is currently realized. Experimentally, it may give rise to (a) temperature-dependent quantum yields, (b) wavelength-dependent quantum yields, (c) triplet reactions requiring a sensitizer of disproportionately high T_1 energy, (d) two-photon reactions ($S_0 + h\nu \rightarrow S_x \rightarrow T_1 + h\nu \rightarrow T_x \rightarrow$ product), depending on the height of the barrier involved.[7–9]

So far, our calculations revealed two general cases where such phenomena are predicted for monomolecular electrocyclic reactions: first, those in which the orbital correlation resembles that in Figure 1 in that it is not the highest occupied molecular orbital of the reactant, but one of the more bonding ones, which becomes antibonding during the reaction (or similarly for the lowest free MO of the reactant or both). Typically, such reactions involve a drastic transformation of the chromophore, and barriers are present both in S_1 and T_1. In addition to I → II, another example for which such behavior is predicted is III → IV.[10] In the second case the orbital "crossover" is normal, but S_1 is not derived from the lowest energy configuration, $1 \rightarrow -1$. This situation arises commonly in aromatic chromophores as a result of strong configuration interaction between singlet $2 \rightarrow -1$ and $1 \rightarrow -2$ excitations. According to our calculations, such lowest singlet state ($2 \rightarrow -1$, $1 \rightarrow -2$, or ^1L_b in Platt's notation) typically correlates with a highly excited state of products. It is only the second singlet state, ^1L_a, which is of $1 \rightarrow -1$ character, that correlates smoothly with the first excited state of the product. The magnitude of the expected barrier for the reaction from S_1 depends on the separation between ^1L_b and ^1L_a. It is usually much smaller than the barrier found for cases such as I → II. For triplet states, the $1 \rightarrow -1$ (^3L_a) state is invariably below $1 \rightarrow -2$, $2 \rightarrow -1$ (^3L_b), and no barrier results.[11] Examples of such reactions are transformations of benzene and naphthalene chromophores into quinoid ones, such as V → VI, where disrotatory opening from S_1 should require "activation energy" (conrotatory opening is forbidden much more strongly yet and lacks the V–O minimum). So far, there seems to be no entirely conclusive experimental evidence to support such predictions. However, Becker, *et al.*,[12,13] have reported that the fluorescence quantum yield of several compounds with benzene or naphthalene chromophores which transform photochemically into quinoid derivatives decreases strongly with decreasing wavelength of exciting light, presumably because the photochemical process competes more efficiently.[14]

We are presently extending our calculations to new systems and searching for experimental evidence to verify our predictions. We hope that this communication will stimulate additional interest in this area.

Acknowledgment. I am very grateful to Professor F. E. Harris, University of Utah, who generously supported part of this work using funds from NSF Grant No. GP-11170.

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[7] When several competing reactions can occur, different product composition would be expected as wavelength of the exciting light or temperature is changed.

[8] The barriers for the processes $A^* \rightarrow B$ and $B^* \rightarrow A$ may be of unequal magnitudes; *e.g.*, the former may require two photons while the latter already proceeds from S_1 at elevated temperatures.

[9] Professor A. Weller suggested to us that two-photon reactions might also proceed in solution *via* triplet–triplet annihilation ($T_1 + T_1 \rightarrow S_x \rightarrow$ product).

[10] During the preparation of this manuscript, Professor J. Meinwald kindly communicated to us that he and his collaborators have indeed found III to behave as predicted[1] (submitted for publication).

[11] We believe that differences between singlet and triplet reactivities can be quite generally understood on the basis of differences in the shapes of potential energy surfaces of S_1 and T_1 due either to differences in configuration interaction, such as those discussed presently, or, more commonly, to the presence of V–O minima in the S_1 but not T_1 surface[3] (which in turn has minima corresponding to biradical structures). A more comprehensive communication on this topic is under preparation.

[12] R. S. Becker and J. Michl, *J. Amer. Chem. Soc.*, 88, 5931 (1966).

[13] R. S. Becker, E. Dolan, and D. E. Balke, *J. Chem. Phys.*, 50, 239 (1969).

[14] Another explanation of these results would be wavelength dependent rate of intersystem crossing followed by a reaction from the triplet state. Becker, *et al.*, consider this unlikely for systems such as the chromenes.[13] However, in other molecules, particularly those with relatively low-lying $n\text{-}\pi^*$ states, this may be an important source of wavelength dependence.

Josef Michl
Department of Physics and Department of Chemistry
University of Utah, Salt Lake City, Utah 84112

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Oxidation by Metal Salts. VII.[1] Syntheses Based on the Selective Oxidation of Organic Free Radicals

Sir:

We wish to report a novel reaction of enolizable ketones with olefins which takes place in the presence of metal oxidants such as manganese(III) and cerium(IV) acetates leading to the formation of γ-keto esters. This reaction, which depends on the selective ability of higher valent metal ions to oxidize organic free radicals, was in turn used to estimate the relative strengths of the various metal oxidants, Cu(II), Ce(IV), and Mn(III).

As a representative example, the reaction of acetone with octene-1 in the presence of manganic acetate under a nitrogen atmosphere was studied in detail. A solution of octene-1 (7.5 mmol), acetone (200 mmol), and manganic acetate (15 mmol) in glacial acetic acid (40 ml) containing 10% potassium acetate was heated at 85° until the brown manganic color had disappeared. Three major products were isolated after work-up: the saturated ketone undecanone-2 (I, 1.13 mmol); an unsaturated ketone[2] $C_{11}H_{20}O$ (II, 0.54 mmol), bp 79–81° (1.5 mm); and a keto acetate[3] $C_{13}H_{21}O_3$ (III, 1.78 mmol), bp 112° (1.0 mm). The relative yields of the three products could be changed by modifying the reaction conditions. The same products were ob-

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[1] Preceding paper by R. M. Dessau, S. Shih, and E. I. Heiba, *J. Amer. Chem. Soc.*, 92, 412 (1970).

[2] Probably a mixture of nonconjugated unsaturated ketones having ir absorption at 1727 cm^{-1} and a complex nmr multiplet in the τ 4.5–4.8 region.

[3] The ir spectrum showed two carbonyl absorptions at 1742 and 1728 cm^{-1}, and the nmr spectrum was consistent with the assigned structure.