to initiate s + a bonding of the cycloaddends. Thus, according to our theory only minor loss of the stereochemistry of the free double bond of the diene cycloadduct is expected in good accord with the results of Bartlett, *et al.*[6]

Finally, we have to account for the orientational selectivity of the nonpolar 2 + 2 cycloadditions. In this case the biradical mechanism makes straightforward predictions. The orientational selectivity of a nonpolar 2 + 2 cycloaddition is correctly predicted to be controlled by the formation of the most stable biradical intermediate. However, one has to be reminded that the biradical mechanism also makes correct predictions for the orientational selectivity of 4 + 2 cycloadditions.[12] In other words, the biradical mechanism accounts for the orientational selectivity of both a presumed two-step and one-step cycloaddition! This certainly makes the reliability of the orientational criterions appear dubious.

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[12] Y. A. Titov, *Russ. Chem. Rev.*, 31, 267 (1962).

Electrocyclic Reactions. III. The Importance of Donor–Acceptor Interactions in Photocycloaddition Reactions

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Contribution from the Department of Chemistry, Princeton University, Princeton, New Jersey 08540. *Received May 7, 1971*

Abstract: The recognition of the donor–acceptor relationship of the cycloaddends leads to the description of the entire spectrum of photochemical cycloadditions. Interaction diagrams are utilized in order to develop our predictions. The Woodward–Hoffmann rules are shown to hold for only parts of the entire photocycloaddition spectrum. The suggestion is made, as in the case of thermal cycloadditions, that most photocycloadditions are concerted and not stepwise as it had been thought before.

The stereochemistry of photocycloaddition reactions has remained for a long time one of the problems in the realm of mechanistic organic chemistry in demand of satisfactory interpretation.[1] The first step toward the solution of the problem was made when Woodward and Hoffman published their formulation of thermally and photochemically allowed concerted reactions.[2] We have already proposed that the thermal Woodward and Hoffmann rules are strictly applicable to only a small segment of the 2 + 2 cycloaddition spectrum and uniformly applicable to the entire 4 + 2 cycloaddition spectrum.[3] We have every reason to believe that a corresponding inadequacy of the Woodward–Hoffmann rules regarding photochemical cycloadditions will also manifest itself. We shall utilize simple perturbation theory results described before to develop some predictive ideas conerning the stereochemistry of photocycloaddition reactions.

I. Theoretical Background

We shall utilize the perturbational approach described before in order to examine photochemical cycloadditions. Accordingly, an interaction diagram is constructed depicting the MO's of the cycloaddends, the electronic configuration of each cycloaddend, and the most important MO interactions between the two cycloaddends. A consideration of energy level proximity effects, or electronic effects, and of orbital overlap effects, or steric effects, then leads us to the determination of the preferred transition state of the reaction.

At this point, it is necessary to consider some important differences between a molecule in a ground state and one in an excited state.

(a) The electronic configuration of an excited molecule is different from the electronic configuration of the same molecule in its ground state. The distribution of the electrons among the MO's of the molecule is different in the excited and in the ground state.

(b) The excited molecule has generally a different geometry than the same molecule in its ground state. Olefinic molecules in their excited state exhibit a twisting of the double bond about their axis. Interaction diagrams are constructed under the assumption that both excited-state and ground-state photocycloaddends are in their ground-state geometry. Accordingly, any drastic deviation of the excited molecule geometry from the geometry of the same molecule in its ground state might create an uncertainty in the accuracy of any predictions made on the basis of such interaction diagrams. This difficulty can be easily circumvented by confining the photoexcited π system undergoing cycloaddition in a ring or any rigid framework. In this fashion the degree of twisting of any double bond about its axis can be restricted and the geometry of the ground and the excited state of the molecule can be considered not to be significantly different. It should be pointed out that in the case of ethylene a twist of the

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[1] P. E. Eaton, *Accounts Chem. Res.*, 1, 50 (1968).

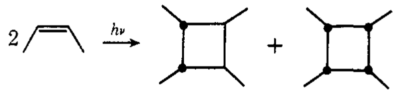
[2] R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 8, 781 (1969).

[3] N. D. Epiotis, *J. Amer. Chem. Soc.*, 94, 1924, 1935 (1972).

two methylene groups out of plane by 20° hardly results in any significant alteration of the energy of the bonding and antibonding π levels of ethylene.[4] Hence, only in cases where olefinic systems react from a nearly perpendicular geometric state would one expect a breakdown in the predictive power of our approach.

(c) A stable ground-state molecule usually has a singlet configuration while an excited molecule can be in either a singlet or a triplet state. The triplet state is energetically lower than the singlet state in most cases. In the framework of our simple perturbation treatment this means that the MO energies of the triplet molecule will be different from the corresponding energies of the singlet molecule in a way compatible with the greater stability of the triplet state. Accordingly, interaction diagrams which are constructed for singlet excited cycloaddends might not be valid for triplet excited cycloaddends if the singlet MO energies substantially differ from the triplet MO energies. This will only happen whenever the singlet–triplet energy splitting is very large. One knows that at least in the case of n–π^* excitation of a cycloaddend the singlet–triplet energy splitting is small.[5] In such a case spin multiplicity effects are not expected to frustrate our analysis. One should be more cautious when π–π^* excitation of a cycloaddend initiates the reaction. This is because the singlet–triplet energy splitting is generally large and, accordingly, spin multiplicity effects might become important. In short, as long as singlet–triplet energy splitting is not large one can disregard spin effects in photocycloadditions discussed on the basis of our simple perturbational model.

After considering some important electronic differences between ground-state and excited-state molecules as related to our perturbation approach, one should consider the nature of orbital overlap in thermal and photochemical cycloadditions. The importance of orbital overlap considerations in determining the preference for an s + s or an s + a cycloaddition will, in general, not be as important in the case of photocycloadditions as in the case of thermal cycloadditions. This assumption is based on the following two observations. Firstly, a photocycloaddition can lead to preferential formation of strained molecules rather than unstrained molecules. This is exemplified by the s + s photodimerization of *cis*-2-butene.[6] The reaction yields syn and anti cyclobutane adducts as shown below. On the basis of orbital overlap considerations at the transition state it is expected that the ratio of anti to syn cycloadducts will be greater than unity. An anti approach of the cycloaddends at the transition state suffers from less nonbonded repulsions between the double bond substituents than the alternative syn approach. The fact that the s + s photodimerization of *cis*-2-butene yields an anti–syn ratio of nearly 0.8 strongly implies that orbital overlap effects are at least not as important in photochemical reactions as they are in thermal reactions. In other words, in a photochemical cycloaddition the cycloaddends are energetically rich enough to overcome nonbonded interactions which are not prohibitingly severe. The relative unimportance of orbital overlap effects might also be suspected in many other reported photocycloadditions.[7] Secondly, in a photocycloaddition the excited cycloaddend has an equilibrium geometry which is, in general, different from the geometry of the ground-state cycloaddend. A general feature of the geometry of unsaturated molecules in their excited state has been recognized to be the twisting of π bonds about their axes. Thus, on the basis of orbital overlap considerations, an s + a cycloaddition of such a photoexcited molecule becomes more favorable and an s + s cycloaddition less favorable when compared to the same reactions occurring under thermal conditions. Hence, one should expect that orbital overlap prohibitions against s + a union of cycloaddends will be significantly reduced when a photocycloaddition takes place. It is also expected that in the latter case bond rotation will preferentially occur within the excited cycloaddend which exhibits a twisted double bond or a twisted π framework. Indeed, the geometry of the excited cycloaddend is the major determinant of the mode of photochemical cycloadditions.



In the subsequent discussions of photochemical cycloadditions we shall use the same alphabetical designations for the appropriate type of cycloaddition as in the case of thermal cycloadditions. We shall simplify the discussion by treating the transition state as an interaction of an excited cycloaddend with a ground-state cycloaddend and neglecting any contribution of charge transfer to the transition state. If the transition state is treated as a resonance hybrid of a no-bond and a charge-transfer structure, *e.g.*, $d^* \cdots a$ $d^+ \cdots a^-$, the same qualitative conclusions about the stereochemistry of the photocycloaddition reaction are reached as in the case where the transition state is treated as an interaction of an excited- and a ground-state cycloaddend, *e.g.*, $d^* \cdots a$ or $d \cdots a^*$.

AD-Type 2 + 2 Photocycloadditions. The interaction diagrams for an AD-like 2 + 2 photocycloaddition are shown in Figure 1. We shall consider three common types of photochemical excitation, n–π^* excitation, π–π^* excitation, and intermolecular charge-transfer excitation. Each type of excitation can involve the donor or acceptor partner of the cycloaddition.[8] It can be seen by inspection of the proximity of the interacting energy levels that in each case the interactions stabilizing the s + s transition state are much stronger than the interactions stabilizing the s + a transition state. Furthermore, orbital overlap is more favorable for s + s union of the cycloaddends rather than s + a

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[4] If one defines the angle of twist in ethylene as θ, then the bonding and antibonding MO's φ_1 and φ_2 have energies $E_1 = \alpha + \beta \cos \theta$ and $E_2 = \alpha - \beta \cos \theta$. For the ground-state molecule $\theta = 0°$, $\cos \theta = 1$, while for the excited twisted molecule $\theta = 20°$, $\cos \theta = 0.94$.

[5] For tabulation of singlet–triplet energy splittings see: S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of the Triplet State," Prentice-Hall, Englewood Cliffs, N. J., 1969.

[6] H. Yamazaki, and R. J. Cvetanovic, *J. Amer. Chem. Soc.*, **91**, 520 (1969).

[7] For example, consider the preferred formation of the syn cyclobutane adduct in some s + s photodimerizations. This might, however, be due to secondary effects like the ones dictating preferential endo rather than exo orientation in the thermal Diels-Alder reaction. In the case of the photodimerization of the 2-butenes such a secondary effect is clearly improbable. For pertinent data on photodimerization stereochemistry and orientation, see: D. J. Trecker, *Org. Photochem.*, **2**, 63 (1969).

[8] The designations donor and acceptor partners are based on the ground-state properties of the two cycloaddends.

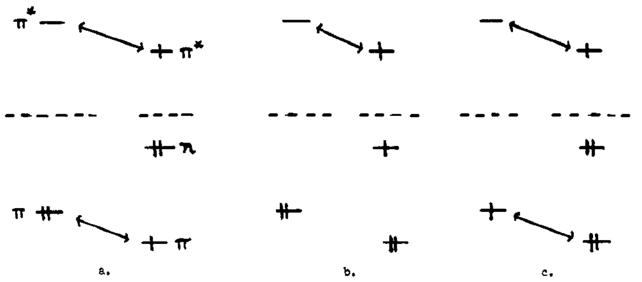
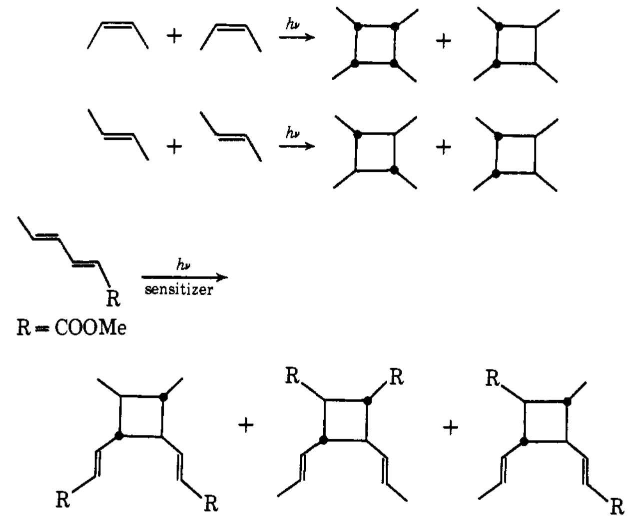


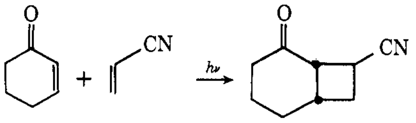
Figure 1. The AD 2 + 2 photocycloaddition initiated by (a) π–π* excitation of the acceptor, (b) n–π* excitation of the acceptor, and (c) intermolecular charge-transfer excitation from the donor to the acceptor. Dominant interactions between the photocycloaddends are indicated by arrows and lead to the stabilization of the s + s transition state. In the cases of π–π* and n–π* excitation of the donor and charge-transfer excitation from the acceptor to the donor analogous interaction diagrams can be constructed leading to identical conclusions as in the cases above.

union of the cycloaddends. Thus, energy level proximity effects and orbital overlap effects both favor an s + s union of the cycloaddends in the case of an AD-like 2 + 2 photocycloaddition reaction. Such reactions are then predicted to occur in an s + s manner and to be highly stereoselective. Experimental results are consistent with our expectations.

(a) 2 + 2 Photodimerizations (AA 2 + 2 Photocycloadditions). All such photocycloadditions are predicted to occur in a highly stereoselective s + s manner. A recent review of photochemical dimerizations covers most of the 2 + 2 photodimerizations studied up to date.[7] They all proceed in an apparent s + s manner regardless of the type of photoexcitation. Two characteristic examples are shown below.[6,9]



(b) 2 + 2 AD-Like Photocycloadditions. AD-like 2 + 2 photocycloadditions or photocycloadditions of two donors or two acceptors are predicted to occur in a stereoselective s + s manner regardless of the type of photoexcitation. A typical example is shown below.[10]



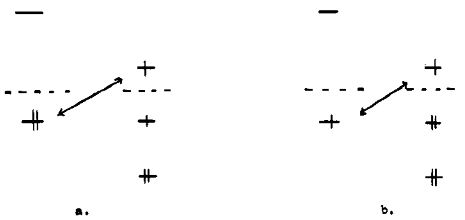


Figure 2. The AX 2 + 2 photocycloaddition initiated by (a) n–π* excitation of the acceptor, and (b) intermolecular charge-transfer excitation from the donor to the acceptor. Dominant interactions are indicated by arrows and lead to the stabilization of the s + a transition state.

AX-Type 2 + 2 Photocycloadditions. The interaction diagrams for an AX-like 2 + 2 photocycloaddition are shown in Figure 2. We shall consider two common types of photochemical excitation which usually involve the acceptor partner of the photocycloaddition. It can be seen by inspection of the degree of proximity of the interacting energy levels that the interactions stabilizing the s + a transition state are much stronger than the interactions stabilizing the s + s transition state. Furthermore, the relative energy of the s + s and s + a transition states due to orbital overlap effects will critically depend upon the pattern of substitution of the two cycloaddends. We distinguish the following two important cases.

(a) AX 2 + 2 Photocycloadditions Involving a Monosubstituted or a Cis Disubstituted Excited Cycloaddend. In such a case, the s + s and s + a transition states are expected to lie close in energy on the basis of orbital overlap considerations. When an s + a union of cycloaddends takes place, the excited cycloaddend, which will undergo bond rotation during the reaction due to its favorable excited state geometry, can be approached by the ground-state cycloaddend in a manner which does not involve severe nonbonded repulsions among the double bond substituents. Specifically, the ground-state cycloaddend will approach the excited-state cycloaddend from the direction of the least hindered side of the double bond, namely, the side of the double bond which displays the two cis hydrogens. Accordingly, an AX 2 + 2 photocycloaddition which involves a monosubstituted or a cis disubstituted excited cycloaddend is expected to occur in an s + a manner since energy level proximity effects strongly favor the s + a over the s + s transition state while orbital overlap effects favor the s + s over the s + a transition state only to a minor extent. It should be emphasized that the factors responsible for the *small* preference of the s + s over the s + a transition state on the basis of orbital overlap considerations are the energy and the geometry of the excited cycloaddend in addition to the substitution pattern of the excited cycloaddend. The former two factors have been discussed in a previous section. The experimental evidence available is in accord with our expectations and typical examples are shown below.[10–13]

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(9) H. P. Kaufmann and A. K. SenGupta, *Justus Liebigs Ann. Chem.*, **681**, 39 (1965).

(10) E. J. Corey, J. D. Bass, R. Le Mahieu, and R. B. Mitra, *J. Amer. Chem. Soc.*, **86**, 5570 (1964).

(11) T. A. Rettig, Ph.D. Thesis, Iowa State University, Ames, Iowa 1965.

(12) A. Cox, P. de Mayo, and R. W. Yip, *J. Amer. Chem. Soc.*, **88**, 1043 (1966); R. L. Cargill and M. R. Wilcott III, *J. Org. Chem.*, **31**, 3938 (1966).

(13) R. Robson, P. W. Gruble, and J. A. Barltrop, *J. Chem. Soc.*, 2153 (1964).

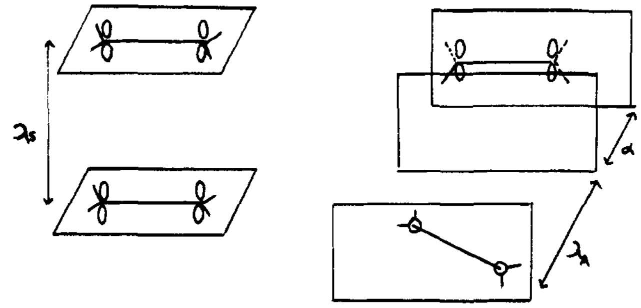


Figure 3. The s + s and s + a transition states in the photocycloaddition of two olefins. The distances λ_A and λ_S are determined by the nonbonded repulsions between the olefin ligands. The distance α is the limiting distance for the approach of the two cycloaddends in an s + a manner.

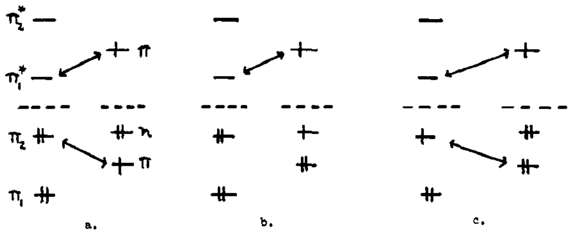
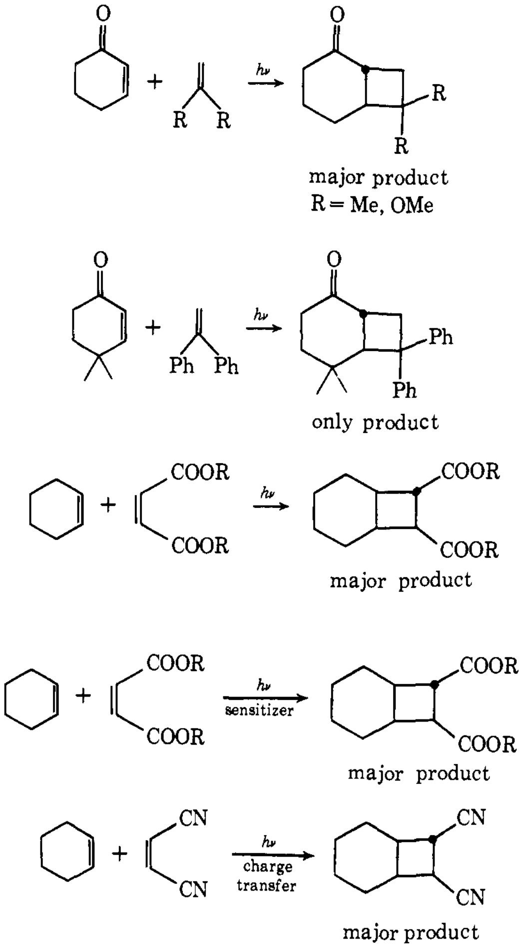


Figure 4. The AM 4 + 2 photocycloaddition initiated by (a) π–π^* excitation of the dienophile, (b) n–π^* excitation of the dienophile, and (c) intermolecular charge-transfer excitation from the diene to the dienophile. Dominant interactions are indicated by arrows and lead to the stabilization of the s + a transition state. In the case of π–π^* and n–π^* excitation of the diene and charge-transfer excitation from the dienophile to the diene analogous interaction diagrams can be constructed leading to identical conclusions as in the cases above.

(b) AX 2 + 2 Photocycloadditions Involving a Trans Disubstituted, Trisubstituted, or Tetrasubstituted Excited Cycloaddend. In such a case the s + a transition state is expected to lie much higher in energy than the s + s transition state on the basis of orbital overlap considerations. When s + a union of the cycloaddends takes place, the excited cycloaddend, which will undergo bond rotation during the reaction due to its favorable excited-state geometry, can only be approached by the ground-state cycloaddend in a manner which involves serious nonbonded repulsions among the double bond substituents. Both sides of the excited cycloaddend's double bond display substituents which will repulsively interact with the ground-state cycloaddend approaching in an s + a manner. In this case one can calculate a limiting ratio of the resonance integrals characteristic of an s + s and an s + a union, γ_S and γ_A, respectively, in a way which was demonstrated in a previous article.[3] In an s + s transition state the two cycloaddends can approach each other up to the equilibrium nonbonded repulsion distance between the substituents of the double bonds. In an s + a transition state the two cycloaddends can approach each other up to a distance which is greater than the distance between the double bond and the double bond substituent of the excited cycloaddend. The parameters involved in the calculation of the limiting γ_S/γ_A ratio are shown in Figure 3. The results of such calculations show that the limiting γ_S/γ_A ratio, which is a measure of the minimum energy difference between the s + s and s + a transition state in terms of orbital overlap effects, is large. Accordingly, the s + s transition state is expected to be strongly favored over the s + a transition state on the basis of orbital overlap considerations. Since energy level proximity effects strongly favor the s + a transition state and orbital overlap effects strongly favor the s + s transition state, we have sought to determine by calculations the preferred mode of union of the cycloaddends. By utilizing model systems we have calculated the relative stabilization energy of the s + s and s + a transition states for different values of the γ_S/γ_A ratio according to well-known formulas of second-order perturbation theory.[14] We have found that for each type of photoexcitation, n–π^*, and intermolecular charge transfer, the s + s and s + a transition states become isoenergetic for a value of the γ_S/γ_A ratio which is smaller than the limiting value of the γ_S/γ_A ratio. This result is primarily due to the appearance of the resonance integral in a square form in the fundamental equations appropriate to the calculation. The conclusion is then reached that orbital overlap effects dominate energy level proximity effects in an AX photocycloadditon involving a trans disubstituted, trisubstituted, or tetrasubstituted excited cycloaddend. Accordingly, such reactions are expected to proceed in an s + s manner. Typical experimental results in accord with our expectations are shown below.[12,13]



AM-Type 4 + 2 Photocycloadditions. The interaction diagrams for an AM-like 4 + 2 photocycloaddition are shown in Figure 4. We shall consider three

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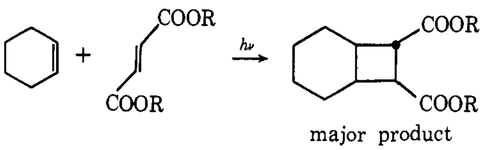
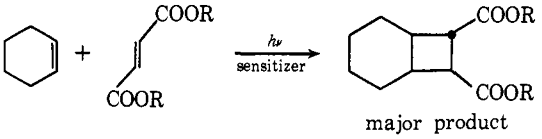
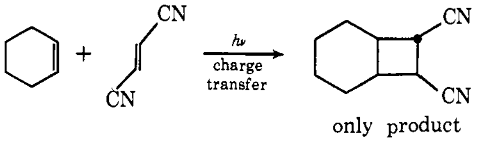
(14) M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969.

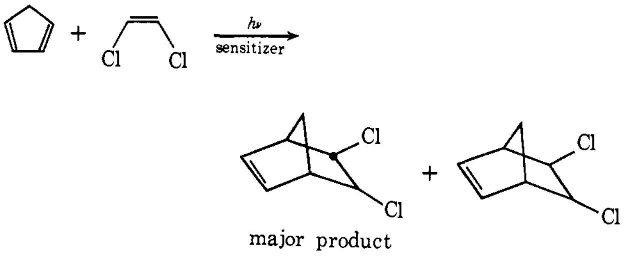






common types of photochemical excitation and each type of excitation can involve the donor or the acceptor partner of the 4 + 2 photocycloaddition. It can be seen by inspection of the degree of proximity of the interacting energy levels that the interactions stabilizing the s + a transition state are much stronger than the interactions stabilizing the s + s transition state. Furthermore, the relative energy of the s + s and the s + a transition states due to orbital overlap effects will critically depend upon the pattern of substitution of the two cycloaddends. We distinguish the following four important cases: (a) AM 4 + 2 photocycloadditions involving a monosubstituted or a cis disubstituted excited olefin; (b) AM 4 + 2 photocycloadditions involving a 1-monosubstituted or a 1,4-trans,trans disubstituted excited diene; (c) AM 4 + 2 photocycloadditions involving a trans disubstituted, trisubstituted, or tetrasubstituted excited olefin; (d) AM 4 + 2 photocycloadditions involving a 1,4-cis,trans disubstituted, 1,4-cis,cis disubstituted, 1,4 trisubstituted, or 1,4 tetrasubstituted excited diene.

In cases a and b the s + s and s + a transition states are expected to lie close in energy as the ground-state cycloaddend can approach the excited partner in an s + a manner from the side of the molecule which bears the cis hydrogens. The situation is analogous to the situation encountered in the case of AX 2 + 2 photocycloadditions. Thus, it is expected that energy level proximity effects will dominate orbital overlap effects and the s + a transition state will be lower in energy than the s + s transition state. A related example drawn from the literature and illustrating our expectations is shown below.[15]



In cases c and d the s + a transition state is expected to lie much higher in energy than the s + s transition state on the basis of orbital overlap considerations. The ground-state cycloaddend can approach the excited partner in an s + a manner at the expense of severe nonbonded repulsions between the substituents of the excited cycloaddend and the ground-state cycloaddend. The situation is analogous to the situation encountered in the case of AX 2 + 2 photocycloadditions. Model calculations indicate that in cases c and d the limiting γ_S/γ_A ratio is greater than the γ_S/γ_A ratio which renders the s + s and s + a transition states isoenergetic when n-π^*, π-π^*, and intermolecular charge-transfer excitation initiates the reaction. Here, as in the case of AX 2 + 2 photocycloadditions, orbital overlap effects dominate energy level proximity effects and the photocycloaddition is expected to proceed in an s + s manner. A related example drawn from the literature and in accord with our expectations is shown below.[15]

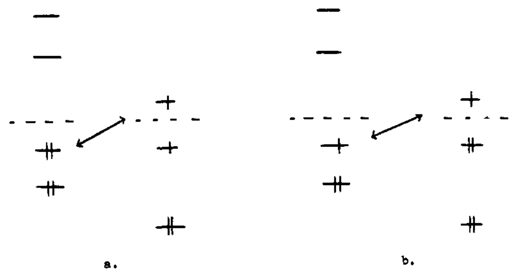
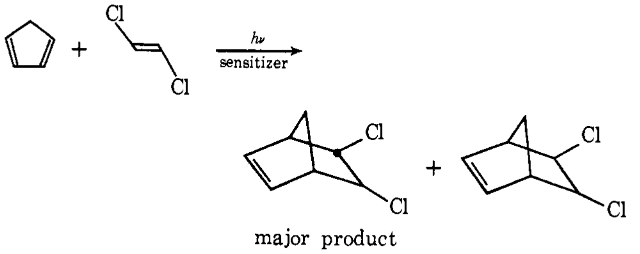


Figure 5. The AX 4 + 2 photocycloaddition initiated by (a) n-π^* excitation of the dienophile, and (b) intermolecular charge-transfer excitation from the diene to the dienophile. Dominant interactions leading to the stabilization of the s + a transition state are indicated by arrows.



AX-Type 4 + 2 Photocycloaddition. The interaction diagrams for an AX-like 4 + 2 photocycloaddition are shown in Figure 5. We shall consider two common types of photoexcitation which usually involve the acceptor partner of the 4 + 2 photocycloaddition. It can be seen by inspection of the degree of proxmity of the interacting energy levels that the interactions stabilizing the s + s transition state are much stronger than the interactions stabilizing the s + a transition state. Furthermore, orbital overlap is more favorable for an s + s union of cycloaddends rather than an s + a one. Thus, energy level proximity effects and orbital overlap effects both favor an s + s union of cycloaddends in the case of an AX-like 4 + 2 photocycloaddition reaction. Berson and Olin have studied the reverse process of a homo-Diels–Alder reaction involving a good electron donor diene and a good electron acceptor diatomic molecule, nitrogen.[16] They discovered that under both thermal and photochemical conditions the reaction occurred in a highly stereoselective s + s manner in

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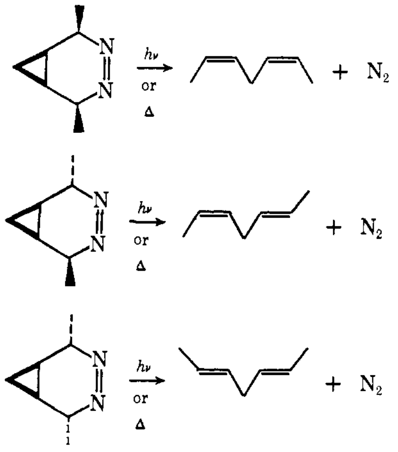
(15) P. D. Bartlett, R. Helgeson, and O. A. Wessel, *Pure Appl. Chem.*, **16**, 183 (1968). One should notice that in this example rotation can occur only in the dienophile moiety since rotation in the excited diene is sterically imposible.

(16) J. A. Berson and S. S. Olin, *J. Amer. Chem. Soc.*, **92**, 1086 (1970).

accordance with our expectations. Their results are shown below.



Conclusion

Recognition of the donor and acceptor properties of cycloaddends leads to a consistent picture of the stereochemical features of photochemical cycloadditions. We summarize our conclusions in Table I. It can be seen that photochemical cycloadditions are part of a reactivity spectrum exactly like their thermal counterparts. The Woodward–Hoffmann rules are applicable only to part of the reactivity spectrum exhibited by 2 + 2 and 4 + 2 photocycloadditions. The biradical mechanisms commonly written in order to rationalize the results obtained in photochemical cycloaddition reactions can now be replaced by concerted mechanisms as long as the spectral properties of photocycloaddition reactions are recognized. For example, a cis and a trans excited olefin can give rise to similar photoadduct mixtures not because of the intermediacy of a common biradical or dipolar species, but because of the relative energies of the s + s and s + a transition states which are dictated by the substitution pattern of the excited olefin. We regard our treatment of the stereochemistry of photochemical cycloadditions only as a first step toward understanding the complexities of such reactions.

Table I. The Spectrum of Photocycloaddition Reactions

Type of Photocycloaddition	Stereochemistry of cycloaddition
2 + 2 AD	s + s
2 + 2 AX	s + a or s + s[a,b]
4 + 2 AM	s + a or s + s[a]
4 + 2 AX	s + s[b]

[a] Depends upon the substitution pattern of the excited cycloaddend. [b] $n\pi^*$ and CT photocycloadditions.

Acknowledgments. This work was generously supported by Princeton University Fellowships (1967–1969), a Monsanto Fellowship (1969–1970), and National Institutes of Health Grant No. AI-07766. The author wishes to thank Professors P. D. Bartlett, J. A. Berson, and R. Hoffmann for their helpful comments and Professor P. von R. Schleyer for stimulating discussions and his interest in this work.

Electrocyclic Reactions. IV. The Importance of Donor–Acceptor Interactions in Photocycloadditions Involving the Carbonyl Group

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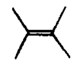
Abstract: Photocycloadditions involving the carbonyl group are examined through the use of interaction diagrams. The ability of the carbonyl group to interact with double bonds *via* its π or n electrons leads to either concerted or stepwise photocycloaddition. The recognition of the donor–acceptor relationship of the cycloaddends leads again to the description of the entire spectrum of photocycloadditions involving the carbonyl group. The Woodward–Hoffmann rules are again shown to be applicable to only a part of the entire spectrum.

Our treatment of the stereochemistry of photocycloaddition reactions will be extended to photocycloaddition reactions of the carbonyl group.[1] Interaction diagrams will be used to develop our predictive ideas.

Photocycloadditions involving union of carbon atoms have been considered previously. Whenever a carbonyl group provides one of the photocycloaddition partners, some important differences should be noted. These differences become apparent by consideration of the model systems, ethylene (**1**) and formaldehyde (**2**).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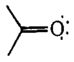
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1 can interact with a photocycloaddend only *via* its π electrons, while **2** can interact with a photocycloaddend either *via* its π or *via* its n electrons. Accordingly, whenever photoexcitation of either photocycloaddition partner obtains, the carbonyl moiety has the option of interacting with the photocycloaddition partner *via* the π or the n electrons, while the olefinic moiety can interact with the photocycloaddition

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[1] N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1941 (1972).