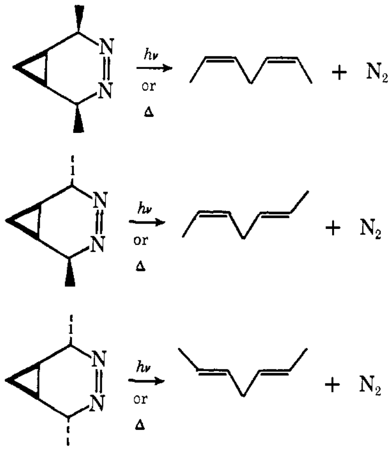
accordance with our expectations. Their results are shown below.



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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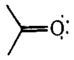

2

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).

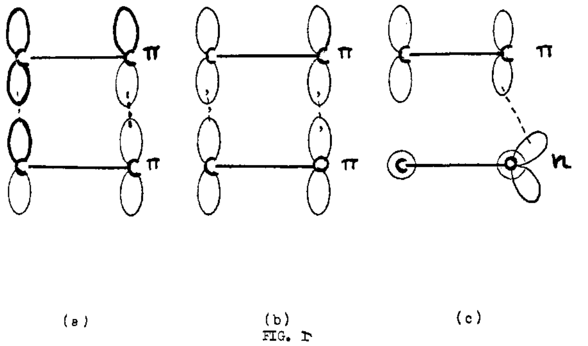


Figure 1. (a) The π–π interaction between two olefins. (b) The π–π interaction between a carbonyl and an olefin. (c) The n–π interaction between a carbonyl and an olefin. It should be noted that π–π interactions give rise to continuous bonding around the uniting termini while n–π interactions give rise to discontinuous bonding around the uniting termini (biradical-like electronic configuration).

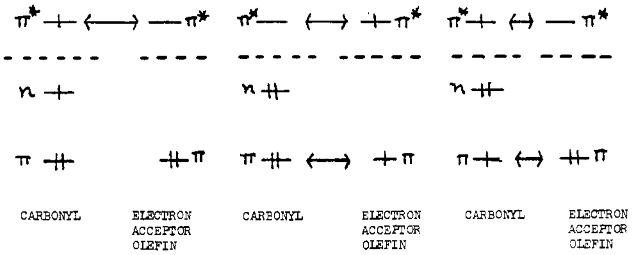


Figure 2. The photocycloaddition of a carbonyl and an electron acceptor olefin. Dominant interactions are indicated by solid arrows. Diagrams are schematic.

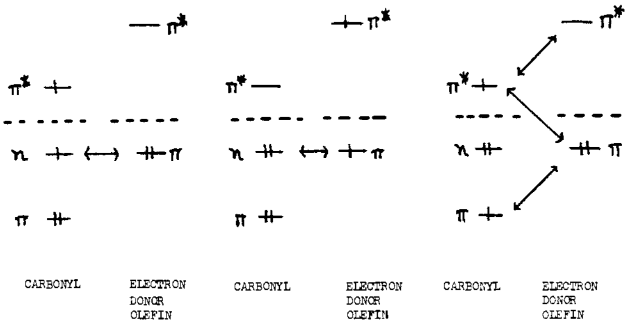


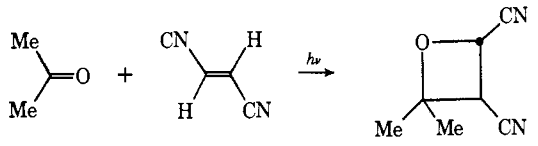
Figure 3. The photocycloaddition of a carbonyl and an electron donor olefin. Crucial interactions are indicated by solid arrows. Diagrams are schematic.

partner only *via* the π electrons. Figure 1 illustrates this.

The electronic differences between a carbonyl and an olefinic moiety suggest that in determining the stereochemistry of the photocycloadditions of a carbonyl group, one should first ascertain whether an n–π or a π–π interaction of the photocycloaddends makes a dominant contribution to the stabilization energy of the transition state. In the former case the photocycloaddition is predicted to be nonstereospecific and the transition state will be biradical-like, while in the latter case the photocycloaddition is predicted to be concerted with the phase properties of the appropriate MO's determining the stereochemistry of the photocycloaddition. Whenever the latter case obtains, the photocycloadditions of carbonyls and olefins can be treated similarly.

The spectrum of the 2 + 2 and 4 + 2 photocycloadditions of the carbonyl group will now be examined in detail. In the three most commonly encountered types of photoexcitation, namely, π–π* and n–π* excitation of the carbonyl group and π–π* excitation of the olefinic photocycloaddition partner, we shall assume that the excited state of one partner attacks the second partner in its ground state.

AD 2 + 2 Photocycloaddition of the Carbonyl Group.[2] Since a carbonyl group is a good electron acceptor, an AD 2 + 2 photocycloaddition will involve a carbonyl and a good electron acceptor. The interaction diagrams appropriate for such photoreactions are shown in Figure 2. It can be seen that the proximity of the interacting energy levels and the phase properties of the corresponding MO's indicate that, irrespective of the type of photoexcitation employed, (a) π–π interactions are stronger than n–π interactions; and (b) the dominant π–π interactions stabilize preferentially the s + s transition state of the photocycloaddition. Accordingly, AD photocycloadditions of carbonyl and an electron acceptor olefin will take place in a highly stereoselective fashion and the major or exclusive product will be derived from the s + s union of the photocycloaddends. These expectations are very nicely confirmed by the work of Turro, *et al.*[3] It was found that photoexcited acetone, 2-pentanone, 2-hexanone, cyclopentanone, and cyclohexanone added in an s + s fashion to *trans*-dicyanoethylene, a good electron acceptor olefin, and photocycloaddition was highly stereoselective.



AX 2 + 2 Photocycloaddition of the Carbonyl Group.[4] Since a carbonyl group is a good electron acceptor, an AX 2 + 2 photocycloaddition will be that of a carbonyl and a good electron donor. The interaction diagrams appropriate for such photoreactions are shown in Figure 3. An examination of the interaction diagrams reveals that in the case of n–π* photoexcitation of the carbonyl or photoexcitation of the olefin a strong interaction between the photocycloaddends will be an n–π interaction, while in the case of a π–π* photoexcitation of the carbonyl the strongest interactions between the photocycloaddends will be π–π interactions. In the former case the reaction is expected to be nonstereoselective, while the latter case is discussed in a separate section of this work. Our expectations find a nice confirmation in the work of Turro, *et al.*, who studied the reaction of triplet and singlet n–π* acetone with *cis*-and *trans*-1-methoxy-1-butene. It was found

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(2) An AD cycloaddition is the reaction of two molecules of comparable ionization potential and electron affinity to form a cycloadduct. The designation of the type of the cycloaddition through the use of the alphabet letters always refers to the ground-state properties of the molecules. The terms donor and acceptor also refer to ground-state properties of the molecules.

(3) J. C. Dalton, P. A. Wriede, and N. J. Turro, *J. Amer. Chem. Soc.*, **92**, 1318 (1970), and references therein.

(4) An AX cycloaddition is the reaction of two molecules of widely different ionization potentials and electron affinities to form a cycloadduct. The designation always refers to ground-state properties of the cycloaddends.

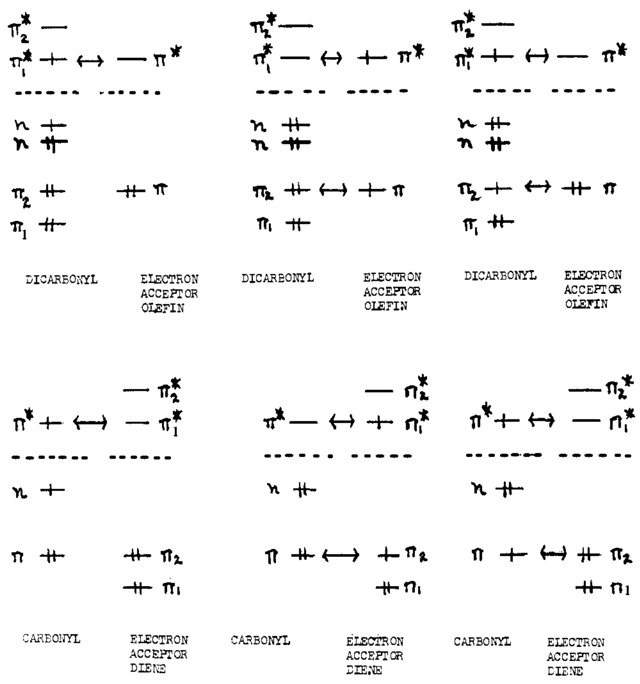
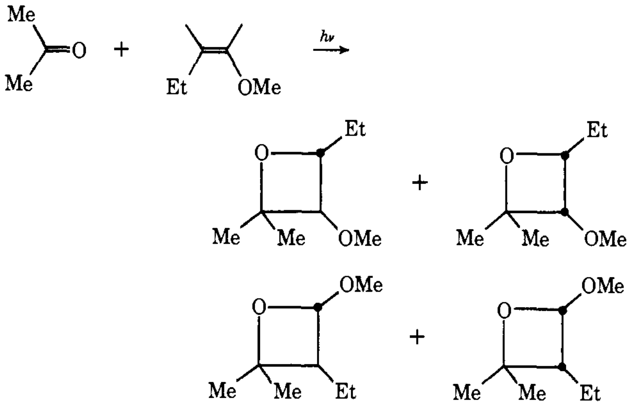


Figure 4. The photocycloaddition of a dicarbonyl and an electron acceptor olefin and the photocycloaddition of a carbonyl and an electron acceptor diene. Dominant interactions are indicated by solid arrows. Diagrams are schematic.

that in both cases the reaction was nonstereoselective and that the stereoselectivity of the singlet reaction was higher than the stereoselectivity of the triplet reaction.[5] It has also been found that the photocycloaddition of benzophenone to the isomeric butenes is also nonstereoselective, in accordance with our expectations.[6] In this case n–π^* excitation of the carbonyl compound is thought with enough certainty to be responsible for the reaction.



AM 4 + 2 Photocycloaddition of the Carbonyl Group.[7] An AM 4 + 2 carbonyl photocycloaddition will be expected in the case of the photocycloaddition of a carbonyl compound and an electron acceptor diene or the photocycloaddition of an α-dicarbonyl compound and an electron acceptor olefin. The appropriate interaction diagrams are shown in Figure 4. An examination of the interaction diagrams reveals that regardless of the type of photoexcitation employed, the strongest interactions between the two photocycloaddends will be π–π interactions. The phase properties of the MO's corresponding to the dominantly interacting energy levels dictate a preferred s + a union of a carbonyl and an electron acceptor diene or a dicarbonyl and an electron acceptor olefin.[8] Unfortunately, no illustrative experimental work appears yet to have been reported.

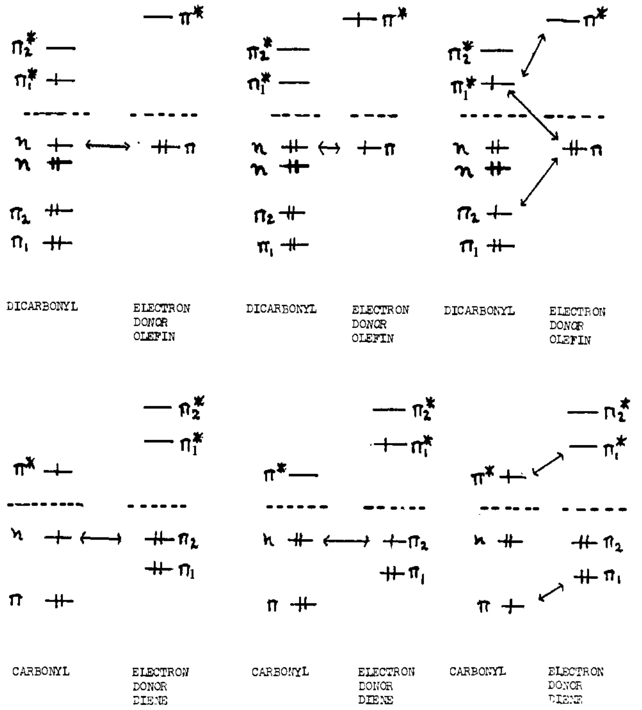


Figure 5. The photocycloaddition of a dicarbonyl and a good electron donor olefin and the photocycloaddition of a carbonyl and a good electron donor diene. Crucial interactions are indicated by solid arrows. Diagrams are schematic.

AX 4 + 2 Photocycloaddition of the Carbonyl Group. An AX 4 + 2 carbonyl photocycloaddition will be the photocycloaddition of a carbonyl compound and a good electron donor diene or the photocycloaddition of an α-dicarbonyl compound and a good electron donor olefin. The appropriate interaction diagrams are shown in Figure 5. An examination of these diagrams reveals that in the case of n–π^* excitation of the carbonyl or the dicarbonyl compound, or, in the case of π–π^* excitation of the diene or the olefin, a strong interaction between the photocycloaddends will be an n–π interaction. On the other hand, in the case of π–π^* excitation of the carbonyl or the dicarbonyl compound the strongest interactions between the two photocycloaddends will be π–π interactions. In the former case the reaction is expected to be nonstereoselective, while the latter case is discussed in a separate section. Several experimental results confirm our expectations. Thus, the reaction of phenanthrenequinone with *trans*- and *cis*-stilbene was found to be slightly stereoselective,[9] while the reaction of phenanthrenequinone with *trans*-

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(5) N. J. Turro and P. A. Wriede, *J. Amer. Chem. Soc.*, **92**, 320 (1970).

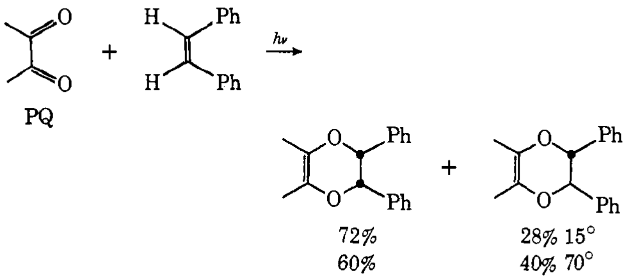
(6) Results of D. R. Arnold, R. L. Hinman, and A. H. Glick quoted in *Advan. Photochem.*, **6**, 301 (1968).

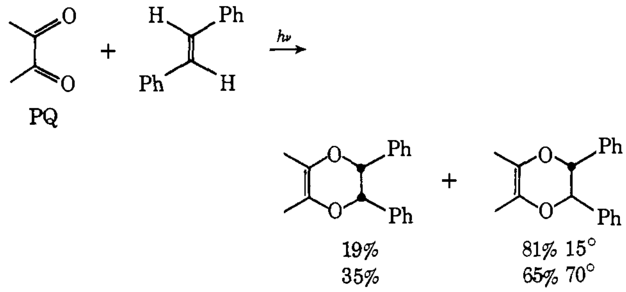
(7) An AM cycloaddition is the reaction of two molecules of moderately different ionization potentials and electron affinities to form a cycloadduct. The designation always refers to ground-state properties of the cycloaddends.

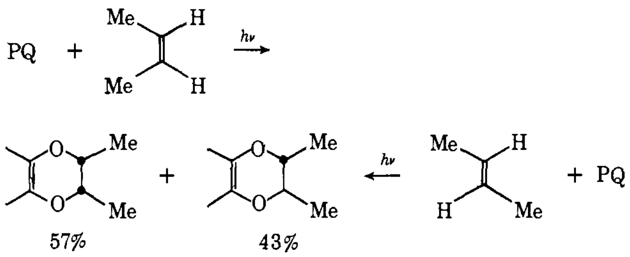
(8) For a discussion of the electronic factors which dictate preferential or nonpreferential bond rotation during an antarafacial thermal union of cycloaddends, see the first paper in this series: N. D. Epiotis, *J. Amer. Chem. Soc.*, **94**, 1924 (1972).

(9) S. Farid, *Chem. Commun.*, 1268 (1967).

and *cis*-butene was found to be completely nonstereoselective.[10] In both cases photoexcitation involves an n–π* transition of the carbonyl or the dicarbonyl compound.







The Limits of the Spectrum of Carbonyl Photocycloadditions. The limits of the spectrum of carbonyl photocycloadditions are represented by the photodimerization of carbonyl groups (AA-type photocycloaddition) and by the photocycloaddition of a strong electron acceptor carbonyl compound and a strong electron donor alkene (AZ type photocycloaddition). It is clear that the stereochemistry of an AA carbonyl photodimerization cannot be operationally defined, in the sense that one can simply not distinguish between an s + s and an s + a union of the partners. On the other hand, the stereochemistry of an AZ photocycloaddition involving a carbonyl-containing compound and an olefin can be operationally defined. The stereochemical differences between an AX and an AZ carbonyl photocycloaddition are simply illustrated through the use of interaction diagrams. Figure 6 shows the interaction diagrams for the AX and AZ 2 + 2 photocycloaddition of an n–π* excited carbonyl and an olefin and also the interaction diagrams for the AX and AZ 4 + 2 photocycloaddition of an n–π* excited dicarbonyl and an olefin. It can be seen that in the case of the AX 2 + 2 photocycloaddition the dominant interactions are n–π interactions, while in the case of the AZ 2 + 2 photocycloaddition the dominant interactions can be π–π interactions. The former give rise to nonstereoselective cycloaddition, while the latter give rise to s + a stereoselective cycloaddition.

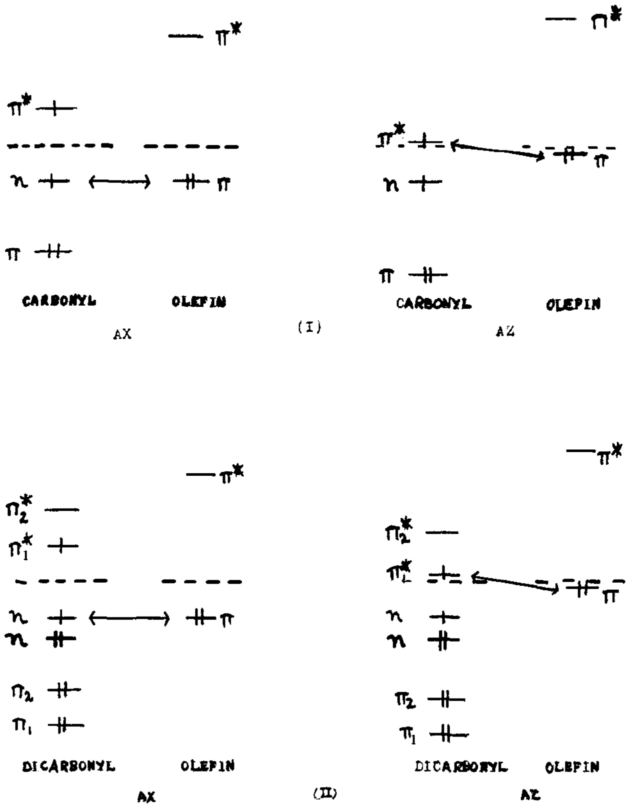


Figure 6. Interaction diagrams illustrating the difference between AX and AZ photocycloaddition of a carbonyl and an olefin (I) and of a dicarbonyl and an olefin (II). Crucial interactions are indicated by solid arrows and the diagrams are schematic.

It can also be seen that in the case of the AX 4 + 2 photocycloaddition the dominant interactions are n–π interactions, while in the case of the AZ 4 + 2 photocycloaddition the dominant interactions can be π–π interactions. The former give rise to nonstereoselective cycloaddition, while the latter give rise to s + s stereoselective cycloaddition. By recognizing the importance of charge transfer in AX and AZ photocycloadditions, it can be shown that the above conclusions are true for any of the three types of photoexcitation we have considered. One can thus generalize that going from an AX to an AZ 2 + 2 carbonyl photocycloaddition, stereoselectivity arising from the preferential s + a union of the photocycloaddends increases. Similarly, in going from an AX to an AZ 4 + 2 photocycloaddition (carbonyl plus diene, or dicarbonyl plus olefin), stereoselectivity arising from the preferential s + s union of the photocycloaddends also increases.

Available experimental results confirm our expectations. The stereoselectivity of three 4 + 2 photocycloadditions is indicated below.[9–11] Thus, as the electron donating power of the donor increases or the electron accepting power of the acceptor increases, *i.e.*, in going toward an AZ photocycloaddition, there is an accompanying increase in the stereoselectivity of the photocycloaddition.

The Importance of Charge Transfer at the Transition State of Carbonyl Photocycloadditions. Our treatment of carbonyl photocycloadditions utilized a simplified description of the transition state by merely considering the interaction of an excited and a ground-

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(10) I. L. Chow and T. C. Joseph, *Chem. Commun.*, 604 (1968).

(11) D. Bryce Smith and A. Gilbert, *ibid.*, 1701 (1968).

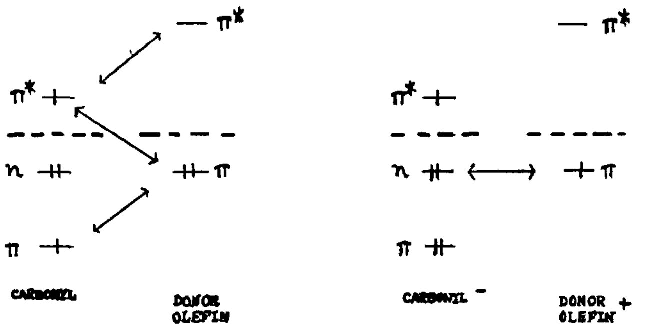
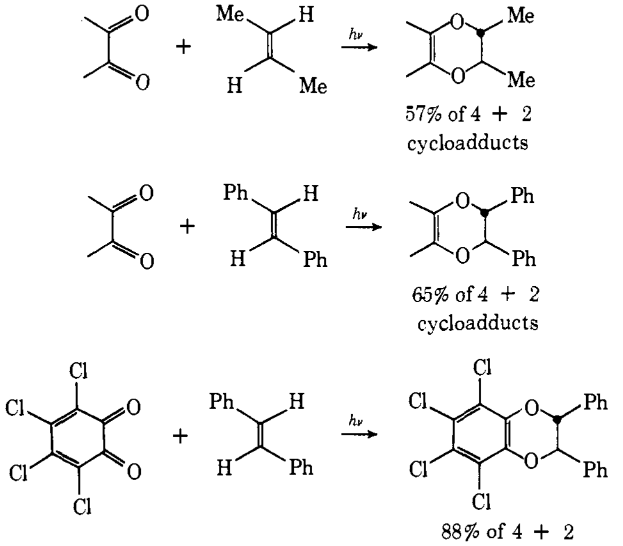


Figure 7. The effect of the charge-transfer contribution to the transition-state interactions between the two photocycloaddends. The charge-transfer contribution to the transition-state interactions is dominant since we are dealing with a donor–acceptor pair. Hence, n–π interactions can be dominant at the transition state. Crucial differences are indicated on the interaction diagrams. Diagrams are schematic.

state photocycloaddend. We avoided using the full description of the transition state, namely that of a resonance hybrid of a no-bond and of a charge-transfer structure, *e.g.*, d···a* (NB) ↔ d⁺···a⁻ (CT). A full treatment of the transition state leads to identical conclusions in all except three cases: the AX photocycloadditions which are initiated by π–π* excitation of the carbonyl moiety. The three reactions of this type are predicted to be nonstereoselective when the contribution of charge transfer at the transition state is taken into consideration. An illustrative case is shown in Figure 7.



57% of 4 + 2 cycloadducts

65% of 4 + 2 cycloadducts

88% of 4 + 2 cycloadducts

Conclusion

We have extended our treatment of photocycloaddition reactions to include photocycloadditions of the carbonyl group; the conclusions are summarized in Table I. The Woodward–Hoffmann predictions are again seen to be applicable only to a portion of the entire spectrum of reactivity exhibited by carbonyl photocycloadditions. It should be noted that our stereochemical analysis is consistent with a transition state in which the contribution of the charge-transfer structure could vary from moderate to predominant. It is expected that the transition state of a carbonyl photocycloaddition will increasingly resemble a charge-transfer complex as one goes from an AD to an AX type of photocycloaddition since the importance of the charge-transfer contributor to the transition-state resonance hybrid increases in this direction.

Table I. The Spectrum of Carbonyl Photocycloadditions

Type of photocyclo-addition	Predicted stereoselectivity	Nature of cycloaddend union
AD 2 + 2	Stereoselective	s + s
AX 2 + 2	Nonstereoselective (biradical-like)	
AZ 2 + 2	Stereoselective	s + a
AM 4 + 2	Stereoselective	s + a
AX 4 + 2	Nonstereoselective (biradical-like)	
AZ 4 + 2	Stereoselective	s + s

Finally, it should be pointed out that Herndon, *et al.*, have also attacked the problem of carbonyl 2 + 2 photocycloadditions by using simple perturbation theory.[12] Their ingenious treatment is different from ours in three important ways. (a) The contribution of charge-transfer structures to the transition state of the cycloaddition reaction is neglected by Herndon, *et al.* Their treatment utilizes as a model the adiabatic interaction of the two cycloaddends while our treatment recognizes the importance of more than one excited configuration in the determination of the stereochemical pathway of a photocycloaddition reaction. (b) The spin multiplicity of the excited cycloaddend is taken into account and the energy of singlet–triplet splitting is assumed to be partitioned in such a way as to equally lower the energy of the nonbonding and antibonding orbitals of the triplet excited carbonyl. This assumption of Herndon, *et al.*, has no apparent quantum mechanical basis. (c) The energy levels of the cycloaddends involved in the model reactions are calculated by the Hückel method and not by reference to experimental ionization potential and spectroscopic measurements as suggested by us. This approach of Herndon, *et al.*, can lead to unreliable conclusions. For example, in the model reaction of ethylene and formaldehyde the nonbonding orbital of formaldehyde is calculated to lie one β unit, *e.g.*, approximately 2.2 eV,[13] above the bonding orbital of ethylene. On the other hand, ionization potential data show that the nonbonding orbital of formaldehyde lies about 0.4 eV below the bonding orbital of ethylene.[14] A number of conclusions arrived at by Herndon, *et al.*, can be rendered invalid because of this reversal in the relative positions of the energy levels of the cycloaddends.

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.

(12) W. C. Herndon and W. B. Giles, *Mol. Photochem.*, 1, 277 (1970).

(13) K. Fukui, K. Morokuma, H. Kato, and T. Yonezawa, *Bull. Chem. Soc. Jap.*, 36, 217 (1963).

(14) K. Watanabe, T. Nakayama, and J. Mottl, *J. Quant. Spectrosc. Radiat. Transfer*, 2, 369 (1962).