is probably too large to allow its detection by the nmr technique. We have estimated the difference in nonbonded repulsions between such a rotamer and rotamer B by employing a Lennard–Jones 6–12 potential function.[28] Idealized geometries, with the nitro group perpendicular to the ring plane in the two rotamers, were assumed, and only atom–atom distances smaller than about 7 Å were taken into account. The coefficient for the r^{-6} term in each potential equation was determined by using the Slater–Kirkwood equation[28,29] and that for the r^{-12} term was obtained by minimizing the energy for a distance equal to the sum of the van der Waals radii of the interacting atoms. The methyl groups were treated as "extended atoms."[28] In this way we obtained an energy difference between the two rotamers of 565 cal/mol, and the populations at 298°K of all four rotamers may be calculated to be $P^{A+C}:P^{B}:P^{X} = 0.70:0.22:0.08$, where P^{X} is the population of the rotamer with all neopentyl groups on the same side of the ring.

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[28] H. A. Scheraga, *Advan. Phys. Org. Chem.*, 6, 103 (1968).

[29] R. E. Carter and J. Sandström, *J. Phys. Chem.*, 76, 642 (1972).

The Regioselectivity of Concerted Cycloadditions

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Abstract: Perturbation theory can be used to predict the preferred orientation (regioselectivity) of concerted cycloadditions. In many, but not all, cases, 2 + 2 thermal cyclodimerizations are expected to occur in a head-to-tail manner and 2 + 2 photodimerizations in a head-to-head manner, if the reactions are concerted. In the same sense, 4 + 2 thermal semipolar photocycloadditions are expected to occur with "meta" orientation and 4 + 2 semipolar photocycloadditions with "para" or "ortho" orientation, if the reactions are concerted. These predictions are compared with experimental evidence, and the mechanistic implications are discussed.

While the stereoselectivity of pericyclic reactions has been the topic of numerous theoretical investigations,[1–8] the regioselectivity of pericyclic reactions has only recently received attention from theoretical chemists.[9] We shall use perturbation theory[10] in order to derive rules concerning the regioselectivity of nonpolar *concerted* 2 + 2 and 4 + 2 cycloadditions.

2 + 2 Dimerizations. We first consider the thermal dimerization of propylene and inquire which of the two possible regiochemical modes of union of the cycloaddends will be preferred. The two distinct regiochemical modes of union are the head-to-head (HH) and the head-to-tail (HT) modes of cycloaddend union. Figure 1a shows the principal MO interactions in the concerted $2_s + 2_a$ thermal dimerization of propylene. The stabilization energy due to orbital interaction for each of the two regiochemical modes is given by

$$\mathrm{SE(HH)} = [4\gamma^2/(E_1 - E_2)](C_{11}C_{21} + C_{12}C_{22})^2 \quad (1)$$

$$\mathrm{SE(HT)} = [4\gamma^2/(E_1 - E_2)](C_{11}C_{22} + C_{12}C_{21})^2 \quad (2)$$

In the expression above, E_1 and E_2 are the energies of the frontier MO's of propylene, γ is the resonance integral of the uniting p atomic orbitals, and C's are AO coefficients with the first index denoting the appropriate MO and the second index denoting the appropriate carbon atom. It becomes clear that regioselectivity will depend on the magnitude of the coefficient terms of eq 1 and 2, and it is easy to show that the coefficient term of eq 2 is greater than the one of eq 1. Calculations show that $C_{12} \simeq C_{21} > C_{11} \simeq C_{22}$. If one makes the substitutions $C_{12} \simeq C_{21} = a$ and $C_{11} \simeq C_{22} = b$, eq 1 and 2 become

$$\mathrm{SE(HH)} = K(2ab)^2 \quad (3)$$

$$\mathrm{SE(HT)} = K(a^2 + b^2)^2 \quad (4)$$

where K equals $4\gamma^2/(E_1 - E_2)$. The inequality $a^2 + b^2 > 2ab$ holds for all positive values of a and b, except $a = b \geq 0$. The conclusion is then reached that SE(HT) > SE(HH) and, accordingly, a concerted thermal dimerization of propylene is predicted to occur in a

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[1] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970; H. C. Longuet-Higgins and E. W. Abrahamson, *J. Amer. Chem. Soc.*, 87, 2045 (1965).

[2] M. J. S. Dewar, *Angew. Chem., Int. Ed. Engl.*, 10, 761 (1971).

[3] H. E. Zimmerman, *Accounts Chem. Res.*, 4, 272 (1971).

[4] K. Fukui, *Accounts Chem. Res.*, 4, 57 (1971).

[5] L. Salem, *J. Amer. Chem. Soc.*, 90, 543, 553 (1968).

[6] C. Trindle, *J. Amer. Chem. Soc.*, 92, 3251, 3255 (1970); T. F. George and J. Ross, *J. Chem. Phys.*, 55, 3851 (1971).

[7] W. A. Goddard III, *J. Amer. Chem. Soc.*, 94, 793 (1972).

[8] N. D. Epiotis, *J. Amer. Chem. Soc.*, 94, 1923, 1935, 1941, 1949 (1972).

[9] (a) J. Feuer, W. C. Herndon and L. H. Hall, *Tetrahedron*, 24, 2575 (1968); (b) W. C. Herndon, *Chem. Rev.*, 72, 157 (1972); (c) O. Eisenstein, T. M. Lefour, and N. T. Anh, *Chem. Commun.*, 969 (1971); (d) J. Bertrán, R. Cabó, and T. Moret, *An. Quim.*, 67, 489 (1971); (e) A. Devaquet and L. Salem, *J. Amer. Chem. Soc.*, 91, 3793 (1969); (f) T. Inukai, H. Sato, and T. Kojima, *Bull. Chem. Soc. Jap.*, 45, 891 (1972); (g) K. N. Houk, *J. Amer. Chem. Soc.*, 94, 8953 (1972); J. Bastide, N. El Grandour, and O. Henri-Rousseau, *Tetrahedron Lett.*, 4225 (1972).

[10] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, N. Y., 1969; see also ref 5.

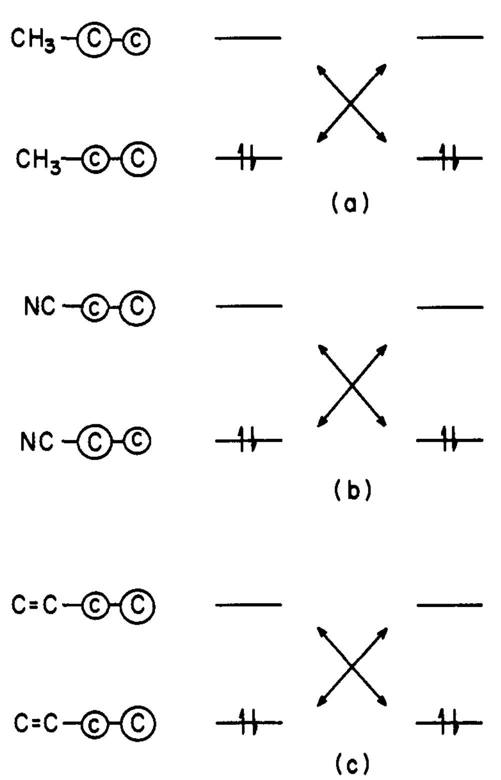

Figure 1. Dominant orbital interactions in thermal nonpolar 2 + 2 concerted cyclodimerizations. Only frontier MO's are shown.

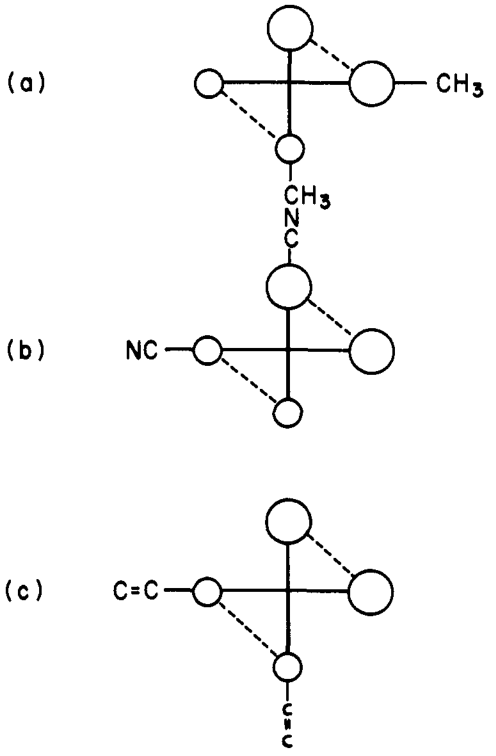

Figure 2. Illustration of the regioselection rule for thermal 2 + 2 concerted cyclodimerizations.

HT fashion. The same conclusions are reached for most type I olefins.

Type I Olefins
$H_2C{=}CHR \quad H_2C{=}CR_2 \quad RHC{=}CR_2$
R = electron-releasing group

Type II Olefins
$H_2C{=}CHW \quad H_2C{=}CW_2 \quad WHC{=}CW_2$
W = electron-withdrawing group

Type III Olefins
$H_2C{=}CHU \quad H_2C{=}CU_2 \quad UHC{=}CU_2$
U = vinyl or phenyl group

We next consider the thermal dimerization of acrylonitrile, and Figure 1b shows the principal MO interactions in the concerted thermal dimerization of acrylonitrile. By using exactly the same type of analysis as in the previous case, we conclude that SE(HT) > SE(HH) and, accordingly, a concerted thermal dimerization of acrylonitrile is predicted to occur in a HT fashion. The same conclusions are reached for most type II olefins.[11]

We next consider the thermal dimerization of butadiene, a typical even conjugated system. Figure 1c shows the principal MO interactions in the concerted thermal dimerization of butadiene. In this case and on account of the pairing theorem the following relationships between the atomic orbital coefficients hold.

$$C_{11} = C_{21} \qquad C_{12} = C_{22}$$

Accordingly, the expressions of the stabilization energies of the two regiochemical modes of union become

$$\mathrm{SE(HH)} = [4\gamma^2/(E_1 - E_2)](C_{11}^2 + C_{22}^2)^2 \qquad (5)$$

$$\mathrm{SE(HT)} = [4\gamma^2/(E_1 - E_2)](2C_{11}C_{22})^2 \qquad (6)$$

The inequality $C_{11}^2 + C_{22}^2 > 2C_{11}C_{22}$ holds for all positive values of C_{11} and C_{22}, except $C_{11} = C_{22} \geq 0$. The conclusion is then reached that SE(HH) > SE(HT). Accordingly, a concerted thermal dimerization of butadiene is predicted to occur in a HH fashion. The same conclusions are reached for any type III olefin.

A derivation of the Woodward–Hoffman rules for stereoselection by means of perturbation theory has already been presented.[2,4,5] A reaction will proceed stereochemically in a manner which renders the phase properties of the frontier orbitals of the reactants compatible. The utility of this simple picture has been amply demonstrated. Our simple analysis of the orientation of pericyclic reactions by means of perturbation theory gives rise to simple rules for regioselection. Specifically, *a reaction will proceed regiochemically in a manner which involves union of the two atoms of highest frontier orbital density and union of the two atoms of lowest frontier orbital electron density.* This is illustrated in Figure 2 for the case of the dimerization of propylene, acrylonitrile, and butadiene. It is interesting to investigate whether the regioselectivity criterion can be used in determining the nature, concerted or nonconcerted, of cycloaddend union.

2 + 2 dimerizations of unsymmetrically substituted olefins are well-known reactions. Unsymmetrical olefins are type I and type II olefins as well as cumulenes and ketenes. Such molecules are predicted to undergo HT dimerization if the reaction is concerted. On the other hand, such molecules are predicted to undergo

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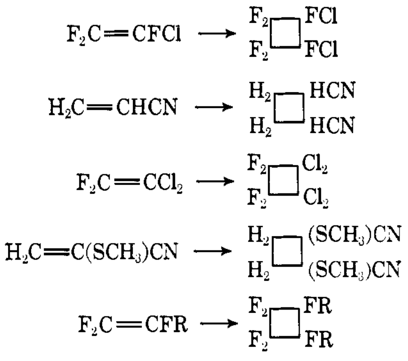
(11) When W is a *conjugatively* electron acceptor group, the relative sizes of the ethylenic HOMO coefficients can be reversed depending on the parametization of the heteroatoms of the W group. Hückel, extended Hückel, and semiempirical calculations differ in the prediction of these HOMO coefficients. If one chooses the alternative set of HOMO coefficients, a situation identical with the dimerization of type III olefins obtains.

HH dimerization if the reaction is stepwise involving diradical intermediates.[12] Hence, in this case the regioselectivity criterion can distinguish a concerted from a nonconcerted reaction. The geometry of the $2_s + 2_a$ transition state is sterically unfavorable and the orbital interactions which stabilize the $2_s + 2_a$ transition state are very weak in the case of 2 + 2 dimerizations because the frontier orbitals of the cycloaddends have substantially different energies. According to these considerations, one would expect the 2 + 2 dimerizations to be nonconcerted and to occur in a HH fashion. Experimental evidence shows that 2 + 2 dimerizations of type I and type II olefins occur in a HH manner and have high activation energies.[12] Recent developments in methods for estimating the entropies and heat capacities of organic molecules have made the calculation of Arrhenius parameters for unimolecular reactions of various molecules possible.[13,14] The thermochemical calculations are carried out by assuming a stepwise mechanism involving diradical intermediates and the calculated activation energies are compared with the experimental ones. Reactions with observed activation energies appreciably lower than those estimated cannot involve diradicals and are probably concerted. By following this type of analysis, Benson and O'Neal concluded that kinetic evidence favors a stepwise mechanism for the thermolysis (reverse 2 + 2 dimerization) of cyclobutane.[13] In summary, the regioselectivity criterion indicates that these reactions are nonconcerted and this is found to be so by application of alternate criteria like the kinetic criterion. Some pertinent examples of the regioselectivity of 2 + 2 dimerizations of unsymmetrical olefins are shown in Scheme I.[12] We want to emphasize that our simple analysis neglects steric effects and dipolar interactions. However, if these effects were dominant they would have also dictated HT union in a concerted process. In other words, interelectronic repulsive effects reinforce rather than weaken our simple analysis.

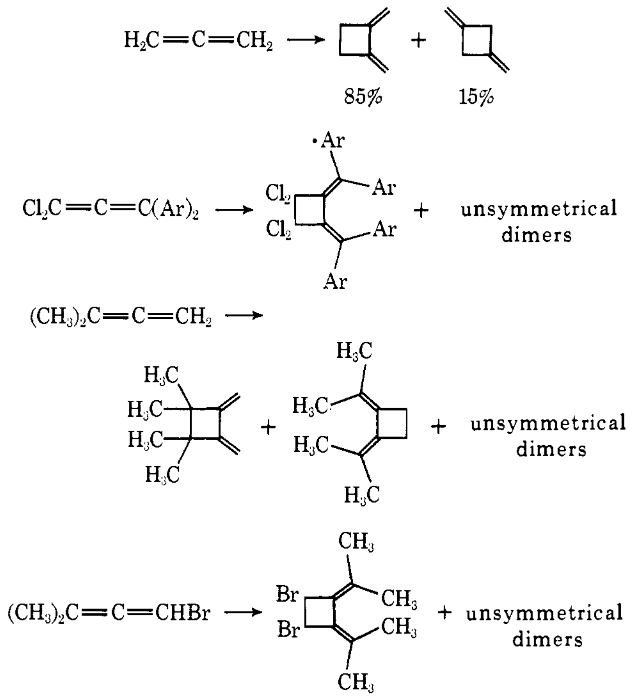
Scheme I



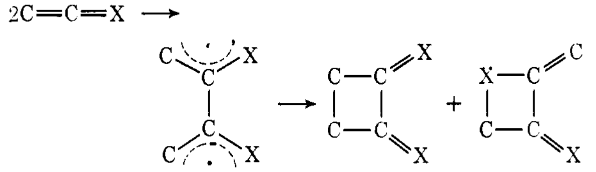
R = Cl, CF_3, CN, Ph

Cumulenes can be regarded as unsymmetrical olefins and their dimerizations have been extensively studied.[15] The reaction is predicted to occur HT, if concerted, and HH, if nonconcerted. In the case of the 2 + 2 dimerization of cumulenes the possibility of concerted $2_s + 2_a$ union exists since the concerted pathway is not as unfavorable sterically as the corresponding pathway involved in the 2 + 2 dimerization of simple unsymmetrical olefins. Recently, studies have been reported which indicate that the 2 + 2 dimerization of allene is nonconcerted.[16] Application of the regioselectivity criterion also indicates that such reactions are nonconcerted. Indeed, many allene dimerizations yield symmetrical HH dimers as well as unsymmetrical dimers. The symmetrical dimerization is indicated to be nonconcerted according to the regioselectivity criterion. Some examples are given in Scheme II.[12]

Scheme II



Heterocumulenes are special types of unsymmetrical olefins. They are known to partake in $2_s + 2_a$ concerted reactions with simple olefins.[17a] Hence, one might expect that their dimerizations might be concerted in nature and, in fact, experimental evidence has been presented in support of this possibility.[17b] Again, a HT orientation is compatible with a concerted reaction, while a HH orientation is compatible with a stepwise reaction. Indeed, a nonconcerted reaction proceeding *via* the intermediacy of the most stable bisallylic radical is expected to give rise to either symmetrical HH dimers or nonsymmetrical dimers but not symmetrical HT dimers (eq 7). Experimentally, it is found



(7)

that in many cases heterocumulenes dimerize to yield both symmetrical and unsymmetrical dimers. The

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(12) J. D. Roberts and C. M. Sharts, *Org. React.*, **12**, 1 (1962), and references cited therein.

(13) H. E. O'Neal and S. W. Benson, *J. Phys. Chem.*, **72**, 1866 (1968).

(14) H. E. O'Neal and S. W. Benson, *J. Chem. Eng. Data*, **15**, 266 (1970).

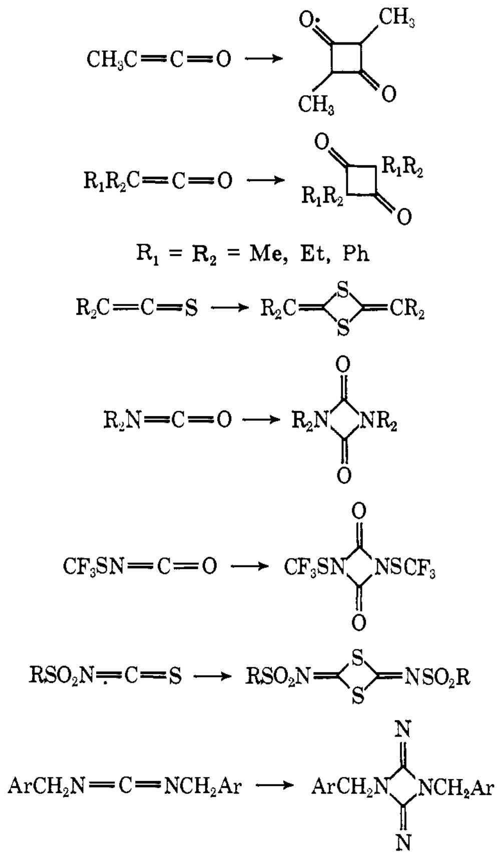
(15) J. E. Baldwin and R. H. Fleming, *Fortschr. Chem. Forsch.*, **15**, 281 (1971).

(16) W. R. Dolbier, Jr., and S. H. Dai, *J. Amer. Chem. Soc.*, **92**, 1775 (1970).

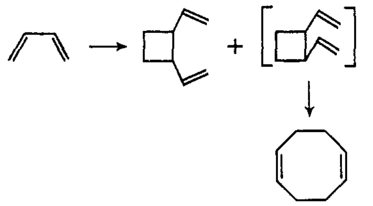
(17) (a) These reactions are illustrated and appropriate references are given in ref 1; (b) R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, **90**, 5342 (1968).

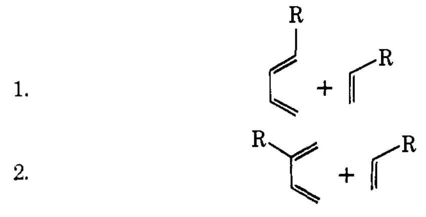
interesting thing is that many symmetrical dimers have a HT orientation, *e.g.*, the regioselectivity criterion indicates that in such cases the reaction probably occurs concertedly. Typical examples are given in Scheme III.[18]

Scheme III

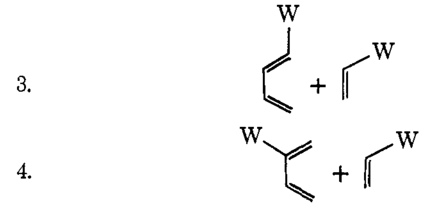


Finally, we come to the case of even alternant type III olefins. In this case the regioselectivity criterion cannot differentiate between a concerted and a nonconcerted addition. Both are predicted to occur HH. Indeed, butadiene dimerizes HH by either of the two mechanisms.[12]



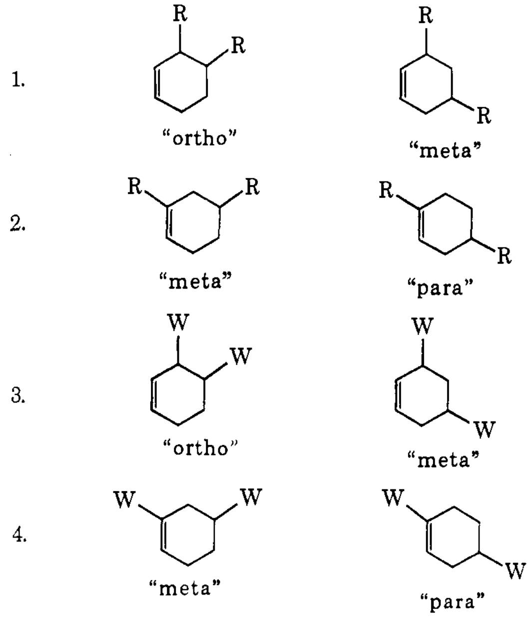


type A semipolar 4 + 2 cycloadditions



type B semipolar 4 + 2 cycloadditions

Chart I



Semipolar 4 + 2 cycloadditions occur when the diene and the dienophile bear substituents which have similar electronic properties. The two general types (A and B) of semipolar 4 + 2 cycloadditions are shown below. In these reactions there are two possible regiochemical modes of cycloaddend union and these are shown in Chart I. We proceed with our analysis as before and we consider a type A semipolar 4 + 2 cycloaddition involving 1-methoxybutadiene and methyl vinyl ether. Figure 3a shows the principal MO interactions involved in a concerted 4 + 2 cycloaddition. By following exactly the same approach as in the case of 2 + 2 dimerizations, we arrive at the conclusion that SE("meta") > SE("ortho") and, accordingly, a concerted semipolar 4 + 2 cycloaddition of this type is predicted to occur in a "meta" fashion. A similar analysis of a type A nonpolar 4 + 2 cycloaddition involving 2-methoxybutadiene and methyl vinyl ether leads to the conclusion that "meta" orientation will be favored over "para" orientation. Figure 4a illustrates how application of our regioselection rule can lead to these predictions.

We next consider a type B semipolar 4 + 2 cycloaddition involving 1-cyanobutadiene and acrylonitrile. Figure 3b shows the principal MO interactions involved in such a reaction. By following exactly the same type of analysis as in the previous case, we conclude that "meta" addition will be preferred over "ortho" addition.[19a] A similar type B semipolar 4 + 2 cycloaddition involving 2-cyanobutadiene and acrylonitrile is somewhat more complicated than the previous cases. In molecules of the type of 2-cyanobutadiene the *relative* magnitude of the C-1 and C-4 coefficients is similar for both HOMO and LUMO. Thus, ap-

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(18) H. Ulrich, "Cycloaddition Reactions of Heterocumulenes," Academic Press, New York, N. Y., 1967, and references cited therein.

(19) (a) Here, as in the case of simple olefins, the relative size of the butadiene HOMO coefficients depends on the parametrization of the heteroatoms of the W group. If one chooses the alternative set of HOMO coefficients, the conclusions are modified accordingly. (b) However, see ref 11.

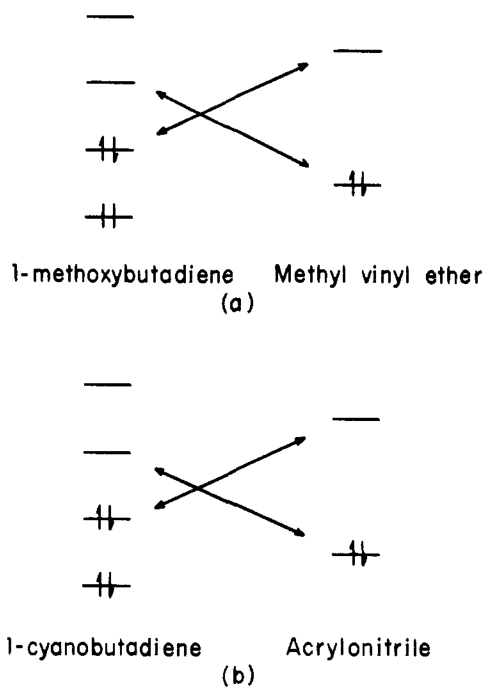
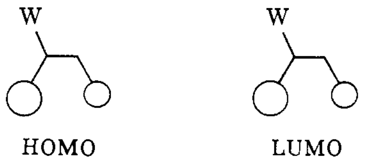


Figure 3. Dominant orbital interactions in thermal semipolar 4 + 2 concerted cycloadditions. Only the perturbed π MO's of butadiene and ethylene are shown.



plication of the regioselection rule tells us that the preferred orientation of the reaction will be "para" if the dominant orbital interaction involves the HOMO of the 2-cyanobutadiene and the LUMO of acrylonitrile and "meta" if the dominant orbital interaction involves the LUMO of the 2-cyanobutadiene and the HOMO of acrylonitrile.[19b] Since both types of HOMO–LUMO interactions are of similar importance,[20] the reaction is predicted to be nonregioselective and give rise to both "meta" and "para" products. In this last case, no clear-cut prediction can be made on the basis of the regioselectivity criterion.

It is interesting to investigate whether the regioselectivity criterion can distinguish a one-step from a two-step semipolar cycloaddition of the type discussed in this section. Such reactions have been studied and their preferred orientation has been determined. As we have seen before, a concerted mechanism is predicted to lead in all cases but one to preferred formation of the "meta" isomer while a stepwise mechanism is predicted to lead to preferred formation of the "ortho" or "para" isomers and this is illustrated in eq 8. The predictions of the stepwise mechanism are based on consideration of the relative stability of the intermediate biradical. Now, it is experimentally found that both type A and type B reactions yield predominantly the "ortho" or "para" isomers and not the "meta" isomer. Application of the regioselectivity criterion indicates that the transition state of such

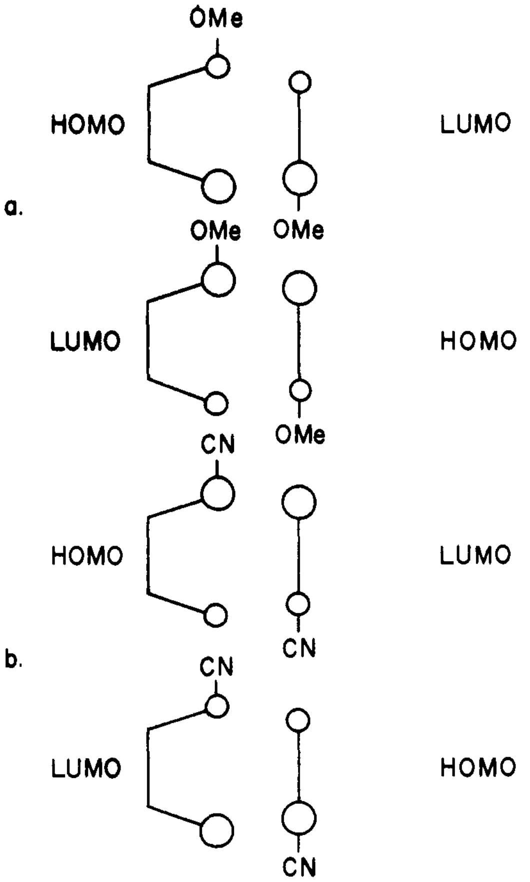
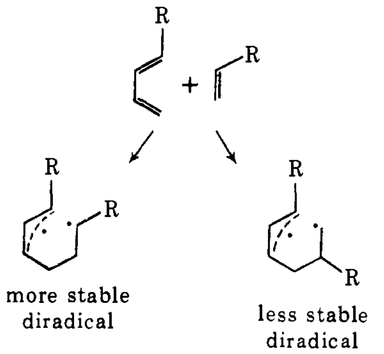
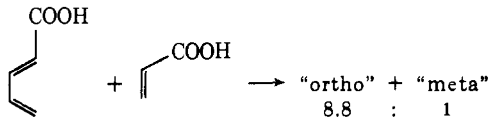


Figure 4. Illustration of the regioselection rule for thermal semipolar 4 + 2 concerted cycloadditions.

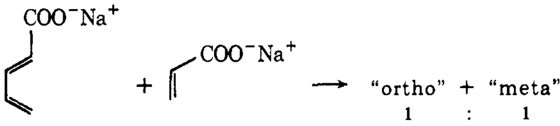


(8)

Diels–Alder reactions involves bond formation which is essentially complete along two union sites and essentially uninitiated at the other two union sites. Some pertinent examples are given in eq 9 and 10.[21]



(9)



(10)

We had previously argued that the best opportunity for stepwise cycloaddition occurs at the nonpolar end

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(20) This occurs because the corresponding energy differences between the interacting orbitals are similar in magnitude.

(21) Y. A. Titov, *Russ. Chem. Rev.*, 31, 267 (1962); R. Husigen, R. Grashey, and J. Sauer in "The Chemistry of Alkenes," S. Patai, Ed., Wiley, New York, N. Y., 1964.

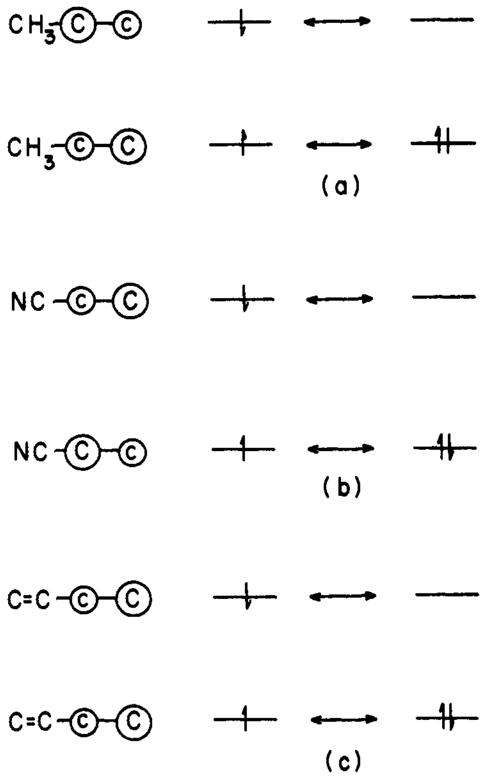

Figure 5. Dominant orbital interactions in nonpolar 2 + 2 photodimerizations. Only frontier MO's are shown.

of the reactivity spectrum because in such instances the orbital interactions which stabilize the concerted pathway are weakest.[8] Hence, it is reasonable to expect that semipolar 4 + 2 cycloadditions proceed *via* a highly asymmetric transition state as indicated by application of the regioselectivity criterion. Here, as in the previous case of the 2 + 2 dimerizations, interelectronic repulsion effects would tend to reinforce rather than upset our simple predictions. There are several indications that these reactions involve a highly asymmetric transition state. For example, Benson and O'Neal have argued on the basis of kinetic evidence that the thermolysis (reverse 4 + 2 dimerization) of vinylcyclohexene is stepwise in nature. As early as 1961, Berson[22] had stated that, "It is conceivable that a graded continuum may be needed to account for the behavior of systems of varying structure, with a completely symmetrical four center mechanism at one end of the scale and a fully developed two step mechanism at the other." Orbital interactions stabilizing the four center transition state are strong at the polar end and weakest at the nonpolar end. In this respect, the conclusion that semipolar 4 + 2 cycloadditions may involve a biradical-like transition state reached on the basis of the regioselectivity criterion seems to be a reasonable one.[23]

2 + 2 Photodimerizations. We now consider the concerted photochemical dimerization of propylene, and Figure 5a shows the principal MO interactions involved in such reaction. The stabilization energy due to orbital interaction for each of the two modes of union of the cycloaddends is given by eq 11 and 12.

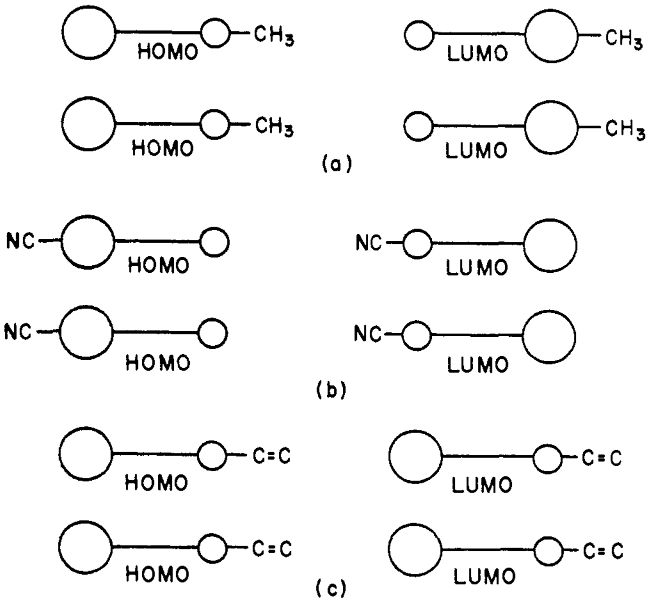

Figure 6. Illustration of the regioselection rule for 2 + 2 concerted photodimerizations.

$$\mathrm{SE(HH)} = (C_{11}C_{11} + C_{12}C_{12} + C_{21}C_{21} + C_{22}C_{22})\gamma \qquad (11)$$

$$\mathrm{SE(HT)} = (2C_{11}C_{12} + 2C_{22}C_{21})\gamma \qquad (12)$$

By using the same substitution technique as before, we can rewrite the equations above as follows

$$\mathrm{SE(HH)} = 2\gamma(a^2 + b^2) \qquad (13)$$

$$\mathrm{SE(HT)} = 2\gamma(2ab) \qquad (14)$$

Since the inequality $a^2 + b^2 > 2ab$ holds for all positive values of a and b, except $a = b = 0$, the conclusion is reached that SE(HH) > SE(HT) and a concerted photodimerization of propylene is predicted to occur in a HH fashion. The same conclusions are reached for any type I olefin.

By following the same approach as above, we conclude that type II and type III olefins will undergo concerted 2 + 2 photodimerization in a HH manner. These conclusions are reached by straightforward application of the regioselection rules enunciated in a previous section.[24] This is illustrated in Figure 6 for the case of propylene, acrylonitrile, and butadiene photodimerization.

An application of the regioselectivity criterion to photochemical reactions requires caution. Specifically, it is known that molecules in their excited states have high dipole moments and dipole–dipole interactions will tend to reverse the HH regioselectivity predicted for the photochemical 2 + 2 dimerization. Steric effects will also operate in the same direction. Thus, in such cases it is very probable that a reaction will be $2_s + 2_s$ concerted but display HT orientation. Hence, in photochemical 2 + 2 dimerizations one expects to find HH orientation mostly in reactions of type III olefins which do not have high dipole moments in their excited states. On the other hand, the regioselectivity of the 2 + 2 photodimerization of type I and type II

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[22] J. A. Berson and A. Remanick, *J. Amer. Chem. Soc.*, **83**, 4947 (1961).

[23] For a theoretical discussion of this problem, see also ref 5.

[24] For a quantitative calculation which substantiates this simple one-electron analysis but also points out its limitations in certain instances, see J. Bertran and G. H. Schmid, *Tetrahedron*, **27**, 5191 (1971).

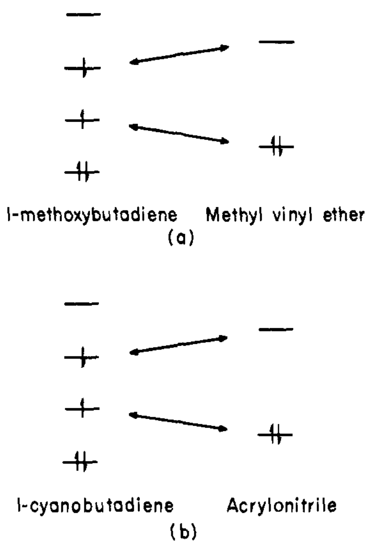


Figure 7. Dominant orbital interactions in semipolar 4 + 2 photocycloadditions. Only the perturbed π MO's of ethylene and butadiene are shown.

olefins will depend on a balance of electron-attractive and electron-repulsive terms. An interesting consequence of this analysis is that HH orientation in photodimerizations is compatible with both diradical and concerted mechanisms. A concerted $2_s + 2_s$ photodimerization is fully expected since it involves first-order orbital interactions which strongly stabilize the pericyclic $2_s + 2_s$ transition state. Hence, it is quite likely that both HH and HT products can arise from concerted union. Thus, although simple regioselection predictions cannot be made, our analysis is useful since it indicates that HH products do not arise necessarily from diradical intermediates as often assumed in the literature.[25] Since this discussion applies to singlet photocycloadditions, it is obvious that defining the multiplicity of the reacting state is essential.

Nonpolar 4 + 2 Photocycloadditions. We now consider a type A semipolar 4 + 2 photocycloaddition involving 1-methoxybutadiene and methyl vinyl ether. The principal interactions involved in this reaction are shown in Figure 7. By following exactly the same approach as in the case of 2 + 2 photodimerizations, we predict that "ortho" orientation will be preferred over "meta" orientation. Similarly, in a type A nonpolar 4 + 2 photocycloaddition of 2-methoxybutadiene and methyl vinyl ether the preferred orientation will be "para" rather than "meta." One can analyze in a similar manner the semipolar 4 + 2 photocycloadditions involving electron-withdrawing groups.

The situation in the case of photochemical semipolar 4 + 2 cycloadditions is like the one encountered in the case of 2 + 2 photodimerizations. Namely, steric effects and dipolar interactions will tend to upset our predictions. Furthermore, a 4 + 2 semipolar photocycloaddition will be less favored than a 2 + 2 photocycloaddition since the former will have to occur s + a and the latter s + s. Thus, it will be difficult to study experimentally the orientation of 4 + 2 semipolar photocycloadditions since the 2 + 2 pathway will dominate.

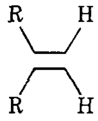
Conclusion

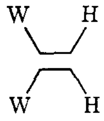
Selection forces in organic reactions can be classified as either strong or weak forces. The forces governing stereoselection are strong and a reaction can be classified as stereochemically "allowed" or "forbidden" in accordance with the Woodward–Hoffmann rules which can be thought of as "strong" stereoselection rules. This occurs because the preferred stereochemistry of a concerted reaction is determined by a numerator term in the perturbation expression for the stabilization energy of the transition state complex which can be additive or subtractive. This term arises out of the expansion of the matrix element between the interacting frontier orbitals and it can be either much greater than zero or near zero depending on the assumed stereochemistry of the transition state. In other words, the stabilization energy difference between two distinct stereochemical arrangements of the reactants at the transition state is comparatively great. On the other hand, the forces governing regioselection are weak, and a reaction *cannot* be realistically classified as regiochemically "allowed" or "forbidden" in accordance with the general rules derived in this paper which can be thought of as "weak" regioselection rules. Indeed, we have seen that in photoadditions steric and dipolar effects will tend to reverse the predicted regioselectivity of a concerted reaction. This occurs because the preferred regiochemistry of a concerted reaction is determined by a numerator term in the perturbation expression for the stabilization energy of the transition state complex which is additive for either regioselection mode. In other words, the stabilization energy difference between two distinct regiochemical arrangements of the reactants at the transition state is comparatively small.

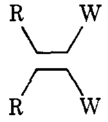
On the basis of the above discussion, one might inquire about the conditions under which the relative stabilization of two distinct regiochemical modes of union is maximized. These conditions can be simply derived. Consider, for example, the case of the 2 + 2 dimerization of two unsymmetrical olefins. As we have seen before

$$\mathrm{SE(HT)} - \mathrm{SE(HH)} \propto (a - b)^2$$

A plot of the difference in stabilization energy for the HT and HH modes of union of two unsymmetrical olefins is shown in Figure 8. It can be seen that regioselectivity is maximal when the two carbon p_z coefficients of the HOMO and LUMO of the olefin differ the most in magnitude. This situation will arise when the substituents are chosen in such a way as to maximize the asymmetry of the electron density of the olefinic π bond. Typical arrangements of substituents around a double bond which give rise to asymmetrical charge distribution is shown below.







The same general conclusions are reached for the case of nonpolar 4 + 2 cycloadditions by following the same reasoning as above.

We have restricted our attention to nonpolar cycloadditions because our approach has been a one-con-

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[25] For example, see D. J. Trecker, *Org. Photochem.*, 2, 63 (1969), and references cited therein.

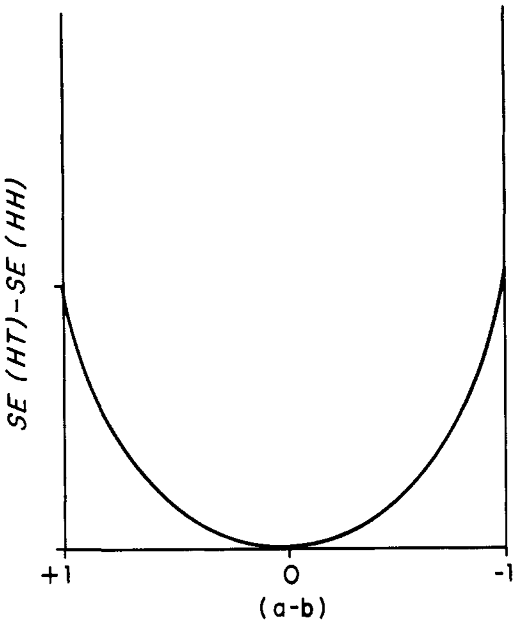
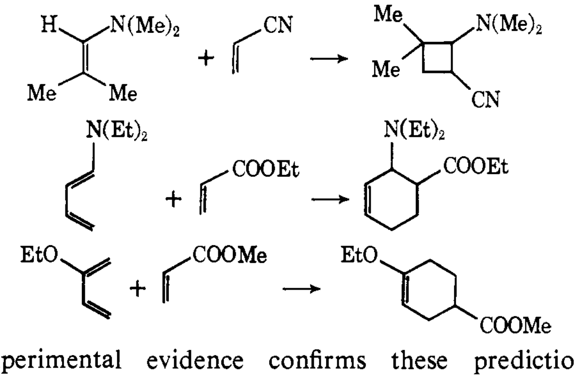


Figure 8. Variation of the stabilization energy difference for HH and HT orientation as a function of the size of orbital coefficients.

figuration, one-electron approach which probably cannot be extended to polar cycloadditions. These latter reactions may involve substantial mixing of ground state and excited configurations of similar energy and a one-configuration approach will most likely fail. However, it is of interest to note that application of the regioselection rules predicts that polar 2 + 2 cycloadditions will occur HT, if concerted, and polar 4 + 2 cycloadditions will occur "ortho" or "para," if concerted. These predictions are illustrated in Figures 9 and 10. Typical experimental results are given in Scheme IV.[21,26]

Scheme IV



Experimental evidence confirms these predictions. However, a check on the stereochemistry of polar 2 + 2 cycloadditions as determined by experiment tells us that these reactions are not concerted in the Woodward–Hoffmann sense. On the other hand, the stereochemistry of polar 4 + 2 cycloadditions has been found experimentally to be in agreement with the Woodward–Hoffmann rules. The Woodward–Hoffmann approach is a one-configuration approach and such an approach suffices to describe $4n + 2$ electron polar reactions but not $4n$ electron polar reactions. These ideas have been systematically pursued in previous papers.[27]

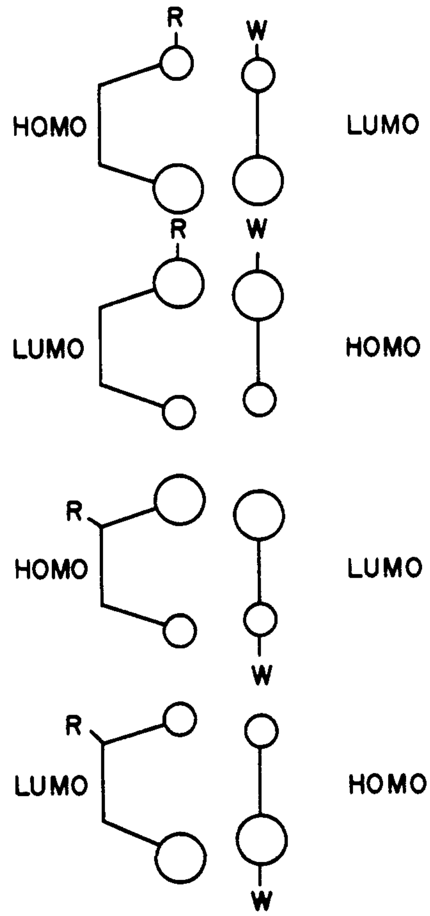


Figure 9. Illustration of the regioselection rule for polar 4 + 2 concerted cycloadditions occurring thermally. Dominant orbital interactions are those between the HOMO of the diene and the LUMO of the olefin.

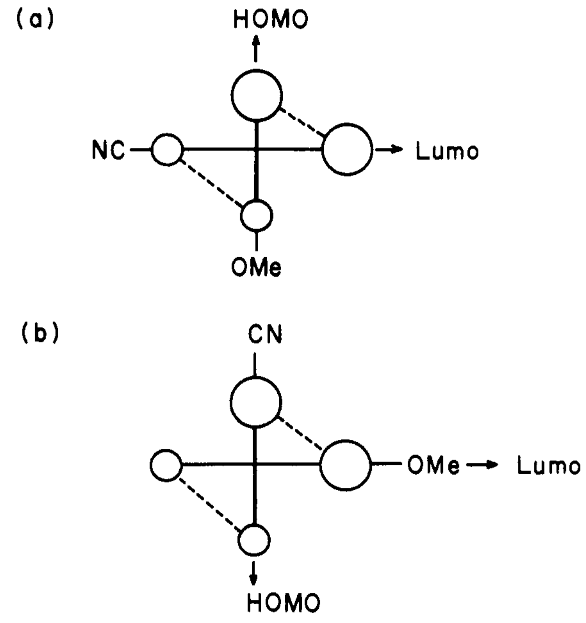


Figure 10. Illustration of the regioselection rule for polar 2 + 2 concerted cycloadditions occuring thermally. Dominant orbital interactions are those between the HOMO of the donor olefin and LUMO of the acceptor olefin.

Finally, it should be pointed out that subtle influences on regioselection, such as subjacent orbital

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(26) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelly, *J. Org. Chem.*, **29**, 801 (1964).

(27) N. D. Epiotis, *J. Amer. Chem. Soc.*, **95**, 1191, 1200, 1206, 1214 (1973); see also R. J. Buenker, S. D. Peyerimhoff, and K. Hsu, *ibid.*, **93**, 5005 (1971), and previous papers in this series; F. S. Collins, J. K. George and C. Trindle, *ibid.*, **94**, 3732 (1972).

effects,[28] might also play a partial role. However, the correlation of the results of our simple treatment with available experimental results[29] seems to be encouraging and could certainly be used as a starting point for more detailed analyses.

Appendix

The crucial orbital coefficients were determined by means of a variety of calculations of a series of representative molecules. Typical olefinic molecules which were calculated included propylene, acrylonitrile, acrolein, fluoroethylene, hydroxyethylene, and aminoethylene and typical butadiene molecules include both the 1 and 2 isomers of cyanobutadiene, carbonylbutadiene, fluorobutadiene, hydroxybutadiene, and aminobutadiene. The generalizations regarding the relative size of the frontier orbital coefficients of various types of olefins and butadienes are based on these calculations and the anomalous cases have been pointed out in footnotes.

Acknowledgment. We are pleased to acknowledge the support of the Research Corporation and the donors of the Petroleum Research Fund, administered by the American Chemical Society.

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(28) J. A. Berson and L. Salem, *J. Amer. Chem. Soc.*, **94**, 8917 (1972).

(29) Professor K. N. Houk has used a similar approach in his studies of the regioselectivity of 1,3-dipolar cycloadditions: K. N. Houk, J. Sims, R. E. Duke, Jr., R. W. Strozier, and J. K. George, submitted for publication; K. N. Houk, J. Sims, C. R. Watts and L. J. Luskus, submitted for publication. We thank Professor Houk for informing us of his results prior to publication.

Molecular Design by Cycloaddition Reactions. V.[1] Photochemical and Thermal Cycloaddition Reactions of Anthracene with Cycloheptatriene

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Received February 5, 1973

Abstract: Irradiations (Pyrex, >290 nm) of anthracene (**1**) with a large excess of cycloheptatriene (**2**) in benzene or ethanol gave a mixture of formal $[_{\pi}6 + {}_{\pi}4]$ (**4**) and $[_{\pi}4 + {}_{\pi}4]$ cycloadducts (**5**) in a moderate yield together with an anthracene dimer (**3**). These products are considered to be formed through a biradical intermediate in the excited π–π^* singlet state. In contrast, the thermal reaction of **1** with **2** afforded only a $[_{\pi}4 + {}_{\pi}2]$ cycloadduct (**10**) in a low yield (8%). Catalytic hydrogenations of these adducts, **4**, **5**, and **10**, gave the corresponding tetrahydro derivatives, **6**, **7**, and **11**, respectively. Irradiations (quartz, >220 nm) of these adducts, **4**, **5**, and **10**, resulted in the cycloreversions to anthracene as well as the interconversions between them. Irradiation (Pyrex, >290 nm) of the thermal adduct **10** in benzene gave the valence isomer **12**, while the photoadducts **4** and **5** were stable under the same conditions. The mechanisms for the formation of the products are discussed.

Recently, Hammond and Taylor[2] have reported on the basis of spectroscopic and kinetic studies that an exciplex is formed in the quenching reactions of fluorescence from anthracene and related aromatic compounds with conjugated dienes.

Although the major decay pathway of the exciplex has been suggested to be nonradiative to their components in the ground state, the possibility of the product formation has not been excluded.[2,3] In fact, some of the numerous photochemical cycloaddition reactions of polynuclear aromatic compounds[4] are suggested to follow the modes of decay of excimers and exciplexes as the chemical processes.[5–10]

The photochemical cycloaddition reactions of anthracene with various unsaturated molecules have been documented to give $[_{\pi}4 + {}_{\pi}2]$[11–13] and $[_{\pi}4 + {}_{\pi}4]$ addition products,[14–16] depending on the nature of the addends and on the reaction conditions. However, there seems to be no studies on the reactions of the conjugated cyclic trienes with anthracene.

As a continuation of our previous reports,[1,17] we have investigated the thermal and photochemical re-

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(1) Part IV of this series: T. Sasaki, K. Kanematsu, Y. Yukimoto, and T. Hiramatsu, submitted to *J. Amer. Chem. Soc.*

(2) (a) D. A. Labianca, G. N. Taylor, and G. S. Hammond, *J. Amer. Chem. Soc.*, **94**, 3679 (1972); (b) G. N. Taylor and G. S. Hammond, *ibid.*, **94**, 3684, 3687 (1972).

(3) L. M. Stephenson and G. S. Hammond, *Angew. Chem., Int. Ed. Engl.*, **8**, 261 (1969).

(4) A. A. Lamola and N. J. Turro, "Energy Transfer and Organic Photochemistry," Interscience, New York, N. Y., 1969, p 171.

(5) (a) T. Sugioka, C. Pac, and H. Sakurai, *Chem. Lett.*, 667, 791 (1972); (b) C. Pac, K. Mizuno, T. Sugioka, and H. Sakurai, *ibid.*, 187, 309 (1973).

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