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$E0,\ E2,\ E4$ = ethylene ratios produced

$R0,\ R2,\ R4$ = metal–ethylene complex ratios at start

$Z0,\ Z2,\ Z4$ = metal–ethylene complex ratios produced

$A0,\ A4$ = 1,7-octadiene ratio

$$E0 = R0(A0 + BA4) + R2A0B$$

$$E2 = B\cdot R0\cdot A4 + D\cdot R2(A0 + A4) + B\cdot R4\cdot A0$$

$$E4 = C\cdot R2\cdot A4 + R4(A4 + B\cdot A0)$$

$$Z0 = A0(R0 + D\cdot R2 + B\cdot R4)$$

$$Z2 = A0(C\cdot R2 + B\cdot R4) + A4(B\cdot R0 + C\cdot RZ)$$

$$Z4 = A4(B\cdot R0 + D\cdot R2 + R4)$$

The *B*, *C*, and *D* factors represent the probabilities of the combination of the *A* and *R* factor producing the desired *E* or *Z* under consideration. The *Z* values became the *R* factors for the next iteration. After approximately 20–30 iterations the calculated ratios become constant and are independent of the assumed starting ratios. Very large isotope effects have a small effect on the calculated values. Only those equilibration steps indicated in the scheme were allowed.
(16) Isolated by centrifugation of the reaction mixture, washed twice with benzene, and used as a suspension in benzene.
(17) The ratio of the *m/e* peaks of 114, 112, and 110 for the starting mixture and the recovered reaction mixture of I and II were compared on spectra determined under identical conditions. The per cent reaction was determined by comparing the ratio of cyclohexene and 1,7-octadiene in the reaction mixture.
(18) The equilibrium ratio was calculated from the equation $(1 + A)^2$ which yields the ratio, $d_4{:}2Ad_2{:}A^2d_0$. Without monohydride equilibration A = II/I. With some equilibration $A = \frac{1}{2}$ the ratio of (ethylene-d_4:ethylene-d_2).
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Robert H. Grubbs,*[22] Patrick L. Burk, Dale D. Carr
Department of Chemistry, Michigan State University
East Lansing, Michigan 48824

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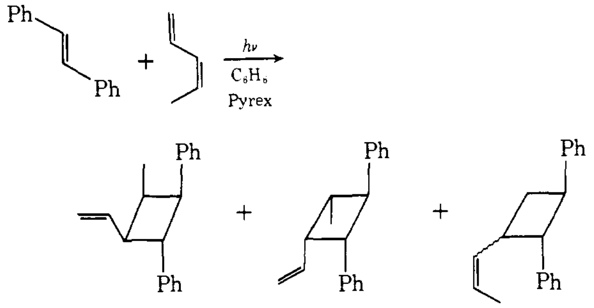
Abnormal Regioselectivity in the Photochemical Cycloaddition of Singlet *trans*-Stilbene with Conjugated Dienes

Sir:

The regioselectivity of 1,2-cycloaddition to conjugated dienes has been investigated for a number of electrophilic species. Such diverse reactions as radical,[1] ionic,[1b] concerted $[_{\pi}2_s + {}_{\pi}2_a]$,[2] 1,3-dipolar,[3] and carbene[3b,4] additions display similar regioselectivities. Addition to *cis-* or *trans*-1,3-pentadiene occurs selectively at the monosubstituted double bond (>90%), whereas addition to 2-methyl-1,3-pentadiene occurs selectively at the disubstituted double bond (70–80%).[5] The observed regioselectivities have been attributed to one or more of the following: (a) formation of the more stable bifunctional intermediate, (b) preferential addition to the sterically less hindered terminus, and (c) addition to the terminus of highest electron density. In spite of the fact that concerted photochemical $[_{\pi}2_s + {}_{\pi}2_s]$ cycloaddition is a symmetry-allowed reaction, there are few examples of concerted 1,2-cycloaddition to conjugated dienes.[8,9] We wish to report that 2 + 2 cycloaddition of the singlet excited state of *trans*-stilbene to conjugated dienes occurs preferentially at the *more* substituted double bond. Application of frontier orbital theory[10] for a concerted 2 + 2 cycloaddition correctly predicts the observed regioselectivities.

Irradiation of *trans*-stilbene in the presence of dienes results in the efficient formation of mixtures of 2 + 2 cycloadducts.[11] Direct irradiation of *cis*-stilbene or triplet sensitized irradiation of either *cis-* or *trans*-stilbene in the presence of dienes results in stilbene cis–trans isomerization, but no cycloaddition. Addition of singlet *trans*-stilbene to the disubstituted double bond of the isomeric 1,3-pentadienes occurs with complete retention of diene and stilbene stereochemistry (eq 1), as is the case for addition of *trans*-stilbene to the isomeric 2-butenes.[12c,13] The regioselectivity of cycloaddition of *trans*-stilbene with several conjugated dienes is given in Table I. Addition to the more substituted double bond predominates in all cases and attains a maximum value of 80% for *cis*-1,3-pentadiene. Since the quantum yields for cycloaddition are high,[11] the regioselectivities reflect relative rates of addition rather than selective partitioning of a 1,4-biradical intermediate. A biradical mechanism[1a,b] appears unlikely in view of the high stereospecificity and abnormal regioselectivity of cycloaddition. It is possible that the stereochemical outcome of the cycloaddition process is determined by the formation of an excited state π-donor-acceptor complex (exciplex) prior to bond formation. The rate of addition of singlet *trans*-stilbene to alkenes displays a negative temperature dependence,[12b] in-



(1)

Table I. Regioselectivity of Cycloaddition and Diene Frontier Orbital Coefficients

	Regioselectivity			Orbital coefficients			
Diene	1, 2%	3, 4%		C_1	C_2	C_3	C_4
4-Methyl-1,3-pentadiene	34	66	HO	0.495	0.294	0.510	0.492
			LU	0.501	0.351	0.441	0.554
trans-1,3-Pentadiene	46	54	HO	0.525	0.337	0.469	0.521
			LU	0.528	0.382	0.437	0.562
cis-1,3-Pentadiene	20	80	HO	0.522	0.339	0.473	0.526
			LU	0.528	0.384	0.437	0,564
2-Methyl-1,3-pentadiene	70	30	HO	0.621	0.429	0.337	0.500
			LU	0.566	0.428	0.407	0.544

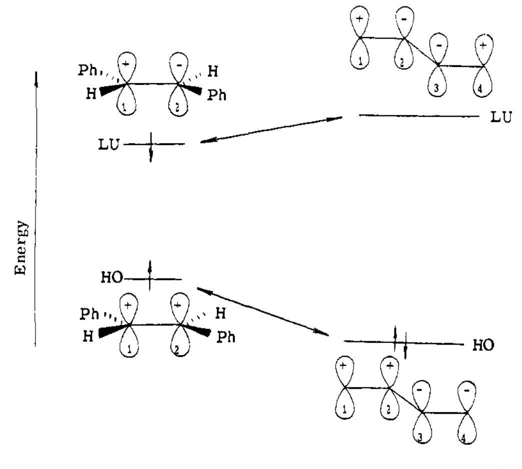


Figure 1. Orbital interaction diagram for excited *trans*-stilbene with butadiene. Relative energies are estimated from ionization potentials and singlet energies.[17a]

dicative of reversible exciplex formation.[16] We observe neither an inverse temperature dependence of the rate constant for quenching *trans*-stilbene fluorescence by dienes nor exciplex emission; however, irreversible exciplex formation cannot be excluded.

Frontier orbital theory[10] has proven useful in predicting the preferred regioisomers and relative reactivities in the Diels–Alder and other cycloaddition reactions.[17] Concerted photochemical 2 + 2 cycloaddition of *trans*-stilbene(s) with a conjugated diene (d) involves the interaction of both the highest occupied (HO–HO) and lowest unoccupied (LU–LU) molecular orbitals (Figure 1). Second-order perturbation theory provides eq 2 for the stabilization energy upon

$$\Delta E = \frac{(C_{\mathrm{HOs1}}C_{\mathrm{HOd1}} + C_{\mathrm{HOs2}}C_{\mathrm{HOd2}})^2\gamma^2}{E_{\mathrm{HOs}} - E_{\mathrm{HOd}}} + \frac{(C_{\mathrm{LUs1}}C_{\mathrm{LUd1}} + C_{\mathrm{LUs2}}C_{\mathrm{LUd2}})^2\gamma^2}{E_{\mathrm{LUs}} - E_{\mathrm{LUd}}} \qquad (2)$$

π-orbital interaction; where C_{HOd1} is the coefficient of the diene C-1 HO orbital, γ is the resonance integral between interacting orbitals, and $E_{\mathrm{HOs}} - E_{\mathrm{HOd}}$ is the energy separation between interacting orbitals (Figure 1). The preferred regioisomers will be determined by the magnitude of the diene HO and LU coefficients. Results of CNDO/2 calculations are given in Table I for several dienes. The HO coefficients for 1,3-pentadiene and 2-methyl-1,3-butadiene are similar to those recently reported for INDO calculations.[17f] Consideration of either the HO or LU coefficients leads to the prediction of preferred addition to the more substituted double bond, in agreement with the experimental results.

There remains the intriguing problem of explaining the preference for addition to the less substituted double bond observed in most diene 1,2-cycloadditions.[1-4] Stepwise (radical or ionic) reactions can be rationalized on the basis of formation of the more stable bifunctional intermediate.[1] The transition states for 1,3-dipolar and ketene additions are most likely asymmetric with substantial polar character.[18] Steric effects may also mitigate against addition to the more substituted double bond. Ketene [$_{\pi}2_s$ + $_{\pi}2_a$] cycloaddition reactions are subject to severe steric demand.[19] The lower regioselectivity of singlet diphenylvinylene carbonate[9] vs. *trans*-stilbene could also be steric in origin. Thus preferred cycloaddition to the more substituted diene double bond may only be observed for concerted reactions with minimal steric demand. Electrophilic singlet carbenes or nitrenes may fulfill these requirements; however, the available evidence is inconclusive.[5-7]

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Frederick D. Lewis,*[20a] Charles E. Hoyle[20b]
Douglas E. Johnson[20c]
Department of Chemistry, Northwestern University
Evanston, Illinois 60201

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Nuclear Magnetic Resonance of Photoexcited Triplet States. I. The Measurement of the Rate of Degenerate Singlet–Triplet Exchange for Anthracene in Solution[1]

Sir:

The NMR spectroscopy of molecules undergoing rapid exchange between diamagnetic and paramagnetic environments is well understood and is exemplified in studies of fast electron transfer between an organic radical ion and its diamagnetic precursor.[2] An entirely equivalent process can be envisioned when molecules undergo photoexcitation, intersystem cross to a triplet state, and decay to the ground state. Indeed, in a little noticed paper, Cocivera reported line broadening in the ^{1}H NMR spectrum of pyrene when the sample was irradiated with ultraviolet light.[3] On the basis of limited experimental data he proposed what is proven here to be an essentially correct mechanism for the line broadening.

In the theory of spin exchange processes it is convenient to distinguish between strong and weak pulse limits depending on the degree of dephasing the rf induced x–y nuclear