Tetrahedron Letters No. 14, pp 1125 - 1128, 1976. Pergamon Press. Printed in Great Britain.

A NEW INDEX FOR PREDICTING THE REACTIVE SITE OF INTRAMOLECULAR PHOTO-CYCLOADDITION

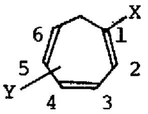
T. Tezuka and O. Kikuchi

Department of Chemistry, The University of Tsukuba
Sakura-mura, Ibaraki 300-31, Japan

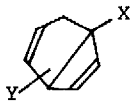
(Received in Japan 5 February 1976; received in UK for publication 24 February 1976)

The perturbation method based on the frontier-orbital coefficients predicts successfully the regiospecificity of the thermally-allowed $4+2\pi$ type cycloaddition.[1-3] There are, however, few attempts to predict the specificity of the photoreaction site.[3a,4] Very recently, Lewis et al. reported that the regiospecificity of the photo $2+2\pi$ cycloaddition of stylene to substituted dienes can be explained by the second-order perturbation method including only the frontier orbitals of the two reactants.[5] This sort of perturbation treatment, however, can not be applicable to the intramolecular problems. We wish to report a new index ΔG_{rs} for predicting the reaction course of the intramolecular cyclization of cycloheptatriene and tropone derivatives.

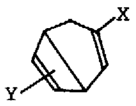
In substituted cycloheptatriene $\underline{1}$, for example, there are two theoretically possible cyclization sites, C_1-C_4 ($\underline{2}$) and C_3-C_6 ($\underline{3}$), both of which are photochemically allowed disrotatory processes.[6] However the direction of cyclization of $\underline{1}$ is distinctly specified in the actual photoreaction depending on the substituted groups. 1-Methoxycycloheptatriene ($\underline{1}$: X=OMe; Y=H) cyclizes exclusively at C_1-C_4 to give bicyclic derivative ($\underline{2}$: X=OMe; Y=H),[7] while 1-carboethoxycycloheptatriene($\underline{1}$:X=COOEt;Y=H) affords only the C_3-C_6 cyclization product($\underline{3}$).[8]



$\underline{1}$



$\underline{2}$



$\underline{3}$

In order to explain the photoreaction courses on the basis of MO method, we defines the ΔG_{rs} value which is derived from the stability gain of the frontier-orbitals. The flow 4 → 5 illustrates that two 2p AO's at the reaction sites, r and s, in 4 construct the σ-orbital in 5 after the cyclization, during which the electron distribution on the two sites changes from non-equivalent to equivalent. In photo-excited cycloheptatriene, the HOMO(ϕ_i) and LUMO(ϕ_k) are singly-occupied orbitals.[9] When the disrotatory cyclization proceeds, the electrons in the two AO's at r and s of ϕ_k(6) must be redistributed equally in the AO's of 7 which may be correlated to the σ-orbital of the product.[6] In this case, the stability gain caused by the redistribution of the electrons is positive, since the electrons are distributed more favourably in 7 than in 6 for the formation of the σ-bonding orbital. The magnetude of the stability gain may be proportional to the difference between LCAO coefficients at r and s of 6, and be expressed by $|q_r^k - q_s^k|$, where $q_r^k = C^2_{rk}$. Contrary to this, the two AO's of ϕ_i(8) loses the stability during the process 8 → 9. The stability gain in this case is $-|q_r^i - q_s^i|$. The total gain of the stability with proceeding the cyclization must be the sum of these terms. It is, thus, proposed that the photo-cyclization occurs selectively at the position having the larger ΔG_{rs} value.

$$\Delta G_{rs} = |q_r^k - q_s^k| - |q_r^i - q_s^i|$$

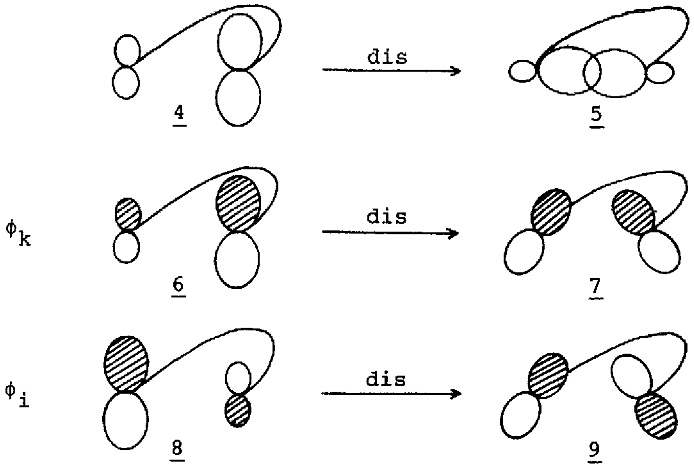
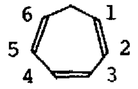
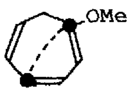
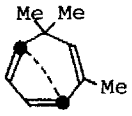


Table 1. ΔG_{rs} values and experimental observations.[*1]

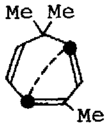
Substituted cyclo-heptatrienes.[*2]	ΔG_{rs}		ΔP_{rs}		Exp.[*3]
	1 - 4	3 - 6	1 - 4	3 - 6	
	0.000	0.000	0.436	0.436	
1 - X	0.085	-0.069	0.428	0.435	10
2 - X	-0.070	-0.004	0.435	0.435	11
3 - X	0.118	-0.060	0.432	0.432	12
1 - Y	-0.085	0.069	0.428	0.435	13
2 - Y	0.070	0.004	0.435	0.435	14
3 - Y	-0.118	0.060	0.432	0.432	15
1 - X ; 4 - Y	0.142	-0.185	0.424	0.427	16
1 - X ; 3 - Y	-0.031	-0.010	0.431	0.433	17
1 - X ; 6 - Y	0.152	-0.152	0.422	0.422	18
2 - X ; 3 - X	0.048	-0.064	0.432	0.436	19



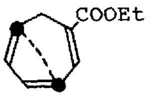
10



11

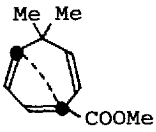


12

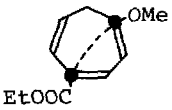


13

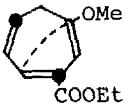
14



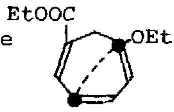
15



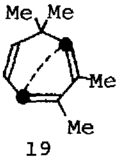
16



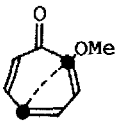
17



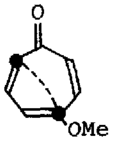
18



19



20



21

---

*1. Huckel MO's were obtained by the inductive-model calcualtions in which the Coulomb integral of the substituted C atom is set as $\alpha = \alpha(C) \pm 0.2\beta(CC)$. Resonance-model calculations were also performed using OMe and COOMe as examples of electron-donating and electron-withdrawing groups, respectively. The results exerted no influence on those obtained by the inductive-model calculations.

*2. X and Y indicate the electron-donating and -withdrawing groups, respectively.

*3. The dotted lines indicate the experimentally identified positions[8,10] of the cyclization, and the black circles, the positions theoretically predicted by ΔG_{rs}.

The ΔG_{rs} values for a number of substituted cycloheptatrienes and tropones were calculated by the Huckel MO method. Some ΔG_{rs} values of substituted cycloheptatrienes are presented in Table 1 as well as the corresponding experimental results.[8,10] All ΔG_{rs} values agree with the experimental evidence except for 17. The photo-cyclization sites in methoxytropones (20 and 21)[10] are also well predicted by the ΔG_{rs} values for the $\pi \rightarrow \pi^*$ excitation obtained by the resonance-model calculation. It is interesting to note that cycloheptatriene[11] and 2-methoxytropone[10] ($\Delta G_{1,4}$=0.000 and $\Delta G_{3,6}$=-0.008), which are known to be inert to the photo-cyclization, give equivalent and zero ΔG_{rs} values for the both directions. The cyclization of 17 would be such a case.

The index ΔP_{rs}, the difference of the bond-orders between the excited and ground states, which has been proposed by Malieu[4b] for predicting the photo-reactive site of intramolecular cyclization fails to give satisfactory prediction (Table 1). From the careful examination, it was found that each term appearing in the second-order perturbation caused by the interaction between r and s could not be a good index for the present purpose. The ΔG_{rs} value proposed here explains not only the substituent effect for the intramolecular photocyclization, but also the empirical selection rule proposed by Brember et al.[8] for the photo-reactivity of substituted cycloheptatrienes.

The authors thank Professor Sigeru Oae for his encouragement.

References and Notes

1) K. Fukui, "Molecular Orbitals in Chemistry, Physics, and Biology" Ed. by P.-O. Lowdin and B. Pullmann, p.513, Academic Press, New York, N.Y. (1964).
2) K.N. Hourk, J. Amer. Chem. Soc., 95, 4092(1973) and references cited therein.
3) (a) W.C. Herndon, Chem. Rev., 72, 157(1972);
   (b) R.F. Hudson, Angew. Chem. Internat. Edit., 12, 36(1973).
4) (a) R. Daudel, "Advances in Quantum Chemistry" 5, 1(1970);
   (b) J.P. Malieu, Photochem. and Photobiology, 5, 291, 301(1966).
5) F.D. Lewis, C.E. Hayle and D.E. Johnson, J. Amer. Chem. Soc., 97, 3626(1975).
6) R.B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry", p.39, Academic Press Inc. (1970).
7) W.G. Borden, O.L. Chapman, R. Swindell, and T. Tezuka, J. Amer. Chem. Soc., 89, 2979(1967).
8) (a) A.R. Brember, A.A. Gorman, and J.B. Sheridan, Tetrahedron Letts., 653 (1971); (b) A.R. Brember, A.A. Gorman, R.L. Leyland, and J.B. Sheridan, ibid., 2511(1970).
9) Cyclization of 1 to 2 or 3 may be originated from the singlet state (Ref. 7).
10) O.L. Chapman, "Advances in Photochemistry" Ed. by W.A. Noyes, G.S. Hammond, and J.N. Pitts, Jr., 1, p.324, Interscience Pub. (1963).
11) R. Srinivasan, J. Amer. Chem. Soc., 84, 3432(1962).