substituents other than the thiazole nuclei without disruption of the chromophore system. This leaves C-3 of pyrrole as the point of attachment between the chromophoric system corresponding to compound VI and the rest of the thiostreptonic acid molecule. The methylene group which appears at 4.42 ppm as a two-proton singlet connects the C-3 of pyrrole with the 2-propionylthiazole; its chemical shift is one expected for CH_2 protons between two aromatic nuclei.

Supporting evidence for the above assignments was found in the nmr spectrum of IV taken in D_2SO_4.[9] A one-proton singlet at 6.84 ppm disappears when the solution is heated. Exchange with deuterium identifies it as the H-4 of pyrrole and allows the assignment of the one-proton singlet at 7.56 ppm as corresponding to the C-5 hydrogen of the 2-propionylthiazole portion.

In the nmr spectrum of IV the H-5 thiazole protons appear as singlets at 7.56, 8.32, and 8.36 ppm. The spectrum of thiostrepton itself exhibits peaks in corresponding positions, suggesting that these three thiazole nuclei are present as such in the parent molecule.

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[9] M. H. Palmer, "The Structure and Reactions of Heterocyclic Compounds," St. Martin's Press, New York, N. Y., 1967, p 276.

[10] National Institutes of Health Predoctoral Fellow, 1967–1969.

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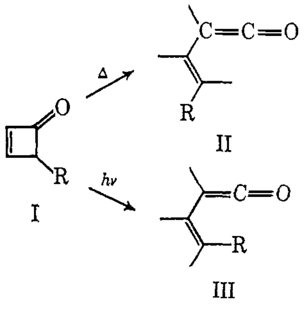
Electronic Control of the Stereospecific Thermal Opening of Cyclobutenones[1]

Sir:

Baldwin and McDaniel[2] have pointed out the difficulty of rationalizing the stereospecific opening of substituted cyclobutenones (I) to α-unsaturated ketenes (II, III) by the Woodward–Hoffmann generalizations.[3]



Nevertheless, since different products are uniquely associated with the ground and excited states of the cyclobutenones, the reactions would seem to be electronically controlled. Because of the lack of helpful symmetry in this problem, it is tedious to construct the correlation diagrams necessary to a full Woodward–Hoffmann analysis; MO calculations at many points along several reaction coordinates would be required. Here we describe an application to the thermal opening of cyclobutenones of a numerical means of by-passing the construction of correlation diagrams, while still reaching a decision whether a certain product can be obtained from a molecule in a given electronic state.

The basis of the Woodward–Hoffmann analyses is that the (adiabatic) perturbation arising from nuclear motion will leave the nodal structure of individual orbitals unchanged, while altering their amplitude from point to point in the molecule. In other words, there exists a topological mapping R which transforms the orbitals associated with geometry A into the orbitals of geometry B. The electronic state B_k of B can be obtained from state A_i of A if the orbitals ϕ_i^A occupied in state A_i are mapped by R into the orbitals ϕ_k^B occupied in the state B_k. For thermal processes, A_i and B_k are the ground states of A and B. The overlap between the wave function for the desired product and the wave function obtained by the application of the mapping to the wave function for the reactant, $S = \langle A\Pi_i R\phi_i^A | A\Pi_k\phi_k^B\rangle$, is a convenient expression of whether the process is allowed. If $S = 1$, the mapping of the orbitals occupied in A produces precisely the orbitals occupied in B. If, however, the mapping of orbitals occupied in A produces one or more orbitals vacant in B, $S = 0$, indicating that the process is forbidden.

To evaluate S, we must form the mapping operator R. According to simple topological notions,[4] a mapping may twist, stretch, bend, or otherwise distort the surface associated with an orbital, but may not cut or puncture the surface if topological invariance is desired. That is, R cannot add or remove nodes in the orbital which it acts upon. The twisting and bending operations are the most important aspects of most concerted reactions, and are relatively simple to describe mathematically. The conrotatory opening of cyclobutenes, for example, consists in large part of twists of the σ-bonded methylenes, with slight bends at the π-bonded carbons. The effect of twists may be simply considered as rotation of the atomic p orbitals, while the effect of bending is simply a rehybridization of the atomic basis. Therefore, the bends and twists can be represented by a series of 4 × 4 unitary transformations mixing the four valence atomic orbitals on each first-row atom.

The determination of the elements of the 4 × 4 transforms can be described only briefly. We are interested in the overlap between wave functions det $(R\phi_1^A R\phi_2^A \ldots) = \det(\phi_1^{B'} \ldots \phi_N^{B'})$ and $\det(\phi_1^B \ldots \phi_N^B)$ where "det" indicates that we form the antisymmetrized product of the orbitals. The overlap is conveniently evaluated by the method of equivalent orbitals,[5] in which the matrix $D_{im} = \langle R\phi_i^A | \phi_m^B\rangle$ is formed. In terms of the mapping transform and the basis functions $D_{im} = \Sigma_{ab} c_{ia}^A R_{ab} c_{mb}^B \langle b|b\rangle$. Here the c_{ia}^A and the c_{mb}^B are the expansion coefficients in the LCAO expression for the orbitals. Assuming that the basis set is orthonormal $D_{im} = \Sigma_{ab} c_{ia}^A R_{ab} c_{mb}^B$. The overlap

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[1] Based on work performed under the auspices of the U. S. Atomic Energy Commission.

[2] J. E. Baldwin and M. C. McDaniel, *J. Am. Chem. Soc.*, **90**, 6118 (1968).

[3] (a) R. B. Woodward and R. Hoffmann, *ibid.*, **87**, 395, 3511 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046, 4389 (1965).

[4] W. J. Thorn, "Topological Structures," Holt, Rinehart and Winston, New York, N. Y., 1966.

[5] H. F. King, R. E. Stanton, H. Kim, R. E. Wyatt, and R. G. Parr, *J. Chem. Phys.*, 47, 1936 (1967).

S is expressed in terms of the roots of the matrix D^+D, which we call d_i; $S = \Pi d_i^{1/2}$. It is convenient to work with the trace of the matrix D^+D; $\mathrm{tr}(D^+D) = \Sigma_i (D^+D)_{ii}$. The trace is simply expressed as the sum of squares of the overlaps of each mapped orbital and its equivalent; $\mathrm{tr}(D^+D) = \Sigma_i d_i = \langle R\phi_i^{\mathrm{A}}|\phi_i^{\mathrm{B}}\rangle^2$. The elements of the R matrix are determined by an iterative maximization of this trace.

The trace is maximized with respect to the angle w_{ab} in the transform $R(a,b)$, in which $R_{aa} = R_{bb} = \cos(w_{ab})$ and $R_{ab} = -R_{ba} = \sin(w_{ab})$ and all other $R_{kl} = \delta_{kl}$. Then the indices a and b are systematically altered in succeeding transformations until the trace converges to its maximum. Details of this numerical procedure will be presented in greater detail elsewhere.

The final values of the roots d_i allow decisions whether a process is allowed. To refer to a familiar example, the thermal opening of cyclobutene to butadiene, we evaluated the roots for the conrotatory and disrotatory modes. The source of the MO's was an ordinary CNDO computation.[6] Nine of the eleven roots corresponded to σ orbitals which were merely reoriented; all these are ≥ 0.99. The remaining roots were related to the π orbitals of butadiene; the conrotatory motion yielded values of 0.63 and 0.63, while the disrotatory motion gave roots of 0.99 and 0.03. Bearing in mind that only an approximate construction of R was attempted, it seems clear that the implications of these calculations, that the disrotatory route is forbidden while the conrotatory route is allowed, are entirely consistent with the well-established behavior of this system.

The application of this method to the thermal opening of 4-methylcyclobutenone (I, with R = Me) is of central interest here. In this case, 11 of the roots corresponded to σ bonds which were merely reoriented, and were indistinguishable from unity whether the *cis* or *trans* ketene was formed. The remaining roots were 0.68, 0.65, 0.81, 0.79, and 0.05 for the thermal formation of the *cis* ketene, and 0.53, 0.89, 0.68, 0.95, and 0.98 for the formation of the *trans* isomer II. The presence of the near-vanishing root for the opening to the *cis* isomer indicates that the process is forbidden; in contrast, the formation of the *trans* ketene is allowed. The conclusions are in accord with the previously established experimental data.[2]

The role of the methyl group (or other 4- substituents) in the opening of cyclobutenones is worth attention in view of the result that *the opening of unsubstituted cyclobutanone is forbidden* according to mapping calculations. It must be assumed that the perturbation on the ring system due to the methyl substituent has the effect of mixing into the ring wave function excited configurations which correlate with the ground state of the ketene. The perturbation is not a strictly repulsive effect which could be ascribed to steric interaction; rather the methyl is attracted to C_3 and repelled from C_2, as shown by the signs of the bond-order matrix. Given this topology of interaction, examination of the signs of the bond order in the ketenes leads to the conclusion that the methyl must be rotated away from the carbonyl group in order that the interactions of the methyl with the remainder of the ketene be of the correct sign. This argument is applicable to both the (+) and (−) optical isomers of methylcyclobutenone, which accounts for Baldwin's recovery of a single *trans* isomer from racemic cyclobutenone. The calculations presented here suggest determination of the relative rates of opening of substituted and unsubstituted cyclobutenones, in order to determine the energetic significance of topological constraints.

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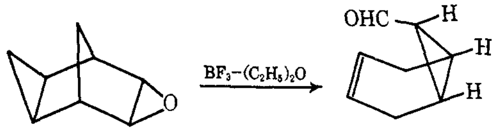
(6) J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965); **44**, 3289 1966).

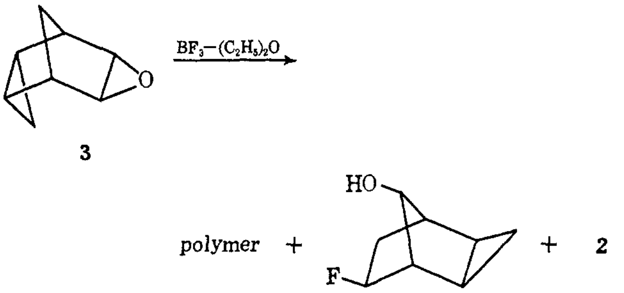
Nucleophilicity of Remote Cyclopropane. The Facile Acid Catalyzed Rearrangement of *exo*-Tricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-Oxide

Sir:

Acid catalysis effects the smooth, rapid conversion of *exo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-oxide (**1**) exclusively to *endo*-7-bicyclo[4.1.0]hept-3-enecarboxaldehyde (**2**). This reaction provides an economical, stereospecific entree to the synthesis of *endo*-7-substituted Δ^3-norcarene derivatives. Contrasted with the behavior of *endo*-tricyclo[3.2.1.0^{2,4}]oct-6-ene *exo*-oxide (**3**), which on treatment with BF_3–$(C_2H_5)_2O$ yields largely polymeric material, this result provides strong support for the suggestion that cyclopropane may function as a nucleophilic neighboring group in this[1,2] and related[3] systems and leads to significant clarification in the structure of the ion which results from such participation. In particular, we are led to infer that cyclopropyl participation in these systems leads to a charge-delocalized ion, which, in the absence of rapid collapse to stable products, can and does isomerize to a charge-localized cation.



1 **2**



3

(80%) **4** (15%) (5%)

The *exo*,*exo*-oxide **1** and the *endo*,*exo*-oxide **3** are obtained in high yield from their respective alkenes[4a] by

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(1) K. B. Wiberg and G. R. Wenzinger, *J. Org. Chem.*, **30**, 2278 (1965).

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(3) P. K. Freeman and D. M. Balls, *Tetrahedron Lett.*, 437 (1967).

(4) (a) H. E. Simmons, E. P. Blanchard, and R. D. Smith, *J. Am. Chem. Soc.*, **86**, 1347 (1964); G. L. Closs and K. D. Krantz, *J. Org. Chem.*, **31**, 638 (1966); (b) K. M. Karach, R. D. Nielsen, and H. W. Rideout, *J. Am. Chem. Soc.*, **82**, 4328 (1960).