The relative configurations of the **1E** and **1N** used were established by base isomerization of the optically active esters used to prepare **1E** and **1N**. After photolysis the alcohols **1E** and **1N** were converted back to the esters to facilitate separation. The rotations of the esters were then taken (at six different wavelengths),[13] and from these values the amounts of bond a and bond b cleavage in the isomerization processes were calculated. In all runs conversion of the starting material to its isomer was kept less than 10%. Recovered starting material from the photolyses and base isomerizations in every case showed no loss of optical activity. Appropriate controls showed that the conversions of the alcohols to the esters gave no epimerization or racemization of the cyclopropanes. The results are shown in Table I. It should be emphasized that the last two columns in the table refer solely to the percentage bond cleavage leading to isomerization.

The data in Table I are striking and permit several conclusions: (1) isomerization of the triplet states of both **1E** and **1N** proceeds almost exclusively via bond a cleavage; (2) the isomerizations observed on direct irradiation, while still proceeding mostly by bond a cleavage, involve a sigificant (19%) amount of bond b fission; furthermore, and very significantly, (3) our data permit us to state definitively that the isomerizations observed on direct irradiation of **1E** and **1N** proceed at least in part (≥17%) by way of the singlet states.

Thus, the triplets of **1E** and **1N** show a very great preference for cleavage of the external bond in accord with expectations based on orbital overlap considerations. In considering the direct irradiation results we note that our data provide no indication as to the extent of the contribution of the triplet states of **1E** and **1N** to the observed isomerizations. However, since the triplets isomerize essentially entirely by bond a cleavage, we may conclusively say that the singlet state isomerizations proceed with a *minimum* of 19% bond b cleavage. It seems likely that the actual percentage of singlet state bond b isomerization is higher than this minimum. The preference for singlet state bond a fission is therefore at most not overwhelming, in line with what one might expect from the previously noted uv data.[15]

Finally, we note that, as is the case with olefins, determining whether the singlet state is responsible for any of the cis–trans isomerization observed upon direct irradiation of arylcyclopropanes is in general extremely difficult. In the present case it is the fortuitous difference in bond cleavage selectivities of the singlet and triplet states which permits the observation of singlet state isomerization. Our results, together with Salisbury's on methylphenylcyclopropane,[1g] indicate cis–trans isomerization may be a general process of the singlet states of alkylarylcyclopropanes.[14]

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(7) However, the situation changes when the aryl group is highly electron withdrawing. Here, as in the ketone case, the conjugative interaction is a spectroscopically detectable function of geometry.[8]

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(11) (a) The cis (**3c**) and trans (**3t**) isomers of 2-vinyl-1-indanol plus several very minor products which were produced in quantities insufficient for identification. The formation of **3c** and **3t** will be discussed in more detail elsewhere. (b) $\Phi_{1N \rightarrow 3c+3t} = 0.022 \pm 0.002$, $\Phi_{1E \rightarrow 3c+3t} \leq 0.003$.

(12) We assume cleavage of the nonconjugated bond c is unimportant. It would be stereochemically equivalent to cleavage of bond a.

(13) In addition CD spectra were taken of each ester from every run to ensure the absence of optical impurities.

(14) Zimmerman and Epling[1f] have evidence for a singlet state cis–trans isomerization in a diphenylvinylcyclopropane.

(15) A discussion of the singlet–triplet selectivity difference will be presented in our full paper.

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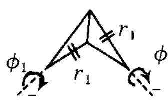
MINDO/3 Study of the Thermolysis of Bicyclobutane. An "Allowed" and Stereoselective Reaction That Is Not Concerted[1]

Sir:

Bicyclobutane (**1**) is known to isomerize on heating to 1,3-butadiene (**2**) with an activation energy of 40.6 kcal/mol.[2,3] Closs and Pfeffer[4] have found that the rearrangements of derivatives of **1** are highly stereoselective in the manner predicted by the Woodward-Hoffmann rules[5] and Evans' principle.[6] It has therefore been generally accepted that these reactions take place by a concerted [$\sigma 2s + \sigma 2a$] mechanism.



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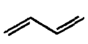
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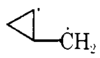

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Although this conclusion seemed logical we became suspicious of it for three reasons. First, preliminary MINDO/2 calculations[7] led to excessively high activation energies. Admittedly this could have been due to the difficulty of studying such a potential surface, using the inefficient geometry procedures then available, but the discrepancy seemed too large for this. Secondly, reactions involving bond breaking require inherent activation, and a reaction involving the simultaneous breaking of two bonds should need double that for breaking of one. Reactions involving the concerted breaking of two bonds are therefore rare.[8] Yet the activation energy for conversion of **1** to **2** is little greater than that (36 kcal/mol[9]) for the analogous conversion of cyclobutene (**4**) to **2** in which only one bond is broken. Thirdly, other studies had led us to the realization that stereochemistry can be retained during reactions that involve intermediates that would be represented classically as biradicals.[10] We have therefore studied the conversion of **1** to **2** using the latest version (MINDO/3[11]) of the MINDO semiempirical SCF MO method together with a new and very efficient procedure[12] for calculating, molecular geometries. Extensive tests[11,13] have shown that this reproduces heats of formation and activation energies with an average error of ca. 5 kcal/mol. Thus the calculated heats of formation of **1** and **2** were in error by −2.1 and 5.8 kcal/mol, respectively. Their calculated geometries[11] were also in reasonable agreement with experiment.

The reaction was first studied using the length of one of the breaking bonds (r_1 in **1**) as reaction coordinate, the energy of the molecule being minimized with respect to all other coordinates for each value of r_1. However, as r_1 was increased, the length of the other breaking bond (r_2 in **1**) remained unchanged as also did the angle (ϕ_2 in **1**) representing the rotational orientation of the second methylene group relative to the rest of the molecule.

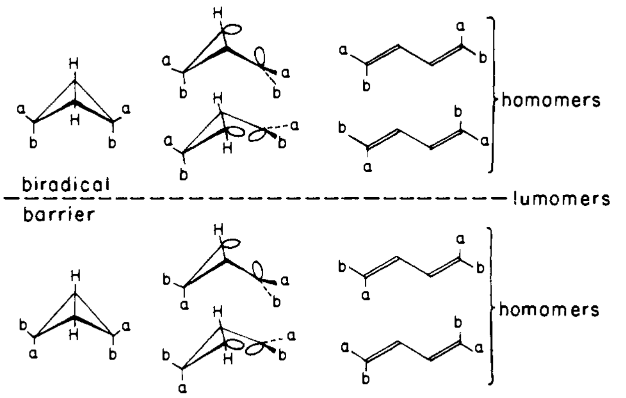
We next treated the system using both r_1 and r_2 as reaction coordinates. When, however, both r_1 and r_2 were increased, the twist angles (ϕ_1 and ϕ_2 in **1**) of the methylene groups remained unchanged and the energy increased steadily. Finally we treated all four variables (ϕ_1, ϕ_2, r_1, r_2) as reaction coordinates, varying all simultaneously. In this way a symmetrical transition state was at last located, apparently analogous to that found by Wiberg[14] but corresponding to an activation energy of 90 kcal/mol. This confirmed the argument that a concerted process of this kind should have a much higher activation energy than that for an analogous one involving breaking of one bond only. The value found was indeed nearly double that (49 kcal/mol) calculated[15] for conversion of **3** to **2**.

We therefore felt confident that the reaction could not be a truly concerted pericyclic process in which both the relevant bonds in **1** break simultaneously but must take place in stages, the transition state corresponding to a situation where one bond has been almost completely broken while the other remains almost intact (cf the Diels-Alder reaction[10]). Such processes cannot be studied by procedures using single determinant wave functions; we therefore repeated the calculations including CI with the lowest doubly excited configuration.[16,17]

With CI, the reaction followed an entirely different course. Here an intermediate was formed which would be represented classically as the biradical (**4**) and which dissociated into **2** almost without activation. The rate-determining step was the formation of **4** from **1** for which we calculated an activation energy of 40.3 kcal/mol in essentially perfect agreement with experiment (40.6 kcal/mol[2,3]).

How then can we explain the stereospecificity of the reaction? As we have pointed out recently,[18] a singlet biradical is an unstable species which must undergo Jahn-Teller distortion to one or other of two more stable isomeric species. These are lumomers[19] of one another and their interconversion via the biradical is a "forbidden" process. Indeed, our calculated structure (**5**) for the intermediate shows it to be a biradicaloid,[18] derived from **4** by a direct coupling between the radical centers. This biradicaloid is a homomer of **1** and of *one* of the butadienes (**2**) that can arise from **1**. Thus **4** retains a "memory" of the structure of **1** and the subsequent conversion to **2** is stereospecific. The situation can be represented schematically as shown in Scheme I.

In order to cross from one set of homomers to the other, the reaction has to pass through a high energy biradical intermediate. However, the barrier to such a "forbidden" process is naturally less, the nearer the species is to the biradical initially. Isomerization of one of the initial biradicaloid species (**6** or **7**) to a lumomeric biradicaloid (**8** or **9**) should occur quite easily. Indeed, we calculate the barrier height to be 8 kcal/mol above **5** which itself is 35 kcal/mol above **1**. Thus the overall activation energy for conversion of **1** to "forbidden" products, violating the Woodward-Hoffmann rules, is calculated to be 43 kcal/mol, only 2.7 kcal/mol above that for the "allowed" reaction. This would correspond, at 200°, to ca. 5% of "forbidden" product. Closs and Pfeffer[4] found that the reactions were indeed stereoselective rather than stereospecific, the proportion of "forbidden" product being 4–7%.



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The Conversion of Benzvalene to Benzene[1]

Sir:

The conversion of benzvalene (**1**) to benzene (**2**) on heating raises several interesting problems. In particular, is this an "allowed"[2-4] process? To the best of our knowledge neither Woodward nor Hoffmann has expressed any definite opinion while Dewar[3] described it as "forbidden" on the