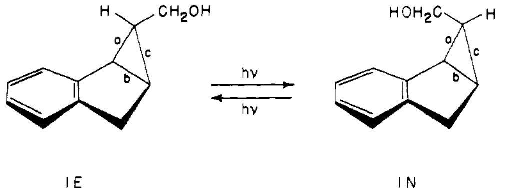
Arylcyclopropane Photochemistry. A Photochemical Probe into the Stereoelectronic Requirements for Excited State Interaction between Aromatic and Cyclopropane Rings in Arylcyclopropanes

Sir:

Both arylcyclopropanes[1] and cyclopropyl ketones[2] have been found to undergo cis-trans isomerization upon irradiation. Studies on the latter compounds have shown that the bond of the cyclopropane ring which is preferentially cleaved during isomerization is that which best overlaps with the π system of the carbonyl group.[2b,3] This finding of selectivity in bond cleavage is in accord with uv studies of cyclopropyl ketones which show (a) that there is a significant interaction between the three-ring and the carbonyl group in the excited state, (b) that this interaction is a sensitive function of the geometric orientation of the cyclopropane ring with respect to the carbonyl group, where for optimum interaction the plane of the π bond of the carbonyl group and that of the three-membered ring should be parallel, giving maximum bond overlap, and (c) in cases where the two cyclopropane bonds adjacent to the carbonyl group do not overlap equally well, alkyl substitution on the β-carbon of that cyclopropane bond which best overlaps with the carbonyl group results in a greater bathochromic shift of the uv spectrum than substitution on the other bond.[4]

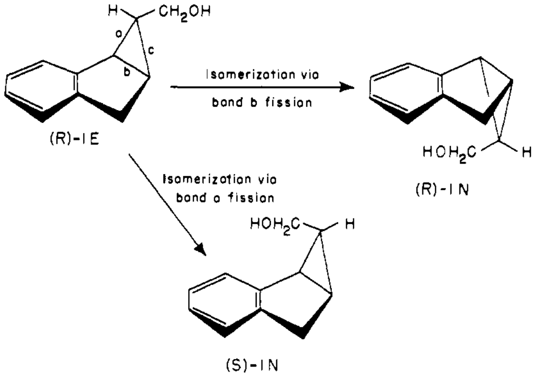
In marked contrast, uv studies of arylcyclopropanes show no evidence for a preferred geometry for conjugative interaction between the aromatic and cyclopropane rings,[5] and a similar situation appears to hold for vinylcyclopropanes.[6,7] The important question therefore arises as to the mode by which the aromatic and cyclopropane rings interact in the photochemical cis-trans isomerization of arylcyclopropanes. The situation could be similar to that with cyclopropyl ketones where a strong preference for cleavage of the bond which overlaps best with the π system is found. On the other hand, the uv studies indicate a rather more indiscriminate cleavage pattern is a strong possibility. In pursuing this problem we have investigated the photochemical cis-trans isomerization of arylcyclopropanes **1E** and **1N**.[9]

Either direct or acetone-sensitized irradiation leads to interconversion of **1E** and **1N** (eq 1). Isomerization quantum yields for the direct irradiations were $\Phi_{1E \rightarrow 1N} = 0.10 \pm 0.01$ and $\Phi_{1N \rightarrow 1E} = 0.13 \pm 0.01$, while for the sensitized irradiations $\Phi_{1E \rightarrow 1N} = 0.13 \pm 0.01$ and $\Phi_{1N \rightarrow 1E} = 0.40 \pm 0.02$. This interconversion between **1E** and **1N** is the only process observed in the sensitized irradiations. The direct irradiations do lead to other products,[11a] but the efficiency of these other processes is much less than that of the **1E** ⇄ **1N** isomerizations.[11b] Significantly, the absence of these other products in the sensitized runs indicates singlet energy transfer from acetone is negligible.



1E 1N (1)

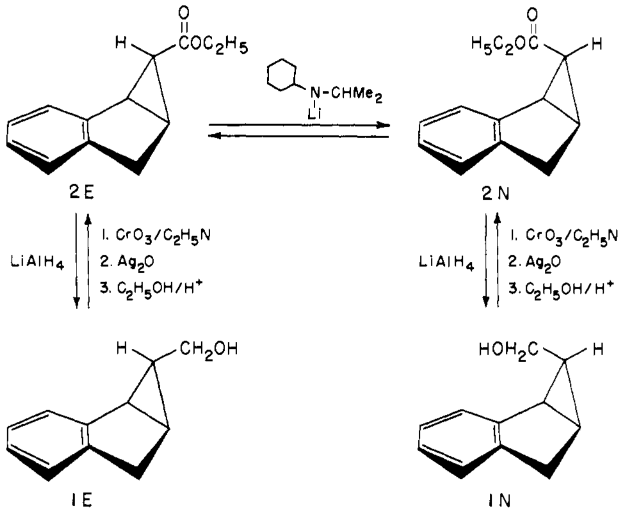
Conversion of **1E** to **1N** could conceivably proceed via initial cleavage of bond a or bond b.[12] The former bond has good overlap with the aromatic ring π system; the latter has very poor overlap. With racemic **1E** the two bond fission processes are indistinguishable. However, with optically active **1E** they may be differentiated, for they lead to different enantiomers of product **1N** (see eq 2; here R and S refer to the configuration at C-1 which bears the hydroxymethyl group). Thus examination of the configuration of **1N** (relative to starting **1E**) produced upon irradiation of optically active **1E** allows one to determine to what extent cleavage of bonds a and b are involved in its formation. The same is true for the **1N** to **1E** conversion.



(2)

We therefore prepared and irradiated optically active **1E** and **1N** and determined the configurations of the isomers produced relative to the starting materials in each case. The mode of configuration correlation is shown in Scheme I.

Scheme I



1E 1N

Table I. Interconversion of 1E and 1N[a]

Reactant rotation[b]	Conditions	Recovered reactant, rotation[b]	Isomerized product, rotation[b] (% racemization)	% bond a cleavage[c]	% bond b cleavage[c]
1E, −113.1 ± 1.2°	Base	−113.1 ± 0.1°	−106.5 ± 0.4°		
	Direct *hν*	−113.2 ± 0.1°	−64.6 ± 0.4° (39.3)	80.6 ± 1.2	19.4 ± 1.2
	Sensitized *hν*	−113.0 ± 0.1°	−103.3 ± 1.6° (3.0)	98.0 ± 3.2	2.0 ± 3.2
1N, −389.0 ± 0.3°	Base	−388.8 ± 0.7°	−428.0 ± 1.5°		
	Direct *hν*	−388.9 ± 0.2°	−262.0 ± 1.8° (38.8)	80.7 ± 0.6	19.3 ± 0.6
	Sensitized *hν*	−388.7 ± 0.4°	−412.4 ± 0.9° (3.7)	98.0 ± 0.6	2.0 ± 0.6

[a] Results given are the average of two different runs in each case. [b] Rotation values given are at 435.83 nm and are for the esters derived from 1E and 1N (see text). [c] These are averages of results obtained at six different wavelengths.

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]

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

References and Notes

(1) See, e.g., (a) G. W. Griffin, J. Covell, R. C. Petterson, R. M. Dodson, and G. Klose, *J. Am. Chem. Soc.*, **87**, 1410 (1965); (b) G. S. Hammond, P. Wyatt, C. D. DeBoer, and N. J. Turro, *ibid.*, **86**, 2532 (1964); (c) S. S. Hixson, *ibid.*, **96**, 4866 (1974); (d) S. S. Hixson and D. W. Garrett, *ibid.*, **96**, 4872 (1974); (e) S. S. Hixson, *J. Chem. Soc., Chem. Commun.*, 681 (1974); (f) H. E. Zimmerman and G. A. Epling, *J. Am. Chem. Soc.*, **94**, 8749 (1972); (g) K. Salisbury, *ibid.*, **94**, 3707 (1972); (h) J. K. Foote, Ph.D. Thesis, University of California at Riverside, 1966.

(2) See, e.g., (a) G. W. Griffin, E. J. O'Connell, and H. A. Hammond, *J. Am. Chem. Soc.*, **85**, 1001 (1963); (b) H. E. Zimmerman, K. G. Hancock, and G. C. Licke, *ibid.*, **86**, 4892 (1968); (c) H. E. Zimmerman, S. S. Hixson, and E. F. McBride, *ibid.*, **92**, 2000 (1970); (d) H. E. Zimmerman and C. M. Moore, *ibid.*, **92**, 2023 (1970); (e) R. C. Cookson, M. J. Nye, and G. Subrahmanyan, *Proc. Chem. Soc., London*, 144 (1964); (f) W. G. Dauben and W. M. Welch, *Tetrahedron Lett.*, 3531 (1971); (g) G. W. Shaffer, *J. Org. Chem.*, **37**, 3282 (1972); (h) H. E. Zimmerman and T. W. Flechtner, *J. Am. Chem. Soc.*, **92**, 6931 (1970).

(3) This selectivity is likewise found for isomerizations of cyclopropyl ketones other than cis–trans isomerization. See W. G. Dauben, G. W. Shaffer, and E. J. Deviny, *J. Am. Chem. Soc.*, **92**, 6273 (1970).

(4) W. G. Dauben and G. H. Berezin, *J. Am. Chem. Soc.*, **89**, 3449 (1967), and references therein.

(5) A. L. Goodman and R. H. Eastman, *J. Am. Chem. Soc.*, **86**, 908 (1964).

(6) C. H. Heathcock and S. R. Poulter, *J. Am. Chem. Soc.*, **90**, 3766 (1968).

(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]

(8) (a) R. C. Hahn, P. H. Howard, S-M Kong, G. A. Lorenzo, and N. L. Miller, *J. Am. Chem. Soc.*, **91**, 3558 (1970); (b) R. M. Kellog and J. Bater, *J. Org. Chem.*, **36**, 2237 (1971).

(9) Studies by Zimmerman and Epling[1f] on a bicyclic diphenylvinylcyclopropane and by Garin and Cooke[10] on a bicyclic vinylcyclopropanecarboxylic acid (and ester) have not probed the overlap question itself because of the presence of more than one conjugating substituent in each case.

(10) D. L. Garin and D. J. Cooke, *J. Chem. Soc., Chem. Commun.*, **33** (1972).

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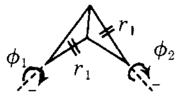
MINDO/3 Study of the Thermolysis of Bicyclobutane. An "Allowed" and Stereoselective Reaction That Is Not Concerted[1]

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 [σ2s + σ2a] mechanism.



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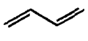

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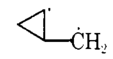

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Although this conclusion seemed logical we became suspicious of it for three reasons. First, preliminary MINDO/2 calculations[7] led to excessively high activation energies. Admittedly this could have been due to the difficulty of studying such a potential 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