pends on the fate of the excited octahedral complex. In the earlier study,[5] the excited complex was assumed to be very rapidly (*i.e.*, within the laser discharge time) converted to the *planar form in its ground state.*[9] The observed relaxation was then ascribed to the reestablishment of equilibrium *via* reactions of the ground-state octahedral and planar forms. In the absence of knowledge of the rate of conversion of the excited octahedral form to the ground-state planar complex or of the genuine relaxation rate for the ground-state complexes this interpretation is open to question. In an effort to resolve this difficulty we independently studied the relaxation of this system using the Raman laser temperature-jump technique.

The same solutions that had been used in the 1.06 μ study were irradiated with 1.41 μ photons, obtained by using liquid nitrogen to Raman shift the 1.06 μ neodymium radiation.[3] The solutions were initially at 23°, and, in the case of H_2O solutions, temperature jumps of 2–3° were produced. The relaxation was again monitored at 440 nm. A typical trace for the H_2O solution is shown in Figure 1(c). Here the direction of the observed relaxation is opposite to that shown in Figure 1(a), but the relaxation time, 0.30 ± 0.02 μsec, is the same as that produced with the 1.06 μ radiation. The direction of the signal change, indicating an increase in the equilibrium concentration of the planar complex, is consistent with the exothermicity of eq 1 ($\Delta H^\circ = -4.8 \pm 0.3$ kcal mol^{-1}).[5] Using 1.41 μ radiation for the H_2O solution favors temperature-jump over nickel photochemistry because of the relative absorbances of the complex and solvent at this wavelength (for H_2O, $A_{1.41} = 10$ cm^{-1}; for the nickel solution, $\epsilon_{1.41} \leq 1\ M^{-1}$ cm^{-1}). A relaxation of the kind found for 1.06 μ (but of smaller amplitude) is, however, seen when the D_2O solution is used at 1.41 μ (Figure 1(d)). Here again excitation of the octahedral nickel complex predominates because of the low absorptivity ($A = 0.07$ cm^{-1}) of D_2O at 1.41 μ.[2]

It is apparent from Figure 1(a), (b), and (c) that the signal changes obtained for photochemical and temperature-jump perturbations are of similar magnitude. For the photochemical perturbation at 1.06 μ the fractional increase in the concentration of planar molecule is given by[10]

$$\frac{\Delta[\mathrm{NiL}^{2+}]}{[\mathrm{NiL}^{2+}]} = \frac{2.3 \times 10^3 \epsilon I_0 K \phi}{N} \qquad (2)$$

where ϵ (the molar absorptivity of the octahedral form at 1.06 μ) is 2.0 M^{-1} cm^{-1}, I_0 (the intensity of the incident laser beam) is 1.5×10^{19} photons cm^{-2} (3 J cm^{-2}), K (the equilibrium constant for reaction 1) is 6.25, N is Avogadro's number, and ϕ is the quantum efficiency for conversion of the excited octahedral complex to the planar form. Expression 2 reduces to 0.75ϕ. Since the observed 440 nm absorbance change corresponds to a 15% increase in the planar concentration, it follows that $\phi \sim 0.2$. In the case of temperature-jump perturbation for the H_2O solution at 1.41 μ, provided that the concentration of the planar form is much less than that of the octahedral, the fractional increase in the concentration of the planar complex is given by expression 3. Here ΔT is the temperature increase produced, 2.5° for 1 J cm^{-2} of 1.41 μ radiation, and ΔH° is the enthalpy change for reaction 1, 4.8 kcal mol^{-1}.

$$-\frac{\Delta[\mathrm{NiL}^{2+}]}{[\mathrm{NiL}^{2+}]} = \frac{\Delta T \Delta H^\circ}{RT^2} \qquad (3)$$

The concentration increase calculated for the planar form is 7%, in satisfactory agreement with the observed absorbance change of 9%. If the absorbance of the solvent at the wavelength of irradiation is less than 0.05, then the temperature jump produced is $\Delta T = 2.3 I_0 A/C$ where C is the heat capacity of the solution and A is the solvent absorbance per centimeter. Consequently the ratio of the displacements by the two perturbations (subject to the above conditions) is

$$-\frac{\Delta_{\text{photochem}}}{\Delta_{\text{temp jump}}} = \frac{7.0 \times 10^{-2}\, \epsilon K \phi T^2 C \lambda}{\Delta H^\circ A} \qquad (4)$$

where the energy units for C and ΔH° are calories and λ, the wavelength of the incident laser beam, is expressed in microns. The above equation neglects any temperature increase arising from absorption of the laser radiation by the solute. Equation 4 predicts the above ratio to be ~50 in H_2O at 1.06 μ, in good agreement with the observed value once allowance is made for the temperature increase resulting from the radiation absorption by the nickel complex.

It is worth reemphasizing that, in the present study, replacing H_2O by D_2O (with 1.41 μ radiation) converts a situation in which a *less* than equilibrium concentration of the planar complex is present immediately after the perturbation into one in which a *larger* than equilibrium concentration of the planar form is produced initially. A similar reversal in the direction of the perturbation is produced in H_2O by changing from 1.41 to 1.06 μ. Further, the agreement of relaxation times obtained by two independent methods is especially significant in that it adds credibility to the interpretation of the photochemically obtained results in terms of the reactions of ground-state species.

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[9] The absorbance changes in Figure 1(a) and (b) may also be explained by postulating that the decay of the excited octahedral nickel complex yields a 440-nm absorbing, nonreactive species. This interpretation seems less plausible than that advanced above.

[10] Equation 2 obtains provided that the 1.06 μ absorbance of the solute is small (less than 0.05).

Photoisomerizations of 2-Methylphenylcyclopropanes to 4-Phenylbutenes. Stereochemistry at the Benzylic Carbon

Sir:

The nature of the transition states in organic reactions is the object of continued investigation. Stereochemical criteria have been of great value in elucidating the nature of organic transition states, and the photochemical isomerization of 2-alkylphenylcyclopropanes to 4-phenylbutenes is amenable to such an experimental test.

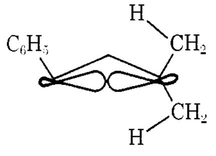
Our working hypothesis was based on two reasonable mechanistic possibilities: (1) a σ^2s + σ^2s con-

Table I

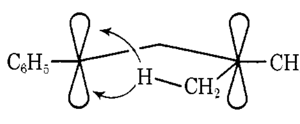
	Optical purity				
	6 (initial)[a,b]	6 (recovered)[a,c]	6 (av)[a]	7[d,e] (obsd)	7 (predicted)
Expt[f] 1	0.75 ± 0.03	0.45 ± 0.04	0.60 ± 0.04	0.59 ± 0.29	0.60
Expt[g] 2	0.75 ± 0.03	0.32 ± 0.04	0.54 ± 0.04	0.5 ± 0.3	0.54

[a] Reading taken at 334 nm. [b] Reading taken before irradiation. [c] Reading taken on material recovered after irradiation. [d] These numbers represent an average of the optical purities calculated for each experiment at 280 and 302 nm. [e] Measured rotations were corrected for incomplete deuteration (91.8% d_1). [f] 48% conversion of **6**, 24% **7** obtained. [g] 62% conversion of **6**, 32% **7** obtained.

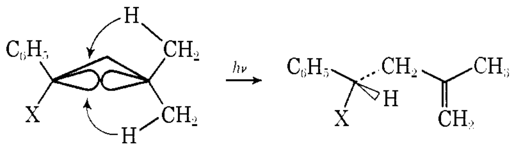
certed cycloaddition[1] or its operational equivalent; (2) a process taking place through a π-cyclopropane intermediate,[2] **2**, arrived at *via* a mixture of disrotatory and conrotatory openings[3] of **1**. The results of these two processes differ significantly with respect to stereochemistry at C1. Whereas the former case predicts net retention of stereochemistry at C1, the π-cyclopropane intermediate possesses a plane of symmetry which would result in equivalent amounts of retention and inversion processes. In a suitably substituted (at C1) phenylcyclopropane these alternatives can be evaluated by virtue of the product asymmetry at the migration terminus, *i.e.*, optically active **3** will afford active **4** *via* the $\sigma^2 + \sigma^2$ route whereas, owing to its symmetry properties, the π-cyclopropane route should result in racemic product.



1



2

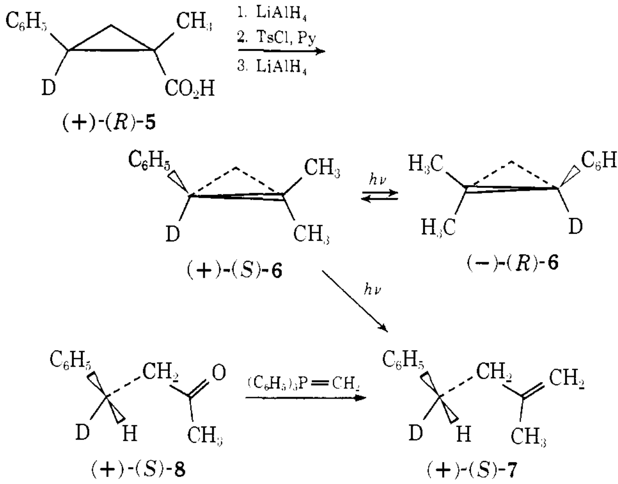


3 4

We chose to conduct our investigation on the deuterated phenylcyclopropane **6** in spite of the fact that product chirality solely[4] due to the presence of deuterium at the asymmetric center was expected to result in low product rotations and attendant experimental difficulties. The system has distinct advantages in that our previous results[3] are directly applicable to these experiments since the presence of deuterium is expected to be a minor mechanistic perturbation,[5] and sufficient literature data are available on related compounds to allow a complete stereochemical correlation.

Preparation of active **6** was accomplished from the resolved acid **5**[6] by the route outlined (Chart I). Irradiation (254 nm) of **6** in isooctane followed by glpc isolation afforded material with a measurable positive rotation at 302 nm indicating that complete racemization had not occurred.[7] More definitive mechanistic conclusions require a knowledge of the optical purities of **6** and **7**. Compound **8**[8,9] ($[\alpha]_D = 0.35 \pm 0.09°$) was converted *via* a Wittig reaction to **7** ($[\alpha]_{302} = 2.0 \pm 0.2°$, $[\alpha]_{280} = 4.3 \pm 0.7°$). Since the conversion of **8** ($[\alpha]_D = 0.44°$) to 1-phenylbutane-*1-d* (**9**, $[\alpha]_D = 0.78°$) has been accomplished[8] and the maximum rotation of **9** is predicted to be $[\alpha]_D = 2.1°$,[4] the maximum rotations of **7** may be calculated to be $[\alpha]_{302} = 6.9 \pm 2.3°$ and $[\alpha]_{280} = 14.8 \pm 5.2°$.

Chart I



Data on the optical purity of starting **6** must reflect the fact that photochemical racemization[10] of starting material competes with product formation. In our calculations we use an average of the optical purities of the starting material before and after reaction. Measurements on the optical purity of **6** showed that it changes in a linear fashion with respect to photolysis time indicating that this approximation is valid. Our results, summarized in Table I,[11] are quite striking and indicate that the reaction takes place with essentially complete retention of optical activity. In addition,

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(1) R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Academic Press, New York, N. Y., 1970.

(2) R. Hoffmann, *J. Amer. Chem. Soc*, **90**, 1475 (1968).

(3) P. H. Mazzocchi and R. S. Lustig, *J. Org. Chem.*, in press. In a series of deuterium labeling experiments we have shown that hydrogen migration in **1** takes place preferentially from the methyl group trans to the benzene ring. The trans:cis migration ratio determined was 63:37. Subsequent mechanistic analysis has been conducted with these results in mind.

(4) D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 127 (1969).

(5) The alternative methyl label at the benzylic carbon might actually change the reaction mechanism. For one example see J. A. Berson and G. L. Nelson, *J. Amer. Chem. Soc.*, **92**, 1096 (1970).

(6) The acid was resolved *via* its ephedrine salt. Details of the synthesis and resolution of **6** will be presented elsewhere.

(7) The low rotations observed for **7** presented a problem in that they could have been due to a minor contamination of **6** which has a much higher rotation. To guard against this active **7** was isolated by preparative glpc, diluted with a large excess of racemic **6**, and reisolated by preparative glpc. The specific rotations of both samples of **7** were within experimental error of each other.

(8) A. Streitwieser, Jr., J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron*, **6**, 338 (1959).

(9) C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Amer. Chem. Soc.*, **88**, 3347 (1966).

(10) Racemization is essentially cis–trans isomerization[3] involving rotation of the benzylic carbon (C1). Rotation at C2 is a nonobservable process in this system.

(11) Rotations were measured on a Perkin-Elmer 141 polarimeter with automatic digital readout. Readings reflect the inherent instrumental error of ±0.002°. For compound **7** (experiment 1) the readings were $\alpha_{302} = 0.012$ and $\alpha_{280} = 0.018$, respectively, in ethanol.

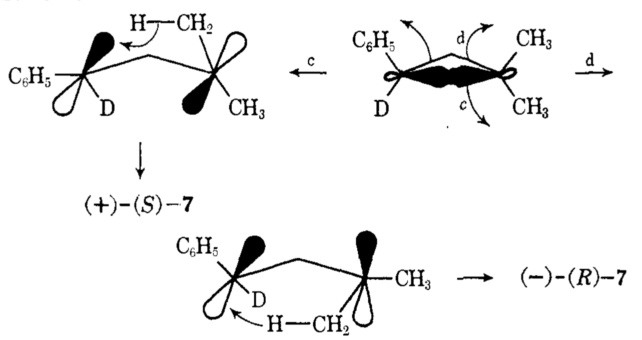
knowledge of the absolute stereochemistry of **6**[12,13] and **7**[14] shows that the reaction takes place with *retention* of *stereochemistry* at the benzylic carbon.

It is worthwhile to carry out a mechanistic evaluation which reflects the minimum retention of stereochemistry value allowed by the error in our data on the optical purity of **7**.[15] Using the extremes of the values for experiment 1 given in Table I for **6** (av) and **7** (obsd) (*i.e.*, 0.64 and 0.30, respectively), it can be calculated that $k_1 = 2.8k_2$, *i.e.*, at a *minimum* retention is faster

$$(+)\text{-}(S)\text{-}\mathbf{7} \xleftarrow[\text{retention}]{k_1} (+)\text{-}(S)\text{-}\mathbf{6} \xrightarrow[\text{inversion}]{k_2} (-)\text{-}(R)\text{-}\mathbf{7}$$

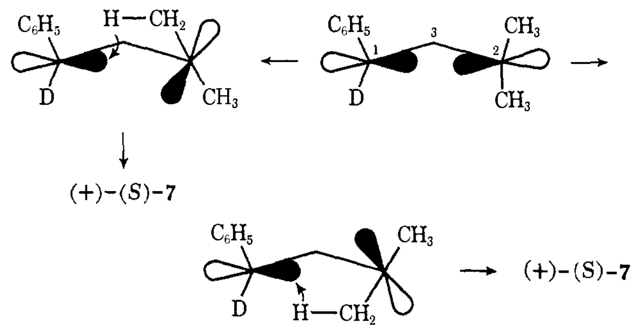
than inversion at the benzylic carbon by a factor of 2.8. In addition to symmetrical intermediates such as **2**,[16] these data also exclude a process where hydrogen migration occurs on ring opening en route to **2**. A pair of disrotatory and conrotatory processes (d and c in Scheme I, respectively) must occur with preferential migration from methyl group trans to the benzene ring. The necessary 63:37[3] trans:cis ratio would result in net *inversion* of stereochemistry, *i.e.*, $k_1/k_2 = 0.6$. A related situation where conrotatory opening (c) results in retention whereas disrotatory opening (d) results in racemization predicts a k_1/k_2 ratio of 2.2, a value excluded by our experimental results.[17]

Scheme I



Although any mechanism or combination of mechanistic pathways which would result in 47% retention of stereochemistry at C1 and 53% racemization will fit the extremes of our experimental data, we consider the following as the most reasonable possibilities. Our data suggest that the probable mechanisms for this reaction be limited to two: a $_{\sigma}2_s + _{\sigma}2_s$ concerted cycloaddition reaction subject to a slight steric effect (and thus the preference for trans migration); a reaction which proceeds through a "diradical" formed essentially by expansion of the C_1–C_3–C_2 bond angle (Scheme II).

Scheme II



In this process rotation around the C_1–C_3 bond must be much *slower* than rotation around the C_3–C_2 bond, a proposal consistent with the relative masses of the rotating groups.[18] The net effect is a cleavage of the C_1–C_2 bond followed by a rocking motion at C_2, subject to a slight steric effect, followed by hydrogen migration.

Both of these mechanisms fit the experimental data (*i.e.*, migration from cis and trans methyl groups and generation of optically active product with retention of stereochemistry) and at present we are not able to distinguish between them.

Acknowledgment. We are grateful to the Center of Materials Research of the University of Maryland for partial support of this work.

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(12) The absolute stereochemistry of (+)-**6** is inferred from knowledge of the absolute stereochemistry of (+)-2,2-dimethylphenylcyclopropane[13] and that of its precursor, *E*-2-phenyl-1-methylcyclopropanecarboxylic acid.[9,13] We have assumed that **5** and **6** will have the same sign and magnitude of rotation as their perhydro analogs. Although this assumption is not strictly correct, the error introduced by it is minor.

(13) I. Tomoskozi, *Tetrahedron*, **22**, 179 (1966).

(14) Inferred from its method of synthesis from (*S*)-**8**.[8,9]

(15) Errors were calculated as D. P. Shoemaker and G. W. Garland outlined in "Experiments in Physical Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1967, p 34, and represent our estimates of the 95% confidence limits. The errors in the optical purity of **7** result from low rotations and small sample sizes for **7** and from rather large errors associated with the optical correlation sequence. Data obtained for experiment 1 were clearly superior to those in experiment 2, since more sample was available, and this is reflected in the larger error and fewer significant figures reported in the latter case. Data from experiment 1 were therefore used in the succeeding arguments.

(16) A 90° diradical, where rotation of C1 (fast) has occurred while rotation of C2 has not occurred, also has a plane of symmetry and is ruled out by these results. In this and all other cases we assume that rotation of the phenyl group away from the cyclopropane ring occurs. Examination of models indicates that the alternative rotation, toward the ring, results in severe steric crowding.

(17) In fact the data from experiment 2 are barely within experimental error of this prediction.

(18) Variation of the rates of rotation in trimethylene diradicals has been demonstrated in thermal systems.[19] Stereospecific product formation due to hindered rotation has also been suggested.[20]

(19) R. G. Bergman and W. L. Carter, *J. Amer. Chem. Soc.*, **91**, 7411 (1969).

(20) J. S. Swenton and A. Wexler, *ibid.*, **93**, 3066 (1971).

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A MINDO/3 Study of the Factors Controlling Configurational Stability in Vinyl and Cyclopropyl Radicals[1]

Sir:

The bent geometry of the vinyl radical **1a**[2] and the nonplanar geometry of the cyclopropyl radical **2a**[3] are now well recognized. Recent reports[4,5] indicate that the barriers to inversion are greater in 1-chloro- (**1b**)

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(2) P. H. Kasai, *J. Amer. Chem. Soc.*, **94**, 5950 (1972), and references cited therein.

(3) See M. J. S. Dewar and J. M. Harris, *J. Amer. Chem. Soc.*, **91**, 3652 (1969); J. Jacobus and D. Pensak, *Chem. Commun.*, 400 (1969).

(4) (a) For a review see L. A. Singer in "Selective Organic Transformations," Vol. II, B. S. Thyagarajan, Ed., Wiley, New York, N. Y., 1972, p 239; (b) M. S. Liu, S. Soloway, D. K. Wedegaertner, and J. A. Kampmeier, *J. Amer. Chem. Soc.*, **93**, 3809 (1971).

(5) (a) T. Ando, H. Yamanaka, F. Namigata, and W. Funasaka, *J. Org. Chem.*, **35**, 33 (1970); (b) L. J. Altman and R. C. Baldwin, *Tetrahedron Lett.*, 2531 (1971). *Cf.*, however, L. A. Singer and J. Chen, *ibid.*, 939 (1971).