

Synthesis and Photoisomerization of Optically Active 2,2-Dimethylphenylcyclopropane-1-*d*

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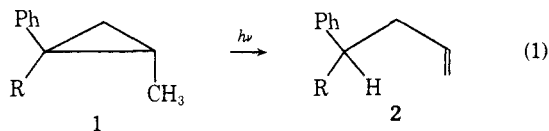
Abstract: Synthesis of (*S*)-(+)-2,2-dimethylphenylcyclopropane-1-*d* was carried out starting from phenylacetic acid-2,2-*d*₂ via a sequence which involved lithium aluminum hydride reduction to 2-phenylethanol-2,2-*d*₂, then, dehydration at 200° (90 mm) over KOD to α -deuteriostyrene. The styrene was converted to its epoxide which was treated with the anion of triethylphosphonopropionate to afford, after hydrolysis, *trans*-2-phenyl-1-methylcyclopropanecarboxylic acid-2-*d*. The acid was resolved via its ephedrine salt and converted to (*S*)-(+)-2,2-dimethylphenylcyclopropane-1-*d* via a hydride reduction, tosylation, reduction procedure. Irradiation of the active cyclopropane afforded optically active (*S*)-(+)-2-methyl-4-phenyl-1-butene-4-*d*. Absolute stereochemistry and optical purity correlations indicate that the hydrogen migration takes place with retention of stereochemistry at the migrating carbon. The mechanism of the reaction is discussed.

In considering the mechanism of the photoisomerization of 2-alkylphenylcyclopropanes,² a point of obvious importance is the stereochemistry at the benzylic carbon. If one considers the possible mechanisms which are reasonable with respect to the stereochemical results at C-2, i.e., that hydrogen migration preferentially (63%) occurs from the methyl *trans* to the benzene ring,^{3a,b} the stereochemistry at C-1 is important for further mechanistic conclusions.

The allowed symmetry controlled routes, the $[\sigma^2s + \sigma^2s]$ and $[\sigma^2a + \sigma^2a]$ processes⁴ (Figure 1), both result in predictable and unique stereochemical results; i.e., the former process would result in retention of stereochemistry, whereas the latter would cause inversion of stereochemistry at the benzylic carbon. The $[\sigma^2a + \sigma^2a]$ process appears to be so sterically demanding that, intuitively, it might be considered an inviable alternative, however, the severe skeletal distortions known to occur in other symmetry controlled reactions would make such an a priori conclusion dangerous.⁵

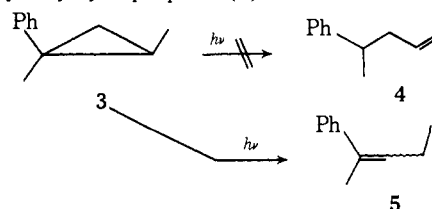
There are a number of nonconcerted processes which could occur through cleavage of the C-1-C-2 bond and subsequent rotation and hydrogen transfer. Here again the possibilities are limited by the known stereochemistry of the reaction at C-2, and the viable alternatives can be further delineated by knowledge of the stereochemistry at C-1. One extreme example is the π -cyclopropane like intermediate⁶ (Figure 1) in which hydrogen migration should occur with equal efficiency to the top and bottom lobes of the sp^2 hybridized orbital at C-1, with concomitant racemization. All transition states in which the p orbital at C-1 in the trimethylene diradical and the migrating hydrogen are symmetrically disposed will tend to give similar results, but these possibilities are best considered with the stereochemical results at C-1 and C-2 in hand.

The photoisomerization reaction (eq 1) is amenable to an

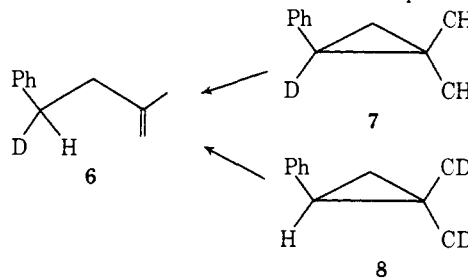


appropriate test for the stereochemical events occurring at C-1; i.e., a suitably C-1 substituted phenylcyclopropane **1** will afford the corresponding 4-phenylbutene with an asymmetric center at the benzylic carbon. In addition to information on the extent of racemization occurring in the reaction, studies on optically active **1** can also afford data on the retention or inversion processes taking place if the absolute stereochemistry of **1** and **2** are known.

Initial attempts at studying the stereochemistry at the benzylic carbon employed a methyl label at C-1 and were fruitless; i.e., irradiation of a mixture of *cis*- and *trans*-1,2-dimethylphenylcyclopropane (**3**) led to none of the desired



product **4** but instead gave a mixture of the styrenes **5**.⁷ In view of this and the fact that methyl labels had been shown to cause mechanistic changes in thermal reactions,⁸ we decided to employ deuterium as a label; i.e., **6** could be optically active because of the H,D nonequivalence at the benzylic carbon. Our choice of substrates was then based on a number of considerations. Substrate **7** was preferable to **8**



since the isotope effect associated with deuterium migration in the latter case would slow the reaction and permit the competing geometrical *cis-trans* isomerization (i.e., racemization, Figure 2) to proceed. Conversely **7** should show $k_H/k_D < 1$ and favor formation of the desired product.⁹ The 2,2-dimethyl system was also chosen in preference to a monomethyl system to diminish the rate of *cis-trans* isomerization which, in the case of optically active **7**, results in racemization. It should be pointed out in this regard that rotation of C-2 (around bond b, Figure 2) is an unobservable event in this system, and only rotations of C-1 around bond a (Figure 2) lead to racemization. In spite of the fact that the low rotations expected for the product **6** and competing geometrical isomerization (racemization) would cause experimental difficulties, this system is particularly attractive since our stereochemical results at C-2^{3a,b} are directly applicable (i.e., they were determined on the same system), and the absolute stereochemistries of **6** and **7** are available via correlation with known compounds (vide infra).

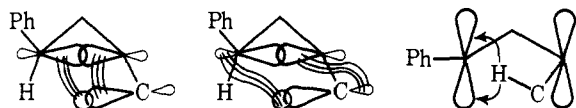
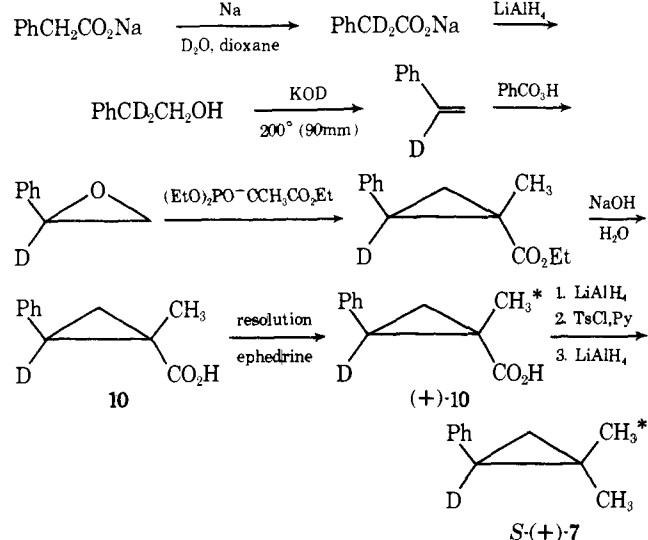


Figure 1. Representation of $[\sigma^2s + \sigma^2s]$, $[\sigma^2a + \sigma^2a]$, and π cyclopropane transition states.

Results

Synthesis of (S)-(+)-2,2-Dimethylphenylcyclopropane-1-d. The desired cyclopropane was synthesized by the procedures outlined in Chart I. Exchange and reduction of



phenylacetic acid were straightforward. The dehydration, under the conditions employed,¹⁰ apparently proceeds with significant E1cB character and results in extensive loss of isotopic label unless precautions are taken; i.e., the alcoholic proton is exchanged with D₂O under acid conditions and dehydration carried out using potassium deuterioxide.

Literature procedures¹¹ were employed to generate the desired deuterated acid **10**. The acid was resolved via its ephedrine salt to give (+)-**10** $[\alpha]^{25\text{D}} 156 \pm 2^\circ$ (*c* 1.5, absolute ethanol) in good agreement with the results of DePuy¹² for optically pure **10** resolved via its brucine salt.¹³ Application of a conventional reduction, tosylation, reduction procedure¹¹ afforded the active deuterated 2,2-dimethylphenylcyclopropane **7** which was purified by preparative GLC.

Optical Purity of 7. Tomoskozi¹¹ had previously prepared the perhydro analog of **7** (**11**) and reported data which, on the basis of the optical purity of his starting acid ($[\alpha]_{\text{D}} 58^\circ$, 37% optically pure), predicted a maximum rotation of $+10.8^\circ$, significantly different from our observed value of $[\alpha]^{20\text{D}} +23.8^\circ$ ¹⁴ obtained on **7** prepared from optically pure acid via the same synthesis.

We ascribe this difference to impurities in the former material; i.e., in our hands, the last reduction step resulted in the formation of significant amounts of 2-methyl-4-phenylbutene which would be removed by our GLC purification but not by the distillation procedure employed by the previous workers. We assume that no racemization has taken place in the conversion of the acid **10** to the hydrocarbon **7**, and that the absolute configurations of (+)-**7** and (+)-**11** are the same since they have identical ORD curves. In addition the resolved ephedrine salts which were precursors to (+)-**7** and (+)-**11** had identical physical properties, identical signs of rotation, and within experimental error identical magnitudes of rotation. Tomoskozi¹¹ originally suggested that the absolute configuration of (+)-**10** at the benzylic carbon was *R* on the basis of an asymmetric synthesis, and

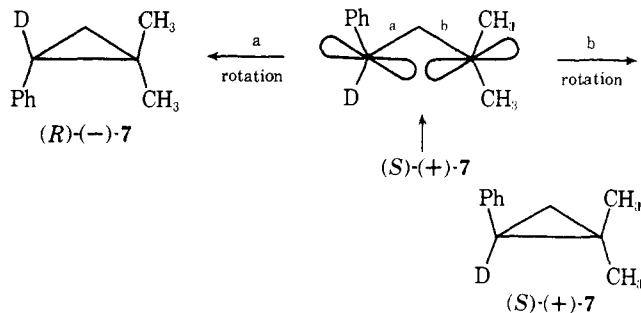
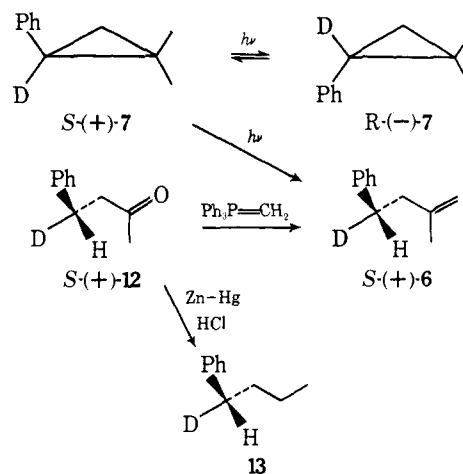


Figure 2. Rotations occurring in the trimethylene diradical intermediate.

this was later independently confirmed.¹² The absolute configurations of (+)-**7** and (+)-**11** are thus *S*. Since pure **11** shows $[\alpha]^{20}_{334} 75 \pm 2^\circ$ (*c* 0.1, isooctane), the deuterated material **7** ($[\alpha]^{20}_{334} 56 \pm 2^\circ$ (*c* 0.1, isooctane)) is 75% optically pure.

Absolute Stereochemistry and Maximum Rotation of 6. The absolute stereochemistry of **6** was established from a correlation with (*S*)-(+)-4-phenyl-2-butanone-4-*d* (**12**) which was first prepared by Streitwieser¹⁵ and later independently synthesized by DePuy¹² who confirmed the stereochemical assignment. We carried out the conversion of (*S*)-(+)-**12** to (*S*)-(+)-**6** via a Wittig reaction (Chart II) which completes the necessary optical correlation.

Chart II



Streitwieser and coworkers¹⁵ have carried out the conversion of the ketone **12** ($[\alpha]_{\text{D}} +0.44^\circ$) to the hydrocarbon **13** ($[\alpha]_{\text{D}} -0.78^\circ$) and, although these authors suggested that the product was nearly optically pure, Eliel and Arigoni¹⁶ have estimated that the maximum rotation of **13** is $[\alpha]_{\text{D}} 2.1 \pm 0.2^\circ$. We have converted **12** $[\alpha]_{\text{D}} +0.35 \pm 0.09^\circ$ to **6** $[\alpha]_{280} +4.3 \pm 0.7^\circ$, $[\alpha]_{302} +2.0 \pm 0.2^\circ$. Using Eliel and Arigoni's¹⁶ value, our sample of compound **12** was of 29% optical purity, and therefore the maximum rotation of **6** is $6.9 \pm 2.3^\circ$ at 302 nm and $14.8 \pm 5.2^\circ$ at 280 nm. It should be noted here that calculation of the maximum rotation of **6** necessitates correlation of compounds whose rotations have been measured under widely varying conditions. Eliel and Arigoni suggest confidence limits of no better than $\pm 10\%$ for such correlations, and we have therefore adjusted all confidence limits accordingly.¹⁷

In defense of the use of the predicted value of 2.1° for the maximum rotation of **13**, it should be pointed out that photoisomerization of (+)-**7** of 75% optical purity afforded **6** with a specific rotation of $[\alpha]_{302} +4.8 \pm 0.8^\circ$, a value greater than twice that obtained for the **6** prepared from **12**. Clearly ours, and the previous preparations of **12**, were of

Table I

	Optical purity				
	7(initial) ^a	7(recovered)	7(av)	6 ^{bc} (obsd)	6(predicted)
Expt 1	0.75 ± 0.03	0.45 ± 0.04	0.60 ± 0.04	0.59 ± 0.29	0.60
Expt 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 These numbers represent an average of the optical purities calculated for each experiment at 280 and 302 nm. ^c Measured rotations were corrected for incomplete deuteration (91.8% *d*₁).

less than 50% optical purity in good agreement with the predictions of 2.1° for the maximum rotation of **13**.

Photolysis of (+)-7. Irradiation of (+)-**7** was carried out in isoctane solution. Aliquots of the reaction mixture were removed at various times, and the rotation of the solution and the concentrations (GLC) of **7** and **6** were monitored and found to vary linearly with time (correlation coefficient >0.98).

At the completion of the reaction, solvent was removed by distillation, and **6** and **7** were isolated by preparative GLC. In the former case, we have guarded against the possibility that the activity in the **6** isolated might be due to a slight impurity of active **7** by diluting the alkene with a 100-fold excess of racemic **7** and reisolating **6**. Both samples of **6** had the same rotations within experimental error.

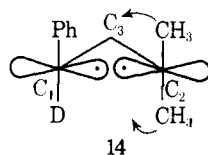
Discussion

The fact that the product obtained on photolysis of optically active **7** has a significant rotation clearly eliminates the possibility of major involvement of symmetrical π -cyclopropane type intermediates. Further, the fact that *S*-(+)-**7** affords (*S*)-(+)-**6** limits mechanisms to those which occur with net retention of stereochemistry at the benzylic carbon.

Since the optical rotation of (+)-**7** changes linearly with photolysis time (correlation coefficient = 0.98) during the course of these experiments, the average optical purity of **7** should be a measure of the maximum optical purity that can be expected for product **6**.

The data in Table I indicate that our best estimate of the stereospecificity of the photoisomerization is 100%, and that this experiment is also completely consistent with hydrogen migration via the $\sigma^2s + \sigma^2s$ transition state.

This result, in conjunction with the known fact that 63% of the hydrogen migrates from the methyl groups *trans* to the benzene ring,^{3a,b} is consistent with only two single mechanism routes, one of which is the $\sigma^2s + \sigma^2s$ route. An alternative is a process which takes place via expansion of the C₁-C₃-C₂ to form biradical **14**. Rotations around the



C₁-C₃ bond in the biradical should be slower than the corresponding rotation around the C₂-C₃ bond because of mass or steric effects.¹⁸ If C₁-C₃ rotation is slow with respect to hydrogen migration, retention of stereochemistry at the benzylic carbon will result. Steric considerations should cause clockwise rotation around C₂-C₃ and thus *trans* migration to predominate. This latter case is indistinguishable, with the data available, from a $\sigma^2s + \sigma^2s$ process. The extremes of the experimental data obtained can probably be made to fit a reaction scheme which proceeds via a mixture of mechanistic routes. A number of these have been discussed and ruled out as viable possibilities earlier.^{3c} Experiments are being conducted which might differentiate stepwise processes from the totally concerted one.

Table II

Trial	<i>c</i> (absolute EtOH), %	[α] _{λ}			
		579.1	546.1	435.8	404.7
1	0.666	0.30			0.75
2	1.04	0.46	0.34	0.67	0.72
3	1.04	0.38	0.44	0.63	0.79

Table III

Trial	<i>c</i> (isoctane), %	[α] ₃₀₂ , deg	[α] ₂₈₀ , deg
1	1.5	1.8	
2	1.5	1.9	
3	1.5	2.0	
4	0.3	1.9	3.7
5	0.3	1.9	4.5
Av:		1.9	4.1

Experimental Section

Infrared (ir) spectra were taken on a Perkin-Elmer 337 or a Beckman IR-8 grating spectrometer, neat or in CCl₄.

NMR spectra were obtained in CCl₄ solution (unless otherwise noted) on a Varian A-60D spectrometer at ambient temperature.

Ultraviolet (uv) spectra were obtained on a Cary 15 spectrophotometer in cyclohexane.

Mass spectra were obtained on a Du Pont 492 double-focusing spectrometer.

GLC was carried out on a Varian Aerograph Model 1200 gas chromatograph or on a Varian Aerograph Model 90-P.

Columns employed in GLC work were: column A, 6 ft × 1/8 in., 2.5% Bentone-34 and 2.5% diisodecyl phthalate (DIDP) on 100-120 mesh Chromosorb G; column B, 5 ft × 3/8 in., 2.5% Bentone-34 and 2.5% DIDP on 100-120 Chromosorb G; column C, 3 ft × 0.25 in., 20% Silicon SE-30 on 60-80 mesh Chromosorb W.

Specific rotations at the sodium D wavelength ([α]_D) were measured at ambient temperature on a Kern full-circle polarimeter in 10-cm cells using a sodium vapor lamp as a light source.

Specific rotations at other wavelengths ([α] _{λ}) were measured at 20° on a Perkin-Elmer 141 polarimeter with digital readout in 10-cm quartz cells using a medium pressure mercury arc lamp as a light source.

Optical rotatory dispersion (ORD) spectra were obtained on a Cary 60 recording spectropolarimeter at ambient temperature using 1 to 3 mm quartz cells and spectro grade isoctane for solvent.

Styrene- α -*d*. The dehydration of phenylethanol- α,α -*d*₂ was accomplished by a modification of the procedure of Halford and Weissmann.¹⁰ Phenylethanol- α,α -*d*₂ (90 g, 0.72 mol) was mixed with 200 ml of dioxane containing 18 ml of D₂O and 1 drop of sulfuric acid and evaporated to dryness. This procedure was repeated two times. The resulting alcohol was flash distilled from 57 g (1 mol) of KOD [oil-bath temperature 180-200° (90 mm)] to afford, after separation of D₂O, 40 g (53%) of styrene- α -*d*.

Styrene- α -*d* Oxide. Styrene- α -*d* oxide was prepared from styrene- α -*d* by the procedure described in ref 19 in 80% yield. The mass spectrum of this material at low ionizing voltage showed that it was 91% *d*₁.

Ethyl (*E*)-2-Methylphenylcyclopropane-2-carboxylate-1-*d*. This compound was prepared by the procedure of Tomoskozi¹¹ employing the styrene- α -*d* oxide. The NMR spectra of both the ester and the acid were identical with those of the perhydro analogs except that the signals due to the benzylic protons at τ 7.25 and 7.10 respectively were absent. The ir spectrum of the acid showed a very

Table IV

Expt	$[\alpha]_{334}^{20}$ ^a starting	% react.	$[\alpha]_{334}^{20}$ ^a recov.	Product 6 ^b			
				α_{302}^{20}	$[\alpha]_{302}^{20}$ ^a	α_{280}^{20}	$[\alpha]_{280}^{20}$ ^a
1	+56 ± 2	48	+34 ± 3	+0.012	+4.8 ± 0.8	+0.018	+7.1 ± 0.8
2	+56 ± 2	62	+24 ± 3	+0.004	+4 ± 2	+0.006	+6 ± 2

^a Error limits (in degrees) are estimated from the rated accuracy of the polarimeter ($\alpha = \pm 0.002^\circ$) and in every case encompass the two or more measurements obtained on different days. ^b Specific rotations (in degrees) of 6 have been corrected for ca. 5% undeuterated 4-phenyl-1-methyl-1-butene.

broad absorption between 3500 and 2000 cm^{-1} with no CD stretch bands identifiable, and a pertinent absorption at 1690 cm^{-1} (C=O stretch).

Resolution of (*E*)-2-Methylphenylcyclopropane-2-carboxylic Acids. (*E*)-2-Methylphenylcyclopropane-2-carboxylic acid-1-*d* and its perhydro analog were resolved by the procedure described. Melting points and specific rotations were identical within experimental error for both.

A solution of 30 g (0.18 mol) of ephedrine in 200 ml of hot hexane was added to 29 g (0.16 mol) of the acid also in 200 ml of hot hexane, and the mixture was immediately filtered. The solid obtained was placed in a Soxhlet extractor cup, and the filtrate plus an additional 200 ml of hexane was used to repetitively extract the solid for 3 days. The solid remaining in the cup was dried under vacuum and recrystallized from water. The precipitate which formed on cooling the hexane solution was filtered and recrystallized from anhydrous ether and then water. These two crops of crystals were combined and dried under vacuum to afford 17.7 g (mp 170.5–172°) of ephedrine salt ($[\alpha]_D +71 \pm 2^\circ$ (*c* 2.20, absolute ethanol)). The salt was partially dissolved in 300 ml of hot water and acidified with concentrated HCl. Ether extracts of the cooled solution were dried over MgSO_4 . Evaporation of the solvent gave 9.3 g (32% of total acid) of (+)-(*E*)-2-methylphenylcyclopropane-2-carboxylic acid, mp 70–73° ($[\alpha]_D +156 \pm 2^\circ$ (*c* 1.53, absolute ethanol)). The yield of the (+)-ephedrine salt could be slightly improved, and a sample of pure (–)-ephedrine salt could be obtained from the hexane soluble fraction by tedious triangular recrystallizations from anhydrous ether and water. In this manner, a 37% yield of (+)-ephedrine salt and a 34% yield of (–)-ephedrine salt [mp 119.5–120°; $[\alpha]_D -96 \pm 2^\circ$ (*c* 1.54, absolute ethanol)] were obtained. The literature value for the maximum rotation of this acid is $[\alpha]_D +155.1 \pm 0.04^\circ$ (*c* 2, absolute ethanol).

2,2-Dimethylphenylcyclopropane-1-*d*. The LiAlH_4 reduction, tosylation, reduction sequence was carried out as described for the hydrocarbon.¹¹

(*E*)-(+)-2-Hydroxymethyl-2-methylphenylcyclopropane-1-*d*: NMR τ 2.83 (s, 5, phenyl), 6.50 (broad, 3, $\text{CH}_2\text{-O}$ and OH), 8.95–9.39 (m, 5, methyl and cyclopropyl) (the signal at τ 7.97 present in the perhydro compound and assigned to the benzylic proton was absent); ir (CCl₄) 3612, 3350, and 2200 cm^{-1} .

(+)-2,2-Dimethylphenylcyclopropane-1-*d*. The distilled product from the LiAlH_4 reduction of the tosylate was purified by preparative GLC on column B (150°) followed by an additional pass on column C (90°). Yields of purified product were <10%: NMR identical with that of the perhydro derivative except signal at τ 8.17 absent; ir (neat) 2050, 2210 cm^{-1} ; MS *m/e* 147 (P, 57%), 132 (100%); ORD first maximum $[\alpha]_{277} 1000^\circ$ ($[\alpha]_D 23.8 \pm 1.3^\circ$). The ORD of (+)-2,2-dimethylphenylcyclopropane also showed its first maximum at $[\alpha]_{277} 1000^\circ$ ($[\alpha]_D 28.5 \pm 1.9^\circ$).

Syntheses of (+)-2-Methyl-4-phenyl-1-butene-4-*d* [(*S*)-(+)-6] and (+)-4-Phenyl-2-butanone-4-*d* [(*S*)-(+)-12]. Compound (+)-12 was prepared by a multistep synthesis starting from mandelic acid according to the basic procedure of DePuy.¹² One important modification was made to DePuy's synthetic scheme involving the conversion of ethyl mandelate to ethyl α -chloro- α -phenylacetate. This conversion was done by the procedure given in ref 20. The product ketone was purified by GLC (column B, 120°).

The NMR spectrum of compound (+)-12 showed resonances at τ 2.89 (s, 5, phenyl), 6.13–7.67 (m, 3, $-\text{CHDCH}_2-$), 8.00 (s, 3, methyl) and was identical with that of an authentic sample of benzylacetone except in the region between 6.1 and 7.7. The ir spectrum showed an important absorption at 1720 cm^{-1} (C=O stretch). The specific rotations measured for compound (+)-12 are given in Table II.

Treatment of (+)-12 with a 20-fold excess of the ylide of methyltriphenylphosphonium bromide in DMSO according to the procedure of Wittig²¹ gave a 70% yield of (+)-6. Compound (+)-6 was purified by preparative GLC (column B, 100°; column C, 140°).

The mass spectrum of (+)-6 showed that it was 95.4% *d*₁.

The average specific rotations (see Table III) were corrected for nondeuterated material ($[\alpha]_{\text{corr}} = [\alpha]/d_1$ content) to give the final values of $[\alpha]_{302} 2.0 \pm 0.2^\circ$ and $[\alpha]_{280} 4.3 \pm 0.7^\circ$.

Photolysis of (+)-2,2-Dimethylphenylcyclopropane-1-*d* [(+)-7]. Compound (+)-7 was photolyzed, and its products were isolated and analyzed according to the general photolysis procedure. Two additional procedures were followed during this experiment.

At measured time intervals during the course of the photolysis, 2-ml aliquots of the reaction mixture were withdrawn, and optical rotation and cyclopropane and product concentrations (GLC) were measured. Calculation of the specific rotation of the cyclopropane at the various intervals was done using the optical rotation and cyclopropane concentration data thus obtained and making the assumption that any contribution to the total rotation of the mixture by the products would be insignificant. Plots of time vs. $[\alpha]_{334}$, (+)-6 vs. $[\alpha]_{334}$, and (+)-7 vs. $[\alpha]_{334}$ were linear.

Special precautions were taken to ensure that the (+)-4-phenyl-2-methyl-1-butene-1-*d* [(+)-6] was free of optically active cyclopropane impurities. After normal purification, compound (+)-6 was diluted with a 100-fold excess of racemic 2,2-dimethylphenylcyclopropane and repurified by GLC. Subsequent to purification, the samples of (+)-6 and (+)-7 were weighed and diluted to a known volume with isooctane in preparation for measurement of specific rotations (Table IV).

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References and Notes

- Abstracted from the Ph.D. Thesis of R.S.L. University of Maryland, 1973.
- (a) H. Kristinsson and G. W. Griffin, *J. Am. Chem. Soc.*, **88**, 378 (1966); (b) *Tetrahedron Lett.*, 3259 (1966); (c) J. Meinwald and D. A. Seeley, *ibid.*, 3739 (1970); (d) L. Ulrich, H. J. Hansen, and H. Shmid, *Helv. Chim. Acta*, **53**, 1323 (1970); (e) P. H. Mazzocchi, R. S. Lustig, and G. W. Craig, *J. Am. Chem. Soc.*, **92**, 2169 (1970).
- (a) P. H. Mazzocchi and R. S. Lustig, *J. Org. Chem.*, **38**, 4091 (1973); (b) previous paper in this issue; (c) *J. Am. Chem. Soc.*, **95**, 7178 (1973).
- R. B. Woodward and R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 781 (1969).
- (a) J. A. Berson and G. L. Nelson, *J. Am. Chem. Soc.*, **89**, 5503 (1967); (b) J. A. Berson, *Acc. Chem. Res.*, **1**, 152 (1968).
- R. Hoffmann, *J. Am. Chem. Soc.*, **90**, 1475 (1968).
- R. S. Lustig, unpublished results.
- J. A. Berson, *Acc. Chem. Res.*, **5**, 406 (1972), and references cited therein.
- In a single experiment, a mixture of 2,2-dimethylphenylcyclopropane and 7 were irradiated. Comparison of the parent peak ratio for starting material and the *m/e* 92/91 ratio for the product indicated an approximate k_H/k_D value of 0.91–0.95 for the reaction. This is appropriate for the hybridization changes involved.
- J. O. Halford and B. Weissmann, *J. Org. Chem.*, **17**, 1646 (1952).
- I. Tomoskozi, *Tetrahedron*, **22**, 179 (1966).
- C. H. DePuy, F. W. Breitbeil, and K. R. DeBruin, *J. Am. Chem. Soc.*, **88**, 3347 (1966).
- We found the resolution with ephedrine to be more convenient than the previously described method using brucine¹² since minor impurities did not cause crystallization difficulties as in the latter case.

- (14) In several cases, it was necessary to calculate $[\alpha]_D$ from specific rotations measured at other wavelengths when this quantity could not be measured directly on available instrumentation. These quantities were obtained by extrapolation of the least-squares line fitting the single term Drude equation (λ^2 vs. $1/[\alpha]_\lambda$) to the sodium D wavelength, see: C. Djerassi, "Optical Rotatory Dispersion", McGraw-Hill, New York, N.Y., 1960, p 5.
- (15) A. Streitwieser, Jr., J. R. Wolfe, and W. D. Schaeffer, *Tetrahedron*, **15**, 338 (1959).
- (16) (a) D. Arigoni and E. L. Eliel, *Top. Stereochem.*, **4**, 143 (1967); (b) *ibid.*, **4**, 151-153 (1967).
- (17) Errors were calculated by the method described by Shoemaker and

- Garland which takes into consideration the probability that sequential errors will cancel. In all cases reported, errors represent 95% confidence limits: D. P. Shoemaker and G. W. Garland, "Experiments in Physical Chemistry", McGraw-Hill, New York, N.Y., 1962, pp 17-37.
- (18) (a) R. G. Bergman and W. L. Carter, *J. Am. Chem. Soc.*, **91**, 7411 (1969); (b) J. A. Berson and J. M. Balquist, *ibid.*, **90**, 7343 (1968); (c) W. von E. Doering and K. Sachdev, *ibid.*, **96**, 1168 (1974).
- (19) H. Hlibert and P. Burt, "Organic Syntheses", Collect. Vol. I, Wiley, New York, N.Y., 1932, p 494.
- (20) E. L. Eliel, M. T. Fisk, and T. Prosser, "Organic Syntheses", Collect. Vol. IV, Wiley, New York, N.Y., 1963, p 169.
- (21) G. Wittig and V. Schoellkopf, *Org. Synth.*, **40**, 40 (1960).

Mechanisms of Electron Demotion. Direct Measurement of Internal Conversion and Intersystem Crossing Rates. Mechanistic Organic Photochemistry^{1,2}

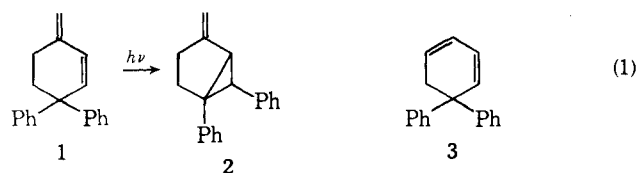
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Abstract: The decay mechanisms of the singlet and triplet excited states of a series of 1-phenylcycloalkenes were investigated. Our previously reported method of computer-assisted single-photon counting was used along with more traditional spectroscopic methods to obtain the total rate of singlet excited-state decay and also that of triplet decay. The singlet decay rate was dissected into rates of fluorescence, of radiationless decay, and of intersystem crossing. Rates were obtained both at 77 K and room temperature. For the triplet excited states, the room-temperature radiationless decay rates increased with ring size and ability of the excited molecule to twist with decrease of the T_1-S_0 energy gap. In the case of the singlet excited states, a similar parallelism was encountered, with one exception, and radiationless decay again correlated with ring size. Here, too, this internal conversion could be related with twisting ability of the excited state, here to minimize the S_1-S_0 energy gap. The implications of these results to organic photochemistry, wherein excited-state reactant most often affords ground-state product, are discussed.

In our previous report,^{2b} we described the development of a method for obtaining exceptionally rapid singlet decay-rate constants. This approach utilized the basic technique of single-photon counting³ along with use of an on-line mini-computer for data collection and processing. The technique allowed direct measurement of singlet decay rates as fast as 10^{10} sec⁻¹. Additionally, a "magic multiplier", based on temperature dependence of fluorescence, allowed amplification of capabilities to deal with rates up to 10^{12} sec⁻¹.

With this method available, we were able to pursue a number of exciting photochemical problems. One fascinating question dealt with the role of molecular flexibility in excited singlet deactivation processes. For example, previously we had postulated,⁴ on photochemical grounds (note eq 1), that the presence of a potentially free rotating double



potential free rotor
reaction only from singlet

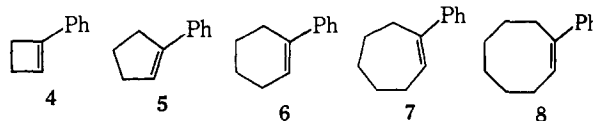
no free rotor
reaction from singlet
and triplet

bond made available a facile deactivation mechanism for triplets; this was termed the free rotor effect. The question remained regarding the extent to which singlet excited states might also avail themselves of this decay route.

These questions were of special interest to us because of their relevance to organic photochemistry. Many years ago

we noted⁵ that most organic photochemical reactions lead directly from excited state of reactant to ground state of product. For some processes, we suggested "electron demotion",⁵ that is, a discrete radiationless decay process. For others, we considered excited state-ground state degeneracies along the reaction coordinate.⁶

Our intention in the present study was an isolation of the decay process in model systems where efficient photochemistry was not to be expected.⁷ With the free rotor effect in mind, we selected the series of 1-phenylcycloalkenes **4-8**, beginning with 1-phenylcyclobutene (**4**) and ending with 1-phenylcyclooctene (**8**). This series promised to allow a correlation of decay rates to excited-state twisting.



Results. Fluorescence Decay Times. The first of three types of experimental data required for this study was the total rates of excited singlet decay (i.e., $^1k_{dt}$). We were interested in rates both at room temperature and 77 K. These were obtained quite readily using the reiterative convolution—single-photon counting method described in our earlier studies.^{2b}

Minor improvements in the apparatus and techniques are detailed in the Experimental Section. The most troublesome pitfall proved to be purification of the phenylcycloalkenes since these were oils at room temperature. The problem was nicely handled by low-temperature recrystallization as described in the Experimental Section. Since even very minor