Photochemical Studies on Deuterium-Labeled 2,2-Dimethylphenylcyclopropanes[1]

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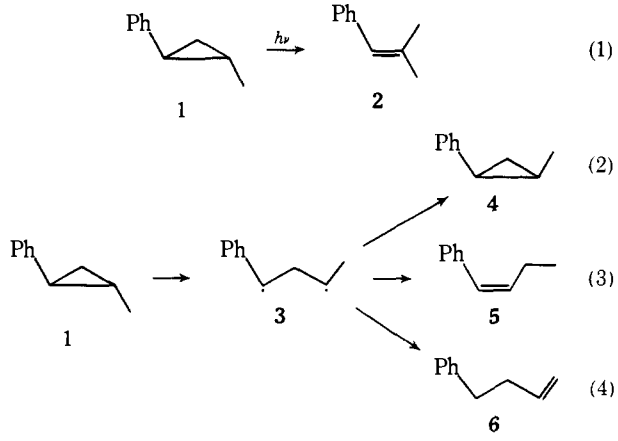
Abstract: The photochemical rearrangement of 2,2-dimethylphenylcyclopropane to 2-methyl-4-phenyl-1-butene was investigated to determined whether hydrogen migration occurred preferentially from the *cis*- or *trans*-methyl group. A series of deuterated phenylcyclopropanes with specific labels in the *cis*- and *trans*-methyl groups was prepared: *cis*-CD_2H,*trans*-CH_3; *cis*-CH_3,*trans*-CD_2H; *cis*-CD_2H,*trans*-CD_2H; *cis*-CH_3,*trans*-CD_3; and *cis*-CD_3,*trans*-CD_3. Hydrogen vs. deuterium migration in each case was measured mass spectrometrically. A series of equations relating the hydrogen vs. deuterium migration ratios to primary (π) and secondary type 1 (α) and type 2 (β) isotope effects and the fraction migration from the *cis*-methyl groups (X) was written. Simultaneous solution of these equations gave the values: $\pi = 1.96$; $\alpha = 1.10$; $\beta = 1.04$; X = 0.37. The clear preference for migration from the *trans*-methyl group and the isotope effects are discussed with respect to possible mechanisms for the reaction.

During the last several years, there has been a great deal of interest and research conducted on the mechanisms of thermal and photochemical reactions particularly with respect to the symmetry controlled concerted or biradical nature of the transition states involved. In particular, the trimethylene biradical derived from cleavage of a cyclopropane bond has been the subject of numerous theoretical[2] and experimental[3] studies. In cases where the potential trimethylene diradical is photochemically generated directly from the cyclopropane, these studies have mostly involved phenylcyclopropanes.

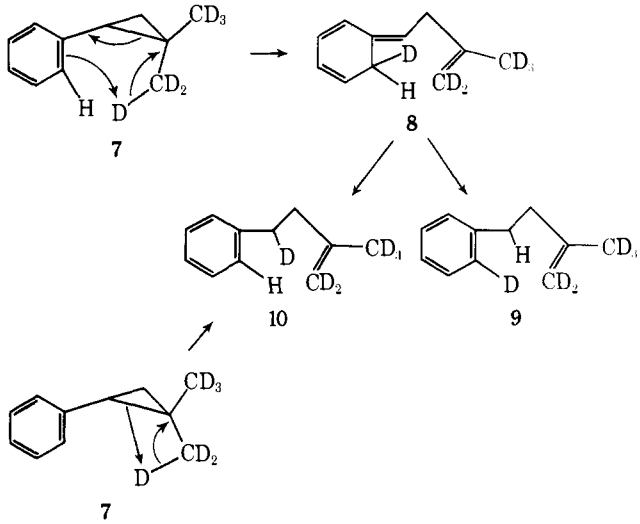
The photochemistry of phenylcyclopropanes is characterized by four general processes: geometrical isomerization;[4] fragmentation to carbenes and styrenes;[5] additions of protic solvents;[6] and structural isomerizations involving hydrogen migration.[7]

The present work involves an investigation on 1,3-hydrogen migrations in 2-alkylphenylcyclopropanes, a reaction first discovered and shown to be common to these systems by Kristinsson and Griffin.[8,9] These reactions are of particular interest, because they possibly represent, if concerted, the first example of a $[\sigma^2s + \sigma^2s]$ sigmatropic hydrogen migration.[10]

Although the major process on irradiation of most substituted phenylcyclopropanes appears to be cis–trans isomerization, a significant portion of most of these reactions proceeds with 1,2-hydrogen migration. Thus *cis*-1,2-diphenylcyclopropane affords the trans isomer, phenylindan, and *cis*- and *trans*-1,3-diphenylpropene.[7] Similarly irradiation of 2-methylphenylcyclopropanes in the gas phase results only in 1,2-hydrogen migration[11] products in addition to efficient geometrical isomerization (eq 1–4).



In their initial reports on the isomerizations of 2-alkylphenylcyclopropanes in solution, Kristinsson and Griffin[8,9] suggested that the reaction was concerted but was best pictured as proceeding through biradical **3** with subsequent hydrogen migration affording product. An alternative mechanism, involving initial hydrogen migration to the ortho position of the aromatic ring, followed by 1,3-hydrogen migration and rearomatization, was also suggested as a possibility by these authors in analogy with the well-known thermal 1,5 homocyclic hydrogen migrations.[12] In order to elucidate the nature of the transition states involved in the 1,3-hydrogen migration process, it was necessary to rule out this latter mechanistic alternative. Our approach[13] was based on the assumption that, if the reaction of **7** proceeded via the



tetraene intermediate **8**, subsequent hydrogen migration should afford a mixture of **9** and **10** with **9** as the major product expected if isotope effects are considered. The direct 1,3-migration process would afford **10** as the sole product. The required hexadeuterio compound **7** was prepared as outlined in Chart I from β,β-bis(methyl-d_3) styrene(**11**) by a modification of the method of Furukawa et al.[14]

Irradiation of an 8.3×10^{-3} *M* solution of 2,2-dimethylphenylcyclopropane (**12**) in cyclohexane afforded the expected **13** in addition to **14**, a previously unreported product of 1,2-hydrogen migration.

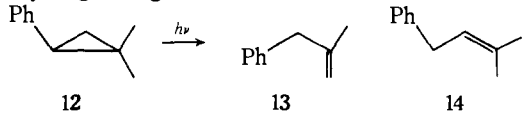
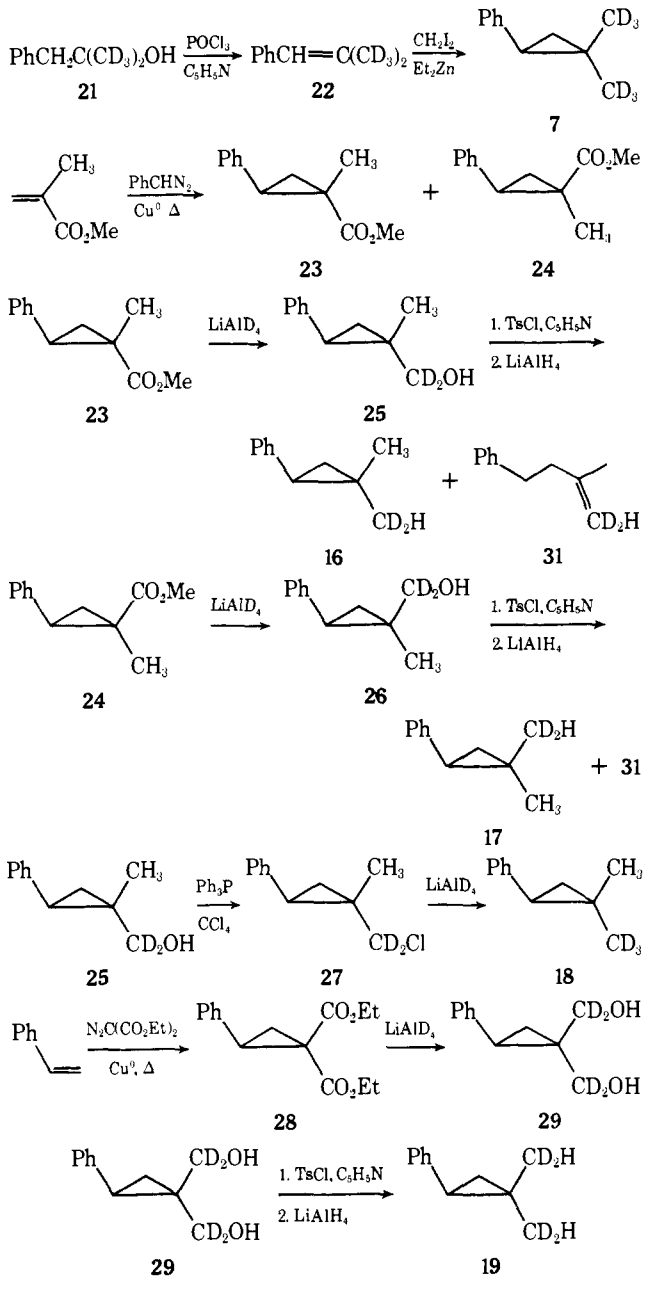


Chart I. Synthesis of Labeled Phenylcyclopropanes



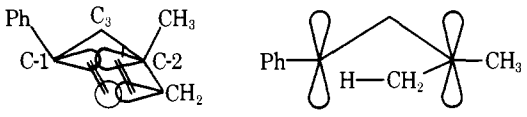


Figure 1. Representation of [σ^2s + σ^2s] and cyclopropane transition states for hydrogen migration.

Irradiation of **7** afforded 2-methyl-4-phenyl-1-butene-d_6 which was identified as **10** on the basis of its NMR spectrum; i.e., the symmetrical A_2B_2 pattern due to allylic and benzylic protons in **13** was replaced by an unsymmetrical (AB_2) pattern integrating for three protons in **10.** Oxidation of the product to benzoic acid, with alkaline permanganate and mass spectral analysis of the methyl ester, confirmed that essentially none of the deuterium resided in the aromatic ring, and that the reaction took place via direct migration to the benzylic position.

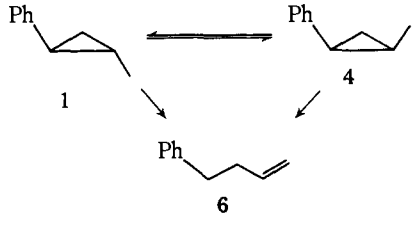
With the 1,3-migration process established, the exact nature of the transition state or intermediate involved in the transformation can be considered. Of the alternatives, the extremes are the concerted [σ^2s + σ^2s] and classical diradical pathway. In the latter case, information on the original locus of the migrating hydrogen is lost because of rotations around the cyclopropyl C–C bonds in the diradical intermediate. Supporting this diradical as the intermediate are spectroscopic studies on diphenylcyclopropanes which suggest that the singlet and triplet excited states have diradical properties.[15] O'Connell[16] has also suggested diradical formation as the means of phosphorescence quenching in phenylcyclopropanes, although he observes no significant changes in the fluorescence spectrum. Conversely, Salisbury[17] observes enhancement of fluorescence in a gas phase study of **1** and suggests that the effect arises from a decrease in the intersystem crossing rate constant. This latter author also describes reactions occurring from the triplet state of **1** as proceeding through diradical **3.**

In the case of the [σ^2s + σ^2s] process (Figure 1), migration from *trans*- and *cis*-alkyl groups should occur with essentially equal frequency with migration from the *trans*-methyl group slightly favored because of steric considerations. Importantly, this alternative requires migration to the internal lobe of the C_1–C_2 orbital at the benzylic carbon; i.e., stereochemistry at C_1 is retained in the product.

Other possible alternatives include π cyclopropane-like intermediates[18] (Figure 1) arrived at via either conrotatory or disrotatory motions of the sp^2 hybridized carbons.

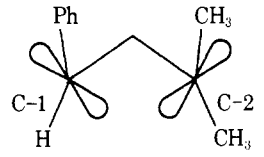
Assuming that rotation of the benzylic carbon always occurs to minimize steric interaction with the benzene ring (i.e., the benzene ring always rotates away from C_2), a conrotatory process will favor migration from a *cis*-alkyl group, whereas disrotation will favor migration from a *trans*-alkyl group. In order to elucidate the nature of the transition states involved in the hydrogen-migration process, it is important that information about the stereochemistry at the migration terminus (C-1) and about the origin of the migrating hydrogen be known (i.e., does migration occur from the *cis*- or *trans*-methyl groups at C-2).

In principle the latter problem may be solved by examining the relative rates of formation of **6** from **1** and **4.** Pre-



liminary experiments by Salisbury[11] and in our laboratory indicate that the major process occurring on irradiation of **1** is geometrical isomerization to **4.** This process is favored to the extent that it would be essentially impossible to determine the origin of the migrating hydrogen since the stereochemistry of the starting material is destroyed before any significant amount of product is formed. In addition these materials have different ground-state energies and conformations which could alter the rates of cleavage to the biradical.

In order to obviate these difficulties, it was decided to conduct a study on labeled 2,2-dimethylphenylcyclopropanes to obtain data on the relative rates of hydrogen migration from *cis*- and *trans*-methyl groups. This system has the advantage that energy absorption, strain, and conformational considerations are common to all the compounds investigated.[20] We had guessed that two methyl groups at C_2 would also decrease the rate of photochemical cis–trans isomerization in **12** vis-a-vis **1**; i.e., either clockwise or counterclockwise rotation around the C_2–C_3 bond in diradical **15** will result in an increase in the steric interaction between



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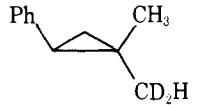
the methyl group and the benzylic carbon. Since 180° rotation of C_1 or C_2 is necessary to interconvert geometrical isomers, to the extent that this steric interaction is important, isomerization will be disfavored. This prediction is, in fact, borne out by the experimental results (vide infra).

The obvious approach of using **12** with stereospecifically deuterium-labeled *cis*- or *trans*-methyl groups is complicated by the attendant primary and secondary isotope effects. Our approach was to investigate a series of stereospecifically deuterium-substituted 2,2-dimethylphenylcyclopropanes to determine both the primary and secondary isotope effects. With these data in hand, we could then obtain the required stereochemical information on the hydrogen-migration process. Syntheses of the required deuterated compounds **7** and **16–19** are outlined in Chart I.

A series of equations was written for compounds **16–19** and for a 1:1 mixture of **7** and **12** (**20**), relating the experimentally measurable (vide infra) ratio of 1,3-hydrogen to 1,3-deuterium migration (H/D) to the theoretical value for this quantity in terms of the primary = π, secondary type I = α, secondary type II = β isotope effects and the fraction of migration originating from the *cis*-methyl group = X.

The process is exemplified for compound **16.** Hydrogen

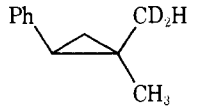


16

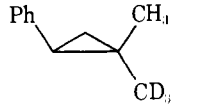
migration from the cis side (X) has a statistical value of 1 and is subject to two type II isotope effects (β^2), whereas migration from the *trans*-methyl (1 − X) may occur with H migration, statistical value = $\frac{1}{3}$, and is subject to two type I effects (α^2), while deuterium migration has a statistical value of $\frac{2}{3}$ and takes place with a primary (π), and a secondary type I effect (α). The equation for the H/D migration ratio observed then becomes

$$H/D = \frac{X/\beta^2 + \frac{1}{3}(1 - X)/\alpha^2}{\frac{2}{3}(1 - X)/\pi\alpha} = \frac{3X\pi\alpha^2 + (1 - X)\pi\beta^2}{2\alpha\beta^2(1 - X)} \quad (5)$$

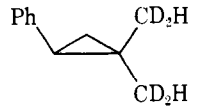
and similar equations (6–9) may be written for compounds **17–20** in terms of H/D values.

17 

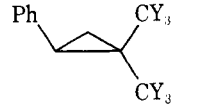
$$H/D = \frac{\pi\beta^2X + (1 - X)3\pi\alpha^2}{2X\alpha\beta^2} \quad (6)$$

18 

$$H/D = \frac{X\pi\alpha^2}{(1 - X)\beta^3} \quad (7)$$

19 

$$H/D = \frac{\pi}{2\alpha} \quad (8)$$

20 

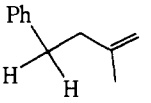
$$H/D = \pi\alpha^2\beta^3 \quad (9)$$

1:1 mixture of
7 (Y = D) and **12** (Y = H)

It should be noted that the isotope effects observed in **16–19** are intramolecular effects, whereas those observed in system **20** are intermolecular effects. This point will be discussed further later.

Product Analysis. Each of the compounds **16–19** and a 1:1 mixture of **7** and **12** were irradiated with 254-nm light in hydrocarbon solvents. Samples were analyzed by GLC, NMR, and mass spectrometry. The crude data are presented in Table I.

Examination of the mass spectra[21] of the deuterated phenylcyclopropanes and 2-methyl-4-phenylbutenes indicated that, whereas the former had a very small *m/e* 91 peak ($C_7H_7^+$), the corresponding peak for the latter compounds was the base peak in the spectrum. Conveniently there was only a small *m/e* 92 peak in the perhydro materials. Since the mass spectrum of **30** showed its base peak at



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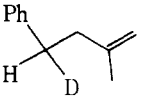

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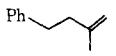
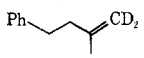
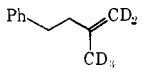
m/e 92 ($C_7H_6D^+$), the *m/e* 92/91 ratio could conveniently be used for determination of the amount of benzylic deuteration.

Table I

Compd	Trial	Solvent	Concn × 10^{-3}	Time, hr	C_3H_6 reacted	% butene formed	% trans isomer	I_{92}/I_{91}[b]	$[D/H]_c$[c]	$[H/D]_c$[d]
16	0			0	0	0	97			
	1	C_5	4.22	0.5	15	5	77	0.465 ± 0.004	0.392	2.49 ± 0.25
	2	C_8	5.73	1	22	7	81	0.454 ± 0.002	0.381	
	3	C_5	4.22	2	45	19	69	0.438 ± 0.004	0.364	
17	0			0	0	0	1			
	1	C_8	6.03	0.5	11	6	18	0.278 ± 0.003	0.198	5.68 ± 0.97
	2	C_8	6.03	2	44	17	31	0.328 ± 0.004	0.250	
18	0			0	0	0	98			
	1	C_8	5.97	0.75	11	3.8	91	0.827 ± 0.002	0.769	1.23 ± 0.12
	2	C_8	5.97	1	17	7.4		0.822 ± 0.005	0.763	
	3	C_8	5.97	2	31	13	76	0.765 ± 0.012	0.704	
	4	C_8	5.97	3	57	18		0.748 ± 0.003	0.687	
	5	C_8	5.97	3	50	22	66	0.699 ± 0.003	0.636	
19	1	C_5	7.05	2	27	9		1.10 ± 0.03	1.05	0.893 ± 0.089
	2	C_5	7.05	5	67	23		1.13 ± 0.01	1.08	
20[e]	1	C_8	3.47	0.5	14	5		0.443 ± 0.002	0.369	
	2	C_8	3.47	0.5	16	6		0.434 ± 0.002	0.360	2.67 ± 0.27

[a] C_8 = isooctane, C_5 = pentane. [b] Error is unbiased standard deviation of at least five measurements. [c] Corrected "normal" *m/e* 92 peak. [d] Extrapolated to 0% conversion or corrected for isotopic impurity. [e] The ratio of 12 to 7 was 1:0976.

Table II

	Intensity trop/parent	Efficiency of trop ion formation (rel to A), %	Intensity trop + 1/trop	% rearranged deuterium
 13	3.04	100	0.083	0.00
 31	2.96	97.4	0.097	1.4
 32	3.14	103	0.108	2.5

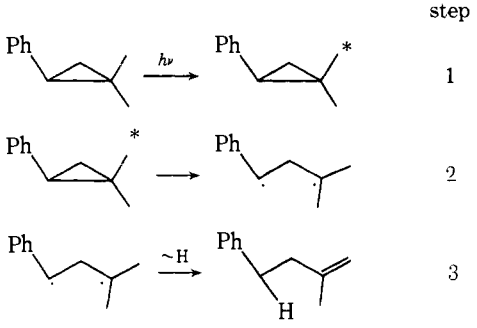
An empirical correction factor for the "normal" *m/e* 92 peak was generated in the following manner. The spectra of a series of mixtures of **13** and **30** were run at 70 eV and at low ionizing voltage. The raw *m/e* 92/91 ratios were plotted against the corrected parent ion intensity ratios,[22] and the equation of the linear least-squares line was used to correct the raw *m/e* 92/91 ratio to [D/H] ratios.

We also considered that deuteration might affect the efficiency of tropylium ion formation, and that there might be significant amounts of deuterium migration from the methyl or vinyl positions to the benzylic positions on electron impact. Examination of the data from the spectra of **13, 31,** and **32** (Table II) indicates that the effects are small in both instances. We have set our error limits for the [D/H] ratios at ±10% to account for possible analytical errors arising from these effects.

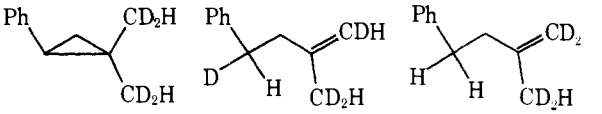
Mass spectral analysis indicated that all of the labeled compounds prepared were >95% deuterated with the exception of **19** which was found to be 92.3% d_4, 4.7% d_3, and 3.0% d_2. The $[D/H]_c$ value was corrected in this case for incomplete deuteration using the assumption that hydrogen was statistically distributed between the two methyl groups. $[D/H]_c$ values for the other compounds were used as obtained without correction.

A more important consideration to the analysis of our results was the cis–trans photochemical isomerization reaction which competes with hydrogen migration. This process effectively destroys the stereochemical integrity of the label in compounds **16, 17,** and **18** as the reaction proceeds. Our procedure was to run the photochemical reaction to different percent conversions and extrapolate the data to zero conversion to obtain the [H/D] ratio for pure starting material. Attempts at using NMR analysis to determine the percentage of cis–trans isomerization proved to be quite inaccurate. Instead we used a graphical technique where the percentage of product formed and the percentage of unreacted starting material, obtained from integration of the GLC traces, were plotted vs. the $[D/H]_c$ value for product isolated from the same samples. The intercept at 0% conversion and 0% product formation correlated quite well, and these numbers are presented as the final [H/D] values.

Scheme I



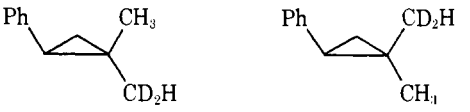
Isotope Effects and Mechanism. Scheme I outlines possible steps in the reaction which must be considered as rate or product determining. Consideration of the results from our isotopically labeled compounds allows some decisions to be made. The fact that **19** gives a nonstatistical product mixture clearly indicates that the hydrogen-migration step is the product-determining step.



19

Statistical ratio:	2	:	1
Observed ratio:	1.12	:	1

It should also be noted that since **16** and **17** differ only in the stereochemistry of their deuterium labels, the isotope effects on product formation should be identical. Clearly the wide variation in product ratios for **16** and **17** (i.e., H/D = 2.49 and 5.68, respectively) can only be accounted for by a hydrogen-migration transient in which the methyl groups are not chemically equivalent.



16 **17**

The intermolecular isotope effects observed for system **20** indicate that isotope effects are also occurring during the rate-determining step of the reaction.[23] The product fractionation observed from system **20** (k_{12}/k_7 = 2.67) could conceivably be due to differences in rate constants of compounds **7** and **12** for steps 1, 2, or 3 (Scheme I). The fact that the uv spectra of these compounds are essentially identical indicates that isotopic fractionation probably is not occurring during the photon-absorption process (step 1). A secondary type II (β) isotope effect of 1.18 per deuterium would be required to account for the observed product ratio if step 2 were rate determining. Unfortunately we could find no values for β isotope effects in closely analogous systems in the literature. Typical values for β effects range from less than ca. 1.0 to 1.4 per methyl-d_3 group for solvolytic reactions.[24] The fact that a β effect of 1.64 per methyl-d_3 group must be invoked to rationalize step 2 as the isotope discriminatory step strongly suggests that step 2 is not rate determining. We believe that step 3 is both product and rate determining. The possible mechanisms differ in that, in the $[\sigma^2s + \sigma^2s]$ process, steps 2 and 3 occur synchronously whereas, in all the other cases considered (vide supra), there are three distinct steps.

The consequences of this conclusion are that the isotope effects which govern the product ratio in the intermolecular experiment are the same as those in the intramolecular experiments. Therefore, eq 9 could, in fact, be used in combination with the four intramolecular equations to solve for X, π, α, and β.

In order to avoid any difficulties in interpretation of the isotope-effect results, we decided to use only the intramolecular results to determine the three isotope effects and X. In principle the four equations (5–8) may be solved simultaneously for the four unknowns. Unfortunately the equations are not independent, and we were forced to solve them via a successive approximation technique which affords values of

$\pi = 1.96 \pm 0.22$, $\alpha = 1.10 \pm 0.05$, $\beta = 1.04 \pm 0.09$, and X = 0.373 ± 0.054.[25] Substitution of these numbers into eq 9 for the intermolecular experiment gives a result which agrees well with the experimental value which suggests that our previous analysis was valid.

One other point must be considered with regard to the isotope-effect values. The numbers obtained are mechanistically prejudicial; i.e., they assume that there is a β effect, but this will be true only in cases where H migration and cyclopropyl bond cleavage occur synchronously. In a stepwise process, there should be little effect (step 3, Scheme I), because of the presence of deuterium in one methyl group, on the rate of migration of hydrogen from the other methyl group; i.e., it is possible that $\beta = 0$.

An alternative solution to eq 5-9 with $\beta = 0$ results in values of $\pi = 2.11$, $\alpha = 1.05$, and the value for X is unchanged.

To our knowledge, these are the first isotope effects obtained for hydrocarbon photochemical reactions, and therefore there are no direct literature analogies. However, the values obtained here have many precedents in ground-state chemistry. Particularly noteworthy is the value for the α effect which has theoretical values from 0.46 to 1.74 and has been shown to be greater than 1.0 for a change in hybridization from sp^3 and sp^2.[26] It is also worth noting that the rather small primary isotope effect is consistent with More O'Ferral's[27] calculations for the highly nonlinear geometry expected for any of the hydrogen-transfer transients, especially the concerted process. We do not intend to extend our isotope-effect values to the point of drawing mechanistic conclusions from them.

The value calculated for X of 0.373 ± 0.054 indicates that 57-68% of the hydrogen which migrates on photoisomerization of 1,1-dimethyl-2-phenylcyclopropane originates from the *trans*-methyl group. This fact clearly excludes the classical 1,3 diradical as a viable intermediate since this transient must give 50% migration from each methyl group. The preference for migration originating from the *trans*-methyl group is completely consistent with a $[\sigma^2s + \sigma^2s]$ transition state in which steric hindrance from the phenyl group partially blocks migration from the *cis*-methyl group. The data also rule out either a conrotatory or disrotatory process as the only route to an intermediate in which hydrogen migration occurs since either of these cases would be stereospecific.

Finally a mixture of dis- and conrotatory processes leading to a π cyclopropane type intermediate may be ruled out when the present results are considered in conjunction with stereochemical results on the benzylic carbon; i.e., the symmetry properties associated with the π-cyclopropane intermediate, Figure 1, would require that hydrogen migration result in racemization at that position, whereas retention of stereochemistry is observed.[20]

Possible mechanisms may be limited to a $[\sigma^2s + \sigma^2s]$ reaction or one in which hydrogen migration takes place on cleavage of the cyclopropyl bond before rotation of the benzylic carbon has proceeded to any great extent. In fact differential rates of rotation around sp^2 hybridized carbons with different substituents in thermally generated trimethylene diradicals are now well documented.[3]

Experimental Section

Infrared (ir) spectra were taken on a Perkin-Elmer 337 or a Beckman IR-8 grating spectrometer. NMR spectra were obtained in CCl_4 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 work 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 × ⅛ in., 2.5% Bentone-34 and 2.5% diisodecyl phthalate (DIDP) on 100-120 mesh Chromosorb G; column B, 5 ft × ⅜ 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; column D, 15 ft × 0.25 in., 15% UCON 50 HB 270× on 80-100 mesh Chromosorb W (AW-DMSC); column E, 2 ft × ⅛ in., 20% UCON LB 1715 on 60-80 mesh Chromosorb W (AW-DMCS).

Synthesis of Phenylcyclopropanes. 2,2-Bis(methyl-d_3)phenylcyclopropane (7). Benzylmagnesium chloride was prepared from 12.7 g (0.1 mol) of benzyl chloride and 2.43 g (0.1 g-atom) of magnesium turnings in 100 ml of anhydrous ether. Acetone-d_6 (4 g, 0.063 mol) in 15 ml of ether was added to the Grignard reagent over a period of 30 min with cooling when necessary. The mixture was refluxed 30 min and then poured into 100 ml of ice-cold, saturated ammonium chloride solution. Ether extracts were washed with saturated sodium bicarbonate, dried, and ether removed in vacuo. Distillation of the residue afforded 9.38 g (95%) of **21**, bp 110-115° (20 mm), which had the following spectral properties: NMR τ 2.80 (s, 5, aromatic), 7.31 (s, 2, benzylic), 8.85 (s, 1, OH); ir (neat) 3570, 3420 (OH stretch), 2220 cm^{-1} (CD stretch).

β,β-Bis(methyl-d_3)styrene (22). Phosphorus oxychloride (10 ml, 0.09 mol) was added to a solution of **21** (9.38 g, 0.06 mol) in 25 ml of pyridine over a period of 30 min. After standing overnight, the mixture was poured into 100 ml of ice-water and extracted with pentane, and the extracts were washed with 10% HCl, saturated $NaHCO_3$, and water. Solvent was removed by rotary evaporation and the residue distilled to give 5.11 g (61%) of a mixture of olefins [bp 71-80° (20 mm)] which was used without further purification. NMR analysis of the olefin mixture indicated that the desired **22** was present in a fourfold excess over its nonconjugated isomer, 2-(methyl-d_3)-3-phenylpropene-*1,1*-d_2.

A modification of the procedure of Furukawa et al.[28] was employed for the preparation of **7**. The entire reaction sequence was carried out in a flame-dried 100-ml round-bottomed flask, equipped with a magnetic stirring bar and condenser topped with a positive-pressure nitrogen inlet and serum cap. All reagents were added via syringe through the serum cap.

Diethylzinc was prepared from 13 g (0.2 mol) of zinc-copper couple made according to the procedure of Smith and Simmons.[29] The couple was dried by heating (150°) at reduced pressure (1 mm) for 20 min. Four milliliters of ethyl iodide was added to the couple and the mixture heated to a vigorous reflux (oil-bath temperature 140°). In ten to thirty minutes, diethylzinc began to form as evidenced by white smoke appearing above the refluxing liquid in the condenser. The flask was cooled, and the remaining ethyl iodide (total 16 ml, 0.2 mol) was added with heating and cooling as necessary. Finally the mixture was heated to 190° for 5 min. Upon cooling, the mixture solidified. A solution of 6.9 g (0.05 mol) of the mixture of olefins in 25 ml of isooctane was added to the diethylzinc, and the reaction mixture was heated (100°). Methylene iodide, 26.8 g (0.1 mol), was very cautiously added to the heated solution over a period of 1 hr. The mixture was stirred and heated 1 additional hr, and then 5 ml of cyclohexene and 2 ml of methylene iodide were added to destroy any excess diethylzinc. After standing at room temperature for 1 day, the mixture was poured into 100 ml of ice-water and suction filtered. Pentane extracts of the filtrate were dried over magnesium sulfate and rotary evaporated, and the residue was vacuum distilled to afford 8.4 g of crude product [bp 80-85° (15 mm)]. Preparative GLC column C, 100°, followed by column D, 130°, afforded pure **7**. The NMR spectrum of **7** was identical with that of **12** except the signal at τ 8.8 was absent, and the multiplet between 9.1 and 9.4 had changed shape and only integrated for two protons. The ir spectrum of **7** showed pertinent CD absorptions at 2060 and 2210 cm^{-1}. Mass spectral analysis indicated that **7** was 95.6% d_6 and showed intense ions at *m/e* 152 (P, 60%), 134 (100%). The uv showed λ_{max} (cyclohexane) 222 nm (ϵ 8390).

Methyl (*E*)-(23) and (*Z*)-2-Methylphenylcyclopropane-2-carboxylates (24). A mixture of the *Z* and *E* cyclopropane esters (**23** and **24**) was prepared by the procedure of Burger et al.[30] GLC analysis (column E, 140°) of the crude reaction product after vacuum distillation indicated that the mixture was ca. 60% **23** and 40% **24**. The crude product was partially separated into its component isomers by spinning-band distillation [bp 104-106° (6 mm)]. Further

purification was achieved by saponification of the esters and recrystallizations of the resultant acids from ethanol–water and then Skelly F.[30] After purification, the acids were reconverted to methyl esters by reaction with diazomethane. This procedure afforded a sample of **24** for subsequent reactions. Although the *E* isomer (**23**) could be obtained in a similar manner, the synthesis described next was more efficient.

The (*Z*)-methyl ester (**24**) showed NMR signals at τ 2.92 (s, 5, phenyl), 6.83 (s, 3, ester methyl), 7.58–8.32 (m, 2, cyclopropyl and benzylic), 8.58 (s, 3, methyl), 8.99 (d of d, 1, cyclopropyl) and a pertinent ir absorption at 1727 cm^{-1} (C=O stretch).

Methyl (*E*)-2-Methylphenylcyclopropane-2-carboxylate (23). Compound **23** was prepared with greater than 90% stereospecificity by the procedure of Tomoskozi.[31] Saponification followed by recrystallizations from ethanol–water and then Skelly F afforded pure (*E*) acid (mp 81–82°), and reaction with diazomethane gave pure **23**. The NMR spectrum of the (*E*)-methyl ester (**23**) consisted of signals at τ 2.87 (s, 5, phenyl), 6.37 (s, 3, ester methyl), 7.25 (d of d, 1, benzylic), 8.38 (d of d, 1, cyclopropyl), 8.79–9.12 (m, 4, cyclopropyl and methyl) and its ir spectrum (CCl_4) showed an absorption at 1726 cm^{-1} (C=O stretch).

Diethyl Phenylcyclopropane-2,2-dicarboxylate (28). To a heated (100°) slurry of styrene and 5 g of copper powder (activated by washing with glacial acetic acid followed by several portions of anhydrous ether) was added 20 g (0.11 mol) of ethyl diazomalonate[32] over a period of 2 hr. The mixture was heated an additional 4 hr and filtered, and excess styrene was distilled at 15 mm. The residue was vacuum distilled through an 8-in. Vigreux column and the fraction boiling between 120 and 125° (0.1 mm), 8.2 g (35%), was collected and identified as **28** on the basis of its spectral properties: NMR τ 2.89 (s, 5, phenyl), 5.88 (q, 2, CH_2 ester), 6.29 (q, 2, CH_2 ester), 6.91 (d of d, 1, benzylic), 7.97 (d of d, 1, cyclopropyl), 8.48 (d of d, 1, cyclopropyl), 8.82 (t, 3, CH_3 ester), 9.25 (t, 3, CH_3 ester); ir (CCl_4) 1729 cm^{-1} (C=O stretch).

General Procedure for Reduction of Phenylcyclopropane Acids and Esters. 2-Hydroxymethyl-1-phenylcyclopropanes were synthesized by lithium aluminum hydride or lithium aluminum deuteride reductions of the corresponding acids or esters according to the procedure of Tomoskozi.[30] The procedure of Micovic and Mihailovic[33] was used to work up the reduction mixtures. Yields of vacuum-distilled products ranged from 60 to 85%. The spectral properties of the crude alcohols prepared in this manner are listed below.

(*E*)-2-(Hydroxymethyl-d_2)-2-methylphenylcyclopropane (**25**): NMR τ 2.83 (s, 5, phenyl), 7.97 (d of d, 1, benzylic), 8.95–9.39 (m, 5, methyl and cyclopropyl), 5.92 (s, 1, OH); ir (CCl_4) 3620, 3330 (OH stretch), 2080, and 2180 cm^{-1} (CD stretch).

(*Z*)-2-(Hydroxymethyl-d_2)-2-methylphenylcyclopropane (**26**): NMR τ 2.92 (s, 5, phenyl), 7.71 (broad s, 1, OH), 8.10 (d of d, 1, benzylic), 8.82 (s, 3, methyl), 9.00–9.55 (m, 2, cyclopropyl); ir (CCl_4) 3600, 3370 (OH stretch), 2080, 2190 cm^{-1} (CD stretch).

2,2-Bis(hydroxymethyl-d_2)-1-phenylcyclopropane (**29**): NMR (acetone-d_6) τ 2.78 (s, 5, phenyl), 6.17 (broad s, 1, OH), 6.68 (broad s, 1, OH), 7.77 (d of d, 1, benzylic), 8.82–9.25 (m, 2, cyclopropyl); ir (KBr) 3340, 3400 (OH stretch), 2080, 2200 cm^{-1} (CD stretch).

General Procedure for Tosylation and Reduction of 2-Hydroxymethylphenylcyclopropanes. The procedure of Fieser and Fieser[34] was used to prepare the tosylates. The tosylates were isolated as dilute ether solutions, dried, and immediately reduced with lithium aluminum hydride according to the procedure of Tomoskozi.[31] The reduction mixtures were worked up in the usual manner and vacuum distilled through a short path distillation apparatus. Further purification was accomplished by preparative GLC (column C, 150°, then column B, 90°). GLC analysis of the distillation residue and long retention time components from the first GLC purification indicated that very little of the starting alcohol was recovered. The short retention time component isolated from the first GLC purification was primarily a mixture of the desired 2,2-dimethylphenylcyclopropane and its isomeric 2-methyl-4-phenyl-1-butene in a ratio of ca. 2 or 3 to 1. For example, tosylation and reduction of (*E*)- or (*Z*)-2-(hydroxymethyl-d_2)-2-methylphenylcyclopropane (**25, 26**) afforded (*E*)- or (*Z*)-2-(methyl-d_2)-2-methylphenylcyclopropane (**16, 17**) and 2-methyl-4-phenyl-1-butene-*1,1*-d_2 (**31**). The yields of purified cyclopropanes were typically less than 10%. The spectral properties of the cyclopropanes prepared by tosylation and reduction are listed below.

(*E*)-2-(Methyl-d_2)-2-methylphenylcyclopropane (**16**): NMR identical with **12** except the methyl signal at τ 8.8 appears as a one proton multiplet; ir (CCl_4) 2090, 2130, 2200 cm^{-1} (CD stretch); MS *m/e* 148 (P, 100%), 133 (96%), 131 (96%); 97.9% D_2.

(*Z*)-2-(Methyl-d_2)-2-methylphenylcyclopropane (**17**): NMR same as **12** except the signal between τ 9.1 and 9.4 appears as a three proton multiplet; ir (CCl_4) 2090, 2120, 2210 cm^{-1} (CD stretch); MS *m/e* 148 (P, 100%), 133 (74%), 131 (69%); 98.3% D_2.

2,2-Bis(methyl-d_2)-1-phenylcyclopropane (**19**): NMR identical with **12** except signals at τ 8.8 and 9.1–9.4 appear as one and three proton multiplets, respectively; ir (CCl_4) 2090, 2120, 2200 cm^{-1} (CD stretch); MS *m/e* 150 (P, 63%), 133 (100%); 92.3% D_4, 4.7% D_3, 3.0% D_2.

(*E*)-2-(Methyl-d_3)-2-methylphenylcyclopropane (18). (*E*)-2-(Chloromethyl-d_2)-2-methylphenylcyclopropane (**27**) was prepared by a modification of the procedure of Lee and Downie.[35] A mixture of 8.5 g of **25** (0.052 mol), 13.9 g (0.053 mol) of dry triphenylphosphine, and 175 ml of carbon tetrachloride was distilled at atmospheric pressure and 50 ml of distillate collected. The remaining reaction mixture was then refluxed under nitrogen for 4 days, filtered, the solvent removed in vacuo, and the residue vacuum distilled to afford two fractions, bp 68–85° (1 mm) (5.6 g), and bp 68–80° (0.2 mm) (3 g). The second fraction was identified as unreacted alcohol. The first fraction was identified as a 4 to 1 mixture of **27** and 4-chloro-4-phenyl-2-methyl-1-butene-*1,1*-d_2 by NMR and was used without further purification. The yield of **27** corrected for unreacted starting material was ca. 75%.

A solution of 4.5 g (0.025 mol) of mixed chlorides in 60 ml of dry THF was added to 0.5 g (0.012 mol) of lithium aluminum deuteride in 60 ml of dry THF and the mixture refluxed for 2 days. After normal work-up, vacuum distillation afforded 1 g of crude **18** [bp 75–79° (14 mm)] and ca. 1 g of unreacted chlorides. Preparative GLC purification (column C, 120°, then column B, 140°) afforded 0.5 g of pure **18** (13% yield from alcohol). No 2-methyl-4-phenyl-1-butene-*1,1,4*-d_3 was detected in the reduction mixture. The NMR spectrum of compound **18** was identical with that of **12** except the signal at τ 8.8 was absent. The ir spectrum showed absorptions at 2200, 2110, 2050 cm^{-1} (CD stretch), and the MS showed major ions at *m/e* 149 (P, 100%), 134 (90%), 131 (86%); 97.2% D_3.

Preparation of 2-Methyl-4-phenyl-1-butene (13), 2-Methyl-4-phenyl-2-butene (33), 2-(Methyl-d_3)-4-phenyl-1-butene-*1,1*-d_2 (32), and 2-(Methyl-d_3)-4-phenyl-2-butene-*1,1,1*-d_3 (34). Compounds **13** and **33** were obtained in a ratio of ca. 3 to 7 in 70% yield by phosphorus oxychloride–pyridine dehydration of the alcohol obtained from the reaction of phenethylmagnesium bromide and hexadeuterioacetone. Procedures analogous to those used in the preparation of β,β-bis(methyl-d_3)styrene were followed. After vacuum distillation, the olefin isomers were separated and purified by preparative GLC (column B, 140°).

The NMR spectrum of compound **13** showed resonances at τ 2.83 (s, 5, phenyl), 5.29 (m, 2, vinyl), 7.00–7.99 (m, 4, benzylic and allylic), 8.26 (m, 3, methyl). The ir showed absorptions at 3070, 3025 (aromatic and olefinic CH stretch), 2970, 2930, 2850 (saturated CH stretch), 885 (olefin CH bend), 743, 695 cm^{-1} (monosubstituted benzene CH out of plane bend). The mass spectrum showed intense ions at *m/e* 146 (P, 33%), 91 (100%).

Compound **33** showed NMR signals at τ 2.90 (s, 5, phenyl), 4.71 (t, 1, vinyl), 6.72 (d, 2, benzylic), 8.72 (m, 6, methyl). The ir showed absorptions at 3020 (aromatic and olefinic CH stretch), 2920, 2850 (saturated CH stretch), 860 (olefin CH bend), 725, 689 (monosubstituted benzene CH out of plane bend).

Compounds **32** and **34** were prepared by the same procedure used for compounds **13** and **33** except acetone-d_6 was utilized.

The NMR spectrum of **32** was identical with that of **13** except the signals at τ 5.29 and 8.26 were absent. The ir spectrum of **32** showed CD stretching bands at 2190, 2225, and 2290 cm^{-1}. The mass spectrum showed major ions at *m/e* 151 (P, 32%), 91 (100%).

The NMR spectrum of **34** was identical with that of **33** except the signal at τ 8.72 was absent. The ir showed CD stretch absorptions at 2200 and 2230 cm^{-1}.

2-Methyl-4-phenyl-1-butene-*1,1*-d_2 (31). Compound **31** was obtained as a side product of the lithium aluminum hydride reduction of the tosylates of (*Z*)- and (*E*)-2-(hydroxymethyl-d_2)-2-methylphenylcyclopropane (**16** and **17**).

The NMR spectrum of compound **31** was identical with that of **13** except the signal at τ 5.29 was absent. The ir showed pertinent absorptions at 2295, 2200 cm^{-1} (CD stretch). The mass spectrum showed intense ions at *m/e* 148 (P, 34%), 91 (100%).

Irradiations. All cyclopropanes were rigorously purified by preparative GLC prior to photolysis. Solutions of the cyclopropanes in spectro grade pentane or isooctane were prepared with concentrations ranging from 3.5×10^{-3} to 7.1×10^{-3} *M*. Undecane was added to these solutions for use as an internal standard for quantitative GLC analysis.

Solutions in either a 2 cm i.d. × 35 cm Vycor tube or a 3 cm i.d. × 30 cm quartz tube sealed with serum caps were extensively purged with pure nitrogen prior to irradiation. Irradiations were carried out using a circular bank containing ten General Electric, 15-W, G15T8 germicidal lamps at ambient temperature.

The extents of the photochemical reactions were determined by analytical GLC employing column A at 90°. The order of elution was (1) solvent, (2) undecane, (3) 2,2-dimethylphenylcyclopropane, (4) 2-methyl-4-phenyl-1-butene, and (5) 2-methyl-4-phenyl-2-butene.

Solvent was removed from the photolysis mixtures by careful rotary evaporation at ambient temperature. The residue obtained was separated into its components by preparative GLC (column B, 120°), and the compounds of interest were further purified by an additional preparative GLC pass (column B, 90°).

Photolysis of 2,2-Dimethylphenylcyclopropane (12). An 8.3×10^{-3} *M* solution of **12** in spectro grade cyclohexane was irradiated in a quartz tube for 9 hr. An approximately 5 to 1 ratio (65%) of 2-methyl-4-phenyl-1-butene (**13**) to 2-methyl-4-phenyl-2-butene (**14**) was detected in the final photolysis mixture. The products were identified by comparison of their ir and NMR spectra with those of authentic samples.

Photolysis of 2,2-Bis(methyl-d_3)-1-phenylcyclopropane (7). An 8.3×10^{-3} *M* solution of **7** in spectro grade cyclohexane was irradiated in a quartz tube for 28 hr to afford an approximately 3 to 1 ratio (48%) of 2-(methyl-d_3)-4-phenyl-1-butene-*1,1,4-d*$_3$ (**10**) to 2-(methyl-d_3)-4-phenyl-2-butene-*1,1,1-d*$_3$ (**34**). Compound **34** was identified by comparison of its ir and NMR spectra with those of an authentic sample.

The structure of **10** was determined on the basis of its spectral properties and chemical degradation. The NMR spectrum consisted of signals at τ 2.86 (s, 5, phenyl) and 7.0–8.0 (m, 3, $-CHDCH_2-$). The ir spectrum showed pertinent absorptions at 2190, 2230, and 2300 cm^{-1} (CD stretch), and the mass spectrum showed intense ions at *m/e* 152 (P, 29%) and 92 (100%).

Compound **10** (25 μl) was oxidized with 1.5 ml of 0.5 *M* permanganate in the presence of 0.2 g of sodium carbonate. The mixture was refluxed for 2 hr, acidified with 50% H_2SO_4 and extracted with ether. The ether extracts were treated with an excess of diazomethane, and the methyl benzoate was isolated and purified by preparative GLC (column C, 80°). The mass spectrum of the methyl benzoate obtained showed a parent peak at *m/e* 136 and a P to P + 1 ratio of 100:9.4. The theoretical P to P + 1 ratio for $C_8H_8O_2$ is 100:8.85.

Acknowledgments. We thank the Research Corporation and the Center of Materials Research of the University of Maryland for partial support of this work and Professor H. L. Ammon of our department for his aid in computer programming.

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