Arylcyclopropane Photochemistry. Effects of Electron-Donating and Electron-Withdrawing Aromatic Substituents on the Photochemical Rearrangements of 1,1-Diarylcyclopropanes

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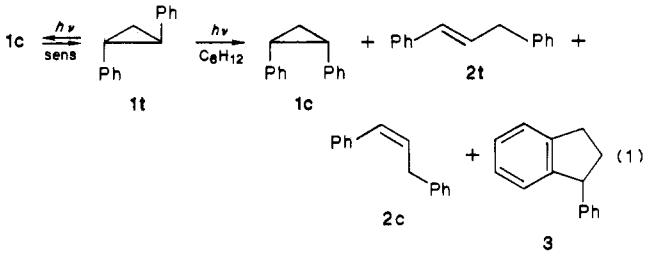
Irradiation of 1,1-diarylcyclopropanes **4a–g**, having substituents X and Y at the para positions of the aromatic rings, afforded 1,1-diarylpropenes **5a–g** and 1-arylindans **6a–f**. The rate constants of these (singlet state) reactions, determined from the reactant fluorescence lifetimes and product quantum yields, were as follows [compound (X, Y), k_5, k_6]: **4a** (CF_3, CF_3), 220×10^6 s^{-1}, 33×10^6 s^{-1}; **4b** (CN, CN), $>130 \times 10^6$ s^{-1}, >30 s^{-1}; **4c** (H, H), 19×10^6 s^{-1}, 7.2×10^6 s^{-1}; **4d** (H, CF_3), 12×10^6 s^{-1}, 3.9×10^6 s^{-1}; **4e** (OMe, CF_3), 7.8×10^6 s^{-1}, 1.5×10^6 s^{-1}; **4f** (Me, Me), 4.1×10^6 s^{-1}, 1.8×10^6 s^{-1}; **4g** (OMe, OMe), 1.6×10^6 s^{-1}, $<0.1 \times 10^6$ s^{-1}. It is concluded that the rate-determining step in the rearrangements is charge-transfer-enhanced cyclopropane ring opening.

The conversion of cyclopropanes to olefins is one of the most commonly observed photochemical reactions of arylcyclopropanes.[1] In many cases this reaction is accompanied by indan formation. The photochemistry of 1,2-diphenylcyclopropane is illustrative[2] (see eq 1).

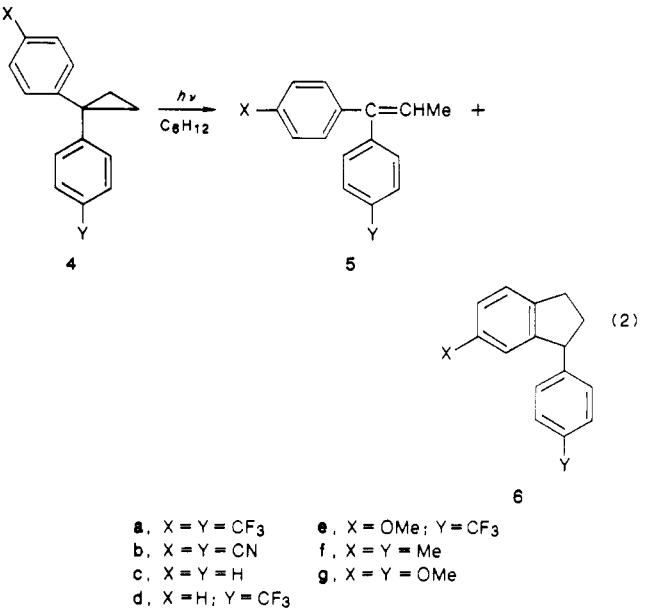


We have been analyzing the mechanisms of reactions occurring from the singlet manifold of arylcyclopropanes by means of substituent effect studies and sought to investigate these two important processes. However, the reactions occurring in the 1,2-diarylcyclopropane system did not appear optimal for study; the parent compound **1t** does not fluoresce[3,4] and derivatives of it might likewise be expected to have very short fluorescence lifetimes. Thus reaction rates would be difficult to measure. Accordingly we selected 1,1-diarylcyclopropanes for study.[5] The unsubstituted compound 1,1-diphenylcyclopropane (**4c**) had been reported to fluoresce normally.[3]

Results

Preparative-scale photolysis of cyclopropanes **4a–g** resulted in every case in formation of a 1,1-diarylpropene (**5a–g**). In most cases a 1-arylindan derivative (**6**) was also produced. See eq 2. With **4e** (X = OCH_3, Y = CF_3) there was a small amount of material produced having a relative GC retention time characteristic of an indan; however, there was insufficient material to allow for isolation and identification. No indan was detected on irradiation of bis(*p*-methoxy) derivative **4g**. Product yields obtained at 50% conversion of cyclopropane are given in Table I.

Quantum yields of product formation at 254 nm were determined by potassium ferrioxalate actinometry. Samples were irradiated and aliquots analyzed by GC at various



intervals. In each case linear plots of the yields of olefin (**5**) and indan (**6**) versus amount of light absorbed were found (at low conversions of cyclopropane). Quantum yields were determined in the range of the plots where <3% reaction had occurred and the plots were linear. The values obtained are shown in Table II. Note that the ratios of quantum yields for formation of **5** and **6** (Table II) do not generally parallel the ratios of their chemical yields at high conversion of **4** (Table I). The major reason for this is no doubt the fact that the diarylpropenes **5** re-form the cyclopropanes **4** on photolysis.[6] This latter process has previously been demonstrated in the case of **5a–c,f**; **5g** did not form **4g**. Of the four alkenes **5a–c,f** that were observed to form cyclopropanes in the previous study,[6] **5f** formed cyclopropane least efficiently. Note that with **4f**—but not **4a–c**—the low-conversion quantum yield ratio (**5**:**6**) is virtually the same as the high-conversion ratio of chemical yields.

Multiplicity Studies. Acetone solutions of cyclopropanes **4a–g** (5 mM) were subjected to prolonged irradiation with predominantly 313-nm light. Under these conditions acetone, acting as both solvent and triplet sensitizer, absorbs nearly all the light. The amount of light absorbed by each sample was determined by valerophenone actinometry.[7] No reaction was detected for any

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Table I. Photolysis of 1,1-Diarylcyclopropanes 4a–g in Cyclohexane

cyclopropane (X, Y)	amt, mmol	time,[a] h	% 5[b]	% 6[b]
4a (CF_3, CF_3)	1.51	1.5	60 ± 3	36 ± 2
4b (CN, CN)	0.28	1.75	52 ± 3	46 ± 2
4c (H, H)	2.57	10	32 ± 2	36 ± 2
4d (H, CF_3)	1.90	7.5	26 ± 1	40 ± 2
4e (OMe, CF_3)	1.71	12	34 ± 2	4 ± 0.5[c]
4f (Me, Me)	2.25	13	46 ± 2	20 ± 1
4g (OMe, OMe)	1.97	16	14 ± 1	*d*

[a] Time required for 50% conversion of cyclopropane. [b] Percent yield based on recovered 4. [c] Identification uncertain. [d] None detected.

Table II. Product Quantum Yields and Reaction Rate Constants for Cyclopropanes 4a–g

cyclopropane (X, Y)	ϕ_5[a]	ϕ_6[a]	$k_{r(5)} \times 10^{-6}$,[b] s^{-1}	$k_{r(6)} \times 10^{-6}$, s^{-1}
4a (CF_3, CF_3)	0.13	0.02	220 ± 40 (12)	33 ± 6
4b (CN, CN)	0.078	0.018	>130[c] (>6.8)	>30[c]
4c (H, H)	0.048	0.018	19 ± 4 (1.0)	>7.2 ± 1.4
4d (H, CF_3)	0.038	0.012	12 ± 2 (0.63)	3.9 ± 0.6
4e (OMe, CF_3)	0.025	0.0047	7.8 ± 1.4 (0.41)	1.5 ± 0.3
4f (Me, Me)	0.013	0.0058	4.1 ± 0.5 (0.21)	1.8 ± 0.2
4g (OMe, OMe)	0.0046	<0.00039[d]	1.6 ± 0.3 (0.084)	<0.1[d]

[a] ±10%. [b] Values in parentheses are relative rates. [c] Lower limit. [d] None detected.

Table III. Fluorescence Maxima, Quantum Yields, and Lifetimes for Cyclopropanes 4a–g[a]

cyclopropane (X, Y)	λ_{max}, nm	ϕ_f (±10%)	τ_s, ns
4a (CF_3, CF_3)	284	0.004	0.6 ± 0.1
4b (CN, CN)	300	0.004	<0.6[b]
4c (H, H)	285	0.013	2.5 ± 0.4
4d (H, CF_3)	296	0.008	3.1 ± 0.4
4e (OMe, CF_3)	315	0.004	3.2 ± 0.5
4f (Me, Me)	292	0.020	3.2 ± 0.3
4g (OMe, OMe)	307	0.032	2.9 ± 0.4

[a] Cyclohexane solution. [b] Upper limit.

of the cyclopropanes. If one assumes that energy transfer from acetone to cyclopropane was 100% efficient and that 5% product formation would be detected, the upper limit for the quantum yield of product (**5**, **6**) formation from the triplet state of any of the cyclopropanes is $<6 \times 10^{-6}$.

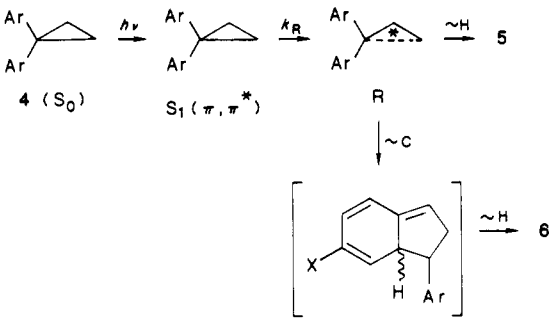
Fluorescence Studies. Reaction Rate Constants. Fluorescence spectra and quantum yields of cyclopropanes **4a–g** are given in Table III. Singlet lifetimes determined by the single-photon-counting technique are also listed. Excited-state reaction rate constants for formation of **5a–g** and **6a–g** were calculated by using the equation $k_r = \phi_r/\tau_s$ (see Table II).

Discussion

All of the cyclopropanes studied (**4a–g**) reacted to form olefins (**5a–g**) on irradiation. Generally, indans (**6**) were also formed. As hoped, reactant fluorescence was observed in every case. Fluorescence lifetimes were measurable in every case except **4b** (CN, CN), for which the lifetime was too short to measure. Accordingly, we had a handle with which to determine reaction rate constants.

Our results clearly show a substantial substituent effect on the rate of conversion of 1,1-diarylcyclopropanes **4** to 1,1-diarylpropenes **5** and 1-arylindans **6**. Electron-withdrawing substituents speed up reaction whereas electron-donating groups slow it down. Interestingly, **4d**, having one unsubstituted and one trifluoromethyl-substituted ring, reacts at almost the same rate as (in fact, somewhat slower than) the unsubstituted compound **4c**. Apparently, the effect of the unsubstituted ring is dominant in determining the reaction rate. A similar conclusion is apparent for **4e** (OMe, CF_3).

Scheme I



There is a close analogy between the present pattern of substituent effects on rate and that found for the photochemical rearrangement of (2-arylcyclopropyl)methyl acetates.[8] The major difference is found with the *p*-methoxy group, which had little effect on the acetate rearrangement but affords substantial inhibition here. We suggest the results are similar because we are in both instances measuring—primarily, at least—the effects of aromatic substituents on the same basic process—cyclopropane ring opening. This step involves conversion of the initially formed excited state S_1, which is primarily an aromatic π,π^* state, to a diradical state, R, having the excitation energy localized in the cyclopropane ring. Subsequent chemistry occurs from the diradical state. The ring-opening step is enhanced by cyclopropane to aromatic ring charge transfer.[8] The finding of similar substituent effects for two such different overall processes is strong evidence for this conclusion.

The mechanism for the conversion of **4** to **5** and **6**, then, is shown in Scheme I. We emphasize that R is drawn and discussed as if it were an intermediate for purposes of discussion only. The ring-opening and hydrogen (carbon) migration processes may well not be separated by an energy minimum. In any case, it is the energetics of ring opening that are dominant in the transition state.

Let us examine our conclusion more closely. Within the framework of Scheme I we see that the k_r's calculated are (assuming formation of R is irreversible) the product of two factors, k_R, the rate constant for formation of diradical state R, and f, the fraction of R that proceeds onward to product, **5** or **6**: $k_r = k_R f$. The substituent effects we observe are therefore the net results of effects on both processes, and the problem is to sort things out. Viewed by themselves, the effects noted here also look consistent with the notion that substituent effects on f are dominant, for the polarization induced in R by *p*-trifluoromethyl and *p*-cyano groups might be expected to favor conversion to **5** and **6**. However, analogy with the acetate rearrangement,[8] where substituent effects on f cannot be the major factor, suggests they play a minor role here as well. Additionally, the very short lifetimes of **4a** (CF_3, CF_3) and **4b** (CN, CN) are consistent with rapid cyclopropane ring opening (k_R).

A word concerning reaction multiplicity is in order. It was concluded from the acetone sensitization studies that the triplets of **4a–g** do not afford **5** and **6** and that therefore the products are singlet derived. This conclusion assumes efficient transfer of triplet energy from acetone to the

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arylpropanes, a fact substantiated in other cases where the arylcyclopropane triplets undergo visible cis–trans isomerization.[8,9]

Experimental Section

General. NMR spectra were recorded on Varian A-60, Perkin-Elmer R12-A, or JEOL FTX-100 instruments using tetramethylsilane as internal standard. Infrared spectra were recorded on a Perkin-Elmer Model 727 spectrophotometer. Ultraviolet spectra were determined with either a Cary Model 12 or Model 14 recording spectrophotometer. Fluorescence spectra were measured with a Perkin-Elmer MPF-44 instrument. Analytical gas chromatography (GC) was carried out with either a Perkin-Elmer Model 990 or a Varian Model 2400 gas chromatograph, both equipped with flame ionization detectors. The columns used for GC were as follows: (1) a 7 ft × $^1/_8$ in. stainless steel column containing 10% C6-DEGS on Anakrom SD, 90/100 mesh; (2) a 5 ft × $^1/_8$ in. stainless steel column containing 4.08% QF-1 on Gas Pack F, 60/80 mesh; (3) a 5 ft × $^1/_8$ in. stainless steel column containing 3% XE-60 on Varaport 30, 100/120 mesh; (4) a 12 ft × $^1/_8$ in. stainless column containing 4% SE-30 on Chromasorb L, 80/100 mesh. Spectral grade cyclohexane used for quantum yield and fluorescence work was further purified by treatment with concentrated sulfuric acid. The preparative-scale photolysis mixtures were fractionated by preparative GC using a Varian Model 700 gas chromatograph equipped with a thermal conductivity detector and a 6 ft × $^3/_8$ in. aluminum column containing 10% DEGS on ABS, 40/60 mesh. Melting points are uncorrected. Thin-layer chromatography was performed with 0.5 mm of silica gel (Kieselgel, containing fluorescent indicator, slurried in water) on 20 × 20 cm glass plates activated by oven-drying overnight at 110 °C. Microanalyses and GC–mass spectra were performed by the University of Massachusetts Microanalysis Laboratory and the University of Massachusetts Mass Spectral Services. Singlet lifetimes were determined at Columbia University. We are grateful to Professor Nicholas J. Turro for making available his singlet photon-counting apparatus and to Dr. Yoshitumi Tanimoto for his technical assistance.

1,1-Bis(*p*-(trifluoromethyl)phenyl)cyclopropane (4a). This procedure was modeled after that of Corey and Chaykovsky.[10] A 50% mineral oil suspension of sodium hydride (50.0 g, 0.287 mol) was washed with pentane under nitrogen, and residual pentane was removed by a brisk flow of dry nitrogen. A 55-mL portion of diimethyl sulfoxide (distilled from calcium hydride) was added, and the mixture was heated to 70 °C for 0.75 h, at which time hydrogen evolution had ceased. The solution was allowed to cool and 55 mL of tetrahydrofuran was added. The flask was then cooled to −15 °C with a 50:50 ethanol:water dry ice mixture. When the reaction solution began to freeze, a solution of 20 g (0.098 mol) of trimethylsulfonium iodide in 80 mL of dimethyl sulfoxide was added over the course of 10 min. When the addition was complete, a solution of 5.0 g (15.9 mmol) of 1,1-bis(*p*-(trifluoromethyl)phenyl)ethylene[11] in 5 mL of tetrahydrofuran was added slowly so as not to elevate the internal temperature above 5 °C. After the addition was complete, the reaction was allowed to stir 2 h at 0 °C and then at room temperature overnight. The reaction mixture was worked up by pouring it into 200 mL of water plus 500 mL of pentane. The organic layer was washed with brine, dried with magnesium sulfate, and concentrated under reduced pressure to give 6.1 g of crude product. Sublimation of the crude solid (100–110 °C, 1 Torr) afforded 5.0 g (96%) of 1,1-bis(*p*-(trifluoromethyl)-phenyl)cyclopropane (**4a**), mp 62.5–63 °C. Spectral data: IR (neat) 3100–2850, 1930, 1610, 1450, 1430, 1400, 1300, 1160, 820, 710, 650 cm^{-1}; NMR ($CDCl_3$) δ 1.39 (s, 4 H, CH_2), 7.30–7.70 (m, 8, H, arom). Anal. Calcd for $C_{17}H_{12}F_6$: C, 61.82; H, 3.66; F, 34.52. Found: C, 61.68, H, 3.45.

1,1-Bis(*p*-bromophenyl)cyclopropane. 1,1-Bis(*p*-bromophenyl)cyclopropane was prepared in the same manner as **4a**. From 14.8 g (0.0437 mol) of 1,1-bis(*p*-bromophenyl)ethylene,[12] 13.8 g (0.287 mol, 50% mineral oil dispersion) of sodium hydride, and 55 g (0.269 mol) of trimethylsulfonium iodide there was obtained 14.4 g (70%) of 1,1-bis(*p*-bromophenyl)cyclopropane, mp 135–137 °C (lit.[13] mp 132.5–133.0 °C). Spectral data for the cyclopropane: IR (KBr) 3100–2875, 1620, 1460, 1380, 1020, 900, 790, 680 cm^{-1}; NMR ($CDCl_3$) δ 1.18 (s, 4 H, CH_2), 7.00–7.47 (m, 8 H, arom).

1,1-Bis(*p*-cyanophenyl)cyclopropane (4b). This procedure is modeled after that of Newman and Boden.[14] A solution of 14.1 g (0.040 mol) of 1,1-bis(*p*-bromophenyl)cyclopropane and 13.0 g (0.144 mol) of cuprous cyanide in 80 mL of *N*-methylpyrrolidinone (vacuum distilled prior to use) was stirred and heated at 180 °C for 2.5 h. The reaction was monitored every 0.25 h by silica gel TLC using chloroform as eluant. Whereas the starting material had an R_f of 0.89 (in hexane, R_f 0.50), the product had an R_f of 0.50. The reaction was worked up by pouring the mixture into 250 mL of benzene and then washing the benzene sequentially with 25% aqueous ethylenediamine (4 × 250 mL), 10% aqueous sodium cyanide (4 × 250 mL), and brine. The benzene solution was dried with magnesium sulfate, filtered, and concentrated under reduced pressure to give 6.20 g of crude 1,1-bis(*p*-cyanophenyl)cyclopropane, which was chromatographed on a 3 × 150 cm silica gel (10% water deactivated) column using benzene as eluant to afford 4.2 g (43%) of 1,1-bis(*p*-cyanophenyl)cyclopropane (**4b**), mp 142–142.5 °C. Spectral data for the cyclopropane: IR (KBr) 3100–2900, 2225, 1600, 1490, 1250, 1000, 910, 840, 810, 740, 620 cm^{-1}; NMR ($CDCl_3$) δ 1.42 (s, 4 H, CH_2), 7.24–7.71 (m, 8 H, arom). Anal. Calcd for $C_{17}H_{12}N_2$: C, 83.58; H, 4.95; N, 11.47. Found: C, 83.49; H, 5.07; N, 11.33.

1,1-Dichloro-2,2-diphenylcyclopropane. This procedure was modeled after that of Kobayashi and Lambert.[15] To a stirred solution of 21.7 g (0.120 mol) of 1,1-diphenylethylene in 74.6 g (0.625 mol) of chloroform were added 50 mL of a 50% aqueous sodium hydroxide solution and 0.4 mL of a 40% methanolic solution of benzyltrimethylammonium hydroxide. The frothy solution was allowed to stir overnight at room temperature. The reaction was diluted with 200 mL of water, and the organic layer was removed. The aqueous phase was extracted with chloroform and then ether. The combined organic solutions were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure to give 28.2 g (81%) of 1,1-dichloro-2,2-diphenylcyclopropane, mp 108–112 °C (lit.[16] mp 107–108 °C, 113–114 °C). Spectral data: IR 3125–2950, 1600, 1450, 1060, 770 cm^{-1}; NMR ($CDCl_3$) δ 2.25 (s, 2 H, CH_2), 7.16 (s, 10 H, arom).

1,1-Diphenylcyclopropane (4c). This procedure was modeled after that of Kobayashi and Lambert.[15] Sodium (20 g) was added in pea-sized pieces over the course of 2 h to an ice-cooled, mechanically stirred solution of 19.2 g (72.9 mmol) of 1,1-dichloro-2,2-diphenylcyclopropane in 200 mL of ether. Simultaneously, and for 0.5 h longer than the addition of sodium, 7 mL of water in 45 mL of methanol was added dropwise. The solution was then filtered through Celite, and the residue was rinsed with ether. The combined filtrate and ether rinses were washed with water and concentrated to give an oil, which by NMR analysis was 75% 1,1-diphenylcyclopropane. Vacuum distillation (115.5–118 °C (1 Torr)) (lit.,[17] 117–117.5 °C (2 Torr)) secured 7.5 g (53%) of the 1,1-diphenylcyclopropane (**4c**). Spectral data for the hydrocarbon: IR (neat) 3000–2900, 1940, 1870, 1800, 1740, 1590, 1490, 1440, 1010, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.292 (s, 4 H, CH_2), 7.140 (s, 10 H, arom).

1-Phenyl-1-(*p*-(trifluoromethyl)phenyl)cyclopropane (4d). 1-Phenyl-1-(*p*-(trifluoromethyl)phenyl)cyclopropane (**4d**) was prepared in the same manner as **4a**. From 5.95 g (24.0 mmol) of 1-phenyl-1-(*p*-trifluoromethyl)phenylethylene, 7.5 g (0.15 mol, 50% oil dispersion) of sodium hydride, and 30 g (0.147 mol) of trimethylsulfonium iodide there was obtained 3.15 g (50%) of 1-phenyl-1-(*p*-(trifluoromethyl)phenyl)cyclopropane (**4d**), bp 135–137 °C (3 Torr). Spectral data for the cyclopropane: IR (neat) 2950–2850, 1620, 1500, 1450, 1410, 1330, 1160, 1010, 930, 840, 750 cm^{-1}; NMR ($CCCl_3$) δ 1.30 (s, 4 H, CH_2), 7.25–7.70 (m, 9 H, arom).

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Anal. Calcd for $C_{16}H_{13}F_3$: C, 73.27; H, 5.00; F, 21.73. Found: C, 73.46; H, 5.24; F, 21.5.

1-(*p*-Methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)-cyclopropane (4e). A solution of (*p*-(trifluoromethyl)phenyl)-magnesium bromide was generated by the addition of 10.1 g (45 mmol) of *p*-bromobenzotrifluoride in 50 mL of ether to 1.00 g (41 mmol) of magnesium turnings. Over a period of 0.5 h, 5.63 g (37.5 mmol) of *p*-methoxyacetophenone in 100 mL of ether was added to the (*p*-(trifluoromethyl)phenyl)magnesium bromide solution. The reaction was quenched by pouring it into 100 mL of saturated aqueous ammonium chloride. The organic layer was washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure to afford 9.30 g (84%) of essentially pure 1-(*p*-methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)ethanol. The alcohol was further purified on preparative silica gel TLC, using dichloromethane as eluant (R_f 0.50) to remove any trace of a biphenyl. Spectral data for the alcohol: IR (neat) 3500 (br), 3100–2850, 1600, 1500, 1400, 1060, 870, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.81 (s, 3 H, CH_3), 3.00 (s, 1 H, OH), 3.65 (s, 3 H, OCH_3), 6.70–7.50 (m, 8 H, arom).

A solution of 7.80 g (27.6 mmol) of the 1-(*p*-methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)ethanol and 0.5 g of *p*-toluenesulfonic acid in 100 mL of benzene was refluxed 1 h with continuous water removal via a Dean–stark trap. The benzene solution was washed with saturated aqueous sodium bicarbonate and brine and dried over magnesium sulfate. Solvent was removed under reduced pressure to afford 7.0 g (96%) of 1-(*p*-methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)ethylene as a yellow oil, which was used directly in the next step. Spectral data for the olefin: IR (neat) 3150–2850, 1600, 1500, 1460, 1400, 1320, 1240, 1160, 900, 830, 730, 650 cm^{-1}; NMR ($CDCl_3$) δ 3.75 (s, 3 H, OCH_3), 5.37 (s, 1 H, =CH*H*), 5.47 (s, 1 H, =CH*H*), 6.76–7.77 (m, 8 H, arom).

The 1-(*p*-methoxyphenyl)-1-(*p*-trifluoromethyl)phenyl)ethylene (6.95 g, 25 mmol) was reacted with 30 g (0.150 mol) of trimethylsulfonium iodide as in the preparation of **4a** to give 3.2 g of crude product. This was chromatographed on a 2 × 25 cm silica gel column using 25% benzene in hexane as eluant to give 2.3 g of product, which was contaminated by a trace (<3% by GC) of starting alkene. The latter was removed by stirring the impure product with 0.2 g (1.2 mmol) of potassium permanganate, 1.0 g (4.6 mmol) of sodium periodate, 0.1 g of potassium carbonate, and 2 mL of water in 25 mL of acetone at 0 °C for 8 h. This oxidation mixture was diluted with 25 mL of water and 100 mL of ether, washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure to give 1.7 g (25%) of 1-(*p*-methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)cyclopropane (**4e**). Cooling to −70 °C induced solidification, and recrystallization from 95% ethanol gave 1.3 g of white crystals, mp 40–40.5 °C. Spectral data for the cyclopropane: IR (neat) 3100–2850, 1600, 1500, 1450, 1400, 1240, 1160, 820, 750, 620 cm^{-1}; NMR ($CDCl_3$) δ 1.282 (s, 2 H, cyclopropyl), 1.292 (s, 2 H, cyclopropyl), 3.772 (s, 3 H, OCH_3), 6.785–7.524 (m, 8 H, arom). Anal. Calcd for $C_{17}H_{15}OF_3$: C, 69.85; H, 5.17. Found: C, 69.92; H, 5.16.

1,1-Dichloro-2,2-bis(*p*-methylphenyl)cyclopropane. As in the preparation of 1,1-dichloro-2,2-diphenylcyclopropane, a mixture of 20.8 g (0.100 mol) of 1,1-bis(*p*-methylphenyl)ethylene,[17] 50 mL of chloroform, 50 mL of 50% aqueous sodium hydroxide, and 0.20 mL of 40% benzyltrimethylammonium hydroxide in methanol was reacted to give 24.5 g (84%) of 1,1-dichloro-2,2-bis(*p*-methylphenyl)cyclopropane, mp 108–109 °C (lit.[18] mp 115 °C). Spectral data for the dihalide: IR (cast film) 3100–2900, 1890, 1500, 1440, 1400, 1300, 1250, 1100, 810, 740 cm^{-1}; NMR ($CDCl_3$) δ 2.20 (s, 2 H, CH_2), 2.25 (s, 6 H, CH_3), 7.02–7.42 (m, 8 H, arom).

1,1-Bis(*p*-methylphenyl)cyclopropane (4f). Sodium (25 g, 1.087 mol) was added in pea-sized pieces over the course of 2 h to an ice-cooled, mechanically stirred flash that contained 19.1 g (0.066 mol) of 1,1-dichloro-2,2-bis(*p*-methylphenyl)cyclopropane in 200 mL of ether. When the sodium addition was complete, 715 mL of methanol was added dropwise over 0.5 h. The solution was filtered through Celite, and the residue was rinsed with ether. The combined filtrate and ether rinses were washed with water and concentrated to give 16.1 g of crude product contaminated with starting material. Vacuum distillation (138–140 °C (1 Torr)) afforded 7.9 g (54%) of the 1,1-bis(*p*-methylphenyl)cyclopropane, mp 26–26.5 °C. Spectra data for the cyclopropane: IR (neat) 3100–2900, 1500, 1440, 1000, 800, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.221 (s, 4 H, CH_2), 2.295 (s, 6 H, CH_3), 7.090 (s, 8 H, arom). Anal. Calcd for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.76; H, 8.16.

1,1-Dichloro-2,2-bis(*p*-methoxyphenyl)cyclopropane. As in the preparation of 1,1-dichloro-2,2-diphenylcyclopropane, a mixture of seven drops of benzyltrimethylammonium hydroxide (in 40% methanol) solution, 2.0 g (8.32 mmol) of 1,1-bis(*p*-methoxyphenyl)ethylene,[19] 20 mL of spectral grade chloroform, and 20 mL of 50% aqueous sodium hydroxide afforded 2.50 g (97%) of 1,1-dichloro-2,2-bis(*p*-methoxyphenyl)cyclopropane, mp 150 °C (lit.[20] mp 141 °C). Spectral data for the dichlorocyclopropane: IR (cast film) 3100–2850, 1600, 1500, 1240, 1160, 1010, 820, 740 cm^{-1}; NMR ($CDCl_3$) δ 2.30 (s, 2 H, CH_2), 3.82 (s, 6 H, OCH_3), 6.80–7.50 (m, 8 H, arom).

1,1-Bis(*p*-methoxyphenyl)cyclopropane (4g). The procedure used was modeled after those of Gassman and Pape.[21] A solution of 12.7 g (41.1 mmol) of 1,1-dichloro-2,2-bis(*p*-methoxyphenyl)cyclopropane in 300 mL of dry THF was added under nitrogen over 0.5 h to a refluxing mixture of 6.29 g (130 mmol) of sodium sand[22] and 50 mL of THF. The nitrogen-blanketed reaction was maintained at reflux for an additional 8 h. The reaction was quenched by the addition of 50 mL of methanol. The solution was diluted with 250 mL of ether and washed with brine. The organic layer was dried over magnesium sulfate, and solvent was removed under reduced pressure to afford, after recrystallization from 95% ethanol, 6.5 g (62%) of 1,1-bis(*p*-methoxyphenyl)cyclopropane (**4g**): mp 124–125 °C (lit.[23] mp 59.5–60.5 °C); bp 182–184 °C (0.03 Torr). Spectral data for the cyclopropane: IR (cast film) 3100–2850, 1570, 1500, 1450, 1415, 1240, 1160, 1010, 820, 740 cm^{-1}; NMR ($CDCl_3$) δ 1.190 (s, 4 H, CH_2), 3.705 (s, 6 H, OCH_3), 6.71–7.16 (m, 8 H, arom). Since the cyclopropane readily decomposes in air, it is best to prepare it immediately prior to use. The 1,1-dichloro-2,2-bis(4-methoxyphenyl)cyclopropane is considerably more stable.

1-Phenyl-1-(*p*-(trifluoromethyl)phenyl)propene (5d). A solution of (*p*-(trifluoromethyl)phenyl)magnesium bromide, generated from 4.8 g (21.3 mmol) of *p*-bromobenzotrifluoride and 0.50 g (20.5 mmol) of magnesium in 50 mL of ether, was reacted with 2.68 g (20 mmol) of propiophenone to give, after ammonium chloride workup, 4.6 g of crude 1-phenyl-1-(*p*-(trifluoromethyl)phenyl)propanol. Purification on silica gel TLC, using chloroform as eluant, afforded 2.25 g (37%) of alcohol: IR (neat) 3400 (br) cm^{-1}. A solution of 1.25 g (4.46 mmol) of the alcohol and 0.25 g of *p*-toluenesulfonic acid in 25 mL of benzene was refluxed in a flask equipped with a Dean–Stark trap for 2 h. The solution was concentrated under reduced pressure to approximately 3 mL and purified by preparative silica gel TLC using cyclohexane as eluant. A total of 0.85 g (73%) of 1-phenyl-1-(*p*-(trifluoromethyl)phenyl)propene (**5d**) was obtained as a mixture of *E* and *Z* isomers. Spectral data for the propene mixture: IR (neat) 3100–2800, 1620, 1500, 1330, 1170, 850, 750 cm^{-1}; NMR ($CDCl_3$) δ 1.723 and 1.755 (two d, J = 7.1 Hz, 3 H, $CHCH_3$), 6.253 and 6.285 (two q, J = 7.1 Hz, 1 H, $CHCH_3$), 7.05–7.72 (m, 9 H, arom).

1-(*p*-Methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)-propene (5e). (*p*-(Trifluoromethyl)phenyl)magnesium bromide, generated from 4.8 g (21.3 mmol) of *p*-bromobenzotrifluoride and 0.50 g (20.5 mmol) of magnesium, was reacted with 3.5 g (21.3 mmol) of *p*-methoxypropiophenone to afford 6.1 g of crude product. Purification was achieved by preparative silica gel TLC using dichloromethane as eluant. A total of 5.3 g (80%) of 1-(*p*-methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)propanol was obtained: IR (neat) 3500 (br) cm^{-1}. A solution of 1.5 g (4.8 mmol) of the alcohol and 0.1 g of *p*-toluenesulfonic acid in 50 mL of

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benzene was refluxed 1 h. The solution was concentrated under reduced pressure to approximately 5 mL and purified by preparative silica gel TLC using 25% benzene in hexane as eluant. A total of 1.30 g (92%) of 1-(*p*-methoxyphenyl)-1-(*p*-(trifluoromethyl)phenyl)propene (**5e**) was obtained as a mixture of *E* and *Z* isomers. Spectral data for the propene mixture: IR (neat) 3100–2850, 1600, 1500, 1460, 1400, 1160, 900, 830, 720 cm^{-1}; NMR ($CDCl_3$) δ 1.703 and 1.771 (two d, J = 7.1 Hz, 3 H, $CHCH_3$), 3.742 and 3.796 (two s, 3 H, OCH_3), 6.130 and 6.178 (two q, J = 7.1 Hz, 1 H, $CHCH_3$), 6.739–7.656 (m, 8 H, arom).

1-Phenylindan (6c). A solution of 10 mL of 2-(2-ethoxyethoxy)ethanol, 0.7 g (12.5 mmol) of potassium hydroxide, 1 mL of 85% hydrazine hydrate, and 1.0 g (4.78 mmol) of 3-phenyl-1-indanone[24,25] was refluxed 1 h. The reaction was diluted with 100 mL of ether, washed with water, dried over magnesium sulfate, and concentrated under reduced pressure. The crude product was chromatographed on a 2.0 × 20 cm silica gel (5% water deactivated) column packed in hexane and eluted with the same; 50-mL fractions were collected. Fractions 3–6 contained 0.42 g (45%) of 1-phenylindan.[26] Spectral data for the indan: IR (neat) 3100–2850, 1600, 1490, 1450, 1070, 1020, 750, 700 cm^{-1}; NMR ($CDCl_3$) δ 1.81–3.00 (m, 4 H, CH_2), 4.327 (m, 1 H, CH), 6.93–7.28 (m, 9 H, arom).

1-(*p*-(Trifluoromethyl)phenyl)indan (6d). (*p*-(Trifluoromethyl)phenyl)lithium, generated from 8.46 mL (22 mmol) of a 2.6 M hexane solution of *n*-butyllithium and 5.6 g (3.5 mL, d = 1.613, 25 mmol) of *p*-bromobenzotrifluoride in 35 mL of dry ether, was reacted with 3.0 g (23 mmol) of 1-indanone to give 5.5 g of crude product. Purification on silica gel preparative TLC (R_f 0.45) using chloroform as eluant afforded 4.0 g (65%) of 1-(*p*-(trifluoromethyl)phenyl)indanol. Spectral data for the alcohol: IR (neat) 3500 (br), 3100–2850, 1610, 1400, 1300, 1160, 820, 710, 650 cm^{-1}; NMR ($CDCl_3$) δ 2.26–2.57 (m, 2 H), 2.87–3.16 (m, 2 H), 3.65 (s, 1 H, OH), 6.97–7.72 (m, 8 H, arom).

A solution of 2.78 g (10 mmol) of the 1-(*p*-(trifluoromethyl)-phenyl)indanol and 0.15 g of *p*-toluenesulfonic acid in 50 mL of benzene was refluxed 2 h. The solution was then washed with saturated aqueous ammonium chloride, dried over magnesium sulfate, and filtered. The solvent was then removed under reduced pressuer to afford 2.0 g (77%) of 1-(*p*-(trifluoromethyl)phenyl)-indene. Spectral data for the olefin: IR (neat) 3100–2850, 1610, 1400, 1300, 820, 710, 650 cm^{-1}; NMR ($CDCl_3$) δ 3.17 (d, J = 2.4 Hz, 2 H, $CHCH_2$), 7.05–7.45 (m, 8 H, arom).

A solution of 2.0 g (7.7 mol) of 1-(*p*-(trifluoromethyl)-phenyl)indene in 75 mL of 95% ethanol was reacted with 0.25 g of 5% palladium on carbon and 65 psi of hydrogen for 4 h in a Parr apparatus. The ethanol solution was then filtered and concentrated under reduced pressure to afford 1.75 g of a yellow oil. This oil was purified on silica gel TLC plates (R_f 0.50) using pentane as eluant to afford 1.5 g (74%) of 1-(*p*-(trifluoromethyl)phenyl)indan (**6d**) as a colorless oil. Spectral data for the indan: IR (neat) 3100–2850, 1610, 1460, 1430, 1410, 1310, 1160, 820, 710, 650 cm^{-1}; NMR ($CDCl_3$) δ 1.73–2.14 (m, 1 H, $CHCH_2CH_2$), 2.22–2.67 (m, 1 H, $CHCH_2CH_2$), 6.75–7.62 (m, 8 H, arom).

Preparative-Scale Photolysis. The following procedure is typical. A solution of 0.500 g (1.51 mmol) of 1,1-bis(*p*-(trifluoromethyl)phenyl)cyclopropane (**4a**) in 110 mL of nitrogen-purged cyclohexane was irradiated with Corex-filtered light from a Hanovia 450-W medium-pressure mercury arc. Progress of the reaction was monitored by GC using column 4 at 130 °C. After 3 h 50% of the **4a** had reacted. Yields of the products **5a** and **6a** as determined by GC are given in Table I. The solution was concentrated and fractionated by preparative GC to give 0.150 g of recovered **4a**, 0.125 g of 1,1-bis(*p*-(trifluoromethyl)phenyl)-propene (**5a**), and 0.079 g of 4',5-bis(trifluoromethyl)-1-phenylindan (**6a**). The propene **5a** was identified by a comparison of NMR and IR spectra and GC retention times with those of an authentic sample available from earlier work.[6] The indan **6a** was identified from its spectral data: IR (neat) 3100–2850, 1620, 1460, 1430, 1330, 1160, 840, 710, 660 cm^{-1}; NMR ($CDCl_3$) δ 1.890–2.278 (m, 1 H, $CHCH_2CH_2$), 2.577–2.844 (m, 1 H, $CHCH_2CH_2$), 3.001–3.163 (m, 2 H, $CHCH_2CH_2$), 4.448 (t, J = 8.4 Hz, 1 H, $CHCH_2CH_2$), 6.97–7.59 (m, 7 H, arom).

Other photolyses were carried out in similar fashion. Yields at 50% conversion are given in Table I. GC columns used were as follows: **4b**, column 3 at 240 °C; **4c**, column 4 at 140 °C; **4d**, column 4 at 130 °C; **4e**, column 2 at 180 °C; **4f**, column 2 at 150 °C; **4g**, column 2 at 205 °C. Products were identified by comparison of NMR and IR spectra and GC retention times with those of authentic samples [1,1-bis(*p*-cyanophenyl)propene (**5b**), 1,1-diphenylpropene (**5c**), 1,1-bis(*p*-methylphenyl)propene (**5f**), and 1,1-bis(*p*-methoxyphenyl)propene (**5g**) were available from an earlier study[6]] except for 4',5-dicyano-1-phenylindan (**6b**) and 4',5-dimethyl-1-phenylindan (**6f**), which were identified by their NMR spectra: **6b** ($CDCl_3$) δ 1.99–2.30 (m, 1 H, $CHCH_2CH_2$), 2.65–2.95 (m, 1 H, $CHCH_2CH_2$), 3.10–3.28 (m, 2 H, $CHCH_2CH_2$), 4.62 (t, J = 8.4 Hz, 1 H, $CHCH_2CH_2$e, 6.96–7.67 (m, 7 H, arom); **6f** ($CDCl_3$) δ 1.400–1.780 (m, 1 H, $CHCH_2CH_2$, 2.461–2.702 (m, 1 H, $CHCH_2CH_2$), 2.900–3.049 (m, 2 H, $CHCH_2CH_2$), 4.25 (t, 1 H, $CHCH_2CH_2$), 6.84–7.26 (m, 7 H, arom).

Quantum Yield Measurements. Solutions of cyclopropanes **4a–g** (0.005 M except for **4b**, where solubility limited the concentration to 0.0025 M) in spectral grade cyclohexane were prepared and 6.5-mL portions were added to quartz tubes fitted with vacuum-tight valves. The samples were subjected to three freeze–pump–thaw cycles at <1 Torr. The samples were then irradiated for intervals of up to 5 min in a merry-go-round apparatus using 254 nm light from a low-presure mercury arc. Actinometry was carried out by simultaneous irradiation of potassium ferrioxalate solutions. The irradiated samples were analyzed by GC using appropriate conditions for each sample. In each case linear plots of the yields of olefin (**5**) and indan (**6**) versus light absorbed were obtained at low conversions of cyclopropane. Quantum yields were determined in the range of the plots where <3% reaction had occurred.

Multiplicity Studies. Nitrogen-purged acetone solutions (0.005 M) of the cyclopropanes **4a–g** were irradiated in a merry-go-round apparatus for 32 h with light from a Hanovia 450-W medium-pressure mercury arc. The light was filtered through 1.5 cm of 1.5 M aqueous $NiSO_4$, 1.5 cm of 1.0 M $CoSO_4$ (separate solutions; 3-cm total path length), and about 3 cm of Pyrex glass. The filter solutions allow for the following transmittance: 6% at 296.7 nm, 20% at 302.5 nm, 62% at 313.0 nm, and 10% at 334 nm.[27] A total of 0.27 einstein of light was absorbed by the samples as determined by simultaneous irradiation of 0.1 M valerophenone in benzene as actinometer.[28] The irradiated samples were analyzed by GC.

Fluorescence Studies. Fluorescence spectra were recorded of spectral grade cyclohexane solutions of cyclopropanes **4a–g**. The solutions were adjusted to an A_{260} of 0.34 and the spectra were recorded with excitation at 260 nm. The relative quantum yields were determined by replotting the data on a scale linear in wavenumber and determining the area under the curves. Absolute quantum yields were determined by comparison with *trans*-3-methyl-1-phenyl-1-butene.[29]

The singlet lifetimes of the cyclopropanes **4b–g** in nondegassed cyclohexane were determined by the single-photon-counting technique using the same solutions used for recording the fluorescence spectra. The lifetime of **1a** was measured by Dr. Charles Dorian in the laboratories of Professor Arthur Halpern at Northeastern University.

Acknowledgment. We thank the National Science Foundation for support of this research.

Registry No. **4a**, 56860-29-8; **4b**, 56860-30-1; **4c**, 3282-18-6; **4d**, 86042-98-0; **4e**, 86042-99-1; **4f**, 56860-31-2; **4g**, 22219-35-8; **5a**, 56860-27-6; **5b**, 56860-28-7; **5c**, 778-66-5; (*E*)-**5d**, 113793-05-8; (*Z*)-**5d**, 113793-04-7; (*E*)-**5e**, 113793-07-0; (*Z*)-**5e**, 113793-06-9; **5f**, 4333-55-5; **5g**, 4663-13-2; **6a**, 86043-02-9; **6b**, 86043-03-0; **6c**, 26461-03-0; **6d**, 86043-04-1; **6e**, 113793-08-1; **6f**, 86043-05-2; $H_2C{=}C(C_6H_4\text{-}p\text{-}CF_3)_2$, 29279-80-9; $H_2C{=}C(C_6H_4\text{-}p\text{-}Br)_2$, 10605-

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43-3; $H_2C{=}C(Ph)_2$, 530-48-3; $H_2C{=}C(Ph)(C_6H_4$-p-$CF_3)$, 345-88-0; p-$BrC_6H_4CF_3$, 402-43-7; p-$MeOC_6H_4COCH_3$, 100-06-1; $MeC(p$-$MeOC_6H_4)(p$-$CF_3C_6H_4)(OH)$, 86767-30-8; $H_2C{=}C(p$-$MeOC_6H_4)(p$-$F_3CC_6H_4)$, 68036-77-1; $H_2C{=}C(p$-$MeC_6H_4)_2$, 2919-20-2; $H_2C{=}C(p$-$MeOC_6H_4)_2$, 4356-69-8; $PhCOCH_2Me$, 93-55-0; $H_3CCH_2C(Ph)(p$-$F_3CC_6H_4)(OH)$, 56431-01-7; H_3CCH_2CO-p-C_6H_4OMe, 121-97-1; $H_3CCH_2C(p$-$MeOC_6H_4)(p$-$F_3CC_6H_4)(OH)$, 113793-09-2; p-$F_3CC_6H_4Li$, 2786-01-8; 1,1-bis(p-bromophenyl)-cyclopropanone, 36714-70-2; 1,1-dichloro-2,2-diphenylcyclopropane, 3141-42-2; 1,1-dichloro-2,2-(p-methylphenyl)cyclopropane, 22125-38-8; 1,1-dichloro-2,2-bis(p-methoxyphenyl)-cyclopropane, 22125-33-3; 3-phenyl-1-indanone, 16618-72-7; 1-indanone, 83-33-0; 1-(p-(trifluoromethyl)phenyl)indanol, 113793-10-5; 1-(p-(trifluoromethyl)phenyl)indene, 113793-11-6.

Arylcyclopropane Photochemistry. Substituent Effects on the Photochemical 1,3-Hydrogen Migration of 1,1-Dimethyl-2-phenylcyclopropane

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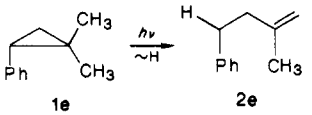
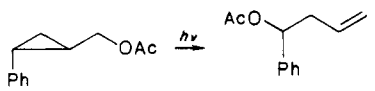
Irradiation of 1,1-dimethyl-2-arylcyclopropanes **1a–g** (Ar = p-$CF_3C_6H_4$ (**1a**), m-$CF_3C_6H_4$ (**1b**), p-$CH_3C_6H_4$ (**1c**), m-$CH_3C_6H_4$ (**1d**), C_6H_5 (**1e**), m-$OCH_3C_6H_4$ (**1f**), p-$OCH_3C_6H_4$ (**1g**)) gave in every case a 2-methyl-4-aryl-1-butene (**2a–g**) via a 1,3-hydrogen migration, accompanied by lesser amounts of a 3-methyl-1-aryl-2-butene (**3a–g**). Rearrangement is a singlet-state process. Rate constants for rearrangement were determined from reactant fluorescence lifetimes and product quantum yields. The rates for rearrangement of **1** to **2** were as follows: **1a**, 25×10^6 s^{-1}; **1b**, 15×10^6 s^{-1}; **1c**, 7.9×10^6 s^{-1}; **1d**, 6.1×10^6 s^{-1}; **1e**, 2.3×10^6 s^{-1}; **1f**, 1.9×10^6 s^{-1}; **1g**, 0.87×10^6 s^{-1}. It is concluded that the energetics of cyclopropane ring opening are important in the rate-determining step of the reaction.

As part of our studies on the mechanisms of photochemical reactions of arylcyclopropanes, we turned our attention to the 1,3-hydrogen migration reaction of 1-alkyl-2-phenylcyclopropanes (eq 1). This reaction was first



1e 2e (1)

noted as a general process by Griffin.[1] Molecular details were later worked out in elegant fashion by Mazzocchi.[2] For us one of the attractive features of the reaction is its formal similarity to the photochemical rearrangement of 2-arylcyclopropylmethyl acetates (eq 2).[3] Our study of



(2)

the effect of aromatic substituents on the latter process had provided unusual and highly informative results, and it was of considerable interest to compare those results on an ionic reaction with a similar study of the reaction **1** → **2**, which does not proceed via an ion-pair mechanism. Accordingly, a series of derivatives of **1** having different substituents in the aromatic ring were prepared and studied.[4]

Results

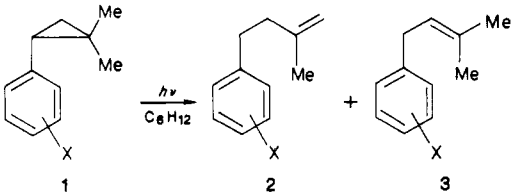
The syntheses of the cyclopropyl reactants **1a–g** and the photoproducts **2a–g** and **3a–g** are described elsewhere.[5]

Preparative-scale photolysis of the 1,1-dimethyl-2-arylcyclopropanes **1a–g** in cyclohexane solution afforded in each case the expected rearranged 2-methyl-4-aryl-1-butene isomers **2a–g** as well as lesser quantities of the 3-methyl-1-aryl-2-butenes **3a–g** (see eq 3). With the p-OCH_3 derivative (**1g**), small amounts of what we tentatively identify as (*E*)- and (*Z*)-3-methyl-1-(p-methoxyphenyl)-1-butene (**4g**) were also detected by GC; however, **4g** was seen only in the preparative-scale photolysis and not in the quantum yield runs. Product yields are given in Table I. The formation of **2e** and **3e** from **1e** had previously been noted by Mazzocchi.[2a] More recently, Zimmerman has reported results qualitatively similar to ours for the photolysis of methoxy derivatives **1f,g**.[6] In all cases products were identified by isolating them and

Table I. Photolysis of 1,1-Dimethyl-2-arylcyclopropanes 1a–g[a]

reactant (X)	% conv	% 2	% 3	% other
1a (p-CF_3)	56	67	8	
1b (m-CF_3)	38	61	7	
1c (p-Me)	44	74	10	
1d (m-Me)	50	53	14	
1e (H)	78	65	16	
1f (m-OMe)	66	50	5	
1g (p-OMe)	70	48	36	11 (4)[b]

[a] Cyclohexane solution. [b] Tentative identifications; see text.



1 2 3 (3)

a, X = p-CF e, X = H
b, X = m-CF f, X = m-OMe
c, X = p-Me g, X = p-OMe
d, X = m-Me

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