43-3; $H_2C{=}C(Ph)_2$, 530-48-3; $H_2C{=}C(Ph)(C_6H_4\text{-}p\text{-}CF_3)$, 345-88-0; $p\text{-}BrC_6H_4CF_3$, 402-43-7; $p\text{-}MeOC_6H_4COCH_3$, 100-06-1; $MeC(p\text{-}MeOC_6H_4)(p\text{-}CF_3C_6H_4)(OH)$, 86767-30-8; $H_2C{=}C(p\text{-}MeOC_6H_4)(p\text{-}F_3CC_6H_4)$, 68036-77-1; $H_2C{=}C(p\text{-}MeC_6H_4)_2$, 2919-20-2; $H_2C{=}C(p\text{-}MeOC_6H_4)_2$, 4356-69-8; $PhCOCH_2Me$, 93-55-0; $H_3CCH_2C(Ph)(p\text{-}F_3CC_6H_4)(OH)$, 56431-01-7; $H_3CCH_2CO\text{-}p\text{-}C_6H_4OMe$, 121-97-1; $H_3CCH_2C(p\text{-}MeOC_6H_4)(p\text{-}F_3CC_6H_4)(OH)$, 113793-09-2; $p\text{-}F_3CC_6H_4Li$, 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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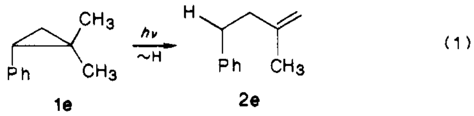
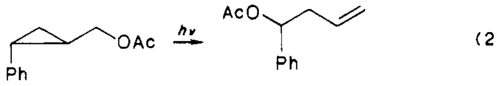
Irradiation of 1,1-dimethyl-2-arylcyclopropanes **1a–g** (Ar = $p\text{-}CF_3C_6H_4$ (**1a**), $m\text{-}CF_3C_6H_4$ (**1b**), $p\text{-}CH_3C_6H_4$ (**1c**), $m\text{-}CH_3C_6H_4$ (**1d**), C_6H_5 (**1e**), $m\text{-}OCH_3C_6H_4$ (**1f**), $p\text{-}OCH_3C_6H_4$ (**1g**)) gave in every case a 2-methyl-4-aryl-1-butene (**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**, $25 \times 10^6\ s^{-1}$; **1b**, $15 \times 10^6\ s^{-1}$; **1c**, $7.9 \times 10^6\ s^{-1}$; **1d**, $6.1 \times 10^6\ s^{-1}$; **1e**, $2.3 \times 10^6\ s^{-1}$; **1f**, $1.9 \times 10^6\ s^{-1}$; **1g**, $0.87 \times 10^6\ s^{-1}$. 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 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 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

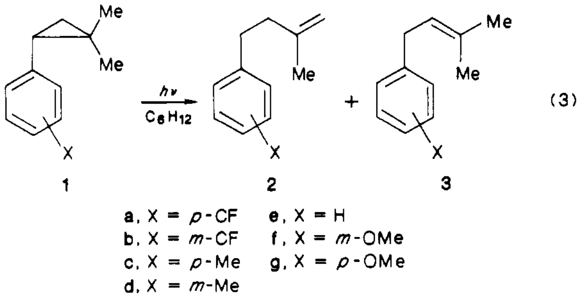
The syntheses of the cyclopropyl reactants **1a–g** and the photoproducts **2a–g** and **3a–g** are described elsewhere.[5]

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.



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[2] (a) Mazzocchi, P. H.; Lustig, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 3707. (b) Mazzocchi, P. H.; Lustig, R. S. *J. Am. Chem. Soc.* **1975**, *97*, 3714.

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Table II. Excited-State Reaction Rate Constants and Product Quantum Yields for Cyclopropanes 1a–g[a]

reactant (X)	ϕ_2[b]	ϕ_3[b]	$k_{r(2)} \times 10^{-6}$,[c] s^{-1}	$k_{r(3)} \times 10^{-6}$, s^{-1}
1a (*p*-CF_3)	0.069	0.0040	25 ± 5 (11)	1.4 ± 0.3
1b (*m*-CF_3)	0.050	0.0042	15 ± 3 (6.5)	1.3 ± 0.3
1c (*p*-Me)	0.030	0.0037	7.9 ± 1.5 (3.4)	0.98 ± 0.18
1d (*m*-Me)	0.026	0.0050	6.1 ± 1.4 (2.6)	1.1 ± 0.3
1e (H)	0.027	0.0045	2.3 ± 0.3 (1.0)	0.38 ± 0.06
1f (*m*-OMe)	0.0094	0.0032	1.9 ± 0.4 (0.83)	0.66 ± 0.12
1g (*p*-OMe)	0.0075	0.0013	0.87 ± 0.12 (0.38)	0.15 ± 0.03

[a] Cyclohexane solution. [b] All quantum yields are ±10%. [c] Values in parentheses are relative rates.

Table III. Fluorescence Maxima, Fluorescence Quantum Yields, and Singlet Lifetimes of Cyclopropanes 1a–g[a]

cyclopropane (X)	fluorescence max, nm	ϕ_f (±10%)	τ_s, ns
1a (*p*-CF_3)	308	0.042	2.8 ± 0.4
1b (*m*-CF_3)	308	0.046	3.3 ± 0.4
1c (*p*-Me)	294	0.089	3.8 ± 0.6
1d (*m*-Me)	299	0.18	4.3 ± 0.8
1e (H)	300	0.28	11.8 ± 1.1
1f (*m*-OMe)	296	0.10	4.9 ± 0.7
1g (*p*-OMe)	306	0.15	8.6 ± 0.8

[a] Cyclohexane solution.

comparing their infrared spectra with those of known samples. Studies of the yields of products **2a–g** and **3a–g** as a function of time (light dose) indicated all were primary photoproducts of **1a–g**.

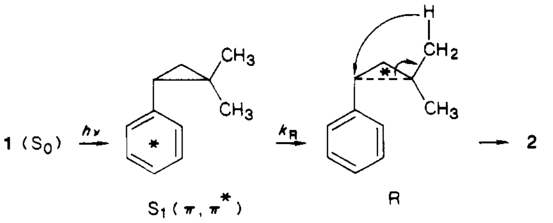
Prolonged irradiation of acetone solutions of cyclopropanes **1a–g** with Pyrex-filtered light resulted in only a small consumption of starting material and no detectable formation of **2a–g** or **3a–g**.

Quantum yields of product formation were determined by using 254-nm light and potassium ferrioxalate actinometry (Table II). Fluorescence quantum yields and singlet lifetimes for **1a–g** were measured and are shown in Table III. Excited singlet state reaction rate constants for formation of **2a–g** and **3a–g** were then calculated by using the equation $k_r = \phi_r/\tau_s$; these are given in Table II.

Discussion

The most notable feature of the results is the enhancement of the rate of conversion of **1** to **2** by the electron-withdrawing trifluoromethyl group; **1a** and **1b** react the fastest of all derivatives studied. The electron-donating methyl groups have a somewhat smaller effect, and methoxy substitution retards reaction somewhat.

These results are nicely in accord with the finding of Blunt et al.[7] that 1,3-hydrogen migration in the diaryldimethylcyclopropanes **5a–e** occurs preferentially to the carbon adjacent to the substituted aryl ring, and, qualitatively at least, the reaction is most efficient with *p*-cyano derivative **5e**.



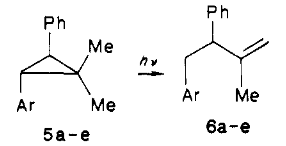
(4)

Table IV. Summary of Effects of Aromatic Substituents on the Rates of Reaction of Arylcyclopropanes

aromatic substituent	effect on reaction rate[a]: acetate rearrangement[b,c]	olefin/indan formation[c]	1,3-H migration[c]
p-CN	lg incr	incr	*e*
m-CN	lg incr	*e*	*e*
p-CF_3	*e*	lg incr	lg incr
m-CF_3	lg incr	*e*	incr
p-Me	no eff	decr	sm incr
m-Me	decr	*e*	sm incr
p-OMe	no eff	lg decr	sm decr
m-OMe	lg decr	*e*	no eff

[a] Effects are relative to reactant with no substituent; lg incr implies a >10× rate in increase; incr, ≥5×; sm incr, ≥2×; sm decr, ≤0.5×; decr, ≤0.2×; lg decr, ≤0.1×; no eff, less than twofold rate change. [b] Reference 3. [c] Reference 8. [d] This work. [e] Not studied.

We have now carried out substituent effect studies on three singlet reactions of arylcyclopropanes: the acetate rearrangement (eq 2),[3] the formation of olefins and indans,[8] and the present reaction (eq 1). The results of all three investigations are qualitatively summarized in Table IV. It is seen that despite substantial differences in the electronic nature of the reactions, their responses to aromatic substitution have a strong element of similarity: electron withdrawal enhances reaction and electron donation has less of an effect or inhibits it. We believe this reflects the fact that at least a major component of the rate-determining step is the same in all cases, i.e., cyclopropane bond stretching to give a diradical species, R, which is subsequently transformed to products. Such a mechanism for the conversion of **1** to **2** is shown in eq 4.



5a–e 6a–e

a, Ar = C_6H_5
b, Ar = *p*-$CH_3C_6H_4$
c, Ar = *p*-ClC_6H_4
d, Ar = *m*-ClC_6H_4
e, Ar = *p*-CNC_6H_4

We have suggested that electron-withdrawing aromatic substituents accelerate ring opening by virtue of the charge-transfer character they induce in S_1.[3] This factor appears to be dominant in all three reactions studied. That there are differences in the magnitude of the response to aromatic substitution (and even direction in the case of methyl substitution) is not surprising when we consider, as noted before,[3,8] that the k_r's measured reflect not only the rate of ring opening to R but also the efficiency of conversion of R to product. And while the former is basically the same process in all the reactions, the latter is not and differences in response to substituents might be expected.

Consider, now, the detailed work by Mazzocchi and Lustig on the conversion of **1e** to **2e**.[2] Their study of **1e** and a series of deuteriated derivatives revealed inter alia the following: (a) hydrogen migration from the *trans*-methyl group is preferred (63:37); (b) reaction proceeds with retention of configuration at the benzylic carbon; (c) **1e** reacts 2.67 times as efficiently as the analogue containing two CD_3 groups instead of CH_3's.

Given the magnitude of the latter isotope effect, the observed difference in reaction efficiency between **1e** and its d_6 analogue was felt by Mazzocchi most likely to be due to an isotope effect on hydrogen transfer and not on bond breaking. It was noted that mechanisms consistent with

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(7) Blunt, J. W.; Coxon, J. M.; Robinson, W. T.; Schuyt, H. A. *Aust. J. Chem.* **1983**, *36*, 565.

(8) Hixson, S. S.; Franke, L. A. *J. Org. Chem.*, in press.

these results were either a concerted $[\sigma 2_s + \sigma 2_s]$ process or a stepwise process somewhat like that detailed in eq 4. Our results indicate the energetics of ring opening are an important factor in determining the overall reaction rate but say nothing about whether the ring-opened species is an intermediate or whether hydrogen migration follows or occurs simultaneously with ring opening. The conclusions of both studies are compatible.

Our conclusions are also in agreement with those of Bender on the analogous 1,3-hydrogen migration of 1,8-dimethylbenzosemibullvalene.[9] In this case there are two a priori options for the reaction and only one is taken. CNDO-CI calculations indicate the course of the reaction is dictated by the energetics of cyclopropane bond breaking.

A final issue to address is that of reaction multiplicity. We conclude from the sensitization studies that reaction proceeds through the singlet manifold: no reaction is observed on triplet sensitization. But this conclusion rests on the assumption that acetone can sensitize the triplet states of **1a–g**. Commonly the only reaction of arylcyclopropane triplets is cis–trans isomerization, an invisible process with the present compounds.[10] So we have no easy handle to tell whether energy transfer has occurred. Fortunately, there are many cases documented where triplet energy transfer from acetone to phenylcyclopropanes analogous to **1a–g** has resulted in observable efficient isomerization,[3,11] and we feel that our assumption that acetone can sensitize the triplet states of **1a–g** is well founded. Also, the rearrangement of the phenanthryl analogue of **1** to the analogous **2** derivative has been shown to be a singlet reaction by Zimmerman.[12]

Experimental Section

Preparative-Scale Photolyses. The following procedure is typical. A solution of 0.417 g (1.95 mmol) of 1,1-dimethyl-2-(*p*-(trifluoromethyl)phenyl)cyclopropane (**1a**) in 160 mL of spectral grade cyclohexane was irradiated 1 h at room temperature with Corex-filtered light from a Hanovia 450-W medium-pressure mercury arc. Nitrogen was bubbled through the solution 0.5 h prior to photolysis and throughout the reaction period. Reaction progress was monitored on a Perkin-Elmer 990 gas chromatograph equipped with a flame ionization detector. A 5 ft × $^1/_8$ in. stainless steel column packed with 2.5% Bentone 34/2.5% diisodecyl phthalate on 100/120 mesh Chromosorb G-NAW and operated at 100 °C was used. Aliquots for analysis were removed at 7.5, 15, 30, and 60 min. Two products, **2a** and **3a**, were noted, the amounts of which increased with time of irradiation. At 60 min GC analysis indicated the reaction mixture contained 0.185 g of **1a**, 0.155 g of **2a**, and 0.018 g of **3a**. The solvent was removed and the products were isolated by preparative GC using a Varian Model 700 gas chromatograph and a 6 ft × $^3/_8$ in. column packed with the same material as the analytical column. The products were identified as 2-methyl-4-(*p*-(trifluoromethyl)phenyl)-1-butene (**2a**) and 3-methyl-1-(*p*-(trifluoromethyl)phenyl)-2-butene (**3a**) by comparison of their infrared spectra with those of authentic samples.[5]

The results obtained with the other cyclopropanes **1b–g** are given in Table I.

Sensitized Photolyses. The following procedure is typical. A solution of 0.248 g (1.70 mmol) of 1,1-dimethyl-2-(*p*-(trifluoromethyl)phenyl)cyclopropane (**1a**) in 160 mL of spectral grade acetone was irradiated for 20 h at room temperature with Pyrex-filtered light from a Hanovia 450-W medium-pressure mercury arc. Nitrogen was bubbled through the solution for 0.5 h prior to photolysis and throughout the reaction period. Progress of the reaction was monitored by GC as in the direct irradiation (see above) with aliquots taken at 1.0 and 20 h. At the end of the run there was 0.237 g of **1a** remaining. No detectable **2a** or **3a** was formed.

Quantum Yield Determinations. Duplicate 6.5-mL cyclohexane (spectral grade, percolated through activated alumina until transparent above 220 nm) solutions of cyclopropanes **1a–g** were placed into quartz tubes and degassed by subjecting them to a minimum of three freeze–pump–thaw cycles. The samples were irradiated in a "merry-go-round" apparatus for 3, 7, or 10 min by a low-pressure mercury arc lamp that emitted light at predominantly 254 nm. The output of the lamp was monitored by potassium ferrioxalate actinometry.

Fluorescence Studies. Fluorescence spectra were determined in a Perkin-Elmer MPF-44A recording spectrophotometer. Solutions of cyclopropanes **1a–g** in spectral grade cyclohexane (see quantum yield determinations) were adjusted to an absorbance of 0.34 at 260 nm, the excitation wavelength used in recording the spectra. Fluorescence quantum yields were determined relative to toluene (assumed to have $\phi_f = 0.14^{13}$) by replotting the emission spectra on a scale linear in frequency and integrating the curves obtained.

Singlet lifetimes were determined by the single-photon-counting technique in the laboratory of Professor J. C. Dalton at Bowling Green State University. Lifetime measurements of **1a–g** were made by using cyclohexane solutions similar to those used in the fluorescence quantum yield measurements except with trifluoromethyl compounds **1a** and **1b** for which the solutions were adjusted to an absorbance of just over 2.0. The trifluoromethyl species were excited at 250 nm; all others were excited at 260 nm. Lifetimes were determined by the curve simulation technique of Demas and Crosby. The data gave a good fit to single-exponential decay.

Acknowledgment. We thank Professor J. C. Dalton for help in performing the fluorescence lifetime measurements.

Registry No. **1a**, 113947-83-4; **1b**, 113947-84-5; **1c**, 93042-78-5; **1d**, 113947-85-6; **1e**, 7653-94-3; **1f**, 90433-21-9; **1g**, 90433-31-1; **2a**, 113947-86-7; **2b**, 113947-87-8; **2c**, 56818-01-0; **2d**, 113947-88-9; **2e**, 6683-51-8; **2f**, 40463-03-4; **2g**, 18491-21-9; **3a**, 113947-89-0; **3b**, 113947-90-3; **3c**, 32094-39-6; **3d**, 113947-91-4; **3e**, 4489-84-3; **3f**, 18272-91-8; **3g**, 4957-18-0.

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[12] Zimmerman, H. E.; Wu, G. S. *Can. J. Chem.* **1983**, *61*, 866.

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