Cyclobutene photochemistry. Substituent effects on the photochemistry of 1-phenylcyclobutene

William J. Leigh and J. Alberto Postigo

Abstract: The photochemistry and photophysics of 1-phenylcyclobutene and five aryl-substituted derivatives have been studied in various solvents at room temperature. All six compounds fluoresce with quantum yields in the 0.2–0.3 range in cyclohexane and acetonitrile solution. 1-Phenylcyclobutene undergoes [2+2]-cycloreversion ($\phi = 0.09$) to yield phenylacetylene upon photolysis in either hydrocarbon or acetonitrile solution, and undergoes (Markovnikov) solvent addition upon irradiation in methanol solution ($\phi = 0.08$) in addition to cycloreversion. Triplet sensitization and quenching experiments indicate that cycloreversion and methanol addition are both excited singlet state processes. None of the six compounds studied undergo ring opening to the corresponding 2-aryl-1,3-butadiene in detectable yield. Quantum yields for cycloreversion in cyclohexane, acetonitrile, and methanol solution and methanol addition have been determined for the six compounds, along with excited singlet state lifetimes. The quantum yields and rate constants for cycloreversion and methanol addition are both enhanced by substitution with electron-donating groups. The variation in the rate constant for [2+2]-cycloreversion with substituent indicates that there is substantial dipolar character developed in the cyclobutenyl σ-bond framework during the reaction, in almost exact correspondence with that developed in the π system during photoprotonation. No deuterium scrambling is observed in 1-phenylcyclobutene-2,4,4-d_3 after photolysis in pentane solution to ca. 80% conversion, indicating that skeletal rearrangements leading to cyclopropyl carbenes do not occur in the direct photolysis of arylcyclobutene derivatives. A pericyclic mechanism for the photocycloreversion reaction is suggested. Triplet–triplet absorption spectra and triplet lifetimes of 1-phenyl-, 1-(*para*-methylphenyl)-, and 1-(*para*-trifluoromethylphenyl)cyclobutene in hydrocarbon solution are also reported.

Key words: photochemistry, cyclobutene, fluorescence, [2+2]-cycloreversion, substituent effects, nanosecond laser flash photolysis, lifetime, triplet state, styrene, photoaddition

Résumé : On a étudié, dans différents solvants et à différentes températures, la photochimie et la photophysique du 1-phenylcyclobutène et de cinq dérivés aryles substitués. Tous ces six composés entrent en fluorescence avec des rendements quantiques de l'ordre de 0,2 à 0,3 en solution dans le cyclohexane et dans l'acétonitrile. Le 1-phénylcyclobutène subit une cycloélimination [2+2] ($\phi = 0{,}09$) pour conduire au phénylacétylène par photolyse en solution dans un hydrocarbure ou dans l'acétonitrile, avec en plus une addition de solvant (de type Markovnikov) par irradiation dans une solution de méthanol ($\phi = 0{,}08$). Les expériences de sensibilisation du triplet et de désactivation indiquent que la cycloélimination et l'addition de méthanol sont toutes deux des états singulets excités. Aucun des six composés étudiés ne conduit par ouverture du cycle au 2-aryl-1,3-butadiène en quantité décelable. On a déterminé, pour les six composés, les rendements quantiques de la cycloélimination dans des solutions de cyclohexane, d'acétonitrile et de méthanol et de l'addition de méthanol ainsi que les temps de vie de l'état singulet excité. La présence de substituants électrodonneurs augmente les rendements quantiques et les constantes de vitesse de la cycloélimination et de l'addition de méthanol. La variation de la constante de vitesse de la cycloélimination [2+2] indique qu'il se développe un caractère dipolaire très marqué dans les liaisons σ du squelette du groupe cyclobutényle au cours de la réaction et cela correspond presqu'exactement au caractère qui se développe dans les systèmes π au cours de la photoprotonation. On n'observe pas de brouillage du au deutérium dans le 1-phénylcyclobutène-2,4,4-d_3 après la photolyse en solution dans le pentane avec une conversion de 80% environ; ceci indique que le réarrangement du squelette conduisant au carbènes du type cyclopropyle ne se produit pas lors de la photolyse directe des dérivés arylcyclobutènes. On suggère un mécanisme péricyclique pour la réaction de photocycloélimination. On rap-

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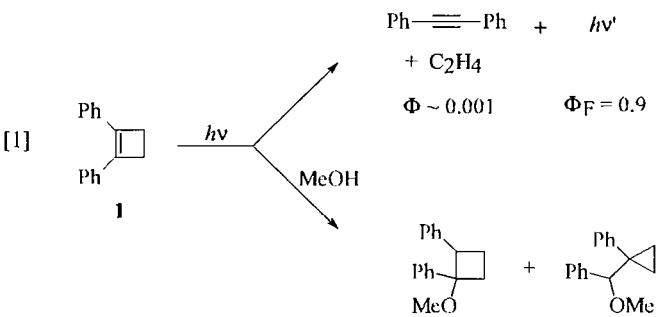
porte également les spectres d'absorption triplet–triplet et les durées de vie du triplet du 1-phenyl-, du 1-(*para*-méthylphényl)- et du 1-(*para*-trifluorométhylphényl) cyclobutène en solution dans un hydrocarbure.

Mots clés : photochimie, cyclobutène, fluorescence, cycloélimination [2+2], effets de substituants, photolyse du laser, durée de vie, l'état triplet, styrène, photoaddition.

[Traduit par le rédaction]

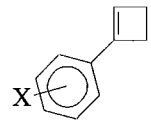
Introduction

The photochemistry of alkyl- and arylcyclobutenes appears to differ in many respects (1, 2). Alkyl-substituted derivatives undergo competing ring opening and [2+2]-cycloreversion upon photolysis in solution. Ring opening is nonstereospecific in most simple cyclobutenes (3, 4), while cycloreversion takes place stereospecifically (5, 6). The quantum yields of these processes vary according to the relative energies of the cyclobutene Rydberg and valence states. Substitution with nonconjugative electron-withdrawing substituents results in a substantial reduction in the quantum yield for cycloreversion and a significant increase in that for ring opening (4). From this it has been concluded that ring opening is a π,π^* singlet



state process, while cycloreversion arises from an excited singlet state with substantial (π,R(3*s*)) Rydberg character. The observation of skeletal rearrangements in the photochemistry of asymmetrically substituted, monocyclic alkylcyclobutenes suggests that cycloreversion may proceed via cyclopropyl carbene intermediates formed by ring contraction (7–9).

While arylcyclobutenes have not been as extensively studied as alkylated derivatives, 1,2-diphenylcyclobutene (**1**) is known to fluoresce efficiently and undergo formal [2+2]-cycloreversion upon photolysis in hydrocarbon solution (see eq. [1]), to the exclusion of ring opening (9–11). This contrasts the behaviour of benzocyclobutenes and Dewar aromatics, which both undergo efficient ring opening upon photolysis in condensed media (12–15). It has been suggested that the failure of arylcyclobutenes to undergo excited state ring opening may be due to simple energetic considerations; the π,π^* singlet state energy is too low to enable cleavage of the cyclobutene C3—C4 bond (1, 2). A second possibility is that the lack of reactivity towards ring opening is for some reason due to polarization of the styrenic C=C bond in the π,π^* excited singlet state. In acyclic and other cyclic phenylalkenes, this polarization is reflected in enhanced basicity and nucleophilicity in the excited state compared to that in the ground state (16–19). This appears to hold true for arylcyclobutenes as well, since photolysis of **1** in alcohol solution results in the formation of ethers consistent with initial protonation of the lowest excited singlet state by the solvent (18).



a: X = 4-OCH_3 *d*: X = 4-OCF_3
b: X = 4-CH_3 *e*: X = 4-CF_3
c: X = H *f*: X = 3-CF_3

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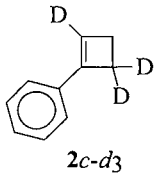
1-Phenylcyclobutene (**2***c*) fluoresces ($\Phi_F = 0.27$) in solution (20) and in the gas phase (21, 22), and affords the styrenic triplet state by intersystem crossing (20, 23, 24). To our knowledge, however, no information on the photochemistry of this molecule exists in the literature. In this paper, we report the results of a study of the effects of aryl substituents on the photochemical and photophysical behavior of 1-phenylcyclobutene, using the series of compounds **2***a–f*. The study of **2***a–f*, which were chosen so as to systematically alter the basicity and polarization of the π,π^* singlet state, was undertaken with several goals in mind. Our primary goals were to determine whether ring opening might become an important mode for excited state decay in phenylated cyclobutenes when the polarization of the C=C bond is altered through appropriate substitution, and to what degree [2+2]-cycloreversion is affected by such alterations in the electronic character of the lowest excited singlet state. The possibility that photocycloreversion proceeds via a similar mechanism to that of alkylcyclobutenes has been investigated with 1-phenylcyclobutene-2,4,4-d_3 (**2***c*–d_3), in which the involvement of a cyclopropylcarbene intermediate should be revealed by scrambling of deuteriums between C4 and C3 in reisolated material after photolysis.

We also wished to examine the effects of substituents on the efficiency of the photoaddition of alcohols to the molecule, as 1-phenylcyclobutene is a rigid analog of styrene, for which the photoaddition of water and alcohols has been studied in detail (19, 25, 26). Styrenes substituted with electron-withdrawing substituents do not undergo photohydration in solution in detectable yield (19, 25, 26). The process involves initial protonation of the excited singlet state, a property that makes electron-donor substituted styrenes useful as precursors for the corresponding 1-phenylethyl cations in time-resolved studies of carbenium ion reactivity (27–29). Presumably, photoprotonation is inefficient in electron-poor analogs because their relatively low excited state basicities render the process too slow to compete effectively with free-rotor excited state relaxation. Thus, arylcyclobutenes may also be potentially suitable as precursors for the study of electron-acceptor substituted benzylic carbenium ions by time-resolved methods. We have studied the photoaddition of methanol to **2***a–f* and have examined the effect of the alcohol on their excited singlet state lifetimes, in order to lay the groundwork for future studies of this type.

Finally, we report the triplet–triplet absorption spectra of 1-phenylcyclobutene (**2***c*) and the 4-methyl- (**2***b*) and 4-trifluo-

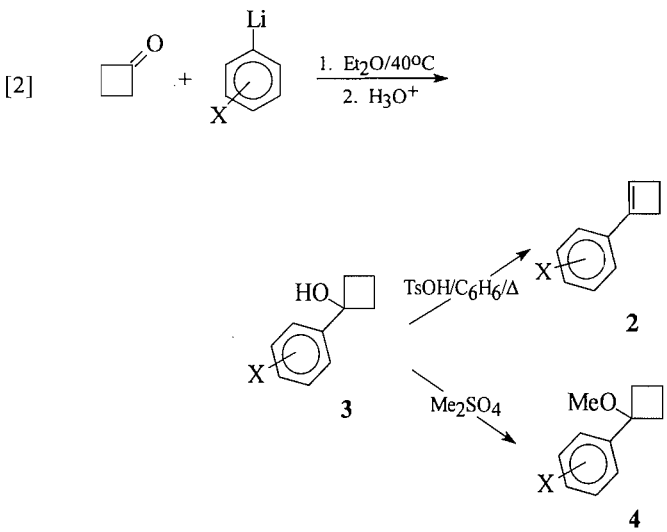


2c-d_3

romethyl- (2*d*) analogs in cyclohexane solution at room temperature, along with rate constants for triplet–triplet energy transfer to *trans*-piperylene, obtained using nanosecond laser flash photolysis (NLFP) techniques. The triplet states of a wide variety of cyclic and acyclic arylalkenes have already been characterized by such methods (23, 30, 31), but that of 1-phenylcyclobutene has not.

Results

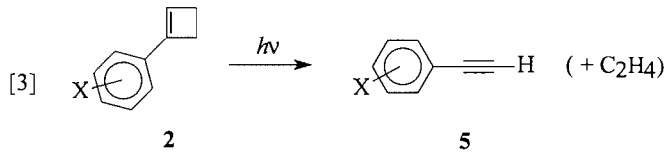
Compounds 2*a–f* were synthesized by addition of the corresponding aryllithium reagent to cyclobutanone, followed by acid-catalyzed dehydration of the intermediate 1-arylcyclobutanol (**3**; see eq. [2]). The cyclobutanols were also methylated to provide authentic samples of the ethers (**4**) anticipated from the photolysis of the arylcyclobutenes in methanol solution.



[2] 1. $Et_2O/40°C$ 2. H_3O^+; $TsOH/C_6H_6/\Delta$; Me_2SO_4

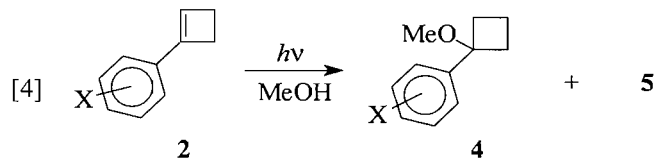
Compound 2*c*–d_3 was synthesized from cyclobutanone-2,2,4,4-d_4 using a similar procedure to that employed for the synthesis of the parent compound (2*c*). ^{1}H NMR analysis of the compound indicated it to be ca. 93% deuterated at positions 2 and 4 of the cyclobutenyl ring.

Direct irradiation of deoxygenated ~0.002 M solutions of 2*a–f* in pentane or dried acetonitrile results in the formation of the corresponding arylacetylenes 5*a–f* in high chemical yield (eq. [3]). In one case (2*f*), the photolysates also contained substantial amounts of two dimeric compounds. The dimers were not isolated, but were tentatively identified as such on the basis of their mass spectra. The yields of the dimers were significant even when the concentration of 2*f* was lowered to 2×10^{-4} M. Irradiation of a pentane solution of 2*f* (2×10^{-4} M) containing 0.02 M 1,3-cyclohexadiene had no effect on the yield of arylacetylene 5*f*, but led to substantial quenching of the formation of the dimeric products.



[3] $h\nu$; (+ C_2H_4)

Photolysis of a deoxygenated 0.05 M solution of 2*c*–d_3 in acetonitrile-d_3 under similar conditions to those above resulted in the formation of phenylacetylene-*d* (5*c–d*), as verified by GC–MS analysis. Integration of the ^{1}H NMR spectrum of the crude mixture after photolysis to ca. 50% conversion afforded a H3/H4 ratio in the remaining starting material which was indistinguishable from that measured in the unphotolyzed material.



[4] $h\nu$, MeOH; + 5

Direct irradiation of deoxygenated ~0.002 M solutions of **2** in methanol results in the formation of the corresponding 1-aryl-1-methoxycyclobutane **4** (eq. [4]), with substantial quenching of the formation of **5** in each case. No other products were observed to be formed in significant yield from photolysis of any of the compounds studied, so long as the conversions were kept below ca. 30%. At higher conversions, small amounts of reduction products of **2** could be detected in the photolysates; these were tentatively identified as the corresponding arylcyclobutanes by GC–MS. Photolysis of similar solutions in the presence of *trans*-1,3-pentadiene (0.01 M) yielded the same products in approximately the same quantum yields as those carried out in the absence of diene.

Quantum yields for formation of **5** (ϕ_5) and **4** (ϕ_4) from direct irradiation of **2** (to ca. 5% conversion) in deoxygenated pentane and methanol solutions, respectively, were determined by potassium ferrioxalate actinometry and are collected in Table 1. Included in this table are quantum yields for the formation of **5** in acetonitrile solution, which were determined for each compound using the quantum yields in pentane as secondary standards. Quantum yields for formation of **5** in methanol solution were estimated based on the relative yields of **5** and **4** obtained upon photolysis of **2** (to 5–12% conversion) in that solvent.

Photolysis of deoxygenated 0.008 M solutions of 2*c* in acetonitrile containing varying amounts of methanol between 0 and 16 M were carried out in a merry-go-round apparatus, and product formation was monitored by GC after ca. 2% conversion. Figure 1(*a*) shows the Stern–Volmer plot for quenching of the formation of phenylacetylene (5*c*) by the alcohol. The slope yields a Stern–Volmer constant of $k_q\tau = 0.046 \pm 0.003$ M^{-1}. Figure 1(*b*) shows a reciprocal plot of the yield of 4*c* obtained in these experiments as a function of methanol concentration. The data were corrected for the formation of a small amount of a product (presumably the alcohol 3*c*) that has the same retention time as the ether under the GC conditions employed, and which is formed in significant yields in acetonitrile in the absence of methanol. The intercept/slope

Table 1. Quantum yields for arylacetylene (**5**) formation from photolysis of **2***a–f* in pentane, acetonitrile, and methanol solution, and for methyl ether (**4**) formation from photolysis of **2***a–f* in methanol solution at 23°C.[a]

2	Substituent	$\phi_5^{pentane}$	ϕ_5^{MeCN}	ϕ_4^{MeOH}	ϕ_5^{MeOH}
a	4-OMe	0.20 ± 0.02	0.18 ± 0.02	0.13 ± 0.02	0.05 ± 0.02
b	4-Me	0.15 ± 0.02	0.12 ± 0.05	0.10 ± 0.02	0.03 ± 0.02
c	H	0.09 ± 0.01	0.09 ± 0.02	0.08 ± 0.01	0.010 ± 0.005
d	4-CF_3	0.07 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.016 ± 0.003
e	4-OCF_3	0.022 ± 0.003	0.035 ± 0.009	0.024 ± 0.007	0.005 ± 0.002
f	3-CF_3	0.0045 ± 0.0006	0.0090 ± 0.0006	0.0006 ± 0.0001	0.0001 ± 0.0001

[a]Determined by electronic actinometry, calibrated with ferrioxalate. ϕ_5^{MeOH} values were estimated from the relative yields of **5** and **4** in methanol solution and the corresponding ϕ_4^{MeOH} values.

Table 2. Fluorescence emission maxima, quantum yields and lifetimes for **2***a–f* in pentane and acetonitrile and fluorescence lifetimes in methanol.[a]

		Pentane			Acetronitrile			Methanol
2	X	λ_F^{max}	ϕ_F[b]	τ_F (ns)[c]	$\lambda_F$max	ϕ_F[b]	τ_F (ns)[c]	τ_F (ns)[c]
a	4-OMe	330	0.20	12.9	331	0.20	10.2	5.6
b	4-Me	335	0.21	12.1	319	0.22	9.7	6.6
c	H	309	0.25	12.2	320	0.24	9.0	7.4
d	4-CF_3	309	0.25	12.1	322	0.27	11.8	11.5
e	4-OCF_3	335	0.30	12.5	337	0.31	11.6	10.8
f	3-CF_3	337	0.31	6.7	331	0.18	7.5	7.0

[a]Determined at 23 ± 1°C.
[b]Errors in fluorescence quantum yields are ca. 20%.
[c]Errors in lifetimes are ca. 10%.

ratio calculated by least-squares analysis of these data affords $k_q\tau = 0.02 \pm 0.01$ M^{-1}; this value should be considered to be a lower limit owing to the poor precision of the data at lower methanol concentrations.

Steady state fluorescence emission spectra of the six compounds were recorded in deoxygenated acetonitrile and pentane solutions at 25°C, as well as in methanol in the cases of **2***b–d*. The emission bands showed minor fine structure in pentane, but were approximately Gaussian in acetonitrile and methanol, with maxima centred at 320–330 nm. Fluorescence quantum yields were determined using naphthalene as a standard ($\phi_F = 0.23$ (32)) (33), and are listed in Table 2.

The phosphorescence emission spectrum of **2***c* was measured in a methylcyclohexane glass at 77 K. The spectrum (not shown) is similar in position and fine structure to that reported by Ramamurthy et al. for the same compound in thallium-exchanged zeolites (24). The phosphorescence lifetime was determined to be 4.1 ± 0.2 ms in methylcyclohexane at 77 K.

Fluorescence lifetimes were determined for **2***a–f* in deoxygenated pentane, acetonitrile, and methanol solutions using the time-correlated single photon counting technique, and are also included in Table 2. The fluorescence of carefully purified samples of **2***b–f* (monitored at the emission maxima) exhibited single exponential decay kinetics, so long as the number of counts acquired for decay acquisition was kept below 5000. In the case of **2***a*, it was necessary to limit acquisition to less than 2000 counts. GC analysis verified that sample photodecomposition was negligible (i.e., <1%) over the course of these experiments in each case. Oxygen quenches the fluorescence of **2***a–c* efficiently; for example, the lifetime of **2***b* in air-saturated acetonitrile is $\tau_s = 6.0$ ns. This allows a rough estimate of $k_q \sim 2 \times 10^{10}$ M^{-1} s^{-1} for the rate constant for quenching of the excited singlet state of this compound by oxygen in this solvent. On the other hand, there is less than a 10% difference in the lifetimes of **2***d,e* and no difference in those of **2***f* in air- and nitrogen-saturated acetonitrile.

Table 3 contains rate constants for fluorescence (k_F^0) and cycloreversion (k_5) in pentane and acetonitrile solution and cycloreversion and methanol addition (k_4) in methanol, calculated using the quantum yield and lifetime data collected in Tables 1 and 2.

Addition of methanol (0–2 M) to deoxygenated solutions of **2***c* in acetonitrile results in a slight reduction in singlet lifetime: ca. 10% over the concentration range studied. Least-squares analysis of a plot of $1/\tau_s$ vs. methanol concentration over the 0–2 M range (Fig. 1(*c*)) affords a slope of $k_q = (5.1 \pm 1.4) \times 10^6$ M^{-1} s^{-1}. Over a larger concentration range, a plot of $1/\tau_s$ vs. [MeOH] is curved, levelling off to a value of 1.35×10^8 s^{-1} ($\tau_s = 7.4$ ns) for the neat alcohol.

Nanosecond laser flash photolysis (NLFP) experiments employed the pulses (248 nm, 16 ns, 40–80 mJ) from a Kr/F_2 excimer laser and a microcomputer–controlled detection system. Flash photolysis of continuously flowing, extensively deoxygenated isooctane solutions of **2***c* (ca. 6×10^{-5} M) gave

Table 3. Rate constants for fluorescence (k_F^0) in cyclohexane and acetonitrile solution, [2+2]-cycloreversion (k_5) in pentane, acetonitrile, and methanol solution, and photoaddition of methanol in neat methanol (k_4).[a]

		Hydrocarbon[b]		Acetonitrile		Methanol	
2	X	k_F^0 ($\times 10^{-7}$ s)	k_5 ($\times 10^{-7}$ s)	k_F^0 ($\times 10^{-7}$ s)	k_5 ($\times 10^{-7}$ s)	k_5 ($\times 10^{-7}$ s)	k_4 ($\times 10^{-7}$ s)
a	4-OMe	1.6 ± 0.2	1.6 ± 0.2	2.2 ± 0.3	2.0 ± 0.2	0.88 ± 0.08	2.3 ± 0.3
b	4-Me	1.7 ± 0.2	1.2 ± 0.2	2.4 ± 0.3	1.3 ± 0.5	0.46 ± 0.05	1.5 ± 0.2
c	H	2.0 ± 0.2	0.74 ± 0.07	2.6 ± 0.3	1.0 ± 0.2	0.14 ± 0.02	1.1 ± 0.2
d	4-CF_3	2.4 ± 0.2	0.58 ± 0.08	3.0 ± 0.4	0.7 ± 0.1	0.14 ± 0.02	0.4 ± 0.1
e	4-OCF_3	3.4 ± 0.3	0.18 ± 0.2	3.6 ± 0.4	0.3 ± 0.1	0.046 ± 0.006	0.2 ± 0.1
f	3-CF_3	4.6 ± 0.5	0.07 ± 0.01	2.9 ± 0.3	0.14 ± 0.02	0.0014 ± 0.003	0.009 ± 0.001

[a]Calculated from quantum yield and lifetime data in Tables 1 and 2.
[b]Fluorescence lifetimes were determined in cyclohexane solution; cycloreversion was determined in pentane solution.

rise to readily detectable transient absorptions in the 300–340 nm region (λ_{max} = 310 nm), which decayed with clean pseudo-first-order kinetics and a lifetime of about 2 μs. Figure 2 shows the transient absorption spectrum obtained from this solution; the insert shows a transient decay trace measured at a monitoring wavelength of 320 nm. Decay traces were collected by signal averaging of four to five separate decays, with correction for the substantial prompt fluorescence emitted by the sample. The presence of oxygen (either added intentionally or due to incomplete deoxygenation) results in substantial reductions in both the initial yield and the lifetime of the transient. The transient is quenched by *trans*-piperylene ($k_q = (1.6 \pm 0.1) \times 10^9$ M^{-1} s^{-1}), and can thus be assigned to the triplet state of **2***c*.

Similar experiments were carried out for 1-(*para*-methylphenyl)- and 1-(*para*-trifluoromethylphenyl)cyclobutene. The triplet–triplet absorption spectrum of **2***b* exhibited λ_{max} = 310 nm, while that of **2***d* was shifted to 320 nm. The triplet lifetimes of both compounds were similar to that of **2***c* in deoxygenated isooctane solution. The triplet–triplet absorptions of **2***b* and **2***d* exhibited similar sensitivities to the presence of oxygen and similar rate constants for quenching by *trans*-piperylene as those from **2***a*. NLFP of extensively deoxygenated solutions containing varying concentrations of **2***d* between 5×10^{-5} and 2×10^{-4} M allowed us to estimate an upper limit of 1×10^9 M^{-1} s^{-1} for the self-quenching rate constant for **2***d*.

Flash photolysis of a deoxygenated, 0.02 M solution of 4-methoxyacetophenone in acetonitrile with a nitrogen laser (337 nm, 6 ns, 4–5 mJ) afforded readily detectable transient absorptions at 385 nm due to formation of the ketone triplet state. The lifetime of the triplet state is quenched upon addition of **2***c* to the solution, with a bimolecular rate constant of $k_q = (2.4 \pm 0.1) \times 10^9$ M^{-1} s^{-1}.

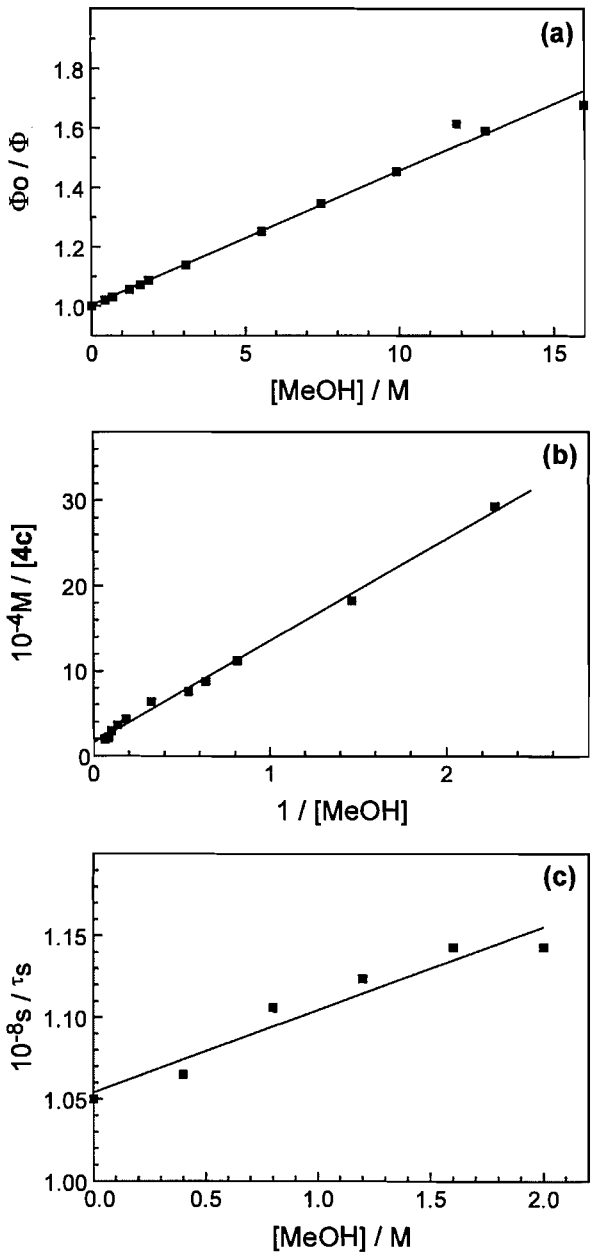
Discussion

The values of ϕ_F (= 0.24) and τ_s (= 12.2 ns) reported here for **2***c* in pentane solution at room temperature are both in reasonable agreement with those reported by Zimmerman et al. for the same compound in methylcyclohexane–isopentane solution at 27°C (ϕ_F = 0.27; τ_s = 15.9 ± 0.9 ns) (20). These workers also reported a value of ϕ_{ISC} = 0.004 for the quantum yield of intersystem crossing in **2***c*, determined by the biacetyl phosphorescence sensitization method (34, 35). Thus, intersystem crossing is over an order of magnitude less efficient than either fluorescence or reaction via [2+2]-cycloreversion (ϕ_{5c} = 0.09), and the combination of these three processes accounts for only about 40% of excited state decay events. Presumably, nonproductive radiationless decay processes account for the rest.

The fluorescence emission maxima of **2***a–f* vary slightly between 320 and 330 nm, but show no regular variation with substituent or solvent throughout the series. On the other hand, the fluorescence quantum yields increase throughout the series in both solvents while the singlet lifetimes decrease, resulting in a fourfold variation in the radiative rate constant k_F^0 (Table 3). The singlet lifetimes are consistently shorter in acetonitrile solution than in pentane for **2***c* and those derivatives bearing electron-donating substituents (**2***a*, *b*). This may be due to the presence of small amounts of water in the polar solvent. Oxygen quenches the lowest excited singlet state of **2***a–c* efficiently ($k_q \sim 2 \times 10^{10}$ M^{-1} s^{-1} for **2***b*), presumably by an electron transfer mechanism (36, 37). In agreement with this, the fluorescence lifetimes of **2***d–f* are approximately the same in air- and nitrogen-saturated solution.

1-Phenylcyclobutene (**2***c*) exhibits readily detectable phosphorescence in a hydrocarbon glass at 77 K, but detection of the triplet in solution at room temperature by nanosecond laser flash photolysis (NLFP) techniques is difficult unless the solutions are *thoroughly* deoxygenated. Presumably, this reflects the rapid quenching of the excited singlet state of **2***c* by molecular oxygen. The triplet–triplet absorption spectrum reported here for **2***c* is similar to that reported previously for 1-phenylcyclopentene (23). The lifetime and UV absorption spectrum of the triplet state of **2***c* appears to be relatively insensitive to substituents on the aryl ring or to solvent polarity. The rate constants for triplet quenching by dienes (e.g., *trans*-piperylene) are significantly slower than the diffusion-controlled rate in both acetonitrile and isooctane, presumably because the triplet energy of **2***c* (ca. 60 kcal/mol (24)) is approximately isothermal with the diene triplet energy. The triplet state of **2***d* is reactive toward dimerization ($k_{sq} \sim 1 \times 10^9$ M^{-1} s^{-1}), but this process proceeds in significant chemical yield only when population of the triplet by intersystem crossing competes

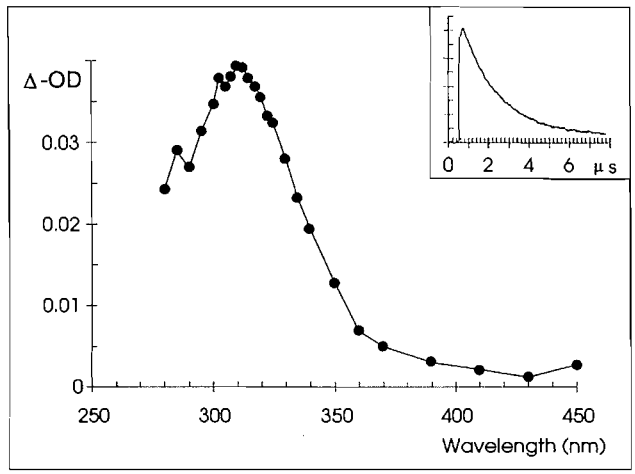
Fig. 1. Quenching of 1-phenylcyclobutene (2*c*) excited singlets by methanol in deoxygenated acetonitrile solution at 23°C: (a) Stern–Volmer plot for the quenching of phenylacetylene (**5***c*) formation; (b) Reciprocal plot for the formation of methyl phenylcyclobutyl ether (**4***c*); (c) quenching of singlet lifetime.



effectively with excited singlet state cycloreversion, as in those derivatives bearing strong electron-withdrawing substituents on the phenyl ring.

Direct irradiation of **2** in aprotic solvents results in the formation of the corresponding phenylacetylene (**5**) in high chemical yield. The reaction is singlet derived, as evidenced by the lack of observable quenching of the formation of **5***c* from photolysis of **2***c* in the presence of diene, and the fact that **5***c* is not formed under triplet sensitization conditions. While there is no significant solvent effect on the quantum yield for cycloreversion for any of the compounds studied (except perhaps for **2***f*), the quantum yields (Table 1) and rate constants (Table 3) for the process decrease markedly throughout the series with increasing substituent electron-withdrawing power.

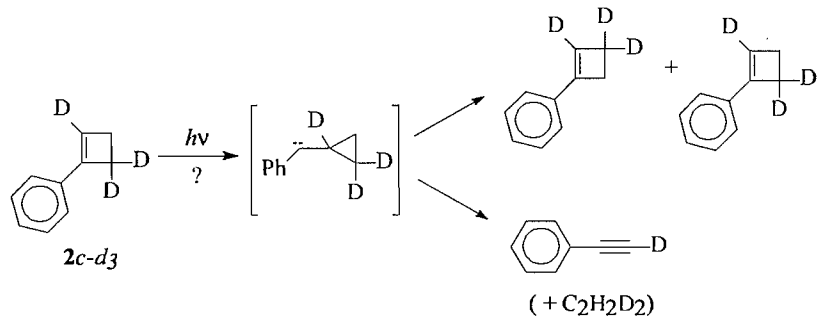
Fig. 2. The triplet–triplet absorption spectrum of 1-phenylcyclobutene (**2***c*) in deoxygenated isooctane solution, obtained by nanosecond laser flash photolysis techniques. The insert shows a representative decay trace, monitored at 320 nm.



The rate constants for cycloreversion of **2** show only a very qualitative correlation with ground-state substituent constants ($\rho = -1.2 \pm 0.5$ ($r^2 = 0.60$) for the data in pentane solution). That of the *meta*-trifluoromethyl substituted derivative **2***f* correlates particularly poorly with the rest of the compounds in the series. The general inadequacy of ground state substituent constants, particularly for *meta* substituents, in describing substituent effects on excited-state reactions of aromatic compounds is well documented (16, 26, 38–43). The cycloreversion rate constants for **2***a–d,f* correlate somewhat better with the σ_{ex} values of Baldry (which are based on the excited state pK_a values of substituted phenols (38)), but still only qualitatively; $\rho_{ex} = -0.9 \pm 0.4$ ($r^2 = 0.69$). Correlation with the $\sigma^{h\nu}$ scale of McEwen and Yates (based on the photoprotonation of substituted styrenes and phenylacetylenes (26)) is not possible owing to the absence of data for electron-withdrawing substituents other than 4-fluoro.

Electrocyclic ring opening to the corresponding 2-aryl-1,3-butadiene does not occur in detectable yield with any of the compounds studied in this work. From this it can be concluded that efficient ring opening requires that the energy of the lowest excited singlet state be significantly higher than the cyclobutenyl C3—C4 bond energy.

Photolysis of **2** in methanol solution results in the formation of the corresponding Markovnikov addition product **4** in high chemical yield. The reaction occurs from the lowest excited singlet state, as evidenced by the lower fluorescence lifetimes observed for **2***a–d* in methanol compared to those in acetonitrile, the substantial quenching of the formation of cycloreversion products in methanol and methanolic acetonitrile, and the fact that the reaction is not quenched by dienes. In the case of **2***c*, the Stern–Volmer constant obtained from the quenching of phenylacetylene formation by methanol in acetonitrile (Fig. 1(*a*)) agrees with that obtained from the reciprocal plot for the formation of cyclobutyl ether **4***c* (Fig. 1(*b*)) within experi-

[5] 

mental error. The Stern–Volmer constant ($k_q\tau = 0.046 \pm 0.003$ M^{-1}) obtained from least-squares analysis of the data in Fig. 1(*a*) affords a quenching rate constant $k_q = 5.1 \times 10^6$ M^{-1} s^{-1}, in satisfactory agreement with the rather imprecise value measured by single photon counting techniques ($k_q = (5.1 \pm 1.4) \times 10^6$ M^{-1} s^{-1}). It is noteworthy that the rate of quenching of the excited singlet state of **2***c* in acetonitrile, as measured by the above techniques, is approximately an order of magnitude faster than that determined in neat methanol solution (4.4×10^5 M^{-1} s^{-1}; from the Φ_{4c} and τ_s-values for **2***c* in methanol). While we cautiously ascribe this to a simple solvent effect, the difference *should* result in curvature in quenching plots taken over the full range of concentrations between neat acetonitrile and neat methanol.

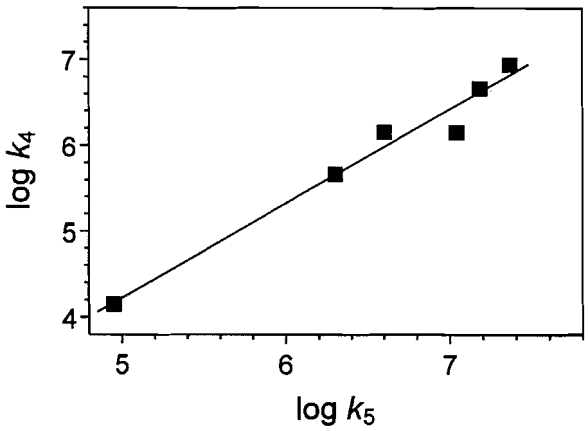
Most aspects of the excited singlet state quenching of **2** by methanol appear to be analogous to those observed for the quenching of the excited singlet states of acyclic and other cyclic styrene derivatives by water and alcohols (16, 25, 44). As anticipated, however, addition to **2** occurs with measurable efficiency even in the derivatives bearing reasonably strong electron-withdrawing groups. As noted previously for styrene, the regiochemistry and substituent effect on the rates of photoaddition of methanol are consistent with significant π-polarization of the C=C bond in the lowest excited singlet state of 1-phenylcyclobutene. Electron-withdrawing substituents on the phenyl ring reduce the polarization of the C=C bond, lowering its basicity and reducing its reactivity toward photoprotonation. In spite of this qualitative similarity to styrene photoadditions, the magnitude of the substituent effect on the process appears to differ significantly in 1-phenylcyclobutene. This can be seen by comparing the span in the rate constants for methanol addition in **2** to those reported by McEwen and Yates for the rates of water-catalyzed photohydration of substituted styrenes in neutral aqueous solution. These were reported to be 1.86×10^4 M^{-1} s^{-1} for styrene itself, 3.80×10^4 M^{-1} s^{-1} for 4-methylstyrene, and 2.45×10^5 M^{-1} s^{-1} for 4-methoxystyrene (26). The corresponding parameters in the present study are the k_4-values calculated from the ϕ_4 and τ_s^{MeOH} values for **2***a–c* in methanol solution (Table 3), after conversion to second-order rate constants by correcting for the solvent concentration (they vary by only a factor of about two throughout the series of three compounds). For the parent compound, the rate of methanol addition to **2***c* in methanol is ~25 times faster than the rate of water addition to styrene in water. The much less pronounced substituent effect on the rates of methanol photoaddition to **2***c* compared to that on the rates of water photoaddition to styrene may be the result of this substantial difference in absolute reactivity, although it will clearly be necessary to study the photochemistry of the two sets of compounds under more similar sets of conditions before reliable conclusions can be made in this regard.

The mechanism of [2+2]-photocycloreversion in arylcyclobutenes is expected to differ from that in alkylcyclobutenes. In the latter case, previous work has led to the conclusion that cycloreversion derives from a π,R(3*s*)-like state (4) and may involve the intermediacy of cyclopropyl carbene intermediates (7). The π,R(3*s*) state in **2** is expected to be substantially higher in energy than the π,π* singlet state (45), and is thus not expected to play a role in the photochemistry of phenylated systems. Indeed, while there is substantial precedent for Rydberg-derived [1,2]-shifts in the photochemistry of aliphatic alkenes and cycloalkenes (17, 46), there appear to be few examples (47) of such processes (yielding carbenes) in phenylalkene photochemistry. Although the excited singlet state behaviour of most of the phenylalkenes that have been studied is dominated by torsional relaxation (so that carbene-derived products might be difficult to detect in significant yield, particularly when the carbene intermediate can revert to the starting olefin), rearrangements of this type have not been observed even in the torsionally constrained phenylcycloalkenes that have been investigated in detail (44, 48).

Nevertheless, it is interesting to note that the efficiency of photocycloreversion in **2** is subject to a similar polar substituent effect as that observed previously for alkylcyclobutene derivatives (4). We thus felt it was important to study the mechanism of the formal [2+2]-cycloreversion reaction of **2** in greater detail. The photochemistry of 2,4,4-trideuterio-1-phenylcyclobutene (**2***c–d*$_3$) in acetonitrile solution was investigated in order to probe for skeletal rearrangements that might be indicative of the intermediacy of a cyclopropyl carbene in the [2+2]-cycloreversion process. If cycloreversion proceeds via such an intermediate (see eq. [5]), then one would expect to observe scrambling of deuterium between positions 3 and 4 of the cyclobutenyl ring, since carbenes of this type are known to undergo ring expansion to the corresponding cyclobutene in addition to fragmentation to alkene and alkyne (49–51). Examination of the ^{1}H NMR spectrum of an irradiated 0.02 M solution of **2***c–d*$_3$ after ca. 50% conversion offers no evidence for significant scrambling of the label between the two positions. We thus conclude that cyclopropyl carbene intermediates are not formed in the direct photolysis of phenylcyclobutenes to a significant extent; the similarity in the substituent effect on the quantum yield of the process to that in alkylcyclobutenes appears to be coincidental.

The substituent effect on k_5 indicates that there is substantial dipolar character developed in the σ-bond framework dur-

Fig. 3. Log–log plot of the rates of methanol addition (k_4) versus photocycloreversion (k_5) in methanol solution for **2***a–f*.



ing the formal [σ_{2s} + σ_{2s}]-cycloreversion reaction, with positive charge developing at C1 of the cyclobutene ring. This is similar to the polarization experienced in the π-bond framework during photoprotonation; a log–log plot of the rate constants for photocycloreversion (in methanol) versus those for solvent photoaddition (Fig. 3) has a slope of 1.1 ± 0.2 (r^2 = 0.970), indicating an almost exact correspondence between the substituent effects on the two processes. It is reasonable to conclude that the photochemical [2+2]-cycloreversion of phenylcyclobutenes is a concerted process, which proceeds through a transition state of considerable dipolar character in the cyclobutenyl σ-bond framework (eq. [6]). In fact, theory predicts that polar factors should have a pronounced effect on the dynamics of singlet [2+2]-cycloreversion and -cycloaddition when the diagonals of the four-atom array are unequal (52, 53). To our knowledge, this is the first experimental verification of this in excited singlet [2+2]-cycloreversion reactions. In contrast to the substantial effect of polar substituents on the rate of the process, there is little variation in rate with solvent polarity in aprotic solvents (Table 3). Surprisingly, there is a substantial reduction in the rates of cycloreversion of all six compounds in methanol compared to acetonitrile; the origins of this intriguing solvent effect are the subject of continued study.

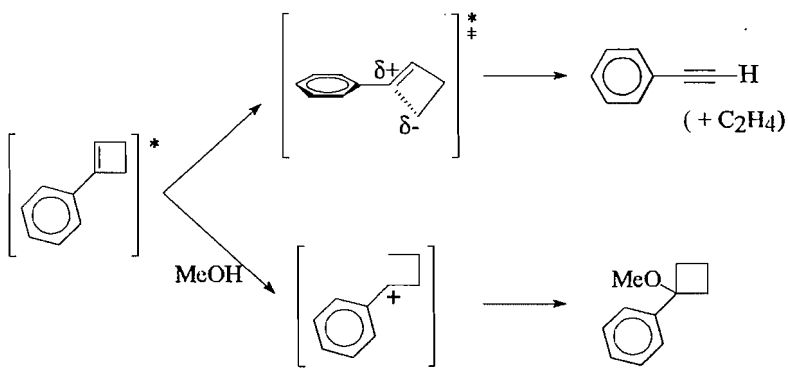
The substantial photoreactivity that **2***a–f* exhibit towards methanol holds considerable promise for studies of the effects of electron-withdrawing substituents on the kinetics of alkene photoprotonation and on the reactivity of the corresponding benzylic carbenium ions. Further work in this area will be directed at more detailed studies of the photoaddition of alcohols to arylcyclobutenes, and toward establishing a more precise comparison between the reactivity of phenylcyclobutenes and simple styrenes toward excited singlet state protonation.

Experimental

^{1}H NMR spectra were recorded on Bruker AC200 (200 MHz) or AC300 (300 MHz) spectrometers in deuteriochloroform solution, and are reported in parts per million downfield from tetramethylsilane. ^{13}C NMR spectra were recorded on the AC200 spectrometer, and ^{19}F NMR spectra were recorded on the AC300; they are reported in parts per million relative to tetramethylsilane and trichlorofluoromethane, respectively. Infrared spectra were recorded in the gas phase using a GC–FTIR system consisting of a Hewlett-Packard 5890 gas chromatograph (equipped with a 5 m × 0.53 mm HP-1 megabore capillary column (Hewlett–Packard, Inc.)) connected through a Biorad GC/C 32 interface to a Biorad FTS-40 FTIR spectrometer. Ultraviolet absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrometer interfaced to an IBM PS/2-286 microcomputer, or on a Hewlett–Packard HP8451 UV spectrometer. Fluorescence emission and excitation spectra were recorded on a Perkin Elmer LS-5 spectrofluorometer, which is also interfaced to the IBM PS/2-286 and controlled by software supplied by the manufacturer. Gas chromatographic analyses were carried out using a Hewlett–Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett–Packard 3396 integrator, and a HP-1 megabore capillary column (12 m × 0.53 mm; Hewlett–Packard, Inc.) or a DB-1 megabore capillary column (30 m × 0.53 mm, Chromatography Specialties). GC–MS analyses were carried out using a Hewlett–Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-1 microbore capillary column (12 m × 0.2 mm; Chromatographic Specialties, Inc.). Exact Masses were determined on a VGH ZABE mass spectrometer and employed a mass of 12.000 000 for carbon. Semipreparative VPC separations employed a Varian 3300 gas chromatograph equipped with 6 ft × 0.25 in. stainless steel columns consisting of (*a*) 5% OV-101 on Supelcoport or (*b*) 10% QF-1 on 80/100 Chromosorb (Supelco, Inc.).

n-Pentane (Baker Photrex), cyclohexane (BDH Omnisolv),

[6]



and barium oxide (Mallinckrodt) were used as received from the suppliers. Acetonitrile (Omnisolv) was dried over calcium hydride and distilled under dry nitrogen. Benzene (Baker Analyzed) was purified by several extractions with concentrated sulfuric acid, followed by distillation through a Vigreux column. Tetrahydrofuran (Baker Analyzed) was refluxed over sodium–benzophenone and distilled immediately prior to use. Dimethyl sulfoxide (Caledon) was dried over potassium hydroxide and distilled under reduced pressure. *p*-Toluenesulfonic acid monohydrate was used as received from Matheson. Bromobenzene, 4-bromotoluene, 4-bromoanisole, 4-bromobenzotrifluoride, 4-trifluoromethoxybromobenzene, 3-bromobenzotrifluoride, cyclobutanone, *n*-butyllithium, and *n*-decane were all used as received from Aldrich Chemical Co. Phenylacetylene and 4-tolylacetylene were used as received from Lancaster Chemicals, Inc.

Preparation of compounds

The cyclobutenes **2***a–f* were prepared by acid-catalyzed dehydration of the corresponding 1-arylcyclobutanol (**3**) (54), which was prepared by addition of the appropriate aryllithium to cyclobutanone in anhydrous ether at −40°C. The aryllithium reagents were prepared as solutions in ether from the corresponding bromoarene by lithium exchange using *n*-butyllithium. In the syntheses of **3***a,b,e*, the exchange was accelerated by sonication of the solutions at room temperature. A typical procedure is described below for the preparation of 1-(4-trifluoromethylphenyl)cyclobutene (**2***d*).

*1-(4-Trifluoromethylphenyl)cyclobutene (2*d)

In an oven-dried 50 mL 2-neck roundbottom flask equipped with a dropping funnel, magnetic stirrer, rubber septum, and nitrogen inlet were placed 4-bromobenzotrifluoride (3.43 g, 0.015 mol) and anhydrous ether (10 mL). The flask was cooled under an atmosphere of dry nitrogen to −40°C with a dry ice – acetone bath, and a 1.6 M hexane solution of *n*-butyllithium (9.5 mL, 0.015 mol) was added dropwise over 1 h. The bath and contents of the flask were then allowed to warm to 0°C over ca. 1 h. The temperature of the resulting yellow solution was again lowered to −40°C, and a solution of cyclobutanone (0.47 g, 0.0067 mol) in anhydrous ether (10 mL) was added dropwise over 1 h. The resulting yellow solution was then allowed to warm to room temperature over a further 1 h. The dark red mixture that resulted was quenched by slow addition of water (20 mL) and then extracted with ether (3 × 10 mL). The combined ether extracts were dried over anhydrous sodium sulfate and filtered. Evaporation of the solvent on a rotary evaporator yielded an orange liquid (1.23 g), which was distilled under vacuum. The major fraction (0.75 g, 0.0035 mol, 70%; bp 87°C (0.3 Torr; 1 Torr = 133.3 Pa); mp 52–54°C), was identified as *1-(4-trifluoromethylphenyl)cyclobutanol* (**3***d*) on the basis of the following spectral data. IR: 3632 (w), 2996 (m), 1328 (s), 1286 (w), 1232 (w), 1172 (m), 1149 (s), 1076 (m), 1017 (w), 846 (w). ^{1}H NMR: δ: 1.55 (br s, 1 H), 1.76 (cplx m, 1 H), 2.08 (brs, 1 H), 2.36 (cplx, m, 2 H), 2.54 (cplx, m, 2 H), 7.62 (s, 4 H). ^{13}C NMR; δ: 12.96, 37.18, 79.60, 125.51, 125.42, 125.36, 125.27, 126.88, 129.0 (q), 156.39. ^{19}F NMR; δ: −62.67. MS, *m/e* (I): 197 (17), 188 (98), 173 (100), 151 (35), 147 (42), 145 (96), 125 (33), 91 (75), 69 (33). Exact Mass, calcd. for $C_{11}H_{11}F_3O$: 216.0762; found: 216.0750.

Significantly higher isolated yields of the cyclobutanols can be obtained using column chromatography (neutral alumina, hexane–ether mixtures) to purify the crude reaction mixtures in the above step.

A solution of **3***d* (0.50 g, 0.0023 mol) and a few crystals of *p*-toluenesulfonic acid in dry benzene (25 mL) was stirred under reflux for 6 h, in a 50 mL roundbottom flask equipped with a glass tube that contained a small thimble filled with granulated calcium chloride and was topped with a reflux condenser. The resulting light brown solution was cooled to room temperature, water (25 mL) was added, and the mixture was extracted with pentane (3 × 10 mL). The combined extracts were washed with saturated aqueous sodium bicarbonate, dried over anhydrous magnesium sulfate, and the solvent was evaporated to yield a light yellow liquid (0.40 g). The product was isolated as a colourless liquid (0.20 g, 0.001 mol, 43%; bp 77°C (1 Torr); mp 20–22°C) by vacuum distillation. Better yields can be obtained by purification of the crude product by column chromatography (neutral alumina; 10% ether in hexane). The product was further purified by semi-preparative gas chromatography, and identified as *1-(4-trifluoromethylphenyl)cyclobutene* (**2***d*) on the basis of the following data. IR: 3056 (w), 2962 (m), 2935 (m), 2852 (m), 1330 (s), 1176 (m), 1149 (s), 1073 (s), 1043 (w), 1019 (w), 900 (w), 846 (m), 765 (w). UV (MeCN), λ_{max}: 260 nm (ε 14 800 M^{-1} cm^{-1}). ^{1}H NMR, δ: 2.40 (m, 2 H), 2.65 (t, J = 4 Hz, 2 H), 6.25 (br s, 1 H), 7.25 (d, J = 8.2 Hz, 2 H), 7.39 (d, J = 8.2 Hz, 2 H). ^{13}C NMR, δ: 26.44, 28.65, 124.32, 125.15, 130.27, 137.89, 145.14, 129.10 (q, CF_3). ^{19}F NMR, δ: −62.70. MS, *m/e* (*I*): 198 (15), 179 (21), 177 (22), 151 (28), 145 (21), 129 (100), 128 (50), 120 (15), 75 (27), 63 (20), 51 (16). Exact Mass, calcd. for $C_{11}H_9F_3$: 198.0656; found: 198.0688.

Cyclobutenes **2***a–c,e,f* were prepared in similar fashion to 2*d*, except that the initial lithium exchange in the cyclobutanol synthesis required less or more vigorous conditions depending on substituent. The yields of the intermediate 1-arylcyclobutanols ranged from 50 to 90% after chromatography, and those of the cyclobutenes from 70 to 90% after isolation by alumina column chromatography. The latter were all subjected to additional purification (>99% by GC) by semipreparative gas chromatography. Spectral and analytical data for the remaining 1-arylcyclobutanols and 1-arylcyclobutenes in the series are listed below.

*1-(4-Methoxyphenyl)cyclobutanol (3*a): IR: 3576 (m), 2966 (s), 2941 (s), 2883 (m), 1610 (m), 1513 (s), 1472 (m), 1298 (m), 1253 (s), 1224 (m), 1175 (m). ^{1}H NMR, δ: 1.66 (cplx m, 1 H), 1.98 (cplx m, 1 H), 2.36 (m, 2 H), 2.55 (m, 2 H), 3.78 (s 3 H), 7.42 (dd, 2 H), 7.77 (dd, 2 H). MS, *m/e* (*I*): 178 (27), 177 (38), 147 (31), 135 (100), 121 (11), 105 (7), 91 (9), 65 (7).

*1-(4-Methoxyphenyl)cyclobutene (2*a): IR: 3009 (w), 2956 (m), 2932 (m), 2851 (m), 1605 (m), 1424 (w), 1300 (m), 1258 (s), 1174 (m), 1056 (w), 1038 (w), 835 (m), 760 (w). UV (pentane), λ_{max}: 261 nm (ε 17 900 M^{-1} cm^{-1}). ^{1}H NMR, δ: 2.50 (m, 2 H), 2.77 (t, 2 H), 3.81 (s, 3 H), 6.13 (t, 1 H), 6.84 (dd, J = 2.2, 6.8 Hz, 2 H), 7.26 (dd, J = 2.2, 6.8 Hz, 2 H). ^{13}C NMR, δ: 26.02, 55.29, 113.74, 124.57, 125.55. MS, *m/e* (*I*): 160 (65), 159 (31), 145 (27), 129 (42), 117 (91), 115 (100), 102 (21), 91 (42), 89 (64), 77 (11), 51 (15). Exact Mass, calcd. for $C_{11}H_{12}O$: 160.0888; found: 160.0904.

*1-(4-Methylphenyl)cyclobutanol (3*b). IR: 3634 (m), 3032 (m),

2994 (s), 2958 (s), 2883 (m), 1621 (w), 1517 (m), 1342 (m), 1243 (m), 1136 (m), 1055 (m), 1021 (m), 818 (m), 720 (m). ^{1}H NMR, δ: 1.66 (cplx m, 2 H), 1.98 (br s, 2 H), 2.37 (s, 3 H), 2.37 (br s, 2 H), 2.54 (br s, 2 H), 7.17 (d, 0.7 Hz, 2 H), 7.37 (d, 0.7 Hz, 2 H). ^{13}C nmr, δ: 12.93, 21.02, 36.80, 109.22, 124.92, 129.09, 136.90, 143.29. MS, *m/e* (*I*): 147 (26), 134 (71), 119 (100), 92 (37), 91 (63), 77 (10), 65 (16). Exact Mass, calcd. for $C_{11}H_{14}O$: 162.1045; found: 162.1037.

1-(4-Methylphenyl)cyclobutene (**2**b): IR: 3057 (m), 3030 (m), 2957 (s), 2932 (s), 2883 (m), 2853 (m), 1510 (m), 1317 (w), 1291 (w), 1241 (w) , 1183 (w), 1117 (w), 899 (w), 822 (m), 754 (m). UV (MeCN), λ_{max}: 258 nm (ε 15 500 M^{-1} cm^{-1}). ^{1}H NMR, δ: 2.27 (s, 3 H), 2.46 (br t, 2 H), 2.72 (t, J = 3.3 Hz, 2 H), 6.15 (br s, 1 H), 7.05 (d, 2 H), 7.18 (d, 2 H). ^{13}C NMR, δ: 21.30, 26.15, 28.75, 102.86, 124.12, 125.96, 128.95, 137.14. MS, *m/e* (*I*): 144 (24), 129 (100), 128 (59), 115 (90), 90 (9), 89 (11), 63 (18), 51 (12). Exact Mass, calcd. for $C_{11}H_{12}$: 144.0939; found: 144.0930.

1-Phenylcyclobutanol (**3**c: mp 40–41°C (54)). IR: 3633 (m), 3073 (m), 3041 (m), 2995 (s), 2960 (s), 1448 (m), 1342 (m), 1242 (m), 1177 (w), 1139 (m), 1026 (m), 899 (m), 761 (m). ^{1}H NMR, δ: 1.68 (cplx m , 1 H), 2.01 (cplx m, 1 H), 2.36 (cplx m, 2 H), 2.56 (cplx m, 2 H), 7.27 (m, 1 H), 7.36 (m, 2 H), 7.49 (m, 2 H). ^{13}C NMR, δ: 12.99, 36.83, 124.93, 127.24, 128.44. MS, *m/e* (*I*): 148 (8), 147 (7), 130 (12), 120 (58), 115 (18), 105 (100), 102 (15), 91 (63), 78 (89), 77 (99), 74 (21), 63 (16), 51 (48).

1-Phenylcyclobutene (**2**c): IR: 3069 (m), 3041 (m), 2958 (s), 2933 (s), 2888 (w), 2852 (m), 1580 (w), 1491 (w), 1244 (w), 1070 (w), 901 (w), 850 (w), 729 (s). ^{1}H NMR (55), δ: 2.51 (m, 2 H), 2.79 (t, 2 H), 6.27 (t, 1 H), 7.31 (m, 5 H). ^{13}C NMR (56), δ: 26.18, 28.72, 124.16, 127.13, 127.36, 128.07, 128.28, 128.64, 135.04, 146.40.

1-(4-Trifluoromethoxyphenyl)cyclobutanol (**3**e): IR: 3630 (w), 2996 (m), 2965 (w), 1513 (m), 1273 (s), 1229 (m), 1186 (m), 1142 (w), 1020 (m), 851 (w). ^{1}H NMR, δ: 1.18 (cplx m, 1 H), 1.63 (br s, 1 H), 1.97 (cplx m, 2 H), 2.11 (cplx m., 2 H), 6.82 (m, 2 H), 7.13 (m, 2 H). ^{13}C NMR, δ: 12.88, 37.06, 76.56, 120.6 (q), 120.83, 127.08, 134.71, 144.92. ^{19}F NMR, δ: −94.59. MS, *m/e* (*I*): 204 (74), 189 (100), 175 (7), 162 (23), 147 (15), 95 (22), 69 (15). Exact Mass, calcd. for $C_{11}H_{11}F_3O_2$: 232.0711; found: 232.0695.

1-(4-Trifluoromethoxyphenyl)cyclobutene (**2**e): IR: 3036 (w), 2968 (m), 2911 (w), 1794 (m), 1597 (m), 1502 (m), 1274 (s), 1226 9s), 1187 (s), 1112 (m), 1023 (w), 901 (m), 836 (m), 790 (m). UV (pentane), λ_{max}: 255 nm (ε 17 400 M^{-1} cm^{-1}). ^{1}H NMR, δ: 2.52 (br d, 2 H), 2.79 (t, 2 H), 6.35 (br s, 1 H), 7.25 (br q, 4 H). ^{13}C NMR, δ: 25.37, 34.94, 118.50, 127.38, 129.56, 130.43, 134.75, 147.80. ^{19}F NMR, δ: −59.08. MS, *m/e* (*I*): 214 (50), 199 (11), 186 (23), 175 (4), 145 (7), 130 (14), 129 (100), 128 (36), 127 (38), 117 (21), 115 (29), 102 (7), 89 (21), 69 (21), 63 (14), 51 (7). Exact Mass, calcd. for $C_{11}H_9F_3O$: 214.0605; found: 214.0593.

1-(3-Trifluoromethylphenyl)cyclobutanol (**3**f): IR: 3633 (w), 3080 (w), 2996 (m), 2956 (m), 2889 (w), 1441 (w), 1330 (s), 1272 (m), 1178 (s), 1147 (s), 1077 (m), 1019 (w), 902 (w), 838 (w), 804 (w), 703 (m). ^{1}H NMR, δ: 1.55 (br s, 1 H), 1.73 (cplx m, 1 H), 2.04 (cplx m, 1 H), 2.34 (cplx m, 2 H), 2.48 (cplx m, 2 H), 7.61 (m, 4 H). ^{13}C NMR, δ: 12.98, 37.15, 76.73, 121.81, 123.98, 124.06, 128.37, 128.92, 130.0 (q), 147.32. ^{19}F NMR, δ: −62.71. MS, *m/e* (*I*): 197 (13), 188 (94), 173 (100), 159 (6), 145 (56), 127 (7), 91 (19), 75 (6). Exact Mass, calcd. for $C_{11}H_{11}F_3O$: 216.0762; found: 216.0750.

1-(3-Trifluoromethylphenyl)cyclobutene (**2**f): IR: 2955 (m), 2816 (m), 1601 (w), 1444 (m), 1348 (m), 1327 (s), 1282 (m), 1256 (m), 1181 (s), 1151 (s), 1076 (m), 981 (w), 891 (w), 799 (m). UV (MeCN), λ_{max}: 254 nm (ε 15 100 M^{-1} cm^{-1}). ^{1}H NMR, δ: 2.54 (m, 2 H), 2.81 (t, J = 4.0 Hz, 2 H), 6.38 (t, J = 1.2 Hz, 1 H), 7.43 (m, 4 H). ^{13}C NMR, δ: 26.38, 28.72, 120.93, 123.89, 127.34, 128.74, 129.36, 146.20. ^{19}F NMR, δ: −63.01. MS, *m/e* (*I*): 198 (23), 179 (11), 177 (46), 151 (40), 129 (100), 128 (40), 120 (9), 75 (9), 63 (4), 51 (5). Exact Mass, calcd. for $C_{11}H_9F_3$: 198.0656: found: 198.0649.

2,4,4-Trideuterio-1-phenylcyclobutene (**2***c*–d_3) was prepared from cyclobutanone-2,2,4,4-d_4 by a similar procedure to that employed for the parent compound. A mixture of cyclobutanone (1.0 g, 0.014 mol), triglyme (15 mL), deuterium oxide (5.0 mL), and potassium carbonate (5.0 g) was stirred for 24 h at 70°C. After cooling, the resulting solution was extracted with ether (5 × 10 mL). The combined organic extracts were dried with anhydrous sodium sulfate, and then distilled through a short Vigreux fractionating column at atmospheric pressure. Once the ether had distilled off, the receiving flask was cooled to −78°C and attached to two consecutive traps immersed in dry ice – isopropanol, and the temperature of the still was allowed to increase gradually. Deuterated cyclobutanone (0.5 g, 51 % yield) and traces of ethyl ether collected in the receiving flask and the traps. ^{1}H NMR analysis of the distillate indicated that the ketone was ca. 80% tetradeuterated. The material was subjected to a second deuteration cycle as described above, after which the α-proton resonances in the ^{1}H NMR spectrum of the isolated material were undetectable by ^{1}H NMR spectroscopy. A solution of the deuterated ketone (0.29 g, 0.0039 mol) in tetrahydrofuran (10 mL) was cooled at −78°C and treated dropwise with phenyllithium (0.0039 mol). The solution was stirred for 30 min at −78°C, allowed to warm to room temperature, and then quenched by dropwise addition of deuterium oxide (3.0 mL). Work-up as described above afforded a slightly yellow oil (0.505 g), which was purified by silica gel column chromatography and tentatively identified as *1-phenylcyclobutanol-2,2,4,4-*d_4 (mp 43–46°C) on the basis of its mass spectrum: MS, *m/e* (*I*): 152 (0.5), 151 (0.8), 150 (0.2), 122 (48), 105 (100), 93 (26), 78 (81), 77 (68), 51 (33), 30 (5), 29 (4), 28 (3), 27 (1).

1-Phenylcyclobutene-2,4,4-d_3 (**2***c*–d_3) was prepared by refluxing a solution of the alcohol from above (0.4 g) in benzene-d_6 (5.0 mL) containing traces of deuterium oxide and *p*-toluenesulfonic acid monohydrate (recrystallized thrice from D_2O) for 5 h. After cooling to room temperature, the solution was washed with a small amount of 5% aqueous sodium hydroxide and dried over anhydrous magnesium sulfate. The solvent was removed on the rotary evaporator to yield a colourless oil (0.35 g), from which **2***c*–d_3 was isolated by semi-preparative VPC after bulb-to-bulb distillation. ^{1}H NMR analysis indicated the compound to be >95% deuterated at the

C2 and C4 positions of the cyclobutene ring. IR: 3074 (m), 3039 (m), 2035 (s), 2291 (w), 2226 (m), 2154 (w), 1954 (w), 1798 (w), 1606 (w), 1493 (m), 1447 (w), 1291 (w), 1019 (w), 753 (s). ^{1}H NMR (CD_3CN), δ: 2.48 (s, 2H), 2.81 (m, 0.12 H), 6.32 (t, 0.05 H), 7.31 (m, 5H). MS, *m/e* (*I*): 133 (81), 132 (100), 131 (79), 119 (9), 118 (21), 117 (45), 116 (44), 103 (81), 79 (11), 78 (12), 77 (30), 76 (26), 75 (21), 67 (11), 66 (12), 65 (14), 52 (16) 51 (36), 50 (18), 39 (13).

The 1-methoxy-1-arylcyclobutanes (**4***a–f*) were prepared by stirring a mixture of the corresponding 1-arylcyclobutanol (0.0009 mol), barium oxide (0.005 mol), iodomethane (0.002 mol), and dry dimethyl sulfoxide (10 mL) for 24 h at room temperature. After addition of 5% aqueous hydrochloric acid, extraction with ether, drying and evaporation of the ether extracts, and finally alumina column chromatography (20% ether in hexane), the compounds were isolated as colourless oils in 75–85% yield. They were identified on the basis of their NMR, IR, and mass spectral data, which are listed below.

1-Methoxy-1-(4-methoxyphenyl)cyclobutane (**4**a): IR: 2995 (m), 2953 (m), 1652 (m), 1616 (m), 1558 (m), 1517 (m), 1510 (s), 1305 (m), 1252 (s), 1178 (m), 1135 (m), 1047 (w), 972 (w), 833 (m), 777 (w). ^{1}H NMR, δ: 1.80 (cplx m, 1H), 1.99 (cplx m, 1 H), 2.46 (cplx m, 2 H), 2.55 (cplx m, 2 H), 2.85 (s, 3 H), 3.76 (s, 3 H), 6.89 (d, 2 H), 7.32 (d, 2 H). MS, *m/e* (*I*): 192 (4), 191 (4), 177 (2), 164 (42), 163 (100), 149 (8), 133 (42), 121 (12), 119 (42), 105 (8), 91 (25), 77 (17), 63 (9). Exact Mass, calcd. for $C_{12}H_{16}O_2$: 192.1150: found: 192.1127.

1-Methoxy-1-(4-methylphenyl)cyclobutane (**4**b): IR: 3031 (m), 2995 (s), 2950 (s), 2885 (m), 2830 (m), 1621 (w), 1516 (m), 1296 (m), 1249 (m), 1137 (s), 1090 (m), 1056 (m), 815 (m), 786 (w). ^{1}H NMR, δ: 1.68 (cplx m, 1 H), 1.97 (cplx m, 1 H), 2.36 (s, 3 H), 2.36 (m, 4 H), 2.92 (s, 3 H), 7.15 (d, J = 7.9 Hz, 2 H), 7.28 (d, J = 7.9 Hz, 2 H). ^{13}C NMR, δ: 12.99, 21.06, 32.88, 50.34, 81.34, 126.29, 128.92, 136.78, 140.10. MS, *m/e* (*I*): 162 (5), 161 (36), 148 (22), 147 (39), 133 (100), 117 (55), 115 (28), 105 (22), 91 (33), 77 (11), 65 (17), 51 (5). Exact Mass, calcd. for $C_{12}H_{16}O$: 176.1201; found: 176.1190.

1-Methoxy-1-phenylcyclobutane (**4**c): IR: 3071 (m), 3037 (m), 2884 (s), 2952 (s), 2914 (m), 2831 (m), 1449 (m), 1289 (m), 1248 (m), 1136 (s), 1090 (m), 1046 (m), 759 (m). ^{1}H NMR, δ: 1.58 (cplx m, 1 H), 1.87 (cplx m, 1 H), 2.32 (cplx m, 4 H), 2.86 (s, 3 H), 7.30 (m, 5 H). ^{13}C NMR, δ: 13.01, 32.80, 50.47, 126.28, 127.14, 128.24. MS, *m/e* (*I*): 161 (3), 134 (37), 133 (100), 115 (6), 104 (31), 91 (34), 77 (35). MS/CI (NH_3), *m/e* (*I*): 131 (100), 148 (50), 162 (4), 180 (5). MS/CI (CH_4); *m/e* (*I*): = 61 (9), 79 (28), 85 (34), 131 (100), 163 (11). HRMS ($M^+ - 1$), calcd. for $C_{11}H_{13}O$: 161.0966; found: 161.0944.

1-Methoxy-1-(4-trifluoromethylphenyl)cyclobutane (**4**d): IR: 2997 (m), 2951 (m), 2834 (w), 1620 (w), 1408 (w), 1323 (s), 1300 (w), 1173 (s), 1147 (s), 1087 (m), 1072 (m), 1018 (m), 842 (s). ^{1}H NMR, δ: 1.67 (m, 1 H), 1.96 (m, 1 H), 2.36 (d, 2 H), 2.39 (double sextet, 2H), 2.92 (s, 3 H), 7.57 (q, J = 8.4 Hz, 4 H). ^{13}C NMR, δ: 12.90, 32.80, 50.67, 81.26, 125.28, 125.36, 125.42, 126.55, CF_3 not observed. ^{19}F NMR, δ: −62.67. MS, *m/e* (*I*): 202 (27), 210 (61), 182 (11), 172 (27), 161 (28), 151 (25), 145 (42), 133 (100), 103 (22), 75 (8). Exact Mass, calcd. for $C_{12}H_{13}F_3O$: 230.0918; found: 230.0900.

1-Methoxy-1-(4-trifluoromethoxyphenyl)cyclobutane (**4**e): ^{1}H NMR, δ: 1.65 (m, 1 H), 1.98 (m, 1 H), 2.40 (d, 2 H), 2.42 (m, 2 H), 2.93 (s, 3 H), 7.02 (m, 4 H). ^{13}C NMR, δ: 12.86, 32.70, 50.63, 78.60, 120.90, 127.14, 134.90, 144.60. MS, *m/e* (*I*): 245 (3), 230 (6), 218 (48), 217 (100), 188 (45), 175 (15), 161 (15), 133 (36), 119 (18), 91 (9), 77 (6), 69 (15). Exact Mass, calcd. for $C_{13}H_{13}F_3O_2$: 246.0868; found: 246.0901.

1-Methoxy-1-(3-trifluoromethylphenyl)cyclobutane (**4**f): IR: 3080 (w), 2997 (m), 2952 (m), 2833 (w), 1489 (w), 1439 (w), 1335 (s), 1270 (s), 1177 (s), 1145 (s), 1100 (m), 1077 (m), 1042 (w), 901 (w), 802 (w). ^{1}H NMR, δ: 1.65 (cplx m, 1 H), 1.95 (cplx m, 1 H), 2.36 (d, 2 H), 2.39 (m, 2 H), 2.92 (s, 3 H), 7.60 (m, 4 H). ^{13}C NMR, δ: 12.88, 32.71, 50.62, 81.23, 122.92, 124.05, 128.82, 129.62, 144.49. ^{19}F NMR, δ: −62.69. MS, *m/e* (*I*): 215 (8), 202 (58), 201 (98), 172 (40), 159 (25), 151 (40), 145 (33), 133 (100), 103 (22). Exact Mass, calcd. for $C_{12}H_{13}F_3O$: 230.0918; found: 230.0901.

Irradiations were carried out on a 0.5 mL scale in 3 in. × 5 mm quartz tubes, in a Rayonet reactor containing one RPR-254 lamp. For the purposes of product identification, photolyses were taken to ca. 40% conversion, and the products identified by GC–MS, GC–FTIR, and GC coinjection with authentic samples in the cases of phenylacetylene (**5***c*), 4-tolylacetylene (**5***b*), and 4-trifluoromethylphenylacetylene (**5***d*). (57) Identification of the other substituted phenylacetylenes was based on their GC retention times, the prominent parent ion and characteristic fragmentation patterns in their mass spectra (58), and their characteristic IR spectra (obtained by GC–FTIR analyses of the crude photolysis mixtures). Mass and gas phase infrared spectral data for the five substituted phenylacetylenes are given below.

4-Methoxyphenylacetylene (**5**a) *(59)*: IR: 3318 (s), 3083 (w), 3031 (w), 2957 (w), 2925 (w), 2838 (w), 2110 (m), 1650 (w), 1598 (m), 1581 (m), 1508 (s), 1489 (s), 1461 (m), 1443 (m), 1290 (m), 1245 (m), 1180 (m), 1103 (w). MS (58); *m/e* (*I*): 132 (80), 131 (75), 117 (27), 101 (39), 90 (20), 50 (20).

4-Methylphenylacetylene (**5**b) *(59)*: IR: 3317 (s), 3084 (w), 3031 (w), 2962 (m), 2925 (m), 2866 (w), 2111 (m), 1508 (s), 1261 (s), 1215 (m), 1103 (m), 1020 (m), 826 (m), 650 (s), 603 (s), 529 (s). MS, *m/e* (*I*):= 116 (75), 115 (100), 89 (40), 74 (20), 63 (35), 50 (29).

4-Trifluoromethylphenylacetylene (**5**d) *(57)*: IR: 3314 (s), 3083 (m), 3060 (w), 3035 (w), 2928 (w), 2112 (m), 1601 (m), 1575 (w), 1489 (s), 1444 (m), 1401 (w), 1325 (m), 1223 (m), 1172 (m), 1132 (m), 1102 (w), 1071 (m). MS: *m/e* (*I*): 170 (100), 169 (25), 151 (40), 120 (40), 99 (10), 75 (20), 74 (20).

4-Trifluoromethoxyphenylacetylene (**5**e): IR: 3314 (s), 2980 (s), 2828 (s), 2869 (m), 2855 (m), 2112 (w), 1671 (w), 1597 (w), 1574 (w), 1489 (m), 1445 (m), 1380 (w), 1261 (s), 1227 (m), 1100 (s), 1070 (m), 1025 (s). MS, *m/e* (*I*): 186 (100), 167 (30), 120 (17), 117 (15), 99 (20), 85 (15), 75 (25), 74 (31).

3-trifluoromethylphenylacetylene (**5**f) *(57)*: IR: 3314 (s), 3076 (m), 3035 (w), 2923 (w), 2114 (w), 1602 (w), 1579 (s), 1485 (s), 1430 (s), 1348 (s), 1272 (s), 1223 (m), 1174 (s), 1131 (s),

1088 (s), 914 (m). MS: *m/e* (*I*): 170 (100), 169 (30), 151 (40), 120 (42), 99 (10), 75 (20), 74 (30), 69 (10).

Quantum yields were determined by electronic actinometry using a system similar to that described previously (60), and 260 nm excitation. The system was calibrated daily with potassium ferrioxalate. Samples were contained in round (1 cm × 2.54 cm) Suprasil UV cells, which were sealed with rubber septa and deoxygenated with a stream of dry nitrogen prior to photolysis. Quantum yields were calculated from the slopes of plots of product concentration versus accumulated photon counts. Product concentrations were determined by GC relative to an internal standard (*n*-decane) and were corrected for relative FID response factors using working curves.

Relative quantum yield determinations and Stern–Volmer studies were carried out using a Rayonet reactor equipped with a merry-go-round and one 253.7 nm Hg lamp. Relative yields of methyl phenylcyclobutyl ether (**4***c*) from photolysis of **2***c* in methanolic acetonitrile solution were corrected for a small amount of dark reaction for each methanol concentration studied, and for the formation of a product (with identical retention time to **4***c*) in runs carried out in the absence of methanol.

Fluorescence lifetimes were measured at ambient temperature (22–25°C) using a PTI LS-100 single photon counting system and a hydrogen flash lamp. Cuvettes were constructed from 1 cm × 1 cm square Suprasil tubing (Vitro Dynamics Ltd.) and were constricted to 7 mm round tubing at the top of the cell. The cuvettes were sealed using a rubber septum, and the solutions, 0.001–0.005 M in **2**, were deoxygenated with a stream of dry nitrogen for at least 60 min prior to the experiment. Fluorescence decays were recorded using 260 nm excitation and a monitoring wavelength corresponding to the emission maximum of the cyclobutene in the particular solvent being studied. Decays were recorded with 5000–10 000 counts in the maximum channel, and were deconvoluted and analysed using the software provided by the manufacturer. In general, the decays were fit to single or double exponential functions in order to obtain the best possible fit. In cases where the data fit best to a two exponential function, the second component comprised less than ca. 10% of the decay. In each case, the lifetimes reported are the average of at least two independent determinations, the results of which invariably differed by less than 5%. The solutions were checked by GC immediately after determination of the lifetime to verify that no appreciable photodecomposition of the sample occurred during the experiment.

Nanosecond laser flash photolysis experiments employed the pulses (248 nm, ca. 16 ns) from a Lumonics 510 excimer laser filled with F_2/Kr/He mixtures or those (337 nm, ca. 6 ns) from a Lumonics 761M excimer laser filled with N_2/He mixtures, and a microcomputer-controlled detection system (61, 62). Solutions of **2***b–d* were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.3 (6×10^{-5} M), and were made to flow continuously from a calibrated 100 mL capacity reservoir through a 3 × 7 Suprasil flow cell. The solutions were deoxygenated with a stream of dry nitrogen in the reservoir for 45 min prior to and continuously throughout flash photolysis experiments. Quenchers were added directly to the reservoir by microlitre syringe as aliquots of standard solutions. Quenching rate constants were calculated by linear least-squares fits of decay rate versus quencher concentration data using Inplot 4.0 (Graphpad, Inc.). Errors are reported as twice the standard deviations obtained from these analyses.

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