

Laser Flash Photolysis Study of Arylcyclopropylcarbenium Ions: Cation Stabilizing Abilities of Cyclopropyl and Phenyl Groups

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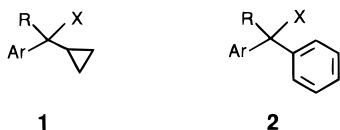
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Abstract: Arylcyclopropylcarbenium ions, $\text{Ar}(\text{c-Pr})\text{CH}^+$, were generated as transient intermediates by laser flash photolysis (LFP) of *trans*-2,3-diphenylaziridinimines of aryl cyclopropyl ketones in 2,2,2-trifluoroethanol (TFE). The carbocations are thought to arise by way of diazo compounds and carbenes. Rate constants for the unimolecular decay in TFE and for the bimolecular reaction with methanol in TFE were obtained for $\text{Ar}(\text{c-Pr})\text{CH}^+$ and for analogous arylphenylcarbenium ions, ArPhCH^+ . Within these series, the cation stabilizing abilities of cyclopropyl and phenyl groups are found to be similar in magnitude. However, cyclopropyl responds more strongly than phenyl to increasing electron demand. Hence cyclopropyl is superior to phenyl in cation stabilizing ability for $\text{Ar} = \text{Ph}$ but inferior to phenyl for $\text{Ar} = 4\text{-MeOC}_6\text{H}_4$.

Introduction

The effects of cyclopropyl and phenyl groups on the kinetic and thermodynamic stability of carbocations have been a matter of some dispute.¹ The solvolysis rates of **1** exceed those of **2**

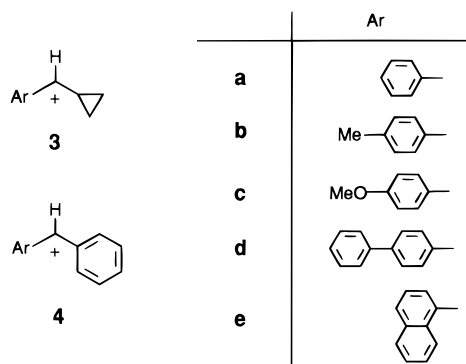


by factors of 3×10^2 ($\text{R} = \text{Me}$) to 1×10^4 ($\text{R} = \text{H}$).² Ion cyclotron resonance data in the gas phase³ and pK_R^+ values in solution⁴ also support the notion that cyclopropyl is superior to phenyl in stabilizing the positive charge. On the other hand, the ^{13}C chemical shifts of the cationic centers for phenyl- and cyclopropyl-substituted carbocations (e.g., Ph_2CH^+ $\delta = 198.7$, $\text{c-PrCH}^+\text{Ph}$ $\delta = 225.7$) indicate better delocalization by phenyl than by cyclopropyl groups.⁵

Solvolysis rates are influenced by ground state effects of the substrates (**1** and **2**). Charge distributions, as reflected by ^{13}C chemical shifts, may not correlate with thermodynamic and/or kinetic stabilities of the carbocations. The discrepancies caused by such effects should be resolved by measuring the absolute rates for electrophilic reactions of the carbocations **3** and **4**, respectively. This approach was pioneered by Dorfman et al. in their pulse radiolysis studies of **1-OH** and **2-OH**.⁶ The primary species formed in pulse radiolysis is the solvent cation radical which reacts with solutes in a dissociative charge transfer

to give eventually carbocations. The reported transient spectra indicate that **3a** and **4a** were in fact generated by this technique. However, solvents (1,2-dichloroethane or dichloromethane) and nucleophiles (trialkylamines) had to be used which led to near-diffusional rates (k ranging from 9×10^8 to $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$). Thus, differences in reactivity tend to be blurred, as was observed for **4a** and benzyl cations.

In view of the limitations inherent to pulse radiolysis, an alternative method, applicable in protic media, was clearly desirable. The present work describes the flash photolytic generation of arylcyclopropylcarbenium ions **3**. The reaction rates of **3** are compared with those of diarylcarbenium ions **4**. The k_4/k_3 rate ratios thus obtained are close to unity, with a tendency to increase as the aryl group Ar becomes more electron donating.



Results and Discussion

A variety of diarylcarbenium ions have been generated by laser flash photolysis (LFP) of diarylcarbinyl esters and ethers, via photoheterolysis of the C–O bond.⁷ We used acetate precursors to generate **4a–e** in 2,2,2-trifluoroethanol (TFE). The spectroscopic and kinetic data for **4a–c** were in excellent agreement with those reported in the literature (Table 1). Unfortunately, analogous precursors failed to produce transient

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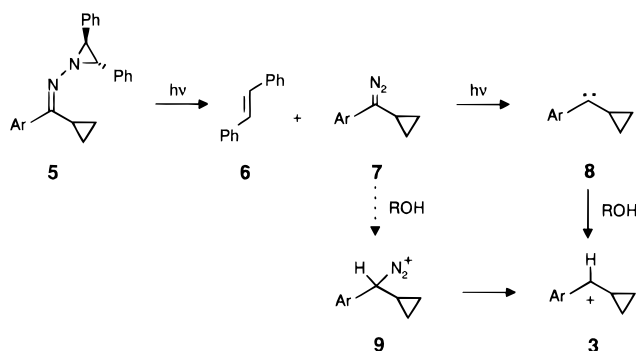
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Table 1. Spectroscopic and Kinetic Data for Arylcyclopropylcarbenium Ions **3** and Arylphenylcarbenium Ions **4** in Oxygen-Saturated TFE^a

Ar	3			4		
	λ_{max} (nm)	k_{TFE} (s ⁻¹)	k_{MeOH} (M ⁻¹ s ⁻¹)	λ_{max} (nm)	k_{TFE} (s ⁻¹)	k_{MeOH} (M ⁻¹ s ⁻¹)
a Ph	345	1.6×10^6	3.2×10^7	435	3.4×10^6 (3.2×10^6) ^b	4.2×10^7
b 4-MeC ₆ H ₄	370	2.2×10^5	5.1×10^6	450	2.8×10^5 (2.7×10^5) ^c	5.8×10^6
c 4-MeOC ₆ H ₄	385	1.4×10^4	9.4×10^4	455	1.5×10^3 (1.2×10^3) ^b	8.1×10^4
d 4-PhC ₆ H ₄	440	2.2×10^5	5.1×10^6	515	2.3×10^5	5.2×10^6
e 1-naphthyl	500	1.9×10^5	4.8×10^6	575	2.2×10^5	4.9×10^6

^a The precision of rate constants is ~5%, the reproducibility ~10%. ^b Kirmse, W.; Kilian, J.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 6399. ^c Reference 6a.

Scheme 1

spectra of the arylcyclopropylcarbenium ions **3**. (A weak signal of **3c**, the most stable species, was obtained by LFP of the appropriate acetate.) In the diarylmethyl series, the quantum yields of carbocations were found to increase linearly with their pK_R^+ values.⁸ As a rule, replacement of phenyl with cyclopropyl enhances the pK_R^+ of carbocations by ca. 2 units.^{4,9} Hence the reluctance of **1**-OAc ($R = H$) to undergo photoheterolysis comes as a surprise. We speculate that excitation of **1**-OAc may lead to rupture of C–C rather than C–O bonds. Cyclopropylmethylbenzene has long been known as a photolabile compound.¹⁰

For an alternative source of carbocations **3**, we resorted to the *trans*-2,3-diphenylaziridinimines **5** (Scheme 1). Analogues of **5** were widely employed as diazo precursors in thermal reactions (Eschenmoser fragmentation)¹¹ but have rarely been photolyzed.¹² Precedent with *N*-alkyl- and *N*-arylaziridines suggests the intermediacy of azomethine ylides.¹³ However, no evidence for a two-step mechanism was found in the case of **5**.

In protic solvents (ROH), carbocations **3** can arise from diazo compounds **7** by two routes: (i) light-induced extrusion of

nitrogen, followed by proton transfer from ROH to the carbenes **8**, and (ii) protonation of **7** to give diazonium ions **9** which lose nitrogen with formation of **3**. The carbene route was recently confirmed for the diaryl series where the lifetime of the diazo compounds ($\sim 10^2$ s) excludes significant protonation by ROH in the microsecond regime of LFP experiments.¹⁴ In the case of **7**, there is also evidence for intervention of the carbenes **8** (see below). However, since the reaction rate of **7** in TFE is not known, the diazonium route to **3** remains a viable alternative.

Preparative photolyses of **5** in MeOH or TFE afforded nearly quantitative yields of *E*-stilbene (**6**), which undergoes light-induced *E* $\rightleftharpoons$ *Z* isomerization, cyclization, reduction, and addition of ROH on prolonged irradiation. Decomposition of the diazo compounds **7** leads to the ethers Ar(c-Pr)CHOR (57–68% in MeOH, 41–57% in TFE), along with small amounts ($\leq 5\%$) of 1-arylcyclobutenes. The latter are known to arise by rearrangement of arylcyclopropylcarbenes **8**.¹⁵ Photolysis of **5c** in cyclohexane afforded 43% of 1-(*p*-methoxyphenyl)-cyclobutene. In protic solvents, reaction of the carbene **8** with ROH predominates over the relatively “slow” ring expansion.¹⁶

LFP of **5** in TFE produced the permanent absorption of **6** at 300 nm as well as transient spectra at longer wavelengths, as exemplified in Figure 1. The transient absorptions are assigned to the carbocations **3** on the basis of the following evidence: (i) The absorption maxima of **3a** (345 nm) and **3b** (370 nm) in TFE are in excellent agreement with data from the literature (343 and 366 nm, respectively, in fluorosulfonic acid at -75°C).¹⁷ (ii) The transients are not affected by the presence of oxygen but are effectively quenched by nucleophiles according to second-order kinetics. Even the most stable species, **3c**, was found to react with azide at a diffusion-controlled rate ($k = 1.0 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ in acetonitrile–water 2:1).

As to the origin of **3**, the following observations are relevant: (i) The decay of **3** (inset a in Figure 1) indicates that the cation is fully formed during the laser pulse (20 ns). There is no evidence for a dark reaction, such as $7 \rightarrow 9 \rightarrow 3$, after the laser pulse. (ii) The yield of **6**, as measured by the optical density (OD) at 300 nm, increases linearly with the laser dose

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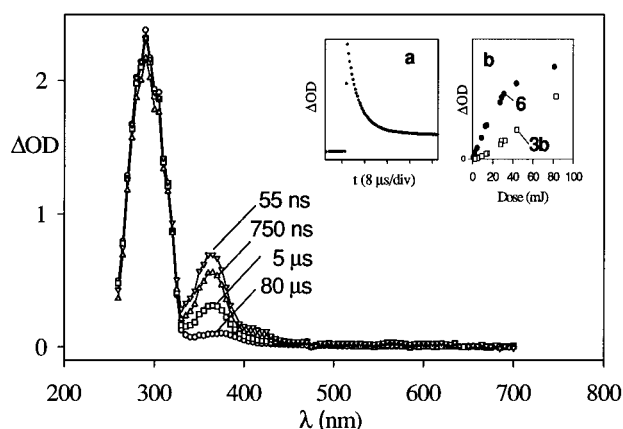


Figure 1. Time-dependent absorption spectra obtained after laser excitation (248 nm, 20 ns, 95 mJ/pulse) of **5b** (0.10 mM) in oxygen-saturated TFE. Inset a: decay of **3b**, recorded at 370 nm. Inset b: yields of **6** and of **3b** (scaled by a factor of 5) as a function of the laser dose (mJ/pulse), recorded 70 ns after LFP of **5b** (0.097 mM) in oxygen-saturated TFE.

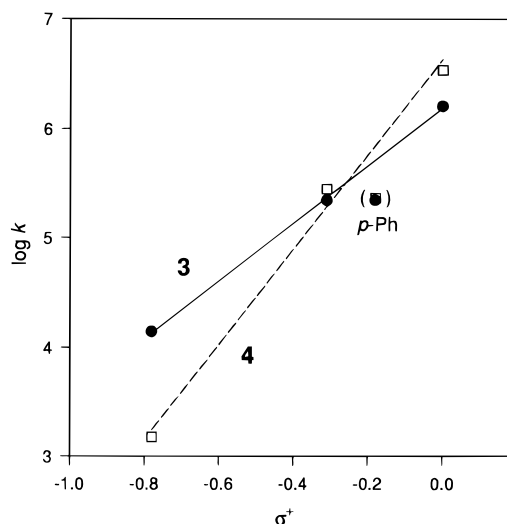


Figure 2. Hammett plots of $\log k_{\text{TFE}}$ versus σ^+ . The correlation lines shown are for **3a–c** (●, —) and **4a–c** (□, ---).

up to ~40 mJ and then levels off, due to depletion of **5** (inset b in Figure 1). Analogous plots for the yield of **3** are upward curved at low laser doses, pointing to the biphotonic sequence $7 \rightarrow 8 \rightarrow 3$.

In order to assess the reactivity of carbocations **3** and **4**, rate constants for the pseudo-unimolecular decay in TFE and for the bimolecular reaction with methanol (≤ 0.2 M) in TFE were estimated (Table 1). For $[\text{MeOH}] \leq 0.2$ M, k_{obs} correlates linearly with $[\text{MeOH}]$ while upward curvature is found at higher concentrations. The rate constant ratios k_4/k_3 are close to unity for most of the cations studied. With increasing rate of solvent capture, k_4/k_3 increases, more strongly for the weak nucleophile TFE than for the good nucleophile MeOH (the reactivity of MeOH toward **3** and **4** exceeds that of TFE by factors of $\geq 10^2$ if the molarity of neat TFE, 13.84 M, is taken into account). These data indicate that cyclopropyl is superior to phenyl in stabilizing “electron-poor” cations (**3a** vs **4a**) while the reverse holds for “electron-rich” cations (**3c** vs **4c**). The different electron-donating tendencies of cyclopropyl and phenyl groups are also reflected by the reaction constants for **3a–c** ($\rho^+ = 2.64$, $r = 0.999$) and **4a–c** ($\rho^+ = 4.34$, $r = 0.996$), obtained by plotting $\log(k_{\text{TFE}})$ vs σ^+ (Figure 2). The data for both **3d** and **4d** deviate from the correlation lines thus defined (a tentative explanation is given below). Inclusion of the data for **3d** and

4d leads to $\rho^+ = 2.48$ ($r = 0.977$) for **3a–d** and $\rho^+ = 4.14$ ($r = 0.983$) for **4a–d**. The ρ^+ values for nucleophilic capture of **3** and **4** differ in sign and ranking order from those reported for solvolyses of **1** ($R = \text{H}$, $X = \text{OPNB}$, $\rho^+ = -3.61$)^{2a} and **2** ($R = \text{H}$, $X = \text{OPNB}$, $\rho^+ = -3.18$)¹⁸ respectively. Since the less reactive carbocations are formed faster, these changes are in accordance with expectation.

Rates constants for nucleophilic capture (k_{nuc}) and solvolysis (k_{solv}) can lead to divergent estimates for the relative stability of carbocations. In terms of eqs 1–3, $\Delta G_{\text{solv}}^\ddagger$ is fully affected

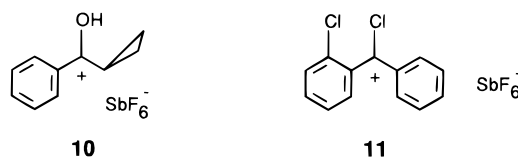


$$\Delta G_{\text{solv}}^\ddagger = G_1^\ddagger - G_{\text{S}} \quad (2)$$

$$\Delta G_{\text{nuc}}^\ddagger = G_2^\ddagger - G_{\text{R}^+} \quad (3)$$

by substrate (S) energies while product (P) energies influence $\Delta G_{\text{nuc}}^\ddagger$ but slightly. Therefore, the relative stability of carbocations is mirrored more accurately by $\Delta \Delta G_{\text{nuc}}^\ddagger$ than by $\Delta \Delta G_{\text{solv}}^\ddagger$.

According to Table 1, $\Delta G_{\text{nuc}}^\ddagger$ is nearly the same for **3a** (9.0 kcal/mol) and **4a** (8.5 kcal/mol) whereas $\Delta G_{\text{solv}}^\ddagger$ for **1** (24.8 kcal/mol)¹⁹ differs substantially from that for **2** (29.1 kcal/mol)²⁰ (these data refer to $R = \text{H}$, $X = \text{ODNB}$, 80% acetone, 25 °C). For an explanation, we focus on the great demand of carbocations for conjugative stabilization which is not shared by the neutral substrates. Optimal geometries, with bisected cyclopropane rings and coplanar phenyl groups, are rarely attained, due to adverse steric interactions. The crystal structure of **10** shows that the plane of the cyclopropane ring bisects the carbocation plane perfectly whereas the plane of the phenyl ring is twisted by $\sim 27^\circ$.²¹ The phenyl twist angle (Φ_{Ph}) of **10** should be regarded as an upper limit for **3a** which lacks the electron-donating HO group of **10**. Analogously, we assume twist angles of $\leq 27^\circ$ for both phenyl groups of **4a**. Some support comes from the crystal structure of **11**, which shows $\Phi_{\text{ClPh}} = 41^\circ$ and $\Phi_{\text{Ph}} = 16^\circ$, despite electron donation from $\alpha\text{-Cl}$.²²



The ionization of covalent substrates involves conformational changes and bond breaking which occur in concert but can be formally dissected. Simplified pictures for **1** and **2** are shown in Scheme 2. Since the relative energies of the carbocations **3a** and **4a** agree closely, conformational changes, $1 \rightarrow 1'$ and $2 \rightarrow 2'$, must account for the difference in $\Delta G_{\text{solv}}^\ddagger$ of **1** and **2** ($R = \text{H}$). Promotion of cyclopropylmethylbenzene (**1**, $R = X = \text{H}$) from its ground state ($\Phi_{\text{C-Pr}} = 29^\circ$, $\Phi_{\text{Ph}} = 91^\circ$) to the geometry of **10** requires 9.5 kcal/mol, as calculated with the MMX force field. The X-ray structure of diphenylmethane ($\Phi_{\text{Ph}} = 64^\circ$ and 71°)²³ is only 0.3 kcal/mol above the MMX

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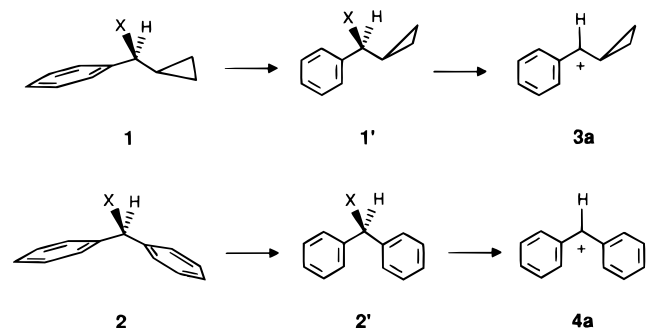
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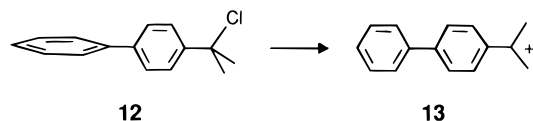
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Scheme 2



minimum. Promotion of **2** ($R = X = H$) to phenyl twist angles of 27° requires 12.3 kcal/mol, ca. 3 kcal/mol more than is needed for **1**. The difference in promotion energies increases, in favor of **1**, for smaller twist angles (e.g., ca. 6 kcal/mol for 25°). In summary, the difference in ΔG_{solv}^+ of **1** and **2** ($R = H$) is attributed to the following trends: (i) The bisected conformation of the cyclopropane ring in **1** is easily attained. (ii) The approach of phenyl groups to coplanarity is energetically less demanding for **1** than for **2**.

As discussed above, k_{solv} and k_{nuc} do not correlate for substrates whose ionization involves variable changes in conformational energy. This principle should also apply to the solvolysis of *p*-substituted cumyl chlorides from which the values of σ_p^+ were derived.²⁴ In order to achieve enhanced conjugation, the biphenyl group of the cation **13** will be less twisted than that of the substrate **12**. As a consequence, the log k_{nuc} data for biphenyl-4-ylcarbenium ions, such as **3d** and **4d**, are poorly accommodated by σ_p^+ (Figure 2).



Conclusion

The flash photolytic generation and study of arylcyclopropylcarbenium ions **3** has been achieved, using the aziridinimines **5** as precursors. In the series of *secondary* cations **3** and **4**, the stabilizing abilities of cyclopropyl and phenyl groups are found to be similar in magnitude. Some variation in k_4/k_3 is observed, however, since cyclopropyl responds more strongly to increasing electron demand than phenyl. Divergent rate ratios for the solvolytic generation and nucleophilic capture of **3** and **4** are explicable in terms of the conformational changes that occur on ionization of the substrates **1** and **2**, respectively.

Experimental Section

General Methods. Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^1H NMR spectra were obtained at 80 (Bruker WP 80) and 400 MHz (Bruker AM-400). Chemical shifts are reported in δ relative to tetramethylsilane. IR spectra were recorded on a Perkin-Elmer 881 instrument. Gas chromatography (GC) was performed by the use of a Siemens Sicromat equipped with glass capillary columns. High-pressure liquid chromatography (HPLC) was carried out with LDC (Milton Roy) chromatographs and refractometric detection. 2,2,2-Trifluoroethanol (TFE) was dried with Na_2SO_4 and then distilled over NaHCO_3 to remove traces of acid impurities.

For the laser flash photolysis (LFP) experiments, we used a Lambda Physik EMG103MSC excimer laser (KrF*) which emitted ≈ 20 ns pulses of 248 nm light. The substrate solutions had optical densities

(OD) at 248 nm of 0.8–1.5/cm. The solutions were flowed through a 2×4 mm Suprasil quartz cell. The light-induced optical transmission changes were digitized in parallel by Tektronix 7612 and 7912 transient recorders interfaced with a DEC LSI11/73+ computer which also process-controlled the apparatus and preanalyzed the data. Final data analysis was performed on a Microvax I connected to the LSI.

Preparation of *trans*-2,3-Diphenylaziridinimines **5.** To a solution of arylmagnesium bromide, obtained from the appropriate aryl bromide (79 mmol) and magnesium turnings (2.0 g, 83 mmol) in ether (100 mL), was added dropwise a solution of cyclopropanecarbonitrile (5.0 g, 74.5 mmol) in ether (40 mL). The mixture was heated at reflux for 5 h. Methanol (18 mL) was then added at room temperature, and stirring was continued for 30 min. With exclusion of moisture, the precipitate of methoxymagnesium bromide was filtered off, and the solution was concentrated in vacuo. The imine thus obtained was used without purification.

To a solution of the arylcyclopropylmethanimine (2.0 mmol) in anhydrous benzene (10 mL) was added 1-amino-*trans*-2,3-diphenylaziridine²⁵ (0.42 g, 2.0 mmol). The mixture was stirred at room temperature (for **5a–c**) or at 35°C (for **5d,e**). When the evolution of ammonia had ceased (2–4 h), the solution was concentrated in vacuo. The residue was flash-chromatographed (neutral Al_2O_3 , ether), and the ether was evaporated in vacuo. HPLC (polyosil 60–5- NO_2 , ether–hexane) afforded two isomers, A and B (presumably *syn/anti*), of each aziridinimine. The isomers are distinguished mainly by the ^1H NMR signals assigned to 2-H and 3-H (δ 3.1–4.1).

5aA: 38%; oil; IR (film) 1603, 1495 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 238$ nm ($\epsilon = 7500$); ^1H NMR (CDCl_3) δ 0.4–1.0 (m, 4 H), 1.5–1.9 (m, 1 H), 3.2 (br. s, 1 H), 3.6 (br. s, 1 H), 7.0–7.4 (m, 15 H). **5aB:** 41%; oil; IR (film) 1602, 1495 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 235$ nm ($\epsilon = 7200$); ^1H NMR (CDCl_3) δ 0.1–0.9 (m, 4 H), 2.2–2.5 (m, 1 H), 3.8 (br. s, 2 H), 6.9–7.5 (m, 15 H).

5bA: 44%; mp 87°C ; IR (KBr) 1601, 1450 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 249$ nm ($\epsilon = 16\,300$), 308 nm ($\epsilon = 1900$); ^1H NMR (CDCl_3) δ 0.4–1.0 (m, 4 H); 1.4–1.8 (m, 1 H), 2.30 (s, 3 H), 3.20 (br. s, 1 H), 3.50 (br. s, 1 H), 6.9–7.4 (m, 14 H). **5bB:** 38%; oil; IR (film) 1603, 1451 cm^{-1} ; $\lambda_{\text{max}} = 249$ nm ($\epsilon = 17\,200$), 308 nm ($\epsilon = 2200$); ^1H NMR (CDCl_3) δ 0.0–0.9 (m, 4 H); 1.1–1.5 (m, 1 H), 2.30 (s, 3 H), 3.80 (br. s, 2 H), 6.9–7.5 (m, 14 H).

5cA: 29%; mp 58°C ; IR (KBr) 1601, 1507, 1448 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 247$ nm ($\epsilon = 16\,200$); ^1H NMR (CDCl_3) δ 0.5–1.2 (m, 4 H), 1.5–1.8 (m, 1 H), 3.35 (br s, 1 H), 3.65 (br s, 1 H), 3.82 (s, 3 H), 6.80 (d, $J = 9$ Hz, 2 H), 7.1–7.4 (m, 10 H), 7.45 (d, $J = 9$ Hz, 2 H). **5cB:** 59%; oil; IR (film) 1607, 1511, 1452 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 245$ nm ($\epsilon = 15\,800$); ^1H NMR (CDCl_3) δ 0.1–1.0 (m, 4 H), 2.1–2.5 (m, 1 H), 3.80 (s, 3 H), 3.90 (br s, 2 H), 6.75 (d, $J = 9$ Hz, 2 H), 7.08 (d, $J = 9$ Hz, 2 H), 7.2–7.5 (m, 10 H).

5dA: 31%, mp 102°C ; IR (KBr) 1596, 1486, 1448 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 256$ nm ($\epsilon = 24\,000$); ^1H NMR (CDCl_3) δ 0.5–1.1 (m, 4 H), 1.6–1.9 (m, 1 H), 3.30 (br s, 1 H), 3.50 (br s, 1 H), 7.1–7.6 (m, 19 H). **5dB:** 37%; mp 51°C ; IR (KBr) 1600, 1486, 1449 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 257$ nm ($\epsilon = 23\,400$); ^1H NMR (CDCl_3) δ 0.0–0.9 (m, 4 H), 2.1–2.5 (m, 1 H), 3.85 (br s, 2 H), 7.1–7.6 (m, 19 H).

5eA: 44%; oil; IR (film) 1602, 1497, 1451 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 223$ nm ($\epsilon = 53\,600$); ^1H NMR (CDCl_3) δ 0.5–1.0 (m, 4 H), 1.7–2.0 (m, 1 H), 3.1 (br s, 2 H), 6.4–7.8 (m, 17 H). **5eB:** 40%, mp 50°C ; IR (KBr) 1587, 1498, 1450 cm^{-1} ; UV (MeCN) $\lambda_{\text{max}} = 221$ nm ($\epsilon = 54\,600$); ^1H NMR (CDCl_3) δ 0.0–1.0 (m, 4 H), 2.6–3.0 (m, 1 H), 3.8 (br d, $J = 5$ Hz, 1 H), 4.1 (br d, $J = 5$ Hz, 1 H), 6.72 (dd, $J = 7$ and 2 Hz, 1 H), 7.2–7.8 (m, 16 H).

Photolyses of Aziridinimines **5.** Solutions of **5** (0.75 mM) in methanol or TFE were irradiated (120 W medium-pressure mercury arc, quartz vessel, 20°C). The product distributions were monitored by GC (6.6 m OV1, $80 \rightarrow 220^\circ\text{C}$). At low conversions, the major products were *trans*-stilbene (**6**) and the ether **14** or **15**, depending on the solvent (Table 2). After 1 h, $\sim 93\%$ of **6** had been converted into *cis*-stilbene (38%), phenanthrene (38%), 2-methoxy-1,2-diphenylethane (**6**),²⁶ *trans,trans,trans*-tetraphenylcyclobutane (7%),²⁷ and *cis,trans*-

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Table 2. Products (%) Obtained on Photolysis of Aziridinimines **5**^a

	 14 R = CH ₃ 15 R = CH ₂ CF ₃	 16	 17	 6
5a , MeOH	65	4	4	98
5a , TFE	53	5	6	97
5b , MeOH	62	4	7	99
5b , TFE	57	5	9	97
5c , MeOH	57	8	5	96
5c , TFE	36	1	5	96
5d , MeOH	68	1	3	95
5d , TFE	45	3	3	93
5e , MeOH	63	1	2	95
5e , TFE	41	1	2	93

^a Extrapolated to $t = 0$.

cis-tetraphenylcyclobutane (4%).²⁸ ¹H NMR (CDCl₃) of **14a**: δ 0.1–1.4 (m, 5 H), 3.25 (s, 3 H), 3.55 (d, $J = 8$ Hz, 1 H), 7.35 (br s, 5 H). ¹H NMR (CDCl₃) of **14b**: δ 0.2–0.8 (m, 4 H), 1.0–1.4 (m, 1 H), 2.34 (s, 3 H), 3.23 (s, 3 H), 3.52 (d, $J = 8$ Hz, 1 H), 7.1–7.4 (m, 4 H). ¹H NMR (CDCl₃) of **14c**: δ 0.1–0.8 (m, 4 H), 1.0–1.3 (m, 1 H), 3.22

(s, 3 H), 3.51 (d, $J = 7$ Hz, 1 H), 3.82 (s, 3 H), 6.85 (d, $J = 9$ Hz, 2 H), 7.22 (d, $J = 9$ Hz, 2 H). ¹H NMR (CDCl₃) of **14d**: δ 0.2–0.8 (m, 4 H), 1.1–1.5 (m, 1 H), 3.31 (s, 3 H), 3.60 (d, $J = 7$ Hz, 1 H), 7.3–7.7 (m, 9 H). ¹H NMR (CDCl₃) of **14e**: δ 0.2–0.8 (m, 4 H), 1.3–1.7 (m, 1 H), 3.29 (s, 3 H), 4.32 (d, $J = 8$ Hz, 1 H), 7.4–8.3 (m, 7 H). ¹H NMR (CDCl₃) of **15b**: δ 0.2–0.7 (m, 4 H), 1.1–1.3 (m, 1 H), 2.35 (s, 3 H), 3.61 (dq, $J = 12.2$ and 8.6 Hz, 1 H), 3.72 (dq, $J = 12.2$ and 8.6 Hz, 1 H), 3.80 (d, $J = 7.8$ Hz, 1 H), 7.16 (d, $J = 8.2$ Hz, 2 H), 7.20 (d, $J = 8.2$ Hz, 2 H). ¹H NMR (CDCl₃) of **15c**: δ 0.2–0.7 (m, 4 H), 0.85 (m, 1 H), 3.61 (dq, $J = 12.5$ and 8.5 Hz, 1 H), 3.69 (dq, $J = 12.5$ and 8.5 Hz, 1 H), 3.77 (d, $J = 8.1$ Hz, 1 H), 3.80 (s, 3 H), 6.89 (d, $J = 8.7$ Hz, 2 H), 7.24 (d, $J = 8.7$ Hz, 2 H). ¹H NMR (CDCl₃) of **15d**: δ 0.3–0.8 (m, 4 H), 1.2–1.3 (m, 1 H), 3.71 (dq, $J = 12.2$ and 8.8 Hz, 1 H), 3.79 (dq, $J = 12.2$ and 8.8 Hz, 1 H), 3.89 (d, $J = 8.0$ Hz, 1 H), 7.3–7.5 (m, 4 H), 7.6 (m, 5 H). ¹H NMR (CDCl₃) of **15e**: δ 0.2–0.8 (m, 4 H), 1.4–1.8 (m, 1 H), 3.7 (q, $J = 9$ Hz, 2 H), 4.58 (d, $J = 8$ Hz, 1 H), 7.4–8.4 (m, 7 H).

Minor amounts of the ketones **16a**, **16b**,²⁹ **16c**,³⁰ **16d** [mp 103 °C; IR (KBr) 1660 cm⁻¹; ¹H NMR (CDCl₃) δ 0.9–1.4 (m, 4 H), 2.5–2.9 (m, 1 H), 7.3–7.8 (m, 7 H), 8.10 (d, $J = 8$ Hz)], and **16e**³¹ were also detected (Table 2). 1-Phenylcyclobutene (**17a**) was identified by comparison with an authentic sample.³² Photolysis of **5c** in cyclohexane afforded 43% of 1-(4-methoxyphenyl)cyclobutene (**17c**): ¹H NMR (CDCl₃) δ 2.50 (m, 2 H), 2.78 (m, 2 H), 3.82 (s, 3 H), 6.13 (t, $J = 2$ Hz, 1 H), 6.85 (d, $J = 8$ Hz, 2 H), 7.30 (d, $J = 8$ Hz, 2 H). The remaining cyclobutenes were tentatively assigned on the basis of their retention times.

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