Methoxy-Substituted Stilbenes, Styrenes, and 1-Arylpropenes: Photophysical Properties and Photoadditions of Alcohols

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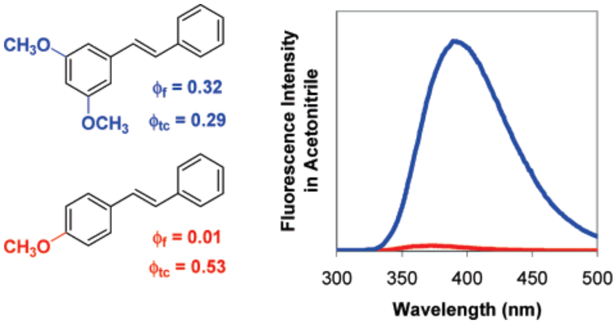

The photochemistry of *trans*-stilbene and four methoxy-substituted stilbene derivatives has been investigated in a variety of solvents. The fluorescence of all five trans isomers was quenched by 2,2,2-trifluoroethanol (TFE). Upon irradiation of the five substrates in TFE, the products derived from photoaddition of the solvent were detected. Nuclear magnetic resonance spectroscopy of the products formed by irradiation in TFE-OD indicated that the proton and nucleophile are attached to two adjacent atoms of the original alkene double bond. Irradiation of the corresponding methoxy-substituted styrenes and *trans*-1-arylpropenes in TFE produced the analogous solvent adducts. The photoaddition of TFE proceeded with the general order of reactivity: styrenes > *trans*-1-arylpropenes > *trans*-stilbenes. Transient carbocation intermediates were observed following laser flash photolysis of the stilbenes in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). The results are consistent with a mechanism that involves photoprotonation of the substrates by TFE or HFIP, followed by nucleophilic trapping of short-lived carbocation intermediates. Compared to the other stilbene derivatives, *trans*-3,5-dimethoxystilbene displayed a large quantum yield of fluorescence and a low quantum yield of trans−cis isomerization in polar organic solvents. The unique photophysical properties of *trans*-3,5-dimethoxystilbene are attributed to formation of a highly polarized charge-transfer excited state (μ_e = 13.2 D).

Introduction

The photochemistry of *trans*-stilbene (*E*-1,2-diphenylethene, *trans*-**1a**) has been extensively investigated by many research groups and has been fundamental in the understanding of the excited-state behavior of arylalkenes.[1] Following excitation to S$_1$, the main deactivation pathway for this substrate is twisting about the central C═C bond. This activated bond torsion process results in formation of a short-lived species which possesses a perpendicular geometry. Subsequent internal conversion to the ground-state surface yields either the original trans isomer (no net reaction) or the isomer *cis*-**1a** (net trans−cis isomerization) in approximately equal amounts. As a result of the highly efficient trans−cis photoisomerization of *trans*-**1a** in room-temperature alkane solvents (ϕ_{tc} = 0.40),[2] the substrate displays only weak fluorescence (ϕ_f = 0.04).[3] Many investigations have focused on hindering the twisting motion by immobilizing the substrate in high-viscosity solvents[4] or in low-temperature glass

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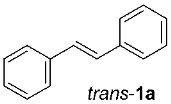
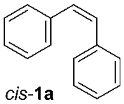
matrixes[5]—these changes lead to smaller quantum yields of isomerization and larger quantum yields of fluorescence. Analogues of *trans*-**1a** in which excited-state bond torsion is completely inhibited by bridging covalent bonds are highly fluorescent.[6]


trans-**1a**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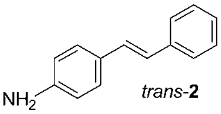
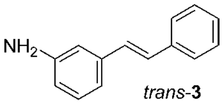
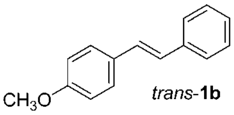


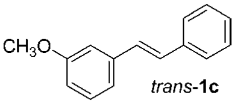
trans-**2**



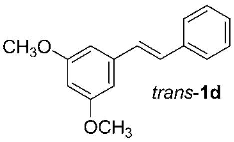
trans-**3**



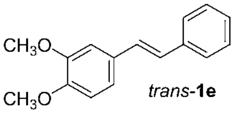
trans-**1b**



trans-**1c**



trans-**1d**

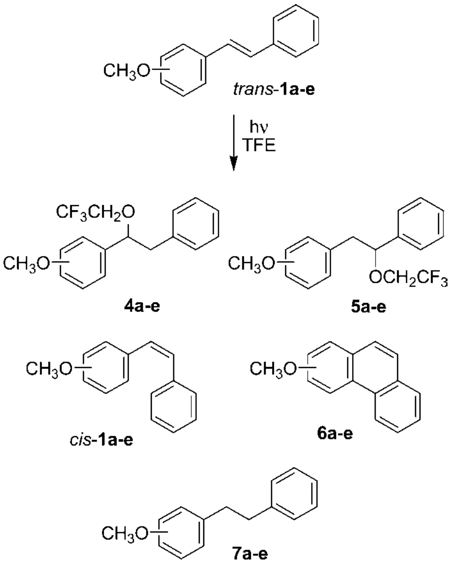


trans-**1e**

Another mechanism for reducing excited-state bond torsion has been established by the detailed investigations of aminostilbene photochemistry by Lewis and co-workers.[7] The "meta-amino effect" is best demonstrated by the very different photophysical properties of *trans*-4-aminostilbene (*trans*-**2**: $\phi_{tc} = 0.52$, $\phi_f = 0.03$) and *trans*-3-aminostilbene (*trans*-**3**: $\phi_{tc} = 0.23$, $\phi_f = 0.40$) in hexane solution.[7b] The reduced quantum yield of isomerization of *trans*-**3** compared to either *trans*-**1a** or *trans*-**2** was taken as evidence that electron-donating meta substituents provide *electronic* inhibition of the C=C twisting motion. This hypothesis was further substantiated by the experimentally determined activation energies for the excited-state bond torsion process. Whereas the energy barrier for twisting of the *trans*-**2** excited state is identical to that of unsubstituted *trans*-**1a** ($E_{act} = 3.5$ kcal/mol), the barrier for the *m*-amino derivative *trans*-**3** is much higher ($E_{act} = 7.0$ kcal/mol).[7b] Even more recent work by Lewis and co-workers has demonstrated that an analogous meta effect exists for methoxy- and hydroxystilbenes.[8]

Our own interest in stilbene photochemistry was initiated by a study of the photoaddition of alcohols to *trans*-**1a** and the methoxy-substituted stilbene derivatives *trans*-**1b**−**d**.[9] The products resulting from the irradiation of *trans*-**1a**−**e** in 2,2,2-trifluoroethanol are displayed in Scheme 1. Although solvent adducts were also detected following irradiation of the substrates in methanol, the photoaddition reaction proceeded much more rapidly in TFE.[10] Our results indicated that the solvent addition reaction occurred more readily for substrates possessing *m*-methoxy substituents. Furthermore, the more reactive substrates (*trans*-**1c** and *trans*-**1d**) also displayed very high quantum yields of fluorescence and exceptionally long singlet lifetimes in acetonitrile solution. We rationalized this connection between photophysical properties and photochemical reactivity as being due to differences in the heights of the barriers for excited-state bond torsion, i.e., a *m*-methoxy effect. According to this explanation, those substrates with longer singlet lifetimes are more reactive toward TFE because the excited stilbene effectively has more time to enter into a bimolecular reaction. A corollary to this theory is that the very short lifetimes of the corresponding cis isomers should preclude their ability to undergo photoaddition chemistry.[11]

SCHEME 1. Products Detected Following Irradiation of *trans*-1a−e in TFE



Although our initial studies were successful in describing many aspects of the photochemical reactivity of methoxystilbenes, some important issues still deserved closer investigation. In the first place, a better understanding of this apparent *m*-methoxy effect seemed desirable. We now report detailed photophysical characterization (absorption maxima, extinction coefficients, fluorescence maxima, singlet lifetimes, fluorescence quantum yields, and trans−cis isomerization quantum yields) for *trans*-**1a**−**e** in six solvents of varying polarity. In addition, these same experiments have been performed for the analogous methoxy-substituted styrenes **8b**−**e** and *trans*-1-arylpropenes *trans*-**9b**−**e**. Taken together, these results provide a much better understanding of the factors that influence the excited-state properties of methoxy-substituted arylalkenes.

The second focus of the current research was the mechanism of the TFE photoaddition reactions. The acid-catalyzed photoaddition of water to a variety of substituted styrene derivatives

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(10) Earlier results from our laboratory (Roberts, J. C.; Pincock, J. A. *Can. J. Chem.* **2003**, *81*, 709−722) have shown that solvent adducts **4** and **5** cannot interconvert during the steady-state irradiation experiments.

(11) Although the photophysical measurements indicate that the trans isomers are the reactive substrates, rapid trans-cis isomerization does occur during the steady-state irradiation experiments; see ref 9 for the yield-versus-time plots for the irradiations of *trans*-**1a**−**e** and *cis*-**1a**−**e** in TFE.

TABLE 1. Summary of Photophysical Data for Stilbene Derivatives *trans*-1a−e in Acetonitrile

substrate	λ_{max} (abs) (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (fluor) (nm)	$\lambda_{0,0}$ (nm)	τ_s (ns)	φ_f[a]	φ_{tc}[b]
trans-**1a**	295, 307	28500, 27600	350	328	0.07[c]	0.023[d]	0.45[e]
trans -**1b**	302, 317	28700, 27700	374	344	0.04[f]	0.007[g]	0.53
trans -**1c**	295	25800	359	336	0.93[h]	0.16[i]	0.39
trans -**1d**	299, 306	30100, 29800	390	341	16.9	0.32	0.28
trans -**1e**	301, 321	20600, 24700	385	353	<0.5[j]	0.035	0.59

[a] 295 nm excitation, relative to $\phi_f = 0.0433$ for *trans*-**1a** in hexanes, ref 3. [b] Determined by steady-state irradiation at 300 nm relative to $\phi_{tc} = 0.40$ for *trans*-**1a** in cyclohexane, ref 2. [c] From ref 15 (in hexane). [d] Literature value $\phi_f = 0.016$, ref 16. [e] Literature value $\phi_{tc} = 0.45$, ref 16. [f] From ref 8b (in THF). [g] Literature values $\phi_f = 0.031$ (cyclohexane) and 0.040 (THF), ref 8b. [h] Literature value $\tau_s = 0.78$ ns (THF), ref 8b. [i] Literature values $\phi_f = 0.23$ (cyclohexane) and 0.26 (THF), ref 8b. [j] Below the time resolution of the instrument.

has been extensively investigated by Yates and co-workers.[12] For methoxy-substituted styrenes, the established mechanism involves photoprotonation of a zwitterionic excited state, followed by nucleophilic trapping of a carbocation intermediate by the solvent. These reactions proceed more rapidly for 3-methoxystyrene than for 4-methoxystyrene.[13] In work that is particularly relevant to our own studies, McClelland and co-workers employed styrene photoprotonation as a method for the generation and subsequent observation of arylmethyl carbocations in TFE and in 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP).[14] Although the photoaddition of TFE to methoxystilbenes can also be explained by a photoprotonation mechanism,[9] Laarhoven and co-workers have reported that the photoaddition of methanol to stilbene does not proceed via carbocation intermediates.[15] In light of this disagreement, we have performed a variety of mechanistic experiments, including laser flash photolysis studies, designed to probe the nature of any reactive intermediates involved in the photoaddition reactions.

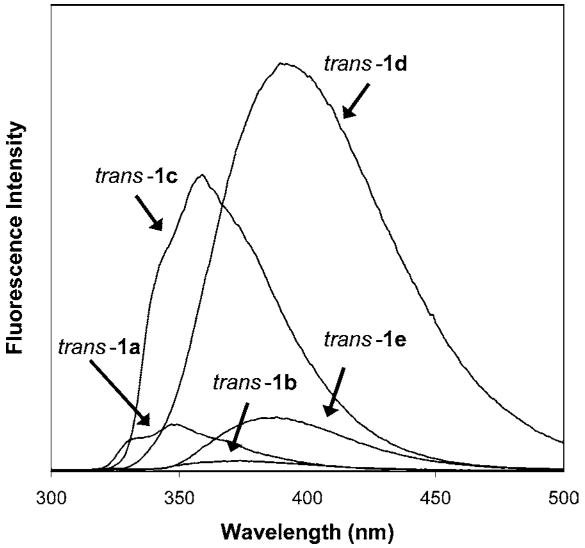

FIGURE 1. Fluorescence spectra of *trans*-**1a**−**e** in acetonitrile solution.

Results

Photophysical Properties: Stilbenes. A compilation of the photophysical properties of *trans*-**1a**−**e** in acetonitrile solution is provided in Table 1. Many of these values were reported in our earlier communication,[9] but have been included now for ease of reference. The absorption spectra (Supporting Information) are all quite similar and are typical of substituted stilbene derivatives: absorption maxima (λ_{max} (abs)) in the range of 295−320 nm and extinction coefficients (ϵ_{max}) on the order of 25000−30000 M^{-1} cm^{-1}. Closer examination of the λ_{max} (abs) values in Table 2 indicates that the para-methoxy substrates *trans*-**1b** and *trans*-**1e** absorb at slightly longer wavelengths than *trans*-**1c** and *trans*-**1d**, which possess only meta substituents.

The fluorescence spectra of *trans*-**1a**−**e** in acetonitrile solution are shown in Figure 1. In contrast to the absorption spectra, the fluorescence behavior of the substrates is not uniform—altering the position of the methoxy substituents induces significant changes in both the wavelength and intensity of fluorescence from the stilbene chromophore. A comparison of the monosubstituted compounds shows that the para isomer (*trans*-**1b**, λ_{max} (fluor) = 374 nm) fluoresces at a longer wavelength than the meta isomer (*trans*-**1c**, λ_{max} (fluor) = 359 nm). Surprisingly, the two disubstituted compounds fluoresce at very nearly the same wavelength (*trans*-**1d**, λ_{max} (fluor) = 390 nm; *trans*-**1e**, λ_{max} (fluor) = 385 nm). Fluorescence quantum yields were determined by comparing the intensity of fluorescence for a given substrate to that of *trans*-**1a** in hexanes, which was chosen as the reference system for these studies.[3] The values in Table 1 (and the spectra in Figure 1) clearly indicate that substrates possessing *m*-methoxy substituents are highly fluorescent in comparison to the parent *trans*-**1a**. The very strong fluorescence of the di-*m*-methoxy derivative *trans*-**1d** is particularly striking (ϕ_f = 0.32). In contrast, the *p*-methoxy substrate *trans*-**1b** displays only weak fluorescence. That the fluorescence of *trans*-**1e** (3,4-dimethoxy, $\phi_f = 0.04$) is intermediate between that of *trans*-**1b** (4-methoxy ($\phi_f = 0.007$) and *trans*-**1c** (3-methoxy, $\phi_f = 0.16$) appears to indicate a conflict between the effects of *p*- and *m*-methoxy substituents.

Quantum yields of trans−cis isomerization were obtained by performing steady-state irradiations of the trans isomers in acetonitrile solution. At low conversions (generally <10%), the increase in the yields of the cis isomers were linear in time as determined by GC−FID analysis; the yield versus time plots for these irradiations are shown in Figure 2. The slopes of these plots were assumed to be proportional to the quantum yield of trans−cis isomerization for each substrate. Again, the unsubstituted compound *trans*-**1a** was taken as the reference (ϕ_{tc} = 0.40 in cyclohexane at room temperature using 313 nm excitation).[2] The reliability of this method is indicated by the fact that our value for *trans*-**1a** in acetonitrile ($\phi_{tc} = 0.45$) is an exact match with the measurement reported by Muzzucato.[16] The ϕ_{tc} values in Table 2 are clearly dependent on the position of the methoxy substituents. In comparison to the unsubstituted compound, the *p*-methoxy derivative *trans*-**1b** displays a larger

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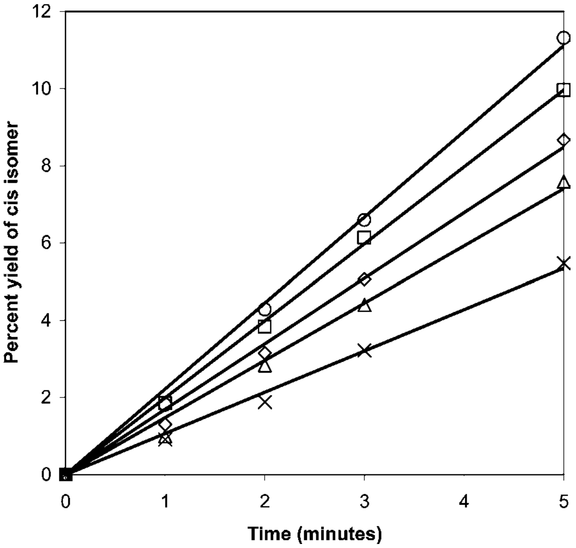

FIGURE 2. Yield of cis isomer formation as a function of time during the irradiation (300 nm) of *trans*-**1a**−**e** in acetonitrile solution: *trans*-**1a** (diamonds), *trans*-**1b** (squares), *trans*-**1c** (triangles), *trans*-**1d** (crosses), *trans*-**1e** (circles).

quantum yield of trans−cis isomerization ($\phi_{tc} = 0.53$). The presence of *m*-methoxy substituents has the opposite effect: both *trans*-**1c** ($\phi_{tc} = 0.39$) and *trans*-**1d** ($\phi_{tc} = 0.28$) isomerize less readily than *trans*-**1a**. Given these trends, the very high quantum yield of isomerization for *trans*-**1e** (3,4-dimethoxy, $\phi_{tc} = 0.59$) is somewhat surprising.

Importantly, the values in Table 1 support the established[1] relationship between ϕ_f and ϕ_{tc}: those substrates with higher quantum yields of isomerization are more weakly fluorescent than those which display smaller values of ϕ_{tc}. In this regard, the differences between the values for the 4-methoxy derivative *trans*-**1b** ($\phi_f = 0.007$, $\phi_{tc} = 0.52$) and the 3-methoxy derivative *trans*-**1c** ($\phi_f = 0.16$, $\phi_{tc} = 0.39$) are particularly striking. The singlet lifetimes of the five substrates, determined by single photon counting techniques, also corroborate the quantum yield measurements. The two substrates with the smallest quantum yields of isomerization display the longest singlet lifetimes (*trans*-**1c**, $\tau_s = 0.9$ ns; *trans*-**1d**, $\tau_s = 17$ ns). The singlet lifetimes of *trans*-**1a**, *trans*-**1b**, and *trans*-**1e** could not be determined using our single photon counting apparatus (time resolution limit 0.5 ns), but the very short lifetimes of these three substrates are consistent with their high quantum yields of isomerization ($\phi_{tc} \geq 0.45$) and low quantum yields of fluorescence ($\phi_f \leq 0.04$). The singlet lifetimes of *trans*-**1a** (0.07 ns in hexane)[17] and *trans*-**1b** (0.05 ns in THF)[8b] have been reported in the literature, and these values are included in Table 1 as points of reference.

To investigate the effect of solvent polarity on the excited states of *trans*-**1a**−**e**, the photophysical properties of these substrates were determined in a series of six solvents of varying polarity (cyclohexane, di-*n*-butyl ether, diethyl ether, ethyl acetate, 2-propanol, and acetonitrile). The absorption maxima and extinction coefficients of *trans*-**1a**−**e** were essentially unchanged through the series of six solvents; the values in acetonitrile (Table 1) are representative. In contrast, the fluorescence maxima (λ_{max} (fluor)) of several substrates displayed a significant solvent dependence; the values for *trans*-**1a**−**e** are displayed in Table 2. Note that the amount of variation in the fluorescence wavelength with solvent polarity is not the same for all five stilbenes; the fluorescence maximum of *trans*-**1a** is essentially the same in all six solvents, while the fluorescence maximum for *trans*-**1d** undergoes a bathochromic shift of 26 nm in acetonitrile compared to cyclohexane.

TABLE 2. Fluorescence Maxima (λ_{max} (fluor)) for *trans*-1a−e in a Series of Six Solvents

solvent	*trans*-**1a**	*trans*-**1b**	*trans*-**1c**	*trans*-**1d**	*trans*-**1e**
cyclohexane	349	364	358	364	372
dibutyl ether	349	367	358	372	375
diethyl ether	349	366	357	374	373
ethyl acetate	349	366	358	382	382
2-propanol	348	365	357	382	374
acetonitrile	350	374	359	390	385

TABLE 3. Ground- and Excited-State Dipole Moments for *trans*-1a−e

compd	$\mu_g{}^a$ (D)	$\mu_e{}^b$ (D)
trans -**1b**	1.6	6.8
trans -**1c**	1.3	3.2
trans -**1d**	1.3	13.2
trans -**1e**	0.6	8.7

[a] Calculated using the Gaussian 98 software package (B3LYP/6-31G(d), optimized geometries). [b] Determined from solvatochromic analysis as described in the Supporting Information.

The solvatochromic behavior displayed by some substrates in Table 2 has been observed previously for many other compounds, including substituted stilbene derivatives.[7,8] In those cases, the results have been successfully analyzed by using the Lippert−Mataga treatment.[18] This technique provides values for the dipole moments of the emissive excited states (μ_e), which can possess substantial charge-transfer character. We suspected that the involvement of charge-transfer excited states might play an important role in the photochemistry of *trans*-**1a**−**e**, so the Lippert−Mataga treatment of these substrates was pursued. Table 3 provides values of μ_g (calculated) and μ_e (experimental) for *trans*-**1b**−**e**; complete details of this analysis are provided in the Supporting Information. Our values for the excited-state dipole moments of *trans*-**1b** and *trans*-**1c** are reasonably close to the values previously reported by Crompton and Lewis (μ_e = 5.4 and 3.6 D, respectively).[8b] The results in Table 3 indicate that the emissive excited states of the methoxy-substituted *trans*-stilbenes have larger dipole moments than do the corresponding ground states. The very large change in dipole moment that accompanies excitation of the *trans*-**1d** is the most obvious example of this effect ($\mu_g = 1.3$ D, $\mu_e = 13.2$ D).[19]

In addition to their solvatochromic fluorescence maxima, *trans*-**1a**−**e** display a variety of other solvent-dependent photophysical properties; the fluorescence quantum yields of these substrates in the six solvents are given in Table 4. The quantum yields of isomerization were only determined in cyclohexane and acetonitrile, and these values are provided in Table 5. Notably, our experimentally determined isomerization quantum

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[19] The substantial increase in the dipole moment of the *trans*-**1d** excited state has been reported previously: Hara, M.; Tojo, S.; Majima, T. *J. Photochem. Photobiol. A: Chem.* **2004**, *162*, 121−128. However, we note that these authors reported values for other photophysical properties of *trans*-**1d** in acetonitrile ($\phi_f = 0.023$, $\tau_s = 4$ ns) that are not consistent with our measurements. At this time, we have no explanation for these differences.

TABLE 4. Fluorescence Quantum Yields (ϕ_f) for *trans*-1a−e in a Series of Six Solvents

solvent	*trans* -**1a**	*trans* -**1b**	*trans* -**1c**	*trans* -**1d**	*trans* -**1e**
cyclohexane	0.038	0.022[a]	0.18[b]	0.18	0.060
dibutyl ether	0.042	0.020	0.20	0.26	0.050
diethyl ether	0.035	0.015	0.18	0.27	0.051
ethyl acetate	0.032	0.013	0.18	0.29	0.046
2-propanol	0.030	0.011	0.15	0.27	0.041
acetonitrile	0.023	0.007	0.16	0.32	0.035

[a] Literature value $\phi_f = 0.031$, ref 8b. [b] Literature value $\phi_f = 0.23$, ref 8b.

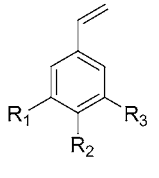
TABLE 5. Isomerization Quantum Yields (ϕ_{tc}) for *trans*-1a−e in Cyclohexane and Acetonitrile

solvent	*trans* -**1a**	*trans* -**1b**	*trans* -**1c**	*trans* -**1d**	*trans* -**1e**
cyclohexane	0.40[a]	0.39[b]	0.32[c]	0.29	0.41
acetonitrile	0.45[d]	0.53	0.39	0.28	0.59

[a] Reference value from ref 2. [b] Literature value $\phi_{tc} = 0.40$, ref 2. [c] Literature value $\phi_{tc} = 0.31$, ref 2. [d] Literature value $\phi_{tc} = 0.45$, ref 16.

yields for *trans*-**1b** and *trans*-**1c** in cyclohexane ($\phi_{tc} = 0.39$ and 0.32, respectively) are excellent matches with the literature values reported by Güsten and Klasinc ($\phi_{tc} = 0.40$ and 0.31, respectively).[2] The results in Tables 4 and 5 indicate that the excited states of *trans*-**1b**, *trans*-**1c**, and *trans*-**1e** all undergo more efficient trans-cis isomerization in more polar solvents (i.e., ϕ_{tc} (cyclohexane) < ϕ_{tc} (acetonitrile)) while also becoming less fluorescent (i.e., ϕ_f (cyclohexane) > ϕ_f (acetonitrile)). The important exception to this trend is *trans*-3,5-dimethoxystilbene, *trans*-**1d**: the quantum yield of isomerization for this substrate is essentially the same in either solvent ($\phi_{tc} = 0.29$), and the fluorescence quantum yield of *trans*-**1d** is *increased* substantially in more polar solvents. Note that trans-**1c** and *trans*-**1d** display identical fluorescence quantum yields in cyclohexane ($\phi_f = 0.18$). However, whereas the fluorescence of *trans*-**1c** falls to $\phi_f = 0.16$ in acetonitrile, the fluorescence of *trans*-**1d** increases to $\phi_f = 0.32$. The solvent dependence of the singlet lifetimes of these substrates is also intriguing. The singlet lifetime of *trans*-**1c** is virtually solvent-independent ($\tau_s = 0.7$ ns in cyclohexane, 0.9 ns in acetonitrile), while the singlet lifetime of *trans*-**1d** is much longer in the more polar solvent ($\tau_s = 3.7$ ns in cyclohexane, 16.9 ns in acetonitrile).[20]

Photophysical Properties: Arylalkenes. The results described in the previous section clearly demonstrate that there are significant differences between the photophysical properties of *trans*-**1a**−**e**. To determine whether these differences are general for all methoxy-substituted arylalkene derivatives, the corresponding styrenes (**8a**−**e**) and *trans*-1-arylpropenes (*trans*-**9a**−**e**) have also been investigated.[21] Based on the fact that these two classes of substrates possess the same chromophore, they were expected to have very similar photophysical properties. The utility of the arylpropenes lies in the potential to determine isomerization quantum yields; photochemical isomerization of the styrenes represents a degenerate rearrangement (i.e., reformation of starting material). The experimentally determined photophysical properties of the styrenes are provided in Table 6, and the data for the arylpropenes are given in Table 7.



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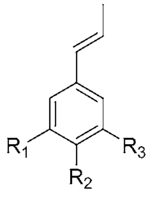

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a: $R_1 = R_2 = R_3 = H$

b: $R_1 = R_3 = H, R_2 = OCH_3$

c: $R_1 = OCH_3, R_2 = R_3 = H$

d: $R_1 = R_3 = OCH_3, R_2 = H$

e: $R_1 = R_2 = OCH_3, R_3 = H$

The extinction coefficients for the $S_0 \rightarrow S_1$ transitions of the eight arylalkenes are about an order of magnitude lower in magnitude than those of the methoxy-substituted stilbene derivatives (absorption and fluorescence spectra are provided as Supporting Information). This observation is consistent with the extended π-conjugation that is present in the stilbenes but not in the arylalkenes. Note that the data in Tables 6 and 7 were obtained using 295 nm excitation, so as to facilitate comparison with the stilbene results (vide supra, Table 1). Neither of the two unsubstituted compounds (**8a** and *trans*-**9a**) absorb significantly at 295 nm, and so these substrates have not been included in Tables 6 and 7.[22] For those cases where literature values[23−25] are available for comparison with our results, the agreement between the two values is very good.

The results in Tables 6 and 7 corroborate the prediction that the styrenes and *trans*-1-arylpropenes should display very similar photophysical properties. For example, the fluorescence maxima of identically substituted styrenes and *trans*-1-arylalkenes are quite similar (i.e., λ_{max} (fluor) **8x** $\approx$ λ_{max} (fluor) *trans*-**9x**). The same statement can be made for many of the other measurements. Perhaps not surprisingly, the properties of the corresponding stilbenes (*trans*-**1b**−**e**, Table 2) are quite different from those of either the styrenes or the *trans*-1-arylpropenes. In general, the stilbene derivatives display longer wavelength emission maxima, shorter singlet lifetimes, and smaller quantum yields of fluorescence when compared to the styrenes and *trans*-1-arylpropenes. The quantum yields for trans-cis isomerization are also much greater for the stilbenes than for the *trans*-1-arylpropenes.

The fluorescence maxima of the eight substrates (**8b**−**e** and *trans*-**9b**−**e**) appear at shorter wavelengths when compared to the corresponding methoxystilbenes; this observation is consistent with the shorter-wavelength absorption maxima of the former compounds. For any given arylalkene, the position of λ_{max} (fluor) is also quite insensitive to the polarity of the medium; no attempts were made to determine the solvatochromic behavior of these substrates. The fluorescence quantum yield measurements also deserve some mention. In particular, the 3,5-dimethoxy substrates **8d** and *trans*-**9d** display the *lowest* fluorescence intensities for either set of compounds (in acetonitrile, $\phi_f = 0.15$ and 0.05, respectively). These results are especially interesting given that the fluorescence of *trans*-3,5-dimethoxystilbene (*trans*-**1d**) was the *highest* of the five stilbenes investigated (vide supra, Table 2). Apart from the low

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(20) An important note regarding the fluorescence decay of *trans*-**1d** in acetonitrile is that the mathematical fit to the data is greatly improved through the use of a biexponential model: τ_s (short) = 3.8 ns (36%), τ_s (long) = 18.6 ns (64%). We are now in the process of characterizing this interesting behavior in much greater detail.

(21) Note that for all three classes of substrate (stilbenes, styrenes, and arylpropenes), the methoxy substitution pattern is provided by the letter in the structure label (i.e., *trans*-**1b**, **8b**, and *trans*-**9b** all possess a 4-methoxy substituent, and so forth).

(22) We have repeated all photophysical measurements of **8a**−**e** and *trans*-**9a**−**e** using 254 nm excitation; these results are provided in the Supporting Information.

(23) Condirston, D. A.; Laposa, J. D. *Chem. Phys. Lett.* **1979**, *63*, 313−317.

(24) Lewis, F. D.; Bassani, D. M.; Caldwell, R. A.; Unett, D. J. *J. Am. Chem. Soc.* **1994**, *116*, 10477−10485.

(25) Lewis, F. D.; Zuo, X. *J. Am. Chem. Soc.* **2003**, *125*, 8806−8813.

TABLE 6. Summary of Photophysical Data for Methoxy-Substituted Styrenes 8b−e in Cyclohexane and Acetonitrile

compd	solvent	λ_{max} (abs)[a] (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (fluor)[a] (nm)	τ_s[b] (ns)	ϕ_f[b,c]
8b	cyclohexane	259, 290 (sh), 302 (sh)	19000, 2500, 1500	322	6.6	0.33
	acetonitrile			323	6.3	0.21
8c	cyclohexane	249, 295	9400, 2300	327	6.8	0.32
	acetonitrile			330	7.8	0.28
8d	cyclohexane	256, 299	9800, 2000	341	3.8	0.12
	acetonitrile			350	6.9	0.5
8e	cyclohexane	261, 293, 309 (sh)	14300, 5300, 3300	331	3.3	0.32
	acetonitrile			334	3.2	0.29

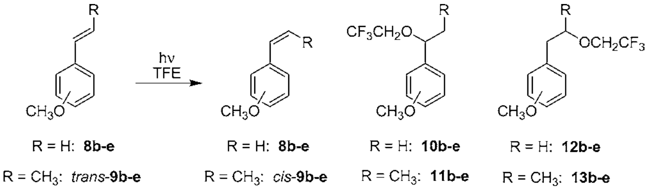
[a] Shoulders of absorption spectra are labeled (sh). [b] Values obtained following excitation at 295 nm. [c] Standard value: $\phi_f = 0.0433$ for *trans*-**1a** in hexane, ref 3.

TABLE 7. Summary of Photophysical Data for Methoxy-Substituted Arylpropenes *trans*-9b−e in Hexane and Acetonitrile

compd	solvent	λ_{max}(abs)[a] (nm)	ϵ_{max} (M^{-1} cm^{-1})	λ_{max} (fluor)[b] (nm)	τ_s[b] (ns)	φ_f[b,c]	φ_{tc}[d]
trans-**9b**[e]	hexane	258, 292 (sh), 305 (sh)	19800, 2100, 1200	328	7.9[f]	0.35[g]	0.10[h]
	acetonitrile			330	8.7[i]	0.27	0.12[j]
trans-**9c**	hexane	252, 293	11800, 2400	325	5.9	0.31	0.07
	acetonitrile			327	6.5	0.24	0.10
trans-**9d**	hexane	257, 296	12100, 1900	338	1.5	0.04	0.03
	acetonitrile			343	2.9	0.05	0.05
trans-**9e**	hexane	259, 290, 308 (sh)	16300, 5200, 3200	334, 333	3.7	0.35	0.12
	acetonitrile				4.0	0.28	0.14

[a] Shoulders of absorption spectra are labeled (sh). [b] Values obtained following excitation at 295 nm. [c] Standard value: $\phi_f = 0.0433$ for *trans*-**1a** in hexane, ref 3. [d] Determined by steady-state irradiation at 300 nm relative to $\phi_{tc} = 0.40$ for *trans*-**1a** in cyclohexane, ref 2. [e] Literature values obtained using 281 nm excitation, ref 20. [f] Literature value 8.5 ns. [g] Literature value 0.42. [h] Literature value 0.12. [i] Literature value 7.2 ns. [j] Literature value 0.13.

SCHEME 2. Products Detected Following Irradiation of 8b−e and *trans*-9b−e in TFE



fluorescence quantum yields of the 3,5-dimethoxy substrates, the methoxystyrenes and *trans*-1-arylpropenes show remarkably similar fluorescence intensities. Such behavior differs significantly from *trans*-**1a**−**e**, for which the quantum yields of fluorescence spanned nearly 2 orders of magnitude.

Photoaddition of TFE to Arylalkenes. To completely assess the photochemistry of **8b**−**e** and *trans*-**9b**−**e**, these substrates were irradiated in TFE solution (Scheme 2). The very low absorbance of the unsubstituted compounds (styrene **8a** and *trans*-1-phenylpropene *trans*-**9a**) at the maximum output of the lamps (300 nm) once again prevented detailed investigations of these substrates. As was expected based on previous studies by McClelland and co-workers,[14] the major product detected following irradiation of styrenes **8b**−**e** in TFE was the corresponding Markovnikov ether **10**.[26] Irradiation of *trans*-**9b**−**e** using the same conditions led to formation of the corresponding cis isomers and the Markovnikov solvent adducts **11b**−**e**. Surprisingly, small amounts (<5%) of the anti-Markovnikov ethers **13** were detected following irradiation of *trans*-**9c** and *trans*-**9e** (**12** or **13** were not detected for any other substrates). The values for percent conversion of arylalkene to solvent adducts are provided in Table 8, and the yield versus time plots are included in the Supporting Information. To facilitate comparisons between the reactivity of the different structure types (styrenes, *trans*-1-arylpropenes, and *trans*-stilbenes) toward TFE, Table 8 also includes values for percent conversion of stilbenes *trans*-**1a**−**e**.[27] The data in Table 8 indicate that, for a given substituent position, the order of substrate reactivity in TFE is styrene > arylpropene > stilbene. This trend appears to hold for all twelve substrates, although the very low reactivity of *trans*-**9c** is a notable exception. For the stilbene and arylpropene structure types, the 3,5-dimethoxy substrates are the most reactive compounds; for the styrenes, the 3,4-dimethoxy substrate (**8e**, 96% conversion) is slightly more reactive than the 3,5-dimethoxy substrate (**8d**, 82% conversion).

TABLE 8. Percent Conversion of Styrenes (8b−e), Arylpropenes (*trans*-9b−e), and Stilbenes (*trans*-1a−e) to the Corresponding TFE Adducts

structure type	substituent	compd[a]	% conversion[b,c]
styrene	4-methoxy	**8b**	33
	3-methoxy	**8c**	57
	3,5-dimethoxy	**8d**	82
	3,4-dimethoxy	**8e**	96
arylpropene	4-methoxy	*trans*-**9b**	20
	3-methoxy	*trans*-**9c**	3
	3,5-dimethoxy	*trans*-**9d**	48
	3,4-dimethoxy	*trans*-**9e**	29
stilbene	unsubstituted	*trans*-**1a**	5
	4-methoxy	*trans*-**1b**	4
	3-methoxy	*trans*-**1c**	20
	3,5-dimethoxy	*trans*-**1d**	39
	3,4-dimethoxy	*trans*-**1e**	7

[a] The unsubstituted styrene (**8a**) and arylpropene (*trans*-**9a**) derivatives do not absorb appreciably at 300 nm, so the photoaddition chemistry of these substrates was not investigated. [b] Percent conversion of starting material to solvent adducts following 300 nm irradiation of substrate for 2 min in TFE. [c] For *trans*-**1b**−**e** and *trans*-**9b**−**e**, the values correspond to conversion of the mixture of trans and cis isomers to solvent adducts.

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(26) Small amounts (<5%) of unidentified compounds were also detected by GC−MS. Based on their long retention times and large molecular weights (*m*/*z* > 300), these products are tentatively assigned to dimers and oligomers of the arylalkenes.

(27) Note that the percent conversion values reported in Table 8 are for 2 min of irradiation in TFE, whereas the values in ref 9 were for 10 min of irradiation in TFE.

TABLE 9. Quenching of Fluorescence Quantum Yields ϕ_f and Singlet Lifetimes τ_s by TFE for Styrenes (8b−e), Arylpropenes (*trans*-9b−e), and Stilbenes (*trans*-1a−e)

compd[a]	φ_f (AcN)[b]	φ_f (TFE)[b]	φ_f ratio[c]	τ_s (AcN)	τ_s (TFE)	τ_s ratio[c]
8b	0.21	0.02	12.2	6.3	<0.5[d]	> 12.6
8c	0.28	0.15	1.8	7.8	4.6	1.7
8d	0.15	0.02	9.6	6.9	0.9	8.1
8e	0.29	0.05	6.4	3.2	0.7	4.5
trans-**9b**	0.27	0.20	1.4	8.7	6.6	1.3
trans-**9c**	0.24	0.23	1.0	6.5	6.3	1.0
trans-**9d**	0.05	0.03	1.8	2.9	2.3	1.3
trans-**9e**	0.28	0.20	1.4	4.0	3.1	1.3
trans-**1a**	0.023	0.01	2.3	<0.5[d]	<0.5[d]	
trans-**1b**	0.007	0.006	1.1	<0.5[d]	<0.5[d]	
trans-**1c**	0.16	0.08	1.9	0.93	0.63	1.5
trans-**1d**	0.32	0.029	11.1	16.9	1.64	10.3
trans-**1e**	0.035	0.026	1.4	<0.5[d]	<0.5[d]	

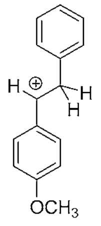
[a] The unsubstituted styrene (**8a**) and arylpropene (*trans*-**9a**) derivatives do not absorb appreciably at 295 nm, so these substrates were not investigated. [b] 295 nm excitation, relative to $\phi_f = 0.0433$ for *trans*-**1a** in hexanes, ref 3. [c] Calculated as value (TFE)/value (acetonitrile). [d] Shorter than the time resolution of the instrument.

Quenching of Excited States by TFE. An important observation from our previous investigations was the quenching of the strong fluorescence of *trans*-**1d** in mixtures of TFE and acetonitrile.[9] The strong upward curvature of a Stern−Volmer plot for fluorescence quenching versus the percentage of TFE in acetonitrile (0−100%) indicated that the quenching mechanism does not follow a simple bimolecular process. We estimated that the quenching of *trans*-**1d** occurs with a rate constant of 9×10^6 M^{-1} s^{-1} in the range of 0−20% TFE and 1×10^8 $M^{-1}s^{-1}$ in the range of 80−100% TFE. Similar experiments with deuterated TFE (TFE-OD) provided a quenching ratio of $k_{TFE}/k_{TFE-OD} = 3{:}1$ in the high concentration regime. Finally, irradiations of *trans*-**1d** in mixtures of TFE and acetonitrile indicated a strong correlation between the fluorescence quenching process and the formation of photoaddition products **4d** and **5d** (vide supra, Scheme 1).

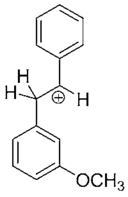
To establish that the excited states of the other substrates are also quenched by TFE, fluorescence quantum yields and singlet lifetimes were determined for all thirteen compounds in TFE solution. These results are displayed in Table 9, along with the same values for the substrates in acetonitrile solution. Quenching ratios were calculated by dividing the quantum yield or singlet lifetime in TFE by the corresponding value in acetonitrile. For those cases where both quantum yields and singlet lifetimes are available for both solvents, the quenching ratios determined by either method are remarkably consistent. Taking the stilbenes as an example, the ratios determined by fluorescence quantum yields (1.9 for *trans*-**1c** and 11.1 for *trans*-**1d**) are quite close to those determined using singlet lifetimes (1.5 for *trans*-**1c** and 10.3 for *trans*-**1d**). This implies that the quantum yield ratios should be reliable for those substrates possessing very short singlet lifetimes (<0.5 ns).

The quenching ratios in Table 9 indicate that the singlet excited states of the styrenes, arylpropenes, and stilbenes are quenched by TFE. However, there is not always a good correlation between the magnitude of fluorescence quenching (Table 9) and the yield of solvent adduct from the steady-state irradiations (Table 8). Considering each structure type separately, the order of fluorescence quenching matches the order of reactivity quite well for the arylpropenes *trans*-**9b−e**. The same is true for the methoxystilbenes *trans*-**1b−e**, although the unsubstituted compound *trans*-**1a** is not as reactive as would be expected based on the fluorescence quenching results. Surprisingly, the quenching of styrenes **8b−e** does not match the solvent addition reactivity: 4-methoxystyrene **8b** reacts with the *slowest* rate of the four substrates (33%) but displays the *highest* quenching ratio (ϕ_f ratio = 12.2). In addition, the quenching ratios are not consistent between different structure types: *trans*-**9d** undergoes solvent addition more rapidly than *trans*-**1d** (48% and 39%, respectively), but the fluorescence of the latter substrate is more easily quenched by TFE (ϕ_f ratios = 1.8 and 11.1, respectively).

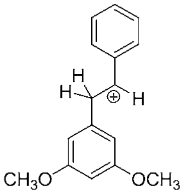
Laser Flash Photolysis. Previous investigations by McClelland and co-workers employed laser flash photolysis (LFP) of a variety of substituted styrenes in solutions of TFE and 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) to generate the corresponding arylethyl cations. These cations displayed absorption maxima in the range of 315−345 nm and decayed with rate constants on the order of 10^2−10^5 s^{-1} in HFIP. The transient species were rapidly quenched by nucleophiles, such as azide and bromide ions. Only those cations possessing highly stabilizing *p*-methoxy substituents were successfully observed in TFE—this observation was attributed to the higher nucleophilicity of TFE relative to HFIP,[28] which results in more rapid quenching of cations in the former solvent. Indeed, the stabilized 4-methoxyphenethyl cation underwent much faster decay in TFE ($k_{TFE} = 4 \times 10^5$ s^{-1}) than in HFIP ($k_{HFIP} = 2 \times 10^2$ s^{-1}). With hopes of directly observing the reactive intermediates involved in the photochemical addition of TFE to *trans*-**1b−e**, we subjected these four substrates to LFP excitation at 308 nm using a nanosecond laser system. Based on the structures of the major products from the irradiations in TFE,[9] cations **14b−e** were suspected to be the likely reactive intermediates. To compare the properties of all four cations in the same solvent, HFIP was employed for the LFP experiments.



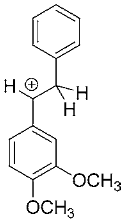
14b



14c



14d



14e

A representative kinetic trace of the change in optical density (ΔOD) at 320 nm following 308 nm excitation of *trans*-**1d** in HFIP is provided in Figure 3. The intense signal bleaching is attributed to the efficient trans−cis isomerization process; the cis isomers possess much smaller extinction coefficients at the monitoring wavelengths for all LFP experiments reported herein. This bleaching effect, which is general to all four methoxy-substituted stilbene derivatives, complicates the use of LFP for these substrates. Clearly, the substituted styrenes employed by McClelland and co-workers were much better suited to LFP studies—photoisomerization of those substrates would result in re-formation of the same compounds. Regardless of the signal bleaching effect for the stilbene experiments, rate constants for transient decay were successfully determined for all four substrates, Table 10. The inset in Figure 3 displays a plot of

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(28) N_{OTs} = 0.06 for ethanol, −3.07 for TFE, and −4.27 for 97% HFIP. Bentley, T. W.; Llewellyn, G. *Prog. Phys. Org. Chem.* **1990**, *17*, 121−158.

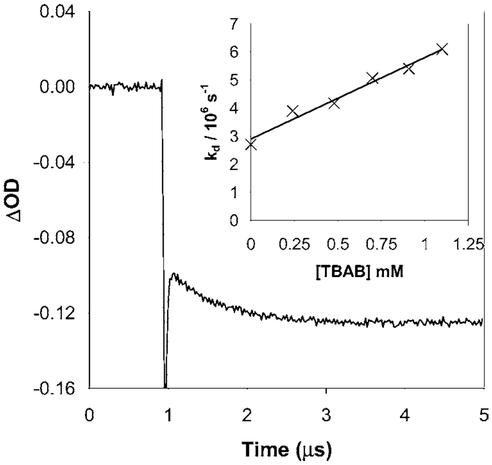

FIGURE 3. Kinetic decay trace at 320 nm following 308 nm LFP of *trans*-**1d** (inset: rate constant for cation decay versus concentration of tetrabutylammonium bromide, TBAB).

TABLE 10. Compilation of Data for Cations 14b−e in HFIP Solution: Absorption Maxima, Rate Constants for Decay in Pure HFIP, and Bimolecular Rate Constants for Quenching by Bromide Ion

compd	cation	λ_{max} (abs) (nm)	k_{HFIP} (s^{-1})	k_{Br} (M^{-1} s^{-1})
trans-**1b**	**14b**	340	4×10^3	7.8×10^8
trans-**1c**	**14c**	315	3×10^6	1.1×10^9
trans-**1d**	**14d**	320	3×10^6	2.9×10^9
trans-**1e**	**14e**	350	1×10^4	7.4×10^8

the rate constant for decay of cation **14d** versus the concentration of bromide ion in HFIP. Similar experiments for the other three substrates provided the bimolecular rate constants for quenching of cations **14b**−**e** by bromide ion, also included in Table 10.

The results in Table 10 are fully consistent with a reaction mechanism that proceeds via photoprotonation of the methoxystilbene excited states, followed by nucleophilic trapping of a carbocation intermediate by the solvent. The transient intermediates display all the important characteristics of carbocations: more facile observation in HFIP than in TFE, rapid quenching by nucleophiles, and absorption maxima that are quite similar to those reported by McClelland and co-workers.[14] The data also indicate that the cations derived from *trans*-**1b** and *trans*-**1e** are more highly stabilized than those derived from *trans*-**1c** and *trans*-**1d**. Indeed, cations **14b** and **14e** have longer wavelength absorption maxima, and react more slowly with either HFIP or bromide ion. These observations support the cation structure assignments (**14b**−**e**) that were made on the basis of the major products from the irradiations of *trans*-**1b**−**e** in TFE, especially with regard to the highly stabilizing *p*-methoxy substituents that are present in cations **14b** and **14e**. Although the steady-state irradiations and LFP experiments were performed in two different solvents (TFE and HFIP, respectively), the same solvent photoprotonation mechanism appears to operate in both cases.

Irradiations in TFE-OD. Although the LFP results support the proposed photoprotonation mechanism for addition of TFE to the methoxystilbenes, Laarhoven and co-workers have previously determined that the photochemical addition of methanol to *trans*-**1a** *does not* occur via protonation of excited states.[15] Instead, these researchers proposed a photoaddition mechanism involving two competitive pathways: (1) direct addition of methanol across the central alkene unit and (2) rearrangement of the *trans*-**1a** singlet state via a 1,2-hydride shift, followed by insertion of the resulting carbene intermediate into the O−H bond of the solvent.[29] Observations that led the authors to these conclusions included the failure of excess acid to either quench the fluorescence of *trans*-**1a** or increase the yield of solvent adduct upon steady-state irradiation in methanol. However, the most important experiment in these studies was the irradiation of *trans*-**1a** in deuterated methanol (CH_3OD). ^{1}H NMR analysis of the product mixture indicated that both the deuterium and the methoxy nucleophile were incorporated on the *same* carbon of the resulting solvent adduct.

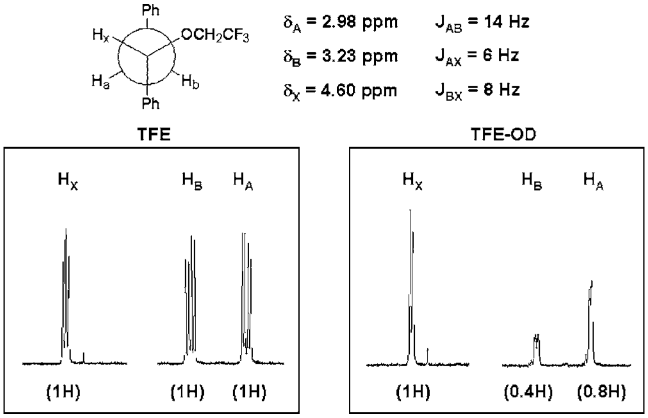

FIGURE 4. Newman projection for photoproduct **4a** and ^{1}H NMR analysis of the ABX protons of the product formed in TFE (left) or TFE-OD (right).

To examine the possibility that formation of cations **14a**−**e** might occur in competition with a carbene insertion mechanism, we performed steady-state irradiations of *trans*-**1a**−**e** in TFE-OD. The results obtained for *trans*-**1a** provide a good introduction to these experiments, which are not straightforward to interpret. Figure 4 displays a Newman projection of the preferred conformation for photoproduct **4a**, with the two phenyl rings at a dihedral angle of 180°. Also provided are the chemical shifts and coupling constants for the three protons, as well as the relevant portions of the ^{1}H NMR spectra of **4a** following irradiation of *trans*-**1a** in either TFE or TFE-OD. The geminal protons are diastereotopic—the chemical shifts and coupling constants for **4a** are consistent with previous ^{1}H NMR studies of 1,2-diphenylethanol by Kingsbury and Thornton.[30] The product formed by irradiation of *trans*-**1a** in TFE also gives the expected 1:1:1 ratio for the integrations of the three protons.

Following irradiation of *trans*-**1a** in TFE-OD, the ^{1}H NMR spectrum of **4a** is significantly modified (Figure 4, spectrum on right). The signals of all three protons are reduced to doublets, and the integrations are altered as well. These changes indicate that incorporation of deuterium does occur, but also that the location of incorporation is not always the same. Conceptually, the photochemical addition of TFE-OD to *trans*-**1a** might result in any one of the three protons in **4a** being "replaced" by deuterium.[31] Thus, there are three isomers for the structure of

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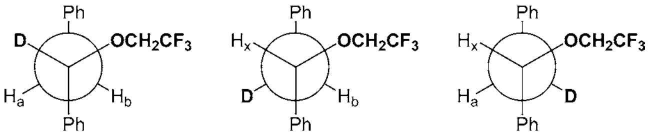
(29) The carbene-insertion mechanism is well-established for the photoaddition of alcohols to simple aliphatic alkenes. This process is thought to involve (π, R(3s)) Rydberg states, which react by processes that are characteristic of radical cations. Kropp, P. J. In *CRC Handbook of Photochemistry and Photobiology*; Horspool, W., Lenci, F., Eds.; CRC Press: Boca Raton, 2004; pp 9-1−9-11.

(30) Kingsbury, C. A.; Thornton, W. B. *J. Org. Chem.* **1966**, *31*, 1000−1004.



15 (insertion product)

16 (anti-addition product)

17 (syn-addition product)

FIGURE 5. Three isomers of **4a** that may be formed by photoaddition of TFE-OD to *trans*-**1a**.

TABLE 11. ^{1}H NMR Analysis of the Products Formed by Irradiation of *trans*-1a−e in TFE and TFE-OD

substrate	product[a]	% insertion[b]	% anti	% syn
trans-**1a**[c]	**4a**[c]	39	22	39
trans-**1a**	**4a**	12	28	60
trans-**1b**	**4b**	0	47	53
trans-**1c**	**5c**	6	27	67
trans-**1d**	**5c**	2	26	73
trans-**1e**	**4e/5e**	0[d]	43/33	57/67

[a] See Scheme 1 for product structures. [b] Highest possible yield of carbene insertion product; see text for details. [c] Data for irradiations in methanol and methanol-*O-d* (which result in formation of the corresponding methanol adducts). [d] The H_X signals for the two products formed by irradiation of *trans*-**1e** overlap, so the relative amount of carbene insertion product cannot be determined.

deuterated **4a** (Newman projections shown in Figure 5), each of which should result from a distinct mechanistic pathway. Structure **15** corresponds to the product that would be formed via the rearrangement−carbene insertion mechanism proposed by Laarhoven and co-workers. The other two isomers represent either anti (**16**) or syn (**17**) addition of TFE-OD across the alkene bond of *trans*-**1a**. That the experimentally determined integration of H_A (0.8H) is larger than that of H_B (0.4H) indicates a preference for syn addition, i.e., the ratio of H_A to H_B provides a method for determining the relative amounts of **16** and **17**. The relative amount of **15** is more difficult to assess—formation of this product results in a decrease in the integration of H_X relative to those of H_A and H_B. Table 11 provides the calculated yields of the carbene insertion, anti addition, and syn addition products for the irradiations in TFE-OD (complete details for these calculations are included in the Supporting Information).

The first entry in Table 11 is from the reaction of *trans*-**1a** in methanol and methanol-*O-d*, the reaction investigated by Laarhoven and co-workers in their original study. The spectra obtained from this reaction were easily the most difficult to analyze of all the experiments—the very low yield of the solvent adduct and the overlapping signal from product **7a** (bibenzyl) made reliable integration of the important peaks problematic. Despite these difficulties, the calculated percentages of the three reaction pathways (39% insertion, 22% anti addition, 39% syn addition) are in fact very close to the values reported Laarhoven and co-workers (47% insertion, 24% anti addition, 29% syn addition). The reasonable agreement between these results is an excellent indication that the measurements reported in the current work are reliable, especially given the fact that the spectra obtained for the TFE/TFE-OD irradiations are far superior to those from the methanol reactions.

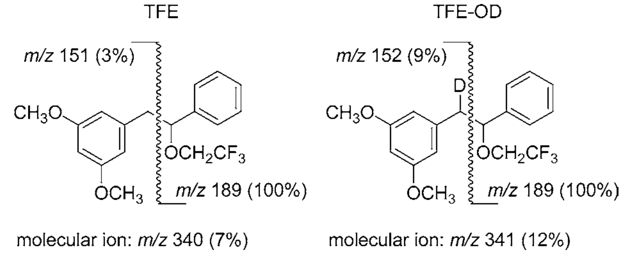


FIGURE 6. Observed GC−MS fragmentation of photoproduct **5d** when formed by irradiation in TFE (left) or in TFE-OD (right).

The results for the irradiations in TFE-OD support all aspects of our proposed[9] mechanism for addition of the solvent to the substituted stilbene derivatives. The relative importance of the carbene insertion product is much lower for the irradiation of *trans*-**1a** in TFE-OD (12%) than in methanol-*O-d* (39%). The calculated amounts of carbene insertion product are even less for the methoxystilbenes *trans*-**1b**−**e** (6−0%) and are essentially zero considering the error involved with determining accurate integrations for the three peaks. Therefore, the carbene insertion mechanism, which accounts for 40−50% of the product formed in methanol solution, appears to be of negligible importance for the TFE irradiations. This solvent dependence may be attributed to the ability of TFE to act as a photoprotonation reagent and thereby react with an excited substrate prior to the 1,2-hydride shift that initiates the carbene insertion mechanism. The relationship between the relative amounts of syn and anti addition products and the position of the methoxy substituent is also quite interesting. In particular, the relative amount of syn addition is lower for the substrates possessing *p*-methoxy substituents compared to those with *m*-methoxy substituents. For example, syn = 53% for *trans*-**1b** (4-methoxy) and 73% for *trans*-**1d** (3,5-dimethoxy).

The absence of substantial carbene insertion product following irradiation of *trans*-**1a**−**e** in TFE-OD was also supported by GC−MS analysis of the reaction mixtures. As indicated in our previous communication,[9] the solvent adducts **4** and **5** lend themselves particularly well to GC−MS techniques. The molecular ions of these products undergo preferential fragmentation to generate the arylmethyl cations that are alkoxy-substituted, presumably due to the enhanced stability of these ions over the alternatives. Importantly, the mass-to-charge ratios (*m*/*z*) for these ions are characteristic of the regiochemistry of the photoaddition reactions. Following irradiation of a given substrate in TFE-OD, the molecular ion of the product is increased by one mass unit, but the mass of the trifluoroethoxy-substituted arylmethyl cation fragment is unchanged. In those cases where the other possible arylmethyl cation is also detected in the GC-MS spectrum, a one unit increase in the mass-to-charge ratio of that fragment is observed. The observed fragmentation of **5d** provides a good example of these results, Figure 6.

Irradiations of styrenes **8b**−**e** and arylpropenes *trans*-**9b**−**e** in TFE-OD were also performed. In all eight cases, the GC−MS spectra of the deuterated (TFE-OD) photoaddition products were consistent with incorporation of the deuterium and the trifluoroethoxy nucleophile on *different* carbons of the original arylalkene double bond. For the photoproducts derived from styrenes **8b**−**e**, these assignments were also confirmed by analysis of the ^{1}H NMR spectra. Unfortunately, the ^{1}H NMR

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(31) McClelland and co-workers have reported that methoxy-substituted aromatics are capable of undergoing ring-protonation following irradiation in HFIP (Mathihvanan, N.; Cozens, F.; McClelland, R. A.; Steenken, S. *J. Am. Chem. Soc.* **1992**, *114*, 2198−2203). However, none of the ^{1}H NMR spectra discussed in the current report showed evidence for ring-incorporation of deuterium, and attempts to observe cyclohexadienyl cations (λ_{max} > 350 nm) by LFP were unsuccessful.

spectra of the photoproducts derived from *trans*-**9b**−**e** were complicated by the additional coupling to the terminal methyl group, and also by the presence of several conformations of similar energy. As a result of these issues, the peaks of interest in the ^{1}H NMR spectra consisted of multiplets that were difficult to integrate reliably. Thus, analysis of the arylpropene products rests solely on the GC−MS spectra, which are included in the Supporting Information.

Discussion

***m*-Methoxy Effect: Photophysical Characteristics.** As discussed in the Introduction, Lewis and co-workers have established that *m*-amino substituents are capable of increasing the barrier for torsional deactivation of the *trans*-stilbene singlet excited state. By examining the temperature dependence of the singlet lifetimes for *trans*-stilbene (*trans*-**1a**) and *trans*-3-aminostilbene (*trans*-**3**) in hexane solution, the activation energies for this process have been estimated as 3.5 and 7.5 kcal/mol, respectively.[7b] Because of these differences, the photochemical trans−cis isomerization of *trans*-**3** in cyclohexane is quite inefficient (ϕ_{tc} = 0.09) when compared to *trans*-**1a** (ϕ_{tc} = 0.40). The lower quantum yield of isomerization for *trans*-**3** also results in a very long-lived, highly fluorescent excited singlet state (τ_s = 7.5 ns, ϕ_f = 0.78). By way of comparison, measurements for *trans*-4-aminostilbene in cyclohexane (ϕ_{tc} = 0.49, ϕ_f = 0.05) indicated that the barrier for excited-state bond torsion of this substrate is quite similar to that of *trans*-**1a**. The properties displayed by methoxystilbenes *trans*-**1b**−**e** are consistent with a similar perturbation of the torsional barrier by *m*-methoxy substituents. In cyclohexane, *trans*-3-methoxystilbene (*trans*-**1c**) does have a smaller quantum yield of trans−cis isomerization (ϕ_{tc} = 0.32) and larger quantum yield of fluorescence (ϕ_f = 0.18) when compared to *trans*-stilbene itself. However, the effect of the 3-methoxy substituent on the stilbene chromophore is clearly not as large as for the 3-amino substituent; these differences are likely due to the more potent electron-donating ability of the amino group.[8b]

The photophysical properties of substituted stilbene derivatives also depend on solvent polarity. Waldeck and co-workers have determined that the barrier for excited-state bond torsion of *trans*-**1a** is decreased from 3.5 kcal/mol in hexane[1] to 2.6 kcal/mol in polar nitrile solvents.[32] This effect, which has been explained by a model involving polarization of the torsional barrier, appears to explain the observation by Muzzucato[16] that *trans*-**1a** isomerizes more efficiently in acetonitrile (ϕ_{tc} = 0.45) than in hexanes (ϕ_{tc} = 0.40). We were intrigued by the possibility of observing similar solvent dependence on the properties of *trans*-**1a**−**e**. A comparison between the properties of *trans*-**3** (3-amino)[7b] and *trans*-**1c** (3-methoxy) is interesting in this regard: upon increasing solvent polarity, the *increase* in isomerization efficiency is much larger for *trans*-**3** (ϕ_{tc} = 0.09 in cyclohexane, 0.23 in acetonitrile) than for *trans*-**1c** (ϕ_{tc} = 0.32 in cyclohexane, 0.39 in acetonitrile). A possible explanation for these differences may lie in the experimentally determined excited-state dipole moments (μ_e = 11.9 D for *trans*-**3**, μ_e = 3.2 D for *trans*-**1c**). Assuming that similar differences in polarization may exist for the excited-state torsional barriers of these two substrates, solvent polarity should have a greater effect on the properties of *trans*-**3**. To investigate this idea more closely, Table 12 provides a compilation of the excited-state dipole moments (μ_e) and quantum yields of isomerization for *trans*-**1a**−**e**. Four of the five substrates display a clear relationship between excited-state dipole moments and the increase in isomerization efficiency upon changing from nonpolar cyclohexane to polar acetonitrile. As shown in Figure 7, a plot of the difference in the isomerization quantum yields (i.e., ϕ_{tc}(AcN) − ϕ_{tc}(Cyc)) versus excited state dipole moment is linear for these four substrates, with a surprisingly high correlation coefficient of $r^2 = 0.961$.[33] Given that these two properties were determined using very different experimental techniques (vide supra), incidental correlation would appear to be quite unlikely. Although the mathematical relationship that governs this correlation is not clear, these trends do support the hypothesis that the magnitude of μ_e dictates the influence of solvent polarity on the isomerization process.

TABLE 12. Excited-State Dipole Moments μ_e and Quantum Yields of Isomerization ϕ_{tc} for *trans*-1a−e in Cyclohexane (Cyc) or Acetonitrile (AcN)

compd	μ_e[a] (D)	ϕ_{tc}(Cyc)[b]	ϕ_{tc}(AcN)[b]	ϕ_{tc}(AcN) − ϕ_{tc}(Cyc)
trans-**1a**	0	0.40	0.45	0.05
trans-**1b**	6.8	0.39	0.53	0.14
trans-**1c**	3.2	0.32	0.39	0.07
trans-**1e**	8.7	0.41	0.59	0.18
trans-**1d**	13.2	0.29	0.28	0.00

[a] Calculated from analysis of solvatochromic data, Table 3. [b] Determined by steady-state irradiation at 300 nm, Table 5.

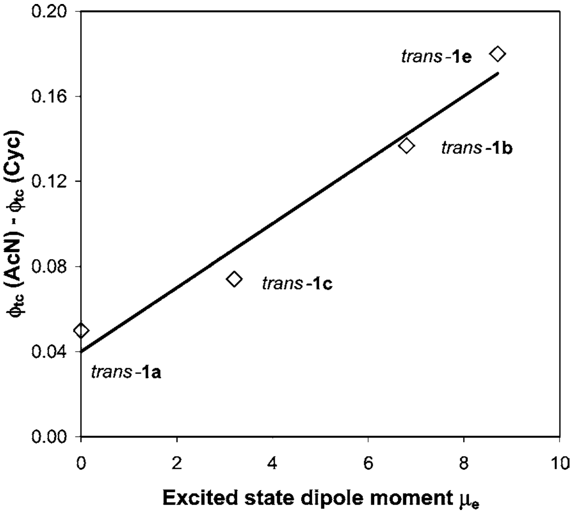

FIGURE 7. Plot of the difference between isomerization quantum yields in acetonitrile and cyclohexane versus the excited-state dipole moment for *trans*-**1a**, *trans*-**1b**, *trans*-**1c**, and *trans*-**1e**.

An important point in the data analysis discussed above is that the 3,5-dimethoxy substrate *trans*-**1d**, which behaves differently in almost all respects from the other stilbenes, has not been included in Figure 7. Although this substrate has the highest dipole moment of the five compounds (μ_e = 13.2 D), the quantum yield of isomerization is the same in both cyclohexane and acetonitrile (ϕ_{tc} = 0.29). Furthermore, the excited state of *trans*-**1d** becomes *more* fluorescent in polar solvents (ϕ_f = 0.18 in cyclohexane, 0.32 in acetonitrile). Given these very different results, the failure of *trans*-**1d** to fit the trend in Figure 7 is not surprising. The very large values of μ_e,

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(32) Sivakumar, N.; Hoburg, E. A.; Waldeck, D. H. *J. Chem. Phys.* **1989**, *90*, 2305−2316.

(33) Removing *trans*-**1a** from Figure 7 improves the correlation to r^2 = 0.997. Alternatively, the data may indicate an upward curvature.

ϕ_f, and τ_s that have been measured for *trans*-**1d** are characteristics of stilbene derivatives which possess charge-transfer excited states.[1d] These unusual excited-state properties make *trans*-**1d** an interesting substrate for further investigations; we are presently completing experiments designed to provide a better understanding of the photochemistry of this substrate in particular and also of a number of substituted *trans*-3,5-dimethoxystilbenes.

The photophysical properties of substituted styrenes and *trans*-1-arylpropenes are also dependent on the height of the barrier for excited-state bond torsion. Lewis and co-workers have determined the barriers for both styrene **8a** (6.6 kcal/mol in methylcyclohexane)[25] and *trans*-1-phenylpropene *trans*-**9a** (8.8 kcal/mol in hexane, 8.0 kcal/mol in acetonitrile).[24] The larger barriers for excited-state bond torsion in these substrates lead to less-efficient singlet state bond torsion (compared to *trans*-**1a**). Instead, isomerization occurs to a large extent by intersystem crossing to the triplet state, followed by barrierless bond torsion. Although the rate constants of intersystem crossing for *trans*-**1a** ($k_{isc} = 3.9 \times 10^7$ s^{-1})[1a] and *trans*-**9a** ($k_{isc} = 4.7 \times 10^7$ s^{-1})[24] are similar, the larger barrier for bond rotation in *trans*-**9a** makes intersystem crossing the major decay pathway for this compound ($\phi_{isc} = 0.60$). The effects of various aryl substituents on the photophysical properties of arylpropenes have also been determined previously. The presence of either electron donating or electron withdrawing substituents appears to lower the barrier, particularly in polar solvents; *trans*-1-(4-methoxyphenyl)propene (5.6 kcal/mol in hexane, 4.2 kcal/mol in acetonitrile) and *trans*-1-(4-cyanophenyl)propene (5.6 kcal/mol in hexane, 2.6 kcal/mol in acetonitrile) are representative examples.[24] The absorption and fluorescence spectra and singlet lifetimes of substituted styrenes, including **8b** and **8c**, have been reported by Yates and McEwen in their study of the acid-catalyzed photohydration of these compounds in water.[13]

Our photophysical measurements involving methoxystyrenes **8b**−**e** and arylpropenes *trans*-**9b**−**e** are consistent with most aspects of the literature results described in the preceding paragraphs. As a result of the larger torsional barriers that these substrates should possess, the singlet lifetimes, quantum yields of fluorescence, and quantum yields of isomerization are more uniform than those of the stilbene derivatives. In general, these substrates display longer singlet lifetimes, larger quantum yields of fluorescence, and (in the case of the *trans*-1-arylpropenes) smaller quantum yields of isomerization. The minimal effect of solvent polarity on these properties is another consequence of the larger barriers for excited state bond torsion. One interesting observation that is not explained by the literature data is the unusually low quantum yields of fluorescence for the 3,5-dimethoxy substrates (**8d** and *trans*-**9d**). For the arylpropenes, most substrates displayed quite strong fluorescence in either hexanes or acetonitrile ($0.35 \geq \phi_f \geq 0.24$) except for *trans*-**9d** ($\phi_f = 0.05$). This large difference is particularly intriguing, given that the 3,5-dimethoxy substrate in the stilbene series (*trans*-**1d**) displayed the *highest* quantum yield of fluorescence ($\phi_f = 0.32$) of those five substrates. In addition to the low fluorescence displayed by *trans*-**9d**, the substrate also gives the smallest isomerization quantum yield of the *trans*-1-arylpropenes. Taken together, these observations may imply that the 3,5-dimethoxy system undergoes a deactivation process that results in return to the ground state for the styrene and arylpropene systems, but instead forms a highly fluorescent charge transfer state in the presence of a second phenyl ring (i.e., in the stilbene system). Although the much longer singlet lifetime of *trans*-**1d** in polar acetonitrile ($\tau_s = 16.9$ ns) compared to nonpolar cyclohexane ($\tau_s = 3.6$ ns) supports this hypothesis, further experiments are required to fully characterize the excited-state behavior of this interesting substrate.[20]

***m*-Methoxy Effect: Photoaddition Chemistry.** Two main aspects of the TFE photoaddition reactions need to be considered: the reason(s) for the differences in substrate reactivity and the actual mechanism that converts excited states to solvent adducts. In our original studies, the relative reactivities of *trans*-**1a**−**e** were assumed to depend solely on the singlet lifetime of the substrate in question. The more detailed experiments provided in the current report demonstrate that this hypothesis is generally correct, but that additional factors are also important. Fluorescence quenching results confirm that the excited singlet states are reactive toward TFE, and there is no evidence that TFE reacts with any other excited species. The relative order of reactivity observed for the three main structure types (styrenes > arylpropenes > stilbenes, see Table 8) is consistent with a strong correlation between the photoaddition chemistry and the magnitude of the singlet lifetimes. The low reactivity of the stilbenes is due to these substrates having smaller barriers for excited state bond torsion when compared to the styrenes or arylpropenes. As a result of these differences, the stilbenes undergo rapid trans−cis isomerization in competition with the solvent addition reaction. In addition to providing a mechanism for deactivating the reactive excited state, the trans−cis isomerization process obviously results in formation of the cis isomers. Importantly, the cis and trans isomers of all five stilbenes are expected to have quite different photophysical properties. In particular, the lifetimes of the cis isomers are even shorter than the corresponding trans isomers; the values for *trans*-**1a** ($\tau_s = 0.07$ ns)[17] and *cis*-**1a** ($\tau_s = 0.001$ ns)[34] should be representative.[35] Based on these differences, the cis isomers are estimated to be an order of magnitude less reactive toward TFE than the corresponding trans isomers. Thus, efficient trans−cis isomerization not only provides a mechanism for deactivation of the reactive excited state of the trans isomers, but also produces the cis isomers, which have attenuated reactivity toward TFE. Eventual cis−trans isomerization allows a pathway for reformation of the more reactive trans isomers during the steady-state irradiations. Essentially the same argument can be used to explain the observation that photoaddition of TFE to arylpropenes *trans*-**9b**−**e** occurs more slowly than for styrenes **8b**−**e**, even though both structure types have quite similar photophysical properties. Excited-state bond torsion leads to trans−cis isomerization of the arylpropenes but results in reformation of the starting material in the case of the styrenes. The reported[24] singlet lifetimes of *trans*-**9a** ($\tau_s = 11.8$ ns) and *cis*-**9a** ($\tau_s = 2.6$ ns) suggest that the cis-arylpropenes should be less reactive toward photoaddition of TFE.

The high reactivity of *trans*-**1d** (3,5-dimethoxy) toward TFE is clearly related to the unique photophysical properties displayed by this substrate. The very long singlet lifetime ($\tau_s = 16.9$ ns) and very high excited-state dipole moment ($\mu_e = 13.2$

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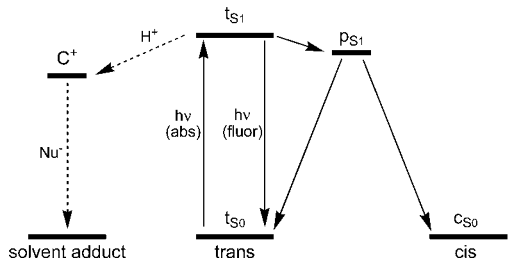
[34] (a) Abrash, S.; Repinec, S.; Hochstrasser, R. M. *J. Chem. Phys.* **1990**, *93*, 1041−1053. (b) Todd, D. C.; Jean, J. M.; Rosenthal, S. J.; Ruggiero, A. J.; Yang, D.; Fleming, G. R. *J. Chem. Phys.* **1990**, *93*, 8658−8668.

[35] Lewis and co-workers have demonstrated that the *m*-amino effect does extend the lifetime of the *cis*-stilbene chromophore. However, the lifetimes of these species still do not exceed those for the corresponding trans isomers. For example, in alkane solvents at 200 K, $\tau_s = 7.3$ ns for *trans*-**3** (ref 7b) and $\tau_s = 1.9$ ns for *cis*-**3** (ref 7c).

D) for *trans*-**1d** are ideally suited to rapid photoprotonation and solvent adduct formation. That the reactivity of the methoxystilbenes depends in part on the dipole moment of the excited state is not surprising; excited states possessing substantial charge transfer should be rapidly quenched by protic solvents, such as TFE. However, those substrates which possess large excited state dipole moments also display higher isomerization quantum yields (particularly in polar solvents, vide supra), so there is certainly a competition between the two effects. This competition is best demonstrated by *trans*-**1e** (3,4-dimethoxy), which has both a high excited-state dipole moment ($\mu_e = 8.7$ D) and a high trans−cis isomerization quantum yield ($\phi_{tc} = 0.59$ in acetonitrile). As a result of the conflicting effects of μ_e on the reactivity of *trans*-**1e** in TFE, the reactivity of this substrate (7% conversion after 2 min) is intermediate between that of *trans*-**1c** (20%, $\mu_e = 3.2$ D, $\phi_{tc} = 0.39$) and *trans*-**1b** (4%, $\mu_e = 6.8$ D, $\phi_{tc} = 0.52$). These results indicate that, although the quantum yield of isomerization of *trans*-**1e** is larger than that of *trans*-**1b**, the higher dipole moment of the former substrate makes it more reactive toward TFE. Conversely, the low quantum yield of isomerization (and longer singlet lifetime) of *trans*-**1c** makes this substrate more reactive in the photoaddition experiments, even though it possesses a less polarized excited state.

The position of methoxy substituents also dictates the relative rates at which the benzylic carbocation intermediates undergo nucleophilic attack by solvent. The LFP experiments in HFIP are consistent with the cations (**14b**−**e**) that would be formed by photoprotonation of *trans*-**1b**−**e** en route to the corresponding solvent adducts (**4b**, **5c**, **5d**, **4e**). Those cations possessing *p*-methoxy substituents (1**4b** and 1**4e**) react more slowly with nucleophiles than those cations that are unsubstituted (**14c** and **14d**). Inspection of the products formed by irradiation of *trans*-**1a**−**e** in TFE-OD showed that very little (if any) solvent adduct is formed via a competitive carbene insertion mechanism, which was originally proposed for the photoaddition of methanol to *trans*-**1a**.[15] Further analysis of the ^{1}H NMR spectra of the deuterated products provided the relative amounts of syn and anti addition products. These results are consistent with the relative reactivity of cations **14b**−**e**, as determined by the LFP experiments. The more reactive cations **14c** and **14d** gave higher yields of the syn addition product (≈70% syn) when compared to the less reactive cations **14b** and **14e** (≈50−60% syn). The equal amounts of syn and anti addition product from **14b** and **14e** are consistent with the formation of free carbocations in solution, with little diastereoselectivity for reaction with the nucleophile. In contrast, the increased amount of syn addition for **14c** and **14d** implies that these less-stabilized cations undergo rapid nucleophilic attack by the trifluoroethoxy anion derived from the *same* molecule of TFE involved in the initial photoprotonation step. An alternative explanation for these results is that the "anti" addition product is actually formed via syn addition to the cis isomers, which would be formed in greater yield from those substrates with high quantum yields of trans−cis isomerization (i.e., *trans*-**1b** and *trans*-**1e**). However, the second explanation is inconsistent with the majority of results presented in this report, and also fails to explain the different amounts of syn addition for the two products derived from *trans*-**1e** (**4e** 57% syn, **5e** 67% syn). The first mechanistic explanation easily accounts for this observation: the cation required for formation of addition product **5e** does not possess a stabilizing 4-methoxyphenyl substituent, and should display essentially the same reactivity as **14c** and **14d**. These ideas are supported by the very similar amounts of syn addition for all three products (**5c** 67% syn, **5d** 73% syn, **5e** 67% syn).

SCHEME 3. Energy State Diagram for the Deactivation of Excited-State *trans*-Arylalkenes



Conclusions

Scheme 3 provides a summary for the connection between the photophysical properties and photoaddition chemistry of the substrates discussed in this report. Excitation of the ground-state trans isomer results in formation of a short-lived singlet excited state ($t_{S0} \rightarrow t_{S1}$). In aprotic solvents, the preferred deactivation pathway for t_{S1} is excited-state bond torsion to a perpendicular intermediate ($t_{S1} \rightarrow p_{S1}$) followed by internal conversion to the ground-state cis or trans isomer. Deactivation of t_{S1} can also occur by fluorescence. In ionizing solvents such as TFE and HFIP, t_{S1} may undergo protonation to yield a carbocation intermediate C^+, which is in turn trapped by solvent-derived nucleophiles. Substrates possessing meta-methoxy substituents display a propensity toward photoprotonation, likely due to higher barriers for torsional deactivation of t_{S1}. The photochemically generated carbocation intermediates react in the same manner as those cations produced by ground-state chemistry. Finally, we propose that t_{S1} is the sole precursor to C^+; alternative reaction pathways involving either p_{S1} or excited states of the corresponding cis isomer (not shown) are not supported by the available data.

Experimental Section

Syntheses. The syntheses of *trans*-**1a**−**e** have been reported previously.[9] Of the five styrene derivatives selected for the current investigations, only 3,5-dimethoxystyrene **8d** was not commercially available. This compound was prepared by combination of the methylmagnesium iodide Grignard reagent with 3,5-dimethoxybenzaldehyde, followed by dehydration of the alcohol intermediate. The unsubstituted *trans*-1-phenylpropene *trans*-**9a** was also commercially available. The syntheses of the four methoxy-substituted *trans*-1-arylpropenes were accomplished using the same route as for **8d**, but using ethylmagnesium iodide with the appropriate methoxyphenyl aldehydes. Separation of the *trans*-1-arylpropenes from their cis isomers by flash chromatography techniques was not possible, but fortunately GC−FID analysis indicated that the reaction mixtures contained ≥90% of the trans isomers in all cases. Complete details regarding the synthesis and characterization of these substrates (**8d**, *trans*-**9b**, *trans*-**9c**, *trans*-**9d**, and *trans*-**9e**) are provided in the Supporting Information.

Photophysical Measurements. Fluorescence spectra were determined using solutions for which $A = 0.25$ at the incident wavelength (either 295 or 254 nm). All fluorescence spectra were corrected, and quantum yields of fluorescence were obtained by comparing the integrated area of a given sample to that of the appropriate reference. Many values of ϕ_f for *trans*-**1a** have appeared in the literature, with slight variations depending on the excitation wavelength, solvent, and temperature.[1] The chosen reference value for the samples excited at 295 nm is $\phi_f = 0.0433$, obtained by Saltiel and co-workers for *trans*-**1a** in hexane solution at 26.6 °C using an excitation wavelength of 294 nm.[3] Slight differences between excitation wavelengths (295 nm versus 294 nm) and temperature (25.0 °C versus 26.6 °C) should not affect our results greatly.[36] For those samples excited at 254 nm (specifically the styrenes and arylalkenes reported in the Supporting Information), the reference value is $\phi_f = 0.25$ for styrene **8a** in cyclohexane.[25] Our method for calculating quantum yields of fluorescence also accounted for differences in the absorbance of the sample and reference solutions, although the experimental differences were generally quite small (less than 0.02 absorbance units, or 10%). Singlet lifetimes were measured by monitoring fluorescence decay using a time-correlated single photon counting apparatus with a hydrogen flash lamp of pulse width about 1.8 ns. All fluorescence data (steady-state and time-resolved) were obtained using a path length of 1 cm and samples that were degassed by three freeze−pump−thaw cycles before being thermostated at 25 °C. As indicated in the Results, quantum yields of trans−cis isomerization were obtained by steady-state irradiation of optically dense solutions (1×10^{-2} M) using one 300 nm low-pressure mercury lamp in a photochemical reactor (solutions thermostated at 25 °C). The rate of cis isomer formation was linear in time for low conversion irradiations (<10% conversion of trans isomer), and the quantum yields were determined using *trans*-**1a** in cyclohexane ($\phi_{tc} = 0.40$) as a reference.[2]

Steady-State Irradiations. A 1×10^{-3} M solution (50 mL) of the substrate of interest in TFE was thermostated at 25 °C in a quartz reaction vessel and purged with nitrogen for 30 min. Irradiations were performed in a photochemical reactor with 10 low-pressure mercury lamps (300 nm emission). Aliquots taken during the reaction were analyzed by GC−FID in order to determine peak areas for each component in the reaction mixture. The peak areas were converted to percentages based on the initial peak area of the starting material, and these percentages were then normalized for each sample. Identification of many photoproducts was achieved by analysis of their GC−MS spectra; these data are included in the Supporting Information.

LFP Experiments. LFP was performed using a XeCl excimer laser (308 nm, 75 mJ/pulse, 8 ns pulse width) with solutions having an absorbance of 0.4 at the incident wavelength. These solutions were prepared by adding a small volume (≈5 μL) of concentrated acetonitrile stock solution to a 0.7 cm cuvette with 2 mL of the fluorinated solvent.[37] This method required good mixing of each sample prior to irradiation in order to ensure homogeneous solutions. Further mixing of the sample was performed before every laser flash, but even with this technique the high reactivity of the substrates toward trans−cis isomerization restricted every sample to less than three flashes each. For the experiments involving quenching of the cations by bromide ion, portions of a concentrated solution of tetrabutylammonium bromide in HFIP (0.01 M) were added to the sample before mixing. The quenching rate constants (k_{Br}) were determined from the slopes of the plots of k_d versus [Br$^-$] for six different concentrations of bromide ion.

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Supporting Information Available: The synthesis and characterization of **8d** and *trans*-**9b**−**e**, the absorption spectra for all 15 substrates (*trans*-**1a**−**e**, **8a**−**e**, and *trans*-**9a**−**e**), the experimental Stokes' shifts and details regarding the Lippert−Mataga analysis for *trans*-**1a**−**e**, the fluorescence spectra of **8a**−**e** and *trans*-**9a**−**e**, the GC−MS characterization of the solvent adducts, the yield versus time plots for the irradiations of **8b**−**e** and *trans*-**9b**−**e**, details regarding the analysis of TFE/TFE-OD irradiation mixtures by ^{1}H NMR, and the Cartesian coordinates and absolute energies for the Gaussian calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) The ϕ_f values reported in ref 9 were determined using a different fluorescence standard. The current values are preferred on the basis of the very close match between our experimental conditions and those in ref 3 (excitation wavelength, temperature, etc.). Importantly, either set of data provides the same mechanistic conclusions.

(37) Surprisingly, the absorbance spectra of all substrates were slightly blue-shifted (5−10 nm) in TFE compared to acetonitrile solution. Although this change did not have a large effect on the laser experiments, the fluorescence quenching studies required the use of more concentrated TFE solutions in order to keep the same absorbance (0.25) for the quantum yield determinations. The difference in concentration is not expected to alter the results significantly.