The photochemistry of 1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethyl ethanoate in alcohol solvents: A search for carbocation rearrangements

J.C. Roberts and J.A. Pincock

Abstract: The photochemistry of the title compound **1** in methanol and 2,2,2-trifluoroethanol has been examined. In both solvents two ether products were obtained: one (**18**) resulting from trapping of the carbocation **2** (expected from photosolvolysis of **1**), and the other (**19**) from the carbocation **3** (expected after rearrangement by hydride migration of cation **2**). The substituted *trans*- and *cis*-stilbene derivatives **20** and **21** were also primary photoproducts. Analysis of product yields as a function of time revealed that the ether product **19** was formed by secondary photolysis of the stilbene derivatives, presumably by a pathway involving excited state protonation. Nanosecond laser flash photolysis results demonstrated that substituted *trans*-stilbene **20** was produced on the same time scale as the laser pulse.

Key words: ester photochemistry, stilbene photoadditions, carbocation rearrangements.

Résumé : On a étudié la photochimie du composé mentionné dans le titre **1** dans le méthanol et dans le 2,2,2-trifluoroéthanol. Dans les deux solvants on obtient deux éthers : L'un deux (**18**) résulte du piégeage du carbocation **2** (produit attendu de la photolyse du composé **1**), et l'autre (**19**) provient du carbocation **3** (produit attendu d'un réarrangement par migration d'un ion hydrure du cation **2**). Les dérivés *trans* et *cis* des stilbènes substitués **20** et **21** sont également des photoproduits primaires. L'analyse des produits obtenus en fonction du temps, révèle que l'éther **19** résulte d'une photolyse secondaire des dérivés du stilbène, vraisemblablement selon un chemin impliquant la protonation de l'état excité. Les résultats de la photolyse éclair au laser, avec des impulsions de l'ordre de la nanoseconde, démontrent que le *trans*-stilbène substitué **20** est produit dans la même échelle de temps que l'impulsion laser.

Mots clés : photochimie d'un ester, photoadditions du stilbène, réarrangements de carbocations.

[Traduit par la Rédaction]

Introduction

The photochemical generation of carbocations by cleavage of arylmethyl leaving group σ bonds ($ArCR_2$-LG) is currently of considerable interest (1). One focus has been on the mechanism for formation of the arylmethyl cation with the two possibilities being either (*i*) direct heterolytic cleavage to an ion pair from the excited singlet state, or (*ii*) excited state homolytic cleavage followed by rapid redox electron transfer converting the first formed radical pair to an ion pair (2). Product studies have been extensively used to probe these two possible pathways. Another focus has been the direct observation of arylmethyl cations by laser flash photolysis (LFP) techniques (3), which has provided information regarding the reactivity of these species, in particular their rates of reaction with various nucleophiles and solvents.

The observation of products resulting from rearrangements of carbocations is a well-established phenomenon in ground state chemistry and appears in early chapters of all modern text books on introductory organic chemistry. The driving force for these rearrangements is formation of a more stable cation from a less stable one, with both 1,2-carbon and hydrogen migrations as well-known examples. We hoped to apply the above two photochemical techniques to observe a hydride shift by both product studies and directly by LFP. We chose the substrate **1** and the cations **2** and **3** as targets (eq. [1]).

The idea behind this choice is that the 3,5-dimethoxyphenyl chromophore efficiently promotes the photochemical

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Dedicated to Professor Don Arnold for his contributions to chemistry. We have both enjoyed and benefited from our many interactions with him as a colleague, friend, and research supervisor (JAP, 1972–1973; JCR, 1997–1998).

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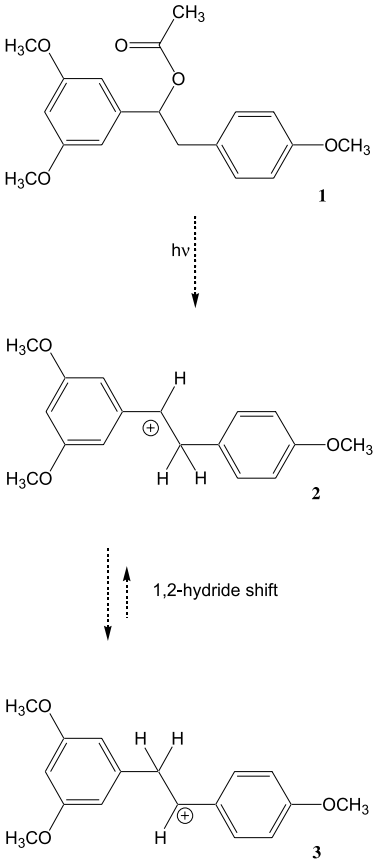


generation of carbocations via C—O bond cleavage (4, 5). For instance, the yield of ion-derived products from the photolysis of 3,5-dimethoxybenzyl acetate in methanol is 60% with a quantum yield of 0.37 (6). A rate constant for this excited state bond cleavage has not been determined because the lack of fluorescence precludes determination of the excited singlet state lifetime, but we estimate that the rate constant is greater than 1×10^9 s^{-1}. If it is formed, carbocation **2** is expected to rearrange rapidly to the more stable isomer **3** by a hydride shift. The difference in stability for the two cations can be demonstrated by the relative rates of solvolysis for 4-methoxybenzyl tosylate and 3,5-dimethoxybenzyl tosylate (1:1 × 10^5 in 80% aqueous acetone at 25°C) (7). Finally, the 4-methoxybenzyl cation has a characteristic absorption band at 340 nm that has been used previously to study its reactivity by LFP (8). Therefore, if **3** is formed from **2**, the time evolution of its growth could be observable.

A similar approach has been reported recently by Lee-Ruff and co-workers (9). In the first example (9), photolysis of the vicinal diol **4** in acetonitrile, methanol, and 2,2,2-trifluoroethanol (TFE) gave the radical-derived product **5**, along with the pinacol rearrangement product **6** (Scheme 1). The proposed mechanism proceeds through the cations **7** and **8**. The efficient formation of **7** results from the previously reported high photochemical reactivity of 9-hydroxyfluorene derivatives to give fluorenyl cations which are not stabilized by aromatic delocalization because they have $4n$ π electrons (10). The cation **7** was observed by LFP, and its unimolecular rearrangement to **8** (not observed) was found to have a rate constant of 5×10^5 s^{-1} in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP). In a second example (11), the irradiation of the 9-fluorenol derivative **9** in methanol gave the ether **10** (28%) and the elimination product **11** (7%). However, the ether **12** (which would have been formed after a 1,2-hydride shift converting **13** to **14**) was not detected in the reaction mixture (Scheme 2). When **9** was submitted to strong acid conditions at –78°C, **13** was detected spectroscopically, but **14** was not observed until the solution was warmed to room temperature. Quenching of the cold or warmed solution with methanol gave **10** or **12**, respectively. The authors rationalized these observations by suggesting that cation **14** is not formed by a 1,2-hydride shift, but rather by a deprotonation–protonation sequence involving the by-product **11** (a process which is only possible in the strong acid experiments). This suggests that the activation barrier for rearrangement of **13** to **14** is high enough to prevent the process from competing with rapid quenching by methanol when **13** is generated photochemically.

Results

Synthesis of ester 1

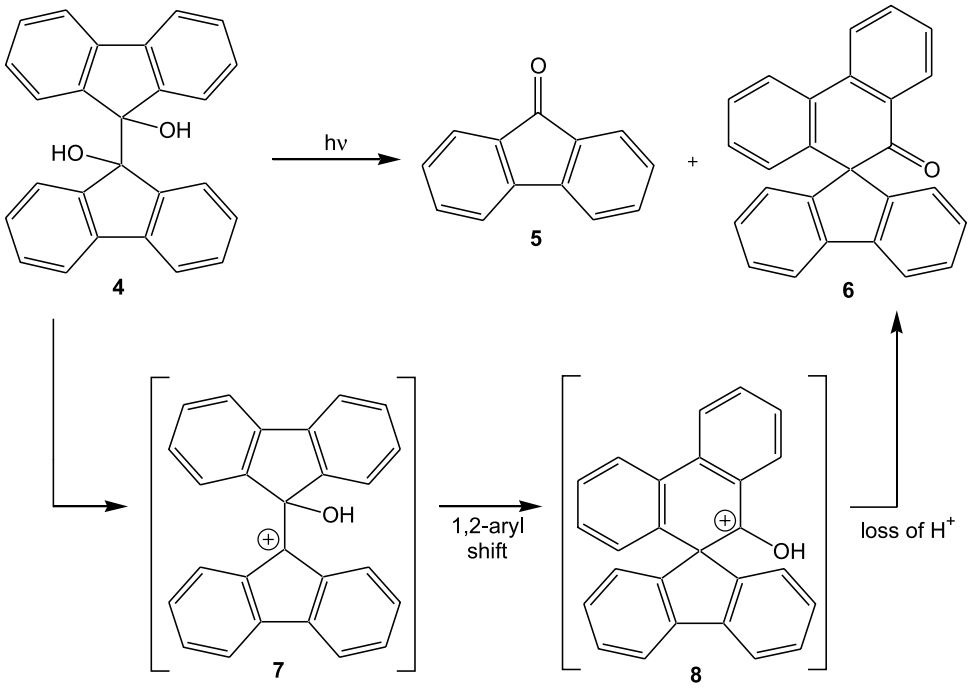
Arylmethyl esters such as **1** are easily accessed by esterification of the corresponding alcohols, and therefore, alcohol **15** was identified as the direct precursor that was required for the preparation of **1**. For the synthesis of **15**, a Grignard reaction between 3,5-dimethoxy-bromobenzene **16** and 2-(4-methoxyphenyl)ethanal **17** was chosen. As shown in Scheme 3, the bromide **16** was synthesized by a Sandmeyer reaction (12) in a low yield (33%) that is consistent with literature precedent (13). The aldehyde **17** was prepared in 74% yield over three steps by Darzens' sequence from 4-methoxybenzaldehyde as reported by Macchia and co-workers (14). Grignard coupling of **16** with **17** gave **15** (96% yield), and esterification by the procedure of Steglich and Neises (15) gave the desired ester **1** (70% yield). Details of the procedures are in the *Experimental* section.

A methanolic solution of ester **1** had absorption maxima at 274 nm ($\varepsilon = 3600$ M^{-1} cm^{-1}) and 280 nm ($\varepsilon = 3300$ M^{-1} cm^{-1}). Excitation of **1** at 274 nm results in fluorescence with λ_{max} at 298 nm, and the 0,0 band is at 288 nm (415 kJ mol^{-1}). Since 3,5-dimethoxybenzyl acetate itself does not fluoresce, this observation is attributed to the 4-methoxyphenyl chromophore, which will absorb competitively with the more reactive portion of the molecule. To check for any interaction between the two chromophores, the absorption spectra of 4-methylanisole and 1-(3,5-dimethoxyphenyl)ethyl ethanoate were recorded and normalized. Summation of the normalized spectra resulted in a slightly higher absorption (8%) than was observed at the λ_{max} of **1** (274 nm). No increased absorption was observed at longer wavelengths. Therefore, the competitive absorption between the two chromophores may decrease the quantum yield of the reaction, but there does not appear to be any strong ground-state interaction between them.

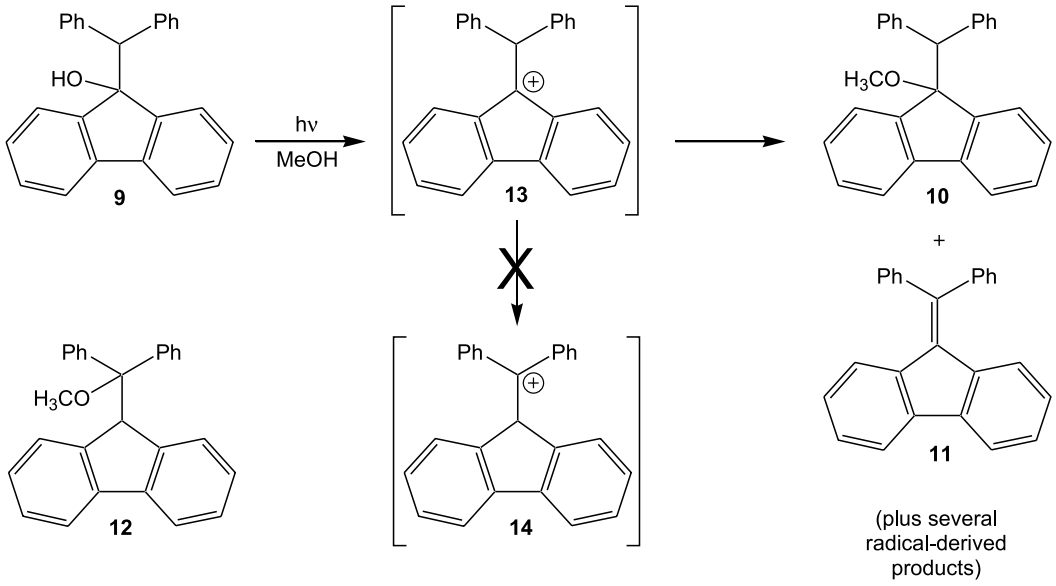
Photolysis of ester 1 in methanol

Photolysis of a nitrogen-saturated solution of **1** in methanol using a Rayonet reactor and 254 nm lamps afforded a

Scheme 1. Formation of ketone **6** via the photochemical pinacol rearrangement of cation **7**.



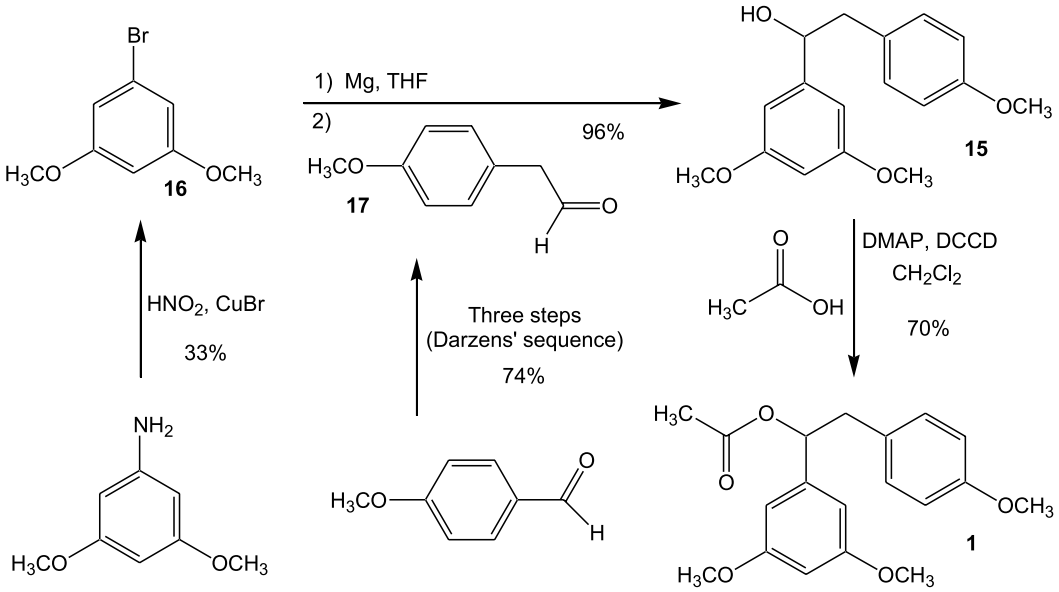
Scheme 2. The photochemistry of fluorenol **9** in methanol.



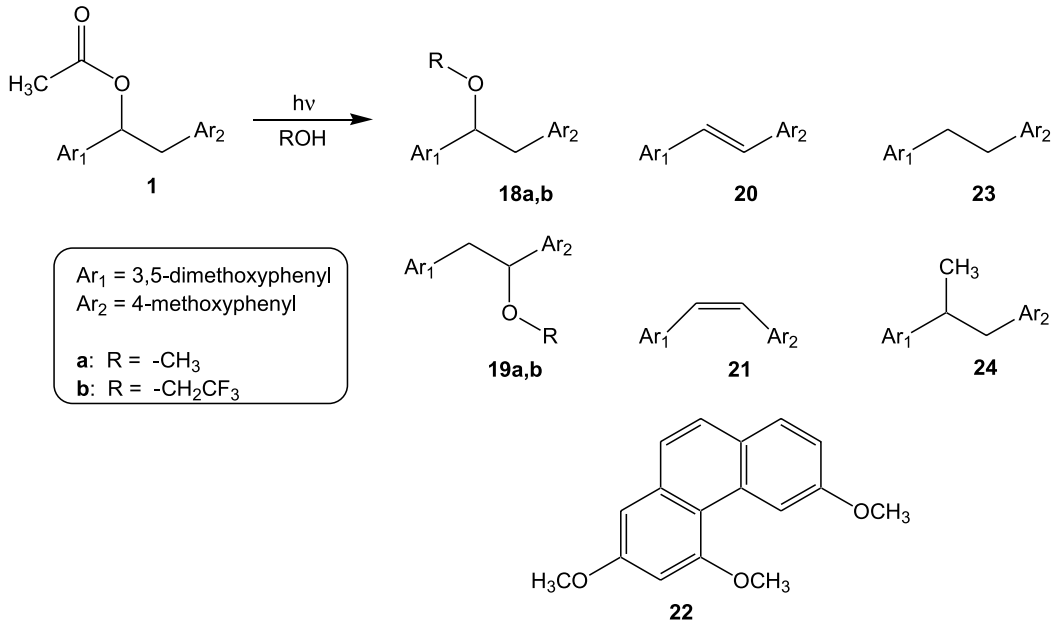
mixture of seven products after irradiation for 1 h (Scheme 4). Figure 1 shows the normalized product yields as a function of time. Preliminary identification of the products was made on the basis of their mass spectra (GC–MS). Pure samples were obtained either by independent syntheses or by isolation following photochemical reactions (vide infra). The reaction was also monitored by gas chromatography with a flame ionization detector (GC-FID). The GC-FID response was calibrated using each of the pure samples, allowing the accurate calculation of product yields (Table 1). Further details on the methods used to obtain accurate values for the product yields can be found in the *Experimental* section.

As shown in Fig. 1 and Table 1, almost 90% of **1** is consumed after 1 h of irradiation, and by this time there is very little change in the relative percentages of the products over time. For the purposes of the current project, the methyl ethers **18a** and **19a** (R = CH_3) are of the greatest interest, since they are the products that would be formed from nucleophilic attack of the solvent on carbocations **2** and **3**. Although the yield of **19a** is difficult to measure at low conversions, the ratio of **18a** to **19a** appeared to decrease with

Scheme 3. The synthesis of 1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethyl ethanoate **1**.



Scheme 4. Products detected following the photolysis of ester **1** in methanol and TFE.



time until a steady state ratio of 21:1 was reached; after only 10 min, however, **18a**:**19a** = 33:1.

The substituted stilbenes **20** and **21** are clearly primary photoproducts, but at low conversions the *trans* isomer is formed in higher yield than the *cis* (*trans*:*cis* = 2:1 at 2% conversion). The two isomers then photoequilibrate to a ratio of 1:1 at high conversion of **1**. The substituted phenanthrene **22** is produced by secondary photochemistry — a photochemically allowed conrotatory electrocyclic reaction of the *cis*-stilbene **21**, followed by oxidation of the dihydrophenanthrene intermediate. This reaction has been well-established for the photochemistry of other electron-rich stilbene derivatives (16). Finally, products **23** and **24** are radical-derived by-products of the reaction.

As noted above, the identification of most products was made by comparison with authentic samples. Ether **18a** was synthesized by reaction of alcohol **15** with sodium hydride and iodomethane. To produce **19a** in a similar alkylation method, the required alcohol **25** was synthesized by Grignard coupling of 4-bromoanisole and 2-(3,5-dimethoxyphenyl)ethanal **26** (the aldehyde, in turn, was prepared by the Darzens' sequence from 3,5-dimethoxy-benzaldehyde). The substituted *trans*-stilbene **20** was produced by dehydration of **15** with *p*-toluenesulfonic acid in benzene. Photo-

Fig. 1. Product yields as a function of time for the photolysis of ester **1** in methanol (Note: compounds **23** and **24** have been removed for improved clarity).

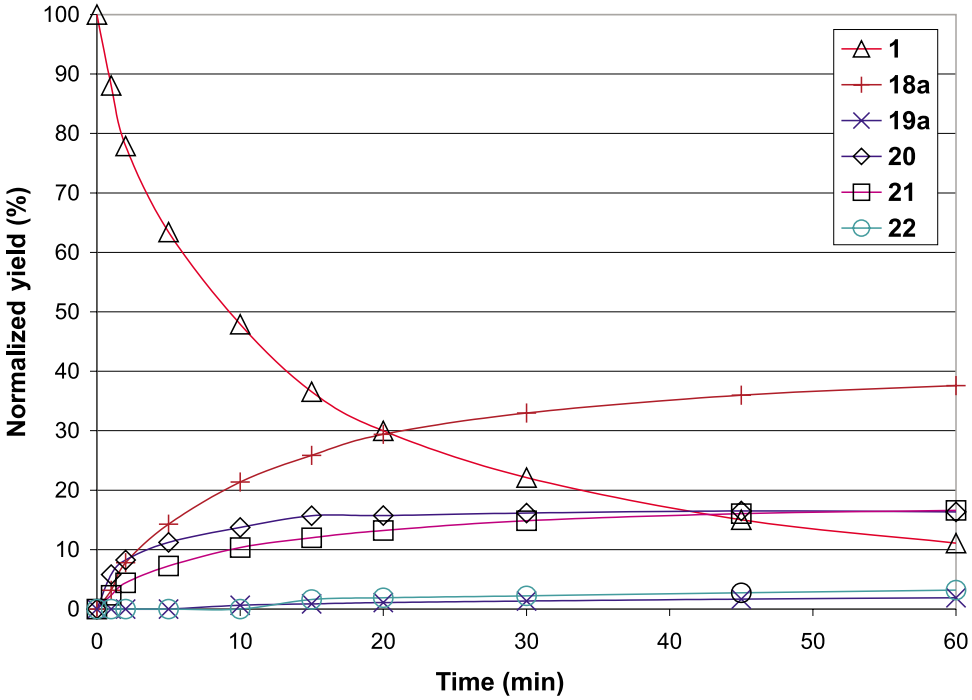


Table 1. Product yields after photolysis of ester **1** for 1 h in methanol and TFE.

Solvent	% Conversion[a]	**18**[b]	**19**[b]	**20**	**21**	**22**	**23**	**24**
Methanol (R = CH_3)	89	42	2	18	19	4	5	10
TFE (R = CH_2CF_3)	82	30	27	13	13	5	4	7

[a]Product yields are normalized to 100% because mass balances were essentially quantitiative; see the *Experimental* section for complete analysis details.
[b]For R = CH_3, products are designated **18a** and **19a**. For R = CH_2CF_3, products are designated **18b** and **19b**.

chemical *cis–trans* isomerization of **20** in acetonitrile provided access to the substituted *cis*-stilbene **21** in a steady-state ratio of *trans*:*cis* = 1:2 (Pyrex filter, 280 nm cut-off). Finally, irradiation of **20** in an aerated solution of methanol gave the substituted phenanthrene **22** after purification by column chromatography. Complete synthetic procedures for all of these compounds are included in the *Experimental* section.

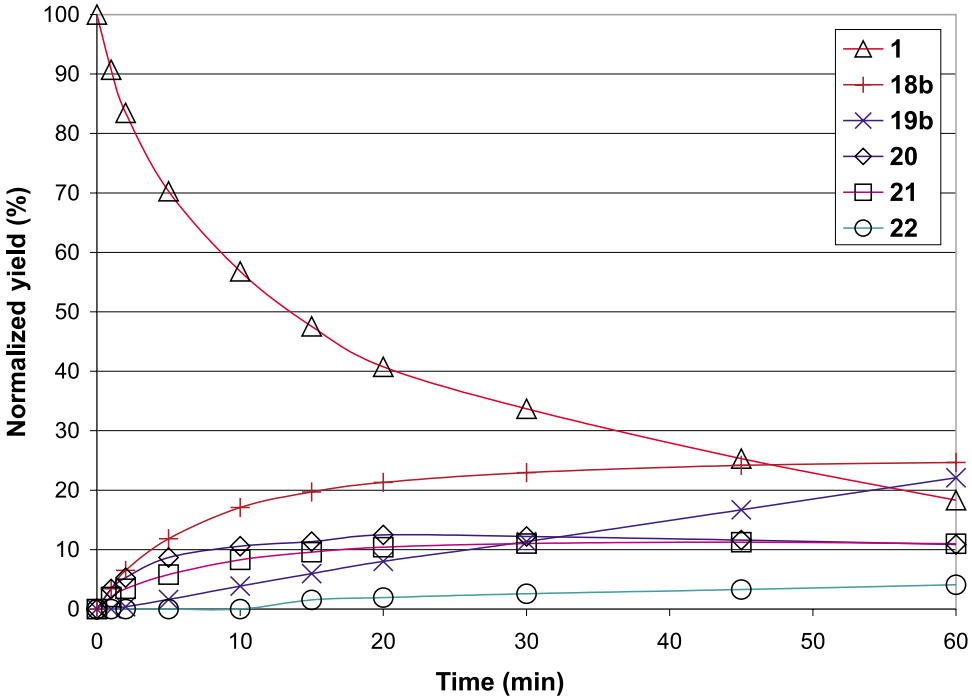
An issue of some concern was whether or not **18a** could react by secondary photochemistry, and thereby revert to carbocation **2**. To this end, a nitrogen-saturated solution of **18a** in methanol was irradiated. Although the ether was consumed (25% conversion after 1 h, 47% after 5 h), only the reduction product **23** was detected. This is clearly a result of radical, not cation, intermediates. Column chromatography of the reaction mixture after a high-conversion photolysis of **18a** provided a convenient method for isolating larger amounts of pure **23** than were obtained following photolysis of **1** in methanol.

Photolysis of ester 1 in TFE

With hopes of prolonging the lifetime of cation **2**, and thereby allowing more time for the rearrangement to **3**, the photochemistry of **1** in TFE was examined under the same conditions as the experiments in methanol. Figure 2 shows the normalized product yields as a function of time. As indicated in Scheme 4 and Table 1, the same photoproducts were formed, keeping in mind that the addition of TFE to cations **2** and **3** leads to the ethers **18b** and **19b** (i.e., with R = CH_2CF_3). The synthesis of both trifluoroethyl ethers was accomplished from alcohols **15** and **25** using a modification of the Mitsonobu reaction developed by Falck and coworkers (17). Attempts to alkylate either **15** or **25** using NaH–DMSO and 2-bromo-1,1,1-trifluoroethane gave no detectable amounts of the desired ethers. Just as in the case of the ether **18a** (R = CH_3), **18b** (R = CH_2CF_3) was also checked for its photochemical reactivity (this time in TFE). Consumption of the ether was observed (29% conversion after 1 h), and compound **23** was again the only product detected. None of the isomeric ether **19b** was detected, confirming that **18b** is not sufficiently reactive to give carbocation intermediates.

Although the % conversion of **1** over 1 h is essentially the same in methanol and TFE (89 vs. 82%) the product yields do show some significant differences. As discussed earlier for the reaction in methanol (R = CH_3), the ratio of the ether

Fig. 2. Product yields as a function of time for the photolysis of ester **1** in TFE (Note: compounds **23** and **24** have been removed for improved clarity).



product derived from cation **2** (**18a**) to the product derived from cation **3** (**19a**) is 21:1 after 1 h. The analogous ratio for **18b**:**19b** (the reaction in TFE, R = CH_2CF_3) is 30:27 (approximately 1:1), supporting the possibility that the less nucleophilic solvent (TFE) perhaps allows more time for the 1,2-hydride shift to occur. However, examination of Fig. 2 reveals that the ratio of **18b**:**19b** is not constant. In fact, the changes in the relative amounts of the ether products during the photolysis of **1** are much more pronounced in TFE (**18b**:**19b** = 16:1 after 2 min; 1:1 after 1 h) than in methanol (**18a**:**19a** = 33:1 after 10 min, 21:1 after 1 h).

With the intention of observing the growth of cation **3** directly, a solution of **1** in TFE was subjected to LFP at 266 nm. As shown in the representative spectrum (Fig. 3), an intense absorption band was observed from 280 (the lowest wavelength used) to 350 nm, with a maximum of approximately 300 nm. Importantly, the signal did not decay over any time window investigated with the laser system (10 ns to 50 μs). The same signal was observed in solutions that were purged with either oxygen or nitrogen. To explore the idea that the signal might be due to a transient species that decays over a much longer time period, a solution of **1** in TFE was submitted to 50 laser pulses, and monitored using a conventional UV–vis spectrometer. The signal did not decay after 30 min, indicating that this signal is not due to a reactive intermediate, but rather to a strongly absorbing photoproduct. Comparison of the laser spectrum with the UV absorption spectra of the isolated products **18**–**23** suggests that *trans*-stilbene **20** (λ_{max} = 303 nm, ε_{max} = 29 000 M^{-1} cm^{-1}) is the compound responsible for the absorption (Fig. 4).

Also shown in Fig. 4 is the absorption spectrum of **1**. At the maximum light output of the lamp used for the photolysis experiments (λ = 254 nm), the extinction coefficient of **20** (ε_{254} = 3030 M^{-1} cm^{-1}) is more than three times larger than that of **1** (ε_{254} = 800 M^{-1} cm^{-1}). Furthermore, **20** absorbs much more strongly than **1** at longer wavelengths. This means that when the photolysis of **1** has proceeded to the point that [**1**] < 3[**20**], the majority of the light will be absorbed by **20**. The results from the photolysis of **1** in the two solvents suggest that this condition would be met between 10 and 15 min after starting the photolysis.

At this point, an important issue must be addressed. Because the formation of **20** during LFP of the ester **1** makes the direct observation of cations **2** and **3** virtually impossible, the use of product yields in assessing the importance of rearrangement becomes critical. If the excited state of **20** is sufficiently reactive to photochemical addition of the alcohol solvent to give the ethers **18** and **19**, then any conclusions about cation rearrangements will be incorrect. To address this point, the photochemistry of **20** in methanol and TFE was examined.

Photolysis of substituted *trans*-stilbene 20 in methanol and TFE

The formation of **20** during the photolysis of **1** corresponds to the loss of acetic acid from the parent ester. For this reason, 1 equiv of acetic acid was added to the solution of **20** in either solvent before irradiation, so as to reproduce the reaction conditions as accurately as possible. No product formation was observed after stirring the solutions of **20** in methanol or TFE with added acetic acid for 48 h in the dark, thus, ensuring that **20** does not react by ground-state chemistry during the time frame of the photolysis experiment.

Photolysis of **20** in the two solvents gave a mixture of four products (Scheme 5). All of the products have already been observed during the photolysis of **1**, and so calibrated

Scheme 5. Products detected following the photolysis of substituted *trans*-stilbene **20** in methanol and TFE.

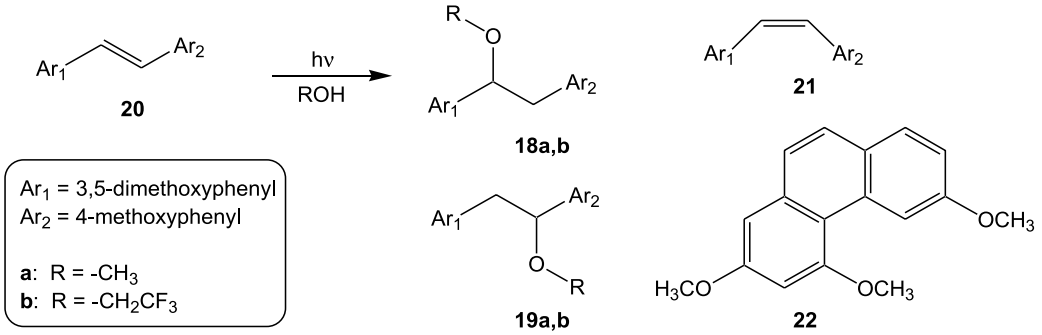


Fig. 3. Change in optical density following LFP at 266 nm of ester **1** in TFE.

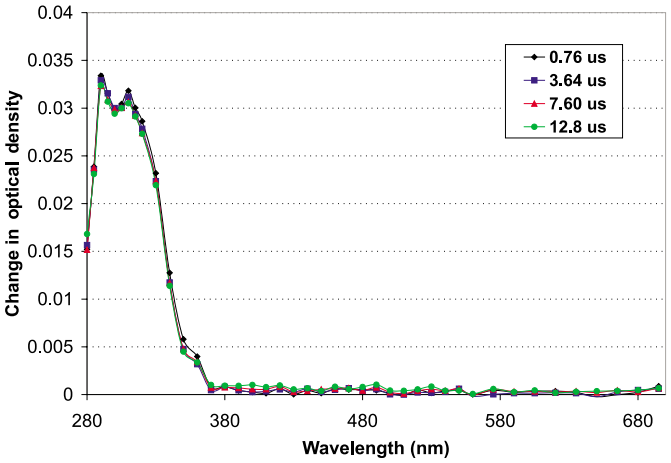
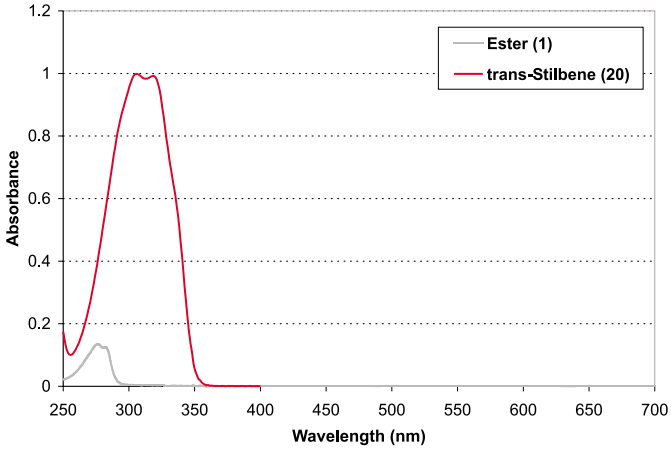


Fig. 4. Comparison of the absorption spectra of ester **1** and substituted *trans*-stilbene **20** (both 3.45 × 10^{-5} M in methanol).



product yields were calculated (Table 2). The normalized product yields as a function of time are shown in Figs. 5 (methanol) and 6 (TFE). In striking contrast to the ester **1**, which exhibits very similar reactivity in either methanol or TFE, **20** reacts much faster in TFE than in methanol. After 1 h, the % conversion of **20** in methanol is 48%, whereas the % conversion is 80% after the same time in TFE. In both solvents, the substituted stilbene isomers approach the steady state composition of 1:1 and then disappear simultaneously, although this process occurs much more rapidly in TFE. Another important observation is that the ether products observed require the formation of both carbocations **2** and **3** by photochemical protonation of **20**. Furthermore, in contrast to the results for **1**, the ethers produced from nucleophilic attack on the rearranged carbocation **3** (i.e., **19a** and **19b**) are formed in greater yield than their isomeric counterparts (**18a** and **18b**). In fact, **18a** was not detected even after 5 h of irradiation. These results strongly suggest that cation **3** is formed rapidly upon photolysis of **20** in methanol and TFE.

Discussion and conclusions

The general mechanism that has been developed for ester photochemistry seems to hold for ester **1**. Both ion- and radical-derived products are formed. The results from the photolysis of **1** in methanol and TFE initially suggested that the desired 1,2-hydride shift occurred as was predicted (eq. [1]). This was based on the idea that TFE, being a less nucleophilic solvent, would promote the formation of carbocation **3** from carbocation **2**. The difference in the final product ratios (**18**:**19**) seemed to support this idea. However, closer inspection of the data revealed that this ratio is not constant over the course of the experiment. For the reaction in methanol, **18a**:**19a** = 33:1 after 10 min, and 20:1 after 60 min. The change is even more drastic for the photolysis in TFE: after 2 min **18b**:**19b** = 16:1, but after 1 h the ratio is **18b**:**19b** = 1:1. The change in the relative amounts of the products that result from nucleophilic attack on carbocations **2** and **3** indicates that a secondary photochemical reaction occurs during the steady-state photolysis of **1**. One possible explanation is that the ethers **18** decay over the course of the photolysis experiments involving **1**. Although these ethers were shown to be photochemically active in the control experiments, they appear to react too slowly to account for the observed change in the **18**:**19** ratio. Furthermore, the presence of several strongly absorbing compounds in the same reaction mixture will make absorption by the ethers **18** even less likely. Indeed, the only experiment in which decay of either **18a** or **18b** was detected was during the photolysis of **20** in TFE (Fig. 4). The yield of **18b** does decrease over the final 2 h of the experiment (4 to 2%), but only after most of the substituted stilbenes have been converted to products.

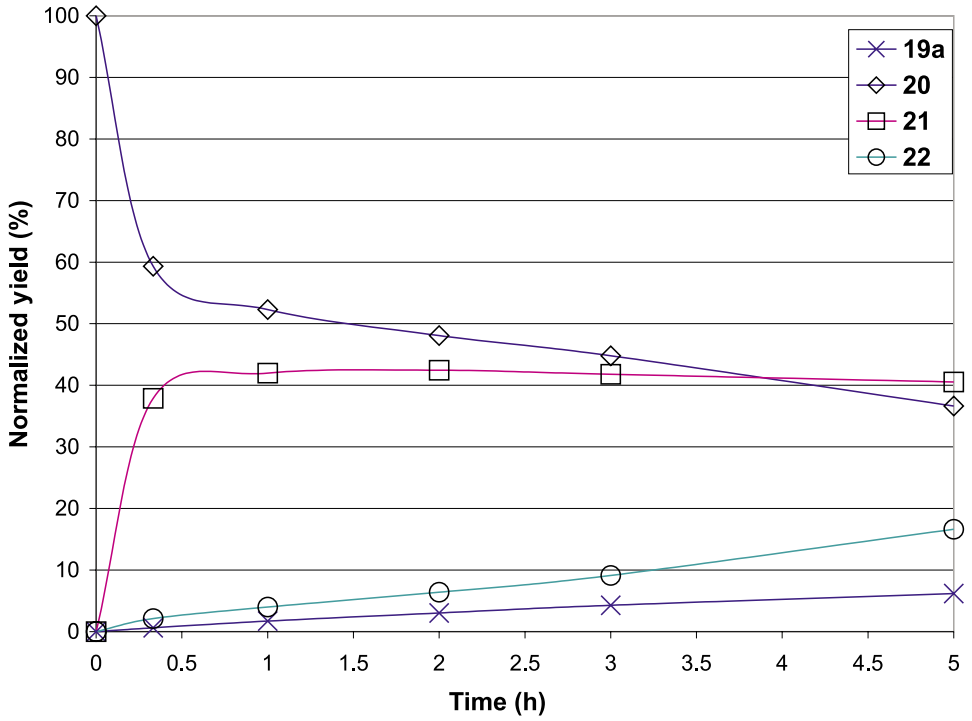
A much more satisfying explanation of the observed change in the **18**:**19** ratio is that secondary photochemistry provides an alternative pathway for the formation of the

Table 2. Product yields after photolysis of substituted *trans*-stilbene **20** in methanol and TFE.

Solvent	Time (h)	% Conversion[a]	**18**[b]	**19**[b]	**21**	**22**
Methanol (R = CH_3)	1	48	0	4	88	8
Methanol (R = CH_3)	5	63	0	10	64	26
TFE (R = CH_2CF_3)	1	80	4	60	27	9
TFE (R = CH_2CF_3)	4	95	2	87	3	8

[a]Product yields are normalized to 100% because mass balances were essentially quantitiative; see the *Experimental* section for complete analysis details.
[b]For R = CH_3, products are designated **18a** and **19a**. For R = CH_2CF_3, products are designated **18b** and **19b**.

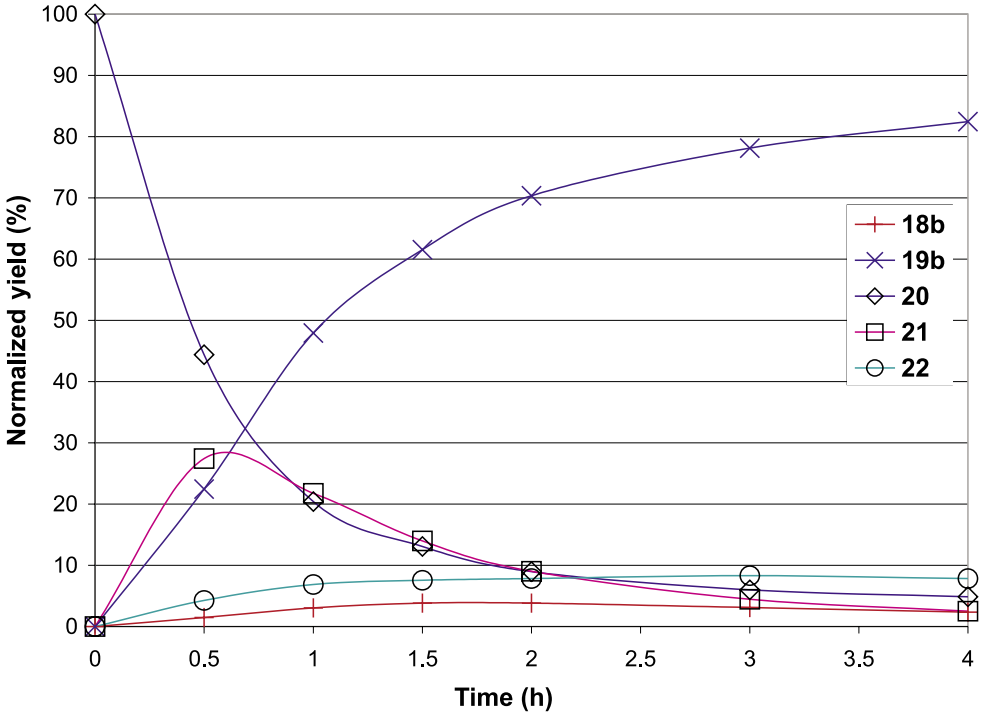
Fig. 5. Product yields as a function of time for the photolysis of substituted *trans*-stilbene **20** in methanol.



products derived from the cation **3**, specifically the ethers **19**. As shown in the control experiments involving **18a** and **18b**, there is no pathway for converting **18** to **19**. Rather, the secondary photochemical reaction is addition of the solvent to the excited state of the substituted *trans*-stilbene **20**. As clearly shown by the steady-state photolysis results, cation-derived products (i.e., **18** and **19**) can be formed in reasonable efficiency from **20** under the same reaction conditions used for the photolysis of ester **1**. Furthermore, this reaction favours the ethers **19** over **18**, which is the reverse of the regiochemistry observed for the photolysis of **1**. The LFP experiments demonstrate that **20** is formed rapidly upon irradiation of **1**, and will be available to absorb competitively with **1** very early in the photolysis experiments involving the ester. Therefore, as the substituted *trans*-stilbene **20** accumulates during the photolysis of **1**, the photochemistry of **20** will become more important, and **19** (formed primarily from **20**) will eventually be formed more rapidly than **18** (formed primarily from **1**). Indeed, even if the formation of **20** did not make the observation of benzylic carbocations by LFP impossible (by obscuring the wavelengths of interest), the observation of a signal corresponding to cation **3** would not be conclusive evidence for the rearrangement of interest. Unfortunately, the rapid formation of **20** upon photolysis of **1** makes the ester a poor substrate for the investigation of cation rearrangements. Our results are similar to those of Lee-Ruff and co-workers (11) (Scheme 2), where the desired cation rearrangement is too unfavourable to compete with rapid quenching by the alcohol solvent (either by nucleophilic attack or by deprotonation). However, the photochemistry of **1** is further complicated by the fact that the by-products themselves react by secondary photochemistry, making reliable assessment of the rearrangement extremely difficult.

There are several other points that need to be addressed for a thorough understanding of the photochemistry of **1** and its photoproducts. Firstly, although deprotonation of cation **2** or **3** appears to be the most likely pathway for formation of **20**, more study is needed to rule out other mechanisms. Work is in progress to examine the possibility that substituted stilbenes **20** and **21** are produced by either a radical pathway or by concerted photochemical elimination of acetic acid from **1**. In addition, the 1,2,2-trimethyl derivative of **1** is currently being synthesized. This substrate may allow the observation of a rearrangement without the complications present for **1** because rearrangement and nucleophilic trap-

Fig. 6. Product yields as a function of time for the photolysis of substituted *trans*-stilbene **20** in TFE.

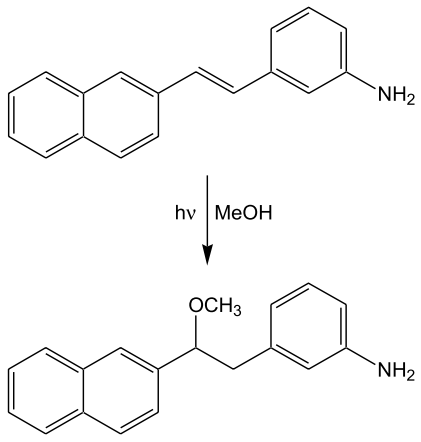


ping may be the only reactions available for the initial carbocation.

Secondly, the photochemical addition of alcohols to substituted stilbenes needs to be investigated in much greater detail. At first, the reaction appears to be analogous to the photohydration of substituted styrenes that has been studied extensively by McEwen and Yates (18), who demonstrated that excitation of 3-methoxystyrene in water gave the Markovnikov addition product faster than 4-methoxystyrene (another example of the photochemical meta effect). Additional support for the presence of a carbocation intermediate in such photochemical additions was provided by McClelland and co-workers (19), who found that laser flash photolysis of 4-methoxystyrene in TFE produced a transient absorption signal at 340 nm that was attributed to the corresponding cation. However, the presence of a second aromatic ring in the single chromophore of the substituted stilbenes makes the assessment of substituent effects much more complicated than for substituted styrenes (with regards to both the rate of the reaction and the regiochemistry of the addition).

A survey of the literature indicates that the photochemical addition of methanol to a variety of substituted stilbenes was first observed by Laarhoven and co-workers (20). In contrast to the results for substituted styrenes, the yield of stilbene–solvent adduct was found to be independent of acid concentration. This suggested that protonation of the singlet excited state is not the rate-limiting step in the photochemical addition of methanol to substituted stilbenes. With the aid of experiments conducted in deuterated methanol, the authors concluded that the addition of methanol to stilbenoid systems occurs via two competing mechanisms: (*i*) direct addition across the central bond; and (*ii*) rearrangement of the excited state via a 1,2-hydride shift to give a carbene intermediate, which then inserts directly to the methanol O—H(D) bond. However, the influence of electron-rich substituents in the meta position was never addressed (the only compound examined with meta substitutents was the symmetric 3,3′-dimethylstilbene). In more recent work, Lewis et al. (21, 22) have made several detailed studies of the effect of electron-donating substituents (mostly amino) on the fluorescence behaviour of substituted stilbenes and related compounds. These results indicate that stilbenes with electron-donating meta-substituents have longer singlet lifetimes and higher fluorescence quantum yields than the para-substituted analogues. Furthermore, the authors attribute this observation to a higher barrier for bond torsion in the meta-substituted cases. Addition of methanol was only observed in one case (21) (eq. [2]). However, methanol was not employed as a solvent for many of the photophysical studies that were of interest to the authors, so the reaction may in fact be more general.

[2]



From the results of the current study, just how the photochemistry of **20** fits with the examples in the literature is not yet clear. The rapid addition of the solvent (TFE in particular) appears to be because of the two meta substituents (the 3,5-dimethoxyphenyl ring), while the preferred regiochemistry is governed by the para substituent (4-methoxyphenyl ring). We had originally believed that the increased reactivity of **20** in TFE compared to methanol could be attributed to the greater effective acidity of the former solvent, which might lead to more rapid protonation of the excited state. However, the study by Laarhoven and co-workers (20) seems to indicate that the mechanism of solvent addition may be even more complicated. Clearly, a larger set of stilbene derivatives is required to confidently assess the factors controlling the reaction. This work is currently in progress.

Experimental

General procedures

Melting points were determined on a Fisher–Johns apparatus and are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded in deuterated chloroform on a Bruker AC 250F instrument, and chemical shifts are reported as parts per million (ppm) relative to tetramethylsilane internal standard. The coupling constants of the ABX systems observed in several compounds were analysed by matching the line positions with those of simulated spectra. Gas chromatography was performed on a Perkin-Elmer Autosystem XL instrument (controlled by a computer with TurboMass and TurboChrom software) with one Turbomass detector and one FID (both columns: Supelco 30 m/0.25 mm MDN-5S 5% phenyl methylsiloxane, film thickness 0.50 μm). For GC–MS, the injection volume was 1 μL; mass spectral data are reported in units of mass over charge (*m*/*z*) with intensities relative to the base peak (in brackets). For GC-FID, an injection volume of 2.5 μL was used. The same temperature program was used for both detectors: 60°C for 1 min, ramp at 20°C/min to 240°C, hold at 240°C for 20 min. Ultraviolet spectra were recorded on a Varian–Cary Bio 100 spectrometer.

Methanol, water, ethyl acetate, and hexanes were all distilled prior to use. Dichloromethane, benzene, dimethylsulfoxide (DMSO), TFE, pentane, and the deuterated solvents were all reagent grade, while acetonitrile was HPLC grade (these solvents were used without extra purification). Tetrahydrofuran (THF) was distilled from sodium–benzophenone, and then a second time from lithium aluminium hydride before being kept under nitrogen. All starting materials were supplied by Aldrich Chemicals, with the exception of 3,5-dimethoxyaniline and 3,5-dimethoxybenzaldehyde (Avocado Chemicals). Thin layer chromatography was performed using plates from Eastman-Kodak. Preparative chromatography was performed using 60–250 mesh silica gel from Silicycle.

Synthetic procedures

3,5-Dimethoxybromobenzene (16)

This compound was prepared from the diazonium ion made from 3,5-dimethoxyaniline using the procedure described (12) for the synthesis of *o*-bromochlorobenzene, yield 33%: mp 64–65°C, lit. (13) mp 64–66°C. ^{1}H NMR δ: 6.66 (d, 2H, J = 2.4 Hz), 6.37 (t, 3H, J = 2.4 Hz), 3.76 (s, 6H). ^{13}C NMR δ: 161.2, 123.0, 109.8, 99.8, 55.5. GC–MS *m*/*z*: 218 (82.6), 216 (100.0), 108 (69.7), 79 (41.6), 77 (56.2), 63 (48.9), 51 (26.3).

2-(4-Methoxyphenyl)ethanal (17)

This compound was prepared from 4-methoxybenzaldehyde by glycidic ester condensation as described (14), yield of 74% over three steps: ^{1}H NMR δ: 9.66 (d, 1H, J = 2.4 Hz), 7.09 (d, 2H, J = 8.5 Hz), 6.88 (d, 2H, J = 8.5 Hz), 3.75 (s, 3H), 3.57 (d, 2H, J = 2.4 Hz). ^{13}C NMR δ: 199.8, 159.0, 130.8, 123.9, 144.4, 55.2, 49.6. GC–MS *m*/*z*: 121 (100), 91 (20.5), 78 (23.9), 77 (31.2), 51 (12.2).

1-(3,5-Dimethoxyphenyl-2-(4-methoxyphenyl)ethan-1-ol (15)

For this reaction, all glassware was dried in an oven and purged with nitrogen gas prior to use. Liquid transfers were performed using a cannula needle under positive pressure. A solution of 3,5-dimethoxybromobenzene **16** (4.00 g, 18.4 mmol) in THF (20 mL) was prepared, and then transferred to a dropping funnel atop a three-necked 100 mL round-bottomed flask containing magnesium turnings (2.68 g, 110 mmol) in THF (5 mL). Approximately 10% of the aryl halide solution was run into the flask, along with a small crystal of iodine. After 15 min of stirring, the yellow colour of the iodine disappeared, and the mixture began to reflux. The remaining solution in the dropping funnel was added to the magnesium over 15 min, and the mixture was refluxed for 30 min after the addition was complete. After cooling to room temperature, the resulting orange solution was transferred under nitrogen to a clean three-necked flask.

A solution of 2-(4-methoxyphenyl)ethanal **17** (2.76 g, 18.4 mmol, distilled under vacuum prior to use) in THF (20 mL) was prepared. The solution was then added dropwise to the solution containing the Grignard reagent, and the resulting mixture was refluxed for 30 min after the addition was complete. After cooling to room temperature, the yellow solution was poured into a separatory funnel containing saturated ammonium chloride solution (100 mL) and dichloromethane (50 mL). The layers were separated, and the aqueous portion was extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with distilled water and saturated sodium chloride solution (2 × 75 mL each). After drying over anhydrous magnesium sulfate and filtering, the solvent was removed under reduced pressure to give 5.10 g of the product alcohol (96%). Further reactions were performed using the crude material, although characterization was performed using a sample recrystallized from ethyl acetate – hexanes, mp: 97–99 °C. ^{1}H NMR δ: 7.09 (d, 2H, J = 8.6 Hz), 6.83 (d, 2H, J = 8.6 Hz), 6.49 (d, 2H, 2.4 Hz), 6.36 (t, 1H, J = 2.4 Hz), 4.76 (m, 1H, J_1 = 8.5 Hz, J_2 = 4.9 Hz, J_3 = 2.4 Hz), 3.77 (s, 9H), 2.95 (m, 1H, J_1 = 13.7 Hz, J_2 = 4.9 Hz), 2.89 (m, 1H, J_1 = 13.7 Hz, J_2 = 8.5 Hz), 2.07 (d, 1H, J = 2.4 Hz). ^{13}C NMR δ: 160.8, 158.4, 146.5, 130.5, 130.0, 113.9, 103.8, 99.6, 75.4, 55.4, 55.3, 45.1. GC–MS *m*/*z*: 271 (5.6), 270 (35.8), 167 (13.1), 139 (35.8), 122 (100.0), 121 (49.9), 77 (16.0). HR-MS calcd.: 288.1361; found: 288.1357 ± 0.0008.

1-(3,5-Dimethoxyphenyl)-2-(4-methoxyphenyl)ethyl ethanoate (1)

This compound was prepared using the method of Steglich and Neises (15). A solution of *N*,*N*-dimethyl-4-aminopyridine (63 mg, 0.52 mmol) and acetic acid (312 mg, 5.2 mmol) in dichloromethane (25 mL) was prepared, and then added to a solution of 1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethan-1-ol **15** (1.5 g, 5.2 mmol) in dichloromethane (30 mL). After the resulting solution was cooled in an ice bath, 1,3-dicyclohexylcarbodiimide (1.17 g, 5.67 mmol) was added in one portion. The resulting mixture was stirred at 0°C for 5 min, and then allowed to stir at room temperature for 3 h. The urea precipitate was filtered off, the solvent was removed under reduced pressure, and the residue was taken up in dichloromethane (50 mL) and filtered again. The clear solution was then washed with 0.5 M hydrochloric acid and distilled water (2 × 25 mL each). The organic material was then dried with anhydrous magnesium sulfate, filtered, and the solvent removed under reduced pressure to give a clear oil. The oil was adsorbed onto silica for column chromatography. Using 5% ethyl acetate – hexanes as the eluant provided 1.5 g of a solid product, which was recrystallized from the same solvent mixture to give 1.2 g of colourless crystals (70%), mp: 68–69°C. ^{1}H NMR δ: 7.03 (d, 2H, J = 8.6 Hz), 6.78 (d, 2H, J = 8.6 Hz), 6.40 (d, 2H, J = 2.4 Hz), 6.37 (t, 1H, J = 2.4 Hz), 5.81 (m, 1H, J_1 = 7.9 Hz, J_2 = 6.1 Hz), 3.77 (s, 3H), 3.75 (s, 6H), 3.08 (m, 1H, J_1 = 14.0 Hz, J_2 = 7.9 Hz), 2.97 (m, 1H, J_1 = 14.0 Hz, J_2 = 6.1 Hz), 2.02 (s, 3H). ^{13}C NMR δ: 170.1, 160.7, 158.3, 142.6, 130.5, 129.1, 113.6, 104.6, 99.7, 76.7, 55.3, 55.2, 42.1, 21.2. GC–MS *m*/*z*: 270 (41.5), 167 (49.1), 139 (20.3), 121 (100), 77 (14.9). HR-MS calcd.: 330.1467; found: 330.1461 ± 0.0008.

1-(3,5-Dimethoxypheny)-2-(4-methoxyphenyl)-1-methoxyethane (18a)

A 60% sodium hydride – oil suspension (0.08 g of suspension, 0.002 mmol NaH) was washed with hexane to remove the oil. After decanting the washes, the residue was taken up in DMSO (2 mL) and added to a solution of 1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethan-1-ol **15** (0.288 g, 1.00 mmol) in DMSO (5 mL). The mixture was stirred at room temperature for 30 min, and then a solution of methyl iodide (0.284 g, 2.00 mmol) in DMSO (5 mL) was added dropwise. After stirring the solution for 3.5 h, distilled water (12 mL) was added slowly to quench the reaction. The organic layer was drawn off, and the aqueous portion was extracted with dichloromethane (3 × 10 mL). The combined organic material was washed with distilled water (3 × 25 mL), dried with anhydrous magnesium sulfate, and filtered. Removal of the solvent under reduced pressure gave 0.25 g of material, which was adsorbed onto silica for column chromatography. Elution using 2.5% ethyl acetate – hexanes gave the pure ether (0.098 g, 32%). Characterization was performed on a sample that was further purified by bulb-to-bulb distillation. ^{1}H NMR δ: 7.03 (d, 2H, J = 6.7 Hz), 6.78 (d, 2H, J = 6.7 Hz), 6.38 (m, 3H), 4.21 (dd, 1H, J_1 = 5.5 Hz, J_2 = 7.6 Hz), 3.77 (s, 3H), 3.75 (s, 6H), 3.20 (s, 3H), 3.01 (dd, 1H, J_1 = 7.6 Hz, J_2 = 13.7 Hz), 2.82 (dd, 1H, J_1 = 5.5 Hz, J_2 = 13.7 Hz). ^{13}C NMR δ: 160.8, 158.0, 144.4, 130.4, 113.5, 104.6, 99.6, 85.4, 56.9, 55.3, 55.2, 43.8. GC–MS *m*/*z*: 303 (0.8), 302 (4.4), 271 (1.5), 270 (6.3), 182 (10.4), 181 (100.0), 121 (12.1). HR-MS calcd.: 302.1518; found: 302.1522 ± 0.0008.

1-(3,5-Dimethoxypheny)-2-(4-methoxyphenyl)-1-(trifluoroethoxy)ethane (18b)

This compound was prepared using the method of Falck et al. (17). To a solution of 1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethan-1-ol **15** (0.300 g, 1.04 mmol) in benzene (20 mL) was added 1,1′-(azodicarbonyl)dipiperidine (0.525 g, 2.08 mmol). The flask was purged with nitrogen for 10 min, and tri(*n*-butyl)phosphine (0.421 g, 2.08 mmol) was added. After stirring the reaction mixture for another 15 min, TFE (1.04 g, 10.4 mmol) was added. The mixture was stirred at room temperature for 1 h, and the solvent was then removed under reduced pressure. The residue was taken up in dichloromethane, filtered, and the liquid then adsorbed onto silica gel for column chromatography. Elution with 5% ethyl acetate – hexanes gave the desired product (0.154 g, 40% yield). ^{1}H NMR δ: 7.03 (2H, d, J = 8.6 Hz), 6.78 (d, 2H, J = 8.6 Hz), 6.38 (s, 3H), 4.43 (dd, 1H, J_1 = 5.5 Hz, J_2 = 7.3 Hz), 3.77 (s, 3H), 3.75, (s, 6H), 3.64 (m, 2H), 3.09 (dd, 1H, J_1 = 14.0 Hz, J_2 = 7.3 Hz), 2.86 (dd, 1H, J_1 = 14.0 Hz, J_2 = 5.5 Hz). ^{13}C NMR δ: 161.0, 158.2, 142.6, 130.5, 129.7, 124.0 (q, J = 278.6 Hz), 113.5, 104.6, 100.1, 84.9, 66.0 (q, J = 34.3 Hz), 55.3, 55.2, 43.5. GC–MS (*m*/*z*): 371 (1.5), 370 (7.9), 270 (6.8), 250 (11.6), 249 (100.0), 166 (22.1), 121 (81.1). HR-MS calcd.: 370.1392; found: 370.1392 ± 0.0008.

2-(3,5-Dimethoxyphenyl)ethanal (26)

The sodium salt of 3-(3,5-dimethoxyphenyl)glycidic acid was prepared in two steps (62% yield) using the same procedures as described for the synthesis of 2-(4-methoxyphenyl)ethanal **17** (14). Decarboxylation of the sodium salt was accomplished using the method of Bullimore et al. (23), giving the desired aldehyde in 20% yield (12% over three steps). ^{1}H NMR δ: 9.69 (t, 1H, J = 2.4 Hz), 6.40 (t, 1H, J = 1.8 Hz), 6.35 (d, 2H, J = 1.8 Hz), 3.77 (s, 6H), 3.58 (d, 2H, J = 2.4 Hz). ^{13}C NMR δ: 199.2, 161.3, 134.0, 107.6, 99.3, 55.3, 50.7.

1-(4-Methoxyphenyl)-2-(3,5-dimethoxyphenyl)ethan-1-ol (25)

A solution of 4-bromoanisole (1.04 g, 5.55 mmol) in THF (10 mL) was prepared under nitrogen, and then transferred to a dropping funnel atop a three-necked 100 mL round-bottomed flask containing magnesium turnings (0.81 g, 33.3 mmol). Approximately 10% of the aryl halide solution was added to the magnesium along with an iodine crystal, and the reaction began within 10 min. The remaining aryl halide solution was added over 5 min, and the resulting mixture was heated to reflux for 30 min after the addition was complete. After cooling to room temperature, the resulting orange solution was transferred under nitrogen to a clean three-necked flask.

A solution of 2-(3,5-dimethoxyphenyl)ethanal **26** (1.00 g, 5.55 mmol) in THF (10 mL) was added dropwise to the Grignard reagent, and the resulting mixture was refluxed gently for 30 min. The mixture was then cooled, and added to a separatory funnel containing saturated ammonium chlo-

ride (50 mL) and dichloromethane (25 mL). The layers were separated, and the aqueous portion was extracted with dichloromethane (2 × 50 mL). The combined organic extracts were washed with water and saturated sodium chloride (2 × 25 mL each), and then dried with anhydrous magnesium sulfate. Removal of solvent under reduced pressure gave a crude oil, which was purified by column chromatography (10% ethyl acetate – hexanes, eluant) to give the desired product (1.00 g, 63% yield). ^{1}H NMR δ: 7.26 (d, 2H, J = 8.5 Hz), 6.87 (d, 2H, J = 8.5 Hz), 6.33 (s, 3H), 4.81 (dd, 1H, J_1 = 8.5 Hz, J_2 = 4.9 Hz), 3.78 (s, 3H), 3.73 (s, 6H), 2.92 (m, 2H, J_1 = 8.5 Hz, J_2 = 4.9 Hz, J_3 = 13.7 Hz), 2.12 (s, 1H). ^{13}C NMR δ: 160.7, 159.0, 140.6, 136.1, 127.2, 113.7, 107.4, 98.6, 74.7, 55.3, 55.2, 46.3.

2-(3,5-Dimethoxypheny)-1-(4-methoxyphenyl)-1-methoxyethane (19a)

A 60% sodium hydride – oil suspension (0.083 g of suspension, 2.08 mmol NaH) was washed with hexane to remove the oil. After decanting the washes, the residue was taken up in DMSO (5 mL) and added to a solution of 2-(3,5-dimethoxyphenyl)-1-(4-methoxyphenyl)ethan-1-ol **25** (0.300 g, 1.00 mmol) in DMSO (10 mL). The mixture was stirred at room temperature for 30 min, and then a solution of methyl iodide (0.295 g, 2.08 mmol) in DMSO (5 mL) was added dropwise. After stirring the solution for 5 h, distilled water (15 mL) was added slowly to quench the reaction. The organic layer was drawn off, and the aqueous portion was extracted with dichloromethane (3 × 20 mL). The combined organic material was washed with distilled water and saturated sodium chloride solution (2 × 20 mL each), dried with anhydrous magnesium sulfate, and filtered. Removal of the solvent under reduced pressure gave 0.34 g of material, which was adsorbed onto silica for column chromatography. Elution using 5% ethyl acetate – hexanes gave the pure ether (0.24 g, 32%). Characterization was performed on a sample that was further purified by bulb-to-bulb distillation. ^{1}H NMR δ: 7.15 (d, 2H, J = 8.5 Hz), 6.87 (d, 2H, J = 8.5 Hz), 6.29 (t, 1H, J = 1.8 Hz), 6.26 (d, 2H, J = 1.8 Hz), 4.27 (dd, 1H, J_1 = 6.2 Hz, J_2 = 7.4 Hz), 3.80 (s, 3H), 3.71 (s, 6H), 3.17 (s, 3H), 3.06 (dd, 1H, J_1 = 13.4 Hz, J_2 = 7.4 Hz), 2.80 (dd, 1H, J_1 = 13.4 Hz, J_2 = 6.2 Hz). ^{13}C NMR δ: 160.4, 159.1, 140.9, 133.6, 128.0, 113.7, 107.4, 98.3, 84.4, 56.5, 55.2 (two signals), 45.0. GC–MS (*m*/*z*): 302 (not observed), 286 (9.3), 270 (6.7), 165 (11.5), 151 (29.8), 122 (9.2), 121 (100.0). HR-MS calcd.: 302.1518; found: 302.1526 ± 0.0008.

2-(3,5-Dimethoxypheny)-1-(4-methoxyphenyl)-1-(trifluoroethoxy)ethane (19b)

This compound was prepared using the method of Falck et al. (17). To a solution of 2-(3,5-dimethoxyphenyl)-1-(4-methoxyphenyl)ethan-1-ol **25** (0.300 g, 1.04 mmol) in benzene (20 mL) was added 1,1′-(azodicarbonyl)dipiperidine (0.525 g, 2.08 mmol). The flask was purged with nitrogen for 10 min, and tri(*n*-butyl)phosphine (0.421 g, 2.08 mmol) was added. After stirring the reaction mixture for another 15 min, TFE (1.04 g, 10.4 mmol) was added. The mixture was stirred at room temperature for 1 h, and the solvent was then removed under reduced pressure. The residue was taken up in dichloromethane, filtered, and the liquid then adsorbed onto silica gel for column chromatography. Elution with 5% ethyl acetate – hexanes gave the desired product (0.210 g, 55% yield). ^{1}H NMR δ: 7.16 (d, 2H, J = 9.2 Hz), 6.30 (d, 2H, J = 9.2 Hz), 6.31 (t, 1H, J = 1.8 Hz), 6.29 (d, 2H, J = 1.8 Hz), 4.50 (dd, 1H, J_1 = 5.5 Hz, J_2 = 7.3 Hz), 3.80 (s, 3H), 3.72 (s, 6H), 3.62 (m, 2H), 3.14 (dd, 1H, J_1 = 14.0 Hz, J_2 = 7.3 Hz), 2.83 (dd, 1H, J_1 = 14.0 Hz, J_2 = 5.5 Hz). ^{13}C NMR δ: 160.5, 159.6, 140.1, 132.0, 128.1, 124.0 (q, J = 278.6 Hz), 114.0, 107.4, 98.8, 84.1, 65.8 (q, J = 34.3 Hz), 55.3, 55.2, 44.8. GC–MS (*m*/*z*): 370 (1.1), 271 (5.8), 270 (27.6), 220 (10.6), 219 (100.0), 135 (27.3). HR-MS calcd.: 370.1392; found: 370.1389 ± 0.0008.

trans-*1-(3,5-Dimethoxyphenyl)-2-(4-methoxyphenyl)ethene (20)*

A solution of 1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethan-1-ol **15** (4.00 g, 13.9 mmol) in benzene (600 mL) was prepared in a three-necked round-bottomed flask. A portion of *p*-toluenesulfonic acid (0.29 g, 1.5 mmol) was added, and the solution was heated to reflux with stirring. Water was removed from the mixture by way of a Dean–Stark trap. After 6 h, analysis by GC–MS indicated that 97% of the starting material had reacted, and the reaction mixture was allowed to cool to room temperature. The solution was then washed with distilled water, and saturated sodium chloride solution (2 × 200 mL each). A portion of benzene (100 mL) was used to reextract the aqueous washes. The combined organic material was then dried with anhydrous magnesium sulfate, filtered, and the solvent was removed under reduced pressure to give an orange oil. Isolation of the desired product was achieved using column chromatography with 20% ethyl acetate – hexanes (eluant). Recrystallization of the resulting product from pentane gave white crystals (1.27 g, 34% yield), mp 55–57°C, lit. (24) mp 53–54°C. ^{1}H NMR δ: 7.43 (d, 2H, J = 8.6 Hz), 7.05 (d, 1H, J = 16.5 Hz), 6.91 (d, 1H, J = 16.5 Hz), 6.90 (d, 2H, J = 8.6 Hz), 6.65 (d, 2H, J = 2.4 Hz), 6.38 (t, 1H, J = 2.4 Hz), 3.83 (s, 9H). ^{13}C NMR δ: 161.0, 159.4, 139.7, 129.9, 128.7, 127.8, 126.6, 114.1, 104.3, 99.6, 55.4, 55.3. GC–MS *m*/*z*: 271 (17.6), 270 (100.0), 269 (15.5), 239 (19.7), 224 (13.0), 196 (12.7), 195 (12.33), 165 (10.3), 153 (12.4), 152 (17.6), 141 (10.5). HR-MS calcd.: 270.1256; found: 270.1263 ± 0.0008.

cis-*1-(3,5-Dimethoxyphenyl)-2-(4-methoxyphenyl)ethene (21)*

A solution of *trans*-1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethene **20** (0.40 g, 1.5 mmol) in acetonitrile (340 mL) was prepared in a large photolysis reaction vessel, and purged with nitrogen for 30 min. A 450 W, medium-pressure Hanovia mercury lamp with a Pyrex filter (300 nm cut-off) was employed to irradiate the solution for 30 min. Analysis by GC-FID indicated that by this time the mixture had achieved a photostationary state consisting of a 2:1 ratio of the *cis* and *trans* isomers. The solvent was removed under reduced pressure, and the residue was prepared for column chromatography. Separation of the isomers was achieved using 2.5% ethyl acetate – hexanes (eluant), and the pure *cis* isomer was isolated as a clear oil (0.15 g, 38% yield). ^{1}H NMR δ: 7.19 (d, 2H, J = 8.5 Hz), 6.78 (d, 2H, J = 8.5 Hz), 6.52 (d, 1H, J = 12.2 Hz), 6.44 (d, 1H, J = 12.2 Hz), 6.43 (d, 2H, J = 2.4 Hz), 6.32 (t, 1H, J = 2.4 Hz), 3.78 (s, 3H), 3.67 (s, 6H). ^{13}C NMR δ: 160.6, 158.7, 139.5, 130.3, 130.2, 129.6, 128.7, 113.5, 106.6, 99.7, 55.2. GC–MS *m*/*z*: 271

(16.44), 270 (100.0), 269 (17.5), 239 (22.5), 224 (14.5), 165 (10.6), 153 (12.7), 152 (18.6), 141 (10.6), 127 (11.2), 115 (14.6). HR-MS calcd.: 270.1256; found: 270.1254 ± 0.0008.

2,4,6-Trimethoxyphenanthrene (22)

A solution of *trans*-1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)ethene **20** (0.30 mg, 1.1 mmol) in methanol (340 mL) was prepared in a large photolysis reaction vessel. To promote the formation of the desired product, no nitrogen was used. A 450 W, medium-pressure Hanovia mercury lamp with a Pyrex filter (280 nm cut-off) was employed to irradiate the solution for 7 h. The solvent was removed under reduced pressure, and the residue was adsorbed onto silica and placed at the top of a dry-flash column (2 cm diameter, 7.5 cm length). Elution with 2.5% ethyl acetate – hexanes gave 0.10 g of a white solid. Recrystallization from methanol gave the desired product as clear crystals (0.076 g, 25% yield), mp 111–113°C. ^{1}H NMR δ: 9.08 (d, 1H, J = 2.8 Hz), 7.76 (d, 1H, J = 8.8 Hz), 7.65 (d, 1H, J = 8.6 Hz), 7.49 (d, 1H, J = 8.8 Hz), 7.17 (dd, 1H, J_1 = 2.8 Hz, J_2 = 8.6 Hz), 6.88 (d, 1H, J = 2.7 Hz), 6.74 (d, 1H, J = 2.7 Hz), 4.10 (s, 3H), 3.99 (s, 3H), 3.95 (s, 3H). ^{13}C NMR δ: 161.9, 160.0, 158.2, 158.1, 136.0, 131.6, 129.4, 128.1, 124.5, 115.4, 114.7, 109.6, 101.3, 99.0, 55.8, 55.4, 55.3. GC–MS (*m*/*z*): 269 (18.1), 268 (100.0), 225 (16.4), 210 (22.7), 152 (15.6), 139 (18.2). HR-MS calcd.: 268.1099; found: 268.1112 ± 0.0008.

1-(3,5-Dimethoxypheny)-2-(4-methoxyphenyl)ethane (23)

A solution of 1-(3,5-dimethoxyphenyl)-2-(4-methoxyphenyl)-1-methoxyethane **18a** (0.0523 g, 0.173 mmol) in methanol (50 mL) was prepared and poured into a quartz reaction vessel. After purging with nitrogen gas for 30 min, the stirred solution was irradiated for 5 h at 25°C. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (2.5% ethyl acetate– hexanes, eluant) to give the desired product (0.020 g, 42% yield). ^{1}H NMR δ: 7.10 (d, 2H, J = 8.5 Hz), 6.83 (d, 2H, J = 8.5 Hz), 6.33 (s, 3H), 3.79 (s, 3H), 3.77 (s, 6H), 2.84 (s, 2H). ^{13}C NMR δ: 160.7, 157.87, 144.3, 133.8, 129.4, 113.8, 106.5, 97.9, 55.3, 55.2, 38.5, 36.8. GC–MS (*m*/*z*): 273 (2.1), 272 (11.4), 151 (2.0), 122 (9.1), 121 (100.0).

2-(3,5-Dimethoxypheny)-1-(4-methoxyphenyl)propane (24)

This photoproduct was not synthesized or isolated; thus, the identification rests solely on the GC–MS spectrum (*m*/*z*): 287 (2.3), 286 (12.0), 165 (15.0), 122 (10.2), 121 (100.0). The molecular ion of *m*/*z* 286 and the major fragment ions of *m*/*z* 165 and *m*/*z* 122 (the two possible benzylic carbocations that may be formed by cleavage of the molecular ion) strongly support the assignment.

Photolysis procedures

In all four photolysis reactions, a similar procedure was used. The solid starting material (**1**: 100 mg, 0.30 mmol; **20**: 50 mg, 0.20 mmol) was placed in a 100 mL volumetric flask, and the flask was filled to the mark with the solvent of interest. After the substrate was fully dissolved, the solution was poured into a quartz reaction vessel and purged with nitrogen for 30 min. The solution was thermostated at 25°C with an immersion circulating water tube, and mixed with a magnetic stirrer. In the reactions involving **20**, an equimolar amount of acetic acid (11 μL, 0.20 mmol) was added to the solution, and the solution was stirred overnight to check for the presence of ground-state reactions (none were found). The photolyses were performed using a Rayonet reactor with 10 low-pressure mercury lamps (254 nm emission). While the reaction was in progress, 1 mL samples were analyzed using the GC conditions outlined above.

The purified photoproducts were used to obtain calibrations for the GC-FID response of each compound as a function of concentration. These calibrations were then used to convert the peak areas from the reaction chromatograms to concentrations. The concentrations of the components were then converted to percentages based on the initial concentration of the starting material and the amount of material consumed during the reaction.

Laser flash photolysis of **1** was performed using a 2.28×10^{-4} M solution in TFE, which had an absorbance of 0.45 at 266 nm. A portion of this solution was excited using a Continuum Nd:Yag NY-61 laser (266 nm, <8 ns/pulse, ≤15 mJ/pulse). Several time domains (10 ns to 50 μs) were used, as well as three different conditions: air-saturated, nitrogen-saturated, and oxygen-saturated.

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