The photochemistry of 3,3′,4,4′-tetramethoxy- and 4-hydroxy-3,3′,4′-trimethoxystilbene — models for stilbene chromophores in peroxide-bleached, high-yield wood pulps

William J. Leigh, T. Johnathan Lewis, Vincent Lin, and J. Alberto Postigo

Abstract: The photochemistry of the title compounds has been investigated in ethanol and tetrahydrofuran solution under aerobic and anaerobic conditions. Direct irradiation of *trans*-3,3′,4,4′-tetramethoxystilbene (*trans*-**1**) in deoxygenated ethanol leads to the rapid establishment of a photostationary state with the *cis* isomer, and the slower formation of the ethyl ether corresponding to addition of ethanol across the olefinic C=C bond and cyclobutane dimers. The same products are formed upon photolysis in the presence of oxygen under the same conditions but, in addition, two isomeric tetramethoxyphenanthrenes and 3,4-dimethoxybenzaldehyde are formed. Photolysis of *trans*-**1** in oxygenated tetrahydrofuran leads to the same products in different relative yields. Quantum yields for *cis,trans* photoisomerization, phenanthrene formation, and addition of ethanol have been determined by ferrioxalate actinometry. Direct irradiation of *trans*-4-hydroxy-3,3′,4′-trimethoxystilbene (*trans*-**2**) in ethanol solution also results in rapid *cis–trans* isomerization and the formation of (three) isomeric phenanthrene derivatives in photolyses carried out in the presence of oxygen, although the material balance is low. The various products of photolysis of *trans*-**2** have been independently synthesized by desilylation of the products isolated from photolysis of *trans*-4-*tert*-butyldimethylsiloxy-3,3′,4′-trimethoxystilbene (*trans*-**3**) under similar conditions. Fluorescence-quenching experiments have been carried out to determine the relative rates of quenching of the excited singlet states of *trans*-**1** and *trans*-**2** by alcohols and oxygen. The formation of aldehydes is proposed to arise via reaction of superoxide ion with stilbene radical cations, which are formed by electron-transfer quenching of the stilbene excited singlet state by oxygen.

Key words: stilbenes, lignin, photochemistry, photooxidation.

Résumé : On a étudié la photochimie des composés mentionnés dans le titre en solutions dans l’éthanol et le tétrahydrofurane, dans des conditions tant aérobiques qu’anaérobiques. L’irradiation direct du *trans*-3,3′,4,4′-tétraméthoxystilbène (*trans*-**1**) dans de l’éthanol désoxygéné conduit à la création rapide d’un état photostationnaire avec l’isomère *cis* et à une formation plus lente de l’éther éthylique correspondant à l’addition de l’éthanol sur la double liaison C=C oléfinique ainsi que des dimères cyclobutanes. Les mêmes produits se forment lors de la photolyse dans les mêmes conditions, en présence d’oxygène; toutefois, il se forme de plus deux tétraméthoxyphénanthrènes isomères ainsi que du 3,4-diméthoxybenzaldéhyde. La photolyse du *trans*-**1** dans du tétrahydrofurane oxygéné conduit à la formation des même produits avec des rendements relatifs différents. On a déterminé les rendements quantiques de la photoisomérisation *cis*, *trans*, de la formation du phénanthrène et de l’addition de l’éthanol par actinométrie ferrioxalate. L’irradiation directe du *trans*-4-hydroxy-3,3′,4′-triméthoxystilbène (*trans*-**2**) en solution dans l’éthanol effectuée en présence d’oxygène conduit aussi à une isomérisation *cis–trans* rapide et à la formation de (trois) dérivés phénanthrènes isomères, même si la balance des produits est faible. Les divers produits de photolyse du *trans*-**2** ont été synthétisés par des voies indépendantes par désilylation des produits isolés de la photolyse du *trans*-4-*tert*-butyldiméthylsiloxy-3,3′,4′-triméthoxystilbène (*trans*-**3**) dans des conditions semblables. On a effectué des expériences de désactivation de la fluorescence pour déterminer les vitesses relatives de désactivation des états singulets excités des composés *trans*-**1** et *trans*-**2** par les alcools et l’oxygène. On suggère que la formation des aldéhydes résulte de la réaction de l’ion superoxyde avec les cations radicaux du stilbène qui se forment par une désactivation du transfert d’électron de l’état singulet excité du stilbène par l’oxygène.

Mots clés : stilbènes, lignine, photochimie, photooxydation.

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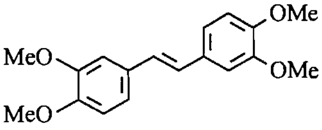
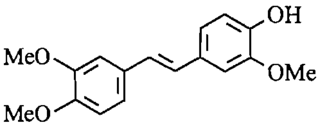
Introduction

The development of an understanding of the mechanisms of the various chemical processes responsible for the photochemical yellowing of lignin-rich pulp and paper products, and discovering ways of inhibiting these processes, is a matter of considerable commercial importance and intense current interest (1). It is generally agreed that oxidative processes involving the conversion of phenoxy radicals to quinonoid species represent the main contributor to photoyellowing, and various mechanisms for the formation of phenoxy radicals from photolysis of the more abundant chromophore types present in lignin, such as α-phenoxycarbonyl and -benzyl alcohol moieties, have been proposed (2–7).

Relatively little attention has yet been paid to the less-abundant chromophores that are present in lignin-rich papers as a result of condensation reactions that take place during alkaline bleaching processes. Castellan et al. have described qualitative results from the irradiation of several model compounds of this general type, stilbenes, benzofurans, biphenyls, diarylmethanes, and alkenylphenols, adsorbed on filter paper and in solution (8). This study was confined to measurements of the rates of photoinduced discolouration of the paper as a function of adsorbate and photolysis time. Interestingly, two of the compounds that proved to be most active under these conditions were *trans*-3,3′,4,4′-tetramethoxystilbene (*trans*-**1**) and *trans*-4-hydroxy-3,3′,4′-trimethoxystilbene (*trans*-**2**).



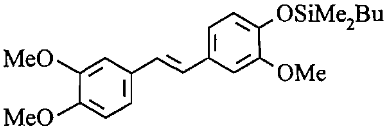
trans-**1**



trans-**2**

Zhang and Gellerstedt have reported the results of a more detailed investigation of the photochemistry of *trans*-2 on filter paper (9, 10). Using natural sunlight as an excitation source, they verified the substantial photoreactivity of this compound under these conditions, and isolated several dimers and a highly coloured *ortho*-quinonoid compound from the photolysis mixture. Interestingly, no evidence for the formation of the *cis* isomer or phenanthrene derivatives — the normal products expected from irradiation of stilbene derivatives (11–13) — was reported. While other explanations are possible, the "unusual" photoreactivity of **2** under these conditions may be due to the reaction medium being microcrystalline; the [2+2] photodimerization of stilbene and other phenylalkene derivatives in the crystalline solid phase is well documented (14). It remains to be determined whether these results are relevant to the photochemistry of stilbene chromophores in the amorphous molecular environment provided by natural lignin.

As part of a study designed to evaluate the importance of phenolic polyalkoxystilbenes and their photoproducts in contributing to the photoyellowing of lignin-rich materials, we report the results of the direct irradiation of **1**, **2**, and *trans*-4-*tert*-butyldimethylsiloxy-3,3′4′-trimethoxystilbene (*trans*-**3**) in ethanol and tetrahydrofuran solutions in the presence and absence of oxygen. The latter compound was prepared primarily as a synthon to aid in the preparation and isolation of the various phenanthrene derivatives expected from photooxidation of *trans*-**2**. We also report fluorescence-quenching studies of *trans*-**1**, *trans*-**2**, and a tetramethoxyphenanthrene derivative derived from the photooxidation of *trans*-**1**, which allows an assessment of the effects of oxygen and proton donors on the photochemistry of these compounds.



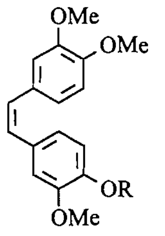
trans-**3**

Results

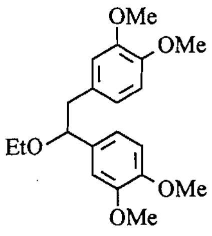
Compounds *trans*-**1** and *trans*-**2** were synthesized according to the published procedures, while *trans*-**3** was synthesized by silylation of *trans*-**2** with *tert*-butyldimethylsilyl chloride. The latter compound exhibited spectroscopic and analytical data consistent with its proposed structure (see Experimental section). The ultraviolet absorption spectra of *trans*-**1** and *trans*-**2** exhibit maxima at ~335 nm in tetrahydrofuran (THF) solution. No changes in the spectra could be detected upon saturating the solutions with oxygen.

The three compounds were irradiated as solutions (0.002–0.015 M) in 95% ethanol and dry tetrahydrofuran (THF), under both nitrogen and oxygen atmospheres, with the progress of the reactions monitored by capillary GC, GC–MS, and ^{1}H NMR spectroscopy. Photoproducts were isolated by thick-layer chromatography, after both short and long irradiation times, and identified on the basis of spectroscopic data (vide infra). As expected, establishment of a photostationary state with the corresponding *cis* isomer is substantially more rapid than the formation of other products and, with broadband irradiation through a Pyrex filter, the photostationary states are rich in the *cis* isomer in all cases. Quantitative detection of *cis*-**2** was carried out by ^{1}H NMR spectroscopy in deuterated solvents, as the compound was found to undergo facile thermal isomerization to *trans*-**2** in the GC injector port at the temperatures required for GC analysis of the mixtures.

In nitrogen-saturated ethanol solution, prolonged irradiation of *trans*-**1** and *trans*-**3** led to isolable yields of solvent-addition products, which were identified as **4** and **5**, respectively; the latter consisted of a mixture of two regioisomers, which were not further separated. GC analysis of the photolysates during the very early stages of photolysis verified that the formation of these products accompanies photoisomerization to the *cis* isomers. Cyclobutane dimers **6**–**8** were also isolated; their yields were generally higher in irradiations carried out using the higher stilbene concentrations, but the concentration dependence was not examined in detail. These products could not be detected by GC analysis under the conditions employed, but were readily detectable in the ^{1}H NMR spectra of the crude reaction mixtures. Irradiation of oxygen-saturated ethanol solutions led to the additional formation of phenan-



cis-**1** (R = Me)
cis-**2** (R = H)
cis-**3** (R = Si^tBuMe_2)



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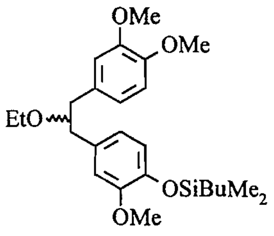

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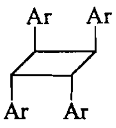

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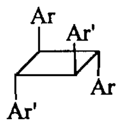
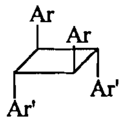


7*a*

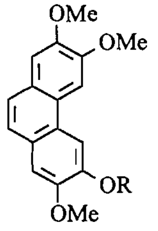


8*a*,*b*

Ar = 3,4-dimethoxyphenyl

a Ar' = 4-($Me_2{}^tBuSiO$)-3-methoxyphenyl

b Ar' = 4-hydroxy-3-methoxyphenyl



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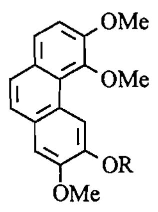

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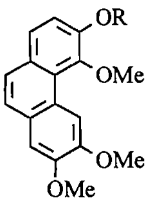
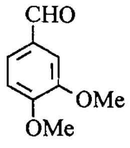


11

a R = Me
b R = H
c R = Si^tBuMe_2



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threne derivatives **9**–**11**, which were isolated by thick-layer chromatography, and 3,4-dimethoxybenzaldehyde (**12**). Minor yields of **9**–**11** were also obtained in the nitrogen-atmosphere experiments, but this was shown to be due to diffusion of air into the irradiation cells during the course of the experiment. Irradiation in THF solution under similar sets of conditions afforded the same products, with the exception of **4** and **5**. Prolonged irradiation of both *trans*-**1** and *trans*-**3** resulted in the development of a yellow colour and the formation of several minor products in each case. These could be detected by GC and GC–MS, but could not be isolated owing to their small yields; GC–MS data for some of these compounds are included in the Experimental section. Small amounts of highly coloured fractions containing mixtures of relatively polar minor products were generally obtained from the thick-layer plates, but the amounts were too low to warrant further attempts at separation. The infrared spectra of these mixtures showed them to be rich in carbonyl absorptions.

Prolonged irradiation of oxygen-saturated ethanol or THF solutions of *trans*-**2** led to the development of a deep yellow-brown colour, complex product mixtures, and poor material balances. Phenanthrenes **9***b*–**11***b* were identified as photoproducts on the basis of GC coinjections of authentic samples, which were synthesized by desilylation of **9***c*–**11***c* with tetrabutylammonium fluoride. In addition, a cyclobutane dimer (**8***b*) was isolated in low yield from irradiation in THF solution.

Table 1 summarizes the products obtained from irradiation of the three compounds under the various conditions employed, along with their chemical yields and material balances, as estimated by a combination of GC and ^1H NMR analysis of crude reaction mixtures.

The phenanthrenes **9**–**11** were identified on the basis of their ^1H and ^{13}C NMR, mass, and UV absorption spectra; NMR was particularly useful for the regiochemical assignments of individual sets of regioisomers. Compound **9***a* could be easily distinguished from **10***a* by NMR, owing to σ_v molecular symmetry. Phenanthrene **9***c* could be readily distinguished from **10***c* and **11***c* from the aromatic proton region in the ^1H NMR spectra, and by comparison to the spectra of **9***a* and **10***a*. Two of the compounds (which, coincidentally, elute together under our GC conditions) show singlets at $\delta \sim 9.2$ (due to the C4 ring proton) and must therefore possess alkoxy substitution at the 5-position of the phenanthrene ring system; by default, the compound without a singlet at $\delta \sim 9.2$ can be assigned to **9***c*. The aromatic region of the ^1H NMR spectrum of this compound compares quite favourably with that in the spectrum of the symmetrical tetramethoxyphenanthrene derivative **9***a*; the spectrum shows single-proton singlets at 7.76 and 7.88 ppm, a two-proton singlet at 7.53 ppm, and single-proton singlets at 7.19 and 7.20 ppm. This should be compared with the spectrum of **9***a*, which shows two-proton singlets at 7.79, 7.55, and 7.21 ppm. ^1H nOe experiments were employed to distinguish between **10***c* and **11***c*. The C7/C8 protons give rise to an AX splitting pattern, with doublets at ca. 7.2 and 7.6 ppm. Irradiation of the *tert*-butyl methyl singlets at $\sim$1.08 ppm results in nOe enhancement of the singlet at 9.2 ppm for the compound assigned as **10***c*, and enhancement of the doublet at δ7.15 for the compound assigned as **11***c*. Irradi-

Table 1. Product yields from irradiation of stilbenes **1–3** in 95% ethanol and THF under various conditions.[a]

Conditions				Products		
Compound	Solvent	Conc/M	Conversion (%)	Phenanthrenes	Others	Material balance (%)
trans-**1**	EtOH–N_2	0.002	30[c]	**9***a* (6%); **10***a* (5%)	**4** (19%)	n.d.
	THF–N_2	0.001	1	[d]	[d]	100
	EtOH–O_2	0.002	90[c]	**9***a* (26%); **10***a* (24%)	**4** (8%); **12** (32%)	51[e]
	THF–O_2	0.013	58[c]	**9***a* (21%); **10***a* (26%)	**12** (8%) + unident. (3%)	92[e,f]
trans-**2**	EtOH–O_2	0.003	5[c]	—	**12** (5%)	n.d.
	THF–N_2	0.001	1[g]	[d]	[d]	100
	THF–O_2	0.006	75[c]	**9***b* (19%); **10***b* (12%); **11***b* (22%)	**12** (14%) + unident. (8%)	80[e,f]
trans-**3**	EtOH–O_2	0.005	75[c]	**9***c* (15%); **10***c* (9%); **11***c* (21%)	**5** (15%); **12** (15%)	76[e,f]
	THF–O_2	0.0166	25[c]	**9***c* (5%); **10***c* (4%); **11***c* (11%)	**12** (5%) + unident. (0.25%)	95[e,f]

[a] Determined by GC–MS analysis of crude photolysis mixtures relative to internal standard, with no correction for detector response.

[b] Only those products observed by gas chromatography are reported (dimers **6–8** are undetectable by GC).

[c] The % conversion was determined by GC–MS, and calculated as 100% × (100% − %(*trans*-**1** + *cis*-**1**)$_{\text{final}}$)/(*trans*-**1**)$_{\text{initial}}$.

[d] *cis,trans* Isomerization is the only photoprocess observed at the given conversion.

[e] Calculated as 100 × (%*trans*-**1** + *cis*-**1**)$_{\text{NMR}}$/(%*trans*-**1** + *cis*-**1**)$_{\text{GC-MS}}$.

[f] Most of the deficiency in the material balance was due to formation of cyclobutane dimers.

[g] Calculated as 100% × (%(*trans*-**1** + *cis*-**1**)$_{\text{final}}$)/(*trans*-**1**)$_{\text{initial}}$.

ation of two of the methoxy singlets in the spectrum of the latter compound results in enhancement of the singlet at 9.2 ppm, thus verifying the assignment. Unfortunately, the methoxy singlets are too closely spaced in the 500 MHz spectrum of **10***c* to allow meaningful information to be gleaned from analogous experiments in this case.

Identification of the cyclobutane dimers **6–8** was made on the basis of their ^{1}H NMR and mass spectra (15, 16). The ^{1}H NMR spectrum of the *trans-syn-trans* dimer **6** shows a multiplet at δ ~ 4.4 ppm, which is characteristic of *trans-syn-trans* stereochemistry in stilbene photodimers (15). The spectra of the all-*trans* dimers **7***a* and **8***a,b* show characteristic resonances at δ ~ 3.7 ppm (16, 17). The identities of the isomers **7***a* and **8***a* were established on the basis of their mass spectral fragmentation patterns (18); that of **8***b* was analogous to that of **8***a*. In most cases, the presence of other regio- and (or) stereoisomeric dimers was evident in the crude irradiation mixtures or in chromatographic fractions, but they could not be characterized owing to either the small amounts obtained or to the fact that they were obtained as mixtures with other minor products. The presence of these products is not evident by GC or GC–MS analyses of the crude irradiation mixtures under the conditions employed.

Prolonged photolysis of **1–3** produced several additional minor products that were detectable by GC–MS, and strongly coloured solutions (particularly in the case of **2**). While all attempts to isolate these products have so far proved unsuccessful, their GC retention times and mass spectra suggest them to be demethylation products of the phenanthrenes; i.e., dimethoxyphenanthrenedione and phenanthrenetetrone derivatives. Our efforts to rigorously identify these products are continuing.

Quantum yields for direct *cis,trans* photoisomerization of *cis*- and *trans*-**1** were determined using 300 nm excitation in deoxygenated ethanol and tetrahydrofuran (THF) solution by electronic actinometry using 0.001 M solutions. In ethanol, $\phi_{t\rightarrow c} = 0.35 \pm 0.04$ and $\phi_{c\rightarrow t} = 0.41 \pm 0.04$ while in THF, $\phi_{t\rightarrow c} = 0.40 \pm 0.04$ and $\phi_{c\rightarrow t} = 0.51 \pm 0.06$. The photostationary state is *cis*-**1** / *trans*-**1** = 1.38 ± 0.05 in ethanol solution for 300 nm excitation. The quantum yields for *cis,trans* isomerization matched the quantum yields for disappearance of the starting isomers in both solvents.

Quantum yields for formation of **4**, **9***a*, **10***a*, and **12** in oxygen-saturated ethanol were estimated relative to $\phi_{t\rightarrow c}$ and $\phi_{c\rightarrow t}$ from the slopes of concentration vs. time plots. The values obtained are $\phi_4 = 0.007 \pm 0.003$, $\phi_{9a} = 0.008 \pm 0.003$, $\phi_{10a} = 0.005 \pm 0.002$, and $\phi_{12} = 0.009 \pm 0.004$.

Irradiation of *trans*-**1** was also carried out in the presence of 2,6-di-*tert*-butylphenol as a free radical scavenger. Thus, a solution of *trans*-**1** (0.0054 M), *n*-hexadecane as internal standard, and 2,6-di-*tert*-butylphenol (0.006 M) in dry tetrahydrofuran was oxygenated with a stream of dry oxygen for 10 min, irradiated for 6 h with 300 nm light, and monitored by GC–MS and TLC at 1 h intervals. The formation of aldehyde **12** was evident in the earliest stages of photolysis, but reached a maximum yield that fell off at long (>8 h) photolysis times. Compounds *cis*-**1**, **9***a*, and **10***a* were isolated and identified by comparison with authentic samples obtained from previous photolysis experiments. The mixture contained enhanced amounts (~5% total) of two of the minor products whose mass spectra are consistent with dimethoxyphenanthrenedione structures (see Experimental section). Significantly, no evidence was obtained for the formation of products of more extensive demethylation, under these conditions.

Direct irradiation (300 nm) of an oxygenated, 0.014 M solution of tetramethoxyphenanthrene **10***a* in THF yielded minute amounts of a single unidentifiable product after several hours of photolysis. Irradiation (254 nm) of an oxygenated THF solution containing **10***a* (0.07 M), *trans*-**1** (0.013 M), and *n*-hexadecane as internal standard (under conditions where **10***a* absorbs >99% of the light) yielded a qualitatively similar product distribution to that obtained from photolysis of *trans*-**1** under similar conditions: none of the products was formed in significantly enhanced or reduced yields under these conditions.

Samples of *cis*- and *trans*-**1** adsorbed on filter paper (ca. 0.5% by weight) were irradiated with 300 nm light (in a Rayonet reactor operating at half intensity) under an air atmosphere, extracted into dichloromethane, and analysed by gas chromatography. Photolysis of *trans*-**1** for 1 h under these conditions caused mild yellowing of the paper. GC analysis indicated that ca. 30% of the starting material had been consumed, but only a small amount of *cis*-**1** had formed (~2% of the amount of *trans*-**1** present) and there was no evidence for the formation of phenanthrenes **9***a* and **10***a*. Irradiation of *cis*-**1** under these conditions results in initially rapid conversion to the *trans* isomer, followed by behaviour similar to that observed upon irradiation of the sample of *trans*-**1** as described above.

Fluorescence emission spectra of *trans*-**1**, *trans*-**2**, and 2,3,6,7-tetramethoxyphenanthrene (**9***a*) were recorded in ethanol and THF solution. The spectra were unexceptional; those of *trans*-**1** and *trans*-**2** were indistinguishable from each other and from the spectrum of *trans*-**2** in toluene reported by Zhu and Gray (19), while that of **9***a* is similar to that of phenanthrene itself (20). Attempts were made to determine fluorescence lifetimes for the two stilbene derivatives using the time-correlated single-photon counting technique. In the case of *trans*-**1** in deoxygenated ethanol, fluorescence decay was too fast to be determined accurately with our system. This affixes an upper limit of ca. 0.5 ns for the singlet lifetime of *trans*-**1** in this solvent. In deoxygenated THF solution, fluorescence decay followed single exponential kinetics and exhibited an apparent lifetime of $\tau = 1.2 \pm 0.3$ ns. The lifetime was shortened to 0.9 ns in oxygen-saturated solution. Both values are very close to the limits of reliability of our system, and we do not consider them reliable. Similar results were obtained for *trans*-**2** in deoxygenated THF solution. The fluorescence lifetime of **9***a* was determined to be $\tau = 16.6 \pm 1.8$ ns in nitrogen-saturated THF, and $\tau = 3.5 \pm 0.4$ ns in oxygen-saturated solution under the same conditions.

The steady state fluorescence spectra of *trans*-**1** and *trans*-**2** in THF are quenched upon addition of ethanol, 2,2,2-trifluoroethanol (TFE), 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), or oxygen to the deoxygenated solution. Stern–Volmer quenching experiments led to the $k_q\tau$ values listed in Table 2.

Table 2. Stern–Volmer constants ($k_q\tau$/M^{-1}) for fluorescence quenching of *trans*-**1** and *trans*-**2** by ethanol (EtOH), 2,2,2-trifluoroethanol (TFE), and 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) in deoxygenated THF solution at 23°C.[a]

Alcohol	EtOH	TFE	HFIP	O_2
trans-**1**	0.13 ± 0.02	0.18 ± 0.03	0.27 ± 0.03	29 ± 9
trans-**2**	0.26 ± 0.04	0.36 ± 0.04	0.46 ± 0.03	47 ± 12

[a] Errors in the $k_q\tau$ values are given as twice the standard deviation from least-squares analysis of the Stern–Volmer plot.

Discussion

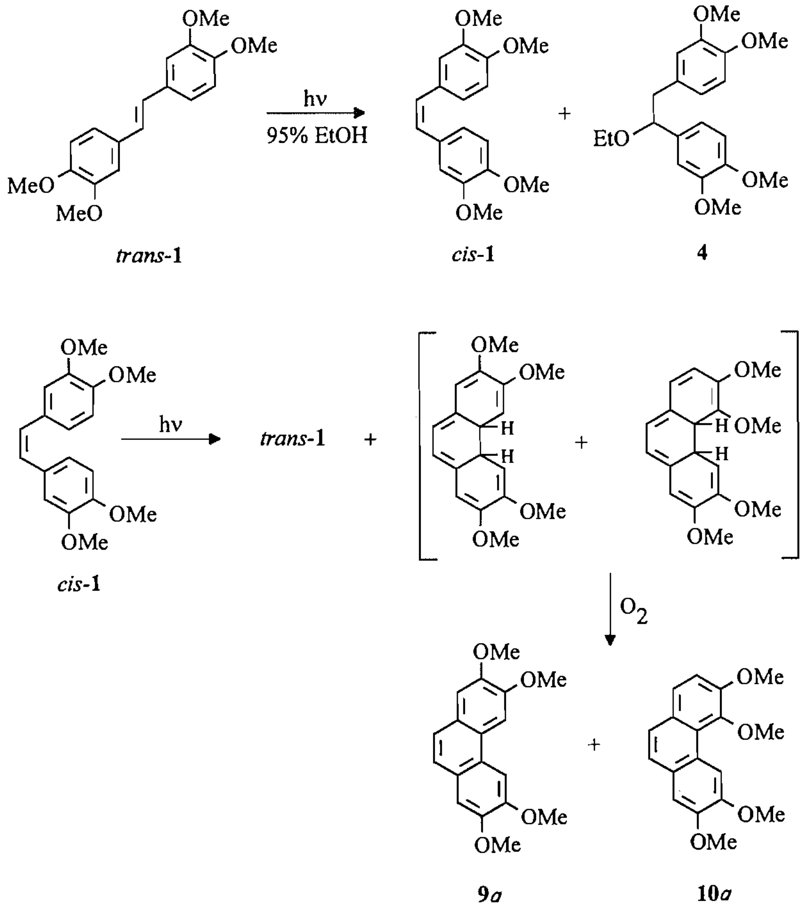
The general features of the photochemistry of *trans*-**1** and *trans*-**3** in solution are typical of the photochemistry of stilbene derivatives (11–13). *cis*,*trans* Photoisomerization occurs with relatively high efficiency, leading to a photostationary state that is rich in the *cis* isomer for 300 nm excitation; in rigorously deoxygenated, non-protic solvents, *cis*,*trans* isomerization is the only productive photoprocess detectable at short irradiation times. In the presence of oxygen, *cis*,*trans* isomerization is accompanied by the formation of 3,4-dimethoxybenzaldehyde (**12**) and phenanthrene derivatives (**9**–**11**), with efficiencies some two orders of magnitude lower than that of *cis*,*trans* isomerization. Phenanthrene derivatives are well known to be formed by a mechanism involving oxidation of 4a,4b-dihydrophenanthrene intermediates formed by photoelectrocyclic ring-closure of the *cis* isomer of the stilbene (11, 21). In the absence of oxidizing agents, these intermediates undergo thermal or photochemical cycloreversion to the *cis*-stilbene derivative from which they were formed. Thermal cycloreversion is relatively rapid; at room temperature in fluid solution, their lifetimes range from seconds to a few hours depending on substituent (21). Thus, the direct detection of these compounds in the present cases is not expected to be straightforward with the analytical methods employed in this work. The relevant chemistry is illustrated for *trans*-**1** in Scheme 1.

While compounds identifiable as 3,4,5,6-tetrasubstituted phenanthrene derivatives could not be detected in the irradiation mixtures from **1**–**3**, there appears to be little regioselectivity in the formation of the 2,3,6,7-tetrasubstituted regioisomer over the 2,3,5,6-isomer(s), at least according to GC analysis. Evidently, this lack of regioselectivity in the photocyclization of *meta*-substituted stilbene derivatives is common (11, 21).

The formation of ethyl ethers **4** (from **1**) and **5** (from **3**) in ethanol is presumably the result of excited singlet state quenching by protonation of the electron-rich stilbene double bond, followed by trapping of the resulting carbenium ion by the solvent. Photoprotonation of phenylalkenes is well documented (22–28), and is known to be enhanced by the presence of electron-donating aromatic substituents. The process occurs with relatively low efficiency (compared to *cis*,*trans* isomerization) in **1** and **3**, but competes effectively with phenanthrene formation and oxidative cleavage in the presence of oxygen. An upper limit for the rate constant for photoprotonation of *trans*-**1** by ethanol in THF solution is on the order of 5×10^8 M^{-1} s^{-1} (assuming a singlet lifetime of 1 ns), which seems reasonable considering the structure of the molecule compared to those of other phenylalkenes for which quantitative data exist in the literature (22–24, 28). It is interesting to note that the rate constant for this process varies by less than a factor of two for EtOH, TFE, and HFIP for both *trans*-**1** and -**2**, in spite of the fact that the pK_a's of the three alcohols vary substantially. To our knowledge, there are, unfortunately, no data available in the literature with which to compare these results.

The irradiations of *trans*-**1**–**3** in oxygenated ethanol solutions lead to lower yields of phenanthrenes than those obtained in oxygenated THF solutions at similar concentrations. As discussed above, the formation of ethyl ethers, corresponding to addition of ethanol across the olefinic C=C bond, provides a productive deactivation pathway for the excited states of *trans*-**1**–**3** that is not available in THF, but this accounts for only a fraction of the differences in the phenan-

Scheme 1.



threne yields in the two solvents. The main contributor appears to be a higher propensity for dimer formation in the protic solvent. Similar solvent effects on stilbene photodimerization have been documented previously (18).

The formation of 3,4-dimethoxybenzaldehyde (**12**) as a primary product of photolysis of **1** in oxygen-saturated solution most likely results from the reaction of the olefin radical cation with superoxide ion, formed as a result of electron transfer quenching of the excited singlet state of the stilbene by molecular oxygen. There is a considerable body of evidence that supports this conclusion. First, the sensitized photooxygenation of stilbene derivatives with cyanoaromatics and *some* dye sensitizers (e.g., methylene blue) has been shown to proceed by an electron transfer mechanism (29–31), in which electron transfer quenching of the excited sensitizer by the olefin, followed by reduction of molecular oxygen by the sensitizer radical anion, results in the ultimate formation of oxidative cleavage products through reaction of the olefin radical cation and superoxide ion. The initial product of this reaction is thought to be the corresponding 1,2-dioxetane (29–32), although evidence that an ozonide may be involved in these reactions has also been reported (33). In the present cases, we believe that the mechanism for formation of superoxide and stilbene radical cation is direct electron transfer quenching of the excited singlet state of the stilbene by molecular oxygen. This is supported by fluorescence-quenching experiments (Table 2), which indicate that oxygen quenching of *trans*-**1** and -**2** proceeds at the diffusion-controlled rate (note that the Stern–Volmer constants reported in Table 2 indicate a quenching rate constant of (2–5) × 10^{10} M^{-1} s^{-1}, assuming singlet lifetimes of 1 ns for the two stilbene derivatives). The oxidation potential of **1** ($E_{½}^{ox}$ = 0.82 V vs. SCE in acetonitrile;[2] a similar value can be expected for **2**) is clearly low enough that photoinduced electron transfer to molecular oxygen will be strongly exothermic. Once formed, $\mathbf{1}^{\cdot+}$ and $O_2^{\cdot-}$ can react to yield dioxetane **13** directly. This mechanism is related to that proposed for the photooxygenation of electron-rich styrenes and other arenes, which has been shown in some cases to proceed via direct excitation of a charge transfer complex between the arene and molecular oxygen (34, 35). However, no evidence for the formation of analogous charge transfer complexes could be obtained from the UV absorption spectra of *trans*-**1** and -**2** in oxygen-saturated THF or acetonitrile solution.

Another possible mechanism for the formation of **13** might involve generation of singlet oxygen ($^1O_2$) by back-electron-transfer of the initially produced radical ion pair (this should also produce the excited triplet state of **1**), followed by reaction of $^1O_2$ with ground state **1** (9). We believe that this mechanism can be discounted, on the basis that the relative yield of **12** (the product of decomposition of the presumed intermediate **13**) does not appear to be enhanced when the photolysis of

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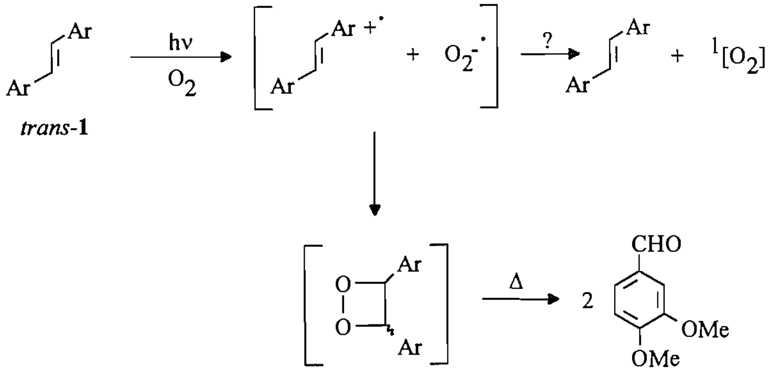
[2] We thank Professor M.S. Workentin for the oxidation potential measurement.

Scheme 2.



12

1 is sensitized by phenanthrene 9*a*. The phenanthrene can be expected to be a much more efficient sensitizer for the formation of superoxide ion (and thus $^1O_2$, by this mechanism) because of its longer singlet lifetime and lower oxidation potential compared to *trans*-**1** (36); fluorescence quenching experiments indicate that the excited singlet state of **9***a* is quenched just as rapidly by molecular oxygen as those of *trans*-**1** and -**2**. Phenanthrene **9***a* also has the potential of producing $^1O_2$ directly by triplet–singlet energy transfer, because intersystem crossing is expected to be efficient (37). In fact, the product distribution obtained in this experiment is similar to that produced in the direct irradiation of *trans*-**1**, suggesting that the dominant mechanism for reaction involves singlet energy transfer from **9***a* to **1**.

Thus, we suggest the tentative mechanism shown in Scheme 2 for the formation of **12** from photolysis of *trans*-**1** in oxygen-saturated solution. Further work is clearly required in order to conclusively identify the reactive oxygen species involved in the reaction, and to fully understand the mechanism(s) by which it is formed.

Of the three lignin-model stilbenes whose photochemistry has been investigated in the present work, **2** is the most relevant to the stilbene chromophores present in lignin-rich materials (10). It is also the most difficult to study because of the large number of minor, unisolable products produced upon its irradiation. Nevertheless, it is clear that UV irradiation of this compound in solution *does* result in the formation of products analogous to those produced from **1** under similar conditions: phenanthrenes derived from photocyclization/oxidation of the *cis* isomer, and products derived from oxidative cleavage of the olefinic double bond. Highly coloured (presumably) quinonoid materials are also formed, but in significantly higher yields than those obtained from photolysis of **1** or **3**.

The irradiation of **2** in solution bears only marginal resemblance to that obtained when the compound is adsorbed on filter paper (9). In the latter case, the main products are cyclobutane dimers and dimethoxybenzaldehyde **12**; minor products are reported to include a dimeric ether from addition of the phenolic OH in **2** across the double bond in a second molecule (which is related to the ethanol-addition products observed in the present work), and a stilbenequinone. In contrast to the solution phase results described here, no phenanthrene derivatives were reported. Furthermore, we observe the formation of only very minor amounts of compounds, tentatively identifiable as stilbenequinones, in the photolysis of **2** in oxygen-saturated solution. On the basis of our results for *trans*-**1**, it seems likely that the absence of phenanthrenes as photoproducts in the irradiation of *trans*-**2** on filter paper is due to the fact that the photostationary state consists of <5% of the *cis* isomer under these conditions. We believe that the extremely low *cis*-**1** content in the photostationary state for the filter paper irradiations is probably due to the reactant existing in a microcrystalline environment in which the *trans* isomer is thermodynamically favoured. The same is likely to be true for **2** under these conditions.

Summary and conclusions

Irradiation of polyalkoxystilbene derivatives in solution in the presence of oxygen leads to *cis,trans* isomerization, polyalkoxyphenanthrene formation, oxidative cleavage of the olefinic double bond, dimerization, and the formation of small amounts of highly coloured, carbonyl-containing compounds. The formation of phenanthrene derivatives is the result of photoelectrocyclization of the corresponding *cis*-stilbene isomer, followed by oxidation, and is a well-known reaction in stilbene photochemistry. For monochromatic 300 nm excitation in solution, the *cis*/*trans* photostationary state is rich in the *cis* isomer, so that cyclization to yield phenanthrene derivatives occurs with significant efficiency. The photostationary state obtainable with broadband irradiation with >300 nm light is undoubtedly lower in *cis* content, since the UV absorption spectra of the *cis* isomers extend slightly further to the red. However, our experiments show that phenanthrene formation still proceeds readily under these conditions.

Both the stilbenes and their phenanthrene photoproducts are powerful photoreductants, and are potentially capable of initiating oxidative processes involving reaction of superoxide ion and (or) singlet oxygen with *other components* in the natural lignin matrix. Defining the extent to which this might contribute to lignin photoyellowing is the subject of continuing investigation in our laboratory.

Experimental section

^{1}H NMR spectra were recorded on Bruker AC200, AC300, or AM500 spectrometers in deuteriochloroform solution, while ^{13}C NMR spectra were recorded on the Bruker AC200 or AM500 spectrometers. Spectra reported for new compounds were recorded on the AM500 spectrometer unless otherwise noted, and are reported in parts per million relative to tetramethylsilane. Infrared spectra were recorded in carbon tetrachloride solution on a Biorad FTS-40 FTIR spectrometer or as the neat samples in the case of liquids. Ultraviolet absorption spectra were recorded on a Perkin Elmer Lambda 9 spectrometer interfaced to an IBM PS/2-286 microcomputer, or on a Hewlett–Packard HP8451 UV spectrometer. Fluorescence emission and excitation spectra and fluorescence lifetimes were recorded on a Photon Technologies Inc. LS-100 spectrofluorometer/single-photon counting system, which is controlled by a 486-33 PC using software provided by the manufacturer. Single-photon counting experiments employed a hydrogen flashlamp.

Gas chromatographic analyses were carried out using a Hewlett–Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett–Packard 3396 integrator, and a DB-1 megabore capillary column (5 m × 0.53 mm; Chromatographic Specialties, Inc.). GC–MS analyses were carried out using a Hewlett–Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 microbore capillary column (30 m × 0.2 mm; Chromatographic Specialties, Inc.). Exact Masses were determined on a VGH ZABE mass spectrometer and employed a mass of 12.000 000 for carbon. Thick-layer chromatographic separations employed a Chromatotron (Harrison Research, Inc.) and 2 or 4 mm silica gel 60 (E. Merck) thick-layer plates.

Preparative photolyses were performed using a Hanovia 450 W medium-pressure mercury lamp and a Pyrex immersion well (at 20°C), or a Rayonet reactor equipped with 14 RPR-3000 Å lamps and a 120 mL capacity Pyrex container (at 27°C). Analytical-scale photolyses employed the latter in conjunction with a merry-go-round; samples (ca. 0.5 mL) were contained in 5 × 80 mm Pyrex tubes that were sealed with rubber septa. Experiments carried out using 254 or 419 nm radiation employed the Rayonet reactor equipped with 6 RPR-2537 or 10 RPR-4190 lamps, respectively.

Tetrahydrofuran (Caledon Reagent grade) was dried over sodium metal and distilled prior to use. Benzene (Fisher Reagent) was purified by several extractions with concentrated sulfuric acid, rinsed with dilute sodium bicarbonate solution, predried over sodium sulfate, and distilled from sodium metal. Methanol (Fisher Reagent) was distilled from magnesium. Ethanol (95%) was purchased from Caledon Chemical Co. and distilled prior to use. Absolute ethanol was purchased from BDH and distilled from magnesium. Pentane (BDH Omnisolv) was used as received from the supplier. *N,N*-Dimethylformamide (Caledon) was dried over potassium hydroxide and distilled prior to use. Neutral alumina, dichloromethane, diethyl ether, ethyl acetate, hexanes, potassium carbonate, potassium bicarbonate, anhydrous sodium sulfate, and HPLC-grade water were all used as received from Fisher Chemical Co. Benzophenone, *n*-butyllithium, *tert*-butyldimethylsilyl chloride, 3,4-dimethoxybenzylalcohol, *n*-hexadecane, imidazole, methylene blue, thionyl chloride, triphenylphosphine, and vanillin acetate were all used as received from Aldrich Chemical Co.

trans-3,3′,4,4′-Tetramethoxystilbene (*trans*-**1**) and *trans*-4-hydroxy-3,3′,4′-trimethoxystilbene (*trans*-**2**) were synthesized according to the method of Castellan et al. (8). They exhibited melting points (*trans*-**1**; mp 154.6–155.0°C; *trans*-**2**; mp 129.6–130.1°C) and spectroscopic data that were similar to the reported data in both cases.

trans-4-*tert*-Butyldimethylsiloxy-3,3′,4′-trimethoxystilbene (*trans*-3)

In a 100 mL round-bottom flask equipped with a condenser and magnetic stirrer were placed *trans*-**2** (1.0 g, 0.001 mol), *tert*-butyldimethylsilyl chloride (0.63 g, 0.0042 mol), imidazole (0.60 g, 0.0083 mol), and dry dimethylformamide (7 mL). The mixture was stirred at room temperature for 24 h, with periodic monitoring by thin-layer chromatography on neutral alumina using 15% ethyl acetate in hexane as the eluant. The product mixture was diluted with ether (15 mL), washed with water (2 × 5 mL), dried with anhydrous sodium sulfate, and filtered. Evaporation of the solvent yielded a slightly yellow solid, which was recrystallized from hexane–ethanol to yield colourless crystals of the desired product (1.18 g, 84%; mp 70.0–71.3°C); UV (ethanol) $\lambda_{max}(\varepsilon)$: 203 nm (36 800), 332 nm (39 400); IR: 3030 (s), 2960 (w), 2840 (w), 1601 (w), 1514 (s), 1465 (m), 1251 (s), 1027 (w), 902 (w) 815 (w); ^{1}H NMR, δ: 0.15 (s, 6H), 0.99 (s, 9H), 3.84 (s, 3H), 3.88 (s, 3H), 3.96 (s, 3H), 6.89 (d, 2H), 6.91 (m, 6H); ^{13}C NMR, δ: –4.6, 18.6, 25.7, 55.5, 55.9, 55.9, 108.7, 109.7, 111.3, 119.5(2), 121.0, 126.6, 126.9, 130.8, 131.5, 144.8, 148.7, 149.1, 151.1; MS, *m/e* (*I*): 400 (44), 343 (24), 328 (100), 286 (90), 271 (13), 73 (9). Exact Mass, calcd. for $C_{23}H_{32}SiO_4$: 400.207; found: 400.2076.

Preparation and isolation of photoproducts

(i) From irradiation of trans-*1*

(a) Irradiation of trans-*1 in 95% ethanol*

A continuously oxygenated solution of *trans*-**1** (0.30 g, 1.0 mmol) in 95% ethanol (500 mL) was placed in a Pyrex immersion well system and irradiated for 0.5 h with a 450 W medium-pressure mercury lamp. GC analysis of the mixture indicated the presence of five compounds, which were subsequently identified (in order of increasing retention time) as *cis*-**1**, **4**, **10***a*, *trans*-**1**, and **9***a*. The solvent was distilled in vacuo to yield a yellow solid residue, which was placed on the Chromatotron and eluted with a 0–7.5% ethyl acetate – hexane gradient. The five compounds eluted in the order **10***a* < *cis*-**1** < *trans*-**1** < **4** < **9***a* under these conditions. Compounds *cis*-**1**, **9***a*, and **10***a* were isolated in >90% purity as solids, and recrystallized several times from ethyl acetate – hexane mixtures. Compound **4** was isolated in ca. 80% purity after several repeated elutions, and finally isolated as a colourless oil by cyclic medium-pressure column chromatography on a 1 in. × 10 in. Merck Lobar silica gel column using 9% ethyl acetate in dichloromethane as the eluant. The purified yields of the five compounds were: *cis*-**1** (0.045 g), *trans*-**1** (0.055 g), **4** (0.061 g), **9***a* (0.065 g), **10***a* (0.020 g). They were identified on the basis of the following spectroscopic data.

cis-*3,3′4,4′-Tetramethoxystilbene* (cis-*1*): 0.045 g, 0.15 mmol, 15%, mp 119.3–120.2°C); UV (ethanol) $\lambda_{max}(\varepsilon)$: 200 nm (33 200), 296 nm (12 700); IR: 3030 (s), 2961 (w), 2839 (w), 1582 (w), 1513 (s), 1464 (m), 1421 (w), 1267 (s), 1140 (m), 1027 (m); ^{1}H NMR (300 MHz), δ: 3.71 (s, 6H), 3.90 (s, 6H), 6.40 (s, 2H), 6.77 (m, 2H), 6.90 (m, 4H); ^{13}C NMR, δ: 55.6, 55.8, 55.9, 108.6, 110.9, 111.3, 111.8, 119.5, 121.8, 126.7, 128.7, 130.2, 130.7, 148.1, 148.4, 148.7, 149.1; MS, *m/e* (*I*): 300 (100), 285 (20), 225 (10), 181 (8), 152 (9), 128 (11). Exact Mass, calcd. for $C_{18}H_{20}O_4$: 300.1374; found: 300.1377.

*1-Ethoxy-1,2-bis(3,4-dimethoxyphenyl)ethane (**4**)*: 0.061 g, 18%. UV (ethanol), $\lambda_{max}(\varepsilon)$: = 202 nm (79 560), 229 nm (19 750), 279 nm (6760); IR: 3059 (w), 2968 (s), 2968 (s), 2836 (s), 1591 (w), 1516 (w), 1262 (w), 1155 (w); ^{1}H NMR (300 MHz), δ: 1.2 (t, 3H), 2.8 (dd, 1H), 3.05 (dd, 1H), 3.75 (s, 3H), 3.80 (s, 6H), 3.85 (s, 3H), 4.3 (t, 1H), 6.5–6.8 (m, 6H); ^{13}C NMR, δ: 14.2, 15.3, 22.5, 44.5, 55.7, 55.8, 61.0, 64.1, 83.2, 109.5, 110.6, 110.8, 133.0, 119.3, 121.4, 131.2, 135.0, 147.4, 148.3, 149.0; MS (NH_3 CI), *m/e* (*I*): 364 (5), 301 (100), 195 (95), 151 (8).

*2,3,6,7-Tetramethoxyphenanthrene (**9a**)*: 0.065 g, 22%, mp 178.9–179.4°C; UV (ethanol), $\lambda_{max}(\varepsilon)$: 218 nm (26 960), 254 nm (52 430), 285 nm (32 460), 299 nm (20 240); IR: 3011 (s), 2960 (w), 2836 (w), 1512 (s), 1481 (s), 1255 (s), 1197 (s), 1160 (s), 1112 (m), 1041 (w); ^{1}H NMR, δ: 4.02 (s, 6H), 4.12 (s, 6H), 7.21 (s, 2H), 7.55 (s, 2H), 7.79 (s, 2H); ^{13}C NMR, δ: 55.9, 56.1, 102.8, 108.4, 124.3, 126.4, 128.3, 148.8, 149.3; MS, *m/e* (*I*): 298 (100), 283 (5), 255 (10), 240 (12), 225 (10), 212 (7), 169 (8), 139 (5), 126 (6). Exact Mass, calcd. for $C_{18}H_{18}O_4$: 298.1205; found: 298.1225.

*2,3,5,6-Tetramethoxyphenanthrene (**10**a)*: 0.020 g, 7%, mp 98–100°C; UV (ethanol), $\lambda_{max}(\varepsilon)$: 261 nm (65 600), 312 nm (12 590); IR: 3010 (s), 2960 (w), 2839 (w), 1514 (s), 1472 (s), 1422 (w), 1268 (s), 1241 (s), 1137 (w), 1103 (s), 1050 (w); ^{1}H NMR, δ: 3.96 (s, 3H), 4.03 (s, 3H), 4.04 (s, 3H), 4.08 (s, 3H), 7.22 (s, 1H), 7.28 (d, 1H), 7.49 (d, 1H), 7.55 (d, 1H), 7.63 (d, ^{1}H), 9.22 (s, 1H); ^{13}C NMR, δ: 55.5, 56.3, 59.8, 107.8, 108.5, 112.2, 123.6, 124.0, 124.4, 124.7, 125.0, 127.6, 128.2, 145.9, 148.2, 148.5, 150.7; MS, *m/e* (*I*): 298 (100), 283 (25), 255 (20), 240 (30), 225 (15), 197 (20), 169 (10), 139 (13), 126 (18), 87 (8), 63 (8). Exact Mass, calcd. for $C_{18}H_{18}O_4$: 298.1205; found: 298.1225.

(b) Irradiation of trans-*1 in THF*

A solution of *trans*-**1** (0.19 g, 0.63 mmol) and *n*-hexadecane (5.65 mg, 0.025 mmol) in dry tetrahydrofuran (5 mL) was placed in a Pyrex tube sealed with a rubber septum, oxygenated with a stream of dry oxygen for 10 min, and then irradiated for 4.5 h with 300 nm light (Rayonet reactor, 14 lamps, 27°C), with periodic bubbling of oxygen through the solution. GC analysis of the photolysis mixture indicated that the conversion of the starting material to products was ca. 80%. The photolysate consisted of a mixture of 3,4-dimethoxybenzaldehyde (**12**) (8%), *cis*-**1** (41%), **9***a* (11%), **10***a* (22%), and *trans*-**1** (17%), in order of increasing retention times. *cis*- and *trans*-**1** were found to be thermally stable under the gas chromatographic conditions employed. The identity of **12** was established by GC–MS and after chromatographic isolation from the mixture (vide infra).

After a total of 7.5 h of irradiation (resulting in a deep yellow solution), there was a further enrichment of the product mixture in **9***a*, **10***a*, and **12**, and a concomitant decrease in the concentration of **1**. At this point the material balance accounted for (by GC and GC–MS analyses) was only ca. 80%.

Two minor products were detected by GC–MS analysis after 4.5 h of irradiation; they were also present after 7.5 h of irradiation in higher concentrations (~3% of the total). Their GC retention times were similar to those of **9***a* and **10***a*. The two products exhibit the following GC–MS data, consistent with their having 1,2,6,7- and 2,3,6,7-phenanthrenetetrone structures: *m/e* (*I*): 238 (12), 221 (2), 167 (100), 151 (4), 139 (78), 124 (21), 108 (12), 95 (6), 77 (8), 71 (21), 65 (3), 51 (2); *m/e* (*I*): 238 (13), 220 (0.5), 167 (100), 151 (1), 139 (77), 124 (17), 108 (10), 95 (7), 77 (7), 71 (10), 65 (2), 51 (5).

The ^{1}H NMR spectrum of the crude photolysis mixture (7.5 h irradiation) revealed the presence of unaccounted-for resonances in the δ3.5–4.5 range; with the assumption that these are due to the cyclobutane ring protons of photodimers, integration indicated that they accounted for ca. 15% of the total material.

The solvent was distilled under vacuum, and the yellow oil that remained was chromatographed on the Chromatatron using a 2 mm silica gel plate. Elution with 10% ethyl acetate – hexane afforded **10***a* (0.063 g, 33%), *cis*-**1** (0.013 g, 7%), *trans*-**1** (0.007 g, 4%), **9***a* (0.038 g, 20%). Further elution with 35% ethyl acetate – hexane afforded two additional compounds. 3,4-Dimethoxybenzaldehyde (**12**, 0.004 g, 2%) was identified by comparison to an authentic sample, while cyclobutane dimer **6** was identified on the basis of the following.

cis,trans,trans-*1,2,3,4-Tetra(3,4-dimethoxyphenyl)cyclobutane (**6**)*: 0.057 g, 30%. ^{1}H NMR, δ: 3.63 (s, 6H), 3.78 (s, 6H), 4.27 (s, 2H), 6.49 (s, 1H), 6.50 (s, 1H), 6.65–6.90 (cplx m, 4H); ^{13}C NMR, δ: 47.54, 55.81, 55.97, 110.82, 112.09, 118.88, 120.04, 133.64, 147.36; MS, *m/z* (*I*): 601 (1), 300 (100), 285 (9), 151 (5); MS (NH_3 CI), *m/z* (*I*): 618 (100), 301 (45), 300 (54).

(c) Irradiation of trans-*1 in the presence of 2,6-di*-tert-*butylphenol*

A solution of *trans*-**1** (0.243 g, 0.81 mmol), *n*-hexadecane (16.9 mg, 0.0747 mmol), and 2,6-di-*tert*-butylphenol (0.186 mg, 0.901 mmol) in dry tetrahydrofuran (15.0 mL) was placed in a 20.0 mL Pyrex container, sealed with a rubber septum, oxygenated with a stream of dry oxygen for 10 min, and then irradiated for 6 h with 300 nm light (Rayonet reactor, 12 lamps, 27°C). The reaction was monitored by GC–MS and TLC at 1 h intervals. Compounds *cis*-**1**, **9***a*, **10***a*, and **12** were formed in similar relative yields to those in irradiations in the absence of the phenol at irradiation times of less than 6 h. The yield of **12** was reduced substantially, however, at long irradiation times. Two new minor products, of GC retention times similar to those of **9***a* and **10***a*, were detected in the mixture after short irradiation times. These were tentatively identified on the basis of GC–MS as 5,6-dimethoxyphenanthrene-2,3-dione (*m/z* (*I*): 268 (100), 253 (81), 238 (3), 225 (31), 210 (90), 195 (11), 182 (1), 167 (47), 152 (8), 151 (9), 139 (33), 113 (5), 63 (5)) and 6,7-dimethoxyphenanthrene-2,3-dione (*m/z* (*I*): 268 (100), 253 (21), 225 (33), 210 (41), 195 (7), 182 (36), 167 (6), 152 (14), 139 (38), 75 (2), 63 (1)).

After 5 h of continuous irradiation the mixture showed an intense yellow color. The solvent was distilled under vacuum, and the yellow oil that remained was chromatographed on the Chromatotron using a 2 mm silica gel plate. Elution with 10% ethyl acetate – hexane allowed isolation of **10***a* (0.048 g, 20%), *cis*-**1** (0.041 g, 17%), *trans*-**1** (0.036 g, 15%), and **9***a* (0.029 g, 12%). Continued gradient elution to 30% ethyl acetate afforded **12** (0.024 g, 10%) and two new compounds (0.024 g, 5% each). The FT-IR spectrum of these compounds (CCl_4) showed the presence of carbonyl absorptions in the 1650–1710 cm^{-1} range, but their GC retention times did not match those of the two minor products observed in the crude reaction mixture (vide supra). Continued gradient elution to 50% ethyl acetate afforded **6** (0.007 g, 3%) and a third minor component (0.007 g, 3%) that is presumably an isomer of **6**.

(ii) From irradiation of trans-*3*

(a) Irradiation of trans-*3 in 95% ethanol*

A continuously oxygenated solution of *trans*-**3** (1.0 g, 2.5 mmol) in 95% ethanol (500 mL) was irradiated under similar conditions to those described above for *trans*-**1**. A single product, subsequently identified as *cis*-**3** (vide infra), was observed by GC analysis during the first 30 min of photolysis. Continued irradiation resulted in the slower formation of four other compounds that eluted between *cis*- and *trans*-**3** under the GC conditions employed (order of elution: *cis*-**3** < **5** < **11***c* = **10***c* < **9***c* < *trans*-**3**), and the development of a dark yellow colour. The irradiation was stopped after 1 h (ca. 75% conversion of *trans*-**3**), and the solvent was removed on the rotary evaporator to yield a brown oil. The mixture was chromatographed on the Chromatotron using a 4 mm silica gel thick-layer plate that was first deactivated with triethylamine, using an ethyl acetate – hexane gradient (1–8% ethyl acetate). The products eluted in the order **10***c* < *cis*-**3** < **11***c* < **9***c* < **5** < *trans*-**3**. Compounds *cis*-**3** and **10***c* were isolated in pure forms as a colourless oil and a crystalline solid, respectively. Compounds **9***c* and **11***c* initially eluted together, but could be separated with subsequent passes through the plate. Compound **9***c* was obtained as a colourless solid after recrystallization from ethyl acetate – hexane. Compound **11***c* was obtained as a pale yellow, low-melting solid that resisted further attempts at purification by either chromatography or recrystallization. Compound **5** was obtained as a colourless solid after two recrystallizations from hexane. Isolated chemical yields and spectroscopic properties of these materials are listed below. The material balance was typically less than 50% from photolyses in ethanol solution.

cis-*4–*tert-*Butyldimethylsiloxy-3,3′,4′-trimethoxystilbene (*cis-*3)*: 0.112 g, 0.28 mmol, 11%; mp 53–55°C. UV (ethanol), $\lambda_{max}(\varepsilon)$: 201 nm (52 400), 281 nm (13 900); IR: 3001 (m), 2954 (s), 2932 (s), 2857 (s), 1509 (s), 1465 (s), 1289 (s), 1128 (s), 1031 (s), 899 (s), 839 (s); ^{1}H NMR, δ: 0.11 (s, 6H), 0.97 (s, 9H), 3.60 (s, 3H), 3.63 (s, 3H), 3.84 (s, 3H), 6.43 (s, 2H), 6.75 (m, 6H); ^{13}C NMR, δ: −4.7, 18.5, 25.7, 55.3, 55.5, 55.8, 110.8, 111.7, 112.6, 120.6, 121.8, 128.6, 128.9, 130.2, 131.1, 144.2, 148.1, 148.3, 150.5; MS, *m*/*e* (*I*): 400 (40), 343 (25), 328 (100), 253 (4), 209 (7), 149 (7), 73 (8). Exact Mass, calcd. for $C_{23}H_{32}SiO_4$: 400.2070; found: 400.2069.

*1(2)-Ethoxy-1-(3-(*tert-*butyldimethylsiloxy)-4-methoxyphenyl)-2-(3,4-dimethoxyphenyl)ethane (5)*: 0.070 g, 0.16 mmol, 6%, mixture of regioisomers. *Major isomer* (67%): ^{1}H NMR, δ: 0.10 (s, 6H), 0.96 (s, 9H), 1.13 (t, 3H), 2.76 (quint, 1H), 3.04 (dd, 1H), 3.34 (m, 2H), 3.76 (s, 3H), 3.82 (s, 3H), 3.84 (s, 3H), 4.27 (m, 1H), 6.65 (cplx m, 6H); ^{13}C NMR, δ: −4.57, 15.34, 18.47, 25.72, 44.57, 55.35, 55.85, 55.94, 64.11, 83.32, 109.45, 110.61, 113.73, 119.27, 120.34, 121.66, 132.07, 134.97, 143.22, 148.26, 148.93, 150.30. *Minor isomer* (33%): ^{1}H NMR, δ: 0.13 (s, 6H), 0.97 (s, 9H), 1.13 (t, 3H), 2.76 (quint, 1H), 3.04 (dd, 1H), 3.34 (m, 2H), 3.66 (s, 6H), 3.73 (s, 3H), 4.27 (m, 1H), 6.65 (m, 6H). *Mixture*: UV (ethanol) $\lambda_{max}(\epsilon$: 202 nm (50 900), 286 nm (11 100), 332 nm (19 260); IR (mixture): 3001 (m), 2954 (s), 2932 (s), 2857 (s), 1509 (s), 1465 (s), 1289 (s), 1128 (s), 1031 (s), 899 (s), 839 (s); MS, *m*/*e* (*I*): 446 (3), 400 (45), 389 (15), 343 (26), 328 (100), 313 (7), 295 (57).

*6-(*tert*-Butyldimethylsiloxy)-2,3,5-trimethoxyphenanthrene (**11**c)*: 0.057 g, 0.14 mmol, 6%; mp 51–53°C; UV (ethanol), $\lambda_{max}(\varepsilon)$: 201 nm (62 800), 260 nm (72 560); IR: 3030 (s), 2959 (m), 2933 (m), 1514 (s), 1470 (s), 1423 (m), 1265 (s), 1239 (s), 1085 (s), 838 (s); ^{1}H NMR (300 MHz), δ: 0.27 (s, 6H), 1.09 (s, 9H), 3.92 (s, 3H), 4.02 (s, 3H), 4.10 (s, 3H), 7.16 (m, 2H), 7.52 (m, 3H), 9.20 (s, 1H); ^{13}C NMR, δ: −4.4, −0.3, 18.3, 25.8, 55.7, 55.8, 59.3, 107.9, 108.7, 120.5, 124.0, 124.6, 124.8, 125.3, 128.3, 128.4, 128.7, 147.3, 148.2, 148.4, 148.6; MS, *m*/*e* (*I*): 398 (20), 326 (100), 163 (10), 73 (12), 57 (6). Exact Mass, calcd. for $C_{23}H_{30}SiO_4$: 398.1914; found: 398.1910.

*3-(*tert*-Butyldimethylsiloxy)-2,5,6-trimethoxyphenanthrene (**10**c)*: 0.11 g, 0.28 mmol, 11%; mp 95–97°C; UV (ethanol), $\lambda_{max}(\varepsilon)$: 202 nm (17 900), 261 nm (38 400); IR: 3030 (s), 2959 (m), 2934 (m), 1599 (m), 1512 (s), 1469 (s), 1275 (s), 1247 (s), 1103 (s), 1049 (m); ^{1}H NMR (300 MHz), δ: 0.25 (s, 6H), 1.07 (s, 9H), 3.94 (s, 6H), 4.0 (s, 3H), 7.21 (m, 2H), 7.50 (m, 3H), 9.15 (s, 1H); ^{13}C NMR, δ: −4.6, −0.5, 18.5, 25.8, 55.3, 56.4, 59.8, 108.6, 112.2, 118.8, 123.9, 124.3, 124.8, 125.3, 127.7, 129.2, 144.7, 146.3, 150.9, 151.0; MS, *m*/*e* (*I*): 398 (25), 341 (22), 326 (100), 311 (15), 268 (15), 163 (8), 134 (7), 89 (7), 73 (12), 57 (10). Exact Mass, calcd. for $C_{23}H_{30}SiO_4$: 398.1914; found: 398.1910.

*3-(*tert*-Butyldimethylsiloxy)-2,6,7-trimethoxyphenanthrene (**9**c)*: 0.083 g, 0.21 mmol, 8%; mp 95.0–96.8°C; UV (ethanol), $\lambda_{max}(\varepsilon)$: 255 nm (90 600), 286 nm (38 700); IR: 3030 (s), 2958 (m), 2934 (m), 1509 (s), 1478 (s), 1434 (m), 1272 (s), 1197 (s), 903 (s), 866 (m), 811 (m); ^{1}H NMR (300 MHz), δ: 0.23 (s, 6H), 1.06 (s, 9H), 3.94 (s, 3H), 4.02 (s, 3H), 4.09 (s, 3H), 7.18 (s, 2H), 7.52 (s, 2H), 7.76 (s, 1H), 7.88 (s, 1H); ^{13}C NMR, δ: −4.5, −4.4, −0.01, 0.30, 18.6, 25.8, 55.3, 55.8, 55.9, 103.0, 108.3, 108.7, 112.8, 124.2, 124.6, 126.2, 127.2, 145.3, 148.7, 149.2; MS, *m*/*e* (*I*): 398 (23), 341 (20), 326 (100), 240 (4), 163 (12), 73 (5). Exact Mass, calcd. for $C_{23}H_{30}SiO_4$: 398.1914; found: 398.1915.

GC analysis of exhaustively irradiated solutions of **3** in oxygenated THF indicate the primary relative phenanthrene yields to be similar to those obtained in ethanol solution. However, irradiation in THF allows isolation of **9***c*–**11***c* in significantly higher chemical yields than are obtained from irradiations in ethanol.

(b) Irradiation of trans-*3 in THF*

A solution of *trans*-**3** (1 g, 2.5 mmol) in dry tetrahydrofuran (15.0 mL) was oxygenated with a stream of dry oxygen for 10 min and then irradiated with 300 nm light (Rayonet reactor, 12 lamps, 27°C). The reaction was not monitored, but instead was stopped after 12 h of continuous irradiation. A deep orange solution was obtained. The solvent from the reaction mixture was evaporated and the remaining dark orange oil was chromatographed using a 2-mm-thick Chromatotron plate that had previously been treated with triethylamine (5 drops in 600 mL of eluent). The less polar fractions (that eluted with 10:90 ethyl acetate:hexanes, containing **9***c*-**11***c*, *cis*-**3** and *trans*-**3**) represented 50% of the photolyzed material.

Continued gradient elution to 35% ethyl acetate afforded four additional fractions, the first and fourth of which consisted of single components. They were identified as the following on the basis of spectral data.

trans-*1,2-Bis(3,4-dimethoxyphenyl)*-cis,trans-*3,4-bis(4-*tert-*butyldimethylsiloxy-3-methoxyphenyl)-cyclobutane (7*a*)*: first fraction (oil), 0.201 g, 20%; ^{1}H NMR, δ: 0.055 (s, 6H), 0.93 (s, 9H), 3.54 (s, 3H), 3.64 (s, 3H), 3.76 (s, 3H), 4.25 (br s, 2H), 6.45 (d, 1H, J = 1.83 Hz), 6.52 (d, 1H, J = 1.97 Hz), 6.62 (dd, 1H, J = 1.87 Hz, J = 8.15 Hz), 6.65 (d, 2H, J = 8.10 Hz), 6.68 (dd, 1H, J = 2.0 Hz, J = 8.28 Hz); ^{13}C NMR (125.8 MHz), δ: −4.80, 18.31, 25.62, 47.31, 47.39, 55.34, 55.45, 55.63, 110.31, 112.00, 112.76, 119.92, 120.13, 120.18, 133.67, 134.45, 143.11, 147.16, 148.37, 150.23; MS, *m/z* (*I*): 550 (12), 501 (10), 400 (100), 354 (10), 328 (71), 300 (7), 284 (7), 151 (7); MS (NH_3 CI), *m/z* (*I*): 818 (38), 568 (20), 502 (11), 401 (100), 301 (21), 151 (15).

cis-*1,3-Bis(3,4-dimethoxyphenyl)*-trans,trans-*2,4-bis(4-*tert-*butyldimethylsiloxy-3-methoxyphenyl)-cyclobutane (8*a*)*: 4th fraction (oil), 0.191 g, 19%; ^{1}H NMR, δ: 0.073 (s, 6H), 0.96 (s, 9H), 3.55 (s, 3H), 3.63 (s, 3H), 3.78 (s, 3H), 4.23 (s, 1H), 4.24 (s, 1H), 6.46 (d, 1H, J = 1.99 Hz), 6.50 (d, 1H, J = 1.91 Hz), 6.59 (dd, 1H, J = 1.99 Hz, J = 8.13 Hz), 6.63 (d, 1H, J = 8.08 Hz), 6.67 (d, 1H, J = 8.28 Hz), 6.71 (dd, 1H, J = 1.99 Hz, J = 8.25 Hz); ^{13}C NMR, δ: −4.73, 18.36, 25.68, 47.38, 47.58, 55.39, 55.71, 55.76, 110.71, 112.79, 112.03,, 120.14, 120.10, 133.76, 134.44, 143.16, 147.23, 148.45, 150.35; MS, *m/z* (*I*): 501 (3), 400 (100), 343 (22), 328 (57), 310 (3), 286 (12), 195 (10), 73 (8); MS (NH3 CI), *m/z* (*I*): 818 (100), 569 (8), 464 (5), 402 (76), 328 (20).

The second fraction consisted of a mixture of two carbonylic compounds, which were tentatively identified as stilbenequinones on the basis of ^{1}H and ^{13}C NMR spectroscopy of the mixture, but they could not be rigorously identified. The third fraction consisted of a mixture of **12** and dimer **8***a*.

(iii) *From irradiation of* trans-*2*

(a) *Irradiation of* trans-*2 in 95% ethanol*

An oxygenated solution of *trans*-**2** (0.50 g, 1.7 mmol) in 95% ethanol (500 mL) was irradiated under similar conditions to those described above. GC and GC–MS analysis of the crude mixture after 15 min irradiation revealed the presence of a single product that was identified as *cis*-**2** (vide infra). Continued irradiation (30 min total) resulted in the solution turning yellow, and GC analysis indicated there to be substantial loss of volatile material with only a slight apparent increase in the yield of *cis*-**2** relative to the amount of *trans*-**2** present. The solvent was distilled from the reaction mixture under vacuum, yielding a dark yellow oily solid (0.49 g). ^{1}H NMR analysis of the crude photolysate indicated a *cis*-**2**/*trans*-**2** ratio of ca. 3:1.

The reaction mixture was chromatographed on a 4 mm silica gel thick-layer plate and eluted with dichloromethane. This allowed recovery of 0.013 g of *trans*-**2**, the first compound to elute. The second fraction consisted of *cis*-**2** (0.018 g) contaminated with a small amount of the *trans* isomer, as determined by ^{1}H NMR spectroscopy. GC analysis of this mixture indicated it to consist of *cis*-**2** and *trans*-**2** in a ~1:1 ratio, but lowering the injector temperature resulted in correspondingly higher amounts of the *cis* isomer in the mixture. ^{1}H NMR analysis of the mixture after storage for 24 h in the dark at room temperature indicated complete thermal isomerization to the *cis* isomer. The remaining material consisted of two dimeric products and **12**; these were isolated from the photolysis of *trans*-**2** in THF (vide infra).

cis-*4-Hydroxy-3,3′,4′-trimethoxystilbene (*cis-*2*)*: mp 131.9–132.3°C; UV (ethanol), $\lambda_{max}(\varepsilon)$: 200 nm (26 150), 303 nm (9780); GC/FTIR: 3564 (br m), 2983 (s), 2939 (m), 1724 (s), 1384 (s), 1325 (m), 1186 (s), 1143 (m), 957 (w), 919 (w); ^{1}H NMR (300 MHz), δ: 3.68 (s, 3H), 3.69 (s, 3H), 3.87 (s, 3H), 5.57 (s, 1H), 6.45 (s, 2H), 6.80 (m, 6H); ^{13}C NMR (AM500), δ: 55.80, 55.82, 55.89, 108.01, 108.56, 111.24, 114.48, 119.43, 120.11, 126.27, 149.08; MS, *m/e* (*I*): 286 (100), 271 (13), 211 (6), 168 (5), 165 (4), 143 (8), 77 (7), 45 (38). Exact Mass, calcd. for $C_{17}H_{18}O_4$: 286.1205; found: 286.1208.

Extended photolysis of **2** in oxygenated ethanol solution resulted in substantial loss of volatile material, the appearance of small amounts of three new products, and the development of a deep orange-brown colour. Attempts to isolate the three new products by thick-layer chromatography were unsuccessful.

Phenanthrenes **9***b*–**11***b* were prepared by desilylation of the corresponding *tert*-butyldimethylsiloxy compound **9***c*–**11***c*. For example, **9***c* (0.05 g, 0.18 mmol), tetra-*n*-butylammonium fluoride (0.066 g, 0.25 mmol), and tetrahydrofuran (0.25 mL) were placed in a 5 mL round-bottom flask and stirred at room temperature for 30 min, with periodic monitoring of the progress of reaction by thin-layer chromatography (silica gel, 15% ethyl acetate in hexane). The solvent was removed under vacuum, saturated aqueous ammonium chloride (5 mL) was added, and the mixture was extracted with anhydrous ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and stripped of solvent on the rotary evaporator. The resulting yellow oil was chromatographed on a silica gel column, eluting with hexane (~100 mL) to remove unreacted starting material and other silicon-containing compounds, and then a 25% ethyl acetate – hexane mixture. Compound **9***b* was obtained as a colourless solid (0.033 g, 0.16 mmol, 93%) and recrystallized from ethyl acetate – hexanes and ethyl acetate. GC coinjection with crude mixtures from photolysis of **2** verified its presence in the photolysate. A similar procedure was employed for the synthesis of **10***b* and **11***b* from **10***c* and **11***c*, respectively.

*6-Hydroxy-2,3,7-trimethoxyphenanthrene (9*b*)*: mp 155–158°C; UV (ethanol), $\lambda_{max}(\varepsilon)$: 254 (65 800), 286 nm (29 470); IR: 3542 (m), 3030 (s), 1512 (s), 1480 (s), 1436 (m), 1266 (m), 1197 (s), 1159 (s), 1111 (m), 1041 (m), 864 (m); ^{1}H NMR, δ: 4.01 (s, 3H), 4.03 (s, 3H), 4.08 (s, 3H), 5.90 (s, 1H), 7.19 (s, 2H), 7.51 (s, 2H), 7.79 (s, 1H), 7.96 (s, 1H); ^{13}C NMR, δ: 55.90, 55.96, 103.10, 105.99, 107.65, 108.17, 123.96, 124.32, 124.36, 125.14, 126.10, 126.35, 145.60, 146.39, 148.81, 149.18; MS, *m*/*e* (*I*): 284 (100), 269 (13), 241 (14), 198 (8), 142 (12). Exact Mass, calcd. for $C_{17}H_{16}O_4$: 284.1048; found: 284.1047.

*6-Hydroxy-2,3,5-trimethoxyphenanthrene (11*b*)*: mp 157.3–159.1°C; UV (THF) $\lambda_{max}(\varepsilon)$: 274 nm (20 180), 260 (25 600); IR (KBr): 3363 (br), 1601 (s), 1513 (s), 1474 (s), 1423 (s), 1370 (m), 1254 (s), 1154 (s), 1076 (s), 1042 (s), 860 (s), 779 (s); ^{1}H NMR, δ: 3.81 (s, 3H), 3.96 (s, 3H), 4.00 (s, 3H), 6.05 (br s, 1H), 7.14 (s, 1H), 7.18 (d, 2H, J = 3.8 Hz), 7.20 (s, 1H), 7.46 (m, 2H), 8.82 (s, 1H); ^{13}C NMR, δ: 55.76, 55.83, 60.29, 107.79, 108.06, 115.44, 122.12, 122.87, 124.08, 125.58, 125.94, 127.56, 128.49, 143.01, 147.69, 148.64, 148.94. MS, *m*/*z* (*I*): 284 (100), 269 (22), 241 (19), 226 (16), 198 (10), 181 (7), 142 (20), 121 (5), 71 (13), 57 (16). Exact Mass, calcd. for $C_{17}H_{16}O_4$: 284.1048; found: 284.1052.

*3-Hydroxy-2,5,6-trimethoxyphenanthrene (10*b*)*: mp 147.4–149.6°C; UV (THF), $\lambda_{max}(\varepsilon)$: 255 nm (88 000), 287 nm (37 500), 301 (21 000); IR (KBr): 3416 (br), 1516 (s), 1474 (s), 1456 (m), 1427 (m), 1370 (m), 1270 (s), 1101 (s), 1053 (m), 818 (m); ^{1}H NMR, δ: 3.90 (s, 3H), 3.95 (s, 3H), 3.98 (s, 3H), 5.74 (br s, 1H), 7.13 (s, 1H), 7.20 (d, 1H, J = 8.7 Hz), 7.39 (d, 1H, J = 8.8 Hz), 7.43 (d, 1H, J = 8.7 Hz), 7.52 (d, 1H, J = 8.7 Hz), 9.09 (s, 1H); ^{13}C NMR, δ: 55.82, 56.68, 59.79, 107.63, 112.27, 112.78, 124.38, 124.54, 124.68, 124.81, 125.03, 127.99, 128.21, 145.07, 146.54, 146.71, 151.16; MS, *m*/*z* (*I*): 284 (100), 269 (59), 241 (11), 226 (8), 181 (9), 155 (10), 139 (9), 126 (7), 84 (14). Exact Mass, calcd. for $C_{17}H_{16}O_4$: 284.1048; found: 284.1049.

(b) Irradiation in THF

A solution of *trans*-**2** (0.261 g, 0.91 mmol) and *n*-hexadecane (0.169 g, 0.075 mmol) in dry tetrahydrofuran (15.0 mL) was oxygenated with a stream of dry oxygen for 10 min and then irradiated with 300 nm light (Rayonet reactor, 12 lamps, 27°C). The reaction was monitored by GC–MS analysis for 8 h at 1 h intervals. The formation of **9***b*, **10***b*, **11***b*, and **12** was observed to proceed linearly as a function of irradiation time.

After 5 h of irradiation, the solution had turned light yellow; GC analysis of the product mixture indicated it to consist of **12** (14%), **9***b* (19%), *trans*-**2** (12%), and **10***b*+**11***b* (12%). After 8 h of irradiation, the presence of other volatile minor products in the photolysate accounted for 8% of the mixture, as determined by GC–MS analysis. The retention times and mass spectral data of two of these products (ca. 4% each) coincide with those found for the two phenanthrenetetrones detected in the photolysis of *trans*-**1** (vide supra).

The solvent was distilled from the photolysate under vacuum, and the dark orange oil that remained was chromatographed on the Chromatotron using a 2 mm silica gel plate and gradient elution with ethyl acetate – hexane. Compounds *cis*-**2** and *trans*-**2**, **9***b*–**11***b*, and **12** were isolated, as well as one other fraction that contained a mixture of two dimeric compounds. This was followed by a fraction containing a single component, which was tentatively identified as cyclobutane dimer **8***b* on the basis of ^{1}H NMR and MS evidence.

cis-*1,3-Bis(3,4-dimethoxyphenyl)-*trans,trans-*2,4-bis(4-hydroxy-3-methoxyphenyl)-cyclobutane (8*a*)*: 4th fraction (oil), 0.191 g, 19%; ^{1}H NMR, δ: 3.64 (s, 6H), 3.74 (s, 3H), 4.69 (s, 2H), 6.36 (s, 1H), 6.37 (s, 1H), 6.71 (cplx m, 4H); MS, *m*/*e* (*I*): 571 (1), 501 (1), 400 (51), 328 (60), 288 (39), 286 (51), 195 (100), 152 (31), 73 (29).

Irradiation of phenanthrene 10*a* under various conditions

A solution of **10***a* (2.1 mg, 0.007 mmol) in THF (0.5 mL) was placed in a Pyrex tube, sealed with a rubber septum, oxygenated with a stream of dry oxygen for 10 min, and then irradiated for 7 h with 300 nm light (Rayonet reactor, 12 lamps, 25°C), with monitoring of the photolysate at 1 h intervals by GC–MS. After 7 h of irradiation, only a single minor photoproduct could be detected (0.5 %, shorter retention time than **10***a*, M^+ = 330), in addition to remaining **10***a*.

A solution of **10***a* (10.1 mg, 0.034 mmol), *trans*-**1** (2 mg, 0.0066 mmol), and *n*-hexadecane (0.068 mg, 0.0003 mmol) in dry THF (0.5 mL) was placed in a quartz NMR tube, sealed with a rubber septum, and oxygenated with a stream of dry oxygen for 10 min. The solution was irradiated with 254 nm light ($[\varepsilon_6/\varepsilon_{trans\text{-}1}]_{254\ \mathrm{nm}}$ = 55), and monitored at 20 min intervals by GC–MS. Compounds *cis*-**1**, **9***a*, and **12** were observed to form in similar relative yields to those produced upon irradiation of *trans*-**1** under similar conditions (vide infra). No new products could be detected in significant yields after photolysis to 50% (total) conversion of **1**.

Photostationary state and quantum yield determinations

Quantum yields were determined using an electronic actinometry system similar to that reported by Leigh and Arnold (38), using 300 nm light from a 100 W xenon lamp attached to a high-intensity monochromator. A Corning CS 7-54 glass filter was employed to remove the higher order spectral lines. The system was calibrated prior to each experiment by ferrioxalate actinometry. Solutions were contained in round Suprasil UV cells (1.0 × 2.54 cm) that were sealed with rubber septa. The samples were deoxygenated with a stream of nitrogen or oxygen for 15 min prior to photolysis, and stirred throughout using a 6 mm Teflon-coated magnetic stirrer. Product formation was followed by GC relative to *n*-eicosane as an internal standard. Relative FID response factors were determined for both *trans*- and *cis*-**1** by construction of working curves. Product yields were determined from plots of product concentration vs. accumulated photon counts. Quantum yields for the formation of **4** (in ethanol) and phenanthrenes **9***a* and **10***a* (in O_2-saturated solution) were estimated from runs ca. 10 times longer than those employed for the determination of quantum yields for *cis,trans* isomerization. The linearity of the system over these longer time scales was not, however, verified.

For photostationary state determinations, 10^{-3} M solutions of *cis*- and *trans*-**1** were purged for 15 min with a stream of nitrogen, and irradiated alternately in the system described above, with periodic monitoring of the course of reaction by GC. The irradiation was continued until the ratios of *cis*-**1**/*trans*-**1** in the two solutions achieved a common value (*cis*-**1**/*trans*-**1** = 1.38 ± 0.07).

Steady state fluorescence quenching experiments

Fluorescence spectra were recorded using $\sim 5 \times 10^{-6}$ M solutions of the stilbenes or phenanthrenes in dry THF containing various amounts of absolute ethanol, TFE, or HFIP, in 1 × 1 cm Suprasil quartz cuvettes that were sealed with rubber septums. The solutions were deoxygenated prior to recording the spectra by bubbling with a stream of dry nitrogen for a constant period of time. A fresh solution was employed for each spectrum recorded, and fluorescence intensities were estimated from the integrated emission spectra. For oxygen-quenching experiments, aliquots of standard solutions of *trans*-**1** and *trans*-**2** were placed in 10 mL volumetric flasks, and then premixed nitrogen–oxygen mixtures were bubbled through the solutions, topping the flasks up to the mark with fresh solvent when evaporation resulted in some loss. The compositions of the gas mixtures were controlled with a Matheson 73510-600 gas proportioner. Oxygen concentrations were calculated using a value of 0.0101 M for the concentration of oxygen in oxygen-saturated THF at 25°C (39).

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