

Reactive Structures in Wood and High-yield Pulp. IV.* Daylight-induced Oxidation of Stilbene Structures in the Solid State

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In order to mimic the light-induced yellowing of stilbene structures present in hydrogen peroxide bleached high-yield pulps, two monohydroxystilbenes have been synthesized and irradiated with daylight in the solid state on filter paper.

The key step in the reaction sequence seems to be an electron transfer–proton transfer process leading to the formation of a stilbene phenoxyl radical. Subsequent oxidation gives rise to a cation which can add water and after loss of methanol is converted into an *ortho*-quinone. By hydrogen donation and subsequent addition to the stilbene double bond, thiol groups like that in mercaptoacetic acid could be used to capture all radical species formed, and thus prevent the formation of coloured products. Other major reaction pathways leading to the formation of non-coloured products were also identified.

Among the various structures present in lignin, stilbenes are the most sensitive and reactive in light-induced discolouration reactions.^{1,2} It has been shown that stilbenes with free phenolic hydroxy groups are the cause of the photo-induced darkening of some wood species.³ In our previous work,^{2,4} it was found that significant amounts of diguaiacylstilbene-type structures were formed in high-yield pulps from spruce, mainly during hydrogen peroxide bleaching but also during grinding or disc refining. Such stilbenes are easily formed from 1,2-diarylpropane-1,3-diol structures in lignin by elimination of water and formaldehyde and they constitute the major type of leucochromophoric structure present in hydrogen peroxide-bleached high-yield pulps.

The formation of stilbenes from diarylpropane structures during high-yield pulping and peroxide bleaching has been demonstrated in model compound studies.^{5,6} Recently, it was also reported that unbleached stone groundwood exhibits a weak fluorescence which, after bleaching with hydrogen peroxide, considerably increases in intensity with an emission maximum at 440–450 nm when irradiated at 350 nm.⁷ This observation can be well explained by the formation of stilbenes, which are strong fluorophores, in the pulp during hydrogen peroxide bleaching.⁸ It has also been reported that during photo-yellowing the decrease in brightness of an irradiated pulp sample was accompanied by a decrease in its fluorescence intensity,⁹ indicating that stilbenes were photo-

chemically converted into coloured structures as well as into other non-fluorescent structures during the irradiation.

The photochemistry of stilbenes has been studied extensively although most of the work has been carried out in organic solvents. Thus, the mechanism of colour formation from phenolic stilbenes during irradiation in the solid state is not understood in detail. It has been proposed, however, that coloured phenanthrene derivatives might be formed from stilbenes through oxidative photocyclization.¹⁰

In the present work, two monohydroxystilbenes, models for stilbenes present in wood and high-yield pulp fibre lignin, were synthesized and used to study the mechanism of photo-yellowing in the solid state. In addition, a mechanism for photostabilization of stilbenes was investigated by performing irradiation experiments in the presence of thioglycolic acid.

Experimental

Instrumental analyses. HPLC analyses and separations were performed on a Beckman system with dual channel detection at 280 and 350 nm, respectively. A Nucleosil 120-5 (5 μ , 4.6 \times 100 mm) column was used with a gradient of petroleum ether and ethyl acetate as the mobile phase. The two isomers of compound **2.03** were separated using a reversed-phase column (Lichrospher 100-5, RP18) with a mixture of water and methanol as the

* Part III, see Ref. 2.

mobile phase. NMR spectra were run on Bruker AC 250 and AM 400 instruments. GC-MS analyses were carried out on a Finnigan 4000 mass spectrometer interfaced with a Finnigan 9610 gas chromatograph.

Model compounds. 4-Hydroxy-3,3',4',5-tetramethoxystilbene (**2**) was prepared from a mixture of syringaldehyde (5 g), homoveratric acid (4 g), triethylamine (20 ml) and acetic anhydride (40 ml) (Fig. 1). After reflux for 1 h, the solvent was removed by azeotropic evaporation with toluene under reduced pressure. Sodium hydroxide (4 g) dissolved in water (50 ml) was added to the residue and the mixture was rotated in a water bath at 80°C for 3 h. After saponification, the solution was acidified by the addition of 10% hydrochloric acid and the stilbenecarboxylic acid was extracted with ethyl acetate.

After removal of the solvent, the stilbenecarboxylic acid was dissolved in newly distilled quinoline (60 ml) and 50 mg of copper chromite were added. The mixture was heated in a distillation flask and after removal of approximately 10 ml of solvent the mixture was kept under reflux for 30 min. A further volume of solvent (approx. 35 ml) was then carefully distilled off under reduced pressure. After being cooled to room temperature, the mixture was dissolved in dichloromethane and washed with 10% hydrochloric acid (2 × 100 ml) and saturated sodium bicarbonate solution. The washing liquors were extracted with dichloromethane and the combined dichloromethane solution was dried and evaporated. The stilbene (6.0 g, yield 69% based on syringaldehyde) was purified by recrystallization from ethanol (m.p. 150–153°C). ¹H NMR (acetone-*d*₆): δ 3.82 (3 H, s, OMe), 3.87 (3 H, s, OMe), 3.88 (6 H, s, 2 × OMe), 6.89 (2 H, s, H₂ and H₆), 6.93 (1 H, d, *J* = 8.3, H₅), 7.05 (1 H, dd, *J*₁ = 8.3, *J*₂ = 1.9, H₆), 7.05 (2 H, s, ethylenic H), 7.21 (1 H, d, *J* = 1.9, H₂), 7.37 (1 H, s, OH). ¹³C NMR (acetone-*d*₆): δ 56.1 and 56.6 (OMe), 104.8 (C₂ and C₆), 110.1 (C₂), 112.8 (C₅), 120.4 (C₆), 127.0 and 127.9 (ethylenic C), 129.7 (C₁), 131.9 (C₁'), 136.8 (C₄), 148.9 (C₃ and C₅), 150.0 and 150.6 (C₄' and C₃'). MS: *m/z* 316 (*M*⁺, 100%), 301 (25%).

4-Hydroxy-3,3',4'-trimethoxystilbene (**1**) was prepared in an analogous way using vanillin and homoveratric acid as starting materials (Fig. 1). M.p. 129–130°C. ¹H NMR (acetone-*d*₆): δ 3.81 (3 H, s, OMe), 3.86 (3 H, s, OMe), 3.90 (3 H, s, OMe), 6.84 (1 H, d, *J* = 8.1, H₅), 6.92 (1 H,

d, *J* = 8.3, H₅'), 7.00–7.06 (4 H, m, H₆ and H₆' as well as ethylenic H), 7.21 (2 H, m, H₂ and H₂'), 7.68 (1 H, s, OH). ¹³C NMR (acetone-*d*₆): δ 56.2 and 56.3 (OMe), 110.0 and 110.2 (C₂ and C₂'), 112.9 (C₅'), 116.0 (C₅), 120.4 and 120.9 (C₆ and C₆'), 126.8 and 127.7 (ethylenic C), 130.9 (C₁), 132.0 (C₁'), 147.3 (C₄), 148.6 (C₃), 150.1 and 150.6 (C₄' and C₃'). MS: *m/z* 286 (*M*⁺, 100%), 271 (25%).

Irradiation experiments. The stilbene model compound (31.6 mg) was dissolved in 10 ml of acetone. Filter paper (Munktell No. 00M, 5.5 cm) sheets were soaked in the acetone solution for 30 s. The stilbene content in the soaked filter paper was then about 0.4%. After air evaporation of the solvent, the paper was exposed to outdoor summer sunlight in the Stockholm area for 15 min on each side and at ambient temperature. Subsequently, the paper was extensively extracted with ethyl acetate by soaking. The resulting reaction mixtures were immediately separated by HPLC. Some irradiation experiments were also carried out with mercaptoacetic acid (1% on paper) added to the filter paper together with the stilbene. For reference purposes, a bleached stone groundwood pulp was also irradiated in the presence of mercaptoacetic acid.

Product identification. Structures of identified products of the HPLC separation are shown in Fig. 2. Compounds **1.01a** and **1.01b** (mixture of two isomers). ¹H NMR (acetone-*d*₆): δ 3.62 (12 H, s, OMe), 3.65 (12 H, s, OMe), 3.70 (12 H, s, OMe), 4.39 (8 H, m, methine H), 6.62–6.85 (24 H, m, aromatic H), 7.29 (2 H, s, OH). ¹³C NMR (acetone-*d*₆): δ 48.1 and 48.2 (methine C), 56.0 and 56.2 (OMe), 112.3, 113.4, 113.9, 115.2, 121.1, 121.6, 133.6, 135.0, 145.6, 147.9, 148.6 and 149.9 (aromatic C).

Compounds **1.01a** (diacetate) and **1.01b** (diacetate) (mixture of two isomers). MS: *m/z* *M*⁺ not observed, 328 (25%), 314 (2%), 300 (5%), 286 (100%), 272 (9%), 271 (18%).

Compounds **1.02a** and **1.02b** (mixture of two isomers). ¹³C NMR (acetone-*d*₆): δ 53.0 and 53.2 (methine C), 56.2 and 56.3 (OMe), 111.7, 112.3, 113.0, 115.8, 120.2, 121.7, 135.4, 136.7, 146.2, 148.3, 149.2 and 150.4 (aromatic C).

Compounds **1.02a** (diacetate) and **1.02b** (diacetate) (mixture of two isomers). ¹H NMR (CDCl₃): δ 2.30

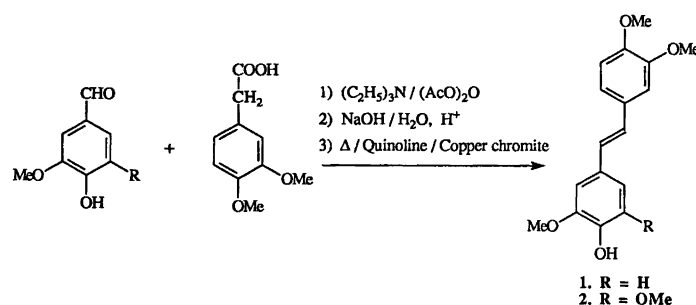


Fig. 1. Synthetic route to the stilbenes used in this work.

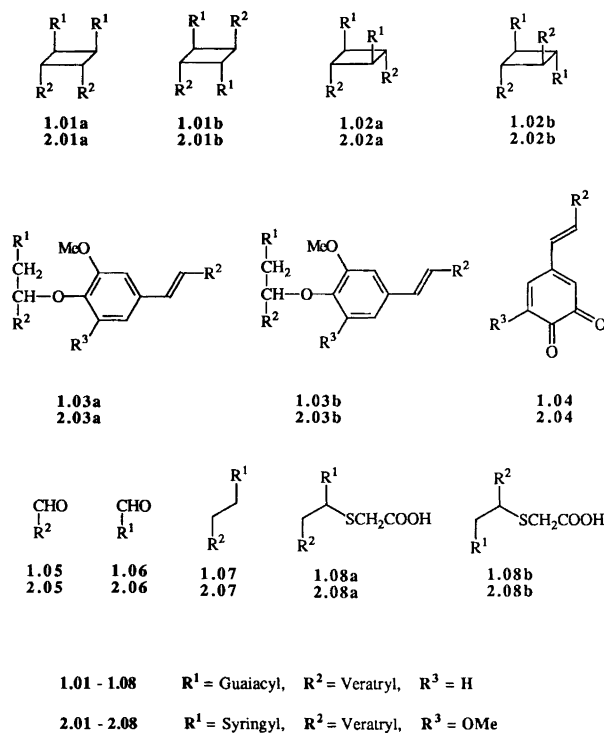


Fig. 2. Structures of products identified in this work.

(12 H, s, OAc), 3.54 (8 H, m, methine H), 3.73 (12 H, s, OMe), 3.81 (12 H, s, OMe), 3.87 (12 H, s, OMe), 6.75–7.00 (24 H, m, aromatic H). MS: m/z M^+ not observed, 356 (3%), 328 (41%), 314 (7%), 300 (34%), 286 (100%), 272 (25%).

Compounds **1.03a** (acetate) and **1.03b** (acetate) (mixture of two isomers). $^1\text{H NMR}$ (acetone- d_6): δ 2.21 (6 H, s, OAc), 3.10 (2 H, m, methylene H_a), 3.30 (2 H, m, methylene H_b), 3.74 (6 H, s, OMe), 3.76 (6 H, s, OMe), 3.77 (6 H, s, OMe), 3.80 (6 H, s, OMe), 3.84 (6 H, s, OMe), 3.91 (3 H, s, OMe), 3.92 (3 H, s, OMe), 5.49 (2 H, m, methine H), 6.77–7.19 (28 H, m, aromatic and ethylenic H). MS: m/z 614 (M^+ , 2%), 435 (2%), 421 (1%), 329 (20%), 328 (10%), 287 (82%), 286 (100%).

Compound **1.04** was reduced to 3,4-dihydroxy-3',4'-dimethoxystilbene by treatment with sodium borohydride. MS of the compound (as the acetate) was recorded. MS: m/z 356 (M^+ , 42%), 314 (61%), 272 (100%).

4-Hydroxy-3,3',4'-trimethoxy-1,2-diphenylethane (**1.07**). MS: m/z 288 (M^+ , 12%), 151 (100%), 137 (35%).

Compounds **1.08a** and **1.08b** (as acetylated methyl esters) (mixture of two isomers). $^1\text{H NMR}$ (CDCl_3): δ 2.28 (3 H, s, OAc), 2.30 (3 H, s, OAc), 2.90–3.15 (8 H, m, methylene H), 3.63 (3 H, s, OMe), 3.65 (3 H, s, OMe), 3.69 (3 H, s, OMe), 3.74 (3 H, s, OMe), 3.79 (3 H, s, OMe), 3.63 (3 H, s, OMe), 3.83 (3 H, s, OMe), 3.85 (3 H, s, OMe), 3.87 (3 H, s, OMe), 4.19 (2 H, m, methine H), 6.44–6.95 (12 H, m, aromatic H). MS of **1.08a**: m/z 434 (M^+ , 17%), 283 (34%), 241 (100%), 167 (16%), 151

(59%). MS of **1.08b**: m/z 434 (M^+ , 9%), 287 (12%), 255 (100%), 241 (14%), 181 (22%), 151 (19%), 137 (8%).

Compounds **2.01a** and **2.01b** (mixture of two isomers). $^1\text{H NMR}$ (CDCl_3): δ 3.65 (6 H, s, OMe), 3.67 (6 H, s, OMe), 3.70 (12 H, s, OMe), 3.71 (12 H, s, OMe), 3.807 (6 H, s, OMe), 3.812 (6 H, s, OMe), 4.25 (8 H, m, methine H), 5.31 (2 H, s, OH), 5.33 (2 H, s, OH), 6.30–6.75 (20 H, aromatic H).

Compounds **2.01a** (diacetate) and **2.01b** (diacetate) (mixture of two isomers). MS: m/z M^+ not observed, 374 (1%), 358 (21%), 332 (2%), 316 (100%), 301 (12%), 300 (6%).

Compounds **2.02a** (diacetate) and **2.02b** (diacetate) (mixture of two isomers). $^1\text{H NMR}$ (CDCl_3): δ 2.327 and 2.331 (12 H, s, OAc), 3.54 (8 H, m, methine H), 3.727 (12 H, s, OMe), 3.735 (12 H, s, OMe), 3.817 (6 H, s, OMe), 3.826 (6 H, s, OMe), 3.87 (6 H, s, OMe), 3.88 (6 H, s, OMe), 6.47 (4 H, s, syringyl aromatic H), 6.50 (4 H, s, syringyl aromatic H), 6.77–6.95 (12 H, veratryl aromatic H). MS: m/z M^+ not observed, 416 (1%), 374 (2%), 358 (21%), 332 (14%), 316 (100%), 301 (19%), 300 (40%).

Compound **2.03a** (acetate). $^1\text{H NMR}$ (CDCl_3): δ 2.31 (3 H, s, OAc), 3.12 (1 H, dd, $J_1 = 7.3, J_2 = 13.6$, methylene H_a), 3.41 (1 H, dd, $J_1 = 6.2, J_2 = 13.6$, methylene H_b), 3.69 (6 H, s, OMe), 3.77 (6 H, s, OMe), 3.82 (3 H, s, OMe), 3.85 (3 H, s, OMe), 3.90 (3 H, s, OMe), 3.93 (3 H, s, OMe), 5.39 (1 H, dd, $J_1 = 7.3, J_2 = 6.2$, methine H), 6.34 (2 H, s, syringyl aromatic H), 6.61 (2 H, s, syringyl

aromatic H), 6.67–7.03 (8 H, veratryl aromatic H and ethylenic H).

Compound **2.03b** (acetate). $^1\text{H NMR}$ (CDCl_3): δ 2.30 (3 H, s, OAc), 3.07 (1 H, dd, $J_1 = 7.6$, $J_2 = 13.6$, methylene H_a), 3.40 (1 H, dd, $J_1 = 6.0$, $J_2 = 13.6$, methylene H_b), 3.71 (6 H, s, OMe), 3.75 (3 H, s, OMe), 3.78 (6 H, s, OMe), 3.84 (3 H, s, OMe), 3.90 (3 H, s, OMe), 3.94 (3 H, s, OMe), 5.31 (1 H, dd, $J_1 = 7.6$, $J_2 = 6.0$, methine H), 6.55 (2 H, s, syringyl aromatic H), 6.64 (2 H, s, syringyl aromatic H), 6.69–7.04 (8 H, veratryl aromatic H and ethylenic H).

Compound **2.04**. UV (in ethyl acetate) λ_{max} : 317 nm, 424 nm. $^1\text{H NMR}$ (acetone- d_6): δ 3.878 (3 H, s, OMe), 3.881 (3 H, s, OMe), 3.89 (3 H, s, OMe), 6.15 (1 H, d, $J = 1.8$), 6.75 (1 H, d, $J = 1.8$), 7.03 (1 H, d, $J = 8.3$), 7.19 (1 H, d, $J = 16.2$), 7.26 (1 H, dd, $J_1 = 8.3$, $J_2 = 2.1$), 7.38 (1 H, d, $J = 2.1$), 7.66 (1 H, d, $J = 16.2$). Reduction with sodium borohydride to 3,4-dihydroxy-3',4',5-trimethoxystilbene. MS (of acetate): m/z 386 (M^+ , 39%), 314 (77%), 302 (100%), 287 (12%).

4-Hydroxy-3,3',4',5-tetramethoxy-1,2-diphenylethane (**2.07**). MS: m/z 318 (M^+ , 20%), 167 (74%), 151 (100%).

Compound **2.08a** (acetylated methyl ester). MS: m/z 464 (M^+ , 23%), 313 (22%), 271 (100%), 197 (14%), 151 (54%).

Compound **2.08b** (acetylated methyl ester). MS: m/z 464 (M^+ , 19%), 255 (100%), 181 (20%), 167 (8%).

Results

Synthesis of stilbenes. Two model compounds were used in the present work, 4-hydroxy-3,3',4'-trimethoxystilbene (**1**) and 4-hydroxy-3,3',4',5-tetramethoxystilbene (**2**). These were synthesized by a Knoevenagel synthesis¹¹ which seems to be the most convenient and versatile way of preparing stilbenes of the various methods available.^{11–13} It was found, however, that the reaction step leading to protection of the phenolic hydroxy group could be omitted. The method could therefore be modified so that the saponification step was placed immediately after the condensation step. This simplified procedure gave an overall synthesis yield of around 70% in comparison with the previously published value of 30%. In both cases the *trans* product was formed with only trace amounts of *cis* isomer present.

Photochemical reactions on exposure to daylight. Both stilbenes were found to undergo similar photochemical reactions and to produce a similar pattern of products, although compound **2** was more reactive and gave a stronger colour than compound **1**. The reactions of **2** will be discussed throughout this paper but most of the reactions apply to compound **1** as well unless otherwise stated. From the irradiation of **2**, compounds **2.01–2.06** (Fig. 3) were produced as major products. The yields of the products were estimated as **2.01a** = **2.01b** > **2.02a** =

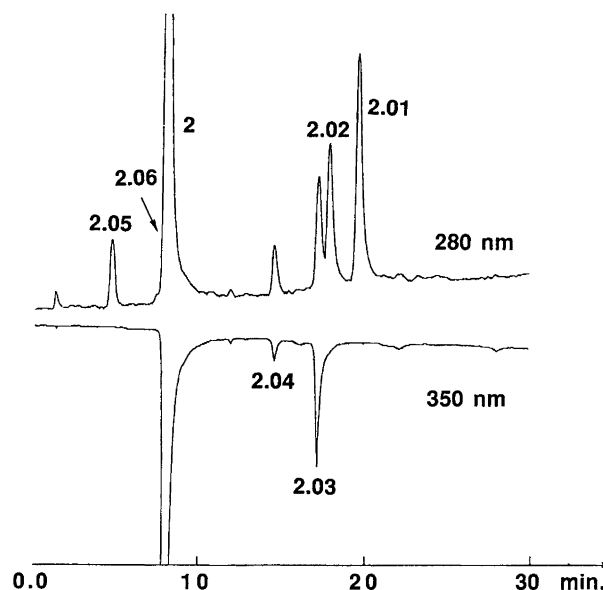


Fig. 3. HPLC chromatogram (with dual channel UV-detection) of reaction products from stilbene **2** after 15 min of irradiation with sunlight.

2.02b \gg **2.03a** = **2.03b** > **2.04** \approx **2.05** \approx **2.06**. A similar product pattern was obtained from stilbene **1**.

The tetraphenylcyclobutanes (**2.01** and **2.02**) were isolated as the predominant products. Their stereochemistry was assigned from the $^1\text{H NMR}$ data.¹⁴ The methine protons of **2.01** gave $^1\text{H NMR}$ signals at around 4.4 ppm, whereas those of **2.02** were found at around 3.5 ppm. The methine carbon signals (from compounds **1.01** and **1.02**) were found at 48.1 ppm and 53.0 ppm, respectively. The two isomers of **2.01** (**2.01a** and **2.01b**) as well as those of **2.02** (**2.02a** and **2.02b**) could not however, be separated by HPLC although their presence could readily be observed by NMR spectral analysis.

The stilbene *o*-quinone (**2.04**) was found to be the structure responsible for the formation of colour, although its yield was estimated to be the lowest among the products identified. TLC analysis clearly indicated that it gave the only visible colour spot in the product mixture. Compound **2.04** showed a reddish colour in solution with λ_{max} at 424 nm. The $^1\text{H NMR}$ spectrum of **2.04** in acetone- d_6 showed very well resolved olefinic and aromatic proton signals, as demonstrated in Fig. 4.

By treatment of **2.04** with sodium borohydride, the corresponding stilbene catechol was produced. It was also found that compound **2.04** could be produced by treatment of stilbene **2** in benzene (with or without the presence of air) with aqueous alkaline potassium ferricyanide, a reagent known to generate phenoxy radicals from phenols.¹⁵ This observation provided evidence that the stilbene phenoxy radical was a key intermediate in the formation of **2.04**. Stilbene **1**, on the other hand, could not be dehydrogenated by aqueous alkaline potassium ferricyanide to give an *o*-quinone, probably because of its higher redox potential.

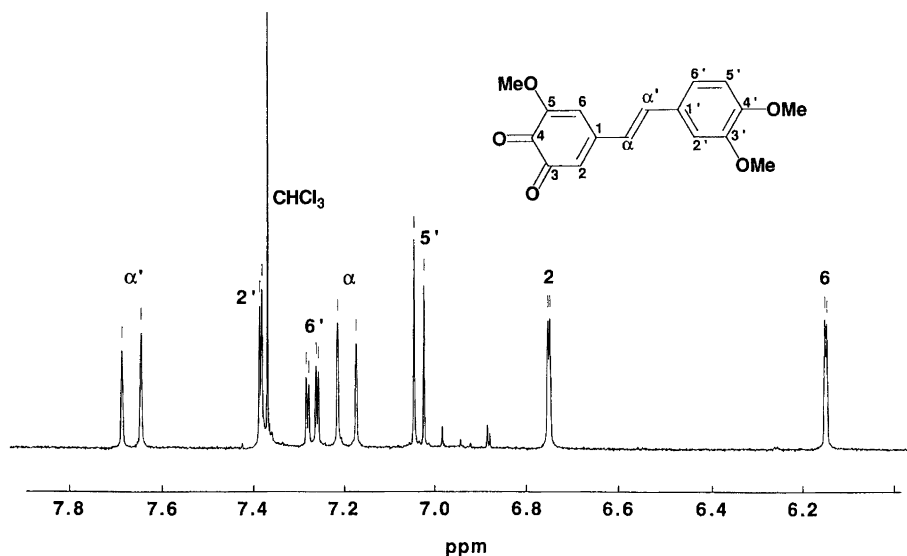


Fig. 4. ^1H NMR spectrum of compound **2.04**.

Photostabilization by added mercaptoacetic acid. It is well known that thiols and other radical scavengers such as ascorbic acid can stabilize high-yield pulps towards photo-induced yellowing.^{16,17} The mechanism behind this stabilization effect has not been studied in detail. A Michael-type addition of a thiol to the enone system of a quinone as well as hydrogen donor mechanisms have, however, been suggested.¹⁶

The photostabilization effect of mercaptoacetic acid present in a filter paper impregnated with the stilbene, as well as in a commercial peroxide-bleached stone groundwood (BSGW) pulp, towards sunlight irradiation was studied. The results are shown in Fig. 5. The BSGW pulp had been stored for several months and some chromophoric structures had probably been formed during that time. Thus, immediately on addition of mercaptoacetic acid to the pulp and exposure to light, a certain bleaching effect was obtained. This resulting brightness level was almost completely retained during the time of expo-

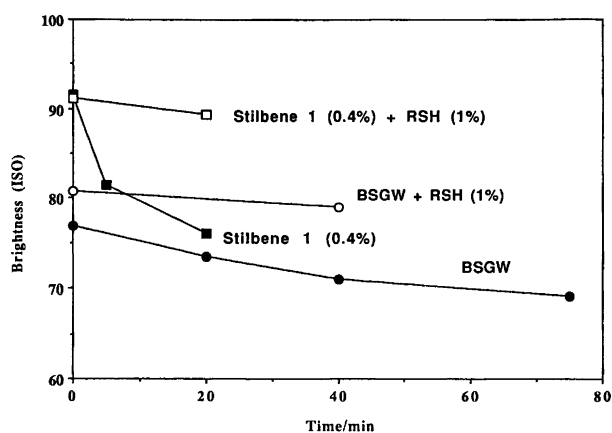


Fig. 5. Brightness stabilization of BSGW and of stilbene 1 (on filter paper) on irradiation with daylight.

sure to daylight whereas, during the same irradiation time, that of the unstabilized pulp decreased by approximately 5 brightness units. As expected, a similar but much stronger stabilization effect was observed in the case of the impregnated filter paper.

After irradiation of filter paper in the presence of stilbene **2** and mercaptoacetic acid, the analysis (Fig. 6) demonstrated a complete absence of compounds **2.03** and **2.04**. Compounds **2.07** and **2.08** were produced together with **2.01** and **2.02** as the predominant products. The relative yields were estimated as **2.01** > **2.02** > **2.08** > **2.07**. In addition, minor amounts of compounds **2.05** and **2.06** were found.

Discussion

Irradiation with daylight. The various products formed on daylight irradiation of a monohydroxystilbene, can be explained according to the reaction sequences outlined in Scheme 1 for stilbene **2**.

The first reaction step, absorption of light, gives rise to an excited singlet state of the stilbene. This may add directly to a second stilbene molecule (in the ground state) giving rise to the cyclobutanes **2.01** and **2.02**.¹⁸ In a com-

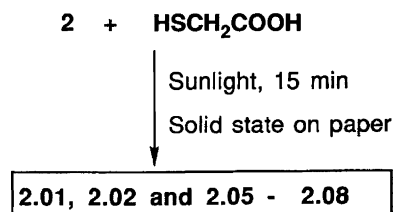
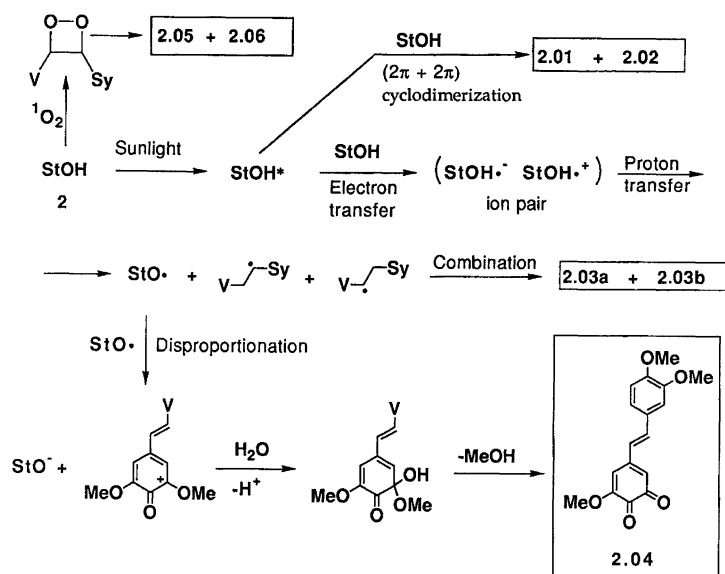


Fig. 6. Structures of major photochemical reaction products after daylight irradiation (15 min) of stilbene **2** on filter paper in the presence of mercaptoacetic acid.



Scheme 1.

peting reaction, the excited singlet may undergo intersystem crossing to form a triplet which in turn can transfer its energy to oxygen with the formation of singlet oxygen. The reaction between singlet oxygen and the stilbene, although being a slow reaction,¹⁹ can lead to the formation of a small amount of a dioxetane structure which is subsequently cleaved with formation of the aldehydes **2.05** and **2.06**.

The excited stilbene molecule may also react with a stilbene molecule in the ground state with the formation of an ion pair in an electron-transfer reaction, a widely observed photochemical process.²⁰ Subsequent proton transfer from $\text{StOH}^{\cdot+}$ to $\text{StOH}^{\cdot-}$ generates a stilbene phenoxyl radical (StO^{\cdot}) and two monohydrostilbene radicals in similar amounts. These radicals may combine with each other to yield coupling products of the aryl ether type as in compounds **2.03a** and **2.03b**.

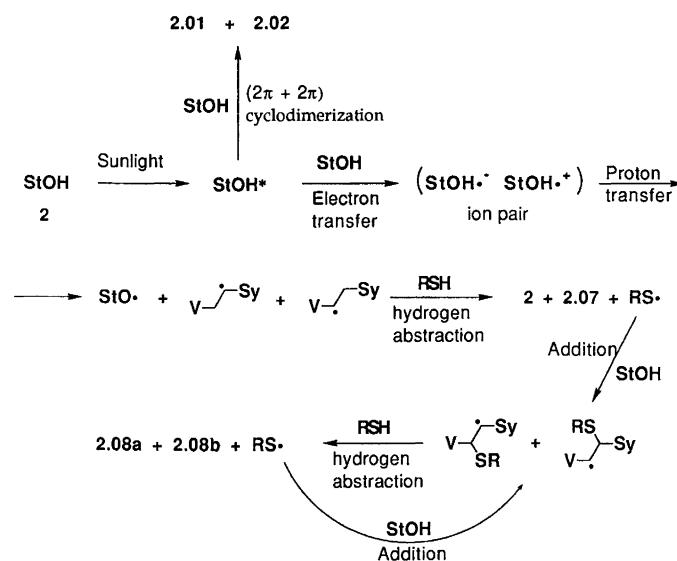
It has been shown previously that, in solution, phenoxyl radicals of the stilbene type may exist in equilibrium with the corresponding dimer.²¹ It is also well known that irradiation of stilbenes in solution will give rise to *cis/trans* isomerization. In the solid state, on the other hand, these options seem to be of less importance and the intermediately formed stilbene phenoxyl radicals stabilize by disproportionation giving rise to the formation of ionic species.²² The subsequent addition of water to the cation followed by elimination of methanol leads to the *o*-quinone **2.04**.

This proposed mechanism is based on the results obtained after 15 min of daylight irradiation. When longer times were employed (several hours), a nitro-substituted stilbene was shown to be formed gradually if the reaction was carried out in the presence of air. Some oxygenated stilbene derivatives were also produced. These reactions will be further addressed in a forthcoming paper.

The formation of cyclobutanes has previously been observed during UV-irradiation of stilbene in benzene solution.¹⁴ A singlet-state excimer was considered to be the reaction intermediate because of the preservation of the stereochemistry of the starting stilbene.^{18,23} It is also known that excited stilbenes undergo $[2\pi + 2\pi]$ cycloaddition to both electron-rich and electron-poor olefinic structures.^{18,23} Therefore, cycloaddition of stilbenes to coniferyl alcohol and coniferaldehyde structures, known to be present in wood and high-yield pulps, leading to the formation of cyclobutane derivatives may be possible reactions during daylight irradiation of high-yield pulps. This type of reaction will not, however, result in the formation of chromophores. Rather, a photobleaching effect can be expected owing to the elimination of both stilbene and coniferaldehyde structures. In high-yield pulps, these types of structure have previously been shown to be responsible for a substantial portion of the absorption of daylight in the near UV wavelength range.²

A key step in the photo-yellowing process seems to be a sequential electron transfer–proton transfer process between an excited- and a ground-state stilbene molecule, generating a stilbene phenoxyl radical and two monohydrostilbene radicals. Further reactions of these entities, leading to the formation of compounds **2.03a** and **2.03b** and (the coloured) compound **2.04**, respectively, do not require the presence of oxygen. Water, on the other hand, plays an important role. Proton transfer reactions from photogenerated radical ion pairs have frequently been observed to occur with excited electron acceptors such as stilbenes in reactions with ground-state donors including amines, methylarenes, alkenes and dienes.²⁴

The *o*-quinone (**2.04**) could also be produced by treatment of stilbene (**2**) in benzene with aqueous alkaline potassium ferricyanide in the absence of oxygen. This



Scheme 2.

observation strongly supports the suggested mechanism of radical disproportionation.

Addition of mercaptoacetic acid. Compounds **2.01** and **2.02** were produced as major products during daylight irradiation of stilbene **2** in the presence of mercaptoacetic acid, indicating that the thiol group did not react directly with the excited state of the stilbene. The protective effect of a thiol group can, however, be explained by its radical trapping ability as outlined in Scheme 2.

The observation that a dihydrostilbene (**2.07**) was produced as one of the predominant products when mercaptoacetic acid was present during irradiation of the stilbene strongly supports the mechanism given in Scheme 1 with a phenoxyl radical and two isomeric monohydrostilbene radicals being generated simultaneously in a sequential electron transfer–proton transfer process. As a consequence, all the radical intermediates were trapped by the thiol group thus preventing the formation of an *ortho*-quinone. Instead, hydrogen abstraction from the thiol group generated thio-radicals which subsequently added to the stilbene double bond in a radical chain reaction to give **2.08a** and **2.08b** as major products.

Conclusions

During daylight irradiation of monohydroxystilbenes in the solid state, cyclobutane derivatives were formed as the major products via a $[2\pi + 2\pi]$ cycloaddition reaction between an excited- and a ground-state stilbene molecule.

It is suggested that the reaction sequence leading to the formation of an *o*-quinone, the only coloured product found, is initiated by a sequential electron transfer–proton transfer process between an excited- and a ground-state stilbene molecule, generating a stilbene phenoxyl

radical and two isomeric monohydrostilbene radicals. A one-electron oxidation of the stilbene phenoxyl radical to a cation is suggested as the second key step. The electron acceptor in this step may be another phenoxyl radical. The stilbene phenoxyl cation formed adds water and eliminates methanol to give the coloured stilbene *o*-quinone. In a competing reaction, the stilbene phenoxyl radicals may combine with the monohydrostilbene radicals giving rise to the formation of dimeric products.

In the presence of a radical scavenger like mercaptoacetic acid, all radical intermediates formed from the stilbene structure are captured and the formation of *o*-quinone structures as well as of dimeric coupling products is prevented.

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