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The Bleaching and Photostabilization of High-Yield Pulp by Sulfur Compounds. II. Reaction of Glycol Mercaptoesters with Model Quinones

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THE BLEACHING AND PHOTOSTABILIZATION OF HIGH-YIELD PULP
BY SULFUR COMPOUNDS. II. REACTION OF GLYCOL
MERCAPTOESTERS WITH MODEL QUINONES.

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ABSTRACT

The reaction of ethylene glycol dimercaptoacetate and pentaerythritol tetramercaptoacetate with *p*-benzoquinone have been investigated, both *in solution and in the presence of cellulose fibers*. In either system, Michael addition is the predominant reaction, leading to decolorization of the quinone by converting it to a substituted hydroquinone. This reaction accounts for the initial bleaching of high-yield pulp produced by these compounds. Handsheets impregnated with these compounds have been irradiated for extended periods of time, and are found ultimately to become more discolored than untreated handsheets. The darkening may be the result of photoinitiated redox chemistry between the Michael adducts and quinones produced in the photodegradation of lignin.

INTRODUCTION

The photoreversion of high-yield pulp has attracted considerable attention, directed both toward understanding the development of color and toward finding some means of brightness stabilization.¹ Prominent

among compounds investigated for stabilizing effects have been the various sulfur compounds originally studied by Cole and Sarkanen^{2,3} and further studied by a number of other groups.^{3-12, 14,15} Recently, we initiated a detailed experimental and computational investigation of the mechanisms by which these compounds produce both stabilizing and bleaching effects when added to high yield pulp. We believe that if the mechanisms are understood at the molecular level, it should be possible to design additives that have these desirable properties but lack the unfortunate odors characteristic of sulfur compounds.

Our initial investigation¹³, involving studies of the reaction of thioglycerol with model quinones, showed that the initial bleaching effect of thioglycerol is produced by Michael addition of the thiol group to quinone chromophores, followed by aromatization of the adducts to colorless hydroquinones. Subsequent oxidation of these hydroquinones by the original quinones explains the redevelopment of color at long exposure times in treated pulp. Our rationalization of these results was considerably aided by data on reaction thermodynamics and redox potentials from semi-empirical and *ab initio* molecular orbital calculations. These data allowed us to understand product regioselectivity, and the direction of redox reactions.

In this paper, we extend our investigations to two other sulfur compounds originally studied by Cole and Sarkanen², the esters of ethylene glycol and pentaerythritol with thiolacetic acid. In their work, the glycol dimercaptoacetate (**1**) was found both to bleach and stabilize, whereas the pentaerythritol ester (**2**) had no bleaching effect and even slightly promoted discoloration.

RESULTS

Initially, we examined the reactions of 1,4-benzoquinone (**3**) with thiols under the same conditions employed in our earlier work: ambient

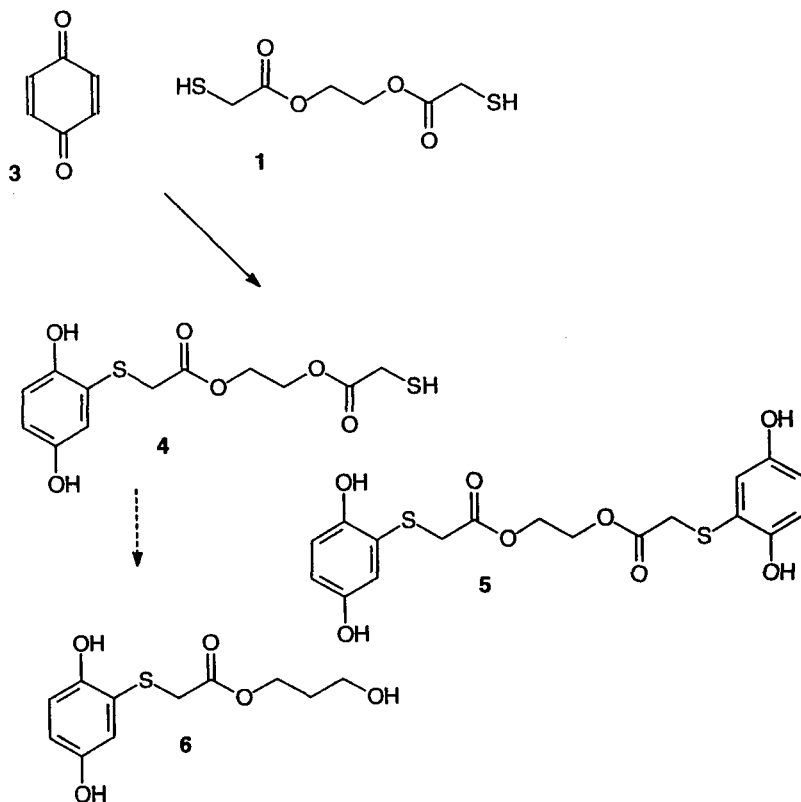


Figure 1: Reaction of benzoquinone with ethylene glycol dimercaptoacetate.

temperature and methanol solution.¹³ The crude reaction mixture was acetylated; the acetylated products were isolated by preparative HPLC and column chromatography as detailed in the experimental section, and their structures were determined by thorough analysis of ^1H and ^{13}C nmr spectra, as described in the Experimental section. For convenience, the products are shown unacetylated.

Two major products (4 and 5) were isolated (Figure 1), corresponding to Michael addition of one or both of the thiol groups of 1 to

TABLE 1

Product Yields from Reaction of Benzoquinone with Ethylene Glycol Dimercaptoacetate^a

Product	Quinone:Thiol Ratio		
	1:2	1:1	2:1
4	74.5 ± 2.8%	44.8 ± 1.1%	~3.5%
5	21.9 ± 0.72%	49.7 ± 0.60%	80.5 ± 4.8%

^a Yields based on quinone

the quinone. A small amount of **6** also was isolated, apparently formed by ester interchange during acetylation of the product mixture.

Varying the ratio of reactants led to the same products, but in different proportions, as shown in Table 1 (quantitation by analytical HPLC). As would be expected, increasing the ratio of **3** to **1** leads to increased formation of the diadduct, **5**.

We found no significant redox chemistry to occur between the initial hydroquinone adducts and unreacted benzoquinone (Figure 2), contrary to our observations with thioglycerol¹³ chemistry. Only at the highest ratio of **3:1**, could we find a small amount (3.1%) of hydroquinone. Traces of a substance which, from its HPLC retention time, could be a disubstituted hydroquinone also were found in this reaction, but the quantities were insufficient for isolation and identification. The absence of redox chemistry suggests either that the Michael reaction of glycol dimercaptoacetate is much faster than that of thioglycerol, or that the redox chemistry is less energetically favorable for the dimercaptoacetate adducts. We did not make rate measurements, but, although qualitative observations suggest the reaction of **1** is indeed faster, semiempirical MO calculations suggest the redox chemistry to be somewhat less favorable (see Discussion).

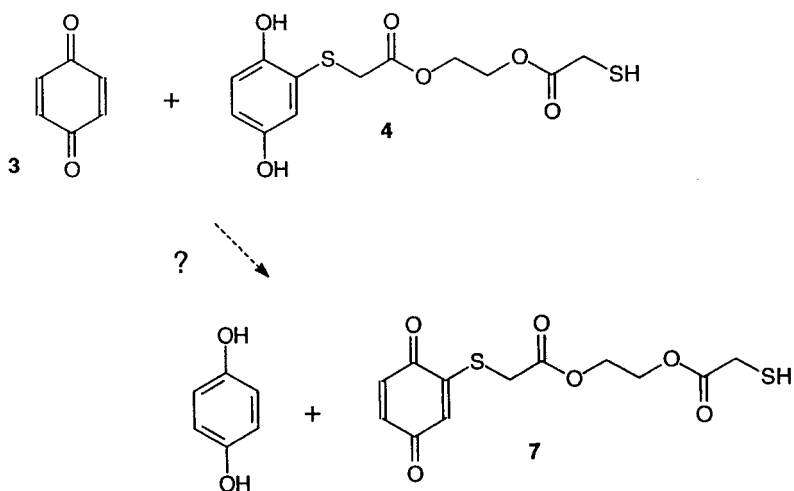


Figure 2: Redox reaction of Michael adduct and benzoquinone

Owing to the lower solubility of the pentaerythritol derivative **2** in polar solvents, reaction of **2** with **3** was carried out in a 1:1 mixture of dichloromethane and methanol. Figure 3 shows the outcome of this reaction, and Table 2 shows the proportions of products at various ratios of the reactants. Again, the dominant mode of reaction is Michael addition of thiol groups to one or more moles of quinone.

Thus, the reactivity of the two thiols toward benzoquinone is quite similar, and similar to the behavior of thioglycerol reported by us earlier¹³, save for the absence of redox chemistry. Yet **1** and **2** seem quite different in their ability to stabilize pulp.² We decided to test whether the presence of cellulose might affect the behavior of **2**, which could easily become entangled in a cellulose matrix. We therefore absorbed **3** and **2** in a 1:1 ratio from dichloromethane/methanol onto air-dried cellulose fibers, and allowed reaction to occur for two hours. The yellow coloration imparted to the fibers by the quinone slowly faded to white. Following extraction with

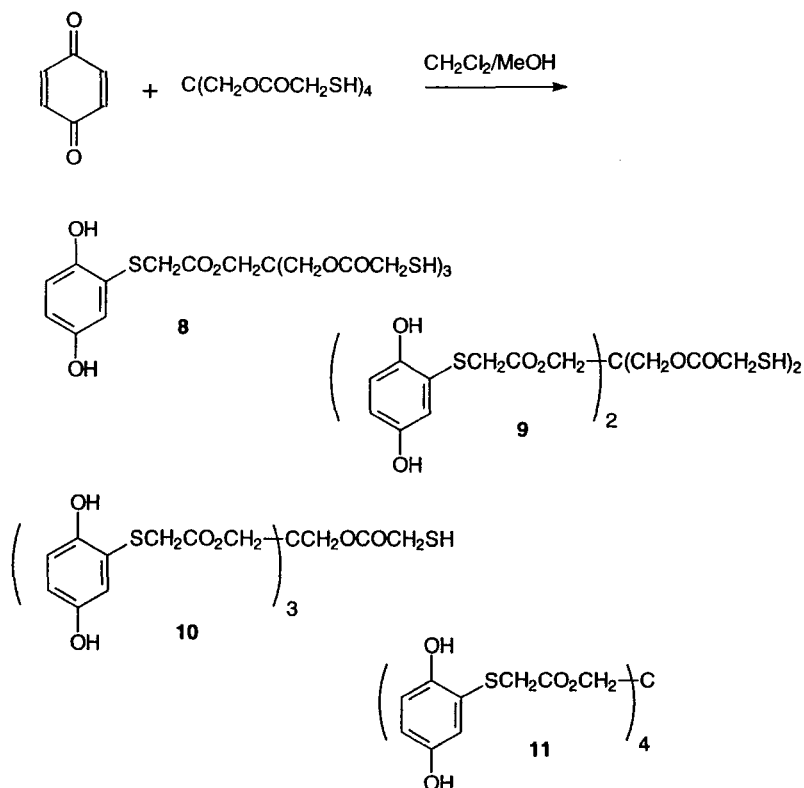


Figure 3: Reaction of benzoquinone with pentaerythritol tetramercaptoacetate

TABLE 2

Reaction of Benzoquinone with Pentaerythritol Tetramercaptoacetate^a

Product	Quinone:Thiol Ratio			
	1:1	2:1	3:1	4:1
8	33.6 ± 1.2%	10.2 ± 0.20%	2.0 ± 0.01%	0
9	45.9 ± 1.7%	30.6 ± 0.21%	13.6 ± 0.06%	0
10	16.1 ± 0.75%	35.9 ± 0.17%	31.2 ± 0.12%	Trace
11	3.2 ± 0.17%	26.8 ± 0.15%	43.7 ± 0.50%	9.2 ± 1.6%

^a Yields based on quinone

multiple portions of dichloromethane, the products were analyzed in the same way as for the solution reactions. The same products were observed: 4.6% **8**; 6.6% **9**; 6.0% **10**; and 36.5% **11**; based on conversion of **3**. The only significant difference from the solution reaction is the greater proportion of **11**, which might be associated with a lesser mobility of **2** and the addition products on the substrate as compared to solution. The implication is that the previously observed² differential stabilizing effect of **1** and **2** might simply result from the poor solubility of **2** in the polar solvents employed in that study.

To pursue this issue further, we prepared handsheets from lightly bleached aspen CTMP, measured their brightness, and impregnated the sheets with **1** or **2** (6% or 12%) from a 1:1 dichloromethane/methanol solvent. After drying, the brightness was measured again, and the sheets were irradiated at 350 nm. Brightness was measured at intervals to a total irradiation time of 66 hours (Figure 4).

The handsheets gained in brightness by about 3 points upon treatment with either **1** or **2**, contrary to the prior² results. At the 6% level, the brightness dropped rapidly upon irradiation; after 8 hours, the thiol-treated sheets were darker than the untreated controls, a position maintained to the end of the irradiation time. In our earlier work¹³ with thioglycerol, we showed that the greater discoloration arose from redox chemistry of the initial Michael adducts producing sulfur-substituted quinones that are darker than those produced by lignin photodegradation. Similar results were obtained at 12% loading. In both cases, although the glycol dimercaptoacetate **1** provided slightly better stabilization in the early part of irradiation, at long irradiation times the handsheets treated with **1** became slightly darker than those treated with **2**.

To assist us in rationalizing the experimental data, we carried out semi-empirical molecular orbital calculations (details in Experimental) on compounds **1**, **3**, **4**, **7**, and hydroquinone. The data are collected in Table 3.

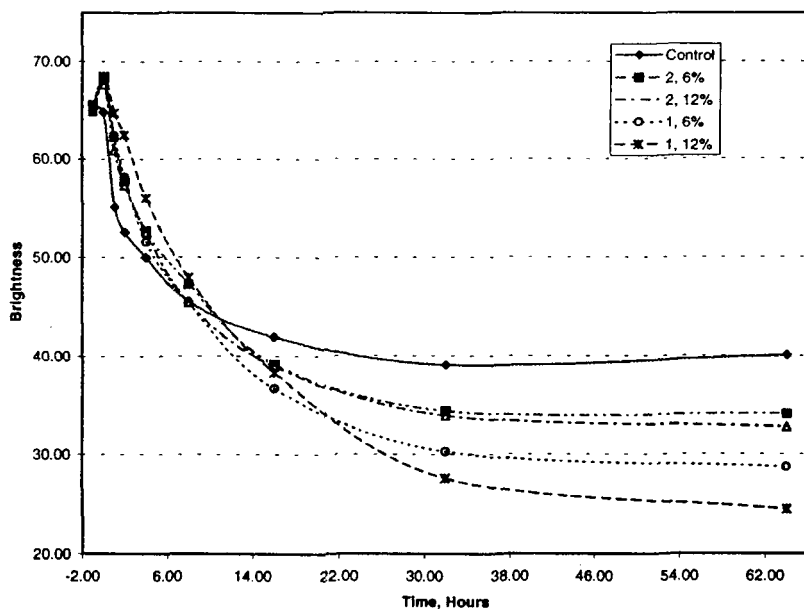


Figure 4: Irradiation of handsheets impregnated with 1 and 2

TABLE 3

Results of Semi-Empirical MO Calculations

Compound	ΔH_f , kcal/mol	$E_o(\text{vib})$, kcal/mol	E_{homo} , eV	E_{lumo} , eV
3	-25.1	55.9	-10.88	-1.74
Hydroquinone	-65.7	69.9	-8.73	0.22
1	-167.7	100.5	-9.21	---
7	-186.0	146.1	-9.20	-1.91
4	-230.6	160.5	-8.63	-0.51

Compounds **1**, **4**, and **7** are extremely flexible, and have a large number of conformers of similar stability. These may be divided, in the case of **1**, into two families, the *gauche* and the *anti*, the lowest energy members of which have energies differing by only a few tenths of a kcal/mol. Similarly, **4** and **7** exist in two families having the side chain either extended away from the ring, or folded back over it. Again, the most stable members of both families have very similar energies. The numbers given in Table 3 are for the slightly more stable *gauche* and folded conformers. The Experimental section contains more information regarding the identification of these families.

DISCUSSION

The initial chemistry of compounds **1** and **2** reacting with benzoquinone is essentially that found earlier for the reaction of benzoquinone with thioglycerol. A Michael addition of the thiol group converts the quinone to a sulfur-substituted hydroquinone. This process is responsible for the initial bleaching effect observed when the compounds are added to high-yield pulp. Although early experiments suggested that **2** did not cause an initial bleach, these observations probably resulted from the low solubility of **2** in polar solvents.

The subsequent behavior of the adducts, **4** and **8**, differs significantly from earlier observations. Adducts of benzoquinone and thioglycerol underwent redox chemistry analogous to that shown in Figure 2, producing sulfur-substituted quinones. These new quinones then underwent further Michael reactions, as long as free thioglycerol was present. Continued production of these quinones, which absorb at longer wavelength than unsubstituted quinones was suggested to be responsible for the eventual photoreversion of treated pulp, which ultimately became darker than untreated pulp.

One possible explanation for the difference in behavior observed in this work is thermodynamic. Using the computed enthalpies of formation from Table 3 (with zero point energy corrections), one calculates that the reaction in Figure 2 is *endothermic* by 3.6 kcal/mol. The corresponding reaction with the thioglycerol adduct was calculated to be *exothermic* by 1.8 kcal/mol.¹³

However, as shown in Figure 4, pulp treated with **1** or **2** still becomes darker than untreated pulp, suggesting that the darker, sulfur-substituted quinones are forming in the photoreversion experiments. One might suggest that the pulp may be facilitating the redox chemistry; however, in our examination of the Michael addition in the presence of pulp, we found no evidence of formation of such quinones. An alternative, which we are now investigating, is that the UV irradiation to which the handsheets are subjected facilitates the electron transfer necessary for oxidation of **4** and **8**. Excitation of an electron from the HOMO of **4** (-8.63 eV) to the LUMO (-0.51 eV) would bring it much closer to the energy of the LUMO of **3** (-1.74 eV), making oxidation of **4** much easier.

Regardless of whether this hypothesis is correct, we can suggest now that the apparent stabilization against reversion provided by thioglycerol and compounds **1** and **2** is illusory, and problems of odor and cost aside, these substances do not represent a realistic way of stabilizing high-yield pulp.

EXPERIMENTAL

Computational Methodology.

The energies cited in Table 3 were obtained from semi-empirical molecular orbital calculations employing the AM1 Hamiltonian, with full geometry optimization. The SPARTAN¹⁶ suite of programs was used for these calculations. Calculation of vibrational spectra including no imaginary frequencies ensured that the structures were minima on the

potential energy surface and yielded the zero point energies (E_0), which are used to correct the energies from 0 K (lowest vibrational state) to 273 K (some vibrational excitation).

The great flexibility of compound **1** and its derivatives **4** and **7** made especially important the task of establishing that we were looking at the global minima. The conformation space of these molecules was explored initially with molecular mechanics, employing a Monte Carlo algorithm. For compound **1**, this search found two families of conformers, one having the carbonyls *anti*- and one having them *gauche*; each family contained several conformers with varying dihedral angles along other bonds. The most stable members of each family were subjected to AM1 calculations, and found to lie within about 0.3 kcal/mol of each other, the *gauche* being slightly more stable. The less favorable steric interactions in the *gauche* appear to be compensated by dipolar attractions.

The conformation space of **4** and **7** was explored in the same way, with similar results. Each has a family of slightly different conformers with the thiodiglycolate chain extended away from the ring, and one with it coiled back over the ring. Again, the most stable conformer of each family was used for the AM1 calculations. The two conformers of **4** differed by 2 kcal/mol in favor of the folded form, owing largely to a hydrogen bond between a ring OH and the glycolate carbonyl, which compensates for unfavorable steric interactions. In compound **7**, the energy difference between the families is negligible, only 0.3 kcal/mol.

Full details of the calculations, including copies of the output files, are available from the authors upon request.

General

Benzoquinone was purchased from Aldrich. Ethylene glycol dimeracetoacetate (EGD) purchased from Evans Chemical was purified by distillation under vacuum (133-137 °C at 1.5 mm). The 2-methoxy-1,4-benzoquinone and thioglycerol disulfide were prepared by methods

previously described.¹³ Solvents and other commercial chemicals were used as received. Elemental analyses were performed by Desert Analytics, Tucson, AZ. NMR spectra were obtained with Varian XL-200 and Gemini 300 spectrometers. GC-MS data were obtained using a Hewlett-Packard 6890 Series GC/MSD, equipped with an HP-5 30 m capillary column. Socorex Calibra micropipettes were used for liquid volume measurements. Cellulose solid supports were prepared by disintegrating Whatman No. 3 filter paper in a commercial blender; the slurry was extracted with methanol and air-dried for a week before use.

HPLC quantification

Analytical HPLC was performed on a Hewlett-Packard 1090 Series II liquid chromatograph equipped with an AllTech analytical silica column (4.7 x 250 mm). The mobile phase was ethyl acetate hexane, 35:65 or 40:60. Preparative separations were accomplished with a Waters 510 HPLC or by standard column chromatography on silica gel. Yields were determined from calibration curves prepared using authentic samples and having correlation coefficients of at least 0.999, and are averages of at least triplicate runs.

General Method for Acetylation.

The substrate (50 - 400 mg) was suspended in excess acetic anhydride (10-15 mL), a few drops of pyridine were added, and the mixture was stirred until the substrate dissolved completely. The mixture then was allowed to stand overnight (ca. 20 h) at room temperature in a covered reaction vessel. The excess acetic anhydride, acetic acid, and pyridine were removed under vacuum (40-60 °C, 2-3 mm). The residue was dissolved in dichloromethane and analyzed directly.

Reaction of 1,4-benzoquinone (3) with EGD (1).

Benzoquinone (109.9 mg, 1.017 mmol) was dissolved in 10 mL of

methanol. To this solution was added a solution of EGD (214.5 mg, 1.020 mmol) in 2 mL of methanol. The solution darkened immediately, and quickly cleared. The mixture was stirred at room temperature for 2 h, and concentrated on a rotary evaporator. The residue was acetylated according to the general procedure. Flash column chromatography on silica gel with 1:1 ethyl acetate: hexane as eluent yielded the acetates of compound **4** (36.5%), **5** (50.2%), and a trace of the acetate of **6**. (Spectral data for acetates) **Compound 4**: ^1H nmr δ (ppm) = 2.30, 2.35 (6H, s, OCOCH_3), 2.39 (3H, s, SCOCH_3), 3.63, 3.69 (4H, s, SCH_2OCO), 4.31 (4H, m, $\text{CO}_2\text{CH}_2\text{CH}_2\text{OCO}$), 7.02 (1H, dd $J = 9$ Hz, 3 Hz, ArH), 7.09 (1 H, d, $J = 9$ Hz, ArH), 7.26 (1H, d, $J = 3$ Hz, ArH); ^{13}C nmr, δ (ppm) = 20.26, 20.55 (OCOCH_3), 29.58 (SCOCH_3), 30.76 ($\text{CH}_2\text{SCOCH}_3$), 34.97 (ArSCH_2), 62.42, 62.57 ($\text{CO}_2\text{CH}_2\text{CH}_2\text{OCO}$), 120.98, 122.85, 123.89, 128.48, 146.60, 147.90 (aryl C), 168.00, 168.32, 168.40, 168.57 (OCO), 193.21 (SCOCH_3); Anal., Calcd. For $\text{C}_{18}\text{H}_{20}\text{O}_9\text{S}_2$, %C = 48.65, %H = 4.50, %S = 14.41; found, %C = 48.40, %H = 4.35, %S = 14.26. **Compound 5**: ^1H nmr, δ (ppm) = 2.28, 2.34 (6H, s, OCOCH_3), 3.60 (4H, s, SCH_2OCO), 4.27 (4H, s, $\text{CO}_2\text{CH}_2\text{CH}_2\text{OCO}$), 7.00 (1H, dd, $J = 9$ Hz, 3 Hz, ArH), 7.08 (1H, d, $J = 9$ Hz, ArH), 7.24 (1H, d, $J = 3$ Hz, ArH); ^{13}C nmr, δ (ppm) = 20.25, 20.54 (OCOCH_3), 34.85 (SCH_2OCO), 62.48 (CO_2CH_3), 120.91, 122.84, 123.74, 128.54, 146.51, 147.90 (aryl C), 168.33, 168.39, 168.53 (OCO); Anal., Calcd. For $\text{C}_{26}\text{H}_{26}\text{O}_{12}\text{S}_2$, %C = 52.52, %H = 4.38, %S = 10.77; Found, %C = 51.92, %H = 4.23, %S = 10.43. **Compound 6**: ^1H nmr, δ (ppm) = 2.05 (3H, s, $\text{CH}_2\text{OCOCH}_3$), 2.29, 2.34 (6H, s, ArOCOCH_3), 3.11 (2H, s, SCH_2OCO), 4.23, 4.31 (4H, m, $\text{CO}_2\text{CH}_2\text{CH}_2\text{OCO}$), 7.02 (1H, dd, $J = 9$ Hz, 3 Hz, ArH), 7.09 (1H, d, $J = 9$ Hz, ArH), 7.26 (1H, d, $J = 3$ Hz, ArH); ^{13}C nmr, δ (ppm) = 20.22, 20.25, 20.57 (OCOCH_3), 35.05 (SCH_2OCO), 61.36, 62.79 ($\text{CO}_2\text{CH}_2\text{CH}_2\text{OCO}$), 120.99, 122.84, 123.90, 128.51, 146.61, 147.90 (Aryl C), 168.34, 168.46, 168.51, 170.24 (OCO); GC-MS (m/z): 370, 328, 286, 182, 154, 87, 43.

Reactions with other ratios of **1** and **3** were conducted and analyzed in the same manner.

Reaction of 1,4-Benzoquinone (**3**) with Pentaerythritol Tetrathioglycolate (PTG; **2**).

PTG (175 mg, 0.404 mmol) was dissolved in 2 mL of dichloromethane. To this solution was added benzoquinone (43.80 mg, 0.405 mmol) in 20 mL of 1:1 methanol and dichloromethane, dropwise over 30 min, with stirring. After stirring at room temperature for an additional 2 h, the mixture was concentrated on a rotary evaporator, and the residue was acetylated according to the standard procedure. Three fractions were isolated from the acetylated residue by column chromatography on silica gel with ethyl acetate/hexane mixtures gradually increasing from 40/60 to 70/30. The fractions were further purified by preparative HPLC (silica gel, ethyl acetate/hexane 40/60), yielding **8** (33.6%), **9** (45.9%), **10** (16.1%), and **11** (3.2%). (Spectral data for acetates). **Compound 8**: ^1H nmr, δ (ppm) = 2.29, 2.33 (6H, s, OCOCH_3), 2.38 (9H, s, SCOCH_3), 3.63 (2H, s, ArSCH_2), 3.64 (6H, s, CH_2SCO), 4.07 (6H, s, $\text{CH}_2\text{OCOCH}_2\text{S}$), 4.11 (2H, s, $\text{ArSCH}_2\text{CO}_2\text{CH}_2$), 7.01 (1H, dd, $J = 10$ Hz, 3 Hz, ArH), 7.09 (1H, d, $J = 10$ Hz, ArH), 7.22 (1H, d, $J = 3$ Hz, ArH); ^{13}C nmr, δ (ppm) = 20.23, 20.54 (OCOCH_3), 29.56 (SCOCH_3), 30.75 (CH_2SCO), 34.63 (ArSCH_2), 41.56 (4° C), 62.48, 62.59 (CO_2CH_2), 121.09, 123.10, 123.37, 128.22, 146.44, 147.93 (Aryl C), 167.60, 168.01, 168.28, 168.51 (OCO), 193.24 (SCOCH_3); Anal., Calcd. For $\text{C}_{29}\text{H}_{34}\text{O}_{15}\text{S}_4$, %C = 46.40, %H = 4.53, %S = 17.07; Found, %C = 46.46, %H = 4.36, %S = 16.68. **Compound 9**: ^1H nmr, δ (ppm) = 2.28, 2.34 (12H, s, OCOCH_3), 2.38 (6H, s, SCOCH_3), 3.62, 3.64 (8H, s, SCH_2), 3.97, 4.02 (8H, s, CO_2CH_2), 7.01 (1H, dd, $J = 9$ Hz, 3 Hz, ArH), 7.08 (1H, d, $J = 9$ Hz, ArH), 7.20 (1H, d, $J = 3$ Hz, ArH); ^{13}C nmr, δ (ppm) = 20.26, 20.57 (OCOCH_3), 29.59 (SCOCH_3), 30.78 (CH_2SCO), 34.61 (ArSCH_2), 41.45 (4° C), 62.49, 62.60 (CO_2CH_2), 121.02, 123.11,

123.27, 128.36, 146.38, 147.96 (Aryl C), 167.60, 168.63, 167.98, 168.51 (O $\overline{C}O$); Anal., Calcd. For C₃₇H₄₀O₁₈S₄, %C = 49.33, %H = 4.44, %S = 14.22; Found, %C = 49.63, %H = 4.31, %S = 13.81. **Compound 10:** ¹H nmr, δ (ppm) = 2.27, 2.33 (18H, s, OCOCH₃), 2.36 (3H, s, SCOCH₃), 3.60 (6H, s, ArSCH₂), 3.62 (2H, s, CH₂SCO), 3.90 (2H, s, CH₂OCOCH₂S), 3.95 (6H, s, ArSCH₂CO₂CH₃), 6.99 (1H, dd, J = 9 Hz, 3 Hz, ArH), 7.08 (1H, d, J = 9 Hz, ArH), 7.20 (1H, d, J = 3 Hz, ArH); ¹³C nmr, δ (ppm) = 20.25, 20.55 (OCOCH₃), 29.59 (SCOCH₃), 30.77 (CH₂SCO), 34.55 (ArSCH₂), 41.36 (4° C), 62.48, 62.59 (CO₂CH₂), 120.94, 123.07, 123.16, 128.44, 146.30, 147.96 (Aryl C), 167.51, 167.91, 168.32, 168.59 (O $\overline{C}O$), 211.48 (SCOCH₃); Anal., Calcd. For C₄₅H₄₆O₂₁S₄, %C = 51.42, %H = 4.38, %S = 12.19; Found, %C = 51.18, %H = 4.15, %S = 12.27. **Compound 11:** ¹H nmr, δ (ppm) = 2.24, 2.30 (24H, s, OCOCH₃), 3.56 (8H, s, ArSCH₂), 3.86 (8H, s, CO₂CH₂), 6.96 (1H, dd, J = 10 Hz, 3 Hz, ArH), 7.05 (1H, d, J = 10 Hz, ArH), 7.17 (1H, d, J = 3 Hz, ArH); ¹³C nmr, δ (ppm) = 20.20, 20.50 (OCOCH₃), 34.49 (SCH₂), 41.27 (4° C), 62.50 (CO₂CH₂), 121.85, 123.01, 123.06, 128.47, 146.23, 147.94 (Aryl C), 167.80, 168.01, 168.27, 168.54 (O $\overline{C}O$) [hindered rotation in a twisted conformation places the thioacetate carbonyls in different environments on the nmr time scale]; Anal., Calcd. for C₅₃H₅₂O₂₄S₄, %C = 53.00, %H = 4.33, %S = 10.67; Found, %C = 52.94, %H = 4.32, %S = 10.35.

Reactions with other ratios of PTG and **3** were conducted and analyzed in the same manner.

Reaction of Pentaerythritol Tetrathio glycolate (2) and 1,4-Benzoquinone (3) on Cellulose.

A solution of **2** (125.3 mg, 0.290 mmol) in 5 mL of dichloromethane and 1 mL of methanol was adsorbed onto 3 g of air-dried cellulose fibers. A solution of **3** (32.09 mg, 0.300 mmol) in 4 mL of methanol was added. The mixture was sealed into a plastic bag, the bag was kneaded for 15 minutes, and then allowed to stand at room temperature for 2 h. The

fibers were extracted with four portions of dichloromethane (25 mL each), and the combined extracts were concentrated on a rotary evaporator. The residue from the concentration was acetylated according to the general procedure, and analyzed by HPLC. The product mixture consisted of 4.6% **8**, 6.6% **9**, 6.0% **10**, and 36.5% **11**; total recovery based on benzoquinone 53.7%.

Brightness Measurements. Handsheets prepared (following TAPPI Standard T218 OM-91) from lightly bleached hardwood (Aspen) CTMP were treated with solutions of **1** or **2** in 1:1 dichloromethane: methanol. The treated sheets and appropriate controls were irradiated at 350 nm in a Rayonet photoreactor at ambient temperatures. ISO brightness¹⁷ was determined using a Technibrite Micro TB-1C brightness meter.

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