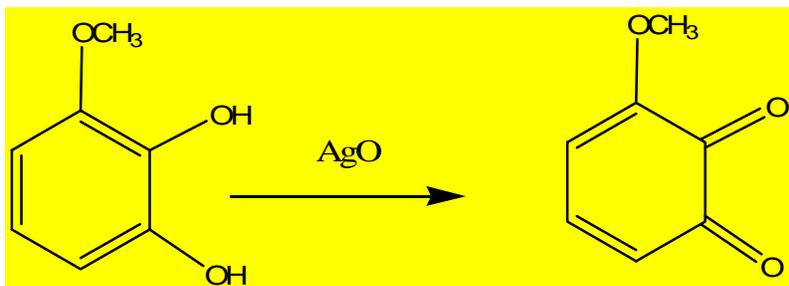
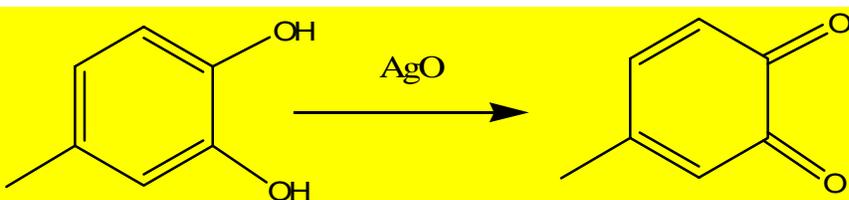


General Guidelines for Synthesis and Purification of Quinone Compounds



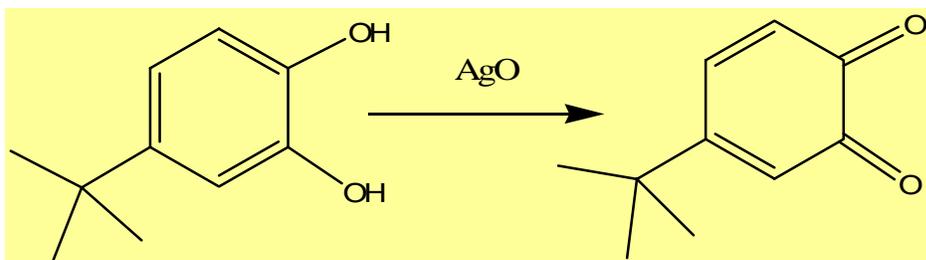
3-Methoxy-1,2-benzoquinone was prepared by silver oxide oxidation of 3-methoxy-catechol.¹ Catechol (2.01 g), 13 g of MgSO₄, and 11.00 g of AgO were combined in 150 mL diethyl ether, stirred

for 1.5 minutes, and then filtered into a round bottom flask. The volume of the solution was reduced by using a rotary evaporator (without a water bath) until dark red needles formed and the product was collected by filtration, washed with cold pentane, and stored in the freezer. The material was dried overnight, under slight vacuum, over P₂O₅.



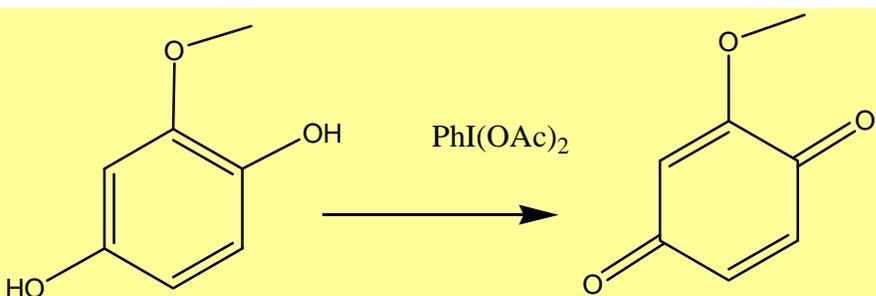
4-Methyl-1,2-benzoquinone was prepared by silver oxide oxidation of 4-methyl-catechol (2.45 g, beige

powder) using 15 g of MgSO₄ and 11.00 g of AgO in 150 mL diethyl ether. The mixture was stirred for 1.5 minutes and then filtered into a round bottom flask. The volume of the solution was reduced to approximately 75 mL by using a rotary evaporator (no water bath). Red needles formed as the solvent volume was reduced and the flask cooled. Pentane, 40 mL, was added to the flask and the solution volume was reduced to approximately 30 mL by a rotary evaporator (without a water bath). Then the product was collected by filtration and washed with cold pentane. The material was dried overnight, under slight vacuum, over P₂O₅. Note: the *ortho*-quinone was found to sublime and decompose when dried under high vacuum.



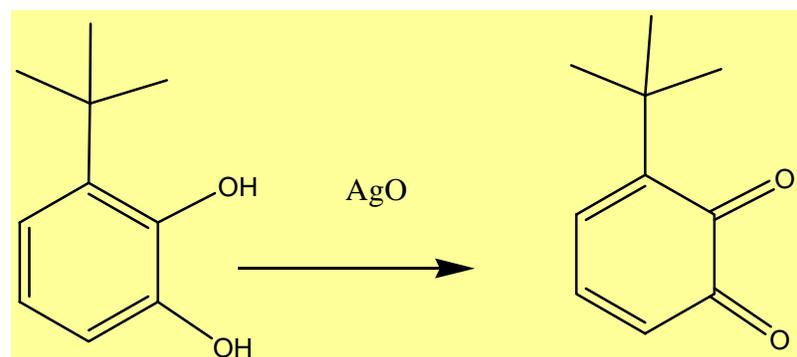
4-*tert*-Butyl-1,2-benzoquinone was prepared by silver oxide oxidation of 4-*tert*-butyl-

catechol (3.93 g, beige/brown powder) using 15 g of MgSO_4 and 10.00 g of AgO in 150 mL diethyl ether. The mixture was stirred for 2 minutes and then filtered into a round bottom flask. Pentane, 200 mL, was added to the flask and the flask was transferred to the freezer (-20°C). Fine brown/purple needles were formed after cooling. The volume of the solution was reduced by a rotary evaporator (without a water bath) to give a large crop of crystals. The collected crystals were washed with cold pentane and dried under vacuum, over P_2O_5 , for 8 hours.



2-Methoxy-1,4-benzoquinone was prepared by phenyliodine (III) diacetate oxidation of 2-methoxyhydroquinone using a procedure similar to Takata and others.ⁱⁱ Methoxyhydroquinone

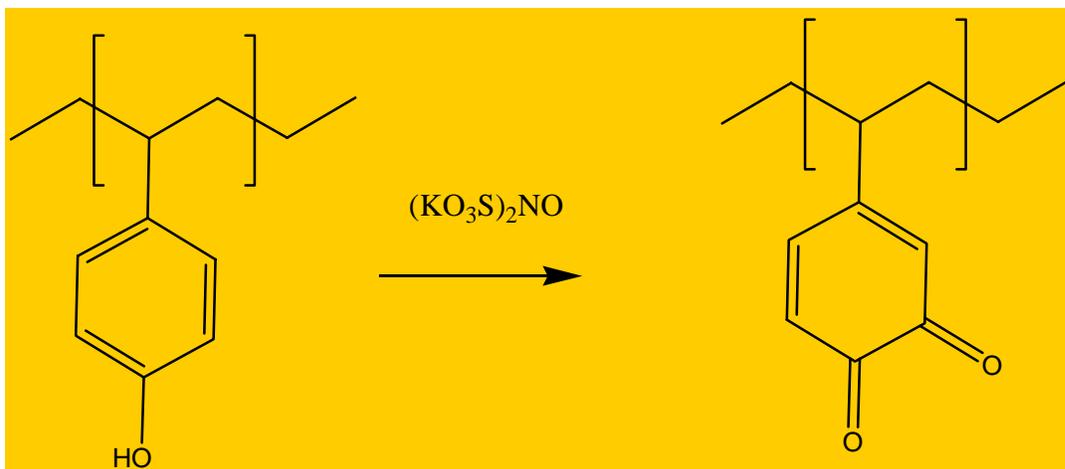
(2.10 g) was dissolved in 150 mL chloroform and 10.00 g of phenyliodine (III) diacetate was added. The solution was stirred for 30 minutes and then the solvent volume was reduced to 30 mL by using a rotary evaporator with a water bath temperature of 40°C . The solution was cooled (-20°C) overnight and yellow crystals formed. The material was recrystallized from 5 mL acetone, collected by filtration and dried under vacuum, over P_2O_5 , for 8 hours.



2-*tert*-Butyl-1,4-benzoquinone was prepared by silver oxide oxidation¹ of 2-*tert*-butyl-hydroquinone. Hydroquinone (1.92 g), 15 g of MgSO_4 and 13.00 g of AgO were combined in 150 mL diethyl ether. The mixture was stirred for 2

minutes and then filtered into a round bottom flask. The volume of the solution was reduced to 5 mL by using a rotary evaporator (without a water bath). The fine golden yellow crystals

were collected by filtration, recrystallized from pentane, and dried under vacuum, over P_2O_5 , for 8 hours.



Poly(4-vinylphenol) was oxidized with Fremy's reagent to give a polymer containing *ortho*-quinone structures. Approximately 2 g of poly(4-vinylphenol)

(MW ~22,000) was dissolved, with stirring, in 100 mL dioxane. Water, 50 mL (pH = 11), and 2.00 g potassium nitrosodisulfonate (Fremy's reagent) were added. A few drops of 1.0 N sodium hydroxide solution were added to the reaction and the resulting solution was stirred vigorously for 30 minutes under an argon atmosphere. The reaction was terminated by adding 50 mL 1.0N HCl. Then 300 mL of water was added, with agitation, to precipitate the polymer. The solution was filtered and the solid was taken up in methanol. Methanol was removed under vacuum to give a brown/red solid.

Quinone Modification of Isolated Lignins

Sodium periodate was used to introduce *ortho*-quinone structures into a residual lignin sample (softwood brownstock, conventional kraft, kappa = 28.). The procedure used was a slight modification of ones previously reported.^{iv} A 517 mg sample of lignin dissolved in 25 mL 90% (v/v) dioxane/water was added to 670 mg sodium periodate dissolved in 10 mL water and the solution was stirred in the dark, at room temperature. After 30 minutes, 100 mL water was added and dioxane solvent was removed by using a rotary evaporator with a water bath temperature of 45°C. The treated lignin was recovered by:

acid precipitation at pH = 2.0, sample freezing, thawing, centrifugation, and then decanting. The recovered lignin was freeze-dried and used for analysis.

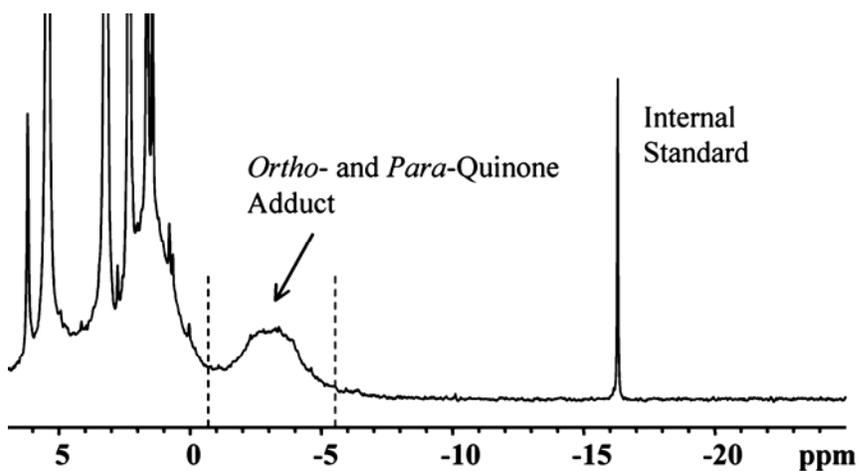
Fremy's reagent (potassium nitrosodisulfonate) was used to introduce quinone structures into a residual lignin sample (softwood brownstock, conventional kraft, kappa = 30.5). Brownstock residual lignin was oxidized using a procedure modified from the literature.⁴ Residual lignin (100 mg) was dissolved in 15 mL of 50 % (v/v) 1,4-dioxane/water adjusted to pH = 8.0 with 0.1 N sodium hydroxide. To the solution was added 450 mg of Fremy's reagent. The resulting mixture was stirred vigorously under an argon atmosphere for 1.5 hours. Excess Fremy's reagent in the reaction mixture was decomposed by adding 5 mL of 1.0 N HCl. The 1,4-dioxane solvent was removed from the reaction mixture by vacuum evaporation at a temperature of 45°C. The modified lignin was recovered by: sample freezing, thawing, and then centrifugation. The recovered lignin was washed once with water (pH = 2.0), freeze-dried and used for analysis.

Phosphorus(31)-NMR: *Ortho*- and *Para*-Quinone Content

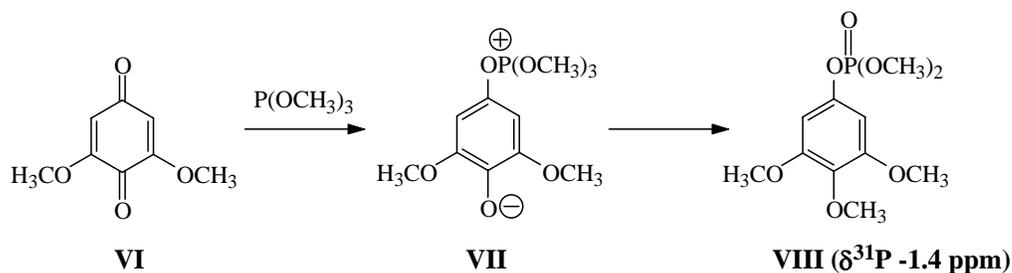
Dry residual lignin (30 mg) was derivatized with 250 μ L trimethylphosphite and 250 μ L anhydrous DMF under an argon atmosphere at room temperature for 2 days. Lignin samples were previously dried under vacuum at 40°C for 24 hours. NMR grade trimethylphosphite was either used from a freshly opened bottle or purified by distillation from solution containing sodium metal.

Derivatized lignin samples were prepared for analysis by removing excess trimethylphosphite under vacuum at 40°C for 3 hours. The treated lignins were dissolved in 450 μ L of solvent consisting of 60% DMSO-*d*₆/pyridine (v/v) containing tri-*meta*-tolylphosphate (0.7 mg/mL) and chromium-acetylacetonate (0.9 mg/mL). Derivatized lignin-quinone structures were hydrolyzed to the open-chain phosphate ester by the addition of 5 μ L water (0.3 mmol per 30 mg lignin). After 12 hours, the ³¹P-NMR spectrum of the resulting solution was acquired with a Bruker 400 MHz NMR spectrometer.

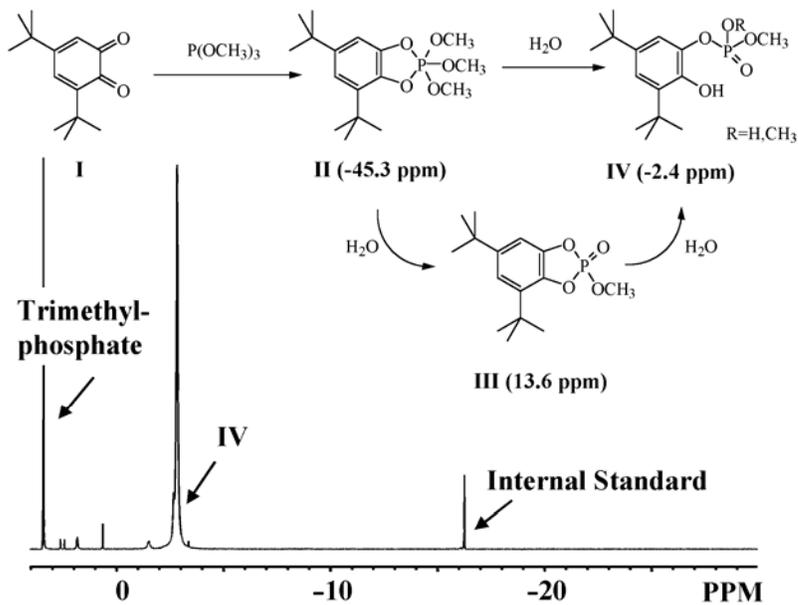
Phosphorus-NMR spectra were acquired under quantitative conditions at 305°K. A 90° pulse was utilized with a 5-second pulse delay along with inverse-gated broad-band proton decoupling. For each spectrum ~1500 scans were collected. The internal standard tri-*m*-tolylphosphate (δ -16.3 ppm) was used both for quantification and as a shift reference. The ^{31}P -NMR chemical shift of tri-*meta*-tolylphosphate in $\text{DMSO-}d_6$ was determined with the aid of 85% H_3PO_4 as an external shift reference. Previously, the chemical shift of tri-*meta*-tolylphosphate was reported as δ -17.3 ppm (CDCl_3 solvent). Quantification of lignin-quinone content was achieved by integrating the areas of the internal standard, δ -15.3 to -17.1 ppm, and the phosphate-ester (quinone adduct) resonance at δ -0.3 to -6.0 ppm.



Phosphorous-NMR spectrum of trimethylphosphite treated residual lignin treated with ClO_2 .



Reaction of trimethylphosphite with 2,6-dimethoxy-1,4-benzoquinone (^{31}P -NMR chemical shifts were determined in this study).



Reaction of trimethylphosphite with 3,5-di-*tert*-butyl-1,2-benzoquinone and the ³¹P-NMR spectrum after treatment and hydrolysis.

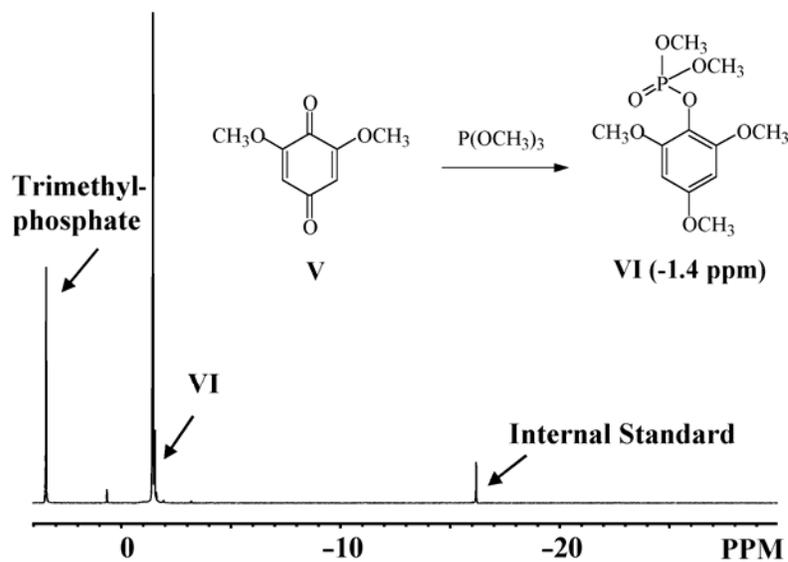
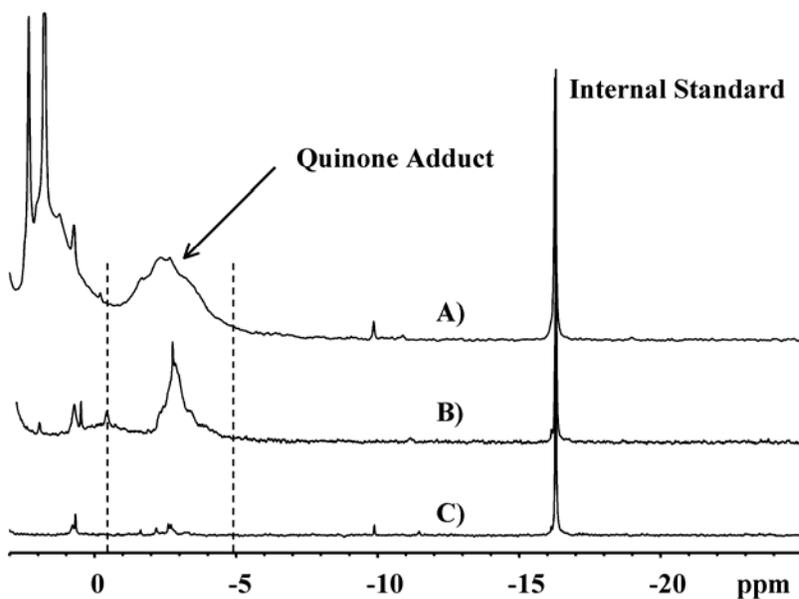


Figure 1. Reaction of trimethylphosphite with 2,6-dimethoxy-1,4-benzoquinone and the ³¹P-NMR spectrum after treatment and addition of water.



^{31}P -NMR spectra of compounds treated with 50% TMP/DMF for 2 days: A) D_0 residual lignin, B) oxidized PVP, and C) PVP.

All chemicals and equipment need to be handled in accordance with MSDS information, the IPST@GT safety manual, and the GA Tech Chemical Hygiene Plan.

References

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- i Cason, J., Chapter 6: Synthesis of Benzoquinones by Oxidation, in *Organic Reactions*, Volume 4, Adams, R., Editor, John Wiley and Sons, New York, (1948).
 - ii Takata, T., Tajima, R., and Ando, W., "Oxidation of Dihydroxy Aromatics by Hypervalent Iodine Oxides: A Facile Quinone Synthesis", *Journal of Organic Chemistry*, **48**, 4764, (1983).
 - iii Wozniak, J., Dimmel, D., and Malcolm, E., "The Generation of Quinones from Lignin and Lignin-Related Compounds", *Journal of Wood Chemistry and Technology*, **9** (4), 491, (1989).
 - iv Furman, G.S., "Contribution of Charge-Transfer Complexes to the Color of Kraft Lignin", Ph.D. Thesis, Institute of Paper Chemistry, Appleton, WI, (1986).