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D.R. Dimmel, X. Pan, and J.J. Bozell

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# PULPING CATALYSTS FROM LIGNIN: PROGRESS AND BARRIERS TO AN ECONOMIC SYNTHESIS

Donald R. Dimmel,<sup>1</sup> Xiaoqi Pan,<sup>1</sup> and Joseph J. Bozell<sup>2</sup>

<sup>1</sup>Institute of Paper Science and Technology, 500 10th St., N.W., Atlanta, GA 30318

<sup>2</sup>National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401 USA

**Abstract.** Oxidation of a lignin model disyringyl dimer with nitrogen dioxide (NO<sub>2</sub>) in the presence of air and N-hydroxysuccinimide (NHS) led to C<sub>1</sub>-C<sub>α</sub> cleavage with the formation of approximately equal amounts of 2,6-dimethoxy-*p*-benzoquinone (DMBQ) and glyceraldehyde-2-syringyl ether-type structures. The result indicates that only the phenolic end syringyl units of a lignin polymer will be converted to DMBQ upon treatment with the current NO<sub>2</sub> reaction conditions. Internal (nonphenolic) lignin units, bonded by β-O-4 linkages, will resist oxidization.

**Keywords.** Nitrogen Dioxide, Lignin Models, Oxidation, Benzoquinones

## INTRODUCTION

We have been investigating the feasibility of preparing low-cost anthraquinone (AQ) catalysts from lignin (1). The synthesis involves oxidation of lignin, or a lignin-related compound, to methoxy-substituted benzoquinones and then treatment of the latter with a diene to generate AQ-type structures (Figure 1). The key to developing a low cost catalyst by this approach is the synthesis yield. The cost at the present time is being hampered by a low yield in the first (oxidation) step.

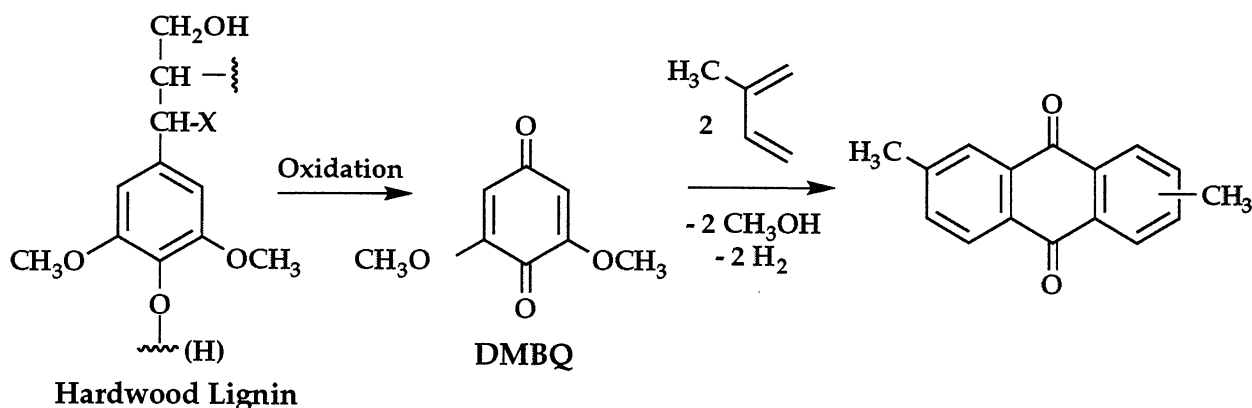


Figure 1. Chemical steps in the conversion of lignin to an AQ (1).

Many syringyl (hardwood) lignin models have been oxidized to 2,6-dimethoxy-*p*-benzoquinone (DMBQ) in high (~90%) yields with nitrogen dioxide (NO<sub>2</sub>) in the presence of air and N-hydroxysuccinimide (NHS) (2). The yields of DMBQ from lignin oxidations are much lower, typically 4-15% for a low-molecular-weight hardwood lignin and <4% for a high-molecular-weight lignin (3). This result suggests that few of the internal (nonphenolic) lignin units are being oxidized. The present study addresses the issue of internal lignin unit reactivity in NO<sub>2</sub> oxidations.

## EXPERIMENTAL

The general experimental conditions related to chromatography analyses, NMR equipment, NO<sub>2</sub>/NHS oxidation conditions, and the preparation of the compounds are described elsewhere (4).

**NO<sub>2</sub> Oxidation of Dimers 1e and 1t.** The NO<sub>2</sub>/NHS oxidation procedure<sup>2</sup> with either dimer 1e or 1t provided a product mixture showing three principal GC signals: DMBQ at retention time 6.3 min, compound 3 at 9.5 min, and compound 2 at 11.3 min. The preliminary structural assignments for 2 and 3 were based on mass spectral data: 3-hydroxy-2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)propanal (2) *m/z* (%) 256 (M<sup>+</sup>, 33), 226 (12), 197 (3), 183 (100), 168 (33), 155 (18), 127 (40), 109 (10), and 95 (18), and 3-hydroxy-2-(4-formyl-2,6-dimethoxyphenoxy)propanal (3) *m/z* (%) 254 (M<sup>+</sup>, 27), 224 (7), 195 (3), 181 (100), 166 (29), 153 (9), 125 (14), 107 (9), and 93 (9). The crude product was dissolved in ethanol and stirred with an excess of NaBH<sub>4</sub> for 2 hr. The solution was neutralized and extracted with chloroform and then ethyl acetate. The extracts were combined and dried over Na<sub>2</sub>SO<sub>4</sub>. An examination of the solution by GC showed that components 2 and 3 had been converted to a single component of retention time 12.4 min. A GC-MS indicated that this compound was 2-(4-hydroxymethyl-2,6-dimethoxyphenoxy)-1,3-propanediol. This compound was identical in GC retention time and MS to a synthesized sample.

## RESULTS AND DISCUSSION

### Model Selection

In order to establish the reactivity of internal lignin units, we decided to examine the yields of DMBQ that result from oxidation of a syringyl-syringyl dimer 1. The dimer was expected to give one equivalent of DMBQ from oxidation of the phenolic A-ring unit. We anticipated that the other oxidation product would be a nonphenolic structure (such as 2) composed of the B-ring joined to the A-ring side chain (Figure 2). The question was whether this structure would also be oxidized under the reaction conditions to give another equivalent of DMBQ. If the dimer provided two equivalents of DMBQ upon treatment with NO<sub>2</sub>/NHS, we rationalized that

internal (nonphenolic) lignin units would also be susceptible to oxidation by  $\text{NO}_2$ . A syringyl-type dimer was selected for study because DMBQ yields are high from the  $\text{NO}_2$  oxidations of syringyl compounds, while monomethoxybenzoquinone yields are generally low for the corresponding oxidation of guaiacyl units (2,5).

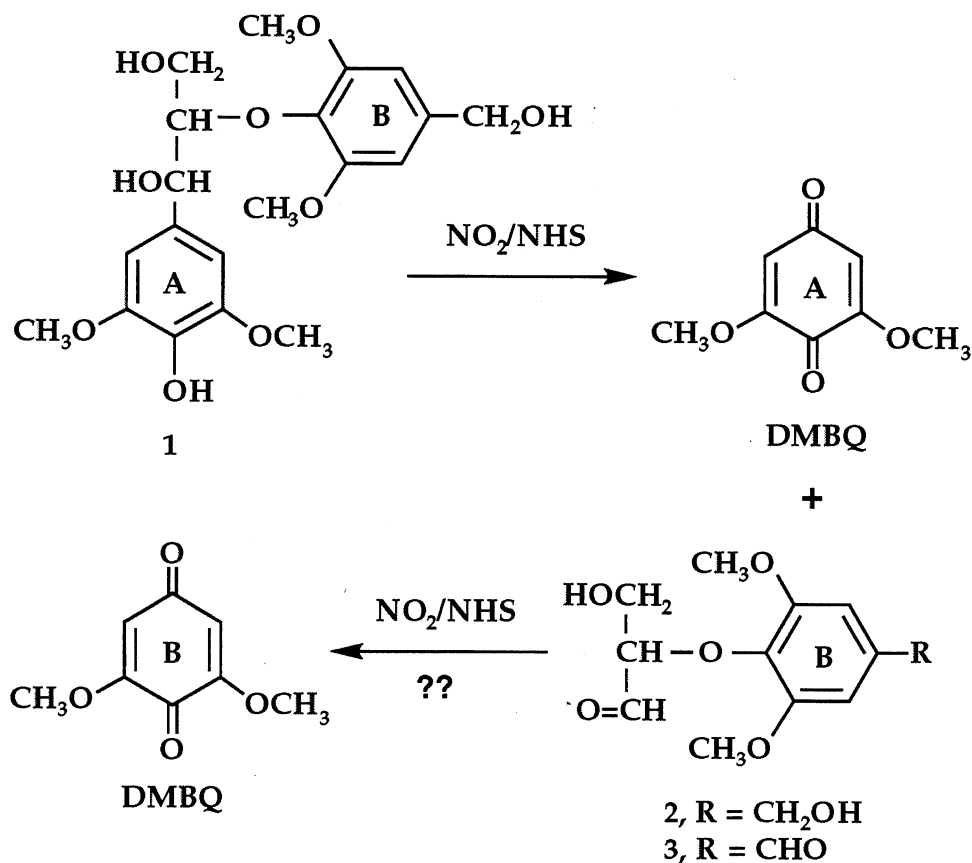


Figure 2. Potential  $\text{NO}_2$  oxidation reactions of syringyl-syringyl dimers.

Syringyl-syringyl dimer **1** was prepared in 52% overall yield by the reactions shown in Figure 3. Compound **1** has been prepared by Miksche in 1973 (6); however, we selected a route analogous to that employed by Katayama et al. to prepare guaiacyl dimers (7). The key step in the synthesis involved condensing 4-O-benzyl syringaldehyde (4) with ester acetal **5**. The acetal group in **5** prevents self-condensation in the presence of base; the benzyl group in **4** prevents ionization of the phenolic-OH in base and thereby facilitates a nucleophilic addition to the aldehyde group.

Both the ester acetal **5** and the resulting condensed acetal product were unstable and, thus, carried into the next step soon after preparation. Acidic hydrolysis of the condensed product gave a 7:1 mixture of stable erythro/threo aldehydes (**6e/6t**). Column chromatography resulted in partial separation of the two aldehydes. The

minor threo isomer was easily crystallized; the major erythro isomer was about 95% pure. The separated isomers were reduced with lithium aluminum hydride to give **7e** and **7t**; these were then hydrogenated to give **1e** and **1t**. The threo isomer again crystallized; it had a sharp melting point (equal to a literature value). The erythro isomer, a solid with a broad melting point range, again resisted various recrystallization attempts. This isomer is reported to be difficult to purify.<sup>8</sup> NMR analysis indicated that the compounds were  $\geq 95\%$  pure.

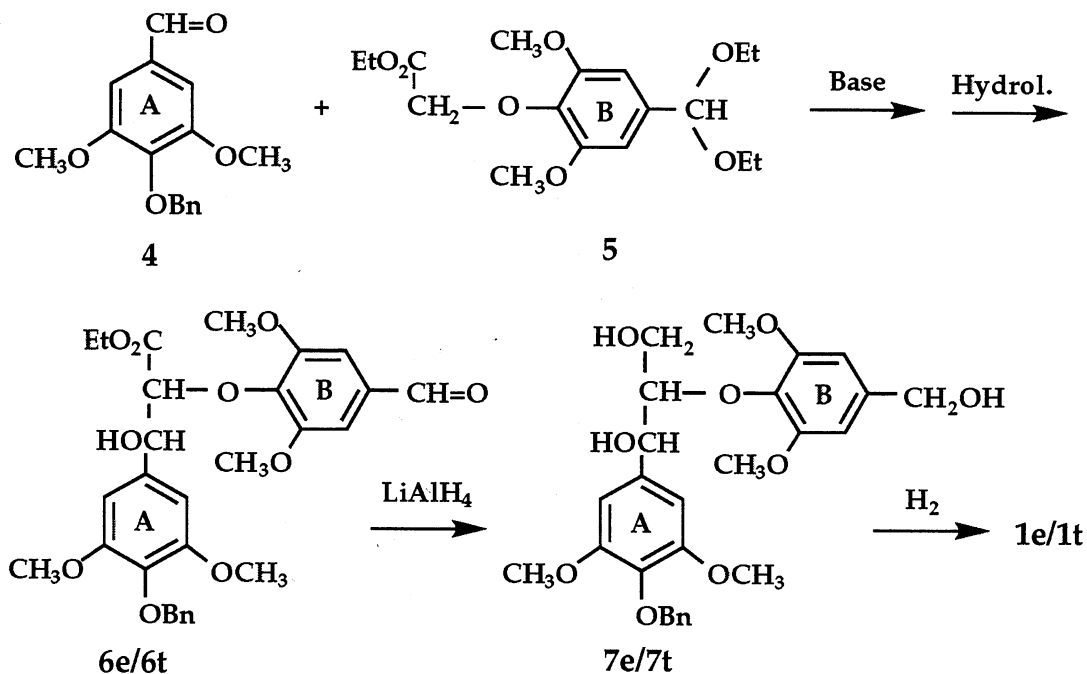


Figure 3. Synthesis of lignin model dimer **1**.

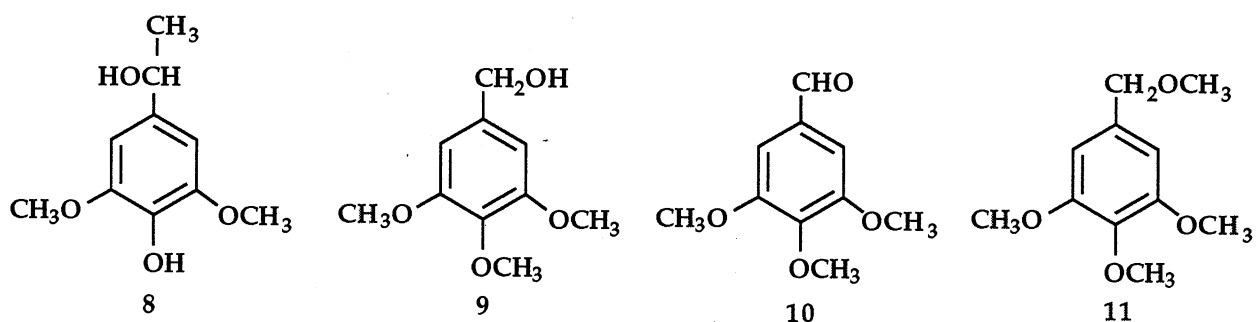
### DMBQ Yields from $\text{NO}_2$ Oxidations

The syringyl dimers **1e** and **1t**, along with monomeric compounds **8** and **9**, were oxidized with  $\text{NO}_2/\text{NHS}$ . The yields of DMBQ from **1e** and **1t** were  $\sim 40$  mole % (0.8 equiv. of DMBQ), as shown in Table 1. The yield difference between the two isomers of **1** was probably due more to a stereochemical difference than to a possible purity difference. The dimer DMBQ yields fit predictions based on the oxidation results of monomers **8** and **9**. The phenolic model,  $\alpha$ -methylsyringyl alcohol (**8**), gave an 0.88 equiv. of DMBQ, while the nonphenolic model, 3,4,5-trimethoxybenzyl alcohol (**9**), provided no DMBQ. The former mimics the A-ring and side chain, while the latter mimics the nonphenolic B-ring of the dimer models. If we consider that the dimers are composed of a "combination" of **8** and **9**, the ceiling yield of DMBQ from the dimer should be  $\sim 45\%$ .

Table 1. Yields of DMBQ from the treatment of dimers **1e** and **1t** and selected monomeric models with excess of NO<sub>2</sub> and NHS in methanol at 22°C for 2 hr.

<u>Compound</u>	<u>DMBQ Yield (%)</u>
Dimer <b>1e</b>	37, 38 <sup>a</sup>
Dimer <b>1t</b>	44, 46 <sup>a</sup>
$\alpha$ -Methylsyringyl Alcohol <b>8</b>	88
3,4,5-Trimethoxybenzyl Alcohol <b>9</b>	0

<sup>a</sup>Duplicate determinations; if both syringyl units in the dimer were completely converted to DMBQ, the yield would be 100%; if one were converted, then 50%.



Gas chromatography/mass spectroscopy (GC/MS) analysis of the NO<sub>2</sub> reaction solution from the nonphenolic model **9** showed starting material (60%) and a signal (40%) which contained two components: an oxidation product 3,4,5-trimethoxybenzaldehyde (**10**) and an (acid-catalyzed) solvent reaction product 3,4,5-trimethoxybenzyl methyl ether (**11**). The results indicate that a free phenolic OH group in the substrate is needed for DMBQ production and that the NO<sub>2</sub> conditions result in some benzyl alcohol oxidation to an aldehyde.

Apart from DMBQ, the product mixture from oxidation of dimer **1** also contained nonphenolic compounds **2** and **3**, that are from the B-ring portion of the molecule. The structures of these components were established by GC/MS and by reduction of each component to the same diol; the latter was also synthesized by a separate route.

The production of aldehydes **2** and **3** indicates that cleavage occurred between C<sub>1</sub>-C <sub>$\alpha$</sub>  without other alterations of the side chain. The dialdehyde component **3** probably is a secondary oxidation product of **2** or an oxidation of the A-ring -CH<sub>2</sub>OH group before oxidative cleavage of dimer **1**.

## CONCLUSIONS

The results obtained from this investigation indicates that the NO<sub>2</sub> oxidation of syringylglycerol-β-syringyl alcohol ether **2** leads to formation of DMBQ and glycer-aldehyde-2-syringyl ether-type structures via a C<sub>1</sub>-C<sub>α</sub> cleavage. It appears that the present NO<sub>2</sub> reaction conditions do not break down β-O-4 linkages and are incapable of oxidative cleavage of nonphenolic units. These conclusions suggest that only phenolic (terminal) syringyl units in a lignin macromolecule will be converted to DMBQ upon NO<sub>2</sub> oxidation. To achieve good DMBQ yields from lignin by NO<sub>2</sub> oxidation, it appears that lignin will have to be degraded into smaller pieces, either before or during the NO<sub>2</sub> oxidation. Such an approach is being taken (3).

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