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DIELS-ALDER REACTIONS OF LIGNIN-DERIVED QUINONES

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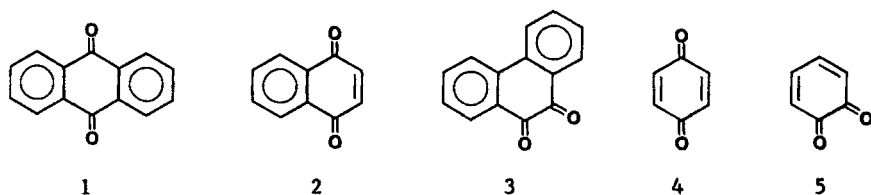
ABSTRACT

The Diels-Alder reactions of methoxy-p-benzoquinone and 2,6-dimethoxy-p-benzoquinone, which may be obtained from lignin and lignin model compounds, and of o-quinones (4-methyl, 4-acetyl, and 4-(1-hydroxyethyl)-o-benzoquinone) were investigated using 2,3-dimethylbutadiene, isoprene and styrene as dienes. Dimethylbutadiene and isoprene were found to be effective reactants, resulting in the generation of several Diels-Alder addition products. Loss of the methoxyl group and the side chain were observed under certain conditions. Reactions of the p-benzoquinones went more smoothly than the reactions of the o-quinones, and product yields were generally higher. Higher yields of anthraquinone products were obtained from 2,6-dimethoxy-p-benzoquinone than from methoxy-p-benzoquinone.

INTRODUCTION

Quinones, and especially anthraquinone (AQ, 1), are well known for their ability to promote pulping at catalytic levels.¹ While not as effective as AQ, naphthoquinone (2) and o-phenanthrenequinone (3) have some pulping catalytic activity. The lower ring members of this homologous series, namely p- and o-benzoquinone (4 and 5), do not promote pulping, presumably because of their low stability in pulping liquors.

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We have found that *p*-benzoquinone compounds can be generated through oxidation of lignin and lignin-related compounds.² We sought ways of building up the rings (homologizing) the simple methoxy substituted *p*-benzoquinones and *o*-benzoquinones to generate effective pulping catalysts from lignin. This paper addresses the homologization of benzoquinones related to lignin. A subsequent paper³ describes the catalytic activity of resulting products.

The Diels-Alder chemistry of some quinones is well known.⁴ As shown in Fig. 1, a homologous quinone synthesis, using the Diels-Alder reaction, involves three steps: the addition of a conjugated diene to a starting quinone, aromatization of the adduct, and oxidation of the resulting quinol to a quinone.⁵

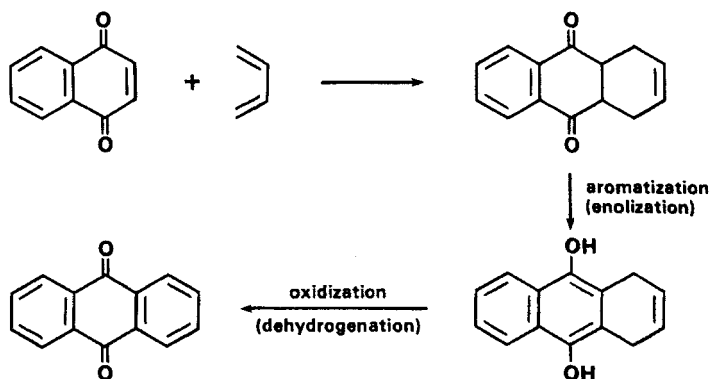


Figure 1. Quinone synthesis using the Diels-Alder reaction.⁵

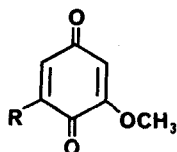
In order to achieve conversion of lignin-related benzoquinones to effective pulping catalysts (which normally have three

rings), we need to react both double bonds of the benzoquinones with dienes, even though one or more double bonds may be deactivated because of attached methoxyl groups. This paper describes the conditions needed to accomplish these homologizations. Yield optimization was not our main goal, but attempts to develop good yield procedures were addressed.

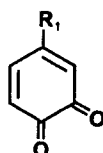
RESULTS AND DISCUSSION

Synthesis of Lignin Model Quinones

The basis for the selection of the benzoquinones studied (6-10) was related to our anticipated ability to generate these quinones from lignin or lignin-related compounds. Through oxidative cleavage of the lignin phenylpropane side chain, methoxy- and dimethoxy-*p*-benzoquinones (6 and 7) can be generated.² However, the samples of 6 and 7 used in this study were synthesized from readily available commercial compounds.^{6,7}



6, R=H
7, R=OCH₃



8, R₁=CH₃
9, R₁=COCH₃
10, R₁=CHOHCH₃

Oxidation of a phenolic hydroxyl group together with an adjacent methoxyl group in a lignin macromolecule would lead to generation of an *o*-benzoquinone. This quinone, of course, would remain attached in the lignin matrix via the propyl side chain. The three *o*-quinones selected for investigation have side chains which represent common features of the side chains actually found in lignin: an α -hydroxyl group, an α -carbonyl group, and a fully saturated carbon atom in the α -position.

It was found that 4-methyl-*o*-benzoquinone (8) could be obtained in low yield (14%) by the oxidation of 4-methylcatechol with silver (II) oxide;⁸ only small amounts of the compound could be isolated at one time. A second procedure involved the oxidation of 4-methylcatechol with *o*-chloranil.⁹ The yield from this reaction was much higher (64%), but the compound readily degraded after a few minutes under room conditions.

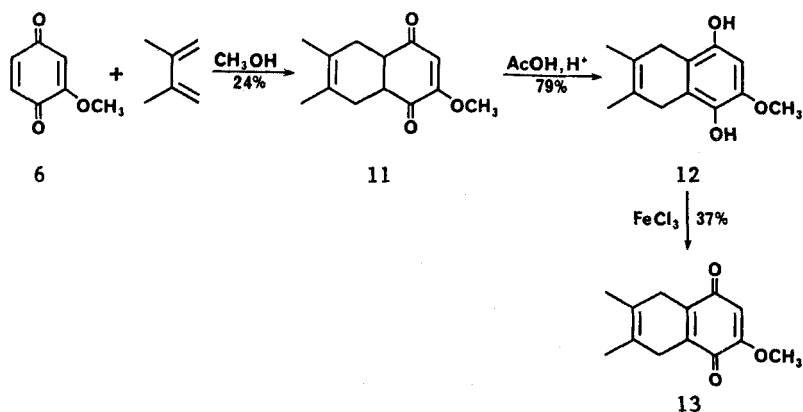
Because of their high reactivity, 4-acetyl- and 4-(1-hydroxyethyl)-*o*-benzoquinone (9 and 10) were not isolated but were generated, in the presence of a diene, through the sodium periodate oxidation of acetovanillone and α -methylvanillyl alcohol.¹⁰ Because sodium periodate can also react with *o*-benzoquinones, the reactions were monitored by GC; ethylene glycol was added after an appropriate reaction time to consume any unreacted sodium periodate.

Diene selection was based on reactivity considerations, ease of product characterization, and possible industrial applications.

Reactions of Methoxy-*p*-Benzoquinone

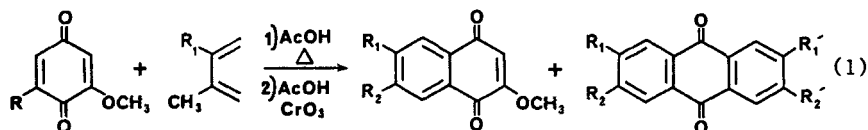
Reaction of 6 with a 50% molar excess of 2,3-dimethyl-1,3-butadiene in methanol¹¹ resulted in a 24% yield of 11 (Scheme 1).

Scheme 1



Enolization of 11 to a hydroquinone, 12, (79 % yield) was achieved by treatment with acid.¹¹ Hydroquinone 12 was oxidized to quinone 13 (37% yield) using ferric chloride in ethanol.¹¹ The overall yield to quinone 13 was only 7%.

By performing the Diels-Alder reaction in acetic acid and directly oxidizing the product with chromic acid,¹² we were able to by-pass several intermediates and obtain naphthoquinone 16 directly in 71% yield (Eq. 1). Unless noted otherwise, this single-pot procedure was employed in all subsequent reactions.



6, R=H 14, R₁=CH₃
7, R=OCH₃ 15, R₁=H

16, R₁=R₂=CH₃
17a, R₁=H, R₂=CH₃
17b, R₁=CH₃, R₂=H

18, R₁=R₁'=CH₃
R₂=R₂'=CH₃
19a, R₁=R₁'=H
R₂=R₂'=CH₃
19b, R₁=R₂'=H
R₁'=R₂=CH₃

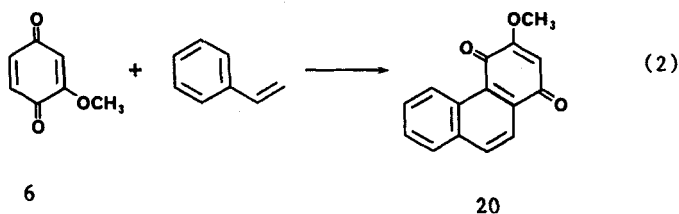
Attempts to obtain an anthraquinone structure by combining methoxy-*p*-benzoquinone with two units of diene were largely unsuccessful. When a 2.5 to 1 mole ratio of diene to dienophile was used and the reaction was run at a higher temperature, tetramethylantraquinone (18) was observed, but only in trace amounts; the major product was still the naphthoquinone, 16.

When 6 and 14 were heated together in the absence of a solvent, only the enolized monoadduct, 12, was obtained (36% yield). This result is significant in that it indicates that following the addition of one unit of the diene, the adduct has a stronger tendency to enolize (11 to 12) than to add another diene unit. A one-step synthesis of an anthraquinone derivative starting with methoxy-*p*-benzoquinone, therefore, would appear to be difficult.

The above results also show the strong influence of the electron donating methoxyl group in the formation of the initial Diels-Alder adducts. Both steric and electronic factors may be

significant in causing reaction to occur much more readily at the unsubstituted double bond of the quinone.

Reaction of methoxy-*p*-benzoquinone with 1.5 equiv. of isoprene (15) gave 17a and 17b in 53% yield (Eq. 1). A complex product mixture (as indicated by gas chromatography) resulted when styrene was reacted with methoxy-*p*-benzoquinone in acetic acid. The reaction without a solvent gave a low (5%) yield of phenanthrenequinone 20 (Eq. 2).



Reactions of 2,6-Dimethoxy-*p*-benzoquinone (7)

Heating a 1.5 to 1.0 mixture of 2,3-dimethyl-1,3-butadiene and 7 in acetic acid, followed by oxidation with chromic acid, gave a product mixture which was approx. 90% naphthoquinone 16 and 10% tetramethylantraquinone 18 (Eq. 1). When a 2.5 to 1 mole ratio of diene to dienophile was used, compounds related to 18 became the major products, but the yield was low.

Heating a mixture of 7 and 1.5 equiv. of isoprene at 114°C for 18 hr resulted in a 19% yield of the mixture of methyl-naphthoquinones 17a and 17b. A small percentage (approx. 6%) of dimethylantraquinone (19a and 19b) was detected by GC/MS. When the mole ratio was increased to 2.5 to 1 and the reaction was run under more vigorous conditions (180°C, 24 hr), the precipitated product was entirely dimethylantraquinone (25-30% yield).

These results indicate that the yields of the diadduct are greater from dimethoxy-*p*-benzoquinone than from methoxy-*p*-benzoquinone, although more vigorous reaction conditions are required. It is apparent that the methoxyl groups are liberated as methanol during the reaction; this gives rise to a quinone, rather than a

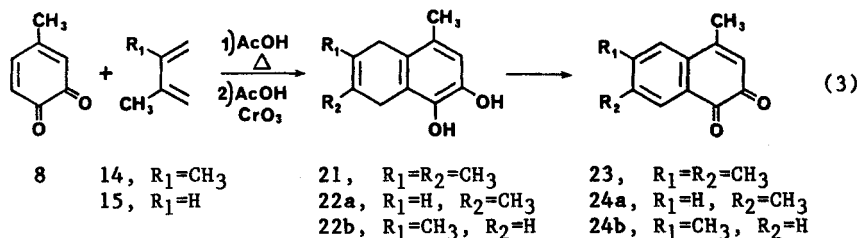
hydroquinone, intermediate and, therefore, favors further Diels-Alder reactions.

Only the starting material was recovered when 7 was heated with styrene even though the conditions were more vigorous than those employed for the corresponding reaction with 6. The additional methoxyl group is quite effective in blocking the addition of styrene to the compound.

Reactions of 4-Methyl-o-benzoquinone (8)

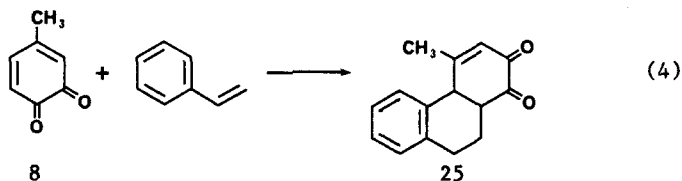
Because of the high reactivity of 8, the Diels-Alder reactions were performed on a freshly prepared, unpurified sample of the compound. Since the amount of 8 employed in the reactions was not determined, yields for the Diels-Alder reactions were based on the 4-methylcatechol used in its preparation.

Reaction of 8 with 2,3-dimethyl-1,3-butadiene was carried out at room temperature for 3 hr in chloroform using a diene to quinone mole ratio of at least 6 to 1 (based on the amount of 4-methylcatechol used).¹³ A 43% yield of an o-naphthohydroquinone, 21, was obtained. Apparently the enolized form of the adduct is more stable than the quinone form, and the initially formed adduct is immediately converted to the hydroquinone form. Oxidation of 21 with o-chloranil in ether¹³ resulted in an 83% yield of o-naphthoquinone 23 (Eq. 3).



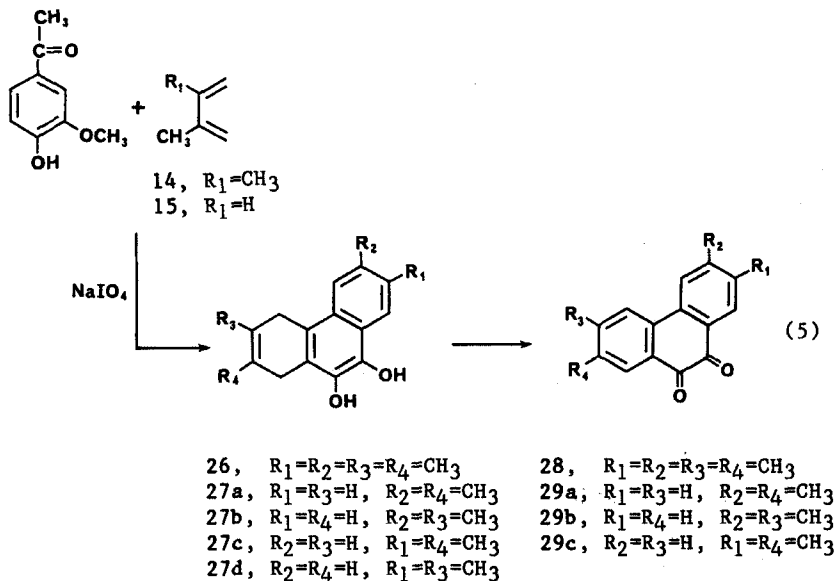
Reaction with isoprene was conducted in a similar manner but with a longer reaction time (17 hr). This resulted in a 32% yield of a mixture of naphthohydroquinones, 22a and 22b. Attempts to

oxidize this mixture with *o*-chloranil to get dimethyl-*o*-naphthoquinones 24a and 24b (Eq. 3) were unsuccessful, yielding only a dark brown tar. Reaction with styrene (20 hr) was similarly performed; the product was not isolated, but analytical data (GC/MS) indicated that the monoadduct, 25, had formed (Eq. 4).



Reactions of 4-Acetyl-*o*-benzoquinone (9)

Benzoquinone 9 was prepared through the sodium periodate oxidation of acetovanillone. This was done in the presence of a diene so that the Diels-Alder reaction would ensue before the *o*-quinone was consumed by other competing reactions. Reaction of 4-acetyl-*o*-benzoquinone with a large excess of 2,3-dimethyl-1,3-butadiene resulted in a red-orange precipitate which was identified as the phenanthrene derivative, 26 (Eq. 5).

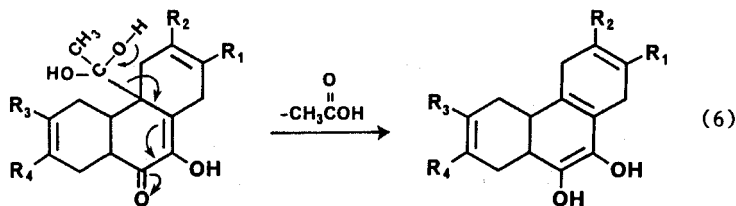


The maximum yield of precipitate obtained from this reaction (using a time of 4 hr) was 29%. It is likely, however, that the yield was even higher since some of the product remained dissolved in the reaction medium. Unfortunately, the reactivity of this compound in chloroform prevented extraction to obtain additional product and determine the true yield.

Oxidation of 26 with chromic acid resulted in a 43% yield of the tetramethylphenanthrenequinone, 28. The fact that 28 was also obtained by simply adding 26 to chloroform indicates that 26 has a strong tendency to form the fully aromatized phenanthrenequinone.

The reaction of 4-acetyl-*o*-benzoquinone with isoprene was performed in a similar manner. The product obtained (14% yield) was identified as phenanthrenediol 27 and is most likely a mixture of the four possible isomers, 27a-27d. Oxidation of 27 with chromic acid resulted in a 70% yield of the dimethylphenanthrenequinone, 29, which is again an isomeric mixture. Isolation and analysis of the 27 isomers were hampered by their strong tendency to form fully aromatized compounds.

The formation of the phenanthrene derivatives 26-29 is significant in that these compounds can only result through elimination of the acetyl side chain. A similar side chain elimination might be expected if an analogous reaction was run using an actual oxidized lignin preparation. A possible mechanism for the side chain loss might involve loss of acetic acid from a hydration carbonyl group, as shown in Eq. 6.



An attempt was made to form the Diels-Alder adduct between 4-acetyl-*o*-benzoquinone and styrene by following the same procedure used for reactions with 2,3-dimethyl-1,3-butadiene and iso-

prene. The only material isolated from the reaction mixture was the starting compound, acetovanillone. Apparently styrene suppresses the formation of the quinone from acetovanillone.

Reactions of 4-(1-Hydroxyethyl)-o-benzoquinone (10)

α -Methylvanillyl alcohol was treated with sodium periodate in an attempt to prepare o-benzoquinone 10. The reaction was performed in the presence of a large excess of 2,3-dimethyl-1,3-butadiene. A mixture of products resulted, of which an o-naphthoquinone and an o-phenanthraquinone (28) indicated 10 had been produced. However, the major (14% yield) isolated product was 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16). In order to get this product, the 1-hydroxyethyl side chain must have been lost, methoxy-p-benzoquinone generated, and diene addition occurred. Side chain loss from guaiacyl compounds containing α -hydroxyl groups is possible during sodium periodate oxidation.¹⁴

The reaction of the sodium periodate-oxidized α -methylvanillyl alcohol with isoprene was performed in a similar manner. A 6% yield of an isomeric mixture of 6- and 7-methyl-2-methoxy-1,4-naphthoquinone (17) was obtained. An attempt to form the Diels-Alder adduct between 4-(1-hydroxyethyl)-o-benzoquinone and styrene was unsuccessful.

Combined Oxidation/Diels-Alder Reactions

An attempt was made to combine an oxidative technique capable of generating quinones from lignin and lignin-derived compounds,² with a Diels-Alder reaction. Oxidation to quinones in the presence of a diene might be effective in trapping shortlived quinones, such as o-quinones. The combination of two steps into one operation might also be advantageous from an economic standpoint in the industrial application of this work.

Some degree of success was achieved with the use of potassium nitrosodisulfonate (Freymy's salt) as an oxidant. Appropriate reaction conditions for a combined Freymy's salt oxidation/Diels-Alder

reaction were established by first using the model compound, α -methylvanillyl alcohol, together with 2,3-dimethyl-1,3-butadiene. The diene was added just prior to the addition of the Fremy's salt. After holding at room temperature for a period long enough to achieve oxidation of the alcohol to methoxy-p-benzoquinone, the mixture was heated to initiate the Diels-Alder reaction. After product isolation and chromic acid oxidation, a 26% yield of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16) was obtained.

A hardwood lignin sample was subjected to the same set of conditions, using both dimethylbutadiene and isoprene. Reactions were conducted both with and without the chromic acid oxidation step. The solutions obtained after precipitation of the lignin were extracted with chloroform to determine if quinone structures were, in fact, being generated. In the dimethylbutadiene reactions, GC/MS analysis showed detectable levels of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16), as well as partially aromatized versions of the compound. In the isoprene reactions, the mixture of 6- and 7-methyl-2-methoxy-1,4-naphthoquinones (17) was detected at very low levels.

SUMMARY AND CONCLUSIONS

The results of this investigation show that a large number of Diels-Alder reactions are possible with lignin-derived quinones. Simple o- and p-benzoquinones can be converted to naphthoquinone, anthraquinone, and phenanthrenequinone products and related derivatives. Yields from reactions using dimethylbutadiene and isoprene can be high; styrene, however, was not found to be a very effective reactant.

Reactions of the methoxy-substituted p-benzoquinones show that the unsubstituted double bond is more reactive than the methoxylated double bond, but the latter will undergo Diels-Alder reaction with subsequent elimination of methanol. The strong ten-

dency of the tetrahydronaphthoquinone product from methoxy-p-benzoquinone to aromatize to a hydroquinone structure prevents further Diels-Alder reactions. Thus, methoxy-p-benzoquinone is less desirable than 2,6-dimethoxy-p-benzoquinone if anthraquinone products are desired.

Reactions of the o-benzoquinones show that the side chain in the 4-position may be eliminated if it contains the appropriate functional group. The loss of side chains containing α -hydroxyl groups and α -carbonyl groups from the lignin model quinones suggests that similar reactions could occur on quinones generated directly from lignin.

Although little attempt was made to optimize product yields, in general, better yields were observed from Diels-Alder reactions of p-benzoquinones than from o-benzoquinones. In the case of potassium nitrosodisulfonate, it was possible to combine the oxidation and Diels-Alder steps. The yield of naphthoquinone from the oxidation of α -methylvanillyl alcohol, however, was only about half of what was achieved through two separate steps. The yield of higher order quinones directly from lignin samples was also quite low.

Overall, the use of Diels-Alder reactions to convert lignin or lignin-related benzoquinones to higher order quinones shows much promise. Because compounds such as anthraquinone are known to catalyze delignification reactions, this finding has important implications in the area of using lignin or lignin-derived compounds in pulping processes.³

EXPERIMENTAL

Melting points were obtained using a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. NMR spectra were recorded on a Jeol FX 100 spectrometer using TMS as an internal reference. Parentheses following the signals indicate the splitting patterns (s = singlet, d = doublet, t = triplet, q =

quartet, m = multiplet, br = broad signal), integration areas, and signal assignments. Mass and NMR spectra were obtained for many compounds indicated in this section but are omitted here because the compounds are "known." The spectra were in complete accord with the assigned structures and can be found in the Ph.D. thesis of author J.C.W. Proton NMR spectra are included when observed and literature melting points differed substantially.

Gas chromatographic (GC) analyses were either done on a Hewlett-Packard 5890A GC or combined with mass spectrometric (MS) analyses and performed on a Hewlett-Packard 5985B GC/MS system. The GC/MS system employed helium (30 mL/min) as the carrier gas, a jet separator at 275°C, a source temperature of 200°C and an ionization voltage of 70 eV. On both instruments a 6-ft, 1/4-in. glass column packed with 3% silicone OV-17 on 100/120 chromosorb W-HP was used.

Synthesis of Lignin Model Quinones

Methoxy-*p*-benzoquinone, 6. The procedure of Erdtman⁶ was used; a 66% yield was obtained: m.p. 143.0-144.5°C [lit.^{6,15} m.p. 143-144°C, 144-145°C].

2,6-Dimethoxy-*p*-benzoquinone, 7. The procedure of Matsumoto and Kobayashi⁷ was used; a 66% yield was obtained: m.p. 253.0-254.0°C.

4-Methyl-*o*-benzoquinone, 8. A 14% yield was obtained through the procedure of Bailey and Dence:⁸ m.p. 74.5-75.5°C [lit.⁸ m.p. 74-76°C]. Larger, but less stable, quantities of 8 were synthesized through the procedure of Ansell, et al.;⁹ the yield was 64%: m.p. 72.5-74.5°C.

4-Acetyl-*o*-benzoquinone, 9, and 4-(1-hydroxyethyl)-*o*-benzoquinone, 10. The procedure of Imsgard, Falkehag and Kringstad¹⁹ was used. Appropriate reaction times were determined through GC analyses of samples which were periodically withdrawn; these indicated the complete reaction of acetovanillone and α -methylvanillyl alco-

hol in approx. 80 min and 1 min, respectively. Because of their reactivity, 9 and 10 were not isolated.

Synthesis of Diels-Alder Adducts

4a,5,8,8a-Tetrahydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinone, 11. The procedure of Ansell, Nash, and Wilson¹¹ was used except that reaction was at 45°C for 18.5 hr; a 24% yield was obtained: m.p. 133.5-134.5°C [lit.¹¹ m.p. 140.0-141.5°C]; ¹H-NMR (CDCl₃) δ 1.62 (s, 6, 6- and 7-CH₃), 2.0-2.5 (br, 4, 5- and 8-H₂), 3.0-3.3 (br, 2, 4a- and 8a-H), 3.78 (s, 3, OCH₃), 5.87 (s, 1, 3-H).

5,8-Dihydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinol, 12. Compound 11 (0.50 g) was dissolved in approx. 2 mL of boiling glacial acetic acid. When 2 drops of concd. HCl was added, a white precipitate immediately formed. This was recrystallized from 95% ethanol to give 0.39 g (79%) of 12: m.p. 212-214°C [lit.¹¹ m.p. 209-211°C]. Compound 12 was also obtained by the reaction of 0.20 g methoxy-*p*-benzoquinone and 0.41 mL of 2,3-dimethyl-1,3-butadiene, without a solvent, at 110°C for 18 hr. Recrystallization from acetic acid and washing with a little cold methanol resulted in 0.11 g (36%) of 12: m.p. 210.5-213.0°C.

5,8-Dihydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinone, 13. Through the procedure of Ansell, Nash, and Wilson,¹¹ a 37% yield was obtained: m.p. 133.0-135.0°C [lit.¹¹ m. p. 151-153°C]; ¹H-NMR (CDCl₃) δ 1.72 (s, 6, 6- and 7-CH₃), 3.00 (s, 4, 5- and 8-H₂), 3.81 (s, 3, 2-OCH₃), 5.86 (s, 1, 3-H).

2-Methoxy-6,7-dimethyl-1,4-naphthoquinone, 16. This and several of the following procedures are adaptations of the procedure of Fieser;¹² glacial acetic acid was used as the reaction medium, and aromatization was achieved through chromic acid oxidation. Methoxy-*p*-benzoquinone (0.50 g) and 2,3-dimethyl-1,3-butadiene (0.63 mL) were added to 23.0 mL of glacial acetic acid and heated at 45°C for 18.5 hr. A chromic acid solution consisting of 1.85 g of Na₂Cr₂O₇·2H₂O and 0.093 mL of H₂SO₄ in 1.16 mL of H₂O was then added, and the temperature was kept at approx. 67°C for 1 hr.

Upon addition of this mixture to approx. 100 mL of a 50% ice/water mixture, the product precipitated; it was washed several times with cold water and then dried over P₂O₅ to give 0.56 g (71%) of 16: m.p. 166.7-167.0°C [lit.¹⁶ m.p. 167-168°C]. Compound 16 was also obtained through the reaction of 0.20 g 2,6-dimethoxy-*p*-benzoquinone and 0.20 mL of 2,3-dimethyl-1,3-butadiene in 3.0 mL of glacial acetic acid at 115°C for 17.5 hr, followed by chromic acid oxidation.

2-Methoxy-6- and 7-methyl-1,4-naphthoquinone, 17a and 17b.

Methoxy-*p*-benzoquinone (0.50 g) and isoprene (0.54 mL) were added to 23.0 mL of glacial acetic acid and heated at 100°C for 18.5 hr. Treatment with chromic acid and product isolation were identical to those used for 16. This resulted in 0.39 g (53%) of a mixture of the isomers 17a and 17b: ¹H-NMR (CDCl₃) δ 2.48 (s, 3, 6- or 7-CH₃), 3.90 (s, 3, 2-OCH₃), 6.13 (s, 1, 3-H), 7.44-7.57 (m, 1, 6- or 7-H), 7.85-8.04 (m, 2, 5- & 8-H); ¹³C-NMR (CDCl₃) ppm 21.6, 21.8 (6- and 7-CH₃), 56.2 (2-OCH₃), 109.4, 109.5 (3-C), 126.0, 126.2, 126.5, 126.6 (5- and 8-C), 128.5, 129.5, 130.7, 131.6 (4a- and 8a-C), 133.6, 134.6, 144.0, 145.2 (6- and 7-C), 159.9, 160.1 (2-C), 179.3, 179.8 (1-C), 184.2, 184.5 (4-C). The isomeric mixture of compounds 17a and 17b was also obtained through the reaction of 0.20 g 2,6-dimethoxy-*p*-benzoquinone with 0.18 mL of isoprene in 3.0 mL of glacial acetic acid at 114°C for 18 hr.

2,3,6,7-Tetramethylantraquinone, 18. Compound 18 was obtained as a by-product of several reactions; it was not isolated. The highest yield was obtained through the reaction of 2,6-dimethoxy-*p*-benzoquinone with 2,3-dimethyl-1,3-butadiene to produce 16. Evidence for 18 was obtained through GC/MS: MS, m/z (rel. intensity), 264 (M⁺,100), 249 (38), 236 (12), 221 (27), 193 (14), 191 (13), 178 (17), 103 (10), 40 (13).

2,6- and 2,7-Dimethylantraquinone, 19a and 19b. Compounds 19a and 19b were obtained as by-products of the reaction between 2,6-dimethoxy-p-benzoquinone and isoprene to give compounds 17a and 17b as described above. They were the only products when the same reaction was run under more severe conditions: 0.20 g of 2,6-dimethoxy-p-benzoquinone and 0.30 mL of isoprene were added to 3.0 mL of glacial acetic acid and heated at 180°C for 24 hr. This was followed by oxidation with chromic acid and precipitation of the product with ice/water as described above. The yield of this reaction was estimated at 25-30%: $^1\text{H-NMR}$ (CDCl_3) δ 2.52 (s, 3, 2- and 6- or 7- CH_3), 7.55 (d with fine splitting, 1, $J = 8$ Hz, 3- and 6- or 7-H), 8.07 (s with fine splitting, 1, 1- and 5- or 8-H), 8.16 (d, 1, $J = 8$ Hz, 4- and 5- or 8-H); MS, m/z (rel. intensity), 236 (M^+ , 100), 221 (32), 208 (26), 207 (12), 193 (14), 179 (16), 178 (26), 165 (53), 89 (27), 76 (10), 63 (15). The additional splitting observed in the $^1\text{H-NMR}$ spectrum is taken as evidence for the formation of an isomeric mixture of compounds 19a and 19b. This was confirmed when recrystallization from methanol resulted in partial separation of the product into two sets of crystals, noticeably different in appearance and melting point.

Compounds 19a and 19b were also obtained through the reaction of the isomeric mixture of 2-methoxy-6- and 7-methyl-1,4-naphthoquinone (compounds 17a and 17b). The naphthoquinone mixture (0.100 g) was added to 3.00 mL of acetic acid and 0.074 mL of isoprene and heated at 150°C for 24 hr. This was followed by chromic acid oxidation and resulted in a reaction yield of 0.022 g (19%).

3-Methoxyphenanthrene-1,4-quinone, 20. The procedure of Inouye and Kakisawa¹⁷ was used to give a 5% yield: m.p. 153-157°C [lit.¹⁶ 168-169°C]; $^1\text{H-NMR}$ (CDCl_3) δ 3.91 (s, 3, 3-O CH_3), 6.09 (s, 1, 2-H), 7.49-9.50 (6, 5-H to 10-H).

5,8-Dihydro-4,6,7-trimethylnaphthalene-1,2-diol, 21. The procedure of Ansell, et al.¹³ was used; the yield was 43% (based on 4-methylcatechol): m.p. 152.5-153.5°C [lit.¹³ m.p. 149-151°C].

5,8-Dihydro-4,6- and 4,7-dimethylnaphthalene-1,2-diol, 22a and 22b. The same procedure that was used to produce 21 was used except that 10 mL of isoprene was used, and the reaction time was 17 hr. Crystallization was achieved from toluene and resulted in 0.92 g (32% based on 4-methylcatechol) of 22. Recrystallization from toluene resulted in light pink crystals: m.p. 149.4-149.5°C; $^1\text{H-NMR}$ (acetone- d_6) δ 1.78, 1.79 (s, 3, 6- or 7- CH_3), 2.05 (s, 3, 4- CH_3), 3.0-3.3 (br, 4, 5- and 8- H_2), 5.55 (m, 1, 6- or 7-H), 6.56 (s, 1, 3-H), 7.30 (br s, 2, 1- and 2-OH); MS, 190 $\underline{m/z}$ (100% rel. intensity) indicative of the molecular ion. Several of the $^{13}\text{C-NMR}$ signals were close together in the aromatic region and were therefore difficult to assign; signals were observed to occur in pairs, however, indicating that a mixture of isomers was produced.

4,6,7-Trimethyl-1,2-naphthoquinone, 23. The procedure of Ansell, et al.¹³ was used; an 83% yield of orange crystals which decomposed at around 112°C was obtained: [lit.¹³ indicates decomposition at 120°C]; $^1\text{H-NMR}$ (CDCl_3) δ 2.33, 2.35, 2.36 (s, 9, 4-, 6-, and 7- CH_3), 6.29 (q, 1, $J = 1$ Hz, 3-H), 7.24 (s, 1, 5-H), 7.87 (s, 1, 8-H).

4a,9,10,10a-Tetrahydro-4-methylphenanthrene-1,2-quinone, 25. The procedure for the preparation of 21 was employed except that 10 mL of styrene was used and the reaction time was 20 hr. Crystallization of the oil remaining after solvent evaporation was unsuccessful. Analysis of the oil by GC/MS, however, indicated that the monoadduct had formed: MS, $\underline{m/z}$ (rel. intensity), 226 (M^+ , 15), 171 (13), 170 (94), 156 (13), 155 (100), 154 (11), 153 (14), 128 (15), 115 (13), 92 (12), 91 (58), 77 (25), 65 (10), 51 (12).

1,4-Dihydro-2,3,6,7-tetramethylphenanthrene-9,10-diol, 26. Immediately following the addition of 0.90 g sodium periodate in 10 mL of distilled water to 0.70 g of acetovanillone dissolved in 10 mL of glacial acetic acid, 10 mL of 2,3-dimethyl-1,3-butadiene was added. The reaction vessel was kept in the dark with stirring for

4 hr. At that time 1 mL of ethylene glycol was added to combine with any unreacted sodium periodate. The red-orange precipitate which formed was filtered and rinsed twice with cold methanol to give 0.32 g (29% based on acetovanillone) of 26. Recrystallization was achieved from methanol. Melting with some decomposition to a dark brown liquid took place at approx. 260°C.

Attempts to analyze 26 were hampered by its reactivity; $^1\text{H-NMR}$ (CDCl_3) obtained in less than 2 min after dissolution showed δ 1.73 (s, 5, 6- and 7- CH_3), 2.26, 2.32 (s, d, 7, 2- and 3- CH_3), 2.9-3.1 (br, 4, 5- and 8- H_2), 7.10, 7.51 (s, 2, 9- and 10-OH), 7.72, 7.76 (s, 2, 1- and 4-H). Although the integration is not correct for the methyl groups, it is very likely that this is due to the fact that the compound had already started conversion to the fully aromatized phenanthrenequinone.

1,4-Dihydro-2,6-, 2,7-, 3,6-, and 3,7-dimethylphenanthrene-9,10-diol, 27. The procedure used to form 27 was identical to that used to produce 26 except that 10 mL of isoprene was used; raw yield was 0.14 g (14% based on acetovanillone): $^1\text{H-NMR}$ (CDCl_3) obtained shortly after dissolution showed δ 1.83 (s, 3, 6- or 7- CH_3), 2.39, 2.45 (s, d, 3, 2- or 3- CH_3), 2.9-3.3 (br, 4, 5- and 8- H_2), 5.55 (m, 1, 6- or 7-H), 7.2-8.0 (m, 5, aromatic H & OH).

2,3,6,7-Tetramethylphenanthrene-9,10-quinone, 28. Compound 26 (0.10 g) was dissolved in 10 mL of glacial acetic acid and then oxidized and isolated as described above to give 0.042 g (43%) of 28: m.p. 250-254°C (with some decomposition); $^1\text{H-NMR}$ (CDCl_3) δ 2.27 (s, 6, 2- and 7- CH_3) 2.35 (s, 6, 3- and 6- CH_3), 7.55 (s, 2, 4- and 5-H), 7.78 (s, 2, 1- and 8-H).

2,6-, 2,7-, and 3,6-Dimethylphenanthrene-9,10-quinone, 29. Compound 27 was oxidized to 29 with chromic acid by following the same procedure described above for the oxidation of 26 to 28. From 0.135 g of 27, 0.093 g (70%) of 29 was obtained: $^1\text{H-NMR}$ (CDCl_3) δ 2.39 (s, 2, 2- and 7- CH_3), 2.46 (s, 4, 3- and 6- CH_3), 7.1-8.0 (m, 6, aromatic H).

Reaction of Compound 10 with 2,3-Dimethyl-1,3-butadiene. Immediately following the addition of 0.64 g of sodium periodate in 7 mL of distilled water to 0.50 g of α -methylvanillyl alcohol dissolved in 7 mL of glacial acetic acid, 7 mL of 2,3-dimethyl-1,3-butadiene was added. After 1 min, 1 mL of ethylene glycol was added to combine with any unreacted sodium periodate. The reaction was then allowed to proceed in the dark with stirring. Reaction at room temp. for 3 hr resulted in 0.093 g of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16, 14% yield based on α -methylvanillyl alcohol). A second reaction run at 45°C for 18.5 hr. generated a brown residue; 0.034 g was filtered from the reaction mixture: m.p. 205-209°C; MS, m/z (rel. intensity), 214 (100), 199 (59), 186 (57), 171 (36), 157 (15), 143 (28), 142 (27), 141 (47), 128 (35), 115 (35), 84 (16), 77 (19), 51 (17), 44 (48). The latter compound was assumed to be 6,7-dimethyl-4-ethylene-1,2-naphthoquinone. Oxidation of the filtrate with chromic acid resulted in a mixture of compounds including the above compound, 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16), and 2,3,6,7-tetramethylphenanthrene-9,10-quinone (28).

Reaction of Compound 10 with Isoprene. The procedure used for the reaction with isoprene was identical to that used for the reaction with 2,3-dimethyl-1,3-butadiene. Reaction at room temperature for 4 hr generated 0.035 g of a mixture of 6- and 7-methyl-2-methoxy-1,4-naphthoquinone (17); the yield was 6%, based on α -methylvanillyl alcohol).

Combined Oxidation/Diels-Alder Reactions

Reaction of α -methylvanillyl alcohol. A 1.00-mmole sample of α -methylvanillyl alcohol² was dissolved in 10 mL of ethylene glycol monomethyl ether and cooled to approx. 0°C in an ice bath. Under a stream of nitrogen, potassium nitrosodisulfonate (Fremy's salt, 3.0 mmole) was added to 20.0 mL of a 0.2M $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$ buffer solution (pH 6.0) which had also been cooled in an ice bath. The diene (2,3-dimethyl-1,3-butadiene, 1.0 ml) was then

added to the α -methylvanillyl alcohol solution, followed immediately by the dropwise addition of the Fremy's salt, using fairly vigorous stirring and a stream of nitrogen to blanket the reaction.

After the addition of the Fremy's salt, the reaction mixture was removed from the ice bath and allowed to come to room temperature. After 2 hr, the reaction residue was suction filtered through a fine sintered-glass Buchner funnel and rinsed with 25 mL of glacial acetic acid. An additional 1 mL of diene was added to the filtrate, and the temperature was raised to 45°C for 18 hr. The mixture was then added to ice/water to precipitate the Diels-Alder addition product. This material was washed with cold water and transferred to a flask with 10 mL of glacial acetic acid for chromic acid oxidation. The addition of the oxidized solution to ice/water caused the precipitation of the final product; 0.26 mmole (26% yield) of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16) was obtained.

Reaction of lignin. The above procedure was repeated with a lignin sample isolated from the acid-catalyzed pulping of aspen with ethanol;² however, the mixture obtained after the 2-hr Fremy's salt oxidation was not filtered, and the additional 1 mL of diene was not added. Both dimethylbutadiene and isoprene were used with 400 mg of lignin. Lignin products obtained both with and without chromic acid oxidation were isolated through the use of centrifugation and freeze dried.

The liquid obtained after precipitation of the lignin was extracted with CHCl_3 (4 X 40 mL), and the extract was washed with saturated NaHCO_3 solution (2 X 40 mL) and water (3 X 40 mL), and dried over anhydrous Na_2SO_4 ; in a few cases the entire reaction mixture was extracted. The extract was then evaporated under reduced pressure and analyzed by GC/MS.

Analyses of the CHCl_3 extracts of the dimethylbutadiene reactions both before and after chromic acid oxidation gave evidence of the production of 2,6-dimethoxy-p-benzoquinone (7)

and 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (16). Analyses of the CHCl_3 extracts of the isoprene reactions before and after chromic acid oxidation also gave evidence of the generation of 2,6-dimethoxy-p-benzoquinone as well as 2-methoxy-6- and 7-methyl-1,4-naphthoquinone (17). One compound, appearing to have a molecular weight of 238, could indicate the formation of the isoprene diadduct; MS, m/z (rel. intensity), 238 (43), 183 (100), 182 (58), 167 (20), 139 (15), 123 (10), 69 (14). This compound appeared as a reaction product before chromic acid oxidation after both 112 and 185°C reactions but was much more predominant at the higher temperature.

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