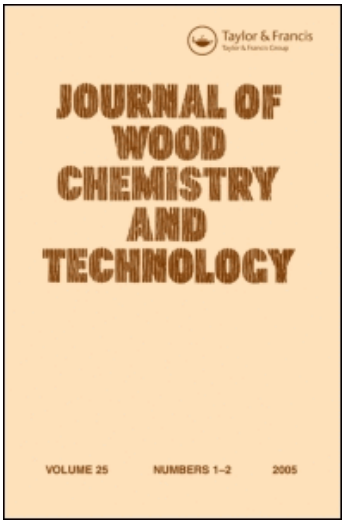

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PULPING CATALYSTS FROM LIGNIN (6). NITROGEN DIOXIDE OXIDATION OF 5-SUBSTITUTED GUAIACYL COMPOUNDS

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ABSTRACT

Bromination was investigated as a potential approach to improve the yield of benzoquinones from lignins by blocking the C_5-position of guaiacyl-type units. The 5-position is a reactive position, often leading to undesirable byproducts when guaiacyl units are oxidized to radical intermediates. The NO_2 reaction of 5-bromovanillin in methanol in the presence of N-hydroxysuccinimde (NHS) provided ~50% yield of 2,6-dimethoxy-*p*-benzoquinone (DMBQ), together with ~4% yield of the expected product, 5-bromo-3-methoxy-*p*-benzoquinone (BMBQ). The NO_2 reaction of 5-chlorovanillin gave a similar result, while 5-iodo- and 5-hydroxymethylvanillin provided poor yields of benzoquinones. The halovanillins gave no benzoquinones in the absence of NHS. A mechanism involving generation of phenolate radicals from NHS radicals can account for these results. During the oxidation, most of the 5-halo groups were converted to 5-methoxy groups by reaction with the solvent; experimental results suggested that the solvolysis occurred with the radical intermediates, before halobenzoquinone production.

A high yield of DMBQ was obtained from a mixture of vanillin and syringaldehyde by treating first with bromine and then with NO_2/NHS. This sequence could be a potential way for improving the yields of benzoquinones from lignins.

INTRODUCTION

Lignin-derived benzoquinones can be used to synthesize anthraquinone pulping catalysts.[1] To date, the best method for generating these benzoquinones is to treat lignins with nitrogen dioxide (NO_2) in air and in the presence of N-hydroxysuccinimde (NHS) in methanol.[2] Two kinds of benzoquinones are possible: monomethoxy-*p*-benzoquinone (MMBQ, **1**) from guaiacyl lignin units and 2,6-dimethoxy-*p*-benzoquinone (DMBQ, **2**) from syringyl lignin units. Previous studies have demonstrated that DMBQ yields are much higher than MMBQ yields from NO_2 oxidations of appropriate lignin model compounds[2] and of different types of lignin.[3] Since guaiacyl lignin units are much more plentiful in nature than are syringyl units,[4] we are limited in the amounts of benzoquinone structures that can be obtained from lignins by this type of oxidation.

The yield differences for the two kinds of lignin units are probably related to the radical nature of the NO_2 reactions. Nitrogen dioxide is known to abstract hydrogen atoms from phenolic hydroxyl groups to generate an oxo radical.[5] A proposed mechanism for an NO_2 oxidation of a lignin unit is shown in Figure 1. The observed high yields of DMBQ from NO_2 oxidations of syringyl units indicate a strong preference for reaction at a C-1 radical site. This is probably related to the ease with which the C-1 substituent can be lost, relative to the C-3 and C-5 methoxyl groups.[6] A guaiacyl unit, on the other hand, has a reactive C-5 radical site[6] which could be susceptible to nitration, oxidation, and/or C_5-coupling (Figure 1). The yield data from NO_2 reactions of guaiacyl structures indicate a strong preference for reaction at C-5, giving rise to 5-nitroguaiacyl-related products, rather than at C-1, which would produce MMBQ.[2]

This paper describes the reactions of 5-halo and 5-hydroxymethyl guaiacyl compounds with NO_2/NHS. The purpose of the research was to examine ways to improve benzoquinone yields from guaiacyl units by the introduction of an appropriate blocking group into the 5-position prior to NO_2 oxidation. Effects of NO_2 reaction conditions and substrate structure are also addressed.

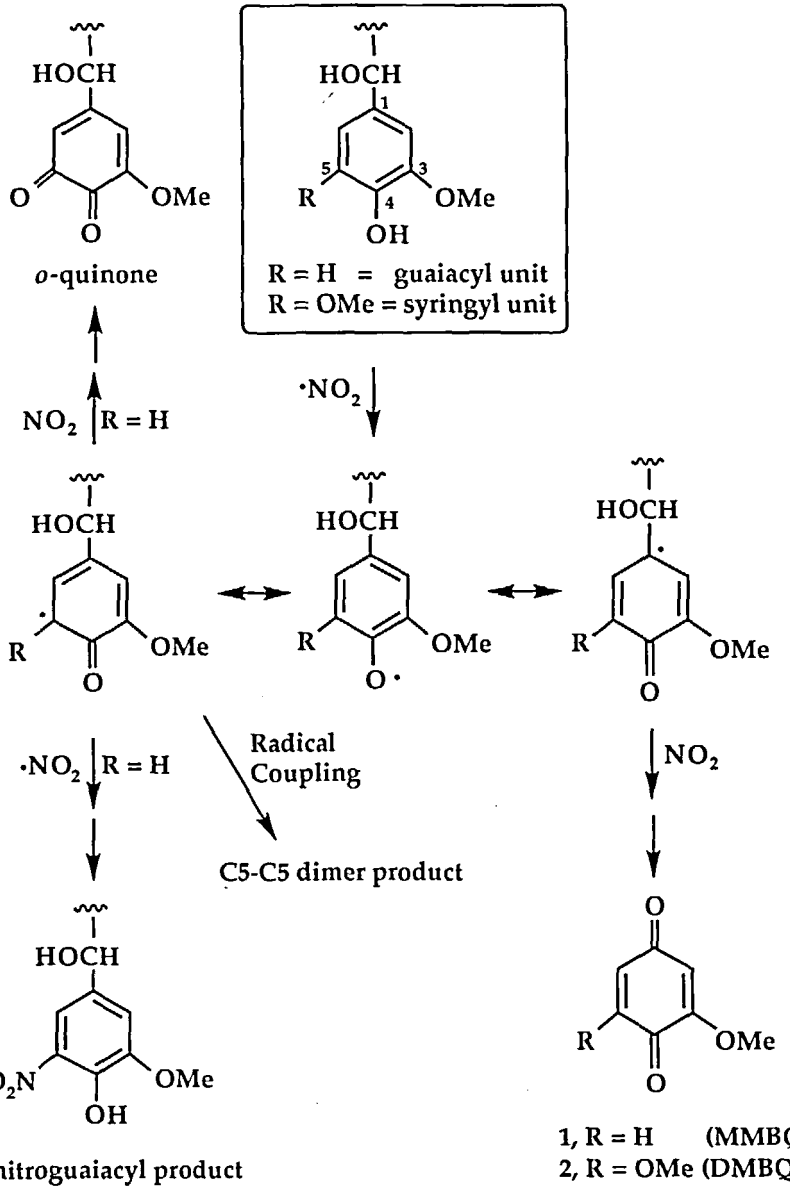
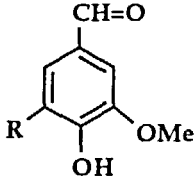


Figure 1. Proposed reaction pathways for an NO_2 oxidation of a lignin unit.

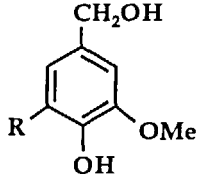
RESULTS AND DISCUSSION

5-Hydroxymethylvanillyl Alcohol

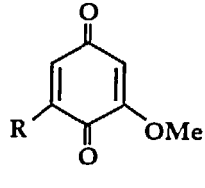
Lignin can be hydroxymethylated by treatment with formaldehyde;[7] therefore, it seemed appropriate to examine the reactivity of a 5-hydroxymethyl guaiacyl compound towards NO_2. The simplest compound to prepare of this type was 5-hydroxymethyl-vanillyl alcohol (**10**). Oxidation of **10** could give an *o*- or *p*-benzoquinone, depending on whether the 5- or 1-hydroxymethyl substituent was eliminated. The actual oxidation of **10** by NO_2/NHS provided a very complex product mixture that did not contain any simple benzoquinones, such as **12**.



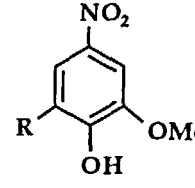
3, R = H
4, R = OCH_3
5, R = NO_2
6, R = CHO
7, R = Br
8, R = Cl
9, R = I



10, R = CH_2OH
11, R = Br



1, R = H
2, R = OCH_3
12, R = CH_2OH
13, R = Br
14, R = Cl
15, R = I



16, R = NO_2
17, R = Br

5-Nitro and 5-Halogenated Guaiacyl Compounds

Other 5-substituents that may be easily introduced into lignin are 5-nitro and 5-halo groups. Table 1 compares the product yields from the oxidation of some selected 5-substituted vanillins with those of vanillin and syringaldehyde. The yields of benzoquinone products from the 5-bromo and 5-chloro guaiacyl derivatives were less than that of the 5-methoxy case (syringaldehyde), but much higher than that of vanillin (which gave mostly nitrated products that did not react further with NO_2/NHS to give a benzoquinone).[2]

Table 1. Product yields from the reactions of vanillin-related compounds with NO_2/NHS at 22°C for 6 hr in methanol.

	Benzoquinone (%)			Nitro products (%)		
Compound	1	2	13[a]	5	16[b]	17[b]
Vanillin 3	4			51	12	
Syringaldehyde 4		84				
5-Bromovanillin 7		50	4			
5-Bromovanillyl alcohol 11		34	18			
5-Chlorovanillin 8		61	1[c]			3[c]
5-Iodovanillin 9		17	trace[c]	20		5[c]
5-Nitrovanillin 5				1[d]	83[d]	

[a]Estimated yield based on an assumed GC response factor = cpd 2.
[b]Estimated yield based on an assumed GC response factor = cpd 5.
[c]The chloro or iodo analog. [d]Data taken from reference 2; no NHS.

Interestingly, the halogenated substrates gave a non-halogenated benzoquinone product (DMBQ). Clearly the C-5 halogen is being replaced by a methoxyl group during the course of the reaction. The new methoxyl group has its origin in the methanol solvent used in the reaction. The only halogenated benzoquinone product observed in significant yield was 5-bromo-3-methoxy-*p*-benzoquinone (BMBQ, **13**) from the oxidation of 5-bromovanillyl alcohol. The corresponding chloro and iodo benzoquinones (**14** and **15**) were observed in only trace amounts in the product mixtures from oxidation of **8** and **9**. The former gave a good yield of DMBQ; the latter gave a poor yield.

Variation in Reaction Conditions

The reaction conditions for the oxidation of 5-bromovanillin were varied to optimize the yield of benzoquinone products (Table 2). Small improvements in DMBQ yields occurred at extended reaction times. The product mixtures were relatively simple, except when elevated

Table 2. Examination of the variation in reaction conditions on the NO_2/NHS oxidation of 5-bromovanillin **7**.

Entry #	Time (hr.)	Temperature (°C)[a]	DMBQ (%)[b]
1	2	22	46
2	4	22	50
3	6	22	57
4	8	22	52
5	14	22	56
6	4	60	14[c]
7	16	0	56
8	6	22 (under N_2)	56

[a]Most experiments were done at room temperature, which was ~22°C.
[b]Also observed were minor amounts of BMBQ (**13**) and trace levels of nitrated products.
[c]Plus a similar quantity of 2-methoxy-4,6-dinitrophenol **16**.

temperatures were employed. At 60°C, ring nitration became competitive with benzoquinone production. In all cases studied, we observed complete consumption of the starting material, 5-bromovanillin **7**. However, we can not account for about 40% of the reaction products; these must have been gaseous or nonvolatile materials, each of which would go undetected by our GC analysis.

The effect of NHS was also probed. When NHS was removed, ring nitration became the dominant reaction. Treatment of 5-bromovanillin with NO_2 at room temperature for six hours gave no detectable benzoquinone products; the product mixture contained 2-bromo-6-methoxy-4-nitrophenol (**17**), 5-nitrovanillin (**5**), and 2-methoxy-4,6-dinitrophenol (**16**) in a relative ratio of 7:1:1. This was an unexpected finding, since DMBQ yields are only slightly reduced when the NO_2 oxidations of syringyl compounds and hardwood lignins are conducted in the absence of NHS.[2,3]

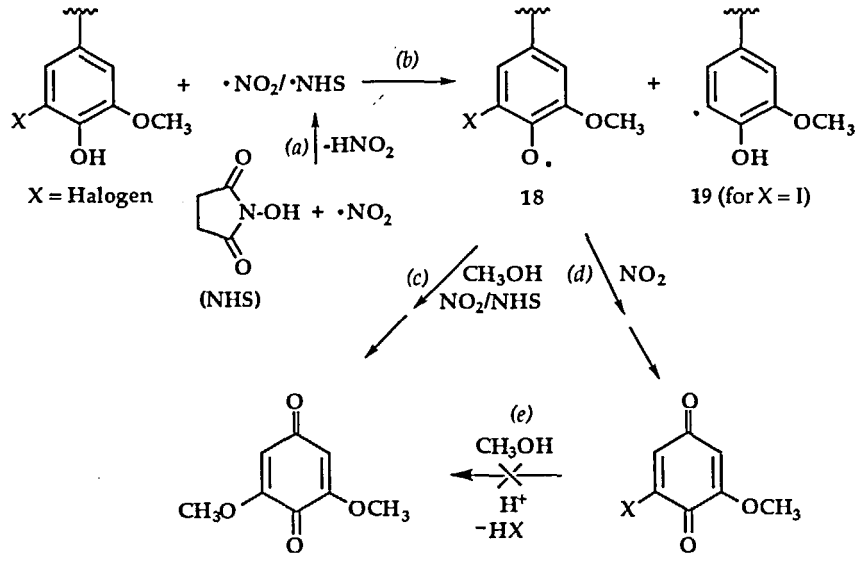


Figure 2. Proposed steps in the reactions of 5-halovanillins with NO_2/NHS.

Mechanistic Studies

Several simple experiments were conducted to learn additional details of the roles of NHS and methanol in NO_2 oxidations. Our solutions are acidic; the abstraction of a phenol hydrogen atom by $\bullet NO_2$ generates HNO_2, which should disproportionate quickly to nitric acid (HNO_3). The acid might catalyze methanol replacement of the halogen group in a 5-halobenzoquinone (Figure 2, step *e*). In order to verify this proposition, we dissolved BMBQ (13) in methanol and then added HNO_3; there was no conversion to DMBQ. Increasing the temperature and acid concentration, and adding chloroform still gave no DMBQ. Thus, it appears that step *e* is not possible under our conditions.

Additional experiments established that DMBQ was not formed when BMBQ was sequentially treated with methanol overnight, fol-

Table 3. Correlation of σ_p substituent values[8] with benzoquinone yields for the NO_2/NHS reactions of 5-substituted vanillins.

5-Substituent	Benzoquinone (%) DMBQ + XMBQ[a]	σ_p	σ_p^+
CH_3O	84	-0.27	-0.78
Cl	62	0.23	0.11
Br	54	0.23	0.15
I	17[b]	0.28	0.14
NO_2	0	0.78	0.79

[a]XMBQ = 5-halo-3-methoxy-*p*-benzoquinone.
[b]This case gave substantial amounts nitrovanillin derivatives.

lowed by NHS for 4 hrs, and finally NO_2 for an additional 16 hrs. A portion of the NHS was consumed in this experiment. Likewise, DMBQ was not formed when the 5-bromovanillin was sequentially treated with methanol overnight and NHS for 4 hrs. However, addition of NO_2 to this mixture produced a 58% yield of DMBQ in 4 hrs. The results indicate that NHS is either vital to the formation of the phenol radical intermediate **18** (Fig. 2, step *b*) or to the conversion of **18** to DMBQ (Fig. 2, step *c*). The chemistry of how **18** gets to DMBQ is not clear to us. Some direct conversion of the 5-halo radical (**18**) to a 5-halobenzoquinone (Fig. 2, step *d*) occurs to a minor extent.

The value of NHS to the success of an NO_2 oxidation varies considerably. Without NHS, the 5-halovanillins are unreactive. For syringaldehyde (5-methoxyvanillin) and lignin, the addition of NHS improves yields by only about 10% (81 → 88% for syringaldehyde and 14 → 15.5% for lignin).[2,3] 5-Nitrovanillin does not give DMBQ under any NO_2 conditions. Thus, the order of DMBQ yields for the NO_2/NHS oxidation of 5-substituted vanillins is CH_3O>Cl>Br>I>NO_2. This order correlates with the substituent's ability to supply electrons by a combination of resonance and polar effects,[8] which is reflected by the substituent's σ_p and σ_p^+ values (Table 3).

The only substituent that appears significantly out of place is iodo. However, the product distribution for 5-iodovanillin suggests that competing reactions are more prominent. The major product is 5-nitrovanillin; this is likely formed by a direct radical displacement of the iodo to give a C-5 radical (19, Fig. 2). Iodo groups are prone to this type of displacement.[9]

The first step in the oxidation of vanillin is most likely hydrogen atom abstraction by either $\bullet NO_2$ or NHS• to give a phenoxy radical, ArO• (Fig. 2, path *b*). The ease of this reaction will be determined by the relative oxidation potentials of the substituted vanillin and the relative reduction potentials of $\bullet NO_2$ and NHS•. These potentials in methanol are not known, but there should be a direct correlation of the reactivity of the 5-substituted vanillins with substituent effects. Syringaldehyde should oxidize more readily than a halo or nitro substituted vanillin. To explain the effects of NHS in NO_2 oxidation reactions, we assume that reduction potential of $\bullet NO_2$ is greater than that of NHS• and that the ability of $\bullet NO_2$ to remove an H-atom (oxidize) a phenol is marginal. For reaction to occur, a highly reactive phenol - one with a low oxidation potential - is needed.

With this premise, we propose that $\bullet NO_2$ generates an ArO• from syringaldehyde because the 5-methoxy substituent is a good stabilizing group when the radical density is on the C-5 position. However, with the other C-5 substituents examined, the oxidation potentials are too high for $\bullet NO_2$ to generate a phenoxy radical. Nitrogen dioxide could be sufficiently reactive to convert some NHS to NHS• (Fig. 2, step *a*). The NHS radical may be capable of abstracting hydrogens from more difficult to oxidize phenols, such as 5-chloro and 5-bromovanillin, to give ArO• and eventually benzoquinones.

In essence, we propose that NHS provides a way to go past a certain energy barrier. Similar chemistry has been observed for the reactions of anthrahydroquinone radical anions ($AHQ^{\bullet-}$) with quinone methides (QM).[10] When a potential of -0.8 volts is applied to a solution of anthraquinone (AQ) and a QM in acetonitrile, partial reduction of AQ (reduction potential -0.95 volts) to $AHQ^{\bullet-}$ occurs; however, direct reduction of the QM (reduction potential -1.15 volts) does not occur

because of the large energy difference of 0.35 volts. Nevertheless, the QM is reduced by the $AHQ^{\bullet}$ in the solution, because the energy separation of 0.2 volts does not restrict reaction. The $AQ \rightarrow AHQ^{\bullet}$ reduction has allowed the $QM \rightarrow QM^{\bullet-}$ to occur with the application of an abnormally low voltage.

The sequence of $\bullet NO_2 \rightarrow NHS\bullet \rightarrow ArO\bullet$ can also explain our previous results involving NO_2 oxidations of lignin models and lignin.[2,3] Small DMBQ yield improvements are observed when NHS is present. Presumably, NHS• is formed and eventually gives rise to a higher concentration of ArO• species, thus favoring benzoquinone production.

Bromination/NO_2 Reaction Sequence for Guaiacyl-based Compounds

The goal of our research was to improve benzoquinone yields from guaiacyl compounds. We sought to learn what the yield improvement would be for a mixture of vanillin and syringaldahyde; such mixtures are produced when lignin is oxidized with copper oxide.[3] A preliminary experiment was conducted with vanillin alone. Bromination of vanillin in acetic acid/sodium acetate buffer rapidly led to 5-bromovanillin 7, which was readily recovered by precipitation in water. The yield of recrystallized product was 76%; the yield of crude product was > 90%. Next, we brominated a 1:1 mole ratio mixture of vanillin and syringaldehyde (4), recovered the resulting crude product mixture by column chromatography, and then reacted it with NO_2/NHS to provide a 75% of DMBQ. This DMBQ yield is in good agreement with the sum of separate contributions for oxidizing a 1:1 mixture of 5-bromovanillin and syringaldehyde.

CONCLUSIONS

Nitrogen dioxide oxidation of vanillin gives a very low yield of the corresponding benzoquinone, but bromination (or chlorination) of vanillin prior to NO_2 reaction increases the yield significantly. Interestingly, the major benzoquinone product from oxidation of 5-

bromo- and 5-chlorovanillin with NO_2 *in the presence of NHS* is DMBQ. The reaction mechanism probably involves NO_2 reaction with NHS to give an NHS radical, and the latter abstracts a hydrogen atom from the 5-halovanillin. The resulting phenolic radical then reacts in an unexplainable way with NHS/methanol to give DMBQ.

A sequence of bromination and NO_2 oxidation could be a potential approach for improving the DMBQ yield from lignin mixtures, *provided* the mixture contained structures similar to vanillin.

EXPERIMENTAL

The general experimental conditions, such as gas chromatography conditions and NMR equipment, have been described earlier.[2] Syringaldehyde **4**, vanillin **3**, 5-nitrovanillin **5**, and 5-bromovanillin **7** were commercial products.[11] Samples of MMBQ (**1**) and DMBQ (**2**) were available from earlier studies.[2] 5-Bromovanillyl alcohol (**11**),[12] BMBQ (**13**),[13] 5-chlorovanillin (**8**),[14] and 5-iodovanillin (**9**)[15] were prepared by standard literature procedures.

Bromination Reactions. A solution of bromine (580 mg, 3.6 mmol) in 1 mL acetic acid was added slowly to a stirred solution of vanillin **3** (415 mg, 2.7 mmol) and sodium acetate (324 mg, 4.0 mmol) in 3 mL of acetic acid. On completion of the addition, sodium hydrosulfite (50 mg, 0.5 mmol) dissolved in 2 mL of water was added to destroy the excess bromine. The reaction mixture was then poured into 30 mL of water containing sodium hydrosulfite (50 mg, 0.5 mmol). The precipitated white solid was recrystallized from ethanol to yield 525 mg (76%) of 5-bromovanillin **7**: mp 163-164°C (Lit.[16] mp 164°C).

Bromination of a mixture of vanillin **3** (159 mg, 1 mmol) and syringaldehyde **4** (191 mg, 1 mmol) was performed as above. The product mixture was purified by silica gel chromatography by sequential elution with hexane, chloroform, and chloroform/methanol mixtures. Evaporation of chloroform and chloroform/methanol solutions gave 463 mg of crude product. This product was subsequently subjected to NO_2 reaction without any further purification.

5-Hydroxymethylvanillyl alcohol (10). 5-Formylvanillin (6) (295 mg, 1.6 mmol) was dissolved in 10 mL of a 1:1 mixture of anh. ethanol and THF; sodium borohydride (300 mg, 8 mmol) was then slowly added with stirring. The reaction mixture was allowed to stir at room temperature for 24 hours. A small amount of acetic acid was added dropwise to destroy the residual sodium borohydride. The reaction mixture was evaporated under reduced pressure, a small volume of methanol was added, and the mixture was evaporated again. This procedure was repeated several times in order to remove the residual acetic acid. The crude product was recrystallized from chloroform, giving 274 mg (93% yield) of **10**: mp 98-100°C (lit.[17] mp 105-106°C). The structure of **10** was further verified by preparing the triacetate of **10** (by treating **10** with acetic anhydride/pyridine): ^{1}H-NMR ($CDCl_3$) δ 2.07, 2.11, and 2.33 (3 s, each a relative area of 3, O<u>Ac</u>), 3.84 (s, 3, OC<u>H</u>$_3$), 5.06 (s, 2, -C<u>H</u>$_2$OAc), 5.08 (s, 2, -C<u>H</u>$_2$OAc), 6.97 (s, 1, Ar<u>H</u>), and 7.02 (s, 1, Ar<u>H</u>); MS (**10** tri-acetate) *m/z* (%) 310 (1, M^+), 268 (10, M-CH_2CO), 208 (100, M-AcOH, CH_2CO), 166 (63, M-AcOH, two CH_2CO), 149 (20), 137 (10), 120 (13), 106(3).

NO_2 Oxidation. The procedure, work-up, and DMBQ analysis has been previously described.[2] Products such as BMBQ (**13**) were identified by direct comparison of GC retention times and mass spectra to an authentic sample: *m/z* (%) 218 (50, ^{81}Br-M^+), 216 (50, ^{79}Br-M^+), 190 (45), 188 (100), 186 (50), 160 (21), 137 (44), 109 (41), and 79 (17). Yields of BMBQ were determined by GC after establishing a response factor relative to an anthraquinone internal standard. Yields of the other halobenzoquinones were determined using an assumed response factor (equal to that of BMBQ). Structural assignments for products were based on mass spectral data:

2-Chloro-6-methoxybenzoquinone (14): *m/z* (%) 174 (44, ^{37}Cl-M^+), 172 (83, ^{35}Cl-M^+), 159 (15), 144 (95), 142 (100), 137 (41), 114 (37), 109 (29), 88 (40), 69 (77), and 53 (39).

2,4-Dinitro-6-methoxyphenol (16): *m/z* (%) 214 (M+, 100), 197 (95), 166 (27), 151 (9), 137 (9), 121 (30), 93 (20), 77 (33), and 53 (47).

2-Bromo-6-methoxy-4-nitrophenol (17): *m/z* (%) 249 (95, ^{81}Br-M$^+$), 247 (100, ^{79}Br-M$^+$), 219 (14), 217 (16), 203 (9), 201 (10), 188 (13), 186 (13), 157 (5), 137 (7), 106 (8), 94 (14), 79 (31), and 53 (27).

2-Chloro-6-methoxy-4-nitrophenol (Cl analog of 17): *m/z* (%) 205 (33, ^{37}Cl-M$^+$), 203 (100, ^{35}Cl-M$^+$), 173 (19), 157 (17), 142 (17), 129 (5), 113 (6), 99 (8), 79 (7), and 65 (13).

2-Iodo-6-methoxy-4-nitrophenol (I analog of 17): *m/z* (%) 295 (100, M$^+$), 265 (8), 234 (11), 205 (5), 177 (5), 122 (16), 107 (8), and 79 (20).

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