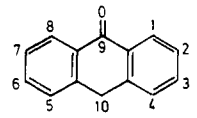
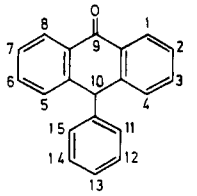
^{1}H NMR spectrum of anthrone[17] (8) shows signals at δ 4.2



8



9a

(2 H, S, H_{10}), 7.37 (6 H, complex, $H_{2,3,4,5,6,7}$), and 8.22 (2 H, d, $H_{1,8}$) whereas 10-phenylanthrone (**9a**) showed signals at δ 4.66 (1 H, S, H_{10}), 6.85 (2 H, d, $H_{4,5}$), 7.39 (4 H, m, $H_{2,3,6,7}$), 7.8 (5 H, complex, $H_{11,12}$, $H_{13,14,15}$), and 8.15 (2 H, d, $H_{1,8}$). Comparison and accurate examination of ^{1}H NMR spectra of **8** and **9a** gave clear and rigid confirmation of the introduction of an aryl group in position 10 of anthrone.

Experimental Section

Melting points are uncorrected. Nuclear magnetic spectra were measured on EM-360 90-MHz spectrophotometer. Infrared spectra were recorded on a Pye-Unicam SP 200-G spectrophotometer. Isolation of products was achieved on a 20 × 15 cm glass plate covered with thin silica gel film. UV absorbances were measured on a Perkin-Elmer 552 spectrophotometer. Elemental analyses were recorded on a Perkin-Elmer 240 C microanalyser.

High-pressure liquid chromatography (HPLC) analyses were performed on a Hitachi apparatus (Japan) supplied with a variable-wavelength monitor (190–600 nm), with a sulfonated silica gel type column, Nucleosil 55 A$^-$, and methanol as a solvent.

Materials. All arenes, α-tetralone, and anthrone were purchased from Aldrich Chemical Co. Silica gel GF_{254} (Type 60) for thin-layer chromatography (Merck) was used in preparative thin-layer chromatography.

Reaction of 1-Tetralone and/or Anthrone with Arenes in the Presence of $AlCl_3$ Catalyst. General Procedure. A sample of 0.061 mol of $AlCl_3$ was added to a solution of 0.01 mol of 1-tetralone or anthrone in 25 mL of the arene in a two-necked flask equipped with a reflux condenser capped with calcium chloride tube, a magnetic stirrer, and a dropping funnel. The reaction mixture was stirred for 48 h at room temperature (RT), decomposed with 10% HCl solution, and extracted with chloroform and methylene chloride; the combined extracts were washed with water, 10% sodium carbonate solution, and again water and dried over magnesium sulfate. The solvents and the unreacted arene were removed by distillation under reduced pressure on a rotatory evaporator, and the residue was subjected for separation and purification to preparative thin layer chromatography. Products were identified as described under each individual run. Results are found in Tables I and II, and the physical data of the products **3a–f** and **9a–f** are depicted in Table III.

The Reactions of an *o*-Quinone Monoimide with Some Phenols

Harold W. Heine,* James A. Ciaccio,† Kenneth G. Carson, and Carol M. Taylor

Department of Chemistry, Bucknell University, Lewisburg, Pennsylvania 17837

Elizabeth A. Williams*

General Electric Company, Corporate Research and Development, Schenectady, New York 12309

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The *o*-quinone monoimide *N*-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (**1**) reacts with 2,6-dimethoxy-, 2,6-dimethyl-, and 2,6-dichlorophenols (**2a–c**) to form *N*-(2,4-dichloro-6-hydroxyphenyl)-*N*-(3,5-dimethoxy-, 3,5-dimethyl-, 3,5-dichloro-4-hydroxy)-4-nitrobenzamides (**3a–c**), respectively. Oxidation of **3a** by **1** and **3b** by DDQ lead to *N*-aryl-*p*-iminoquinones **4a,b**. Oxidative dimerizations by either C–C or C–O coupling occur when **1** is admixed with the sterically hindered 2,6-di-*tert*-butyl-, 2,4-di-*tert*-butyl-, 4-bromo-2,6-di-*tert*-butyl-, and 2,4,6-tri-*tert*-butylphenols.

The reactions of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) with a wide variety of mono- and dihydric phenols have been studied extensively, especially by Becker.[1a–c] Surprisingly, little work has been done on the reactions of *o*-quinones and their derivatives with phenols. A few articles have appeared on the treatment of naphthols with chloranil,[2a–d] but there is only one report on the reactions of *o*-chloranil with phenols[3] and one paper involving the interaction of an *o*-quinone diimide and phenol.[4] This paper describes the reactions of the *o*-quinone monoimide *N*-(2,4-dichloro-6-oxo-2,4-cyclohexadien-1-ylidene)-4-nitrobenzamide (**1**) with substituted monohydric phenols and the subsequent oxidations of some of the *p*-amidophenols that were prepared during the course of this study.

Results and Discussion

Admixing of **1** with 2,6-dimethoxy-, 2,6-dimethyl-, and 2,6-dichlorophenols (**2a–c**) in methanol formed the *p*-amidophenols **3a–c** (Scheme I). The action of 2 equiv of **1** on **2a** or 1 equiv of **1** with **3a** afforded the *N*-aryl-*p*-iminoquinone **4a** (84%) and compound **5**. Reduction of **4a** with sodium borohydride reformed **3a**. No reaction occurred between **1** and **3b,c**; however, **3b** was converted to

† Camille and Henry Dreyfus Teaching and Research Fellow 1988–89.

(1) (a) Becker, H.-D. *J. Org. Chem.* **1965**, *30*, 982. (b) Becker, H.-D. *J. Org. Chem.* **1965**, *30*, 989. (c) Becker, H.-D. *J. Org. Chem.* **1969**, *34*, 1198.

(2) (a) Kasturi, T. R.; Sivaramakrishnan, R. *Proc. Indian Acad. Sci., Sect. A* **1978**, 87A(6), 181. (b) Kasturi, T. R., Sivaramakrishnan, R. *Indian J. Chem. Sect. B* **1978**, 668. (c) Kasturi, T. R.; Arunachalam, T.; Subrahmanyam, G. *J. Chem. Soc. C* **1970**, 1257. (d) Arzeno, H.; Barton, D. H. R.; Reine-Marie, B.-L.; Lusinchi, X.; Pinto, B. M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2069.

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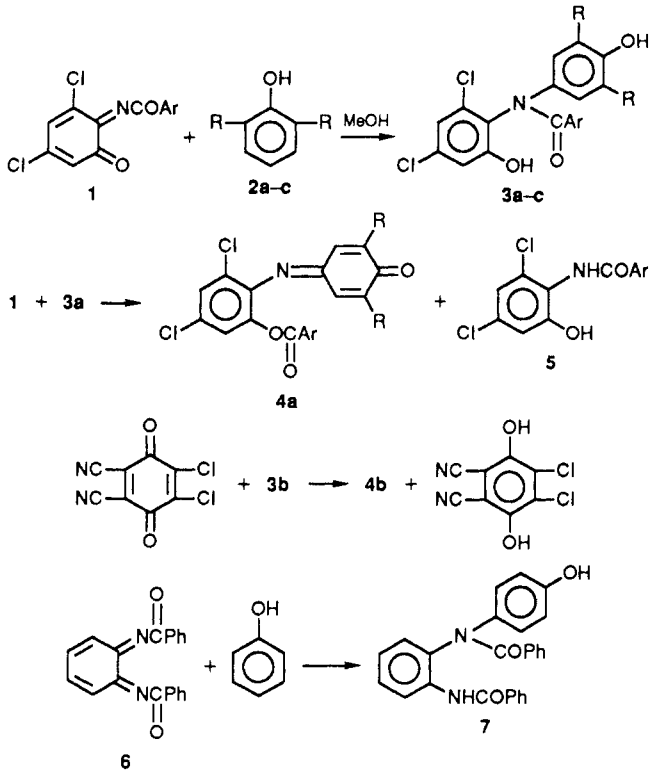
(4) Seto, S.; Nishiyama, Y. *Yakugaku Zasshi* **1962**, *82*, 590; *Chem. Abstr.* **1963**, *58*, 515.

Scheme I[a]



[a] **2a–4a**, R = MeO; **2b–4b**, R = Me; **2c**, **3c**, R = Cl. Ar = *p*-$O_2NC_6H_4$.

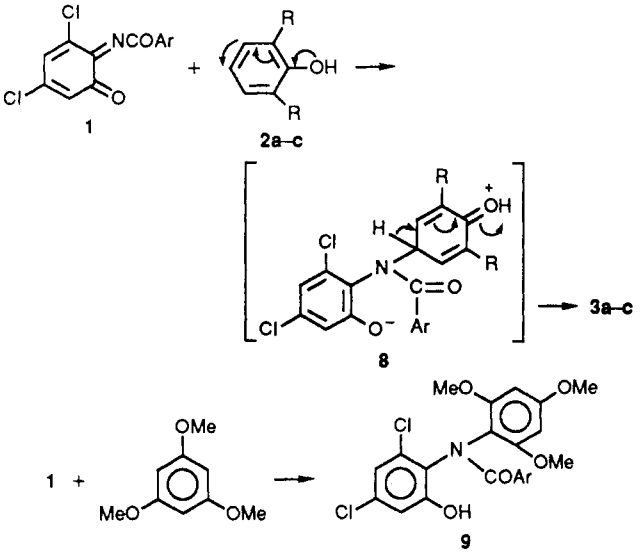
4b by means of DDQ. Attempts to oxidize **3c** to **4c** with DDQ failed. The formation of **3a–c** is analogous to the reaction of phenol with the *o*-quinone diimide **6** to give **7**[4] (Scheme I).

Compounds **3a–c** and **4a,b** were characterized by IR, ^1H NMR, ^{13}C NMR, and mass spectroscopies. The infrared spectra of **3a–c** showed absorption bands for the amido carbonyl moiety at 1665–1635 cm^{-1}, and the ^{13}C NMR spectra exhibited chemical shifts at 156 ppm for the phenolic carbons and at 168 ppm, a value very characteristic for amido carbonyl carbons of compounds bearing the -N(R)C(O)$C_6H_4NO_2$-*p* moiety.[5a–c] The infrared spectra of **4a,b** showed the typical absorption frequency for the ester carbonyl group at 1750 cm^{-1}, and the ^{13}C NMR spectra indicated the presence of a keto carbonyl carbon, an ester carbonyl carbon, and an imino carbon by resonances at 175, 163, and 162 ppm. The keto carbonyl resonance for **4b** was at 187 ppm. The expected molecular ions were observed for **3a–c** and **4a,b**.

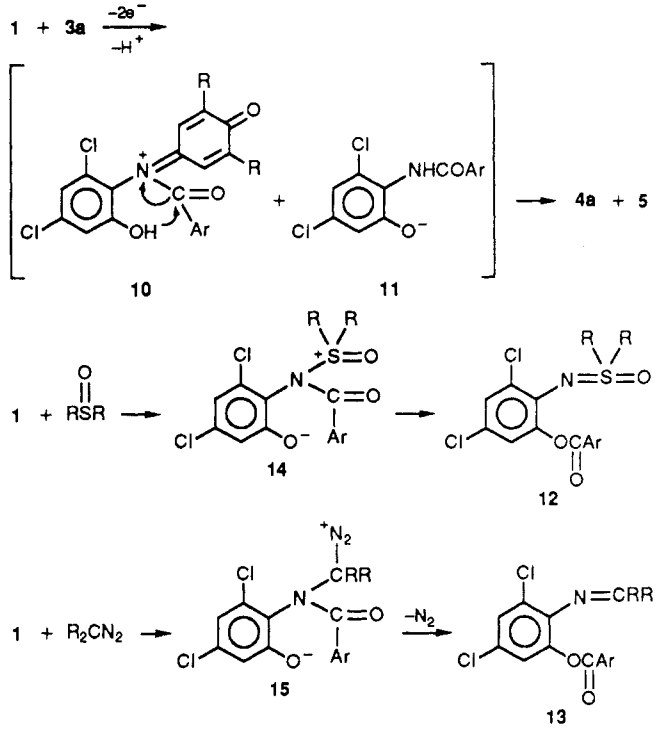
A mechanism to account for the formation of **3a–c** presumes a nucleophilic attack by the electron-rich para carbon of the phenol on the imido nitrogen of **1**, giving rise to the intermediate **8** which subsequently yields **3a–c** (Scheme II). A similar reaction pathway has been suggested previously for the reaction of **1** with 1,3,5-trimethoxybenzene to give **9**[5b] (Scheme II).

A mechanism for the novel oxidation of **3a** to **4a** involves a transfer of two electrons and a proton—formally a hydride ion transfer—from **3a** to **1** to produce the intermediate **10** (R = MeO) and the phenoxide ion **11**. Intermediate **10** subsequently undergoes an N → O acylation with a loss of a proton to **11** to generate **4a** and **5** (Scheme III). The initial electron transfer becomes more difficult with **3b** and requires the higher oxidation potential of DDQ to produce intermediate **10** (R = Me). In the case of **3c** even DDQ does not have a high enough oxidation potential for the overall hydride transfer to occur. Other hydride-transfer reactions of hydroquinones have been described recently.[6] Analogous N → O acylations have been observed when **1** is treated with dialkyl sulfoxides and diazoalkanes.[5d] The products formed, **12** and **13**, respectively, presumably involve the positively charged intermediates **14** and **15**, which bear a close similarity to **10** (Scheme III).

Scheme II



Scheme III



In contrast to the reactions of phenols **2a–c** with **1**, 2,6-di-*tert*-butylphenol (**16**) and **1** formed the known oxidative dimer **17**[7] in 70% yield, the reduced *o*-quinone

(5) (a) Heine, H. W.; Barchiesi, B. J.; Williams, E. A. *J. Org. Chem.* **1984**, *49*, 2560. (b) Heine, H. W.; Olsson, C.; Bergin, J. D.; Foresman, J. B.; Williams, E. A. *J. Org. Chem.* **1987**, *52*, 97. (c) Heine, H. W.; Schairer, W. C.; Suriano, J. A.; Williams, E. A. *Tetrahedron* **1988**, *44*, 3181. (d) Heine, H. W.; Empfield, J. R.; Golobish, T. D.; Williams, E. A.; Garbauskas, M. F. *J. Org. Chem.* **1986**, *51*, 829.

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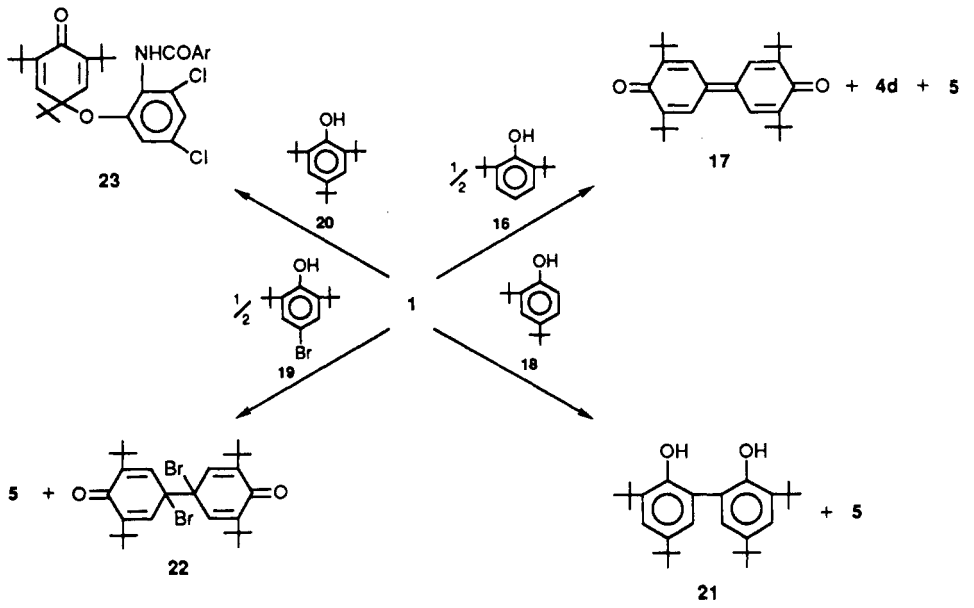
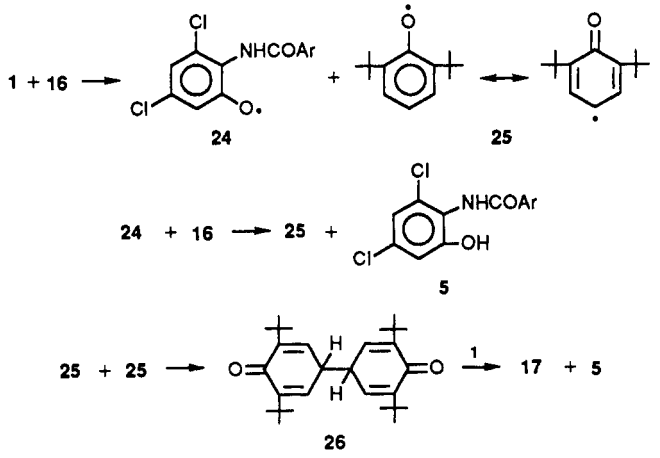
Scheme IV



Scheme V



monoimide **5**, and 5% of the *N*-aryl-*p*-iminoquinone, **4d** (R = $C(Me)_3$) (Scheme IV). Under similar experimental conditions 2,4-di-*tert*-butylphenol (**18**), 4-bromo-2,6-di-*tert*-butylphenol (**19**), and 2,4,6-tri-*tert*-butylphenol (**20**) reacted with **1** to give compounds **21–23**, respectively (Scheme IV).

Compounds **17**, **21–23** are products typical of free-radical processes. As shown by Becker,[1a] compound **22** is also formed when **19** is treated with DDQ. He presented evidence consistent with the view that the latter reaction is initiated by a one-electron transfer from the phenol to DDQ. The formation of **17** can be envisioned as a one-electron transfer from **16** to **1** to produce the radicals **24** and **25** (Scheme V). Further reaction of **24** with **16** generates additional **25**, which dimerizes to **26**. Dehydrogenation of **26** by **1** gives **17** and **5**. Similar schemes can be put forth for the formation of **21–23**. Compound **17** was also formed by treating **16** with *o*-chloranil.[3]

That **1** and **16** formed only 5% of **4d** may be a consequence of the weakening of the conjugation in **16** between the OH group and the ring because of the steric bulk of the tertiary butyl groups. The resultant diminution of electron density on the C-4 carbon of the phenol reduces its ability to bond to the imido nitrogen of **1**. In the case of the reaction of **20** with **1** it is suggested that the generated 2,4,6-tri-*tert*-butylphenoxide radical is trapped by radical **24** to give **23**. Previously it was shown that analogues of **23** were formed when **20** was treated with *o*-chloranil[3] and DDQ.[1a] It is not surprising that a mixed coupling product is formed given that the oxidative dimer of **20** is sterically improbable.[1a]

In summary, treatment of **1** with 2,6-dimethoxy-, 2,6-dimethyl-, and 2,6-dichlorophenols afforded adducts **3a–c**, which were most likely formed by a nucleophilic attack of the phenol on the imido nitrogen of **1**. The adducts **3a,b** could be further oxidized by either **1** (for **3a**) or DDQ (for **3b**) to afford the *N*-aryl-*p*-iminoquinones **4a–b** via a novel N → O acyl migration.

In the case of phenols with either one or two *o*-*tert*-butyl substituents, nucleophilic attack by C-4 carbon of the phenol on **1** is muted due to steric inhibition of resonance; instead, oxidation of the phenols to their corresponding phenoxy radicals take place. These either combine to form dimers or are trapped by **24**. The results are consistent with the idea that the proclivity of phenols toward one-electron oxidation increases with steric crowding in the 2- and 6-positions.[8] The presence of electron-donating substituents in these positions normally enhance the one-electron oxidation of phenols; however, in reactions with **1**, nucleophilic attack by the C-4 of the phenol on the imido nitrogen of **1** becomes the preferred path.

Experimental Section

Materials and Methods. ^1H NMR spectra were recorded at either 89.6 or 300 MHz using JNM-FX90Q and Brucker spectrometers, respectively. ^{13}C NMR spectra were recorded on JNM-FX90Q and Varian XL-300 spectrometers operating at 22.5 and 75.4 MHz, respectively. Chemical shifts are reported relative to internal $SiMe_4$. Infrared (IR) spectra were recorded on either a Perkin-Elmer Model 1300 or Infracord spectrophotometer and were calibrated with a polystyrene standard. Low-resolution mass spectra (MS) were obtained on a Finnigan 4021 spectrometer by using electron impact ionization at 70 eV. High-resolution mass spectra were recorded at the Mass Spectrometer Facility, Department of Chemistry, Pennsylvania State University, and were obtained on a Kratos MS-50 spectrometer at 70 eV. TLC was performed on silica gel (Baker-flex, IB-F) as was flash[9] and fil-

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tration column chromatography (Merck 60, 230–400 mesh). Melting points were determined on a Mel-Temp apparatus and are uncorrected. Elemental analyses were performed by M-H-W Laboratories, Phoenix, AZ. All reactions were carried out under nitrogen in either snap-cap vials or standard laboratory glassware. Methanol was commercial grade and was used without purification. All phenols are commercially available and were also used without further purification.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(4-hydroxy-3,5-dimethoxyphenyl)-4-nitrobenzamide (3a).** A suspension of 2,6-dimethoxyphenol (47 mg, 0.31 mmol) and **1** (100 mg, 0.31 mmol) in 2.5 mL of MeOH was vigorously stirred at ambient temperature for 13 h. The resulting creamy beige suspension was collected to afford 73 mg (50%) of an off-white solid after washing the filter cake with ca. 2 mL of $CHCl_3$. The solid was recrystallized from acetonitrile to afford 50 mg of the adduct as a pale yellow solid [mp 268–270 °C; IR (Nujol mull) 3300 (broad, OH), 1660 (amide C=O) cm^{-1}] which was spectroscopically and chromatographically identical with a sample obtained by treatment of **4a** with $NaBH_4$. Anal. Calcd for $C_{21}H_{16}N_2O_7Cl_2$: C, 52.62; H, 3.37; N, 5.85. Found: C, 52.55; H, 3.76; N, 5.83.

4-[[2,4-Dichloro-6-[(4-nitrobenzoyl)oxy]phenyl]imino]-2,6-dimethoxy-2,5-cyclohexadien-1-one (4a). To an orange suspension of **1** (200 mg, 0.62 mmol) in 2.5 mL of MeOH was added 2,6-dimethoxyphenol (48 mg, 0.31 mmol), and the mixture immediately became a slightly darker orange. After vigorously stirring the mixture for 24 h, the resulting dark red suspension was collected to afford 124 mg (84%) of **4a** as a brick red solid: mp 179–180 °C; ^1H NMR (CD_3COCD_3) δ 8.35 (d, 2 H, J = 9.2 Hz), 8.27 (d, 2 H, J = 9.2 Hz), 7.57 (s, 2 H), 6.35 (d, 1 H, J = 2.2 Hz), 5.95 (d, 1 H, J = 2.2 Hz), 3.78 (s, 3 H), 3.70 (s, 3 H); ^1H NMR ($CDCl_3$) δ 8.27 (d, 2 H, J = 9.2 Hz), 8.24 (d, 2 H, J = 9.2 Hz), 7.44 (d, 1 H, J = 2.2 Hz), 7.26 (d, 1 H, J = 2.2 Hz), 6.26 (d, 1 H, J = 2.2 Hz), 5.78 (d, 1 H, J = 2.2 Hz), 3.78 (s, 3 H), 3.71 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 175.80, 162.58, 161.60, 155.53, 155.37, 151.47, 141.02, 139.85, 133.81, 131.26, 129.91, 127.96, 125.74, 123.90, 122.27, 110.30, 99.63, 56.29; IR (Nujol mull) 1750 (ester C=O), 1685, 1640, 1595, 1530 (NO), 1355 (NO) cm^{-1}; MS m/z (rel. intensity) 476 (10, M^+), 461 (1, $M^+ - CH_3$), 445 (2, $M^+ - OCH_3$), 360 (11), 326 (35), 298 (28), 150 (100), 104 (55), 76 (50). Anal. Calcd for $C_{21}H_{14}Cl_2N_2O_7$: C, 52.84; H, 2.96; N, 5.87. Found: C, 52.71; H, 2.98; N, 5.77.

Sodium Borohydride Reduction of (4a). Alternate Synthesis of 3a. Sodium borohydride (143 mg, 3.8 mmol) was added in small portions over 1 min to a solution of **4a** (100 mg, 0.21 mmol) stirring in 1.5 mL THF and 1.2 mL of absolute EtOH. The resulting dark red mixture was stirred for 1 h and 10 min at room temperature, treated with 20 mL of H_2O, and extracted with Et_2O (3 × 20 mL) and CH_2Cl_2 (2 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated in vacuo to afford 88 mg of a light red solid. Trituration with $CHCl_3$ afforded 62 mg (62%) of **3a** as a pale yellow solid: mp 266–268 °C; ^1H NMR (CD_3COCD_3) δ 8.15 (d, 2 H, J = 8.5 Hz), 7.90 (d, 2 H, J = 8.5 Hz), 7.11–6.88 (m, 2 H), 6.80 (s, 1 H), 6.62 (s, 1 H), 3.78 (s, 3 H), 3.61 (s, 3 H); IR (Nujol mull) 3250 (br, OH), 1665 (amide C=O), 1530 (NO), 1360 (NO) cm^{-1}; MS m/z (rel intensity) 478 (100, M^+), 461 (40, $M^+ - OH$), 296 (40), 170 (25), 150 (90), 104 (60), 76 (35); exact mass calcd for $C_{21}H_{16}N_2O_7Cl_2$ 478.0331, found 478.0332.

Oxidation of 3a with 1. Alternate Synthesis of 4a. To a slurry of **3a** (47 mg, 0.10 mmol) in 2 mL of MeOH was added **1** (32 mg, 0.10 mmol). The resulting dark orange slurry was stirred for ca. 12 h at ambient temperature, after which it became a dark orange-red. Vacuum filtration afforded **4a** as a red solid (27 mg, 57%): mp 179–181 °C; ^1H NMR ($CDCl_3$) δ 8.30 (d, 2 H, J = 9 Hz), 8.20 (d, 2 H, J = 9 Hz), 7.45 (d, 1 H, J = 2 Hz), 7.25 (d, 1 H, J = 2 Hz), 6.27 (d, 1 H, J = 2 Hz), 5.78 (d, 1 H, J = 2 Hz), 3.78 (s, 3 H), 3.71 (s, 3 H); MS and IR spectra were identical with a sample obtained by treating 2,6-dimethoxyphenol with 2 equiv of **1**.

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(4-hydroxy-3,5-dimethylphenyl)-4-nitrobenzamide (3b).** To a vigorously stirred suspension of **1** (200 mg, 0.62 mmol) in 1.5 mL of MeOH was added 2,6-dimethylphenol (75 mg, 0.62 mmol). Upon addition of the phenol, the suspension became a dark orange. After being stirred overnight at ambient temperature, the resulting clear, light orange-yellow mixture was analyzed by TLC (2:1 hex/EtOAc); no unreacted 2,6-dimethylphenol (R_f = 0.9) remained, and a UV-active spot at R_f = 0.6 was present. The mixture was concentrated in vacuo to afford a clear, yellow-amber oil. Trituration with 2–3 mL of $CHCl_3$ afforded 249 mg (91%) of the adduct as a bright yellow solid (mp 147–151 °C). Recrystallization twice from EtOAc/$CHCl_3$ afforded 127 mg of **3b** as a yellow crystalline solid. An elemental analysis of **3b** indicated a solvate had formed with $CHCl_3$ (1 mol of **3b** to 0.8 mol of $CHCl_3$). The resonance for occluded solvent could be seen in the ^{13}C NMR spectrum of **3b**: mp 156–158 °C; ^1H NMR (CD_3COCD_3) δ 8.10 (d, 2 H), 7.78 (d, 2 H), 7.05 (br s, 2 H), 6.91 (br s, 2 H), 2.21 (s, 3 H), 2.08 (s, 3 H); ^{13}C NMR (CD_3SOCD_3) δ 168.65, 167.35, 155.86, 151.80, 148.06, 142.86, 133.87, 133.38, 132.19, 129.42, 127.74, 126.61, 125.68, 124.55, 122.92, 119.73, 115.66, 16.41; IR (Nujol mull) 3300 (br, OH), 1650 (amide C=O), 1530 (NO), 1350 (NO) cm^{-1}; MS m/z (rel intensity) 446 (40, M^+), 429 (10, $M^+ - OH$), 281 (50), 150 (100), 104 (50), 76 (40); exact mass calcd for $C_{21}H_{16}N_2O_5Cl_2$ 446.0433, found 446.0425. Anal. Calcd for $C_{21}H_{16}N_2O_5Cl_2 \cdot 0.8CHCl_3$: C, 48.24; H, 3.13; N, 5.16. Found: C, 48.01; H, 3.35; N, 5.13. (The adduct **3b** was found to be inert to reaction with a second equivalent of **1**.)

***N*-(2,4-Dichloro-6-hydroxyphenyl)-*N*-(3,5-dichloro-4-hydroxyphenyl)-4-nitrobenzamide (3c).** To a solution of **1** (200 mg, 0.62 mmol) in 2.5 mL of CH_2Cl_2 was added 2,6-dichlorophenol (100 mg, 0.62 mmol). TLC (2:1 hex/EtOAc) of the resulting clear orange reaction mixture vs 2,6-dichlorophenol (R_f = 0.8) revealed only a UV-active spot at R_f = 0.4. The solvent was evaporated after 24 h to afford an orange residue. Trituration with benzene afforded 176 mg (59%) of a pale orange solid (mp 110–115 °C). Recrystallization from CH_2Cl_2 afforded 47 mg of **3c** as a white solid. An elemental analysis of **3c** indicated a solvate had formed with CH_2Cl_2 (1 mol of **3c** to 1.5 mol of CH_2Cl_2), mp 145–147 °C: ^1H NMR (CD_3SOCD_3) δ 8.15 (d, 2 H), 7.90 (d, 2 H), 7.41 (br s, 2 H), 6.95 (m, 2 H); ^{13}C NMR (CD_3SOCD_3) δ 168.43, 155.70, 148.44, 148.06, 141.62, 134.19, 133.76, 133.11, 126.55, 126.06, 123.08, 122.11, 120.10, 115.93; IR (Nujol mull) 3290 (br, OH), 1635 (amide C=O), 1530 (NO), 1350 (NO) cm^{-1}; MS m/z (rel intensity) 486 (4, M^+), 469 (0.7, $M^+ - OH$), 301 (3.5), 150 (100), 104 (40), 76 (30); exact mass calcd for $C_{19}H_{10}N_2O_5Cl_4$ 485.9343, found 485.9358. Anal. Calcd for $C_{19}H_{10}N_2O_5Cl_4 \cdot 1.5CH_2Cl_2$: C, 40.00; H, 2.13; N, 4.55. Found: C, 40.13; H, 2.26; N, 4.51. (Adduct **3c** was found to be inert to reaction with a second equivalent of **1**; it was also unreactive to DDQ in MeOH and sodium periodate in MeOH/H_2O.) Adduct **3c** also forms solvates with benzene and $CHCl_3$ (solvent resonances could be seen in the ^1H and/or ^{13}C spectra of **3c**).

Alternative Procedure. To a suspension of **1** (200 mg, 0.62 mmol) in 3 mL of MeOH was added 2,6-dichlorophenol (100 mg, 0.62 mmol). The resulting suspension was vigorously stirred at ambient temperature for 3 days to afford a beige slurry. The solvent was evaporated to afford 330 mg of a wet, beige solid. Trituration with 2–3 mL of benzene afforded 278 mg (93%) of **3c** as a white solid, mp 120–123 °C. Recrystallization from benzene/$CHCl_3$ (ca. 1:10) afforded 148 mg (50%) of **3c** as a white solid, mp 144–145 °C. If the solid is slurried with hot benzene and filtered, the melting point changes dramatically to 238–240 °C. Anal. Calcd for $C_{19}H_{10}N_2O_5Cl_4$: C, 46.75; H, 2.07; N, 5.74. Found: C, 46.75; H, 2.18; N, 5.69. If the high-melting solid is heated with either CH_2Cl_2 or MeOH the lower melting solid (e.g. 144–145 °C) is obtained.

4-[[2,4-Dichloro-6-[(4-nitrobenzoyl)oxy]phenyl]imino]-2,6-dimethyl-2,5-cyclohexadien-1-one (4b). To a solution of **3b** (50 mg, 0.11 mmol) in 2.5 mL of MeOH was added 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ; 28 mg, 0.12 mmol), and the clear, light yellow solution immediately became a dark brown. After 10–15 min, an orange solid began to precipitate from solution, and the mixture was kept at 2 °C for 12 h. Vacuum filtration afforded 19 mg (40%) of **4b** as a fluffy, orange solid, mp 140–143 °C. The filtrate was concentrated in vacuo and triturated with ca. 4 mL of benzene to precipitate 2,3-dichloro-5,6-dicyano-1,4-benzenediol (DDH; 25 mg): IR (Nujol mull) 3300 (br, OH), 2260 (CN) cm^{-1}; MS m/z (rel intensity) 228 (100, M^+), 200 (60), 193 (10), 137 (14), 110 (20), 101 (12), 87 (30), 78 (20),

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36 (10). A 40-mg sample of **4b** was recrystallized from MeOH to afford 28 mg of **4b**: mp 148–149 °C; ^{1}H NMR ($CDCl_3$) δ 8.28 (d, 2 H, J = 9 Hz), 8.20 (d, 2 H, J = 9 Hz), 7.45 (d, 1 H, J = 2.2 Hz), 7.27 (d, 1 H, J = 2.2 Hz), 6.95 (m, 1 H), 6.56 (m, 1 H), 2.00 (sharp mult, 6 H); ^{13}C NMR ($CDCl_3$) δ 187.34, 162.04, 154.88, 142.75, 142.53, 140.85, 136.36, 133.87, 131.26, 130.24, 127.85, 125.47, 123.84, 122.06, 16.14, 15.82; IR (Nujol mull) 1750 (ester C=O), 1640, 1530 (NO), 1360 (NO) cm^{-1}; MS m/z (rel intensity) 444 (8, M^+), 294 (15), 266 (20), 150 (100), 104 (40), 76 (30). Anal. Calcd for $C_{21}H_{14}N_2O_5Cl_2$: C, 56.64; H, 3.18; N, 6.29. Found: C, 56.51; H, 3.15; N, 6.36.

3,3′,5,5′-Tetra-*tert*-butyl-4,4′-diphenoquinone (17) and 4-[[2,4-Dichloro-6-[(4-nitrobenzoyl)oxy]phenyl]imino]-2,6-di-*tert*-butyl-2,5-cyclohexadien-1-one (4d). 2,6-Di-*tert*-butylphenol (95 mg, 0.46 mmol) and **1** (300 g, 0.92 mmol) were dissolved in 2.5 mL of CH_2Cl_2 to afford a clear, dark orange-brown solution. After 45 min, the solution became a darker orange-brown. TLC (10:1 hex/EtOAc) indicated that a small amount of 2,6-di-*tert*-butylphenol (R_f = 0.9) remained unreacted after several hours. After 16 h at ambient temperature, the resulting deep brown solution was found to contain a small amount of undissolved solid. Vacuum filtration afforded 62 mg of a light brown solid which TLC cospotted with an authentic sample of **5**. The filtrate was concentrated down in vacuo to afford 350 mg of an orange-brown solid. The crude solid was dissolved in a minimum amount of benzene and applied to a 6 in. × 20 mm flash silica column and eluted first with 10:1 followed by 4:1 hex/EtOAc. The first eight fractions were combined to afford 67 mg (71%) of diphenoquinone **17** as a brown-orange solid. This sample was spectroscopically identical with a sample of **17** prepared by DDQ oxidation of 2,6-di-*tert*-butylphenol. Fractions 14–24 were combined to afford 13 mg (5%) of adduct **4d** as a red-orange solid, which was spectroscopically identical with a sample of **17** prepared by treatment of 2,6-di-*tert*-butylphenol with DDQ.

17: mp 230–232 °C; ^{1}H NMR ($CDCl_3$) δ 7.72 (s, 4 H), 1.37 (s, 36 H); ^{13}C NMR ($CDCl_3$) δ 186.52, 150.82, 136.30, 125.30, 36.08, 29.69; IR (CH_2Cl_2) 3060 (C=C—H), 2980 (CH_2—H), 1600 (C=O) cm^{-1}; MS m/z (rel intensity) 408 (10, M^+), 393 (5, $M^+ - CH_3$), 351 (10, $M^+ - C(CH_3)_3$), 57 (100), 41 (40).

4d: mp 62–64 °C; ^{1}H NMR ($CDCl_3$) δ 8.26 (d, 2 H), 8.15 (d, 2 H), 7.45 (d, 1 H, J = 2.1 Hz), 7.30 (d, 1 H, J = 2.1 Hz), 6.94 (d, 1 H, J = 2.6 Hz), 6.48 (d, 1 H, J = 2.6 Hz), 1.22 (s, 9 H), 1.18 (s, 9 H); IR (CH_2Cl_2) 3060 (C=C—H), 2980 (CH_2—H), 1760 (ester, C=O), 1660 (C=N or C=O), 1640 (C=N or C=O), 1540 (NO), 1360 (NO) cm^{-1}; MS m/z (rel intensity) 528 (15, M^+), 513 (5, $M^+ - CH_3$), 471 (1, $M^+ - C(CH_3)_3$), 378 (10), 150 (100), 104 (40), 76 (25), 57 (70), 41 (35); exact mass calcd for $C_{27}H_{26}N_2O_5Cl_2$ 528.1213, found 528.1207.

3,3′,5,5′-Tetra-*tert*-butyl-2,2′-dihydroxybiphenyl (21). To a clear, colorless solution of 2,4-di-*tert*-butylphenol (95 mg, 0.46 mmol) in 2 mL of CH_2Cl_2 was added **1** (100 mg, 0.31 mmol). The solution immediately became a dark brown and **5** began to precipitate out of solution after several hours at ambient temperature. TLC of the mixture showed a very faint spot corresponding to unreacted phenol (which is in slight excess; when present in an equimolar amount, all phenol reacts in less than 3 h) after 3 h (R_f = 0.64; 10:1 hexanes/EtOAc). After a total of 15 h, **5** was filtered away (52 mg) and the filtrate was concentrated down and applied to a 1 in. × 15 mm plug of flash silica gel which was eluted with 50 mL of hexanes. Evaporation of the hexanes afforded 62 mg (97%) of dimer **21** as an off-white solid, mp 169–174 °C. The crude solid was dissolved in 5 mL of MeOH and diluted with 5 drops of H_2O; white solid slowly appeared from solution over 15 min. Filtration afforded 25 mg (40%) of dimer **21** as a white solid: mp 190–193 °C; ^{1}H NMR ($CDCl_3$) δ 7.40 (d, 1 H), 7.20 (d, 1 H), 5.30 (br s, 1 H, D_2O exchangeable), 1.50 (s, 9 H), 1.35 (s, 9 H); IR (Nujol mull) 3500 (sharp, OH), 3400 (broad, OH) cm^{-1}; MS m/z (rel intensity) 410 (4, M^+), 395 (5), 354 (2), 339 (6), 190 (6), 57 (100), 41 (40). Dimer **21** was found to be spectroscopically and chromatographically identical with a sample obtained by treatment of the 2,4-di-*tert*-butylphenol with chloranil.[4c]

Bis(1-bromo-3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-yl) (22). 4-Bromo-2,6-di-*tert*-butylphenol (118 mg, 0.41 mmol) was added to a clear, orange solution of **1** (270 mg, 0.83 mmol) in 3 mL of CH_2Cl_2. Progress of the reaction was monitored by TLC (10:1 hex/EtOAc) for disappearance of the phenol (R_f = 0.85) and appearance of the dimer (R_f = 0.95); after 2 days, no phenol remained. Upon evaporation of the solvent, the resulting orange residue was dissolved in ca. 0.5 mL of $CHCl_3$, and the solution was applied to a 1 in. × 15 mm plug of flash silica gel which was subsequently eluted with a mixture of 10:1 hex/EtOAc. Solvent was evaporated to afford 121 mg of a clear, yellow oil. Trituration with ca. 4 mL of MeOH yielded 70 mg (60%) of dimer **22** as a bright yellow, crystalline solid. The substance turned red at ca. 85 °C and melted at 190–195 °C. When dissolved in $CHCl_3$, **22** slowly lost bromine to give 3,3′,5,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**17**). Dimer **22** was spectroscopically and chromatographically identical with a sample obtained by DDQ oxidation of the phenol.[4a]

***N*-[2,4-Dichloro-6-[(1,3,5-tri-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-yl)oxy]phenyl]-4-nitrobenzamide (23).** 2,4,6-Tri-*tert*-butylphenol (58 mg, 0.22 mmol) and **1** (70 mg, 0.22 mmol) were dissolved in 1.5 mL of CH_2Cl_2. The resulting clear deep amber solution was kept at room temperature for 4 days and then concentrated in vacuo to afford 123 mg (95%) of a yellow-brown solid which melted at 163–165 °C. Upon recrystallization of the crude product from MeOH, 55 mg (45%) of monoquinol ether (**23**) was obtained as a fluffy, pale yellow solid: mp 176–177 °C; ^{1}H NMR ($CDCl_3$) δ 8.38 (d, 2 H, J = 8.5 Hz), 8.12 (d, 2 H, J = 8.5 Hz), 7.08 (d, 1 H, J = 2.0 Hz), 6.93 (d, 1 H, J = 2.0 Hz), 6.63 (s, 2 H), 1.25 (s, 18 H), 0.93 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 185.84, 163.69, 154.09, 150.00, 149.84, 139.42, 133.36, 132.98, 128.44, 124.09, 121.70, 115.10, 83.84, 42.04, 35.33, 29.16, 25.73; IR (Nujol mull) 3250 (NH), 1660, 1600, 1590, 1570, 1530 (NO), 1410, 1360 (NO), 1000, 890, 850, 730; MS m/z (rel intensity) 530 (0.6), 515 (0.5), 408 (0.6), 393 (0.5), 262 (5), 247 (20), 205 (3), 150 (75), 104 (50), 93 (30), 76 (40), 57 (100), 50 (30), 41 (80). Anal. Calcd for $C_{31}H_{36}N_2O_5Cl_2$: C, 63.37; H, 6.16; N, 4.78. Found: C, 63.33; H, 6.21; N, 4.85.

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