JOC*Note*

Formation of Dimer-Type Ketals in the Reaction of 2,4,6-Trichlorophenol and 2,4,6-Trichloro-*m*-cresol with Calcium Hypochlorite in Methanol: Conversion to Quinones and Other Compounds†

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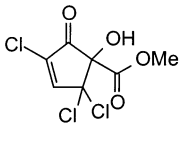
Abstract: 2,4,6-Trichlorophenol (**2**) and 2,4,6-trichloro-*m*-cresol (**5**) react with calcium hypochlorite ($Ca(OCl)_2$) in MeOH to give respectively dimer-type ketals 2-(2′,4′,6′-trichlorophenoxy)-4,4-dimethoxy-6-chlorocyclohexadien-2,5-one (**6**) and 2-(3′-methyl-2′,4′,6′-trichlorophenoxy)-4,4-dimethoxy-5-methyl-6-chlorocyclohexadien-2,5-one (**7**). Ketal **6**, which was too unstable to be isolated, and **7** hydrolyzed in H_2O/HCl to 2-(2′,4′,6′-trichlorophenoxy)-6-chloro-1,4-benzoquinone (**8**) and 2-(3′-methyl-2′,4′,6′-trichlorophenoxy)-5-methyl-6-chloro-1,4-benzoquinone (**9**), respectively. Ketal **6** and quinone **8** were also produced when **2** and $Ca(OCl)_2$ reacted in DMF, followed by addition of MeOH and H_2O, respectively. The mechanisms of these reactions are examined. Conversion of the ketals and quinones to other products is described.

Recently[1] we reported on the formation of ketone-ester **1**, a minor product, in the reaction of 2,4,6-trichlorophenol (**2**) with calcium hypochlorite, $Ca(OCl)_2$, in methanol, MeOH. Compound **1** is an analogue of a ketone-ester derivative (**3**) of Hantzsch's acid (**4**), a compound for



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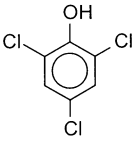

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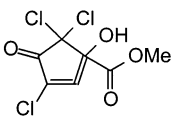

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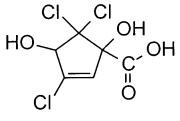

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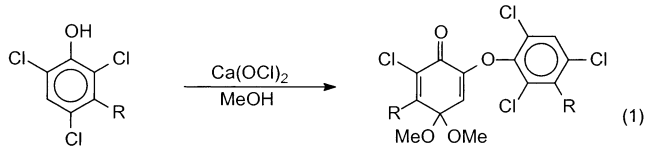
which we described an improved synthesis starting with the reaction of **2** and hypochlorite ion, OCl^-, in basic, aqueous solution. In the current note, we now consider the major products in the reaction of **2** and 2,4,6-trichloro-*m*-cresol (**5**) with $Ca(OCl)_2$ in MeOH, examining their synthesis, the mechanisms involved in the synthesis, and the conversion of some of the major products to other compounds.

The major products in the reaction of **2** and **5** with $Ca(OCl)_2$ are ketals **6** and **7**, respectively (eq 1). Ketal **7** was



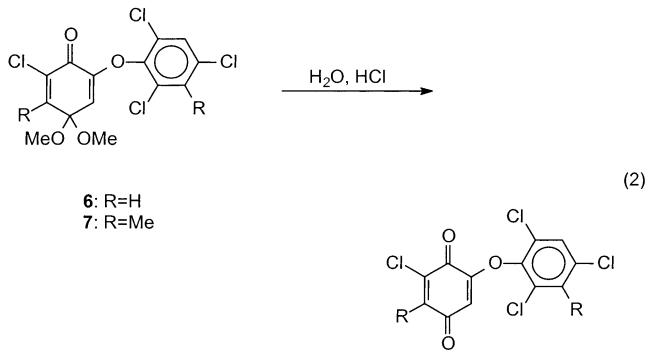
(1)

2: R=H
5: R=Me

6: R=H
7: R=Me

isolated and its structure confirmed by MS (gas chromatography−mass spectrometry; GC-MS), ^1H and ^{13}C NMR, IR (GC-FT infrared spectroscopy; GC-FTIR), HRMS, and elemental analysis. Ketal **6** was unstable and could not be isolated; its structure was confirmed by its MS (M^+; $M - OMe^+$; $M - OMe$, $-Cl^+$; $M - OC_6H_2Cl_3^+$) and IR (OCH_3; CO; C═C) obtained directly from the crude reaction solution.

Ketals **6** and **7**, however, were easily hydrolyzed to their respective substituted quinones (**8** and **9**) in acid solution (eq 2); both quinones were isolated and charac-



(2)

6: R=H
7: R=Me

8: R=H
9: R=Me

terized: **8**, MS, ^1H and ^{13}C NMR, IR, HRMS, and elemental analysis; **9**, MS, ^1H and ^{13}C NMR, IR, HRMS, elemental analysis and X-ray crystallography. Compound **8** has been reported previously as a product in the oxidation of **2** with various metal oxides[2] and nickel peroxide.[3] Our melting point (116.5−118 °C) differed somewhat from the reported melting points 134.5−136 °C[2] and 120−124 °C.[3] We repeated the oxidation of **2** with PbO_2 as reported[2] and obtained **8** as established by its mass spectra (GC-MS); however, the product from **2** and PbO_2 always contained an unknown impurity that we were unable to remove even with column chromatography. Perhaps this impurity was responsible for the high melting point that was reported[2] for **8**.

Reaction of **2** with $Ca(OCl)_2$ in dimethyformamide, DMF, followed by addition of H_2O led directly to quinone

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(1) Heasley, V. L.; Wadley, B. D.; Alexander, M. D.; Anderson, J. D.; Anderson, J. H.; Allen, R. T.; Hernandez, M. L.; Ismail, M. L.; Sigmund, G. A.; Shellhamer. D. F. *J. Org. Chem.* **2000**, *65*, 8111.

(2) Hunter, W. H.; Morse, M. *J. Am. Chem. Soc.* **1926**, *48*, 1615.

(3) Sugita, J. *Nippon Kagaku Zasshi* **1966**, *87*, 741.

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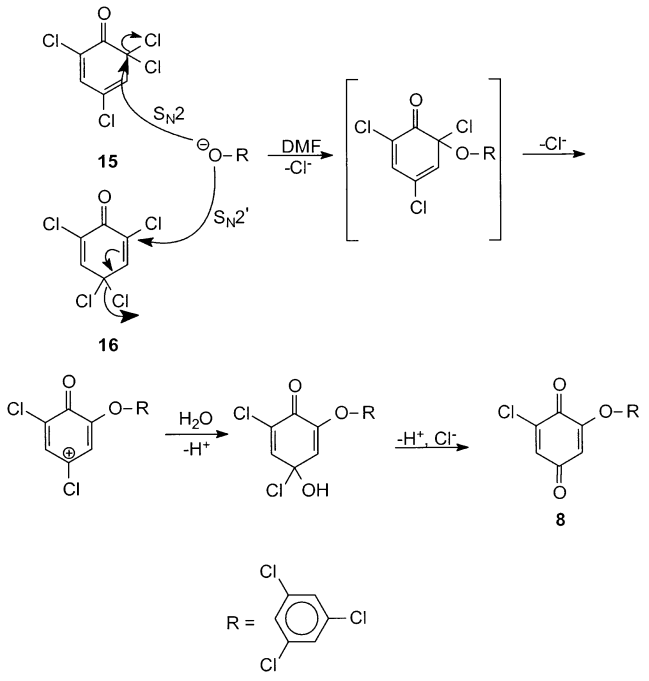
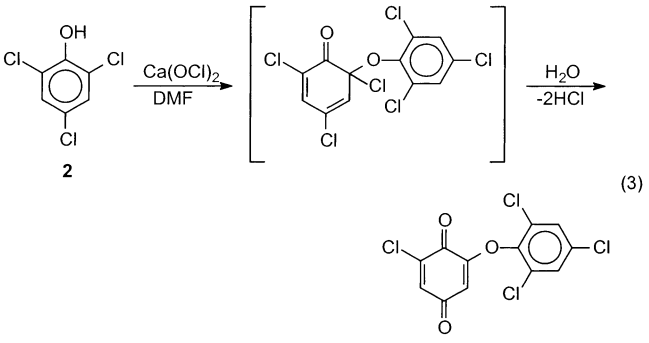
SCHEME 1

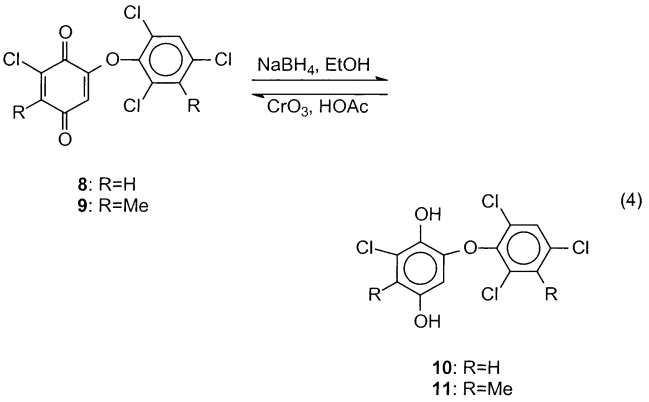


8 (eq 3). An intermediate, tertiary chloride (see Scheme 1) was assumed to be involved in the reaction but was not detected. Direct reaction of **2** with $Ca(OCl)_2$ in H_2O gave only a trace of **8**.



(3)

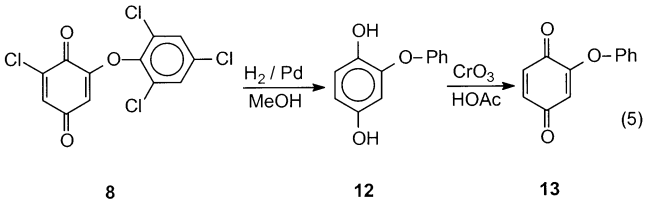
Quinones **8** and **9** were reduced to phenols **10** and **11**, respectively, with sodium borohydride; **10** and **11** were reoxidized with CrO_3/acetic acid (HOAc) to **8** and **9** (eq 4). The structures of **10** and **11** were confirmed as



(4)

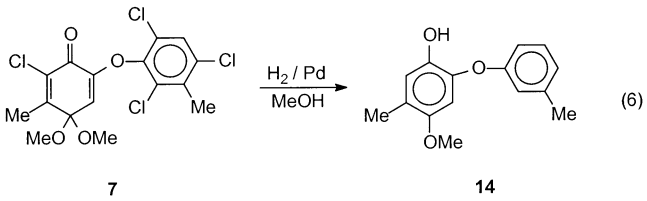
follows: **10**, MS, ^{1}H and ^{13}C NMR, IR, and HRMS; **11**, MS, ^{1}H and ^{13}C NMR, IR, and HRMS.

To establish a possible expanded, synthetic use for the quinones, we examined the hydrogenation (H_2/Pd) of **8** as a model. Hydrogenation of **8** gave dihydrophenol **12**, which was subsequently oxidized to quinone **13** (eq 5). The structure of **12** was confirmed by MS, ^{1}H and ^{13}C NMR, IR, and HRMS; **13** was established by MS, ^{1}H and ^{13}C NMR, IR, and HRMS.



(5)

Direct hydrogenation (H_2/Pd) of ketal **7** gave a substituted phenol (**14**) (eq 6). The structure of **14** was confirmed by MS, ^{1}H and ^{13}C NMR, IR, and HRMS.



(6)

It seemed likely to us that the mechanisms leading to ketals **6**/**7** in MeOH and quinone **8** in DMF involved attack of a trichlorophenoxide ion, from an equilibrium reaction of a trichlorophenol with $Ca(OCl)_2$, on a tetrachlorocyclohexadienone intermediate that was subsequently converted to the ketals by solvolysis. Therefore, to test these mechanisms, we synthesized 2,4,6,6-tetrachloro-2,4-cyclohexadienone (**15**) and 2,4,4,6-tetrachloro-2,5-cyclohexadienone (**16**) according to literature procedures and examined their reactions with sodium 2,4,6-trichlorophenoxide in DMF. Both **15** and **16** reacted with sodium 2,4,6-trichlorophenoxide in DMF, followed by H_2O, to give quinone **8**. Product **8** was not dectected in the GC until the addition of H_2O. As shown in Scheme 1, we suggest an S_N2 attack on **15** and an S_N2' attack on **16** by the 2,4,6-trichlorophenoxide ion to give an intermediate tertiary chloride (undetected on the GC) that hydrolyzed in H_2O to give **8**.[5] Similarly, **15** and **16** and sodium 2,4,6-trichlorophenoxide in DMF, followed by MeOH yielded **6**, presumably by a similar mechanism to that outlined in Scheme 1 for quinone formation. It is not clear why the phenoxide ion prefers to attack at the 2-position for both **15** and **16**; perhaps the orbitals of the carbonyl group, which are known to accelerate an S_N2

(4) Svec, P.; Zbirovsky, M. *Sci. Pap. Inst. Chem. Technol.* **1974**, *21*, 23.

(5) Compound **15** has been shown to rearrange to **16**[4] so it is possible that rearrangement occurred during the reaction. Both compounds **15** and **16** decompose extensively to 2,4,6-trichlorophenol (**2**) and other byproducts in the injection port of the GC and therefore it was impossible to determine the extent of reaction of **15** or **16** prior to addition of H_2O. Our assumption is that the intermediary tertiary chloride also was not detected because of decomposition in the injection port.

reaction, also increase the rate of an S_N2' reaction.[6] The greater preponderance of positive charge at the 4-position, with subsequent attack of H_2O at this position, is probably a result of instability of the charge in the 2-position, adjacent to the carbonyl group.

Experimental Section

Materials. 2,4,6-Trichlorophenol (**2**), calcium hypochlorite, $Ca(OCl)_2$, Pd(30%)/charcoal, and MeOH (anhydrous) were obtained commercially. Sodium 2,4,6-trichlorophenoxide was prepared by mixing the appropriate amounts of sodium methoxide and 2,4,6-trichlorophenol in MeOH, followed by removal of the MeOH under vacuum leaving the dry solid. Sodium 2,4,6-trichlorophenoxide was identified by comparison of its IR spectrum with the literature spectrum. 2,4,6-Trichloro-*m*-cresol (**5**) was prepared by passing Cl_2 into a solution of *m*-cresol in CCl_4 until GC and GC-MS analyses showed that the product was primarily **5**. The solvent was then removed under vacuum and **5** was crystallized by adding ice-cold petroleum ether. Compound **5** was identified by its mp, 44−46 °C; (lit.[7] mp 46 °C).

Instrumentation. Mass spectral data are expressed as *m*/*z* and as relative intensity (%). GC and GC-FTIR analyses were performed under the following conditions: 25 m column of internal diameter 0.20 mm with a methyl silicone stationary phase of 0.33 mm film thickness and programmed from 120 to 220 °C and 10 °C/min.

Reaction of 2 with $Ca(OCl)_2$ in DMF. To 137 mg (0.69 mmol) of **2** in 5 mL of DMF with stirring was added 100 mg of $Ca(OCl)_2$ (0.70 mmol). After 20 min, 10 mL of H_2O and 5 mL of CH_2Cl_2 were added. The CH_2Cl_2 solution was separated and dried over $MgSO_4$. Yield of **8** by GC, 40%.

Reaction of 2,4,6,6-Tetrachloro-2,4-cyclohexadienone (15) and 2,4,4,6-Tetrachloro-2,5-cyclohexadienone (16) with Sodium 2,4,6-Trichlorophenoxide in DMF. To a stirred solution of 80 mg (0.34 mmol) of **15** or **16** in 5 mL of DMF was added 76 mg (0.30 mmol) of sodium 2,4,6-trichlorophenoxide. After 20 min, 10 mL of H_2O and 5 mL of CH_2Cl_2 were added and the organic layer was isolated and dried over $MgSO_4$. The formation of quinone **8** from either **15** or **16** was confirmed by its mass spectrum (GC-MS).

Reaction of 2,4,6,6-Tetrachloro-2,4-cyclohexadienone (15) and 2,4,4,6-Tetrachloro-2,5-cyclohexadienone (16) with Sodium 2,4,6-Trichlorophenoxide in MeOH. The reaction conditions were identical with those described in DMF. The formation of ketal **6** from either **15** or **16** was confirmed by its mass spectrum (GC-MS).

2-(2′,4′,6′-Trichlorophenoxy)-4,4-dimethoxy-6-chlorocyclohexadien-2,5-one (6). Ketal **6** is an intermediate in the synthesis of quinone **8**. Ketal **6** could not be isolated by crystallization and it decomposed and hydrolyzed to **8** when subjected to silica gel. The presence and structure of **6** were confirmed by GC (ret. time, 28 min), GC-MS, and GC-FTIR. MS *m*/*z* (EI) 384, 382 (M^+); 355, 353, 351 (M − OMe); 320, 318, 316 (M − OMe, −Cl, 100); 189, 187 (M − $OC_6H_2Cl_3$). IR (cm^{-1}): CH, 3007; CH_3, 2950; OCH_3, 2836; C=O, 1713; C=C, 1661 and 1620.

2-(3′-Methyl-2′,4′,6′-trichlorophenoxy)-4,4-dimethoxy-5-methyl-6-chlorocyclohexadien-2,5-one (7). 2,4,6-Trichloro-*m*-cresol (**15**, 0.64 g, 1.55 mmol) was dissolved in 20 mL of MeOH. To this stirred solution was added 0.32 g (2.24 mmol) of $Ca(OCl_2)$. After 20 min, ketal **7** was isolated by filtration. Crude **7** was dissolved in CH_2Cl_2 and washed with H_2O to remove inorganic material. The CH_2Cl_2 solution was dried over $MgSO_4$ and the solvent was removed under vacuum. The resulting solid (**7**) was washed with pentane to remove any unreacted starting phenol. Recrystallization for MeOH gave 0.20 g of **7**. Yield: 32%. Mp: 165−168 °C. ^1H NMR (300 MHz): δ 2.09 (s, 3H), 2.49 (s, 3H), 3.15 (s, 6H), 5.3 (s, 1H), 7.47 (s, 1H). ^{13}C NMR (75.4 MHz): 14.7, 17.9, 51.3, 98.5, 116.3, 125.8, 128.8, 129.9, 131.8, 132.7, 135.6, 144.2, 148.7, 152.6, 172.0. MS *m*/*z* (EI): 414, 412, 410 (M^+); 381, 379, 377, 375 (M − Cl); 203, 201 (M − $OC_6HCH_3Cl_3$, 100). HRMS (CI): MH^+, calcd for $C_{16}H_{15}Cl_4O_4$ 410.9724, found 410.9689. IR (cm^{-1}): OCH_3, 2842; C=O, 1703; C=C, 1631. Anal. Calcd for $C_{16}H_{14}Cl_4O_4$: C, 46.64; H, 3.42; Cl, 34.41. Found: C, 46.50; H, 3.40; Cl, 34.50. GC retention time: 46 min.

2-(2′,4′,6′-Trichlorophenoxy)-6-chloro-1,4-benzoquinone (8). 2,4,6-Trichlorophenol (**2**, 0.75 g, 3.80 mmol) was dissolved in 25 mL of MeOH. To this stirred solution was added 0.40 g (2.80 mmol) of $Ca(OCl)_2$. The solution was stirred for 15 min. Ketal **6**, which is present at this point, was converted in situ to **8** by the dropwise addition of 5 drops of concentrated HCl in 35 drops of H_2O. After being stirred for 30 min, the solution was filtered and shaken with 25 mL of CH_2Cl_2 and 50 mL of H_2O. The CH_2Cl_2 layer was separated, dried over $MgSO_4$, and removed under vacuum. The gummy residue was heated with 6 mL of boiling hexane. The hot solution was decanted from insoluble material and the solvent was removed under vacuum to leave another gummy solid. As ice-cold MeOH (5−10 mL) was stirred into the gummy material in an ice bath, 0.41 g of bright-yellow quinone **8** precipitated. Yield of crude **8**: 64%. After recrystallization from $CHCl_3$/hexane (80:20), the yield was reduced to 48%. Mp: 116.5−118 °C. ^1H NMR (300 MHz): δ 5.63 (d, 1H, J = 0.4 Hz), 6.990 (d, 1H, J = 0.40 Hz), 7.46 (s, 2H). ^{13}C NMR (75.4 MHz): 111.2, 129.2, 129.5, 133.3, 133.9, 142.2, 143.7, 154.0, 155.0, 173.2, 184.0. MS *m*/*z* (EI): 342, 340, 338, 336 (M^+); 305, 303, 301 (M − Cl, 100); 277, 275, 273 (M − Cl, −CO). HRMS (EI): M^+, calcd for $C_{12}H_4Cl_4O_3$ 335.8919, found 335.8915. IR (cm^{-1}): CO, 1703; C=C, 1646. Anal. Calcd for $C_{12}H_4Cl_4O_3$: C, 42.65; H, 1.19; Cl, 41.96. Found: C, 42.32; H, 1.48; Cl, 42.28. GC retention time: 21 min.

2-(3′-Methyl-2′,4′,6′-trichlorophenoxy)-5-methyl-6-chloro-1,4-benzoquinone (9). A 100-mg (0.24 mmol) sample of ketal **7** was added to 14 drops of H_2O and 2 drops of concentrated HCl. THF was then added dropwise with stirring until **7** dissolved. After 4 h, 10 mL of CH_2Cl_2 and 20 mL of H_2O were added. The solution was shaken vigorously and the CH_2Cl_2 layer was separated and dried over $MgSO_4$. Removal of the CH_2Cl_2 layer gave 39.5 mg of crude **9**. Yield: 45%. Recrystallization from MeOH gave a return of approximately one-half of the **9**. Mp: 145.0−145.5 °C. ^1H NMR (300 MHz): δ 2.21 (s, 3H), 2.49 (s, 3H), 5.61 (s, 1H), 7.48 (s, 1H). ^{13}C NMR (75.4 MHz): 13.9, 17.9, 110.7, 125.5, 128.9, 129.4, 133.5, 135.9, 138.9, 142.9, 143.5, 154.8, 173.2, 184.0. MS *m*/*z* (EI): 370, 368, 366, 364 (M^+); 333, 331, 329 (M − Cl, 100); 298, 296, 294 (M − 2Cl). HRMS (EI): calcd for $C_{14}H_8Cl_4O_3$ 363.9228, found 363.9214. IR (cm^{-1}): CO, 1703; C=C, 1652. Anal. Calcd for $C_{14}H_8Cl_4O_3$: C, 45.94; H, 2.20; Cl, 38.74. Found: C, 45.49; H, 2.28; Cl, 39.17. The structure of **9** was also confirmed by X-ray crystallography, performed by Molecular Structure Corporation, Houston, TX. GC retention time: 34.7 min.

2-(2′,4′,6′-Trichlorophenoxy)-6-chloro-1,4-dihydroquinone (10). To a stirred solution of 20 mg (0.53 mmol) of $NaBH_4$ in 12 mL of 95% EtOH was added slowly 50 mg (0.15 mmol) of **8**. After the solution was stirred for 10 min, 12 mL of CH_2Cl_2 and 25 mL of H_2O were added and the solution was shaken vigorously. The CH_2Cl_2 layer was separated, dried over $MgSO_4$, and passed through silica gel. The solvent was removed and the crude product was chromatographed with silica gel, using CCl_4/CH_2Cl_2 mixtures. Dihydroquinone **10** (0.35 mg, 0.10 mmol) was obtained in the CH_2Cl_2 fraction. Yield: 70%. Mp: 162−164 °C. ^1H NMR (300 MHz): δ 5.95 (d, 1H, J = 2.8), 6.61 (d, 1H, J = 2.8), 7.68 (s, 2H), 8.20 (s, 1H), 8.22 (s, 1H). (H_2O appeared in the acetone-d_6 solvent at ~3.1 ppm.) The peaks at 8.20 and 8.22 ppm were confirmed as hydroxy protons since they disappeared when D_2O was added to the solvent. ^{13}C NMR (75.4 MHz): 101.5, 111.2, 122.4, 130.2, 130.9, 132.1, 136.9, 146.6, 146.9, 150.9. MS *m*/*z* (EI): 344, 342, 340, 338 (M^+); 307, 305, 303 (M − Cl); 272, 270, 268 (M − 2Cl); 132, 130 (100). HRMS (EI): calcd for $C_{12}H_6Cl_4O_3$ 337.9075, found 337.9071. IR (cm^{-1}): OH, 3485, 3429; C=C, 1614. GC retention time: 38 min. Additional confirmation for the structure of **10** was derived from its oxidation to **8** with CrO_3 in HOAc and H_2O.

(6) Carey, F.; Sundbery, R. *Advanced Organic Chemistry*, 3rd ed.; Plenum Press: New York and London, 1990; p 264

(7) Crowther, H. L.; McCombie, H. *J. Chem. Soc.* **1913**, *103*, 536.

2-(3′-Methyl-2′,4′,6′-trichlorophenoxy)-5-methyl-6-chloro-1,4-dihydroquinone (11). Dihydroquinone **11** was prepared by reduction of **9** with $NaBH_4$ as described with **10**. Yield: 89%. Mp: 177−179 °C. ^{1}H NMR (300 MHz): 2.19 (s, 3H), 2.49 (s, 3H), 5.97 (s, 1H), 7.69 (s, 1H), 7.90 (s, 1H), 8.07 (s, 1H). (H_2O appears in the acetone-d_6 solvent at ∼3.0 ppm.) ^{13}C NMR (75.4 MHz): 12.8, 18.0, 100.6, 118.1, 123.5, 127.6, 129.6, 131.5, 132.3, 136.2, 136.9, 143.7, 144.4, 148.4. MS *m*/*z* (EI): 372, 370, 368, 366 (M^+, 100); 335, 333, 331 (M − Cl); 300, 298, 296 (M − 2Cl). HRMS (EI): calcd for $C_{14}H_{10}Cl_4O_3$ 365.9384, found 365.9393. IR (cm^{-1}): OH, 3509. GC retention time: 68 min. Additional confirmation for the structure of **11** was derived from its oxidation to **9** with CrO_3 in acetic acid and H_2O.

2-Phenoxy-1,4-dihydroquinone (12). 8 (80 mg, 0.24 mmol) or **10** (80 mg, 0.24 mmol) and 95 mg of 30% palladium on charcoal in 15 mL of MeOH were reduced with hydrogen in a Parr bottle. Compounds **8** and **10** required 4.5 and 3.5 h, respectively, for hydrogenation to **12**. MeOH was removed under vacuum to leave a viscous liquid. CH_2Cl_2 was added to remove **12** from a polymeric contaminant. Removal of the CH_2Cl_2 under vacuum gave 45 mg of crude **12** from either **8** or **10**. Yield: 94%. Compound **12** was purified by silica gel as described for **10**. ^{1}H NMR (60 MHz): 6.48 (m, 7H), 8.03 (s, 1H), 8.81 (s, 1H), 9.01 (s, 1H). (H_2O appeared in the DMF-d_7 solvent at ∼3.4 ppm.) The peaks at 8.81 and 9.01 ppm were confirmed as hydroxy protons since they disappeared when D_2O was added to the solvent. ^{13}C NMR (75.4 MHz): 108.8, 117.8, 118.2, 123.2, 130.4, 142.8, 144.3, 151.6, 158.9. MS *m*/*z* (EI): 202 (M^+, 100); 173 (M − HCO); 125 (M − C_6H_5); 96 (M − C_6H_5, −HCO); 77 (C_6H_5). HRMS (EI): calcd for $C_{12}H_{10}O_3$ 202.0624, found 202.0630. IR (cm^{-1}): OH, 3657, 3602. GC retention time: 12 min.

2-Phenoxy-1,4-benzoquinone (13). Compound **13** was prepared by oxidation of **12** as described below. It was isolated as a viscous, yellow liquid by silica gel with hexane/ether. **13** eluted in the 5% ether fraction. ^{1}H NMR (300 MHz): δ 5.73 (d, 1H, J = 2.0 Hz), 6.70−6.85 (m, 2H), 7.07−7.16 (m, 2H), 7.26−7.35 (m, 1H), 7.41−7.51 (m, 2H). ^{13}C NMR (75.4 MHz): 110.9, 120.9, 126.6, 134.5, 137.0, 152.2, 158.5, 181.5, 187.5. MS *m*/*z* (EI): 200 (M^+, 100); 172 (M − CO); 144 (M − CO, −CO). HRMS (EI): calcd for $C_{12}H_8O_2$ 200.0473, found 200.0480. IR (cm^{-1}): CO, 1693, 1672. GC retention time: 10 min.

Oxidation of the Dihydroquinones to the Benzoquinones. The following procedure was used in the oxidations of **10**, **11**, and **12**. The procedure is outlined using the oxidation of **12** to **13**: 40.4 mg (0.21 mmol) of **12** were dissolved in 6 mL of 60% HOAc/H_2O and cooled below 5 °C in an ice bath. To this stirred solution was added 24 mg (0.24 mmol) of CrO_3 in 1 mL of HOAc and 2 mL of H_2O at such a rate that the temperature of the reaction solution did not exceed 10 °C throughout the addition. The benzoquinones began to separate immediately from the solution. After 20 min, 10 mL of H_2O and 5 mL of CH_2Cl_2 were added. The CH_2Cl_2 solution was washed with saturated $NaHCO_3$, dried over $MgSO_4$, and evaporated under vacuum. The crude CH_2Cl_2 solution was passed through silica gel to remove polymeric impurities. The yields for **10** and **11** exceeded 90%; the yield for **13** was not determined but was observed to be high.

2-(3′-Methylphenoxy)-4-methoxy-5-methylphenol (14). Ketal **7** (0.25 g, 0.60 mmol) and 0.30 g of 30% palladium on charcoal were added to 20 mL of MeOH in a Parr hydrogenation bottle. Reduction with hydrogen required 4 h to reduce the chloro intermediates to **14**. The catalyst was removed by filtration and the solvent was removed under vacuum. The residue was dissolved in a minimum of CH_2Cl_2 and passed through silica gel. Removal of the solvent under vacuum gave **14** (22 mg) as a viscous liquid. Yield: 15%. ^{1}H NMR (300 MHz): 2.19 (s, 3H), 2.32 (s, 3H), 3.68 (s, 3H), 6.46 (s, 1H), 6.80−6.91 (m, 4H), 7.17−7.22 (m, 1H), 7.26 (s, 1H). ^{13}C NMR (75.4 MHz): 15.8, 21.4, 56.1, 103.5, 113.9, 117.5, 118.2, 123.6, 123.9, 129.6, 140.1, 141.2, 151.5, 157.5. MS *m*/*z* (EI): 244 (M^+, 100); 229 (M − CH_3); 214 (M − $2CH_3$); 211 (M − CH_3OH). HRMS (CI): calcd for MH^+, $C_{15}H_{18}O_3$ 245.1177, found 245.1178. IR (cm^{-1}): OH, 3600; OCH_3, 2867. GC retention time: 13 min.

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Supporting Information Available: NMR and mass spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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