coupling is observed in the ^{13}C NMR spectra of **4** and **5**[9] for the carbons of the dioxaphospholene ring (J_{POC} = 2.9 Hz for **4**; J_{POC} = 2.6 Hz for **5**).[10] Therefore, the most straightforward pseudorotation route would be the Berry mechanism, in which only Ph, R, and S[11] are used as the pivot, in order to retain axial–equatorial location of the dioxaphospholene ring. However, this dynamic process, given in the circular pathways of Scheme I, will lead to retention of configuration at phosphorus. (The phosphorus configuration in the left circle is related to **6a** and in the right circle to **6b**.) It follows that intermediate structures with a diequatorial location of the dioxaphospholene ring must be invoked to justify the ^{31}P NMR observations. Most likely, (53), in which the phenyl group occupies an equatorial site, is representative for the intramolecular isomerization of (14) into (24) and vice versa.[12]

Conclusion

It is shown with ^{31}P NMR that the pseudorotation of the oxyphosphoranes **4** and **5** involves intermediate structures with a diequatorial orientation of the dioxaphospholene ring. Thus it appears that the pseudorotation of trigonal bipyramidal phosphoranes that are stabilized by a dioxaphospholene ring may very well involve intermediates which are in conflict with the well-known ring-strain rule.

Experimental Section

Spectroscopy. ^{31}P and ^{13}C NMR spectra were run in the FT mode on a Bruker CXP-300 spectrometer, at 121 and 75.3 MHz, respectively. ^{13}C NMR spectra were also run on a Bruker HX-90R spectrometer, at 22.6 MHz. ^{31}P chemical shifts are related to 85% H_3PO_4 as an external standard. Downfield shifts were designated as positive. ^1H NMR spectra were run at 60 MHz on a Hitachi-Perkin-Elmer R-24B spectrometer.

Synthesis. 2,2-Bis(tetrahydrofurfuryloxy)-2-phenyl-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (4). Butanedione (0.5 g, 5.8 mmol) was added slowly to a cooled (0 °C) solution of **6** (1.00 g, 3.2 mmol) in 2 mL of anhydrous CD_3CN that was kept in a 10-mm NMR sample tube. After 10 min, ^{31}P NMR indicated complete conversion into the desired product: ^{31}P NMR δ −42.10, −42.09 (ratio 1:1); ^1H NMR δ 0.92–2.50 (8 H, m, $H_{2'}/H_{3'}$), 2.33 (6 H, s, CH_3), 3.13–4.77 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 7.11–8.03 (5 H, m, Ar H).

2,2-Bis(tetrahydrofurfuryloxy)-2-phenyl-4,5-bis(trifluoromethyl)-1,3,2-dioxaphosphol-4-ene (5). Hexafluorobiacetyl (0.39 g, 3.0 mmol) was bubbled slowly through a cooled (0 °C) solution of **6** (0.5 g, 1.6 mmol) in 2 mL of anhydrous CD_3CN that was kept in a 10-mm NMR sample tube. After 20 min, ^{31}P NMR indicated complete conversion into the desired product: ^{31}P NMR δ −49.62, −49.70 (ratio 1:1); ^1H NMR δ 1.03–1.77 (8 H, m, $H_{2'}/H_{3'}$), 3.00–4.03 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 6.50–8.05 (5 H, m, Ar H).

Phenylbis(tetrahydrofurfuryloxy)phosphine (6). A mixture of tetrahydrofurfuryl alcohol (20.4 g, 0.2 mol), triethylamine (20.2 g, 0.2 mol), and 120 mL of anhydrous diethyl ether was added over 60 min to a cooled (0 °C) and stirred solution of phenyldichlorophosphine (17.9 g, 0.1 mol) in 100 mL of anhydrous diethyl ether. After completion of the addition, the reaction mixture was refluxed for 2 h. The precipitated triethylamine hydrochloride was removed by filtration. After removal of the solvent, the oily residue was distilled under reduced pressure to yield phenylbis(tetrahydrofurfuryloxy)phosphine (46 mmol, 46%) as a colorless viscous liquid, bp 150–154.5 °C (0.005 mm). Anal. Calcd for $C_{16}H_{23}PO_4$: C, 61.94; H, 7.42. Found: C, 62.13; H, 7.34. ^{31}P NMR δ 158.82, 158.77, 158.68 (ratio 2:1:1); ^1H NMR δ 1.37–2.20 (8 H, m, $H_{2'}/H_{3'}$), 3.45–4.33 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 7.17–7.87 (5 H, m, Ar H).

Phenylbis(tetrahydrofurfuryloxy)phosphine Oxide (7). During 15 min, an ozone–oxygen (15:85) stream was bubbled slowly through a solution of **6** (1.00 g, 3.2 mmol) in anhydrous bromobenzene that was kept in a 10-mm NMR sample tube. ^{31}P NMR indicated complete formation of **7**. Anal. Calcd for $C_{16}H_{23}PO_5$: C, 58.90; H, 7.06. Found: C, 58.78; H, 6.94. ^{31}P NMR δ 21.30, 21.21, 21.12 (ratio 1:2:1); ^1H NMR δ 1.00–1.80 (8 H, m, $H_{2'}/H_{3'}$), 3.00–3.57 (4 H, m, $H_{1'}$), 3.57–4.03 (6 H, m, $H_{4'}/H_{5'}$), 6.53–8.05 (5 H, m, Ar H).

Phenylbis(tetrahydrofurfuryloxy)phosphine Sulfide (8). A mixture of **6** (3.1 g, 10 mmol), sulfur (0.34 g, 1.3 mmol of S_8), and 50 mL of anhydrous toluene was refluxed for 4 h. Evaporation of the solvent afforded **8** as a yellowish oil. Anal. Calcd for $C_{16}H_{23}PO_4S$: C, 56.14; H, 6.73. Found: C, 55.64; H, 6.45. ^{31}P NMR δ 92.18, 92.05, 91.95 (ratio 1:2:1), ^1H NMR δ 1.00–1.70 (8 H, m, $H_{2'}/H_{3'}$), 2.92–3.82 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 6.80–7.68 (5 H, m, Ar H).

Oxyphosphorane 9. This model compound was prepared from ethyl α-isopropylideneacetoacetate[13] and **6**, according to Gorenstein and Westheimer:[8] ^{31}P NMR δ −19.71, −19.94, −20.02 (ratio 2:1:1); ^1H NMR δ 0.83 (3 H, t, CH_3(Et), J = 7.0 Hz), 1.00–2.03 (8 H, m, $H_{2'}/H_{3'}$), 1.47–1.62 (6 H, s, $PC(CH_3)_2$), 1.88 (3 H, s, CH_3), 2.90–3.70 (10 H, m, $H_{1'}/H_{4'}/H_{5'}$), 3.80 (2 H, q, CH_2(Et), J = 7.0 Hz), 6.77–7.67 (5 H, m, Ar H).

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Registry No. **4**, 98170-48-0; **5**, 98170-49-1; **6**, 7526-34-3; **7**, 98170-50-4; **8**, 98170-51-5; **9**, 98170-52-6; butanedione, 431-03-8; hexafluorobiacetyl, 685-24-5; tetrahydrofurfuryl alcohol, 97-99-4; phenyldichlorophosphine, 644-97-3; ethyl α-isopropylideneacetoacetate, 35044-52-1.

Supplementary Material Available: ^{31}P NMR spectra (121 MHz) of (i) **6** in CD_3CN, (ii) **6** in CD_3CN after addition of the chiral shift reagent tris[3-((trifluoromethyl)hydroxymethylene)-*d*-camphorato]europium(III), (iii) **4** in $(CD_3)_2CO$, (iv) **5** in $(CD_3)_2CO$, and (v) **9** in $(CD_3)_2CO$ (1 page). Ordering information is given on any current masthead page.

(9) The ^{13}C NMR spectra of **4** and **5** give rise to crowded patterns at δ 25–31 and 60–70. However, the olefinic carbons of the dioxaphospholene ring could be clearly identified. The spin–spin coupling constants of these nuclei with phosphorus were obtained by comparison of the ^{13}C NMR spectra recorded at 22.6 and 75.3 MHz.

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(11) R and S are used as abbreviations for tetrahydrofurfuryloxy with *R* and *S* configuration at $C_{4'}$, respectively.

(12) Low-temperature ^{31}P NMR spectra of **4** and **5** in CD_2Cl_2 do not show any decoalescence phenomena for temperatures as low as −70 °C.

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Novel Oxidative Coupling of Monophenols in the System of Cupric Chloride–Oxygen–Alcohol

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In a previous paper,[1] we reported the oxidative chlorination of naringenin (4′,5,7-trihydroxyflavanone) by the cupric chloride–oxygen–alcohol system. Extending this

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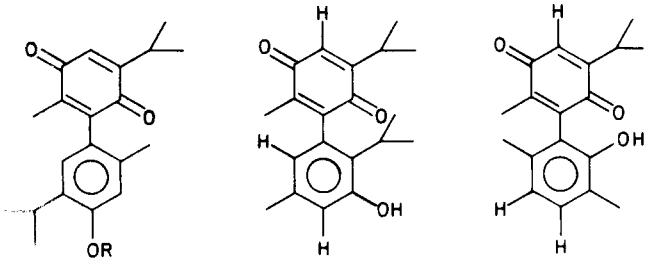
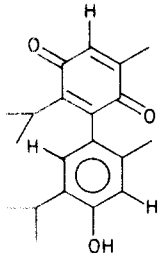
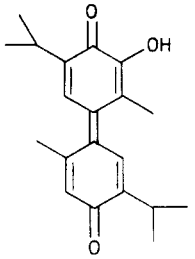
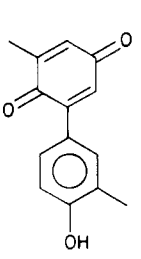
investigation to the oxidation of the monophenols thymol, o-cresol, 2-naphthol, 2,6-dimethylphenol, and 2,6-di-*tert*-butylphenol by the same system, novel coupling products were isolated. This is of interest concerning the laccase–O_2 system[2] and oxidative phenol coupling. Although oxidation of thymol[3] has been studied previously by using ferric chloride in aqueous solvent and 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ) in benzene,[4] our coupling products have not been reported. This reaction will be a novel and simple method to prepare coupled quinoid compounds from phenols in one step. Equimolar amounts of phenols and anhydroud cupric chloride were mixed in various solvents. Oxidation was carried out by bubling O_2 through the solution with stirring at 60 °C for 24–48 h. The products were examined by TLC (benzene–ethyl acetate, 10:1 v/v). In case of thymol three spots were detected by exposure to iodine vapor or spraying with concentrated H_2SO_4. These products were isolated by silica gel column chromatography.

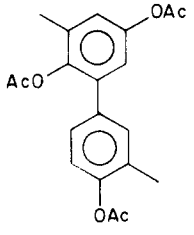
One of them (R_f 0.45) was found to be 2-(4-hydroxy-5-isopropyl-2-methylphenol)-6-isopropyl-3-methyl-1,4-benzoquinone (**1a**). The IR and UV spectra indicated that it had both a *p*-quinoid structure and a phenyl group in the molecule. The MS spectrum revealed the following

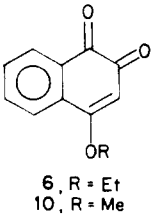












for **1a**: *m/e* 312 (M^+), 297 (M^+ – Me), 284 (M^+ – CO), 269 (M^+ – Me – CO). It also revealed the presence of a typical *p*-quinoid structure.[5] The ^1H NMR spectrum corresponded to the structure of **1a** and its acetate **1b**, which was given quantitatively by reacting it with acetic anhydride and pyridine. Two singlet aromatic protons of **1a** (δ 6.54 and 6.68) were shifted downfield (δ 6.89 and 6.94) by acetylation,[6] so the hydroxyl group is bound at the para position of the ring. Three other isomers (**1c**, **1d**, and **1e**) can be envisioned. Two of them (**1c** and **1d**) would have ortho and meta coupled protons in the aromatic region in the ^1H NMR spectrum, but in our ^1H NMR spectrum such meta or ortho coupled protons did not appear. Also Gills reagent[7] was negative to this compound. This indicates that the position para to the hydroxyl group is not free. The last isomer (**1e**) has one olefinic proton that should be coupled with the adjacent methyl protons in the ^1H NMR spectrum, but our olefinic proton was not coupled to any other protons. In this structure, the ^1H NMR spectrum of the isopropyl group must occur at a much higher field than δ 1.12 due to anisotropic effect of the neighboring aryl group.[8] From these data, these three isomers can be rejected. The product **2** (R_f 0.77) was identified as thymoquinone by comparing its UV, IR, MS, and NMR spectra with those of an authentic sample. The last compound (R_f 0.88) was confirmed to be 3-hydroxy-5,5′-diisopropyl-2,2′-dimethyl-4,4′-diphenoquinone (**3**). The UV spectrum (440 nm) indicated that a diphenoquinone or an analogous group was formed. The IR spectrum (1660 cm^{-1}) also revealed the presence of a carbonyl group in diphenoquinone which resembles a 1,4-benzoquinoid type.[9] The ^1H NMR and MS spectra were also consistent with the structure **3**. By the oxidation of *o*-cresol, the ortho–para coupling product **4** was selectively obtained. In the ^1H NMR spectrum of **4**, two olefinic proton [δ 6.72 (d, J = 2.6 Hz) and 6.63 (m)] indicated that it was the 1,4-benzoquinoid compound substituted with a 2-methyl group and a 6-aryl group. Reductive acetylation of **4** with zinc powder and acetic anhydride gave the triacetate **5**, which revealed two new aromatic protons with meta coupling [δ 7.15 (d, J = 1.8 Hz) and 7.2 (d, J = 1.8 Hz)]. These results also confirmed the structure of **4**. The ^{13}C NMR spectra data (Table I) is consistent with structure **4**.[10]

Table I. ^{13}C NMR Data of the Quinoid 4

C	chem shift, δ	C	chem shift, δ
C_1	187.8	$C_{1'}$	133.0
C_2	146.1	$C_{2'}$	128.4
C_3	132.1	$C_{3'}$	124.6
C_4	187.6	$C_{4'}$	157.2
C_5	130.6	$C_{5'}$	114.9
C_6	145.9	$C_{6'}$	124.7
C_2-Me	16.2	$C_{3'}$-Me	16.0

In the case of 2-naphthol in EtOH, 4-ethoxy-1,2-naphthoquinone (**6**) (65% yield) and 1-chloro-2-naphthol (**7**) (30% yield) were produced. With MeOH instead of EtOH, 4-methoxy-1,2-naphthoquinone (**10**) was obtained in 60% yield. On the other hand, in the oxidation of 2,6-dimethylphenol, 2,6-dimethylbenzoquinone (**8**) (32% yield) and 3,5,3′,5′-tetramethyl-4,4′-diphenoquinone (**9**) (51% yield) were isolated. However in the oxidation of 2,6-di-*tert*-butylphenol, only 3,5,3′,5′-tetra-*tert*-butyl-4,4′-diphenoquinone (**11**) was produced in 70% yield. Our oxidation was more selective compared with the system

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Scheme I

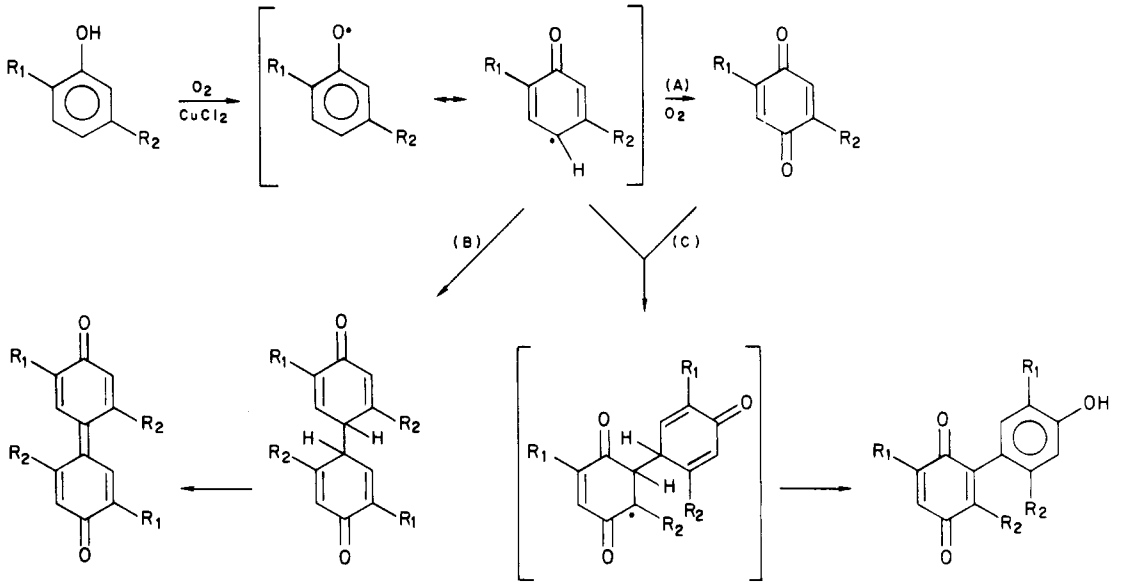

Table II. Effect of Solvent on Phenol Oxidation

solvent	product, %[d] 1a	2	3
methanol	28	10	5
ethanol	65	25	10
butanol	15	50	30
isopropanol	5	24	35
acetonitrile		32	61
DMF		63	30
acetone[b]			
pyridine[c]			

[a] Thymol, 1.5 mmol; $CuCl_2$, 1.5 mmol; solvent, 50 mL, reaction temperature, 60 °C for 48 h. [b] Reaction did not proceed, and the starting materials were recovered. [c] Polymeric products were produced. [d] Isolated yields.

$CuCl–O_2–py$,[11] and our new quinoid compounds were not formed in previous known coupling systems: CuCl/py, $K_3Fe(CN)_6$, PbO_2, $Pb(OAc)_4$, and $FeCl_3$. Scheme I appears to be reasonable in explaining the observed products **1a** and **4** via path C.

Considering solvent effects (Table II), ethanol most favors the formation of the coupling product. Tsuruya and Yonezawa reported that catalytic action would occur in the $CuCl_2$–OEt–phenol complex, which is easily formed in the presence of sodium ethoxide.[12] Since in our case, alcoholic solvent is essential for the formation of the coupling product, it is likely that a similar interaction is occurring.

Experimental Section

All melting points are uncorrected. The ^1H NMR spectra were recorded at 60, 100, and 200 MHz on JEOL FX-60, JEOL JNM-MH-100, and JEOL JNM-FX-200 spectrometers, respectively, using Me_4Si as an internal standard. The ^{13}C NMR spectra were recorded on a JEOL FX-60 spectrometer using Me_4Si as an internal standard. IR spectra were recorded on a JASCO A-3 spectrometer. UV spectra were recorded on a Hitachi EPS-3T spectrometer. Mass spectra were obtained on Hitachi M-60 and Hitachi RMU-7M spectrometers.

Oxidation of Thymol. An example of the general method is given for thymol. To a stirred solution of anhydrous cupric chloride (200 mg, 1.5 mmol) in absolute ethanol (50 mL) was added dropwise a solution of thymol (230 mg, 1.5 mmol) in absolute ethanol (10 mL) under bubbling oxygen at 60 °C. The mixture was subsequently stirred under the same condition for 48 h. The reddish brown reaction mixture was condensed on a rotary evaporator under reduced pressure. The condensed reaction mixture was poured into water (250 mL) and extracted with ethyl acetate. The extract was washed with water (3 × 50 mL), dried (Na_2SO_4), and evaporated to give an oily residue. The products were purified by column chromatography using silica gel. Elution with ethyl acetate and benzene (10:1) gave **1a** (65%), **2** (25%), and **3** (10%) as orange yellow liquids, respectively.

2-(4-Hydroxy-5-isopropyl-2-methylphenyl)-6-isopropyl-3-methyl-1,4-benzoquinone (1a): bp 130 °C (3 mmHg); IR (neat) ν 3400, 2924, 1640, 1605, 1500, 1400, 1320, 1210, 885, 840 cm^{-1}; UV λ_{max} (EtOH) 256 nm (ϵ 10 000), 265 (8600), 287 (1500), 442 (390); ^1H NMR ($CDCl_3$) δ 1.12 (d, 2 H, J = 7.0 Hz), 1.20 (d, 6 H, J = 7.0 Hz), 1.80 (s, 3 H), 1.92 (s, 3 H), 3.08 (m, 2 H), 5.24 (br, 1 H, exchangeable with D_2O), 6.54 (s, 1 H), 6.56 (s, 1 H), 6.68 (s, 1 H); MS, m/e 312.1734 (M^+), calcd for $C_{20}H_{24}O_3$ m/e 312.1726. Anal. Found: C 76.94; H, 7.82. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74.

2-(4-Acetoxy-5-isopropyl-2-methylphenyl)-6-isopropyl-3-methyl-1,4-benzoquinone (1b). Acetylation of **1a** with Ac_2O in pyridine gave a monoacetate **1b**: orange yellow viscous oil; IR (neat) ν 3050, 2924, 1765, 1660, 1610, 1500, 890 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (d, 6 H, J = 7.0 Hz), 1.20 (d, 6 H, J = 7.0 Hz), 1.82 (s, 3 H), 2.04 (s, 3 H), 2.35 (s, 3 H), 3.00 (m, 2 H), 6.60 (s, 1 H), 6.89 (s, 1 H), 6.94 (s, 1 H); MS, m/e 354 (M^+).

Thymoquinone (**2**): mp 44–45 °C (lit.[13] mp 43–45 °C); ^1H NMR ($CDCl_3$) δ 1.54 (d, 6 H, J = 7.0 Hz), 2.05 (d, 3 H, J = 1.65 Hz), 3.00 (h, 1 H, J = 7.0 Hz), 6.52 (d, 1 H, J = 1.25 Hz), 6.60 (q, 1 H, J = 1.65 Hz); IR (neat) ν 2950, 1600, 1610, 1470, 1360, 910 cm^{-1}; MS, m/e 164 (M^+), 149 (M^+ – 15), 136 (M^+ – CO).

3-Hydroxy-5,5′-diisopropyl-2,2′-dimethyl-4,4′-diphenoquinone (3): orange yellow viscous oil; IR (neat) ν 3550, 2950, 1660, 1570, 1400, 870, 760 cm^{-1}; UV (EtOH) λ_{max} 261 nm (ϵ 30 700), 267.5 (30 500), 345 (1000), 440 (26 000); ^1H NMR ($CDCl_3$) δ 1.15 (d, 6 H, J = 7.0 Hz), 1.25 (d, 6 H, J = 7.0 Hz), 2.22 (s, 3 H), 2.28 (d, 3 H, J = 1.16 Hz), 3.25 (m, 2 H), 5.55 (d, 1 H, exchangeable with D_2O), 6.32 (s, 1 H), 6.67 (s, 1 H), 7.32 (s, 1 H); MS, m/e 312 (M^+), 297 (M^+ – Me), 269 (M^+ – Me – CO), 198. Anal. Found: C, 76.72; H, 7.91. Calcd for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74.

Preparation of 6-(4-Hydroxy-3-methylphenyl)-2-methyl-1,4-benzoquinone (4). To a stirred solution of anhydrous cupric chloride (200 mg, 1.5 mmol) in absolute ethanol (50 mL), with oxygen bubbling through the solution at 60 °C, was added *o*-cresol (160 mg, 1.5 mmol) in absolute alcohol (10 mL) in portions over 15 min. The mixture was stirred under bubbling oxygen through

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the solution for 48 h at 60 °C. The usual workup gave a crude product (150 mg), which was chromatographed on a silica gel column. Elution with ethyl acetate–benzene (20:1, v/v) gave **4** (145 mg) as reddish orange yellow needles: mp 149–150 °C; IR (KBr) ν 3400, 2950, 1650, 1618, 1603, 1500, 1275, 1030, 905, 820, 610 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.12 (d, J = 1.54 Hz, C_2Me, 3 H), 2.28 (s, 3 H, C_3Me), 6.63 (m, 1 H, H-3), 6.72 (d, 1 H, J = 2.63 Hz, H-5), 6.84 (d, 1 H, J = 7.62 Hz, H-5′), 7.20 (dd, 1 H, J = 7.62 Hz, J = 1.81 Hz, H-6′), 7.30 (d, 1 H, J = 1.81 Hz, H-2′), 7.55 (br, 1 H, ArOH, exchangeable with D_2O); MS, m/e 228.0801 (M^+), calcd for $C_{14}H_{12}O_3$ m/e 228.0787. Anal. Found: C, 73.50; H, 5.14. Calcd for $C_{14}H_{12}O_3$: C, 73.67; H, 5.30.

Reductive Acetylation of 4. The quinoid compound **4** (200 mg) in acetic anhydride (10 mL) was added with zinc powder (100 mg) and anhydrous sodium acetate (100 mg). The mixture was stirred at 60 °C for 12 h. The reaction mixture was poured into ice–water (500 mL) and extracted with CH_2Cl_2 (100 mL × 3). The extracts were dried over Na_2SO_4 and concentrated. The product **5** (90 mg) was isolated by silica gel chromatography eluted with benzene–ethyl acetate (20:1, v/v): viscous oil; ^1H NMR ($CDCl_3$) δ 2.05 (s, 3 H, ArO*Ac*), 2.15 (s, 6 H, ArO*Ac*), 2.23 (s, 3 H, Ar*Me*), 2.28 (s, 3 H, Ar*Me*), 6.88–7.00 (m, 3 H), 7.15 (d, 1 H, J = 1.80 Hz), 7.20 (d, 1 H, J = 1.80 Hz); IR (neat) 2950, 1760, 1610, 1600, 1500, 1475, 1440, 1380 cm^{-1}. Anal. Found: C, 67.21; H, 5.55. Calcd for $C_{20}H_{20}O_6$: C, 67.40; H, 5.66.

Oxidation of 2-Naphthol. 2-Naphthol (290 mg, 2.0 mmol) was dissolved in 10 mL of absolute ethanol and was added to the ethanol solution (80 mL) of cupric chloride (270 mg, 2.0 mmol) under bubbling oxygen. The reaction solution was stirred for 60 °C for 24 h under bubbling oxygen through the solution, and then the solvent was removed under reduced pressure. The usual workup gave a crude product (382 mg), which was chromatographed over silica gel. The first eluate was concentrated in vacuo to give colorless needles, **6** (107 mg). The last eluate was concentrated and cooled to give 263 mg (65%) of orange yellow crystals, **7**: mp 107–108 °C; IR (KBr) 2990, 1685, 1660, 1615, 1595, 1580, 1250, 1215, 1050, 780, 730, 700 cm^{-1}; ^1H NMR ($CDCl_3$); δ 1.52 (t, 3 H, CH_2CH_3), 4.15 (q, 2 H, CH_2CH_3), 6.20 (s, 1 H, H-3), 7.60–8.20 (m, 4 H, H-5,6,7,8); MS, m/e 202.0625, calcd for $C_{12}H_{10}O_3$ m/e 202.0630; MS, m/e 174 (M^+ – CO), 158 (M^+ – OEt + H).

1-Chloro-2-naphthol (**7**): mp 68–69 °C (lit.[14] 70 °C; IR (KBr) ν 3300, 2925, 1625, 1600, 1500, 1430, 1350, 1000, 810 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.85 (s, 1 H, exchangeable with D_2O), 7.15–8.10 (m, 6 H); this compound was positive to a Beilstein test;[15] MS, m/e 178 (M^+).

Preparation of 4-Methoxy-1,2-naphthoquinone (10). 2-Naphthol (288 mg, 2.0 mmol) and anhydrous cupric chloride (270 mg, 2.0 mmol) in absolute ethanol (50 mL) were used for the synthesis of **10**. The reaction solution was stirred at 60 °C for 35 h under bubbling oxygen through the solution. The reaction mixture was condensed on a rotary evaporator under the reduced pressure. The usual workup gave a crude product (310 mg), which was purified by silica gel chromatography (benzene–ethyl acetate, 10:1) to yield orange yellow crystals (226 mg): mp 152 °C; IR (KBr) 2950, 1682, 1650, 1610, 1598, 1580, 1450, 1250, 730 cm^{-1}; ^1H NMR ($CDCl_3$) δ 388 (s, 3 H), 6.15 (s, 1 H), 7.60–8.20 (m, 4 H); MS, m/e 188 (M^+), 160 (M^+ – CO), 158 (M^+ – OMe + H). Anal. Found: C, 69.98; H, 4.16. Calcd for $C_{11}H_8O_3$: C, 70.20; H, 4.28.

Oxidation of 2,6-Dimethylphenol. 2,6-Dimethylphenol (610 mg, 5.0 mmol) in absolute ethanol (20 mL) and anhydrous cupric chloride (670 mg, 5.0 mmol) in absolute ethanol (80 mL) were added in the same method described for the oxidation of thymol. The reaction solution was stirred at 60 °C for 24 h under bubbling oxygen through the solution. The usual workup and the following silica gel chromatography gave 200 mg of yellow crystals of **8** and 310 mg of reddish brown crystals of **9**.

2,6-Dimethyl-1,4-benzoquinone (**8**): mp 69–70 °C (lit.[16] 72–73 °C); IR (KBr) ν 2980, 1660, 1620, 1445, 1390, 1298, 1185, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.15 (s, 6 H), 7.70 (s, 2 H); ^{13}C NMR ($CDCl_3$) δ 187.55 (C-1), 186.87 (C-4), 145.31 (C-2), 132.89 (C-3), 15.35 (CH_3).

3,3′,5,5′-Tetramethyl-4,4′-diphenoquinone (9): mp 205–207 °C (lit.[17] mp 205.5–208 °C); ^1H NMR ($CDCl_3$) δ 6.41 (s, 4 H), 1.92 (s, 12 H); ^{13}C NMR ($CDCl_3$) δ 187.21 (C-4 and C-4′), 139.10 (C-3 and C-3′), 135.67 (C-1 and C-1′), 129.56 (C-2 and C-2′), 17.07 (4 × CH_3).

3,5,3′,5′-Tetra-*tert*-butyl-4,4′-diphenoquinone (11). 2,6-Ditetra-*tert*-butylphenol (1.018 g, 5.0 mmol) in absolute ethanol (10 mL) and anhydrous cupric chloride (0.672 g, 5.0 mmol) in absolute ethanol were added. The reaction mixture was stirred at 60 °C for 24 h under bubbling oxygen through the solution. The reaction mixture was condensed on a rotary evaporator under reduced pressure. The usual workup and the following silica gel chromatography gave 680 mg (66.8%) of reddish brown crystals of **11**: mp 239–242 °C (lit.[17] mp 242.5–244 °C); IR (KBr) 2950, 1640, 1605, 1570, 1360, 1100, 900 cm^{-1}.

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Registry No. **1a**, 98268-32-7; **1b**, 98268-33-8; **2**, 490-91-5; **3**, 98268-34-9; **4**, 98268-35-0; **5**, 98268-36-1; **6**, 7473-19-0; **7**, 633-99-8; **8**, 527-61-7; **9**, 4906-22-3; **10**, 18916-57-9; **11**, 2455-14-3; thymol, 89-83-8; *o*-cresol, 95-48-7; 2-naphthol, 135-19-3; 2,6-dimethylphenol, 576-26-1; 2,6-di-*tert*-butylphenol, 128-39-2; cupric chloride, 7447-39-4.

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(18) Solvent effect on the oxidation of *o*-cresol (yields of **4**, % are as follows: MeOH (80), EtOH (85), BuOH (34), *i*-PrOH (18). In the solvents acetonitrile, DMF, acetone, and pyridine, **4** was not produced.

Selective Permanganate Oxidation of *cis*- vs. *trans*-2,5-Dihydro-2,5-dimethoxyfuran

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2,5-Dihydro-2,5-dimethoxyfuran, prepared by electrolytic methoxylation of furan[1,2] or by the action of methanolic chlorine or bromine[3,4] on furan is a mixture of cis (**1**) and trans (**2**) isomers, which, on a preparative scale, are difficultly separable by very efficient vacuum fractionation[3,5] (2.5 °C boiling point difference). 2,5-Dihydro-2,5-dimethoxyfuran is most often used in synthesis as a masked 1,4-dialdehyde; therefore, the mixture of stereoisomers is of no great consequence since the stereochemistry of the 2,5-substituents disappears upon hydrolysis.[6,7] For example, the cis 3,4-diols (mixture of **3** and **4**) made from the mixture of cis/trans isomers **1** and **2** upon hydroylsis give *meso*-tartaraldehyde.[7] We needed to synthesize some stereochemically defined model furan compounds derived from **1** and **2** and therefore explored these reactions further.

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