gave **9c** (0.277 g, 95%) as a colorless oil: ^{1}H NMR (CDCl$_3$, 200 MHz), δ 1.22–1.33 (m, 1 H), 1.45–1.71 (m, 2 H), 1.81–1.99 (m, 4 H), 2.18–2.34 (m, 1 H), 2.58–2.75 (m, 2 H), 2.86–3.12 (m, 2 H); ^{13}C NMR (CDCl$_3$) 25.21, 30.86, 32.26, 33.19, 33.39, 39.91, 51.22, 52.25, 54.72, 219.84; mass spectrum, *m/e* (relative intensity) 148 (M$^+$, 22), 120 (22), 105 (22), 104 (60), 92 (71), 91 (100).

Anal. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.12; H, 8.07.

Acknowledgment. This work was supported by the National Institutes of Health (GM 26568). NMR spectra were recorded on a Varian XL-200 instrument purchased with funds provided, in part, by a National Science Foundation Department Instrumentation grant. Mass spectra were obtained on a Hewlett-Packard 5987 GC–MS system purchased with funds provided by the National Science Foundation and Grant 1 510 RR01677 awarded by the National Institutes of Health-BRS Shared Instrument Program.

Registry No. **1a**, 97253-90-2; **1b**, 97253-91-3; **1c**, 91029-50-4; **1d**, 91036-26-9; **1e**, 97253-92-4; *cis*-**2a**, 97254-14-3; *trans*-**2a**, 97253-93-5; *cis*-**2b**, 97254-15-4; *trans*-**2b**, 97253-94-6; **2c**, 97253-95-7; *cts*-**2d**, 97254-16-5; *trans*-**2d**, 97253-96-8; *cis*-**2e**, 97254-17-6; *trans*-**2e**, 97253-97-9; **3a**, 97253-98-0; **3d**, 97253-99-1; **3f**, 97254-00-7; **4a**, 97254-02-9; **4b**, 97277-65-1; **4c**, 97254-03-0; **4d**, 97254-05-2; **5a**, 97254-04-1; **5b**, 94225-53-3; **6b**, 97254-01-8; **7a**, 97277-64-0; **7b**, 97254-06-3; **8a**, 97254-07-4; **8b**, 97254-08-5; **9a**, 97254-09-6; **9b**, 97254-12-1; **9c**, 97254-13-2; **10**, 97254-10-9; **11**, 97254-11-0; 2-$MeC_6H_4CH{=}CHCO_2Me$, 70625-38-6; 2-$(BrCH_2)C_6H_4CH{=}CHCO_2Me$, 70625-62-6; 2-$MeOC_6H_4CO_2Me$, 606-45-1; $BrCH_2CH{=}CH_2$, 106-95-6; $CH_2{=}C(Br)CH_2Br$, 513-31-5; $I(CH_2)_3CH{=}CH_2$, 7766-48-5.

Synthesis of Unsymmetrical Biphenyls by Reaction of Nitroarenes with Phenols

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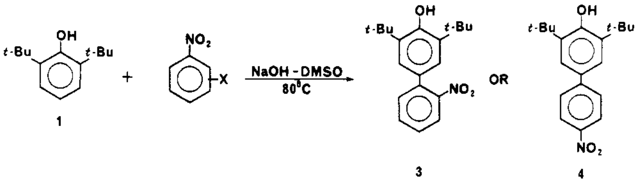
The anion of 2,6-di-*tert*-butylphenol (**1**) behaves as a carbon nucleophile toward nitroarenes bearing leaving groups ortho or para to the nitro group, affording biphenyls by conventional S_NAr processes. However, **1** reacts with *m*-dinitrobenzene (**2**), *o*-nitrobenzonitrile, or *m*-nitrobenzonitrile to give biphenyls by formal displacements of nitroarene hydrogen atoms. This oxidative coupling process also occurs between unhindered phenols, even phenol itself, and compound **2**. Mechanistic features of the oxidative coupling reaction are discussed.

A variety of methods exist for the preparation of biphenyls.[1] In some cases unsymmetrical biphenyls have been synthesized by nucleophilic aromatic substitution reactions involving electron-rich arenes and halonitroarenes.[2] There are also reports of aryl–aryl bond formation by formal nucleophilic aromatic substitution for hydrogen.[3]

Reactions in which an aromatic hydrogen atom is replaced are well documented for nitroarenes and a variety of nucleophiles.[4] They occur via intermediate Meisenheimer complexes which decompose in various ways. Nucleophiles bearing leaving groups at the nucleophilic center give rise to complexes which undergo subsequent elimination.[5] With simpler nucleophiles oxidation of the intermediate complex may occur spontaneously[6] or by addition of an oxidant.[7] Presumably the nitroarene itself functions as the oxidant in the former cases, usually af-

Table I. Nucleophilic Aromatic Substitution Reactions



X	time, h[a]	product	yield, %[b]
2-F	18	3	97
2-Cl	24	3	71
2-Br	4	3	79
2-I	2	3	63[c]
2-NO_2	17	3	64
2-SO_2Ph	20	3	68
3-Cl		no reaction	
3-SO_2Ph		complex product mixture	
4-NO_2	3	4	77
4-SO_2Ph	30	4	69

[a] Reaction times not optimized. [b] Based on weight of crude material from PTLC. [c] A mixture of 3 and unreacted *o*-iodobenzene (22%) was recovered.

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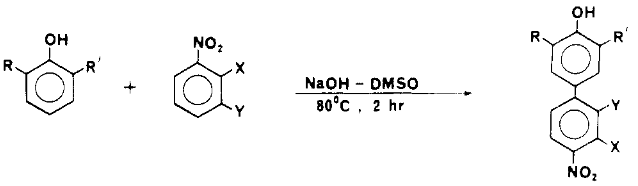
Table II. Oxidative Coupling Reactions



R	R′	X	Y	product	yield, %[a]
$C(CH_3)_3$	$C(CH_3)_3$	H	NO_2	5	69
$C(CH_3)_3$	CH_3	H	NO_2	6	64
CH_3	CH_3	H	NO_2	7	49
H	H	H	NO_2	8	17[b]
$C(CH_3)_3$	$C(CH_3)_3$	H	CN	9	46
$C(CH_3)_3$	$C(CH_3)_3$	CN	H	10	28

[a] Based on weight of crystalline material. [b] Reaction time was 3 h. 3-Nitrophenyl phenyl ether was also obtained (18% yield).

fording products in low yield. Reduction of the nitroarene was demonstrated in the Zimmermann reaction of *m*-dinitrobenzene (2) and acetone by the isolation of *m*-nitroaniline.[6b,c]

Described herein are the syntheses of unsymmetrical biphenyls by two related processes. The first is reaction of the anion of 1 with nitroarenes bearing leaving groups, resulting in nucleophilic aromatic substitution by a ring carbon atom of the phenoxide ion. The second is an oxidative coupling process that occurs in moderate to good yields between 2, *o*-nitrobenzonitrile, or *m*-nitrobenzonitrile and hindered or unhindered phenoxides. Together these methods provide a variety of substituted biphenyls. Available transformations of the nitro and cyano groups as well as the ease of removal of phenolic *tert*-butyl groups[8] render such compounds versatile intermediates.

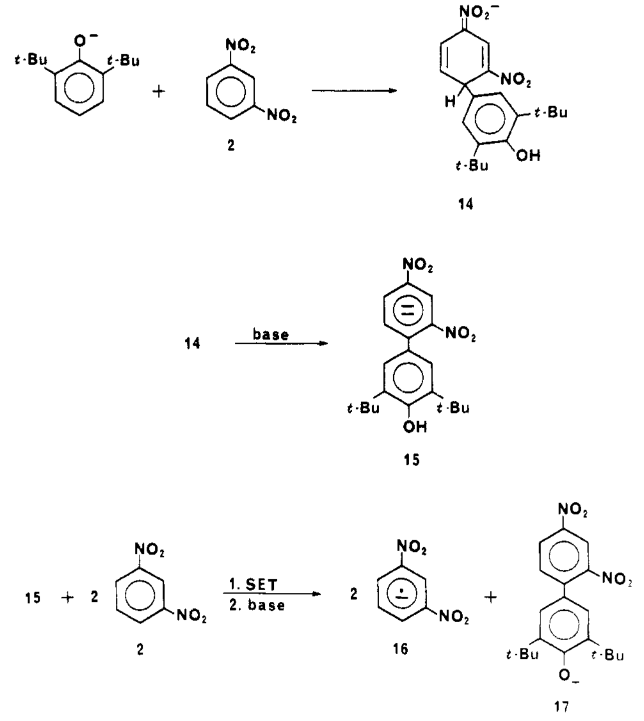
Results and Discussion

Reactions involving displacements of conventional leaving groups by the anion of 1 are shown in Table I. These were conducted by heating mixtures of 1, arene, powdered sodium hydroxide (NaOH), and dimethyl sulfoxide (Me_2SO) at 80 °C for the indicated times.

In each case where a major product was formed, it was a biphenyl. This observation is consistent with the results of Wright and Jorgensen, who isolated biphenyl 4 from the reaction of *p*-chloronitrobenzene and 1 but obtained diphenyl ethers from this nitroarene and 2,6-diisopropylphenol or other less hindered phenols.[2a]

Although most of the reactions in Table I involve displacements of conventional leaving groups such as halide or nitrite ions, both 2- and 4-nitrophenyl phenyl sulfones afforded biphenyls resulting from exclusive displacement of the phenylsulfonyl group. Previous research has revealed that relative leaving group mobility is highly dependent on the substitution pattern of the nitroarene, the nature of the displacing reagent, and the reaction conditions.[9] Most of these studies involved oxygen, nitrogen, or sulfur nucleophiles, but Kornblum reported that the carbanion derived from 2-nitropropane reacts with 4-nitrophenyl phenyl sulfone via nitro group displacement.[9b] Thus, the reactions of the anion of 1 merely exemplify the dependency of group mobility on the character of the nucleophile.

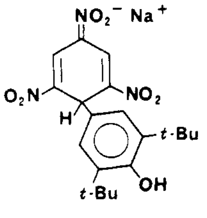
Scheme I



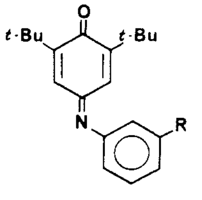
Biphenyls obtained by oxidative coupling reactions are shown in Table II. It is surprising that reactions of 1 or other phenols with particular nitroarenes (Table II) under standard conditions (NaOH in Me_2SO) occur by a formal displacement of hydride ion rather than the typical substitution process. Kornblum found that compound 2 undergoes nitro group displacement on reaction with sulfur nucleophiles.[9b]

The conditions outlined in Table II are not critical. Reaction of 1 and 2 affords biphenyl 5 (yields not quantified) using the following base–solvent combinations: NaOH–dimethylformamide, NaOH–acetonitrile, NaOH–ethanol, potassium *tert*-butoxide–Me_2SO, and sodium hydride–Me_2SO. The yield of 5 from reaction of 1 and 2 under standard conditions is dependent on stoichiometry. When equimolar amounts of reactants or an excess of 1 were used, 5 was obtained in 48% yield. Employing a 50% excess of NaOH and compound 2 afforded 5 in 69% yield.

The number of different nitroarenes that undergo the oxidative coupling reaction appears limited. Nitrobenzene does not react with 1 to produce a biphenyl under standard conditions even at 180 °C. Other nitroaromatic compounds which either do not react with or give complex product mixtures (containing no detectible biphenyls) on reaction with 1 are 2-nitroacetophenone, 9-nitroanthracene, 2-nitronaphthalene, 4-nitrobenzonitrile, and 2-nitrobenzamide. Under standard conditions 1,3,5-trinitrobenzene reacts with 1 to produce the stable Meisenheimer complex 11, which was observed by NMR spectroscopy.



11



12 : R = NO_2
13 : R = H

The results shown in Table II indicate that biphenyl formation by oxidative coupling is not particularly de-

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pendent on hindrance at the phenolic hydroxyl group. Ether formation by phenoxide ion displacement of the nitro group is a competitive process only with phenol itself. It is known that phenoxide ion reacts as an oxygen nucleophile in conventional nucleophilic aromatic substitution (S_NAr) processes[9] but reacts as a carbon nucleophile with polynitroarenes to form stable Meisenheimer complexes.[10] Buncel suggested that attack by the phenoxide ion oxygen atom is the kinetic process, which prevails in S_NAr reactions due to the subsequent irreversible loss of a good leaving group.[11] He also postulated that phenoxide ion attack at a nitroarene ring position bearing a poor leaving group would allow the thermodynamic process, reaction of phenoxide ion as a carbon nucleophile, to compete. Such is the case for the oxidative coupling reactions. In these systems reaction of the phenoxide or substituted phenoxide ions at an unsubstituted position of the nitroarene is followed by hydride loss (oxidation), which is inefficient enough to allow the thermodynamic process to predominate. In conventional S_NAr reactions substituents are displaced more readily from positions ortho and para to the activating nitro group than from meta positions.[9a] Thus only the unhindered phenoxide ion is nucleophilic enough to react with **2** via the S_NAr pathway. It is noteworthy that Kornblum obtained only 3-nitrophenyl phenyl sulfide from the reaction of thiophenoxide ion and **2**.[9b] Presumably the S_NAr process predominates in this case because of the greater nucleophilicity of the sulfur anion compared to that of the oxygen anion.

The reaction of **1** and **2** was explored in some detail to better define mechanistic features. As mentioned earlier, the Zimmerman coupling of acetone and **2** proceeds with reduction of excess **2**.[6b,c] Thus, it seemed likely that the oxidative coupling reactions involve nitroarene reductions. The detailed reaction pathway was suspected to be analogous to that proposed by Guthrie for the reaction of nitrobenzene and potassium *tert*-butoxide,[12] i.e., dianion formation followed by single electron transfers (Scheme I).

A product mixture from the reaction of **1** and **2** was subjected to chromatography in order to isolate and identify minor components. Along with gummy, intractable orange and black materials, the crystalline quinonimine **12** was isolated in 2% yield. The analogous compound **13** was obtained by treatment of **1** with nitrosobenzene, which suggests that **12** arises from reaction of **1** and *m*-nitronitrosobenzene. Processes of this type have been reported previously.[13] These results support the contention that **2** is reduced during the oxidative coupling reaction.

By analogy to Guthrie's proposal,[12] the rate-determining step of the mechanism shown in Scheme I should be formation of dianion **15**. Accordingly, appearance of Meisenheimer complex **14** was found to be rapid compared to generation of product **5**. A deep purple color resulted immediately on addition of powdered sodium hydroxide to a solution of **1** and **2** in Me_2SO, but workup of this solution after a few minutes afforded only a trace of **5**. A similar mixture kept at 80 °C for 2 h attained a deep blue color, and workup afforded **5** in good yield. The UV-visible spectra exhibited absorption maxima at 580 nm for the initially formed, purple species and 670 nm for the final, blue species. Control experiments and comparison with literature values[14] supported assignment of the 580-nm absorption to the Meisenheimer complex **14** and the 670-nm absorption to the anion of biphenyl **5** (**17**).

Complex **14** was also evident in the NMR spectrum of a purple solution made as described above. The freshly prepared solution exhibited very sharp NMR signals for unreacted **1** and **14**, but no signals for unreacted **2**. Presumably this is due to selective exchange broadening by electron-transfer processes.[15] Over a period of 90 min at room temperature the signals for **1** disappeared, leaving only the spectrum of complex **14**. After completion of the reaction by heating for 2 h at 80 °C, exchange broadening of all signals was observed. This effect was most dramatic for the aromatic signals, which appeared as a broad, featureless absorption.

Also implicit in the mechanism shown in Scheme I is the scission of a carbon–hydrogen bond during the rate-determining step (formation of dianion **15**). A deuterium isotope effect was observed in the reaction of **1** with a mixture of **2** and perdeuterated **2**. This study was carried out at room temperature so that only aromatic protons or deuterons situated between two nitro groups would undergo exchange.[16] A control experiment indicated that perdeuterated **2** yields **5** containing either two or three deuterons. The competition experiment produced biphenyls containing zero to three deuterons, with the ratio of $d_0 + d_1$ species to $d_2 + d_3$ species providing a k_H/k_D value of 3.3. This primary isotope effect, similar in magnitude to that reported by Guthrie for the potassium *tert*-butoxide–nitrobenzene reaction,[12] is consistent with a rate-determining dianion formation. However, other processes such as hydride transfer from **14** to **2** cannot necessarily be ruled out.

If the mechanism of the oxidative coupling reaction were strictly analogous to that proposed by Guthrie,[12] then 3 mol of **2** would be consumed for each mole of **5** produced. This is not the case. However, Guthrie carried out his reactions in THF, from which the radical anion of nitrobenzene precipitates. In the present system the radical anion of **2** (**16**) presumably remains in solution and may react further. Protonation of **16** could eventually result in a neutral species, capable of accepting a single election, such as *m*-nitronitrosobenzene. Similar transformations of nitrobenzene have been reported.[17] It is also conceivable that two electrons are transferred to each molecule of **2** to give the dianion, a known species.[18]

Experimental Section

Melting points were determined with a Fischer-Johns hot stage melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded on a Varian EM-390 spectrometer. Chemical shifts are reported in parts per million relative to tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 683 spectrophotometer. UV-visible spectra were obtained on a Varian Cary 219 spectrophotometer. Mass spectra were obtained on a Finnigan 4023 gas chromatograph/mass spectrometer equipped with a 50-m SE-52 fused silica capillary column. Elemental analyses were performed by Huffman Laboratories, Inc., Wheat Ridge, CO.

All reactions were carried out under a nitrogen atmosphere. Me_2SO was dried by storage over 3-Å molecular sieves. Sodium hydroxide was powdered in a nitrogen-purged grinder. Per-

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deuterated *m*-dinitrobenzene was purchased from ICN-KOR isotopes. Petroleum ether refers to the fraction of bp 35–60 °C. Preparative thin-layer chromatography (PTLC) was carried out on commercially prepared silica gel plates (Analtech) and visualization was by ultraviolet light.

Reaction of 2,6-Di-*tert*-butylphenol (1) with 2-Nitrophenyl Phenyl Sulfone. A mixture of 30 mg (0.75 mmol) of powdered sodium hydroxide, 155 mg (0.75 mmol) of 2,6-di-*tert*-butylphenol, 155 mg (0.59 mmol) of 2-nitrophenyl phenyl sulfone, and 1.0 mL of Me$_2$SO was stirred overnight at 80 °C and poured into 10 mL of 1 N HCl. The resulting aqueous mixture was extracted with three 10-mL portions of diethyl ether. Combination, drying (MgSO$_4$), and concentration of the ether layers afforded a residue which was purified by PTLC (eluted with 50% dichloromethane in petroleum ether) to give 131 mg (68% yield) of 3,5-bis(1,1-dimethylethyl)-2′-nitro-(1,1′-biphenyl)-4-ol (**3**):[2b,19] ^{1}H NMR (CDCl$_3$) δ 1.46 (s, 18 H), 5.29 (s, 1 H), 7.16 (s, 2 H), 7.24–7.81 (m, 4 H); IR (neat) 3630, 2880, 1530, 1435, 1360, 1235 cm^{-1}; mass spectrum (70 eV), *m*/*e* (relative intensity) 327 (M$^+$, 12), 312 (24), 57 (100), 41 (40).

Reaction of 2,6-Di-*tert*-butylphenol (1) with *m*-Dinitrobenzene (2). A mixture of 1.2 g (30 mmol) of powdered sodium hydroxide, 4.1 g (20 mmol) of 2,6-di-*tert*-butylphenol, 5.0 g (30 mmol) of *m*-dinitrobenzene, and 40 mL of Me$_2$SO was stirred for 2 h at 80 °C and poured into 400 mL of 1 N HCl. The resulting aqueous mixture was extracted with three 400-mL portions of diethyl ether. Combination, drying (MgSO$_4$), and concentration afforded a residue which was subjected to flash chromatography[20] on 200 g of silica gel (eluted with 25–40% dichloromethane in petroleum ether) and crystallized from hexane to give 5.1 g (69% yield) of yellow 3,5-bis(1,1-dimethylethyl)-2′,4′-dinitro-(1,1′-biphenyl)-4-ol (**5**):[19] mp 170–171 °C; ^{1}H NMR (CDCl$_3$) δ 1.47 (s, 18 H), 5.52 (s, 1 H), 7.20 (s, 2 H), 7.70 (d, 1 H, J = 9 Hz), 8.41 (dd, 1 H, J = 2, 9 Hz), 8.61 (d, 1 H, J = 2 Hz); IR (KBr) 3650, 2980, 1545, 1445, 1356, 1245 cm^{-1}; mass spectrum (70 eV), *m*/*e* (relative intensity) 372 (M$^+$, 6), 357 (19), 57 (100), 41 (36). Anal. Calcd for C$_{20}$H$_{24}$N$_2$O$_5$: C, 64.50; H, 6.50; N, 7.52. Found: C, 64.90; H, 6.63; N, 7.37.

The following compounds were prepared by similar procedures:

3-(1,1-Dimethylethyl)-5-methyl-2′,4′-dinitro-(1,1′-biphenyl)-4-ol (6): mp 154–156 °C; ^{1}H NMR (CDCl$_3$) δ 1.41 (s, 9 H), 2.30 (s, 3 H), 5.10 (s, 1 H), 7.10 (m, 2 H), 7.70 (d, 1 H, J = 9 Hz), 8.45 (dd, 1 H, J = 2, 9 Hz) 8.67 (d, 1 H, J = 2 Hz); IR (KBr) 3525, 2960, 1535, 1350 cm^{-1}; mass spectrum (70 eV), *m*/*e* (relative intensity) 330 (M$^+$, 31), 315 (100), 287 (22), 165 (24), 152 (26), 57 (34), 43 (21), 41 (60). Anal. Calcd for C$_{12}$H$_{18}$N$_2$O$_5$: C, 61.81; H, 5.49; N, 8.48. Found: C, 61.91; H, 5.51; N, 8.27.

3,5-Dimethyl-2′,4′-dinitro-(1,1′-biphenyl)-4-ol (7): mp 182–183 °C; ^{1}H NMR (CDCl$_3$) δ 2.28 (s, 6 H), 4.90 (s, 1 H), 6.98 (s, 2 H), 7.61 (d, 1 H, J = 9 Hz), 8.43 (dd, 1 H, J = 2, 9 Hz), 8.65 (d; 1 H, J = 2 Hz); IR (KBr) 3400, 1540, 1360 cm^{-1}; mass spectrum (70 eV), Me$_4$Si derivative, *m*/*e* (relative intensity) 315 (M$^+$, 9), 73 (100), 45 (24). Anal. Calcd for C$_{14}$H$_{12}$N$_2$O$_5$: C, 58.33; H, 4.20; N, 9.72. Found: C, 58.38; H, 4.17; N, 9.50.

2′,4′-Dinitro-(1,1′-biphenyl)-4-ol (8): mp 166–167 °C, ^{1}H NMR (CDCl$_3$) δ 6.81 (broad s, 1 H), 6.95 (d, 2 H, J = 9 Hz), 7.24 (d, 2 H, J = 9 Hz), 7.69 (d, 1 H, J = 9 Hz), 8.49 (dd, 1 H, J = 2, 9 Hz), 8.70 (d, 1 H, J = 2 Hz); IR (KBr) 3525, 3090, 2960, 1535, 1350 cm^{-1}; mass spectrum (70 eV), TMS derivative, *m*/*e* (relative intensity) 332 (M$^+$, 79), 317 (90), 75 (28), 73 (100), 45 (31). Anal. Calcd for C$_{12}$H$_8$N$_2$O$_5$: C, 55.39; H, 3.10; N, 10.77. Found: C, 55.03; H, 3.11; N, 10.52.

3,5-Bis(1,1-dimethylethyl)-2′-cyano-4′-nitro-(1,1′-biphenyl)-4-ol (9): mp 178–180 °C; ^{1}H NMR (CDCl$_3$) δ 1.50 (s, 18 H), 5.60 (s, 1 H), 7.53 (s, 2 H), 7.79 (d, 1 H, J = 9 Hz), 8.51 (dd, 1 H, J = 2, 9 Hz), 8.70 (d, 1 H, J = 2 Hz); IR (KBr) 3580, 2960, 2240, 1520, 1430, 1355, 1235 cm^{-1}; mass spectrum (70 eV), *m*/*e* (relative intensity) 352 (M$^+$, 37), 337 (79), 57 (100), 41 (33). Anal. Calcd for C$_{21}$H$_{24}$N$_2$O$_3$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.52; H, 6.95; N, 7.90.

3,5-Bis(1,1-dimethylethyl)-3′-cyano-4′-nitro-(1,1′-biphenyl)-4-ol (10): mp 197–199 °C; ^{1}H NMR (CDCl$_3$) δ 1.51 (s, 18 H), 5.56 (s, 1 H), 7.45 (s, 2 H), 7.92 (dd, 1 H, J = 2, 9 Hz), 8.05 (d, 1 H, J = 2 hz), 8.41 (d, 1 H, J = 9 Hz); IR (KBr) 3655, 2980, 2250, 1540, 1445, 1355, 1250 cm^{-1}; mass spectrum (70 eV), *m*/*e* (relative intensity) 352 (M$^+$, 25), 337 (100), 57 (24), 41 (25). Anal. Calcd for C$_{21}$H$_{24}$N$_2$O$_3$: C, 71.57; H, 6.86; N, 7.95. Found: C, 71.35; H, 6.86; N, 7.97.

Isolation of 2,6-Bis(1,1-dimethylethyl)-4-[(3-nitrophenyl)imino]-2,5-cyclohexadien-1-one (12). A product mixture, generated as described above from 1.5 g (38 mmol) of powdered sodium hydroxide, 7.8 g (38 mmol) of 2,6-di-*tert*-butylphenol, 5.0 g (30 mmol) of *m*-dinitrobenzene, and 25 mL of Me$_2$SO, was subjected to flash chromatography on 200 g of silica gel. Elution with 40% dichloromethane in petroleum ether afforded 4.1 g of crude biphenyl **5**. Elution with 60% dichloromethane in petroleum ether gave a red fraction, which was further purified by chromatography on 20 g of neutral alumina (activity grade 3) using 30% dichloromethane in petroleum ether as eluent. Crystallization of the appropriate fraction from dichloromethane–hexane provided 193 mg (2% yield) of bright red **12**: mp 133–138 °C; ^{1}H NMR (CDCl$_3$) δ 1.20 (s, 9 H), 1.35 (s, 9 H), 6.69 (d, 1 H, J = 3 Hz), 7.06 (d, 1 H, J = 3 Hz), 7.20 (m, 1 H), 7.70 (apparent t, 1 H), 7.77 (apparent t, 1 H), 8.20 (m, 1 H); IR (KBr) 2960, 1655, 1535, 1355 cm^{-1}; mass spectrum (70 eV), *m*/*e* (relative intensity) 340 (M$^+$, 15), 323 (68), 91 (32), 77 (28), 67 (37), 65 (21), 57 (88), 41 (100), 39 (26). Anal. Calcd for C$_{20}$H$_{24}$N$_2$O$_3$: C, 70.56; H, 7.11; N, 8.23. Found: C, 70.57; H, 7.19; N, 8.09.

2,6-Bis(1,1-dimethylethyl)-4-(phenylimino)-2,5-cyclohexadien-1-one (13). A mixture of 37 mg (0.93 mmol) of powdered sodium hydroxide, 193 mg (0.93 mmol) of 2,6-di-*tert*-butylphenol, 100 mg (0.93 mmol) of nitrosobenzene, and 1 mL of Me$_2$SO was stirred for 30 min at ambient temperature and poured into 10 mL of 1 N HCl. The resulting aqueous mixture was extracted with three 10-mL portions of diethyl ether. Combination, drying (MgSO$_4$), and concentration of the ether layers afforded a residue which was purified by PTLC (eluted with 40% dichloromethane in petroleum ether) to give 182 mg of red oil. This was identified by spectral data (NMR, IR, MS) as compound **6**.[21]

Meisenheimer Complex 11. A mixture of 19 mg (0.48 mmol) of powdered sodium hydroxide, 100 mg (0.48 mmol) of 2,6-di-*tert*-butylphenol, 102 mg (0.48 mmol) of 1,3,5-trinitrobenzene,[22] and 1.0 mL of Me$_2$SO-d_6 was stirred for 90 min at ambient temperature and filtered. The ^{1}H NMR spectrum of the filtrate was recorded: δ 1.34 (s, 18 H), 5.60 (s, 1 H), 7.07 (s, 2 H), 8.43 (s, 2 H).

Meisenheimer Complex 14. A mixture of 30 mg (0.75 mmol) of powdered sodium hydroxide, 155 mg (0.75 mmol) of 2,6-di-*tert*-butylphenol, 126 mg (0.75 mmol) of *m*-dinitrobenzene, and 1.0 mL of Me$_2$SO-d_6 was stirred for 2 h at ambient temperature and filtered. The ^{1}H NMR spectrum of the filtrate was recorded: δ 1.32 (s, 18 H), 4.72 (d, 1 H, J = 4 Hz), 5.47 (dd, 1 H, J = 4, 10 Hz), 6.61 (dd, 1 H, J = 2, 10 Hz), 6.81 (s, 2 H) 8.31 (d, 1 H, J = 2 Hz).

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Registry No. **1**, 128-39-2; **2**, 99-65-0; **3**, 51572-38-4; **4**, 15138-30-4; **5**, 51572-39-5; **6**, 97211-17-1; **7**, 97211-18-2; **8**, 53398-98-4; **9**, 97211-19-3; **10**, 97211-19-3; **11**, 97211-20-6; **12**, 97211-21-7; **13**, 14329-20-5; **14**, 97211-23-9; *o*-FC$_6$H$_4$NO$_2$, 1493-27-2; *o*-ClC$_6$H$_4$NO$_2$, 88-73-3; *o*-BrC$_6$H$_4$NO$_2$, 577-19-5; *o*-IC$_6$H$_4$NO$_2$, 609-73-4; *o*-NO$_2$C$_6$H$_4$NO$_2$, 528-29-0; *m*-ClC$_6$H$_4$NO$_2$, 121-73-3; *m*-PhSO$_2$C$_6$H$_4$NO$_2$, 18513-19-4; *p*-NO$_2$C$_6$H$_4$NO$_2$, 100-25-4; *p*-PhSO$_2$C$_6$H$_4$NO$_2$, 1146-39-0; PhOH, 108-95-2; *m*-CNC$_6$H$_4$NO$_2$, 619-24-9; *o*-CNC$_6$H$_4$NO$_2$, 612-24-8; 2-nitrophenyl phenyl sulfone, 31515-43-2; nitrosobenzene, 586-96-9; 1,3,5-trinitrobenzene, 99-35-4; 2-methyl-6-*tert*-butylphenol, 2219-82-1; 2,6-dimethylphenol, 576-26-1; 3-nitrophenyl phenyl ether, 620-55-3.

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