Palladium-Catalyzed Coupling of Naphthoquinone Triflates with Stannanes. Unprecedented Nucleophilic Aromatic Substitution on a Hydroxynaphthoquinone Triflate

Antonio M. Echavarren,*[1a] Óscar de Frutos,[1a] Nuria Tamayo,[1b] Pedro Noheda,[1c] and Paloma Calle[1d]

Departamento de Química Orgánica, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain, Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain, and Departamento de Química Física Aplicada, Universidad Autónoma de Madrid, Cantoblanco, 28049 Madrid, Spain

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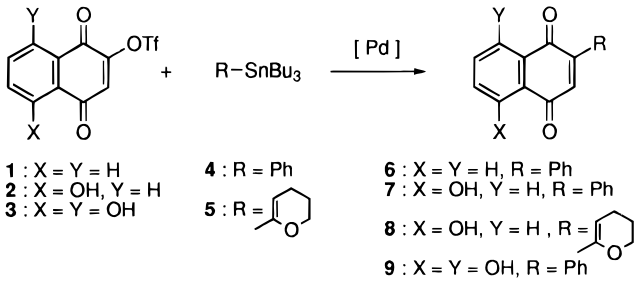
Aryl trifluoromethanesulfonates (triflates), readily prepared from phenols, have been extensively used in recent years as electrophiles in the Stille palladium-catalyzed coupling with organostannanes.[2,3] We have recently applied this type of coupling reaction for the formation of carbon−carbon bonds from anthraquinone triflates.[4] As an extension of this coupling, and as an alternative to the use of 2-bromoquinone electrophiles in palladium-catalyzed coupling reactions,[5] we decided to examine the palladium-catalyzed coupling reaction of 2-[(trifluoromethanosulfonyl)oxy]-1,4-naphthoquinones (2-hydroxynaphthoquinone triflates). As expected, the desired coupling with stannanes proceeds very readily by using a palladium catalyst in the absence of phosphine ligands and LiCl, a common additive in the coupling of triflates.[2,3] Additionally, we have also uncovered an unexpected nucleophilic aromatic substitution on one of the hydroxynaphthoquinone triflates that proceeds under surprisingly mild conditions.

The starting 1,4-naphthoquinone triflates **1**−**3** were readily prepared from 2-hydroxynaphthoquinone,[6] 2-hydroxyjuglone (2,5-dihydroxy-1,4-naphthoquinone),[7] and 2-hydroxynaphthazarine (2,5,8-trihydroxy-1,4-naphthoquinone),[8] respectively, by reaction with triflic anhydride and 2,6-lutidine (1 equiv each) as the base. Phenyltributylstannane (**4**) and dihydropyranyltributylstannane (**5**) were selected as representative aryl- and alkenylstannanes. Triflate **1** reacted with stannane **4** with $Pd(PPh_3)_4$ as the catalyst to give 2-phenylnaphthoquinone (**6**) in 46% yield (Scheme 1). The best coupling yields were realized by using a palladium catalyst without donor phosphine ligands. Thus, by using $Pd_2(dba)_3$·dba as the catalyst in NMP (*N*-methylpyrrolidone) as the solvent, **1** and **4** coupled at room temperature to give **6** in 73% yield. Under these conditions, triflate **2** reacted with stannane **4** to give **7**[5a,c] in 67% yield. Similarly, coupling of **2** with alkenylstannane **5** furnished **8**[5a,c] in 61% yield. Triflate **3** coupled uneventfully with **4** to give 2-phenylnaphthazarine (**9**) in 45% yield. It is worth noting that this coupling reaction proceeds in the absence of added halide sources. In fact, in these cases addition of LiCl, the usual additive employed in the cross coupling of triflates,[2,3] led to the formation of 2-chloro-1,4-naphthoquinones as a result of an addition−elimination reaction,[9] which did not couple with the stannanes under these mild reaction conditions. Thus, for example, a coupling attempted between triflate **3** and stannane **4** with $Pd(dppf)Cl_2$ as the catalyst in DMF in the presence of excess LiCl afforded 2-chloronaphthazarin in good yield.

Scheme 1



The ^1H and ^{13}C NMR spectra of **3** were consistent with the existence of an equilibrium between two tautomers **3a** and **3b** shifted toward this last structure.[10,11] It is interesting to note that, in contrast with related naphthazarins,[12] the ^{13}C NMR spectrum of **3** in $CDCl_3$ at 23 °C showed the carbons, except for C-2 and C-3,[13] coupled to the OH hydrogens (J = 2.3−3.5 Hz).

Surprisingly, as part of the studies on the stability of the naphthoquinone triflates toward nucleophiles, we found that triflate **3** reacted very cleanly with methanol in DMF in the presence of 3 equiv of Et_3N at 23 °C for 3 h to give methyl ether **10** in 86% yield (Scheme 2). A reaction carried out in the absence of DMF as cosolvent led to the formation of a 1:6 mixture of **10** and 2-methoxynaphthazarin, the expected product of addition−elimination reaction.[9] The structure of **10** was supported by the NMR data. In addition, methylation of the free hydroxyl of **10** with methyl iodide and silver oxide yielded dimethyl ether **11** (68%), which showed ^1H and ^{13}C NMR data fully consistent with the assigned structure. Quinone **11** and its regioisomer 5,7-dimethoxy-8-hydroxy-1,4-naphthoquinone were proposed as reasonable structures for one of the methylation products of 2-methoxynaphthazarin.[14] The preparation of **11**, with NMR data different from those reported for the dimethyl ether

(1) (a) Universidad Autónoma de Madrid, Departamento de Química Orgánica (b) Present address: AMGEN Inc., Thousand Oaks, CA. (c) Instituto de Química Orgánica, CSIC. (d) Universidad Autónoma de Madrid, Departamento de Química Física Aplicada.

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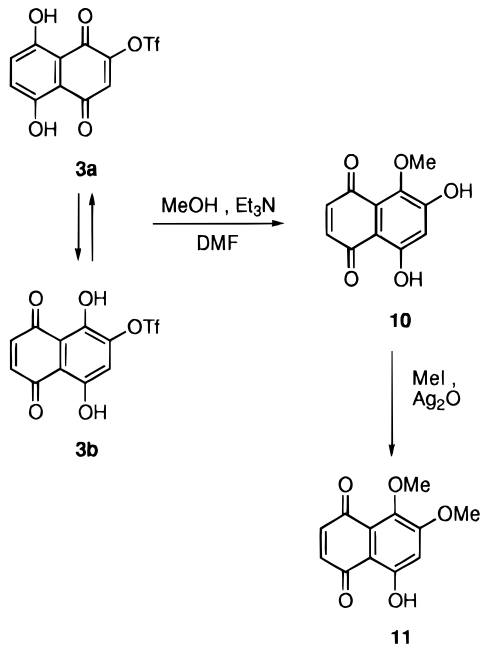
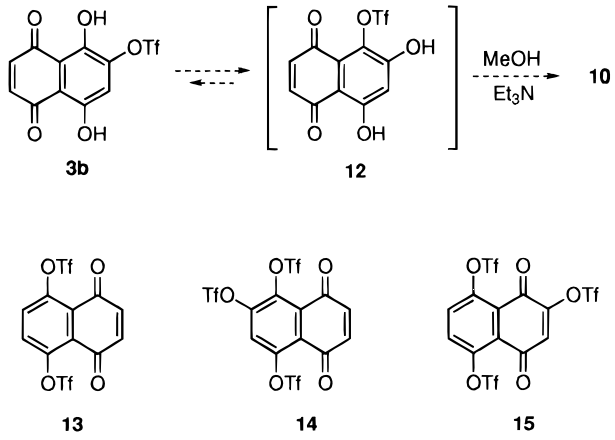
S0022-3263(96)02102-0 CCC: $14.00

Scheme 2



Scheme 3



derived from 2-methoxynaphthazarin, allows the assignment of its structure as 5,7-dimethyl-8-hydroxy-1,4-naphthoquinone. Interestingly, **11** is the only dimethyl ether that could not be prepared by direct methylation of 2-methoxynaphthazarin with methyl iodide and silver oxide.[14]

Formation of **10** formally implies a nucleophilic substitution on **12**, which may arise by an intramolecular triflate rearrangement from **3** (Scheme 3). However, such a sulfonyl migration is, to the best of our knowledge, unprecedented.[15] Additionally, although nucleophilic substitutions at the *peri* position of quinones, particularly anthraquinones, are precedented, these reactions usually proceed under harsh conditions.[9] Furthermore, bistriflate **13**, prepared from naphthazarin by reaction with excess triflic anhydride, did not suffer substitution after being treated with methanol under the conditions in which **3** gives **10**.[16] On the other hand, tristriflates **14** and **15**, obtained by reaction of **3** with excess triflic anhydride or directly from 2-hydroxynaphthazarin, were stable compounds that, unlike their acyl analogues,[17] did not equilibrate after being heated in toluene or DMF for several hours.

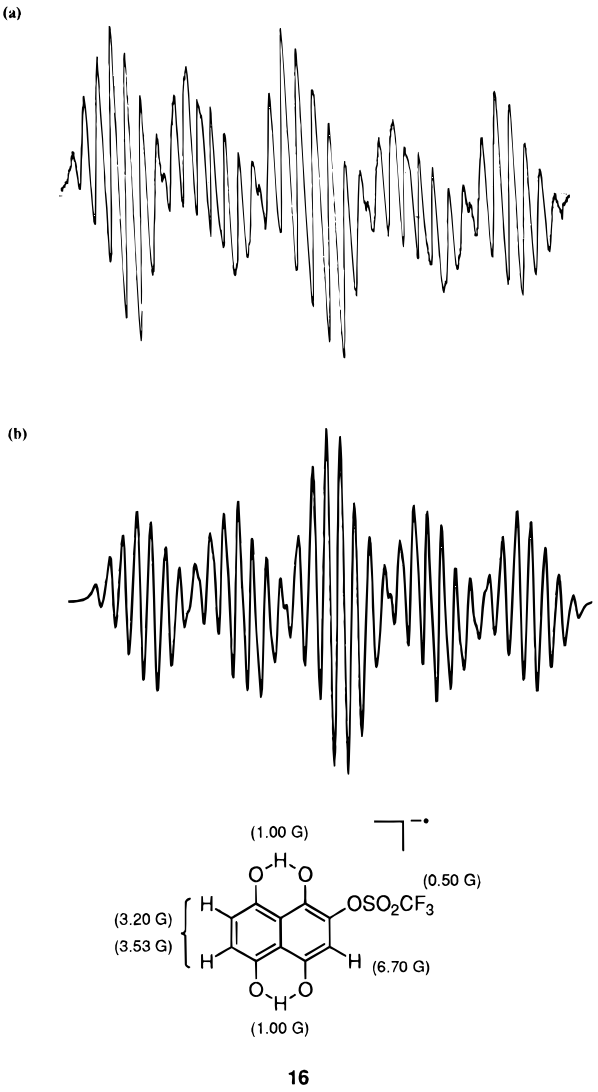


Figure 1. (a) ESR spectrum of the radical anion **16** generated from triflate **3** and Et_3N in DMF. Spectrometer settings: modulation amplitude 2.5×10^{-2} G, receiver gain 6.3×10^3, scan time 16 s. (b) Computer simulation (peak to-peak width of 0.35 G).

A strong coloration appeared immediately after dissolving quinone **3** with Et_3N in DMF, which suggests the formation of a charge-transfer complex.[18] Dissociation of the charge-transfer complex at room temperature led to an ESR-active species for which was assigned structure **16**, the radical anion of **3**. Radical anion **16** gave rise to a signal whose intensity increased with time and was analyzed in terms of six hyperfine splitting constants, $a_1 = 6.70$ G (1H), $a_2 = 3.53$ (1H), $a_3 = 3.20$ G (1H), $a_4 = 1.0$ G (2H), $a_5 = 0.50$ G (3F), by comparing the experimental spectrum with that obtained by computer simulation (Figure 1). Although **16** was stable under the conditions of the ESR experiment, a homolytic cleavage

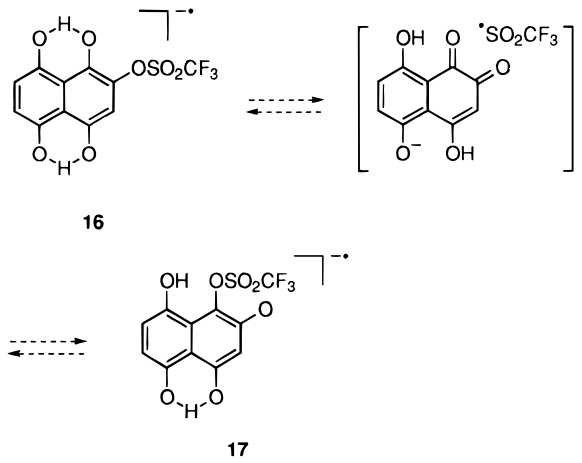
(15) We have recently uncovered another case of sulfonyl migration on calixarene derivatives that proceeds intermolecularly: González, J. J.; Nieto, P. M.; Prados, P.; Echavarren, A. M.; de Mendoza, J. *J. Org. Chem.* **1995**, *60*, 7419.

(16) Traces of product tentatively assigned as 2-methoxy-5,8-bis-[(trifluoromethanesulfonyl)oxy]-1,4-naphthoquinone (*ca.* 10%) were occasionally obtained in these experiments: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.65 (s, 2H), 6.22 (s, 1H), 3.93 (s, 3H).

(17) Acyl migration: (a) Alvarado, S.; Fariña, F.; Martín, J. L. *Tetrahedron Lett.* **1970**, 3377. (b) Brockmann, H.; Greve, H.; Zeeck, A. *Tetrahedron Lett.* **1971**, 1929.

(18) See: Mukherjee, A. K.; Chattopadhyay, A. K. *J. Chem. Soc., Perkin Trans. 2* **1992**, 1081.

Scheme 4



of the triflate leading to an intermediate sulfonyl radical[19] following by recombination could lead to the formation of **17** (Scheme 4). Further reaction of **17** with methanol by a $S_{RN}1$-type mechanism[20] could account for the formation of **10**.

In summary, we have shown that 2-hydroxynaphthoquinones are suitable starting materials for the synthesis of substituted naphthoquinones. In addition, we have found a surprisingly facile nucleophilic aromatic substitution on one of the hydroxynaphthoquinone triflates that may proceed through its radical anion.

Experimental Section

Only the most significant IR absortions and the molecular ions and/or base peaks in the MS are given. "Usual workup" means aqueous treatment, extraction with EtOAc or CH_2Cl_2, drying with Na_2SO_4, filtration, and evaporation. Chromatography was performed with flash grade silica gel. All reactions were carried out under an atmosphere of Ar.

2-Hydroxy-1,4-naphthoquinone,[6] 2,5-dihydroxy-1,4-naphthoquinone,[7] 2,5,8-trihydroxy-1,4-naphthoquinone,[8] and (2,3-dihydro-4*H*-pyran-6-yl)tri-*n*-butylstannane[21] were prepared according to known procedures.

2-[(Trifluoromethanesulfonyl)oxy]-1,4-naphthoquinone (1). To a solution of 2-hydroxy-1,4-naphthoquinone (308 mg, 1.77 mmol), 2,6-lutidine (0.227 mL, 208 mg, 1.95 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (21 mg, 0.18 mmol) in CH_2Cl_2 (35 mL) at 0 °C was slowly added triflic anhydride (0.315 mL, 529 mg, 1.88 mmol). The resulting mixture was stirred at 23 °C for 3 h. After the usual workup and chromatography (20:1 hexane−EtOAc), **1** was isolated as a red solid (353 mg, 65%): mp 101−102 °C; R_f = 0.23 (24:1 hexane−EtOAc); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 8.25−8.10 (m, 2H), 7.90−7.81 (m, 2H), 6.94 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 183.1, 177.1, 151.7, 135.2, 134.7, 131.5, 130.2, 127.3, 126.8 (2C), 118.5 [q, $J(^{13}C-^{19}F)$ = 321 Hz]. Anal. Calcd for $C_{11}H_5F_3O_5S$: C, 43.14; H, 1.65. Found: C, 43.36; H, 1.55.

5-Hydroxy-2-[(trifluoromethanesulfonyl)oxy]-1,4-naphthoquinone (2). To a solution of 2,5-dihydroxy-1,4-naphthoquinone (290 mg, 1.53 mmol), 2,6-lutidine (0.196 mL, 180 mg, 1.68 mmol), and 4-(*N*,*N*-dimethylamino)pyridine (19 mg, 0.15 mmol) in CH_2Cl_2 (35 mL) at 0 °C was slowly added triflic anhydride (0.272 mL, 456 mg, 1.62 mmol). The resulting mixture was stirred at 23 °C for 3 h. After the usual workup and chromatography (10:1 hexane−EtOAc), **2** was obtained as a red solid (391 mg, 79%): mp 109−110 °C; R_f = 0.41 (9:1 hexane−EtOAc); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 11.66 (s, 1H), 7.73−7.65 (m, 2H), 7.34 (dd, J = 6.8, 3.0 Hz, 1H), 6.91 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 188.1, 176.3, 161.8, 152.0, 137.0, 127.0, 126.1, 120.5, 118.5 [q, $J(^{13}C-^{19}F)$ = 321 Hz], 114.3 (one carbon signal was not observed). Anal. Calcd for $C_{11}H_5F_3O$ S: C, 41.00; H, 1.56. Found: C, 41.05; H, 1.49.

5,8-Dihydroxy-6-[(trifluoromethanesulfonyl)oxy]-1,4-naphthoquinone (3). To a solution of 2,5,8-trihydroxy-1,4-naphthoquinone (2-hydroxynaphthazarine) (260 mg, 1.26 mmol) in CH_2Cl_2 (20 mL) at 0 °C were added 2,6-lutidine (0.15 mL, 138 mg, 1.29 mmol) and triflic anhydride (0.22 mL, 369 mg, 1.30 mmol). The mixture was stirred at 0 °C for 5 min and at 23 °C for 1 h. After the usual workup and chromatography (5:1 hexane−EtOAc), **3** was obtained as a dark red solid (355 mg, 83%): mp 142−143 °C; IR (KBr) 1625, 1570 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 12.27 (s, 1H), 12.20 (s, 1H), 7.23 (part A, AB system, J = 9.8 Hz, 1H), 7.19 (part B, AB system, J = 9.8 Hz, 1H), 7.13 (s, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 173.8 (ddd, J = 6.1, 2.9, 2.7 Hz), 173.3 (ddd, J = 5.6, 3.2, 3.0 Hz), 170.9 (dd, J = 2.9, 2.8 Hz), 164.1 (dd, J = 6.8, 2.3 Hz), 148.0 (dd, J = 6.1, 3.6 Hz), 135.9 (dd, J = 168.5, 3.5 Hz), 134.9 (dd, J = 168.8, 3.5 Hz), 124.5 (dd, J = 169.8, 3.8 Hz), 118.5 (q, J = 320.8 Hz), 112.3 (m), 111.56 (m); ^{13}C NMR ($CDCl_3$ + D_2O, 50 MHz) δ 173.8 (dd, J = 6.1, 3.0 Hz), 173.3 (dd, J = 5.6, 3.2 Hz), 170.9 (d, J = 3.0 Hz), 164.1 (d, J = 7.0 Hz), 148.0 (d, J = 5.8 Hz), 135.9 (d, J = 168.5 Hz), 134.9 (d, J = 168.8 Hz), 124.5 (d, J = 168.8 Hz), 118.5 (q, J = 320.8 Hz), 112.3 (m), 111.6 (m); EI-MS m/z 338 (M^+, 100), 261 (8), 205 (32), 177 (95). Anal. Calcd for $C_{11}H_5F_3O_7S$: C, 39.06; H, 1.49. Found: C, 38.69; H, 1.59.

Palladium-Catalyzed Coupling of 1−3. General Procedure. The triflate and $Pd_2(dba)_3$·dba (2.5 mol%) were dissolved in NMP (1.5 mL). After 5 min, the stannane was added (1.2 equiv) dissolved in NMP (1 mL), and the resulting mixture was stirred at 23 °C for 16 h. Usual workup and chromatography (EtOAc−hexane mixtures) furnished the coupled products as orange solids (**6,** 73%; **7**, 67%; **8,** 61%) identical with previously prepared compounds.[5a,c]

5,8-Dihydroxy-2-phenyl-1,4-naphthoquinone (9). This new quinone was prepared according with the general procedure in 45% yield as a red solid: mp 147−148 °C; R_f = 0.53 (5:1 hexane−EtOAc); ^{1}H NMR ($CDCl_3$, 200 MHz) δ 12.85 (s, 1H), 12.57 (s, 1H), 7.63−7.58 (m, 2H), 7.51−7.48 (m, 3H), 7.24 (s, 2H), 7.16 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 179.6, 179.1, 166.3, 165.4, 147.7, 134.3, 133.2, 132.3 (2C), 130.0, 129.3, 128.5, 112.2, 111.9; EI-MS m/z 266 (M^+, 100), 237 (32).

2-Chloro-5,8-dihydroxy-1,4-naphthoquinone. A solution of **3** (30 mg, 0.09 mmol), Pd(dppf)Cl_2 (4 mg, 0.005 mmol), LiCl (11 mg, 0.27 mmol), and phenyltributylstannane (40 mg, 0.11 mmol) was stirred at 23 °C in DMF (3 mL) for 1.5 h. After the usual workup and chromatography, 2-chloronaphthazarin (17 mg, 85%) was obtained as a dark red solid: mp 178−179 °C (lit.[22] 179 °C); IR (KBr) 1620, 1575 cm^{-1}; ^{1}H NMR ($CDCl_3$, 200 MHz) δ 12.41 (s, 1H), 12.37 (s, 1H), 7.29 (s, 1H), 7.29 (part A, AB system, J = 9.6 Hz, 1H), 7.21 (part B, AB system, J = 9.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 177.4 (s), 173.2 (d, J = 7.8 Hz), 167.2 (dd, J = 7.3, 2.2 Hz), 166.5 (dd, J = 7.3, 1.5 Hz), 143.0 (d, J = 5.2 Hz), 134.5 (d, J = 171.2 Hz), 133.3 (dd, J = 167.3, 132.3 Hz), 132.3 (br d, J = 165.8 Hz), 111.5 (br s), 111.34 (m).

5,7-Dihydroxy-8-methoxy-1,4-naphthoquinone (10). To a solution of triflate **3** (45 mg, 0.13 mmol) in DMF (6 mL) and methanol (3 mL) at 23 °C was added triethylamine (0.045 mL, 0.32 mmol). The mixture was stirred at this temperature for 3 h. After the usual workup (washing with aqueous tartaric acid solution) and chromatography (2:1 hexane−EtOAc), **10** was obtained as an orange solid (25 mg, 86%): mp 173−175 °C; IR (KBr) 1665, 1635, 1575 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 12.81 (s, 1H), 11.25 (br s, 1H), 6.94 (part A, AB system, J = 10.3 Hz, 1H), 6.84 (part B, AB system, J = 10.3 Hz, 1H), 6.66 (s, 1 H), 3.94 (s, 3H); ^{1}H NOEDIFF ($CDCl_3$, 300 MHz) (i) irradiation at 3.94 ppm (OMe) led to enhancements of the signals at 6.66 (H-6, 13%), 11.25 (OH, −45%), and 12.81 (OH, −38%), (ii) irradiation at 6.66 (H-6) led to enhancements of the signals at 11.25 (OH, 2%) and 12.81 (OH, 2%); $^{13}C\{^1H\}$ NMR (10:1 $CDCl_3$-CD_3OD, 50 MHz) δ 188.0, 184.2, 161.2, 159.9, 139.7, 137.9, 130.5, 129.0, 110.2, 109.0, 61.1; EI-MS m/z 220 (M^+, 100), 205 (8), 177 (38), 160 (35). Anal. Calcd for $C_{11}H_8O_5$: C, 60.00; H, 3.66. Found: C, 59.71; H, 3.56.

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5,6-Dimethoxy-8-hydroxy-1,4-naphthoquinone (11). A mixture of quinone **10** (90 mg, 0.41 mmol), Ag_2O (116 mg, 0.50 mmol), and iodomethane (0.031 mL, 0.50 mmol) in acetonitrile (10 mL) was heated at 70 °C for 3 h. The solvent was evaporated, and the residue was chromatographed (7:1 hexane−EtOAc) to yield **11** as an orange solid (65 mg, 68%): mp 180−181 °C; IR (KBr) 1660, 1640, 1590 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 12.97 (s, 1H), 6.86 (part A, AB system, J = 10.2 Hz, 1H), 6.79 (part B, AB system, J = 10.2 Hz, 1H), 6.68 (s, 1 H), 3.95 (s, 3H), 3.67 (s, 3H); ^1H NOEDIFF ($CDCl_3$, 300 MHz) (i) irradiation at 3.95 (OMe) led to an enhancement of the signal at 6.68 (H-6, 11%), (ii) no enhancement was observed after irradiation at 3.68 (OMe); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 188.3 (d, J = 10.1 Hz), 183.7 (dd, J = 8.8, 1.9 Hz), 161.6 (d, J = 10.4 Hz), 161.6 (d, J = 1.1 Hz), 145.1 (m), 140.6 (dd, J = 169.0, 1.4 Hz), 137.6 (dd, J = 169.2, 1.2 Hz), 123.0 (d, J = 3.5 Hz), 107.9 (q, J = 3.6 Hz), 105.5 (dd, J = 162.1, 7.8 Hz), 61.2 (q, J = 145.5 Hz), 56.5 (q, J = 145.8 Hz). Anal. Calcd for $C_{12}H_{10}O_5$: C, 61.54; H, 4.30. Found: C, 61.35; H, 4.60.

5,8-Bis[(trifluoromethanesulfonyl)oxy]-1,4-naphthoquinone (13). To a solution of 5,8-dihydroxy-1,4-naphthoquinone (300 mg, 1.58 mmol) in CH_2Cl_2 (40 mL) at 23 °C were added 2,6-lutidine (2.24 mL, 2.06 g, 19.2 mmol) and triflic anhydride (3.22 mL, 5.40 mL, 19.1 mmol). The mixture was stirred at 23 °C for 18 h. After the usual workup and chromatography (5:1 hexane−EtOAc), **13** was obtained as a yellow solid (444 mg, 62%): mp 148−150 °C; IR (KBr) 1670 cm^{-1}; ^1H NMR ($CDCl_3$, 200 MHz) δ 7.69 (s, 2H), 7.02 (s, 2H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 181.1, 146.1, 138.7, 130.0, 125.9, 118.9 [q, $J(^{13}C-^{19}F)$ = 321 Hz]; EI-MS m/z 454 (M^+, 7), 298 (6), 270 (11), 257 (15), 201 (46); HRMS calcd for $C_{12}H_4F_6O_8S_2$ 453.9252, found 453.9251. Anal. Calcd for $C_{12}H_4F_6O_8S_2$: C, 31.72; H, 0.89; S, 14.11. Found: C, 31.79; H, 1.10; S, 13.97.

5,6,8-Tris[(trifluoromethanesulfonyl)oxy]-1,4-naphthoquinone (14) and 2,5,8-Tris[(trifluoromethanesulfonyl)-oxy]-1,4-naphthoquinone (15). Method a. To a solution of 2,5,8-trihydroxy-1,4-naphthoquinone (100 mg, 1.58 mmol) in CH_2Cl_2 (10 mL) at 0 °C were added 2,6-lutidine (0.56 mL, 0.52 g, 4.85 mmol) and triflic anhydride (0.80 mL, 1.34 g, 4.75 mmol). The mixture was stirred at 0 °C for 10 min and at 23 °C for 24 h. After the usual workup and chromatography (7:1 hexane−EtOAc), **14** (73 mg, 25%; R_f = 0.6, 3:1 hexane−EtOAc) and **15** (88 mg, 31%; R_f = 0.5, 3:1 hexane−EtOAc) were obtained as a yellow solids. **14**: mp 234−235 °C dec; IR (KBr) 1720, 1600 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.73 (s, 1H), 7.14 (part A, AB system, J = 11.4 Hz, 1H), 7.06 (part B, AB system, J = 11.4 Hz, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 180.4, 180.0, 146.0, 144.8, 138.9, 138.8, 138.6, 138.3, 123.4 (2C), 118.6 [q, $J(^{13}C-^{19}F)$ = 321 Hz], 118.51 [q, $J(^{13}C-^{19}F)$ = 321 Hz], 118.46 [q, $J(^{13}C-^{19}F)$ = 321 Hz]; EI-MS m/z 602 (M^+, 17), 382 (11), 341 (24), 203 (20); HRMS calcd for $C_{13}H_3F_9O_{11}S_3$ 601.8694, found 601.8691. **15**: mp 185−190 °C; IR (KBr) 1690, 1680 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 7.80 (s, 2H), 7.01 (s, 1H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 50 MHz) δ 179.4, 173.7, 150.4, 146.7, 146.2, 131.5, 130.9, 127.0, 125.6, 124.3, 118.7 [q, $J(^{13}C-^{19}F)$ = 321 Hz, 2C], 118.5 [q, $J(^{13}C-^{19}F)$ = 321 Hz]; EI-MS m/z 602 (M^+, 34), 533 (13), 341 (44) 203 (39); HRMS calcd for $C_{13}H_3F_9O_{11}S_3$ 601.8694, found 601.8672. **Method b.** To a solution of triflate **3** (100 mg, 0.29 mmol) in CH_2Cl_2 (10 mL) at 0 °C were added 2,6-lutidine (0.48 mL, 0.44 g, 3.26 mmol) and triflic anhydride (0.55 mL, 0.92 g, 3.26 mmol). The mixture was stirred at 0 °C for 10 min and at 23 °C for 24 h. After the usual workup and chromatography (7:1 hexane−EtOAc), **14** (48 mg, 27%) and **15** (53 mg, 30%) were obtained as yellow solids.

Radical Anion 16. The paramagnetic species were generated by reaction of a nitrogen-purged solution of **3** (3.4 mg, 1 mmol) with Et_3N (0.2 mL). The mixture, which immediately turned from red to intense violet, was transferred to the ESR cell. The ESR spectrum was recorded at 23 °C on a Varian E-12 spectrometer with 100 kHz field modulation operating at 9.5 GHz microwave frequency, in a flat quartz cell (4 × 1 × 0.1 cm). The microwave power level was kept at 1 mW, the time constant was 0.3 s, the modulation amplitude was 100 kHz, and the scan range was 20 G.

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Supporting Information Available: Copies of the NMR spectra for **9**, **14**, and **15** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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