culture is extracted similarly by using ethyl acetate or, alternatively, by performing continuous extraction with methylene chloride for 24 h. The obtained products are purified by flash chromatography (silica gel, Merck 60H, hexane/ether, 4/3) and bulb-to-bulb distillation. When used, the inhibitors are added to the culture 45 min before substrate 1 addition. The concentration of TEPP for preparative-scale experiments is 0.8 mM (200 μL/L of culture).

6-Undecyltetrahydro-2*H*-pyran-2-one (5-hexadecanolide) (2) was identified by IR, ^1H NMR, and ^{13}C NMR spectroscopy and by comparison with an authentic sample. Mass spectrometry: [M^+] 254; *m/z* 99 (100), 114 (16).

3-Undecyltetrahydro-2*H*-pyran-2-one was characterized by GC/MS of a mixture consisting of 95% of this compound and 5% **2**. Retention times: **3**, 4.4 min; **2**, 4.5 min (OV-1701 column, 230 °C, He flow, 1 bar). GC/MS: [M^+] 254; *m/z* 113 (60), 100 (100), 95 (7), 55 (15), 43 (9), 41 (15).

Selection of Lactone Hydrolase Inhibitors. *A. calcoaceticus* cells were grown, harvested by centrifugation, and disrupted as previously described.[5] A 200-μL (6 mg of P) aliquot was added in 1 mL of phosphate buffer (pH 7.1) at 30 °C containing 1 or 5 mM of the selected potential inhibitor. After 10 min of stirring, 10 μL (11 mg) of δ-valerolactone was added. The medium was extracted 1 h later with 3-mL of ethyl acetate, and the remaining lactone amount was checked by GC analysis using dodecane as internal standard.

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Registry No. (±)-1, 83019-13-0; (*S*)-2, 59812-97-4.

Palladium-Catalyzed Reduction of Aryl Sulfonates. Reduction versus Hydrolysis and Selectivity Control

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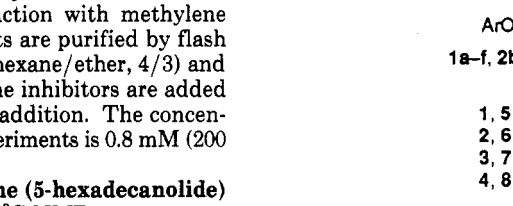
Introduction

Deoxygenation of phenols appears to be an important tool in the field of organic synthesis;[1] palladium-catalyzed reduction of perfluoroalkane sulfonates has arisen in the last few years as an important method with mild reaction conditions and concomitant high chemoselectivity.[2] However, the synthesis of perfluoroalkane sulfonates from the corresponding phenols can sometimes be a major problem[3] in terms of selectivity, stability, and cost. In spite of these drawbacks, to the best of our knowledge, no effort has been carried out to extend the scope of this and related reactions to the more accessible and stable mesylates, tosylates, etc.[4] In this paper we report our results on the palladium-catalyzed reduction of sulfonates **1a–f**, **2b**, **3b**, and **4a–f** to the corresponding arenes **5–8** (Scheme I).[5] We have focused our attention on the study of effects of solvent, reaction conditions, and, mostly, the nature of palladium ligands on the course of reaction.

Scheme I



Results and Discussion

Palladium-catalyzed reductions were performed with a catalyst, generated "in situ", from $Pd(AcO)_2$ and the appropriate ligand. Among the several hydride sources reported in the literature,[6] triethylammonium formate was chosen because of its compatibility with all of our substrates.

Reduction of 1-naphthyl triflate **1a** was reported by Wulff and co-workers to proceed in high yield at 60 °C by using $Pd(PPh_3)_4$ (2 mol %) as catalyst and DMF as solvent.[2c] Under the same experimental conditions, we found that 1-naphthyl sulfonates **1b–f** failed to react; even at 90 °C only a very small amount of naphthalene **5** was formed after 48 h. Concomitant decomposition of the catalyst was observed, suggesting that oxidative addition was too slow. The substitution of PPh_3, with the more electron donating PCH_3Ph_2 and $P(CH_3)_2Ph$ ligands,[7] which in principle should give rise to faster oxidative addition, led only to trace amounts of naphthalene due to complete decomposition of formate.[8] In searching for a more efficient system, we used a 1,3-bis(diphenylphosphino)propane (DPPP) containing catalyst that is very active in alkoxycarbonylation reactions.[9] This complex proved to be a better catalyst for triflate reduction than the one based on PPh_3 (Table I, entries 1–3); its use actually allowed us to carry out reduction of sulfonates **1b–f** in high yields provided that the temperature was 90 °C (entries 4–8). The nature of substituents on the aryl sulfonate moiety affects the reduction, the order of reactivity being *p*-F > H ≫ *p*-Me > *p*-OMe; mesylate **1f** turned out to be as reactive as *p*-methoxybenzenesulfonate **1e**. Substrates **2b** and **3b**, bearing potentially reducible groups such as nitrile and acetyl on the phenyl ring, were completely converted to benzonitrile **6** and acetophenone **7**, respectively (entries

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(5) Sulfonate derivatives **4a–f** of 1-hydroxy-9,10-anthraquinone (**9**) are useful models for determining potential applications of palladium catalysis in the field of anthracyclines, an important class of drugs in anticancer therapy. Arcamone, F. *Doxorubicin Anticancer Antibiotics*; Academic Press: New York, 1981. Arcamone, F. In *Topics in Antibiotic Chemistry*; Sammes, P. G., Ed.; Wiley: New York, 1978; Vol. 2, pp 89–229. Remers, W. A. *The Chemistry of Antitumor Antibiotics*; Wiley Interscience: New York, 1979; Vol. 2, pp 89–229.

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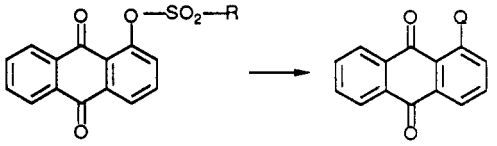
Table I. Palladium-Catalyzed Reduction of Sulfonates 1a–f, 2b, and 3b[a]

entry	substrate	ligand (L/Pd[b])	T, °C	t, h	conversion,[c] %	product (yield,[d] %)
1	**1a**	Ph_3P (4)	40	5	100	**5** (90)
2	**1a**	Ph_3P (4)	18	24	42	**5** (32)
3	**1a**	DPPP (1.1)	18	0.8	100	**5** (92)
4	**1b**	DPPP (1.1)	90	1.5	100	**5** (95)
5	**1c**	DPPP (1.1)	90	2.5	100	**5** (90)
6	**1d**	DPPP (1.1)	90	24	100	**5** (93)
7	**1e**	DPPP (1.1)	90	45	100	**5** (90)
8	**1f**	DPPP (1.1)	90	48	100	**5** (85)
9	**2b**	DPPP (1.1)	90	5	100	**6** (88[e])
10	**3b**	DPPP (1.1)	90	3.5	100	**7** (93[e])

[a] All reductions were run under an argon atmosphere, with 4 equiv of triethylammonium formate and 5 mol % of $Pd(AcO)_2$ in DMF. [b] Molar ratio between ligand and $Pd(AcO)_2$. [c] Determined by GLC. [d] Isolated yield. [e] GLC yield (butyrophenone standard).

Table II. Solvent Effect on Reduction of 4a and 4b[a]



4a, b **8**, Q = H; **9**, Q = OH

entry	substrate	solvent	T, °C	t, h	conversion, %	8/9[c]
1[d]	**4a**	DMF	40	1.8	100	100/0
2	**4b**	DMF	40	20	100	8/92
3	**4b**	dioxane	40	52	100	35/65
4	**4b**	toluene	40	48	72	45/55

[a] Reactions were run under an argon atmosphere with 4 equiv. of triethylammonium formate, 10 mol % of $Pd(AcO)_2$, and 40 mol % of PPh_3; 9,10-anthraquinone (**8**) and 1-hydroxy-9,10-anthraquinone (**9**) are the only products present at the end of the reactions. [b] Determined by HPLC. [c] Molar ratio determined by GLC. [d] With 5 mol % of $Pd(AcO)_2$ and 20 mol % of PPh_3.

9 and 10). These results show chemoselectivity of the method and the synthetic usefulness of arenesulfonates.

Taking advantage of these results, we undertook a comparative study of the reduction of 1-hydroxy-9,10-anthraquinone derivatives triflate **4a** and 4-fluorobenzenesulfonate **4b**. The latter was chosen because the 4-fluorobenzenesulfonyl derivative was the most reactive among sulfonates **1b–f**. Due to the presence of the quinone system, these substrates could be expected to be more activate than the corresponding naphthyl derivatives toward oxidative addition. In fact triflate **4a**, with PPh_3 as the ligand on palladium, was reduced faster than 1-naphthyl triflate **1a** (cf. Table I, entry 1, and Table II, entry 1). The reaction, carried out at 90 °C with the same catalyst, of 4-fluorobenzenesulfonate **4b** afforded only a small amount of 9,10-anthraquinone **8**; 1-hydroxy-9,10-anthraquinone **9** was the major reaction product (Table II, entry 2). A solvent effect on the reduction/hydrolysis ratio was observed, with the amount of reduction product increasing in the order DMF, dioxane, and toluene (entries 2–4). Moreover, in toluene the conversion was incomplete because of decomposition of the catalytic system. The hydrolysis product **9** was not observed following heating of **4b** in DMF in the absence of any metal catalyst or with acetate in place of formate, where palladium is present only as Pd^{II} species. These blank experiments suggest that cleavage of the S–O bond[10] is assisted in some way by the presence of the Pd^0/formate system.[11]

To prevent the cleavage of the S–O bond we studied in some detail the influence of palladium ligands on the reaction course, in both dioxane and DMF, using **4b** as substrate. The results obtained with monodentate phosphines (Table III) show that the selectivity of the reaction is greatly affected by the ligand. In particular, the use of phosphines having the same cone angle (entries 1–7) allows one to separate the electronic effect from the steric one; the amount of reduction product **8** increases with donor properties of the ligand and the best results were obtained with P(*p*-tolyl)$_3$.

Tri-*o*-tolylphosphine was less effective than the para isomer in spite of a comparable basicity, probably because of the larger cone angle of the former (entries 8, 9). These results suggest that a high basicity of the ligand and a cone angle around 145° or less should be the right combination to prevent the formation of **9**. This hypothesis is compatible with the last two entries reported in Table III, where PCH_3Ph_2 (entry 10) and $P(CH_3)_2Ph$ (entry 11) give the reduction product **8** exclusively.

In Table IV are reported the results obtained with chelating biphosphines. For the series 1,1-bis(diphenylphosphino)methane (DPPM),[12] 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP), and 1,4-bis(diphenylphosphino)butane (DPPB), which have similar electronic character, the amount of 9,10-anthraquinone **8** increases with the length of the chain that links the phosphorus atoms[13] (entries

(10) Hydrolysis via S–O cleavage is widely described for nucleophilic attack on aryl sulfonates: (a) Subramanian, L. R.; Hanack, M.; Chang, L. W. K.; Imhoff, M. A.; Schleyer, P. v. R.; Effenberger, F.; Kurtz, W.; Stang, P. J.; Dueber, T. E. *J. Org. Chem.* **1976**, *41*, 4099. (b) McMurry, J. E.; Mohanraj, S. *Tetrahedron Lett.* **1983**, *24*, 2723. (c) D'Rozario, P.; Smyth, R. L.; Williams, A. *J. Am. Chem. Soc.* **1984**, *106*, 5027. (d) Netscher, T.; Scweisinger, R.; Trupp, B.; Prinzbach, H. *Tetrahedron Lett.* **1987**, *28*, 2115.

(11) Stille and Echavarren observed S–O bond cleavage in coupling reactions of aryl triflates with organostannanes using $Pd(PPh_3)_4$ or $Cl_2Pd(PPh_3)_2$ as the catalyst in DMF: Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478.

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Table III. Reduction of 4b with Monodentate Phosphines as Ligand[a]

			Solvent			
			DMF		dioxane	
entry	ligand (L/Pd[b])	cone angle θ,[c] deg	8/9[d]	t, h	8/9[d]	t, h
1	P(*p*-Cl-Ph)$_3$ (2)	145	0/100	1	2/98	24[e]
2	P(*p*-Cl-Ph)$_3$ (3)	145	0/100	4	8/92	44
3	PPh_3 (2)	145	1/99	1.5	8/92	23
4	PPh_3 (3)	145	3/97	9	21/79	35
5	PPh_3 (4)	145	9/91	20	35/65	52
6	P(*p*-tolyl)$_3$ (2)	145	18/82	1.5	80/20	4.5
7	P(*p*-tolyl)$_3$ (3)	145	75/25	3.5	97/3	5
8	P(*o*-tolyl)$_3$ (2)	194	1/99	1	5/95	4
9	P(*o*-tolyl)$_3$ (3)	194	4/96	1.5	10/90	9
10[f]	PCH_3Ph_2 (2)	136	100/0	0.5	100/0	0.5
11[f]	$P(CH_3)_2Ph$ (2)	122	100/0	0.5	100/0	0.5

[a] Reactions were carried out under an argon atmosphere with 4 equiv of triethylammonium formate and 10 mol % of $Pd(AcO)_2$ at 90 °C until conversion was complete; 9,10-anthraquinone (8) and 1-hydroxy-9,10-anthraquinone (9) are the only products present of these reactions. [b] Molar ratio between ligand and $Pd(AcO)_2$. [c] See ref 7. [d] Molar ratio, determined by GLC. [e] Conversion, determined by HPLC, was 75%. [f] Reduction took place at 60 °C.

Table IV. Reduction of 4b with Bidentate Phopshines as Ligand[a]

			solvent			
			DMF		dioxane	
entry	ligand	P–Pd–P angle, deg	8/9[e]	*t*, h	8/9[e]	*t*, h
1	DPPM	≈73[c]	0/100	0.5	0/100	5
2	DPPE	≈85[c]	68/32	0.5	95/5	4
3	DPPP	≈90[c]	98/2	0.35	100/0	0.5
4	DPPB	≥90[d]	96/4	0.35	100/0	1
5	DPPF	≈99[e]	95/5	0.4	100/0	0.4
6	DpTPE	-	55/45	1[f]	85/15	1

[a] Reactions were carried out under an argon atmosphere at 90 °C with 4 equiv of triethylammonium formate, 5 mol % of $Pd(AcO)_2$ and 5.5 mol % of the ligand. [b] Determined by GLC. [c] See ref 13b. [d] See ref 13a. [e] See ref 14. [f] 8 equiv of triethylammonium formate was necessary to achieve a complete conversion.

Table V. Reduction of Sulfonates 4b–f[a]

entry	substrate	*t*, h	product (yield,[b] %)
1	**4b**	0.5	8 (95)
2	**4c**	0.5	8 (92)
3	**4d**	0.5	8 (90)
4	**4e**	0.5	8 (87)
5	**4f**	0.8	8 (89)

[a] All reactions were carried out under an argon atmosphere at 90 °C and with 4 equivs of triethylammonium formate, 5 mol % of $Pd(AcO)_2$, and 5.5 mol % of DPPP in dioxane. [b] Isolated yields.

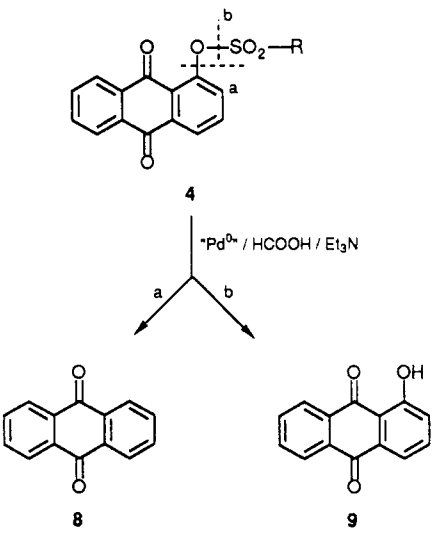
1–4). The same selectivity observed with DPPP and DPPB was achieved with the bulkier 1,1′-bis(diphenylphosphino)ferrocene (DPPF)[14] (entry 5). The presence of electron-releasing groups on phenyl rings, such as in 1,2-bis(di-*p*-tolylphosphino)ethane (DpTPE) (entry 6) does not improve selectivity; thus, electronic effects seem to play a minor role in comparison to steric ones.

On the basis of these results we have extended the reaction to sulfonates **4c–f** (Table V). By working in dioxane and using DPPP as the ligand for palladium, it was possible to obtain the reduction product with complete selectivity in all cases. The effects that favor reduction (scission a, Scheme II) over hydrolysis (scission b, Scheme II) are not easily related to a mechanistic scheme. On the other hand, a competition between oxidative addition on Pd^0 of either C–O or S–O bond cannot be ruled out; further work is necessary in order to confirm this hypothesis.

Conclusion

The reduction of aryl alkane and arene sulfonates using the Pd^0/triethylammonium formate system is subject to subtle influences of substrates, leaving groups, and ligands. With aromatic derivatives such as naphthyl and phenyl, only hydrogenolysis occurs, and these sulfonates prove to be as effective as perfluoroalkanesulfonates. Unlike triflates, quinone alkane- and arenesulfonates exhibit both reduction and hydrolysis of the sulfonate group. An appropriate choice of ligands and solvents prevents hydrolysis and provides completely selective hydrogenolysis.

Scheme II



Experimental Section

Melting points were determined on a Kofler appratus and are uncorrected. Bulb-to-bulb distillations were conducted with a Büchi Kugelrohr apparatus. ^1H NMR spectra were recorded on a BRUKER AM 200 in $CDCl_3$ with tetramethylsilane as an in-

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ternal standard. All IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. The GLC analyses were carried out on a Carlo Erba HRGC 5300 chromatograph equipped with a Nordibond OV-1 column (25 m length, i.d. 0.32 mm) and a flame ionization detector. High-performance liquid chromatography (HPLC) was performed with a SHIMADZU LC-8 apparatus on a LiChrosorb RP-18 (7 μm) column using $CH_3CN/CH_3OH/H_2O$ (52/15/33 by volume) as eluent. Thin-layer chromatography (TLC) was performed on E. Merck precoated silica gel 60 F-254 plates (0.25 mm). Flash chromatography was carried out on Merck silica gel 60 (230-400 mesh), as described by Still.[15] Elemental analyses were performed by the microanalytical laboratory of the Instituto G. Donegani.

1,4-Dioxane and toluene were distilled from sodium and stored over activated 4A sieves. DMF was distilled from calcium hydride and stored over activated 4A sieves.

Aryl Triflates. Compounds **1a** and **4a** were prepared according to literature method.[11]

1-(((Trifluoromethyl)sulfonyl)oxy)naphthalene (1a) (84%): colorless oil; bp (bulb-to-bulb) 108-110 °C (0.4 mmHg); IR (neat) 1600, 1420, 1210 cm^{-1}; ^1H NMR δ 8.10 (br d, J = 8.3 Hz, 1 H), 7.94-7.8 (m, 2 H), 7.68-7.55 (m, 2 H). Anal. Calcd for $C_{11}H_7F_3O_3S$: C, 47.83; H, 2.55. Found: C, 48.07; H, 2.58.

1-(((Trifluoromethyl)sulfonyl)oxy)-9,10-anthraquinone (4a) (88%): yellow solid; mp 151-152 °C; IR (Nujol) 1670, 1580, 1420 cm^{-1}; ^1H NMR δ 8.45 (dd, J = 7.8, 1.2 Hz, 1 H), 8.39-8.20 (m, 2 H), 7.97-7.75 (m, 3 H), 7.63 (d, J = 8.2 Hz, 1 H). Anal. Calcd for $C_{15}H_7F_3O_5S$: C, 50.57; H, 1.98. Found: C, 50.45; H, 2.09.

Aryl Alkane- and Arenesulfonates. The following compounds were prepared in an analogous manner to aryl triflates, substituting trifluoromethanesulfonic anhydride with the corresponding sulfonyl chloride.

1-(((4-Fluorophenyl)sulfonyl)oxy)naphthalene (1b) (92%): white solid; mp 86-88 °C; IR (Nujol) 1450, 1370, 1180 cm^{-1}; ^1H NMR δ 8.10-7.65 (m, 5 H), 7.60-7.31 (m, 3 H), 7.24 (br d, J = 7.6 Hz, 1 H), 7.14 (br t, J = 7.9 Hz). Anal. Calcd for $C_{16}H_{11}FO_3S$: C, 63.57; H, 3.67. Found: C, 63.31; H, 3.64.

1-((Phenylsulfonyl)oxy)naphthalene (1c) (94%): white solid; mp 106-108 °C; IR (Nujol) 1440, 1365, 1180 cm^{-1}; ^1H NMR δ 8.1-7.1 (m, 11 H). Anal. Calcd for $C_{16}H_{12}O_3S$: C, 67.59; H, 4.25. Found: C, 67.50; H, 4.41.

1-(((4-Methylphenyl)sulfonyl)oxy)naphthalene (1d) (90%): white solid; mp 90-92 °C; IR (Nujol) 1450, 1360, 1175 cm^{-1}; ^1H NMR δ 8.35-8.06 (m, 3 H), 7.92-7.58 (m, 5 H), 7.50 (dd, J = 8.1, 1.3 Hz, 1 H), 7.31 (d, J = 8.5 Hz, 2 H), 2.38 (s, 3 H). Anal. Calcd for $C_{17}H_{14}O_3S$: C, 68.44; H, 4.73. Found: C, 68.12; H, 4.42.

1-(((4-Methoxyphenyl)sulfonyl)oxy)naphthalene (1e) (95%): white solid; mp 101-103 °C; IR (Nujol) 1450, 1370, 1180 cm^{-1}; ^1H NMR δ 8.02-7.60 (m, 5 H), 7.53-7.28 (m, 3 H), 7.21 (br d, J = 8.2 Hz, 1 H), 6.90 (br d, J = 9.0 Hz, 2 H), 3.82 (s, 3 H). Anal. Calcd for $C_{17}H_{14}O_4S$: C, 64.95; H, 4.49. Found: C, 64.79; H, 4.41.

1-((Methylsulfonyl)oxy)naphthalene (1f) (85%): colorless oil; bp (bulb-to-bulb) 183-185 °C (0.4 mmHg); IR (neat) 1590, 1370, 1180 cm^{-1}; ^1H NMR δ 8.16 (dd, J = 9.0, 1.0 Hz, 1 H), 7.92-7.69 (m, 2 H), 7.66-7.22 (m, 4 H), 3.16 (s, 3 H). Anal. Calcd for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.53. Found: C, 59.61; H, 4.65.

4-(((4-Fluorophenyl)sulfonyl)oxy)benzonitrile (2b) (89%): white solid; mp 102-104 °C; IR (Nujol) 2230, 1580, 1485, 1370, 1160 cm^{-1}; ^1H NMR δ 7.96-7.75 (m, 2 H), 7.63 (td, J = 8.8, 2 Hz, 2 H), 7.23 (tt, J = 8.2, 1.9 Hz, 2 H), 7.13 (td, J = 8.7, 1.9 Hz, 2 H). Anal. Calcd for $C_{13}H_8FNO_3S$: C, 56.31; H, 2.91. Found: C, 56.46; H, 3.04.

4-(((4-Fluorophenyl)sulfonyl)oxy)-1-acetophenone (3b) (90%): white solid; mp 75-77 °C; IR (Nujol) 1670, 1370, 1150 cm^{-1}; ^1H NMR δ 8.05-7.70 (m, 4 H), 7.36-7.00 (m, 4 H), 2.59 (s, 3 H). Anal. Calcd for $C_{14}H_{11}FO_4S$: C, 57.14; H, 3.77. Found: C, 57.32, H, 3.70.

1-(((4-Fluorophenyl)sulfonyl)oxy)-9,10-anthraquinone (4b) (90%): yellow solid; mp 158-160 °C; IR (Nujol) 1665, 1580, 1370 cm^{-1}; ^1H NMR δ 8.34 (dd, J = 7.8, 1.3 Hz, 1 H), 8.30-8.00 (m, 4 H), 7.89-7.68 (m, 3 H), 7.6 (dd, J = 8.2, 1.3 Hz, 1 H), 7.35-7.15 (m, 2 H). Anal. Calcd for $C_{20}H_{11}FO_5S$: C, 62.82; H, 2.90. Found: C, 62.69; H, 2.78.

1-((Phenylsulfonyl)oxy)-9,10-anthraquinone (4c) (95%): yellow solid; mp 144-146 °C; IR (Nujol) 1665, 1570, 1350 cm^{-1}; ^1H NMR δ 8.32 (dd, J = 7.8, 1.2 Hz, 1 H), 8.27-8.13 (m, 2 H), 8.08-7.98 (m, 2 H), 7.86-7.45 (m, 7 H). Anal. Calcd for $C_{20}H_{12}O_5S$: C, 65.93; H, 3.32. Found: C, 65.99; H, 3.36.

1-(((4-Methylphenyl)sulfonyl)oxy)-9,10-anthraquinone (4d) (94%): yellow solid; mp 156-158 °C; IR (Nujol) 1670, 1580, 1370 cm^{-1}; ^1H NMR δ 8.31 (dd, J = 7.8, 1.2 Hz, 1 H), 8.28-8.10 (m, 2 H), 7.95-7.60 (m, 5 H), 7.53 (dd, J = 8.2, 1.2 Hz, 1 H), 7.40-7.24 (m, 2 H), 2.40 (s, 3 H). Anal. Calcd for $C_{21}H_{14}O_5S$: C, 66.66; H, 3.73. Found: C, 66.82; H, 3.81.

1-(((4-Methoxyphenyl)sulfonyl)oxy)-9,10-anthraquinone (4e) (91%): yellow solid; mp 154-156 °C; IR (Nujol) 1670, 1585, 1370 cm^{-1}; ^1H NMR δ 8.3 (dd, J = 7.8, 1.3 Hz, 1 H), 8.27-8.10 (m, 2 H), 8.00-7.85 (m, 2 H), 7.85-7.66 (m, 3 H), 7.55 (dd, J = 8.2, 1.3 Hz, 1 H), 7.02-6.85 (m, 2 H), 3.8 (s, 3 H). Anal. Calcd for $C_{21}H_{14}O_6S$: C, 63.95; H, 3.58. Found: C, 63.79; H, 3.45.

1-((Methylsulfonyl)oxy)-9,10-anthraquinone (4f) (95%): yellow solid; mp 186-188 °C; IR (Nujol) 1660, 1580, 1360 cm^{-1}; ^1H NMR δ 8.40-8.15 (m, 3 H), 7.90-7.65 (m, 4 H), 3.50 (s, 3 H). Anal. Calcd for $C_{15}H_{10}O_5S$: C, 59.90; H, 3.33. Found: C, 60.15; H, 3.44.

Palladium-Catalyzed Reduction of Aryl Sulfonates. General Procedure (Table I, Entry 1). To a stirred solution of **1a** (1 g, 3.62 mmol) in DMF (25 mL) under an argon atmosphere at room temperature were sequentially added Et_3N (1.46 g, 2.01 mL, 14.48 mmol), formic acid (0.67 g, 55 mL, 14.48 mmol), PPh_3 (0.19 g, 0.724 mmol), and $Pd(AcO)_2$ (0.041 g, 0.181 mol). The reaction temperature was raised to 40 °C. After 5 h the reaction mixture was diluted with methylene chloride (100 mL) and brought to pH 7.0 with sequential washes of 5% aqueous hydrochloric acid (2 × 30 mL) and water, dried (anhydrous Na_2SO_4), filtered, and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/ethyl acetate, 95/5 by volume), affording naphthalene **5** (0.417 g, 90%). This procedure was used in all of the reactions described in Tables I-V. Anthraquinone **8** in Table V was purified by flash chromatography (hexane/ethyl acetate, 8/2 by volume).

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Registry No. **1a**, 99747-74-7; **1b**, 123412-32-8; **1c**, 15161-04-3; **1d**, 68211-49-4; **1e**, 123412-33-9; **1f**, 38262-42-9; **2b**, 123412-34-0; **3b**, 123412-35-1; **4a**, 123412-36-2; **4b**, 123412-37-3; **4c**, 123412-38-4; **4d**, 107035-89-2; **4e**, 123412-39-5; **4f**, 123412-40-8; **5**, 91-20-3; **6**, 100-47-0; **7**, 98-86-2; **8**, 84-65-1; **9**, 129-43-1; DPPP, 6737-42-4; DPPM, 2071-20-7; DPPE, 1663-45-2; DPPB, 7688-25-7; DPPF, 12150-46-8; DpTPE, 70320-30-8; $Pd(AcO)_2$, 3375-31-3; $P(p\text{-}ClPh)_3$, 1159-54-2; $P(p\text{-tolyl})_3$, 1038-95-5; PCH_3Ph_2, 1486-28-8; $P(CH_3)_2Ph$, 672-66-2.

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Decarboxylation of Sodium 1-Nitrocyclopropanecarboxylates. A Facile Synthesis of Nitrocyclopropanes

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Nitroacetic acid is stable in acidic aqueous solution, and its dianion is stable in basic solution, yet in neutral aqueous solution the monoanion (**1**) decarboxylates within seconds to nitronate (**2**).[1] Other acyclic 1-nitrocarboxylic acids behave similarly.[2] However, 1-nitrocyclopropane-

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