mA (current density: 1.6 A/dm^2). After 8.0 F/mol of electricity was passed, the reaction mixture was poured into 100 mL of a saturated sodium chloride solution and extracted with three 50-mL portions of ether. The combined ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated to give an oily material, which was then fractionally distilled to form almost pure 2-methyl-4-methoxyphenol (8) in 42% yield; mp 71–72 °C [lit.[28] mp 71–72 °C].

Registry No. **1a**, 140-39-6; **1b**, 106-42-3; **1c**, 99-87-6; **1d**, 98-51-1; **1e**, 106-43-4; **1f**, 104-93-8; **1g**, 3395-83-3; **2a**, 878-00-2; **2b**, 104-87-0; **2c**, 122-03-2; **2d**, 939-97-9; **2e**, 104-88-1; **2f**, 123-11-5; **2g**, 623-27-8; **3a**, 38177-36-5; **3e**, 1195-44-4; **3g**, 93943-06-7; **4c**, 20185-55-1; **4d**, 26537-19-9; **4f**, 121-98-2; **4g**, 1571-08-0; **5**, 1730-48-9; **6**, 1078-19-9; **7**, 533-18-6; **8**, 5307-05-1.

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Electrochemical Oxidative Dehydrodimerization of Naphthylamines. An Efficient Synthesis of 8,8′-Dianilino-5,5′-binaphthalene-1,1′-disulfonate

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Fluorescent probes have been widely applied in the investigation of the structure and behavior of proteins. One probe that has found extensive use is 8-anilino-1-naphthalenesulfonate (**1**).[1] A related probe, 8,8′-dianilino-5,5′-binaphthalene-1,1′-disulfonate (**2**), is potentially more useful than **1** because it binds more tightly to proteins[2] and has a larger fluorescence quantum yield.[3] However, the current syntheses of **2**,[3–5] by dehydrodimerization of **1** using sodium nitrite, are small-scale, low yield reactions involving tedious purifications.[6]

A number of methods for the synthesis of biaryls have been reported.[7] Many of these, such as the Gomberg reaction[8] and the Ullman reaction,[9] have the disadvantage that the aryl group must have a substituent that is lost during the coupling process. Biaryls can also be prepared by oxidative dehydrodimerization with various metal salts.[7] For example, thallium trifluoroacetate has recently been shown to be an excellent reagent for such transformations of electron-rich aromatic substrates.[7] In addition, electrochemical oxidation of electron-rich aromatic substrates often results in the formation of biaryls.[10] However, the potential of this method has not been extensively developed.

Chart I

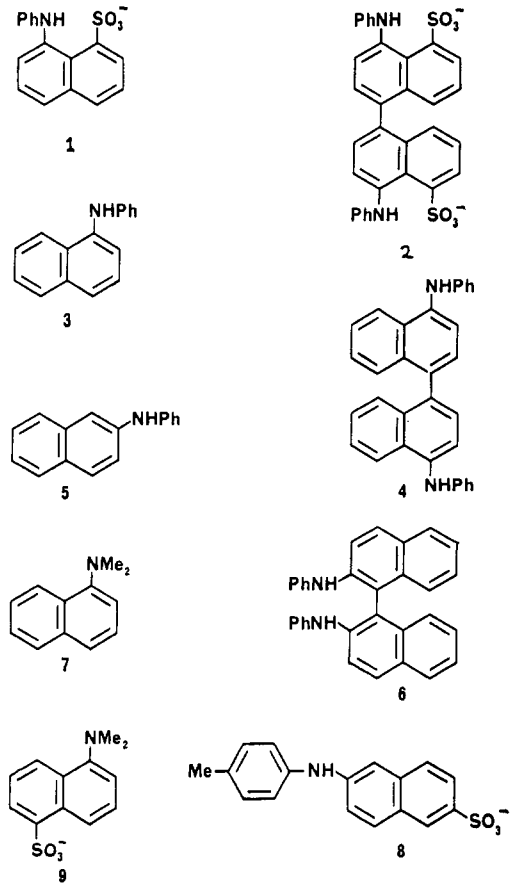

Table I. Yields and Conversions for Various Oxidants Used for the Conversion of 1 to 2

oxidant	yield of 2,[a] %	convn of 1,[b] %
$K_2Cr_2O_7$	1	81
CrO_3	4	46
CoF_3	11	73
$Pb(OAc)_4$	14	69
$NaNO_2$	18	98
$KMnO_4$	20	20
$Tl(C_2F_3O_2)_2$	31	88
anode	50 (30)[c]	92

[a] Yields are calculated on the basis of reacted 1. [b] Amount of 1 that has reacted. [c] Isolated yield.

We report here a convenient synthesis of **2** by electrochemical oxidation of **1**, a comparison of the electrochemical reaction with reactions employing some selected chemical oxidants, and a brief investigation of the scope of the electrochemical reaction with some other naphthylamines.

A solution of **1** in aqueous sodium perchlorate was electrolyzed by using a carbon cloth anode and a copper cathode. Analysis by HPLC showed the formation of a single product. After most of the starting material had reacted, the product was isolated in 30% yield by column

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chromatography. This product was identified as **2** by comparison of its HPLC retention time and its IR, UV–vis, and fluorescence spectra with those of an authentic sample.[6] A similar electrolysis, analyzed by HPLC, showed a 50% yield of **2** at a 92% conversion of **1**.[11] Although the yield was higher, approaching quantitative, at lower conversions of **1**, isolation of the product was easier after most of the starting material had reacted.

The use of a number of chemical oxidants for the conversion of **1** to **2** was also explored (Table I). The best literature method,[5] employing sodium nitrite as the oxidant, gave an 18% yield of **2** by HPLC.[11] The best chemical oxidation method was the one recently developed by Taylor and co-workers,[7] using thallium trifluoroacetate, which resulted in a 31% yield of **2**. All of the chemical oxidations gave lower yields than the electrochemical oxidation.

The electrochemical oxidation of some additional naphthylamines was investigated in order to explore the generality of the reaction. Electrolysis of a solution of *N*-phenyl-1-naphthylamine, (**3**), in acetonitrile with sodium perchlorate as the electrolyte, gave a 35% yield of **4**[11] at a 95% conversion of **3**. After isolation by chromatography, the product was assigned structure **4** on the basis of its high-resolution mass spectrum, which showed it to be a dimer formed from **3** by the loss of two hydrogens, its ^{13}C NMR spectrum, which showed 14 carbons, indicating that the product was a symmetrical dimer, and by comparison of its melting point with the reported value.[12]

A similar electrolysis of *N*-phenyl-2-naphthylamine (**5**) gave a 28% yield of **6**[11] at a 71% conversion of **5**. The product was isolated by chromatography and identified by its high-resolution mass spectrum, which showed it to be a dimer formed from **5** with the loss of two hydrogens, by its ^{13}C NMR spectrum, which showed 14 carbons, indicating a symmetrical dimer, and by comparison of its melting point with the reported value.[13]

The electrochemical oxidation of three additional naphthylamine derivatives was also investigated. HPLC analysis of a solution of **7**, which had been electrolyzed in acetonitrile containing sodium perchlorate, showed the presence of six products. Similarly, electrolysis of **8** in aqueous sodium perchlorate gave five products. These products were not identified. Finally, electrolysis of **9** in aqueous sodium perchlorate solution showed that the starting material had reacted but no products were observed by HPLC.

From the above results it can be seen that electrochemical oxidation can be a useful method for the synthesis of dimeric naphthylamines. In the case of **1**, **3**, and **5**, the reaction is quite clean and proceeds in reasonable yield. The position of coupling is probably controlled by a combination of steric and electronic effects. The fact that no coupling at nitrogen is observed with **1**, **3**, or **5** can be attributed to a steric effect[10e,14] of the phenyl group since anodic oxidation of 1-naphthylamine has been shown to result in some reaction at nitrogen.[15] In addition, the formation of only **6** from **5** is different from the chemical oxidation of **5** with potassium permanganate which resulted in the formation of both **6** and an N-coupled product.[13] The formation of multiple products from **7** and **8** may be due to a less favorable coupling position due to steric and electronic effects or to reaction at the alkyl side chain.[10f]

Experimental Section

Melting points were obtained on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were obtained on a Perkin-Elmer 283 B or a Digilab FTS 20 B spectrometer. Nuclear magnetic resonance spectra were obtained on a Varian EM 360 or a Varian FT 80 spectrometer. Ultraviolet–visible spectra were obtained on a Beckman Acta V spectrometer. Fluorescence spectra were obtained on a Perkin-Elmer MPF-36 spectrometer. High-resolution mass spectra were obtained from the Midwest Center for Mass Spectrometry, Department of Chemistry, University of Nebraska—Lincoln, Lincoln, NE 68588. HPLC analyses were obtained with a Perkin-Elmer Series 2 liquid chromatograph, a Regis reverse-phase C-18 column (300 mm × 4.6 mm), a Perkin-Elmer LC 55 spectrometer as the detector, and a Linear Instruments recorder. Electrochemical reactions employed a Hewlett-Packard Harrison 6443 B D.C. power supply.

Electrochemical Oxidation of Ammonium 8-Anilino-1-naphthalenesulfonate (1). An electrochemical cell, consisting of a beaker, a carbon cloth anode,[16] and a platinum cathode, was charged with 2.14 g (6.77 mmol) of **1** and 100 mL of 0.1 M aqueous $NaClO_4$ solution. The solution was stirred and the applied voltage was increased until current began to flow. The reaction was monitored by HPLC, using a mixture of 99% methanol and 1% water containing 7 g/L of cetyltrimethylammonium bromide as the eluent at a flow rate of 1 mL/min and a detector wavelength of 385 nm. After ca. 2 h the amount of product had reached a maximum. After the solvent was removed, the residue was dissolved in a minimum amount of methanol and chromatographed on a short column of neutral alumina by using methanol as the eluent. The solvent was removed in vacuo and the residue was dissolved in a minimum amount of water. Excess barium acetate was added to precipitate **2** as the barium salt. An excess of K_2SO_4 was added and the precipitated $BaSO_4$ was removed by filtration. The solution was concentrated and the potassium salt of **2** which crystallized was collected. HPLC analysis showed the product to be contaminated with ca. 15% of **1**. Further column chromatography, as described above, gave 0.69 g (30%) of pure **2**: ^{13}C NMR (ppm, D_2O) 145.16 (s), 139.94 (s), 139.38 (s), 136.82 (s), 132.31 (d), 130.31 (d), 129.74 (d), 128.81 (d), 125.00 (d), 123.35 (s), 120.84 (d), 118.01 (d). The HPLC retention time and the IR, UV–vis, and fluorescence spectra of **2** were identical with those of an authentic sample[6] with the exception of a small peak in the carbonyl region of the authentic sample which is probably due to an impurity.

HPLC analysis of a similar electrolysis showed a 92% conversion of **1** and a 50% yield of **2**.

Electrochemical Oxidation of *N*-Phenyl-1-naphthylamine (3). A solution of 1.06 g (4.85 mmol) of **3** in 125 mL of 0.2 M $NaClO_4$ in acetonitrile was electrolyzed as described above, using a graphite rod anode and a copper wire cathode. After ca. 1 h of electrolysis, HPLC analysis, using methanol–water (89:11) as the eluent at a flow rate of 1 mL/min and monitored at 338 nm, showed a 95% conversion of **3** and a 35% yield of **4**.

The solvent was removed in vacuo and the residue was dissolved in CH_2Cl_2. This solution was washed with water and the solvent was removed in vacuo. The residue was dissolved in a minimum amount of CCl_4 and chromatographed on silica gel with CCl_4–hexane (1:1) as the eluent. Several recrystallizations from CCl_4–hexane afforded a pure sample of **4**, mp 183–184 °C (lit.[12] mp 189–190 °C); IR (KBr) cm^{-1}, 3400, 3120–3040, 1590, 1500, 1310, 770, 740, 690; UV ($CHCl_3$) λ_{max} 355 nm; ^{13}C NMR (ppm, $CDCl_3$) 144.85, 138.71, 134.29, 133.52, 129.43, 128.33, 127.81, 127.44, 126.13, 125.57, 121.92, 120.73, 117.75, 115.38; high-resolution mass spectrum, calcd for $C_{32}H_{24}N_2$ 436.1941, found 436.1942.

Electrochemical Oxidation of *N*-Phenyl-2-naphthylamine (5). A solution of 0.558 g (2.55 mmol) of **5** and 1 mL of 0.1 M aqueous ferric nitrate[17] in 125 mL of 0.2 M $NaClO_4$ in acetonitrile

(11) HPLC yields are based on reacted starting material.

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was electrolyzed as described for **3**. After ca. 1 h of electrolysis, HPLC analysis, using methanol–water (92:8) as the eluent at a flow rate of 1 mL/min and monitored at 312 nm, showed a 71% conversion of **5** and a 28% yield of **6**.

The solvent was removed in vacuo. The residue was dissolved in a minimum amount of $CHCl_3$ and chromatographed on silica gel using hexane–CCl_4 (60:40) as the eluent. Several recrystallizations from CCl_4–hexane gave a pure sample of **6**: mp 169–170 °C (lit.[13] mp 167–168 °C); IR (KBr) cm^{-1}, 3390, 3140, 1590, 1495, 1410, 1290, 810, 750, 690; UV ($CHCl_3$) λ_{max} 308 nm; ^{13}C NMR (ppm, $CDCl_3$) 142.69, 140.58, 134.09, 129.56, 129.42, 129.26, 128.26, 127.07, 124.53, 123.50, 122.25, 120.14, 117.96, 116.59; high-resolution mass spectrum, calcd for $C_{32}H_{24}N_2$ 436.1941, found 436.1962.

Electrochemical Oxidation of *N,N*-Dimethyl-1-naphthylamine (7). A solution of 27.3 g (0.159 mol) of **7** in 500 mL of 0.2 M $NaClO_4$ in acetonitrile was electrolyzed, using a carbon cloth anode and a platinum cathode. After 1 h of electrolysis, HPLC analysis, with methanol as the eluent, monitored at 320 nm, showed the formation of six products.

Electrochemical Oxidation of 6-*p*-Toluidino-2-naphthalenesulfonate (8). A solution of 0.903 g (2.73 mmol) of the ammonium salt of **8** in 0.1 M aqueous $NaClO_4$ solution was electrolyzed in a double cell by using a graphite rod anode and a copper cathode. After electrolysis for 1 h, HPLC analysis, using 70% methanol, 30% water containing 7 g/L of cetyltrimethylammonium bromide as the eluent, monitored at 390 nm, showed the presence of five products.

Electrochemical Oxidation of *N,N*-Dimethyl-5-aminonaphthalene-1-sulfonic Acid (9). A solution of 0.343 g (1.37 mmol) of **9** in 100 mL of 0.2 **M** aqueous $NaClO_4$ solution was electrolyzed by using a carbon cloth anode and a copper cathode. Periodic analysis by HPLC, using various percentages of methanol in water containing 7 g/L of cetyltrimethylammonium bromide as the eluent, monitored at 320 nm showed a decrease in the peak due to **9** without the appearance of a new peak.

Chemical Oxidations of Ammonium 8-Anilino-1-naphthalenesulfonate (1). With Sodium Nitrite. This reaction was patterned after the procedure of Farris et al.[3] A solution of 1.02 g (3.23 mmol) of **1** and 1.6 mL of 0.2 **M** aqueous $NaNO_2$ in 20 mL of glacial acetic acid and 20 mL of concentrated hydrochloric acid was stirred at room temperature for 4 h. After removal of the solvent, the residue was quantitatively dissolved in methanol. Analysis by HPLC showed a 98% conversion of **1** and an 18% yield of **2**.

With Potassium Permanganate. The reaction was patterned after the procedure of Bridger et al.[13] A solution of 1.02 g (3.23 mmol) of **1** in 10 mL of acetone was cooled to 0 °C. To this stirring solution was added, over a 6-h period, a solution of 0.166 g (1.05 mmol) of $KMnO_4$ dissolved in a minimum amount of acetone. After the addition was completed, the solution was allowed to warm to room temperature and an excess of 2-propanol was added to destroy any remaining $KMnO_4$. After removal of the solvent, the residue was dissolved in water. Analysis by HPLC showed a 20% conversion of **1** and a 20% yield of **2**.

With Potassium Dichromate. A solution of 1.00 g (3.16 mmol) of **1** in 10 mL of acetone was cooled to 0 °C and a solution of 0.528 g (1.79 mmol) of $K_2Cr_2O_7$ in a minimum amount of water was added over a 6 h-period. After removal of the solvent, the residue was dissolved in water. Analysis by HPLC showed an 81% conversion of **1** and a 1% yield of **2**.

With Chromium Trioxide. A solution of 0.599 g (1.90 mmol) of **1** and 0.096 g (0.96 mmol) of CrO_3 in 100 mL of DMF was heated to reflux for 4 h. Analysis by HPLC showed a 46% conversion of **1** and a 4% yield of **2**.

With Lead Tetraacetate. The reaction was patterned after the procedure of Taylor et al.[7] To a solution of 0.500 g (1.58 mmol) of **1** in 40 mL of glacial acetic acid was added 2 mL of boron trifluoride diethyl etherate and 0.461 g (1.04 mmol) of lead tetraacetate. The solution was stirred at room temperature for 4 h. After addition of 10 mL of 50% hydrochloric acid and 5 mL of methanol, the solvent was removed. The residue was dissolved in 10 mL of concentrated ammonium hydroxide solution. To this was added 10 mL of methanol and 10 mL of water. The lead dioxide was removed by filtration. Analysis by HPLC showed a 69% conversion of **1** and a 14% yield of **2**.

With Cobalt(III) Fluoride. This reaction was patterned after the procedure of Taylor et al.[7] To a solution of 0.558 g (1.77 mmol) of **1** in 100 mL of Me_2SO was added 0.654 g (5.63 mmol) of CoF_3. The solution was heated to 80 °C for 12 h. The solvent was removed in vacuo and the residue was dissolved in methanol. Analysis by HPLC showed a 73% conversion of **1** and an 11% yield of **2**.

With Thallium Trifluoroacetate. The reaction was patterned after the procedure of Taylor et al.[7] To a refluxing solution of 0.214 g (0.678 mmol) of **1** in 20 mL of glacial acetic acid was added, over a 4-h period, a solution of 0.202 g (0.372 mmol) of thallium trifluoroacetate in 20 mL of glacial acetic acid. Analysis by HPLC showed a 71% conversion of **1** and a 31% yield of **2**.

Acknowledgment. We are grateful to Dr. R. F. Nelson, Gates Rubber Co., for helpful discussions and to Dr. R. D. Barrows, Battelle Northwest, for the ^{13}C NMR spectra.

(17) The yield was very poor if a small amount of aqueous ferric nitrate was not added. Addition of larger amounts did not further increase the yield. We are unsure why the ferric nitrate is needed. It is possible that the iron is acting as an electron-transfer mediator or is acting as a catalyst in a chemical step.

Propadieneselone

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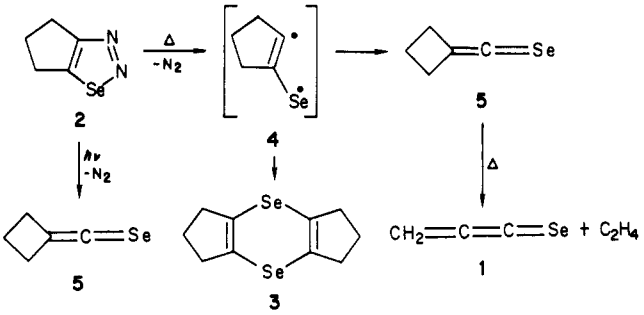
Propadienone and its derivatives have been the subject of recent investigations.[1,2] Nothing is known of the analogous thio- and selenocumulenes. We report the preparation, spectroscopic characterization, and photochemistry of propadieneselone (**1**).



Meier and Voigt[3] showed that cyclopenteno-1,2,3-selenadiazole (**2**) gives dicyclopenteno-1,4-diselenine (**3**) in 27% yield when heated to 140 °C and suggested that **3** is formed by dimerization of diradical **4**. No products derived from loss of selenium were found.

Flash vacuum thermolysis of **2** (500 °C, 10^{-6} torr) with trapping of the products in argon at 12 K gave trimethyleneselenoketene (**5**) in high yield. Intermolecular reactions are excluded under these conditions, and dimer **3** is not formed. Selenoketene **5** was characterized by its infrared spectrum. The intense band at 1746 cm^{-1} is assigned to the C=C=Se stretching mode. This assignment is in good agreement with selenoketene (1695 cm^{-1})[4] and bis(trimethylsilyl)selenoketene (1730 cm^{-1}).[5] Other bands of trimethyleneselenoketene (**5**) appear at 2967 (s), 2863

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