1745–1720, 1680, 1590 cm^{-1}; NMR δ 4.70 (s, 2 H), 4.12 (t, 2 H), 3.85 (ds, 6 H), 2.60 (t, 2 H).

Anal. Calcd for $C_{10}H_{12}NO_5Br$: C, 39.24; H, 3.95. Found: C, 39.28; H, 3.93.

Methyl 1,4,5,6-Tetrahydro-2-[(acetyloxy)methyl]-1-methoxycarbonyl-4-oxo-3-pyridinecarboxylate (3b). The crude bromide **2b** (prepared from 11.3 g, 50 mmol, of pyridinone **1c**) was stirred with 9.8 g (100 mmol) of potassium acetate in 150 mL of dry dimethylformamide at room temperature for 5 h. Water was added and the aqueous solution extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated to 6.8 g of solid. The aqueous solution was further extracted with dichloromethane. The dichloromethane extract was dried ($MgSO_4$) and concentrated to 6.7 g of red oil which was chromatographed on 100 mL dry volumn of silica gel (*ICN Pharmaceuticals* Act III for dry column chromatography). Elution with dichloromethane–ethyl acetate (2:1) gave 4.45 g of crystalline acetate **3b.** Further elution gave 0.7 g of yellow solid which was combined with the ether extract and recrystallized from ethyl acetate to 4.7 g of the acetate **3b** (9.15 g, 64%, mp 100–101 °C): IR ($CHCl_3$) 1755–1725, 1680, 1600 cm^{-1}; NMR δ 5.10 (s, 2 H), 4.10 (t, 2 H), 3.85 (s, 6 H), 2.62 (t, 2 H), 2.05 (s, 3 H).

Anal. Calcd for $C_{12}H_{15}NO_7$: C, 50.53; H, 5.30. Found: C, 50.71; H, 5.30.

Methyl 1,5,6,7-Tetrahydro-3,7-dioxo-3*H*-oxazolo[3,4-*a*]pyridine-8-carboxylate (5). To 285 mg of acetate **3b** (1 mmol) in 3 mL of methanol was added 1.0 mL of 1 M potassium hydroxide in methanol (1 mmol) at −20 °C. After stirring 1.3 h, the mixture was filtered and washed with cold methanol to give 174 mg of the potassium enolate of **5:** NMR (Me_2SO-d_6) δ 6.62 (s), 2.2 (t), the spectrum also showed a singlet at δ 4.72 due to a small amount of lactone **4c;** IR (KBr) 1715, 1645, 1605 cm^{-1} (identical to that of the potassium enolate prepared by treatment of the urethane **5** with potassium hydroxide in methanol). The white solid was partially dissolved in aqueous ammonium chloride and extracted with dichloromethane. The extracts were dried ($MgSO_4$) and concentrated to give pure urethane **5** (98 mg, 46%, mp 152–153 °C): IR ($CHCl_3$) 1815, 1748, 1692, 1600 cm^{-1}; NMR δ 5.48 (s, 2 H), 4.0 (t, 2 H), 3.80 (s, 3 H), 2.70 (t, 2 H); mass spectrum *m/e* (rel intensity) 211 M^+ (73), 180 (100), 179 (80), 153 (34), 151 (18), 59 (13), 55 (43).

Anal. Calcd for $C_9H_9NO_5$: C, 51.19; H, 4.30. Found: C, 51.20, H, 4.24.

1,4,5,6-Tetrahydro-2-(hydroxymethyl)-1-(methoxycarbonyl)-4-oxo-3-pyridinecarboxylic Acid γ-Lactone (4b). To 2.85 g of acetate **3b** (10 mmol) in 40 mL of methanol was added hydrogen chloride gas at room temperature. After stirring 4 h the mixture was cooled to 0 °C and filtered to give the lactone **4b** (1.82 g, 86%, mp 227–228 °C): IR (KBr) 1770, 1745, 1675, 1585 cm^{-1}; NMR δ 5.25 (s, 2 H), 4.22 (t, 2 H), 3.96 (s, 3 H), 2.69 (t, 2 H); chemical ionization mass spectrum *m/e* (rel intensity) 212 (100).

Anal. Calcd for $C_9H_9NO_5$: C, 51.19; H, 4.30. Found: C, 51.23; H, 4.40.

1,4,5,6-Tetrahydro-2-(hydroxymethyl)-4-oxo-3-pyridinecarboxylic Acid γ-Lactone (4c). To 211 mg of lactone **4b** (1 mmol) in 3 mL of methanol was added 1.0 mL of 1 M potassium hydroxide in methanol at room temperature. After 1.6 h the mixture was cooled to 0 °C and 1.1 mL of 1 N hydrochloric acid was added. After 10 min the mixture was filtered to give 146 mg of solid which was recrystallized from methanol–water (1:1) to give the lactone **4c** (76 mg, 50%, decomposition without melting at 340 °C): IR (KBr) 3210, 1740, 1615 cm^{-1}; NMR (Me_2SO-d_6) 8.95 (bs, 0.8 H), 4.80 (s, 2 H), 3.65 (t, 2 H), 2.35 (t, overlaps with Me_2SO-d_5); chemical ionization mass spectrum *m/e* (rel intensity) 154 (100).

Anal. Calcd for $C_7H_7NO_3$: C, 54.90; H, 4.61. Found: C, 54.96; H, 4.71.

Methyl 1,4,5,6-Tetrahydro-1-methyl-4-oxo-2-[(phenylthio)methyl]-3-pyridinecarboxylate (6a). To a mixture of 131 mg of bromide **2a** (0.5 mmol), 70 μL of triethylamine (0.5 mmol), and 2 mL of dimethylformamide was added 57 μL of benzenethiol (0.55 mmol) at 0 °C. After stirring 2 h at 0 °C and 3 h at room temperature, the solvent was removed at about 0.1 mmHg. The residue was taken up in water and extracted with dichloromethane. The extract was dried ($MgSO_4$) and concentrated to 143 mg of oil which crystallized in ether to give the sulfide **6a** (93 mg, 64%, mp 49–51 °C): IR ($CHCl_3$) 1690, 1640, 1553 cm^{-1}; NMR δ 7.3 (m, 5 H), 4.07 (s, 2 H), 3.58 (s, 3 H), 3.50 (t, 2 H), 3.10 (s, 3 H), 2.40 (t, 2 H).

Anal. Calcd for $C_{15}H_{17}NO_3S$: C, 61.83; H, 5.88. Found: C, 61.82; H, 5.85.

Methyl 1,4,5,6-Tetrahydro-2-[(methylthio)methyl]-1-(methoxycarbonyl)-4-oxo-3-pyridinecarboxylate (6b). Lithium thiomethoxide (3.24 g, 60 mmol) was added to a solution of 15.9 g of crude bromide **2b** (50 mmol) in 200 mL of tetrahydrofuran at room temperature. After stirring 6 h, brine was added and the aqueous solution extracted with ether. The ether extract was dried ($MgSO_4$) and concentrated to 11.8 g of oil which was chromatographed on 600 mL dry volume of silica gel (ICN Pharmaceuticals Act III for dry column chromatography). Elution with 1 L of ethyl acetate–petroleum ether (3:1) gave 1.1 g of a mixture of **1c** and the methyl sulfide **6b.** Elution with 1.2 L of ethyl acetate–petroleum ether (2:1) gave the methyl sulfide **6b** (8.0 g, 59%, mp 83–84.5 °C): IR ($CHCl_3$) 1745–1715, 1675, 1585 cm^{-1}; NMR δ 4.10 (t, 2 H), 3.90 and 3.82 (2 s, 8 H), 2.60 (t, 2 H), 2.05 (s, 3 H).

Anal. Calcd for $C_{11}H_{15}NO_5S$: C, 48.34; H, 5.53. Found: C, 48.37; H, 5.64.

Methyl 1,4,5,6-Tetrahydro-1-(methoxycarbonyl)-4-oxo-2-[(phenylthio)methyl]-3-pyridinecarboxylate (6c). Benzenethiol (2.29 g, 20.8 mmol) was added to a solution of 6.36 g (20.8 mmol) of bromide **2b** and 2.1 g (20.8 mmol) of triethylamine in 70 mL of methanol at room temperature. After stirring 17 h the mixture was concentrated, dissolved in water, and extracted with dichloromethane. The extract was concentrated to an oil which crystallized from ethyl acetate–hexane to give the phenyl sulfide **6c** (4.9 g, 70%, mp 87–88 °C): IR ($CHCl_3$) 1745–1715, 1675, 1585 cm^{-1}; NMR δ 7.35 (m, 5 H), 4.30 (s, 2 H), 3.90 (t, 2 H), 3.80 (s, 3 H), 3.62 (s, 3 H), 2.50 (t, 2 H).

Anal. Calcd for $C_{16}H_{17}NO_5S$: C, 57.30; H, 5.11. Found: C, 57.28; H, 5.09.

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Registry No.—**1a,** 68185-61-5; **1b,** 68185-62-6; **1c,** 68185-63-7; **2a,** 68185-64-8; **2b,** 68185-65-9; **3a,** 68185-66-0; **3b,** 68185-67-1; **4a,** 68185-68-2; **4b,** 68185-69-3; **4c,** 68185-70-6; **5,** 68185-71-7; **6a,** 68185-72-8; **6b,** 68185-73-9; **6c,** 68185-74-0; β-alanine methyl ester, 4138-35-6; methyl acetoacetate, 105-45-3; methyl chloroformate, 79-22-1; benzenethiol, 108-98-5; lithium thiomethoxide, 35638-70-1.

References and Notes

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(2) A. G. Schultz, R. D. Lucci, W. Y. Fu, M. H. Berger, J. Erhardt, and W. K. Hagmann, *J. Am. Chem. Soc.*, **100,** 2150 (1978).
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Attempted Benzophenanthridine Syntheses through Chemical and Electrochemical Cyclizations of Naphthylamines and Naphthylimines[1]

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We have synthesized[2] numerous benzophenanthridines using the Kessar cyclization[3] as a key step. This cyclization involves treatment of a bromoimine (e.g., **2**) with $NaNH_2$ in liquid NH_3 and the yields of benzophenanthridines were usually on the order of 30%. We considered that it might be possible to effect the same cyclization in better yield with chemical or electrochemical oxidations. It might also be possible to perform the cyclization directly on the imine (e.g., **1**) and thus obviate the need for preparation of a bromo derivative. We report here the results of VOF_3 and anodic oxidation of **1, 3,** and **4.**

Imine **1** gave benzophenanthridine **5** in a maximum of 30% yield by oxidation with VOF_3 in trifluoroacetic acid (TFA)/

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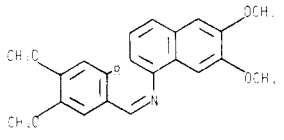
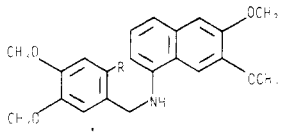
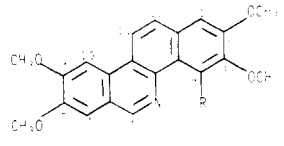
CH_2Cl_2 at 25 °C. The reaction was, however, extremely variable and runs under "identical" conditions or with slight variations often gave less than 10% yield. We were not able to pinpoint the source of variability in these reactions.[4] Different results were obtained when **1** was oxidized with VOF_3 in trifluoroacetic anhydride (TFAA)/CH_2Cl_2. From this reaction, **6** was isolated in 50% yield. In this case, the cyclization reaction was reproducible. It provides a unique entry into 4-substituted benzophenanthridines which may be of value[5] as precursors of biologically stable antitumor benzophenanthridinium salts.



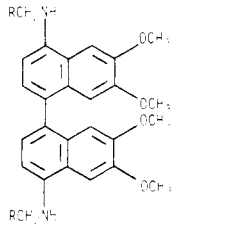
1 R = H
2 R = Br



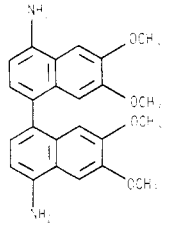
3 R = H
4 R = Br



5 R = H
6 R = COCF$_3$



7 R = 3,4-dimethoxyphenyl
8 R = 2-bromo-4,5-dimethoxyphenyl



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Structure proof of **6** was by analysis and spectral interpretations. High-resolution mass spectrometry established the molecular formula as $C_{23}H_{18}F_3NO_5$. The base peak was at *m/e* 376 which represented loss of CF_3 from the molecular ion. The IR showed a carbonyl peak at 1721 cm^{-1}, which is identical with that observed[6] for α,α,α-trifluoroacetophenone. The UV and ^1H- and ^{13}C-NMR spectra were clearly those of a substituted benzophenanthridine.

In the ^{13}C spectra, benzophenanthridines show three groups of aromatic carbon resonances: a group in the 149–155-ppm region for carbons 2, 3, 4b, 6, 8, and 9; a group in the 115–130-ppm region for carbons 4a, 6a, 10a, 10b, 11, and 12; and a group in the 99–110 region for carbons 1, 4, 7, and 10. For compounds such as **5**, each of the four peaks in the last group are doublets in the off-resonance decoupled spectrum. The off-resonance decoupled ^{13}C spectrum for **6** (taken in Me_2SO-d_6 at 80 °C) showed resonances for the last group at 102.2 d, 108.0 d, 109.9 s, and 110.9 d. Since the 109.9 peak was a singlet, **6** must be substituted at carbon 1, 4, 7, or 10. Confirmatory evidence was obtained from analysis of the other groups. Two peaks are present at 120.4 and 125.6 ppm. These are assignable to carbons 11 and 12 and, since they are doublets, these carbons have not been substituted. Substitution cannot have occurred at carbon 6 since a doublet for that carbon is observed at 147.0 ppm. A final assignment of the trifluoroacetyl substituent to carbon 4 could be made from the ^1H-NMR spectrum. In benzophenanthridines[2,4,7,8] two downfield singlets are always observed, with one below 9 ppm being assigned to the proton at carbon 6 and one just above 9 ppm being assigned to the proton on carbon 4. The ^1H-NMR of **6** showed only one singlet in this region instead of two. This must be assigned to a proton on carbon 6 since the ^{13}C NMR showed that position to be unsubstituted. The trifluoroacetyl group must therefore be at carbon 4 and our product must have structure **6**.

Imine **1** was anodically oxidized under various conditions,[4] but workup yielded only starting imine along with hydrolysis products. **1** was therefore reduced to **3**, which was anodically oxidized (2 F/mol at 1.0 V in CH_3CN with $LiClO_4$ as electrolyate). This reaction yielded 42% of a solid shown (see Experimental Section) to be the dimer **7** by spectral analysis, oxidation to the dimeric imine with MnO_2, and hydrolysis of the latter to 4,4′-bis(6,7-dimethoxy)-1-naphthylamine (**9**). None of the desired cyclization product was obtained.

Since we have found electrochemical cyclization to proceed in good yield at the site of a bromine,[9] the bromoimine **2** was prepared and reduced to the bromoamine **4**. Anodic oxidation of **4** gave 48% of a dimer, **8**, but none of the desired cyclization product was found.

Experimental Section

***N*-(3,4-Dimethoxyphenylmethylene)-1-(6,7-dimethoxy)naphthylamine** (**1**). Equal molar amounts of 6,7-dimethoxynaphthylamine[2] and 3,4-dimethoxybenzaldehyde were heated at reflux in benzene (10 mL/g of aldehyde) with a Dean-Stark trap attached. A drop of trifluoroacetic acid (TFA) was added as a catalyst and heating was continued until analysis showed disappearance of the aldehyde proton (30–45 min). The benzene was evaporated in vacuo and the crude product was recrystallized from ethyl acetate to yield the imine in 90% yield: mp 137.5–139 °C; ^1H NMR ($CDCl_3$) δ 3.94 (s, 3 H), 4.02 (s, 3 H), 6.83–7.79 (m, 3 H), 8.51 (s, 1 H); IR (KBr) 1630 cm^{-1}; UV λ_{max}^{EtOH} (log ϵ) 211 (4.56), 240 (4.70), 276 (4.20), 318 (4.16), 350 nm (4.10). Anal. Calcd for $C_{21}H_{21}NO_4$: C, 71.78; H, 6.02; N, 3.99. Found: C, 71.59; H, 6.08; N, 3.84.

***N*-(2-Bromo-4,5-dimethoxyphenylmethylene)-1-(6,7-dimethoxy)naphthylamine** (**2**) was similarly prepared in 48% yield and was identical with the compound previoulsy synthesized.[2]

***N*-(3,4-Dimethoxybenzyl)-1-(6,7-dimethoxy)naphthylamine** (**3**). To a solution of **1** (1.5 g) in 50 mL of dry, freshly distilled diglyme was added 660 mg of $NaBH_4$. The reaction was performed in a dry 100-mL round-bottom flask equipped with a condenser and a drying tube. After the mixture was heated for 11 h at 95–100 °C, it was poured into cold water (100 mL). Filtration yielded 1.4 g of white crystalline solid (95%). Recrystallization from ethyl acetate gave **3**: mp 154–156.5 °C; ^1H NMR ($CDCl_3$) δ 3.88 (s, 6 H), 3.98 (s, 6 H), 4.42 (br s, 3 H), 6.67 (d of d, J = 4 and 9 Hz, 1 H), 6.91–7.26 (m, 7 H); IR (KBr) 3430, 1590, 1540, 1520 cm^{-1}; UV λ_{max}^{EtOH} (log ϵ) 316 (3.80), 283 (sh, 3.78), 259 (4.48), 221 (4.69), 206 nm (4.58). Anal. Calcd for $C_{21}H_{23}NO_4$: C, 71.37; H, 6.56; N, 3.96. Found: C, 70.92; H, 6.40; N, 3.90.

***N*-(2-Bromo-4,5-dimethoxybenzyl)-1-(6,7-dimethoxy)naphthylamine** (**4**). A mixture of **2** (1.0 g), 40 mL of dry diglyme, and 363 mg of $NaBH_4$ was heated in a dry, moisture-protected 100-mL round-bottom flask for 12 h at 92 °C. Workup as given above yielded the crude product (80%). Recrystallization from ethyl acetate afforded pure **4**: mp 186.5–187.5 °C; ^1H NMR ($CDCl_3$) δ 3.74 (s, 3 H), 3.87 (s, 3 H), 4.01 (s, 6 H), 4.52 (br s, 3 H), 6.55 (d of d, J = 3 and 7 Hz, 1 H), 7.01–7.28 (m, 6 H); IR (KBr) 3410, 1585, 1495 cm^{-1}; UV λ_{max}^{EtOH} (log ϵ) 314, 283 nm. Anal. Calcd for $C_{21}H_{22}NO_4Br$: C, 58.34; H, 5.13; N, 3.24. Found: C, 58.55; H, 5.30, N, 3.11.

2,3,8,9-Tetramethoxybenzo[*c*]phenanthridine (**5**). Dry VOF_3 (180 mg, Alfa Division, Ventron Corp.) was suspended in 8 mL of 5% TFA in CH_2Cl_2 solution (with 2 drops of TFAA added) in a dry 25-mL three-neck round-bottom flask equipped with a N_2 gas inlet, a 10-mL dropping funnel, and a magnetic stirrer. Transfer of the VOF_3 to the flask was accomplished in an N_2-purged glove bag. A solution of 52 mg of **1** in 9 mL of 5% TFA in CH_2Cl_2 was added dropwise to the stirred mixture. After 35 min the solution was poured into 70 mL of aqueous 1% citric acid solution. The solution was adjusted to pH 8 with $NaHCO_3$ and extracted with CH_2Cl_2. The CH_2Cl_2 was evaporated to leave 46 mg of residue which was chromatographed on silica gel (125:2 $CHCl_3$/MeOH) to yield 18.1 mg (30%) of **5** whose UV and NMR spectra and TLC R_f values were identical to an authentic sample.[2]

Attempts to improve the yield on this reaction by using different batches of VOF_3 or TFA (freshly opened, old or of different lot numbers), different reaction times, lower temperatures, and FSO_3H catalysis were unsuccessful. Many times only TLC evidence for product formation in small yield could be observed.

2,3,8,9-Tetramethoxy-4-(trifluoroacetoxy)benzo[*c*]phenanthridine (6). A solution of 1 (257 mg) in 35 mL of 5% trifluoroacetic anhydride in CH_2Cl_2 was added dropwise to a stirred suspension of VOF_3 (880 mg) in 35 mL of the same solvent at 25 °C for 40 min. This was followed by the workup above which yielded 331 mg of crude material. This was chromatographed on silica gel (EtOAc) to yield 230 mg (50%) of **6**: mp 257–260 °C; ^1H NMR ($CDCl_3$) δ 4.07 (s, 3 H), 4.11 (s, 6 H), 4.20 (s, 3 H), 7.41 (s, 1 H), 7.46 (s, 1 H), 7.87 (s, 1 H), 7.88 (d, J = 9 Hz, 1 H), 8.38 (d, J = 9 Hz, 1 H), 9.12 (s, 1 H); IR (KBr) 1721 and 1619 cm^{-1}; UV λ_{max}^{EtOH} (log ϵ) 370 (3.40), 352 (3.54), 328 (sh, 4.03), 313 (4.29), 282 (4.82), 227 nm (4.43); MS m/e (rel intensity) 445.113 (7, calcd for $C_{23}H_{18}NF_3O_5$: 445.114), 376 (100, $M^+ - CF_3$), 360 (12), 332 (7), 188 (11).

4,4′-Bis[*N*-(3,4-dimethoxyphenylmethyl)]-1-(6,7-dimethoxy)naphthylamine (7). Oxidation of **3** was performed in a two-compartment H cell partitioned by a glass frit. The substrate (827 mg) was dissolved in 100 mL of CH_3CN containing 0.1 M $LiClO_4$ electrolyate. A cylindrical platinum electrode was used as the anode and a "Scoopla" as the cathode. The oxidation was performed at 25 °C and at a constant potential of 1.0 V until 2 F/mol were passed. Evaporation of excess CH_3CN (with 5 mL of solvent left at the finish to avoid an explosion from reacting perchloric acid), addition of water (75 mL), extraction with CH_2Cl_2 (3 × 75 mL), and evaporation of the solvent (after drying) gave the crude product (774 mg), which was observed to be a complex mixture by TLC analysis. Chromatography on silica gel ($CHCl_3$) yielded five fractions: fraction 2 (40 mg) was identified as 3,4-dimethoxybenzaldehyde by NMR, fraction 3 (328 mg, 42%) contained the major product **7**, and fraction 4 (282 mg) was observed to be a mixture of **7** and other products.

Fraction 3 was recrystallized from CH_2Cl_2/cyclohexane to give pure **7**: mp 148.5–152 °C; ^1H NMR ($CDCl_3$) δ 3.54 (s, 6 H), 3.93 (s, 12 H), 4.01 (s, 6 H), 4.51 (s, 4 H), 6.70–7.36 (m, 14 H); IR (KBr) δ 3200, 1630, 1595, 1515, 1495 cm^{-1}; MS m/e (rel intensity) 704 (36), 554 (42), 404 (73), 403 (35), 207 (34), 152 (50), 151 (100); UV λ_{max}^{EtOH} (log ϵ) 333 (4.19), 263 (4.61), 221 (4.85), 202 nm (4.92). Anal. Calcd for $C_{42}H_{44}N_2O_8$: C, 71.57; H, 6.29; N, 3.97. Found: C, 70.92; H, 6.56; N, 3.96.

4,4′-Bis[*N*-(2-bromo-4,5-dimethoxyphenylmethyl)]-1-(6,7-dimethoxy)naphthylamine (8). This product was obtained by anodic oxidation at 1.2 V of **4** (799 mg) in 100 mL of CH_3CN containing 0.1 M $LiClO_4$ ($Ag|Ag^+$ reference electrode) until 2 F/mol of current was passed. The crude product (836 mg) was isolated as above. Chromatography on silica gel (EtOAc) gave **8** (48%): mp 134–136 °C (CH_2Cl_2/cyclohexane); ^1H NMR ($CDCl_3$) δ 3.60 (s, 6 H), 3.81 (s, 6 H), 3.92 (s, 6 H), 4.04 (s, 6 H), 4.61 (br s, 6 H), 6.72 (d, J = 8 Hz, 2 H), 6.92 (s, 2 H), 7.15 (s, 3 H), 7.25 (s, 3 H), 7.29 (d, J = 8 Hz, 2 H); IR (KBr) 3200, 1625, 1600, 1500, 1465, 1440, 1390 cm^{-1}; UV λ_{max}^{EtOH} (log ϵ) 331 (4.27), 263 (4.68), 239 sh (4.84), 220 (4.94), 205 nm (5.00). Anal. Calcd for $C_{42}H_{42}N_2O_8Br_2$: C, 58.48; H, 4.91; N, 3.26. Found: C, 58.36; H, 4.90; N, 3.21.

Structures for the dimers could be reasonably assigned based upon the following data. Both dimers could be oxidized (see below) to imine dimers which were then independently hydrolyzed to yield the same dimeric naphthylamine. This meant that dimerization (in both cases) was at a site on the naphthylamine moiety rather than on the dimethoxybenzyl or bromodimethoxybenzyl moieties. A key to the site of dimerization was evident in the ^1H-NMR spectra for the dimers, the imine dimers (see below), and the naphthylamine dimer hydrolysis product. Each had a six-proton singlet for two methoxy groups in the 3.5–3.6-ppm region. This is considerably upfield from any of the other aromatic methoxyls and is a result of one methoxy on each naphthalene by the π-electron cloud of the other naphthalene. The ^1H NMR of the hydrolysis product from both imine dimers was extremely simple and symmetrical (see below). It consisted of two identical pairs of methoxy absorptions, one at 3.60 and the other at 4.07, and an aromatic AB pattern superimposed by two singlets. These data could best be accounted for by assigning structure **9** to the naphthylamine and hence structures **7** and **8** to the electrochemically produced dimers.

Oxidation and Degradation of 7 and 8. **7** (125 mg) was dissolved in 3 mL of $CHCl_3$ containing "active" MnO_2[10] (149 mg) and refluxed for 3.5 h. An additional 10 mL of $CHCl_3$ was added, and the solution was filtered through Celite and evaporated to give the crude product (75%). Recrystallization from CH_3NO_2 gave **4,4′-bis[*N*-3,4-dimethoxyphenylmethylene]-1-(6,7-dimethoxy)naphthylamine:** mp 281–281.5 °C; ^1H NMR ($CDCl_3$) δ 3.60 (s, 6 H), 4.02 (s, 6 H), 4.07 (s, 12 H), 6.87–7.60 (m, 10 H), 7.84 (s, 4 H), 8.67 (s, 2 H); IR (KBr) 1620 cm^{-1}; MS m/e (rel intensity) 700 (34), 280 (16), 209 (15), 208 (22), 207 (100), 166 (14), 151 (24), 111 (16), 109 (12), 97 (33), 95 (31), 85 (23), 83 (32), 81 (19), 71 (47), 69 (42); UV λ_{max}^{EtOH} (log ϵ) 315 (sh), 275, 230, 204 nm. Anal. Calcd for $C_{42}H_{40}N_2O_8$: C, 71.99; H, 5.75; N, 4.00. Found: C, 71.77; H, 6.02; N, 3.86.

In a similar manner, **8** (130 mg) in 10 mL of $CHCl_3$ containing 226 mg of "active" MnO_2 was refluxed for 3 h. Workup as above gave the crude product (75%), which was recrystallized from CH_3NO_2 to give **4,4′-bis[*N*-(2-bromo-4,5-dimethoxyphenylmethylene)]-1-(6,7-dimethoxy)naphthylamine:** mp 285–288.5 °C; ^1H NMR ($CDCl_3$) δ 3.64 (s, 6 H), 4.03 (s, 6 H), 4.08 (s, 12 H), 6.92 (s, 2 H), 7.18–7.55 (m, 6 H), 7.87 (s, 2 H), 8.08 (s, 2 H), 9.05 (s, 2 H); IR (KBr) 1620 cm^{-1}; UV λ_{max}^{EtOH} 332, 289 (sh), 241, 220, 203 nm. Anal. Calcd for $C_{42}H_{38}N_2O_8Br_2$: C, 58.75; H, 4.46; N, 3.26. Found: C, 58.64; H, 4.54; N, 3.05.

Each imine dimer (64 mg) was hydrolyzed for 1 h on a steam bath in 15 mL of EtOH containing 2 drops of concentrated HCl. The solvent was evaporated, 15 mL of $CHCl_3$ was added, and this solution was extracted with 1 M H_2SO_4 (2 × 15 mL). The aqueous layer was separated, made basic with $NaHCO_3$, and extracted with $CHCl_3$. The $CHCl_3$ was dried and evaporated to leave 30 mg of a dark oil which was crystallized from ether to yield **9**: mp 111 °C dec; ^1H NMR ($CDCl_3$) δ 3.60 (s, 6 H), 4.07 (s, 6 H), 6.85 (d, J = 7 Hz, 2 H), 6.89 (s, 2 H), 7.20 (s, 2 H), 7.24 (d, J = 7 Hz, 2 H). Instability of the product precluded the obtaining of additional analytical data.

Registry No.—**1**, 68152-23-8; **2**, 56517-04-5; **3**, 68152-24-9; **4**, 68152-25-0; **5**, 15462-10-9; **6**, 68152-26-1; **7**, 68152-27-2; **8**, 68152-28-3; **9**, 68152-29-4; 6,7-dimethoxynaphthylamine, 52401-42-0; 3,4-dimethoxybenzaldehyde, 120-14-9; 2-bromo-4,5-dimethoxybenzaldehyde, 5392-10-9; 4,4′-bis[*N*-3,4-dimethoxyphenylmethylene]-1-(6,7-dimethoxy)naphthylamine, 68152-30-7; 4,4′-bis[*N*-(2-bromo-4,5-dimethoxyphenylmethylene)]-1-(6,7-dimethoxy)naphthylamine, 68152-31-8.

References and Notes

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Synthesis of 1,2-Glycols via Coupling of the Trimethylsilyl Ethers of Primary Alcohols

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The synthesis of 1,2-glycols is generally approached by two quite different paths: (1) oxidation of olefins by a variety of procedures; or (2) bimolecular reduction of aldehydes and ketones.[1] A third method, oxidative or dehydrogenative dimerization of alcohols (eq 1a), is not useful because of disproportionation of intermediate radicals (eq 1b) or overoxidation (eq 1c).

$$2R_2CHOH \xrightarrow{-2H} 2R_2\dot{C}OH \longrightarrow \begin{cases} HOCR_2CR_2OH & \text{(1a)} \\ R_2CO + R_2CHOH & \text{(1b)} \\ \xrightarrow{[O]} RCO_2H & \text{(1c)} \end{cases}$$

For example, Ladygin and Saraeva[2] have shown that the ratio of coupling to disproportionation is approximately 3/2

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