1,2-Eliminations in a Novel Reductive Coupling of Nitroarenes to Give Azoxy Arenes by Sodium Bis(trimethylsilyl)amide

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General Procedure. Dichloromethane, 1,4-dioxane, N,N-dimethylformamide, ethyl acetate, *n*-hexane hexamethylphosphoramide and tetrahydrofuran were purchased from Mallinckrodt Chemical Co. N,N-dimethylformamide was dried and distilled from MgSO₄ under reduced pressure and then stored in serum-capped bottles over molecular sieves 4A under nitrogen. Hexamethylphosphoramide was dried and distilled from CaH₂ at reduced pressure and then stored under nitrogen over molecular sieves 4A. Ethyl acetate and hexanes were dried and distilled from CaH₂. 1,4-Dioxane and tetrahydrofuran were dried by distillation from sodium and benzophenone under an atmosphere of nitrogen. Nitrobenzene and 2,2'-dinitrobiphenyl were purchased from Merck Inc. Sodium bis(trimethylsilyl)amide, 4-nitroanisole, 3-nitroanisole, 3,4-dimethoxynitrobenzene, *p*-nitrophenetole, 4-nitrothioanisole, N,N-dimethyl-3-nitroaniline, 2,2'-dinitrobiphenyl were purchased from Aldrich Chemical Co.

An explosion-proof oven from Blue M. Electric Co. and the Pyrex combustion tubes (8 × 10 × 200 mm) from Tung Kuang Glassware Industrial Corp. were used to carry out experiments that required high temperature (150 °C).

Analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254), purchased from Merck Inc. Mixtures of ethyl acetate and hexanes were used as eluants. Gas chromatographic analyses were performed on a Hewlett–Packard 5890 Series II instrument equipped with a 25-m cross-linked methylsilicone gum capillary column (0.32 mm i.d.). Nitrogen gas was used as a carrier gas and the flow rate was kept constant at 14.0 mL/min. The retention time t_R was measured under the following conditions: injector temperature 260 °C, initial temperature for column 70 °C, duration 2.00 min, increment rate 10 °C/min, and final temperature for column 250 °C. Gas chromatography and low resolution mass spectral analyses were performed on a Hewlett–Packard 5890 Series II instrument equipped with a Hewlett–Packard 5971A Mass Selective Detector and a capillary

HP-1 column. Purification by gravity column chromatography was carried out by use of Merck Reagents Silica Gel 60 (particle size 0.063–0.200 mm, 70–230 mesh ASTM).

Infrared (IR) spectra were measured on a Bomem Michelson Series FT-IR. The wavenumbers reported are referenced to the polystyrene 1601 cm^{-1} absorption. Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; w, weak. Proton NMR spectra were obtained on a Varian Unity-400 (400 MHz) spectrometer or a Varian Gemini-300 (300 MHz) spectrometer by use of chloroform-*d* as solvent and tetramethylsilane as internal standard. Carbon-13 NMR spectra were obtained on a Varian Unity-400 (100 MHz) spectrometer or Varian Gemini-300 (75 MHz) spectrometer by use of chloroform-*d* as solvent. Carbon-13 chemical shifts are referenced to the center of the CDCl_3 triplet (δ 77.0 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; *J*, coupling constant (hertz). High-resolution mass spectra were obtained by means of a JEOL JMS-HX110 mass spectrometer.

Standard Procedure for the Formation of Azoxy Compounds. A nitroarene (1.0 mmol) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.0 mmol) were added into a Pyrex combustion tube under nitrogen gas. The tube was then sealed by torch and heated in an oven at 150 °C for 12 h. The reaction mixture was diluted with water at room temperature, and extracted with CH_2Cl_2 (4×5 mL). The combined organic layers were washed with saturated aqueous NaCl (5 mL), dried over $\text{MgSO}_4(\text{s})$, filtered, and concentrated under reduced pressure. The residue was purified by gravity column chromatography packed with silica gel to provide the desired azoxy compound.

Azoxybenzene (2a). The standard procedure was followed by use of nitrobenzene (**1a**, 123.5 mg, 1.001 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm $\times$ 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **2a** as a yellow solid in 20% yield: TLC *R_f* 0.73 (20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.37–7.54 (m, 6 H, ArH), 8.13–8.15 (m, 2 H, ArH), 8.27–8.30 (m, 2 H, ArH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 122.27, 125.48, 128.65, 128.74, 129.56, 131.53, 143.94, 148.26; IR (neat) 1478 (s, N=N), 1437 (m, N=N), 1296 (w), 1162 (w), 1071 (w), 1024 (w), 917 (w), 762 (s), 683 (s), 521 (w) cm^{-1} ; MS *m/z* (relative intensity) 198 (M^+ , 67), 169 (46), 152 (4), 141 (24), 115 (11), 105 (9), 91 (35), 77 (100), 65 (17), 51 (34).

4,4'-Dimethoxyazoxybenzene (2b). The standard procedure was followed by use of 4-nitroanisole (**1b**, 152.5 mg, 0.999 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm × 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **2b** as a yellow solid in 45% yield: TLC R_f 0.43 (20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 3.86 (s, 3 H, CH_3), 3.87 (s, 3 H, CH_3), 6.93–6.97 (m, 4 H, ArH), 8.22–8.27 (m, 4 H, ArH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.46, 55.64, 113.57, 113.69, 123.74, 127.77, 137.97, 141.68, 160.17, 161.82; IR (neat) 2932 (w), 2849 (w), 1600 (m), 1501 (m), 1453 (w), 1252 (m), 1154 (m), 1022 (m), 833 (m) cm^{-1} ; MS m/z (relative intensity) 258 (M^+ , 52), 242 (54), 135 (27), 121 (46), 107 (100), 92 (36), 77 (47), 64 (18), 51 (6).

3,3'-Dimethoxyazoxybenzene (2c). The standard procedure was followed by use of 3-nitroanisole (**1c**, 154.5 mg, 1.009 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm × 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **2c** as a yellow solid in 40% yield: TLC R_f 0.50 (20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 3.88 (s, 3 H, CH_3), 3.85 (s, 3 H, CH_3), 6.95 (d, $J = 8.4$ Hz, 1 H, ArH), 7.08 (d, $J = 8.0$ Hz, 1 H, ArH), 7.35–7.40 (m, 2 H, ArH), 7.75 (d, $J = 8.6$ Hz, 1 H, ArH), 7.80 (s, 1 H, ArH), 7.83 (s, 1 H, ArH), 7.88 (d, $J = 8.4$ Hz, 1 H, ArH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 55.41, 55.67, 107.54, 110.04, 114.65, 116.26, 118.03, 118.35, 129.30, 129.43, 145.02, 149.53, 159.61, 159.93; IR (neat) 2362 (m), 1579 (m), 1493 (s), 1459 (s), 1312 (m), 1279 (m), 1142 (w), 1040 (m), 911 (w), 863 (s) cm^{-1} ; MS m/z (relative intensity) 258 (M^+ , 80), 242 (12), 230 (32), 215 (28), 199 (17), 187 (24), 123 (30), 107 (100), 92 (56), 77 (62), 64 (32), 51 (15).

3,3',4,4'-Tetramethoxyazoxybenzene (2d). The standard procedure was followed by use of 3,4-dimethoxynitrobenzene (**1d**, 183.5 mg, 1.002 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm × 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **2d** as a yellow solid in 45% yield: TLC R_f 0.14 (20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 300 MHz) δ 3.84–3.97 (12 H, OCH_3), 6.84–6.94 (m, 2 H, ArH), 7.84–7.98 (m, 4 H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 55.93, 55.97, 56.19, 105.52, 108.04, 109.09, 109.97, 110.30,

111.87, 115.06, 119.25, 119.96, 138.04, 148.26, 150.23; IR (neat) 3339 (w), 2835 (w), 1732 (w), 1597 (m), 1511 (s), 1455 (s), 1278 (m), 1231 (m), 1123 (m), 1018 (m), 806 (m) cm^{-1} ; MS m/z (relative intensity) 318 (M^+ , 24), 302 (45), 275 (7), 151 (22), 137 (100), 122 (8), 108 (11), 92 (9), 79 (21), 66 (5), 51 (7).

4,4'-Diethoxyazoxybenzene (2e). The standard procedure was followed by use of *p*-nitrophenetole (**1e**, 168.1 mg, 1.006 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm $\times$ 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **2e** as a yellow solid in 42% yield: TLC R_f 0.11 (20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 1.40–1.44 (m, 6 H, CH_3), 4.04–4.10 (m, 4 H, CH_2), 6.90–6.95 (m, 4 H, ArH), 8.19–8.26 (m, 4 H, ArH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 14.69, 63.66, 63.90, 113.28, 113.42, 114.70, 114.85, 123.49, 123.86, 127.62, 127.92, 137.82, 141.48, 159.57, 161.19; IR (neat) 2917 (w), 1592 (w), 1510 (s), 1467 (m), 1439 (w), 1267 (s), 1234 (m), 1125 (m), 1022 (m) cm^{-1} ; MS m/z (relative intensity) 286 (M^+ , 100), 270 (27), 229 (10), 151 (13), 135 (39), 121 (81), 107 (71), 93 (19), 79 (15), 65 (26), 52 (10).

4,4'-Bis-methylsulfanylazoxybenzene (2f). The standard procedure was followed by use of 4-nitrothioanisole (**1f**, 168.5 mg, 0.996 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm $\times$ 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **2f** as a yellow solid in 46% yield: TLC R_f 0.53 (20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 2.52 (s, 3 H, CH_3), 2.53 (s, 3 H, CH_3), 7.24–7.30 (m, 4 H, ArH), 8.16–8.21 (m, 4 H, ArH); ^{13}C NMR (CDCl_3 , 75 MHz) δ 14.73, 15.08, 122.43, 123.77, 124.88, 125.23, 125.41, 125.89, 126.14, 140.96, 141.16, 143.65, 145.05; IR (neat) 2913 (w), 1582 (m), 1507 (w), 1484 (m), 1457 (m), 1432 (w), 1090 (m), 826 (s) cm^{-1} ; MS m/z (relative intensity) 290 (M^+ , 75), 274 (66), 151 (20), 137 (33), 123 (100), 108 (23), 90 (12), 79 (20), 45 (26).

3,3'-Azoxybis(*N,N*-dimethyl)benzenamine (2g). The standard procedure was followed by use of *N,N*-dimethyl-3-nitroaniline (**1g**, 166.2 mg, 1.000 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm $\times$ 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **2g** as a yellow solid in 25% yield: TLC R_f 0.48

(20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 2.87–3.02 (m, 12 H, NCH_3), 6.77–6.86 (m, 2 H, ArH), 7.28–7.34 (m, 2 H, ArH), 7.51–7.59 (m, 4 H, ArH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 40.49, 40.71, 105.89, 109.46, 110.07, 113.92, 114.99, 129.02, 129.10, 145.04, 149.65, 150.79; IR (neat) 1613 (m), 1504 (s), 1445 (m), 1428 (w), 1354 (m), 1314 (w), 996 (m), 680 (m) cm^{-1} ; MS m/z (relative intensity) 284 (M^+ , 76), 268 (61), 239 (17), 149 (25), 136 (45), 120 (100), 104 (31), 92 (24), 77 (36), 65 (16), 42 (30).

Benzo[*c*]cinnoline-*N*-oxide (4). The standard procedure was followed by use of 2,2'-dinitrobiphenyl (**3**, 244.7 mg, 1.002 mmol, 1.0 equiv) and sodium bis(trimethylsilyl)amide (1.0 M in THF, 1.10 mL, 1.1 mmol, 1.0 equiv). After 12 h, the reaction mixture was worked up and the residue was purified by chromatography on silica gel (2.2 cm $\times$ 16 cm column, 5% EtOAc in hexanes as eluant) to give pure **4** as a yellow solid in 18% yield: TLC R_f 0.18 (20% EtOAc in hexanes); ^1H NMR (CDCl_3 , 400 MHz) δ 7.66–7.81 (m, 3 H, ArH), 7.90–7.98 (m, 2 H, ArH), 8.34 (d, J = 8.0 Hz, 1 H, ArH), 8.47 (d, J = 8.8 Hz, 1 H, ArH), 8.81 (d, J = 8.8 Hz, 1 H, ArH); ^{13}C NMR (CDCl_3 , 100 MHz) δ 118.24, 121.23, 122.29, 122.38, 126.37, 128.63, 128.89, 129.94, 130.50, 132.59, 137.14, 142.29; IR (neat) 1845 (w), 1587 (w), 1557 (w), 1467 (m, $\text{N}=\text{N}$), 1398 (s, $\text{N}=\text{N}$), 1336 (m), 1220 (m), 923 (m), 762 (s), 718 (s) cm^{-1} ; MS m/z (relative intensity) 196 (M^+ , 27), 166 (20), 151 (15), 140 (48), 126 (11), 113 (23), 98 (28), 87 (43), 74 (61), 63 (100).