Radical Reduction of Aromatic Azides to Amines with Tributylgermanium Hydride

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Supporting information

Table of contents:

Page S2-S3. Experimental procedures.

Pages S4-S8. Analytical and spectral data for new compounds **3a-d**, **4f-h**, **5f-h** and **6i-m**, **o**.

General Procedure for the Preparation of Azides 1a-q. The already known aryl azides **1a-q** were prepared by diazotization of the corresponding anilines **2a-q**, all commercially available (Aldrich) except biphenyl-2,2'-diamine (**2k**),¹ followed by treatment with sodium azide according to a standard procedure.² All the azides were characterized on the basis of physical and/or spectral data. (**1a**,³ **1b**,⁴ **1c**,⁵ **1d**,⁶ **1e**,⁷ **1f**,⁷ **1g**,⁸ **1h**,⁵ **1i**,⁹ **1j**,⁴ **1k**,¹⁰ **1l**,¹¹ **1m**,⁷ **1n**,¹² **1o**,¹³ **1p**,¹⁴ **1q**¹⁵).

1a: R= Cl

1b: R= OMe

1c: R= COMe

1d: R= CN

1e: R= NO₂

1f: R= Cl

1g: R= OMe

1h: R= COMe

1i: R= Me

1j: R= OMe

1k: R= 2-NH₂C₆H₄

1l: R= F

1n

1m: R= Cl

1o: R= COMe

1p: R= Br

1q: R= I

2a: R= Cl

2b: R= OMe

2c: R= COMe

2d: R= CN

2e: R= NO₂

2f: R= Cl

2g: R= OMe

2h: R= COMe

2i: R= Me

2j: R= OMe

2k: R= 2-NH₂C₆H₄

2l: R= F

2n

2m: R= Cl

2o: R= COMe

2p: R= Br

2q: R= I

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General Procedure for the Reactions of Azides 1a-q with Tributylgermanium Hydride. A toluene (15 mL) solution containing the appropriate azide **1** (1 mmol), tributylgermanium hydride (1.1 mmol) and benzenethiol (0.1 mmol) was refluxed for ca 30 min, after which time TLC normally showed the virtual disappearance of the starting substrate. In the case of the azides **1e**, **1p** and **1q** prolongation of the reaction time up to 60 min did not cause any significant change in the ensuing products. After cooling to room temperature, the solvent was removed in vacuo and the residue subjected to chromatographic separation on silica gel by progressive elution with light petroleum/diethyl ether mixtures. Yields of the isolated products are collected in Table 1. The anilines **2** and 3-methyl-2,1-benzisoxazole **7** (Barth, A.; Corrie, J. E. T.; Gradwell, M. J.; Maeda, Y.; Mäntele, W.; Meier, T.; Trentham, D. R. *J. Am. Chem. Soc.* **1997**, *119*, 4149) were identified by spectral comparison with authentic samples. Analytical and spectral data of the unknown germylated anilines **3a-d**, **4f-h**, **5f-h** and **6i-m**, **o** were as follows.

3a

4-Chloro-2-tributylgermylaniline (3a). oil; IR $\nu_{\max}$ (cm^{-1}) 3459 and 3380 (NH_2); ^1H NMR (400 MHz) δ 0.87-0.90 (9 H, m), 1.00-1.05 (6 H, m), 1.33-1.37 (12 H, m), 3.66 (2 H, br s, NH_2), 6.55 (1 H, d, $J = 8.4$ Hz), 7.06 (1 H, dd, $J_1 = 8.4$ Hz, $J_2 = 2.6$ Hz), 7.09 (1 H, d, $J = 2.6$ Hz), ^{13}C NMR (100 MHz) δ 12.8 (CH_2), 13.7 (CH_3), 26.4 (CH_2), 27.3 (CH_2), 116.2 (CH), 123.4 (C), 125.7 (C), 129.2 (CH), 134.4 (CH), 149.4 (C); MS (ESI) (rel inten) 372 $[(M + 6) - 1]^-$ (38), 370 $[(M + 4) - 1]^-$ (100), 368 $[(M + 2) - 1]^-$ (61), 366 $(M - 1)^-$ (36). Anal. calcd for $\text{C}_{18}\text{H}_{32}\text{ClGeN}$: C, 58.35; H, 8.71; N, 3.78. Found: C, 58.46; H, 8.70; N, 3.79.

3b

4-Methoxy-2-tributylgermylaniline (3b). oil; IR $\nu_{\max}$ (cm^{-1}) 3448 and 3368 (NH_2); ^1H NMR (400 MHz) δ 0.84-0.92 (9 H, m), 0.99-1.07 (6 H, m), 1.25-1.43 (12 H, m), 3.43 (2 H, br s, NH_2), 3.75 (3 H, s), 6.60 (1 H, d, $J = 8.6$ Hz), 6.71 (1 H, dd, $J_1 = 8.6$ Hz, $J_2 = 2.9$ Hz), 6.79 (1 H, d, $J = 2.9$ Hz), ^{13}C NMR (100 MHz) δ 13.0 (CH_2), 13.7 (CH_3), 26.5 (CH_2), 27.4 (CH_2), 55.6 (CH_3), 114.4 (CH), 116.2 (CH), 120.9 (CH), 125.6 (C), 144.6 (C), 152.4 (C); MS (EI) m/z (rel inten) 367 ($M^+ + 4$, 16), 365 ($M^+ + 2$, 11), 363 (M^+ , 14), 310 (83), 308 (63), 306 (45), 252 (60), 250 (46), 248 (36), 196 (100), 194 (91), 192 (59), 123 (30). Anal. calcd for $\text{C}_{19}\text{H}_{35}\text{GeNO}$: C, 62.33; H, 9.64; N, 3.83. Found: C, 62.48; H, 9.66; N, 3.82.

3c

4'-Amino-3'-tributylgermylacetophenone (3c). oil; IR $\nu_{\max}$ (cm^{-1}) 3489 and 3366 (NH_2), 1579 (CO); ^1H NMR (400 MHz) δ 0.86-0.96 (9 H, m), 1.01-1.10 (6 H, m), 1.24-1.48 (12 H, m), 2.50 (3 H, s), 4.17 (2 H, br s, NH_2), 6.59 (1 H, d, $J = 8.4$ Hz), 7.77 (1 H, dd, $J_1 = 8.4$ Hz, $J_2 = 2.2$ Hz), 6.86 (1 H, d, $J = 2.2$ Hz), ^{13}C NMR (100 MHz) δ 12.8 (CH_2), 13.7 (CH_3), 17.6 (CH_3), 26.4 (CH_2), 27.3 (CH_2), 113.6 (CH), 121.9 (C), 127.6 (C), 131.0 (CH), 136.7 (CH), 155.5 (C), 196.7 (CO); MS (EI) m/z (rel inten) 379 ($M^+ + 4$, <1), 377 ($M^+ + 2$, <1), 375 (M^+ , <1), 322 (100), 320 (81), 318 (57), 264 (77), 262 (51), 260 (34), 208 (86), 206 (64), 204 (50), 135 (9). Anal. calcd for $\text{C}_{20}\text{H}_{35}\text{GeNO}$: C, 63.53; H, 9.64; N, 3.70. Found: C, 63.47; H, 9.63; N, 3.71.

4-Amino-3-tributylgermylbenzonitrile (3d). oil; IR $\nu_{\max}$ (cm^{-1}) 3494 and 3371 (NH_2), 2214 (CN); ^1H NMR (300 MHz) δ 0.79-0.96 (9 H, m), 0.98-1.09 (6 H, m), 1.20-1.48 (12 H, m), 4.16 (2 H, br s, NH_2), 6.6 (1 H, d, $J = 8.2$ Hz), 7.38 (1 H, dd, $J_1 = 8.2$ Hz, $J_2 = 1.9$ Hz), 7.42 (1 H, d, $J = 1.9$ Hz), ^{13}C NMR (75.45 MHz) δ 12.7 (CH_2), 13.7 (CH_3), 26.3 (CH_2), 27.2 (CH_2), 114.1 (CH), 117.8 (CN), 120.7 (C), 123.5 (C), 133.7 (CH), 139.6 (CH), 154.5 (C); MS (EI) m/z (rel inten) 305 [$(\text{M}^+ + 4) - 57$, 54], 303 [$(\text{M}^+ + 2) - 57$, 47], 301 [$(\text{M}^+ - 57)$, 31], 247 (47), 245 (42), 243 (18), 191 (100), 189 (67), 187 (42), 118 (45). Anal. calcd for $\text{C}_{19}\text{H}_{32}\text{GeN}_2$: C, 63.20; H, 8.93; N, 7.76. Found: C, 63.39; H, 8.92; N, 7.77.

3-Chloro-2-tributylgermylaniline (4f). oil; IR $\nu_{\max}$ (cm^{-1}) 3462 and 3392 (NH_2); ^1H NMR (400 MHz) δ 0.81-0.95 (9 H, m), 1.11-1.24 (6 H, m), 1.28-1.47 (12 H, m), 3.89 (2 H, br s, NH_2), 6.46 (1 H, dd, $J_1 = 7.9$ Hz, $J_2 = 1.1$ Hz), 6.72 (1 H, dd, $J_1 = 7.9$ Hz, $J_2 = 1.1$ Hz), 6.99 (1 H, t, $J = 7.9$ Hz), ^{13}C NMR (100 MHz) δ 13.71 (CH_2), 15.7 (CH_3), 26.4 (CH_2), 27.5 (CH_2), 113.6 (CH), 119.8 (CH), 121.8 (C), 130.2 (CH), 141.9 (C), 153.2 (C); MS (EI) m/z (rel inten) 316 [$(\text{M}^+ + 6) - 57$, 43], 314 [$(\text{M}^+ + 4) - 57$, 100], 312 [$(\text{M}^+ + 2) - 57$, 87], 310 ($\text{M}^+ - 57$, 47), 258 (42), 256 (49), 254 (35), 252 (18), 202 (43), 200 (48), 198 (27), 196 (16), 166 (63), 164 (73), 162 (51), 160 (14), 129 (23), 127 (59). Anal. calcd for $\text{C}_{18}\text{H}_{32}\text{ClGeN}$: C, 58.35; H, 8.71; N, 3.78. Found: C, 58.47; H, 8.69; N, 3.77.

3-Methoxy-2-tributylgermylaniline (4g). oil; IR $\nu_{\max}$ (cm^{-1}) 3485 and 3387 (NH_2); ^1H NMR (400 MHz) δ 0.86-0.94 (9 H, m), 1.01-1.08 (6 H, m), 1.25-1.46 (12 H, m), 3.71 (3 H, s), 3.78 (2 H, br s, NH_2), 6.24 (2 H, dq, $J_d = 8.0$ Hz, $J_q = 1.0$ Hz), 7.06 (1 H, t, $J = 8.0$ Hz); due to the very small isolated amounts the ^{13}C NMR spectrum was not recorded; MS (EI) m/z (rel inten) 367 ($\text{M}^+ + 4$, 3), 365 ($\text{M}^+ + 2$, 2), 363 (M^+ , 2), 310 (100), 308 (75), 306 (61), 252 (82), 250 (49), 248 (42), 196 (69), 194 (54), 192 (35), 166 (48), 164 (42), 162 (29), 123 (27). Anal. calcd for $\text{C}_{19}\text{H}_{35}\text{GeNO}$: C, 62.33; H, 9.64; N, 3.83. Found: C, 62.56; H, 9.62; N, 3.84.

5-Chloro-2-tributylgermylaniline (5f). oil; IR $\nu_{\max}$ (cm^{-1}) 3465 and 3345 (NH_2); ^1H NMR (400 MHz) δ 0.81-0.92 (9 H, m), 0.97-1.05 (6 H, m), 1.26-1.43 (12 H, m), 3.74 (2 H, br s, NH_2), 6.61 (1 H, d, $J = 2.0$ Hz), 6.71 (1 H, dd, $J_1 = 7.9$ Hz, $J_2 = 2.0$ Hz), 7.08 (1 H, d, $J = 7.9$ Hz), ^{13}C NMR (100 MHz)

δ 12.9 (CH_2), 13.7 (CH_3), 26.4 (CH_2), 27.3 (CH_2), 114.6 (CH), 118.3 (CH), 121.3 (C), 136.2 (CH), 139.2 (C), 152.1 (C); MS (EI) m/z (rel inten) 316 [$(\text{M}^+ + 6) - 57$, 33], 314 [$(\text{M}^+ + 4) - 57$, 79], 312 [$(\text{M}^+ + 2) - 57$, 49], 310 ($\text{M}^+ - 57$, 32), 258 (27), 256 (59), 254 (42), 252 (20), 202 (58), 200 (100), 198 (73), 196 (43), 129 (10), 127 (23). Anal. calcd for $\text{C}_{18}\text{H}_{32}\text{ClGeN}$: C, 58.35; H, 8.71; N, 3.78. Found: C, 58.57; H, 8.70; N, 3.76.

5-Methoxy-2-tributylgermylaniline (5g). oil; IR $\nu_{\max}$ (cm^{-1}) 3425 and 3375 (NH_2); ^1H NMR (400 MHz) δ 0.84-0.92 (9 H, m), 0.96-1.02 (6 H, m), 1.28-1.42 (12 H, m), 3.69 (2 H, br s, NH_2), 3.76 (3 H, s), 6.19 (1 H, d, $J = 2.3$ Hz), 6.34 (1 H, dd, $J_1 = 8.2$ Hz, $J_2 = 2.3$ Hz), 7.08 (1 H, d, $J = 8.2$ Hz);

due to the very small isolated amounts the ^{13}C NMR spectrum was not recorded; MS (EI) m/z (rel inten) 367 ($\text{M}^+ + 4$, 3), 365 ($\text{M}^+ + 2$, 2), 363 (M^+ , 1), 310 (64), 308 (61), 306 (49), 252 (62), 250 (45), 248 (28), 196 (100), 194 (75), 192 (56), 123 (29). Anal. calcd for $\text{C}_{19}\text{H}_{35}\text{GeNO}$: C, 62.33; H, 9.64; N, 3.83. Found: C, 62.47; H, 9.62; N, 3.84.

6-Methyl-2-tributylgermylaniline (6i). oil; IR $\nu_{\max}$ (cm^{-1}) 3481 and 3398 (NH_2); ^1H NMR (300 MHz) δ 0.88 (9 H, t, $J = 7.1$ Hz), 0.98-1.08 (6 H, m), 1.25-1.45 (12 H, m), 2.16 (3 H, s), 3.67 (2 H, br s, NH_2), 6.70 (1 H, t, $J = 7.40$ Hz), 7.00-7.12 (2 H, m), ^{13}C NMR (75.45 MHz) δ 13.1 (CH_2), 13.7

(CH_3), 18.0 (CH_3), 26.5 (CH_2), 27.4 (CH_2), 118.2 (CH), 121.5 (C), 122.6 (C), 130.9 (CH), 133.0 (CH), 149.0 (C); MS (EI) m/z (rel inten) 351 ($\text{M}^+ + 4$, 7), 349 ($\text{M}^+ + 2$, 5), 347 (M^+ , 3), 294 (79), 292 (66), 290 (50), 236 (44), 234 (34), 232 (20), 180 (100), 178 (85), 176 (58), 106 (29). Anal. calcd for $\text{C}_{19}\text{H}_{35}\text{GeN}$: C, 65.18; H, 10.08; N, 4.00. Found: C, 65.37; H, 10.06; N, 3.99.

6-Methoxy-2-tributylgermylaniline (6j). oil; IR $\nu_{\max}$ (cm^{-1}) 3477 and 3387 (NH_2); ^1H NMR (300 MHz) δ 0.88 (9 H, t, $J = 7.1$ Hz), 0.97-1.10 (6 H, m), 1.25-1.44 (12 H, m), 3.84 (3 H, s), 3.89 (2 H, br s, NH_2), 6.69-6.80

(2 H, m), 6.82 (1 H, dd, $J_1 = 7.0$ Hz, $J_2 = 1.9$ Hz); ^{13}C NMR (75.45 MHz) δ 13.0 (CH_2), 13.7 (CH_3), 26.5 (CH_2), 27.4 (CH_2), 55.3 (CH_3), 110.4 (CH), 117.9 (CH), 123.2 (C), 126.7 (CH), 140.4 (C), 146.7 (C); MS (EI) m/z (rel inten) 367 ($\text{M}^+ + 4$, 14), 365 ($\text{M}^+ + 2$, 9), 363 (M^+ , 8), 310 (100), 308 (75), 306 (61), 252 (66), 250 (50), 248 (44), 196 (98), 194 (77), 192 (52), 123 (14). Anal. calcd for $\text{C}_{19}\text{H}_{35}\text{GeNO}$: C, 62.33; H, 9.64; N, 3.83. Found: C, 62.56; H, 9.61; N, 3.84.

3-Tributylgermyl[1,1'-biphenyl]-2,2'-diamine (6k). oil; IR ν_{max} (cm^{-1}) 3469 and 3377 (NH_2); ^1H NMR (400 MHz) δ 0.78-0.97 (9 H, t, $J = 7.00$ Hz), 0.99-1.11 (6 H, m), 1.23-1.47 (12 H, m), 6.78 (1 H, dd, $J_1 = 8.0$ Hz, $J_2 = 1.1$ Hz), 6.78 (1 H, dd, $J_1 = 7.3$ Hz, $J_2 = 1.7$ Hz), 6.80-6.86 (2H, m), 7.09 (1H, dd, $J_1 = 7.3$ Hz, $J_2 = 1.7$ Hz), 7.11-7.20 (2H, m), 7.23 (1H, dd, $J_1 = 7.3$ Hz, $J_2 = 1.7$ Hz), ^{13}C NMR (100 MHz) δ 13.1 (CH_2), 13.7 (CH_3), 26.5 (CH_2), 27.4 (CH_2), 115.5 (CH), 118.4 (CH), 118.8 (CH), 123.6 (C), 124.0 (C), 125.1 (C), 128.7 (CH), 131.1 (CH), 131.4 (CH), 134.8 (CH), 144.1 (C), 148.4 (C); MS (ESI) (rel inten) 451 [$(\text{M} + 4) + \text{Na}$] $^+$ (25), 449 [$(\text{M} + 2) + \text{Na}$] $^+$ (15), 447 ($\text{M} + \text{Na}$) $^+$ (11), 429 [$(\text{M} + 4) + 1$] $^+$ (100), 427 [$(\text{M} + 2) + 1$] $^+$ (79), 425 ($\text{M} + 1$) $^+$ (54), 371 (23), 369 (18), 367 (13), 245 (21), 243 (16), 241 (12), 189 (52), 187 (36), 185 (33). Anal. calcd for $\text{C}_{24}\text{H}_{38}\text{GeN}_2$: C, 67.48; H, 8.97; N, 6.56. Found: C, 67.62; H, 8.96; N, 6.54.

6-Fluoro-2-tributylgermylaniline (6l). oil; IR ν_{max} (cm^{-1}) 3482 and 3396 (NH_2); ^1H NMR (400 MHz) δ 0.82-0.94 (9 H, m), 0.9-1.10 (6 H, m), 1.26-1.44 (12 H, m), 3.76 (2 H, br s, NH_2), 6.68 (1 H, ddd, $J_1 = 8.0$ Hz, $J_2 = 7.3$ Hz, $J_{3(\text{H-F})} = 4.6$ Hz, H-4), 6.91-6.98 (2 H, m, H-3, H-5); ^{13}C NMR (100 MHz) δ 13.0 (CH_2), 13.7 (CH_3), 26.5 (CH_2), 27.3 (CH_2), 115.1 (CH, d, $J = 19.1$ Hz), 118.3 (CH, d, $J = 6.1$ Hz), 126.4 (C, s), 130.0 (CH, d, $J = 4.0$ Hz), 138.6 (C, d, $J = 9.7$ Hz), 151.6 (C, d, $J = 242$ Hz). MS (ESI) (rel inten) 378 [$(\text{M} + 4) + \text{Na}$] $^+$ (35), 376 [$(\text{M} + 2) + \text{Na}$] $^+$ (29), 374 ($\text{M} + \text{Na}$) $^+$ (10), 356 [$(\text{M} + 4) + 1$] $^+$ (100), 354 [$(\text{M} + 2) + 1$] $^+$ (92), 352 ($\text{M} + 1$) $^+$ (73). Anal. calcd for $\text{C}_{18}\text{H}_{32}\text{FGeN}$: C, 61.06; H, 9.11; N, 3.96. Found: C, 61.24; H, 9.09; N, 3.97.

6-Chloro-2-tributylgermylaniline (6m). oil; IR ν_{max} (cm^{-1}) 3486 and 3393 (NH_2); ^1H NMR (400 MHz) δ 0.83-0.96 (9 H, m), 0.97-1.10 (6 H, m), 1.22-1.42 (12 H, m), 4.13 (2 H, br s, NH_2), 6.67 (1 H, t, $J = 7.6$ Hz), 7.08 (1 H, d,

$J = 7.8$ Hz), 7.22 (1H, d, $J = 7.3$ Hz), ^{13}C NMR (100 MHz) δ 13.0 (CH_2), 13.7 (CH_3), 26.4 (CH_2), 27.2 (CH_2), 118.7 (CH), 119.4 (C), 124.9 (C), 129.5 (CH), 133.4 (CH), 139.1 (C), 146.6 (C); MS (EI) m/z (rel inten) 373 ($\text{M}^+ + 6$, <1), 371 ($\text{M}^+ + 4$, <1), 369 (M^+ , <1), 316 (39), 314 (87), 312 (72), 310 (44), 258 (43), 256 (63), 254 (43), 252 (28), 202 (47), 200 (100), 198 (61), 196 (44), 166 (9), 164 (33), 162 (25), 160 (18), 129 (7), 127 (14). Anal. calcd for $\text{C}_{18}\text{H}_{32}\text{ClGeN}$: C, 58.35; H, 8.71; N, 3.78. Found: C, 58.40; H, 8.70; N, 3.77.

2'-Amino-3'-tributylgermylacetophenone (6o). oil; IR ν_{max} (cm^{-1}) 3496 and 3317 (NH_2); ^1H NMR (400 MHz) δ 0.88 (9 H, t, $J = 7.1$ Hz), 1.00-1.09 (6 H, m), 1.28-1.42 (12 H, m), 2.58 (3 H, s), 6.56 (2 H, br s, NH_2), 6.64 (1 H, dd, $J_1 = 8.1$ Hz, $J_2 = 7.0$ Hz), 7.32 (1 H, dd, $J_1 = 7.0$ Hz, $J_2 =$

1.5 Hz), 7.72 (1 H, dd, $J_1 = 8.1$ Hz, $J_2 = 1.5$ Hz), ^{13}C NMR (100 MHz) δ 13.0 (CH_2), 13.7 (CH_3), 26.4 (CH_2), 27.3 (CH_2), 28.1 (CH_3), 115.5 (CH), 117.2 (C), 125.7 (C), 132.7 (CH), 140.9 (CH), 154.5 (C), 201.3 (CO). MS (EI) m/z (rel inten) 379 ($\text{M}^+ + 4$, 10), 377 ($\text{M}^+ + 2$, 4), 375 (M^+ , 4), 322 (100), 320 (79), 318 (61), 264 (41), 262 (32), 260 (29), 208 (68), 206 (56), 204 (40), 135 (7). Anal. calcd for $\text{C}_{20}\text{H}_{35}\text{GeNO}$: C, 63.53; H, 9.33; N, 3.70. Found: C, 63.68; H, 9.30; N, 3.71.

The germylanilines **4h** and **5h** were obtained in very small amounts as an unresolved oily mixture and were characterized by GC-MS analysis (starting T: 80 °C [3']; rate: 15 °C / min; final T: 270 °C). The identification was based on spectral analogies with

other germyl compounds. 1st isomer (22.3'): MS (EI) m/z (rel inten) 322 [$(\text{M}^+ + 4) - 57$, 84], 320 [$(\text{M}^+ + 2) - 57$, 70], 318 ($\text{M}^+ - 57$, 48], 208 (48), 206 (33), 204 (25), 135 (47). 2nd isomer (24.5'): 322 [$(\text{M}^+ + 4) - 57$, 48], 320 [$(\text{M}^+ + 2) - 57$, 43], 318 ($\text{M}^+ - 57$, 33], 264 (31), 262 (26), 260 (16), 208 (66), 206 (49), 204 (31), 135 (16). Anal. calcd for $\text{C}_{20}\text{H}_{35}\text{GeNO}$ (mixture of isomers): C, 63.53; H, 9.33; N, 3.70. Found: C, 63.37; H, 9.31; N, 3.71.