Supplementary Material

Reduction of hydrazines to amines with low-valent titanium reagent

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Preparation of hydrazines

Monosubstituted arylhydrazines were prepared from corresponding amines.[1] *N*-Alkyl-*N*-arylhydrazines were prepared from corresponding monosubstituted arylhydrazines.[2] *N*,*N*-Diarylhydrazines[3] and *N*,*N*-dialkylhydrazines[4] were prepared from corresponding secondary amines. *N*-Acyl-*N*-arylhydrazines were prepared from corresponding *N*-arylamines.[5]

General procedure for the preparation of monosubstituted arylhydrazines.[1]

To the mixture of amine (20 mmol) and conc. HCl (15 mL) cooled in an ice-bath was added an aqueous solution of $NaNO_2$ (25%, 5.6 g) slowly. After cooling to -20 ºC, a mixture of $SnCl_2$ (40 mmol) and conc. HCl (10 mL) was added dropwise. After 4 h, the reaction mixture was filtered. The residues were dissolved in aqueous KOH (25%), exacted with ether (3 × 20 mL). The extracts were combined and dried. The volatiles were removed to give corresponding hydrazines.

General procedure for the preparation of *N*-alkyl-*N*-arylhydrazines.[2]

An oven-dried flask was charged with sodium amide (0.43 g, 11 mmol), evacuated, backfilled with argon and then THF (50 mL) was added. The reaction mixture was cooled to 0 ºC, then arylhydrazines (10 mmol) in THF (50 mL) was added dropwise and the resulting mixture was allowed to warm up to room temperature. The reaction mixture was stirred for 6 h at room temperature and turned brown. Methyl iodide (10 mmol) was added at 0 ºC and the reaction mixture was stirred for additional 2 h. Then H_2O (20 mL) was added to remove superfluous sodium amide. To the resulting mixture was extracted with CH_2Cl_2 three times. The extracts were dried over $MgSO_4$. After removal of the solvent, the residue was purified by column chromatography on silica.

General procedure for the preparation of *N*,*N*-diarylhydrazines.[3]

To a mixture of CH_2Cl_2 and Et_2O (250 mL, 4:1 v/v), was added $TiCl_4$ (6.6 mL, 0.06 mol) slowly with stirring to give a yellow complex. Mg powder (1.5 g, 0.06 mol) was added under argon. The mixture was stirred for 2.5 h at room temperature to give a black solution. Then an ethereal solution of *N*-nitrosodiarylamine (0.015 mol) was added to the solution at room temperature with stirring. After 30 min, the reaction was quenched with dil. HCl and the mixture was stirred for 1 h. The resulting solution was made alkaline by addition of NaOH and extracted with Et_2O to give *N*,*N*-diarylhydrazine.

General procedure for the preparation of *N*,*N*-dialkylhydrazines.[4]

N-Nitrosodialkylamine (10 mmol) were dissolved in EtOH (10 mL) under argon. Then aqueous solution of titanium trichloride (40 mmol) was added and the mixture was stirred for 1 h at room temperature. The mixture was basified to pH > 10 by adding aqueous NaOH (20%) dropwise under ice-bath extracted with CH_2Cl_2 repeatedly. The extracts were combined and dried, and the volatiles were removed. The residue was purified by column chromatography on silica to obtain *N*,*N*-dialkylhydrazines .

Procedure for the preparation of other types of substituted hydrazines.

These hydrazines were prepared following the procedures reported in references 6-15.

Characterization data of products

Aniline (1a). Analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.13−7.16 (m, 2H), 6.75 (t, *J* 7.2 Hz, 1H), 6.65 (d, *J* 7.2 Hz, 2H), 3.51 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 149.1, 129.6, 117.6, 115.1; GC−MS (EI, *m/z*): 93 [M^+], identical with commercial sample.

2-Naphthylamine (2a). White solid, mp 112−114 °C (lit.[16] 113−114 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.70 (d, *J* 8.4 Hz, 1H), 7.67 (d, *J* 8.4 Hz, 1H), 7.61 (d, *J* 8.0 Hz, 1H), 7.38 (t, *J* 7.2 Hz, 1H), 7.25 (t, *J* 6.8 Hz, 1H), 7.00 (s, 1H), 6.97 (dd, *J* 8.8 Hz, 2.0 Hz, 1H), 3.85 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 144.1, 135.0, 129.2, 128.0, 127.7, 126.3, 125.7, 122.5, 118.3, 108.5; GC−MS (EI, *m/z*): 143 [M^+].

2-Methoxyanline (3a). Yellow oil, bp 105-106 °C/15 mmHg (lit.[17] 103-104 °C/12 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 6.82 (d, *J* 6.8 Hz, 2H), 6.76 (t, *J* 7.2 Hz, 2H), 3.87 (s, 3H), 3.76 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 147.2, 136.2, 121.1, 118.3, 115.0, 110.3, 55.4; GC−MS (EI, *m/z*): 123 [M^+].

4-Choloroanline (4a). Analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.11 (d, *J* 8.4 Hz, 2H), 6.62 (d, *J* 8.4 Hz, 2H), 3.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 145.0, 129.2, 122.9, 116.4; GC−MS (EI, *m/z*): 127 [M^+], identical with commercial sample.

4-Aminobenzoic acid ethyl ester (5a). Colorless solid. mp 88-89 °C (lit.[18] 88-90 °C), ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.86 (d, *J* 8.4 Hz, 2H), 6.64 (d, *J* 8.4 Hz, 2H), 4.31 (q, *J* 7.2 Hz, 2H), 4.06 (s, 2H), 1.36 (t, *J* 7.2 Hz, 3H); MS (ESI, *m/z*): 165 [M^+].

Cyclohexanamine (6a). Colorless oil, bp 130−131 °C (lit.[19] 132−134 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 2.61−2.67 (m, 1H), 1.82 (d, *J* 12.4 Hz, 2H), 1.57−1.72 (m, 5H), 1.20−1.31 (m, 2H), 1.13−1.17 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 50.3, 36.6, 25.5, 24.9; GC−MS (EI, *m/z*): 99 [M^+].

Piperidine (7a). Analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 2.78 (s, 4H), 2.19 (s, 2H), 1.52 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 47.1, 26.7, 24.8; GC−MS (EI, *m/z*): 85 [M^+], identical with commercial sample.

***N,N*-Diisobutylamine (8a).** Colorless oil, bp 135−136 °C (lit.[20] 137−138 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 2.38 (d, *J* 6.8 Hz, 4H), 1.71−1.78 (m, 2H), 1.32 (brs, 1H), 0.98 (d, *J* 6.8 Hz, 12H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 58.0, 28.1, 20.6. GC−MS (EI, *m/z*): 129 [M^+].

***N,N*-Dicyclohexylamine (9a).** Analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 2.54 (t, *J* 10.8 Hz, 2H), 1.57−1.85 (m, 11H), 0.96−1.27 (m, 11H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 52.9, 34.1, 26.1, 25.2; GC−MS (EI, *m/z*): 181 [M^+], identical with commercial sample.

***N*-Cyclohexylaniline (10a).** Colorless oil, bp 137-139 °C/10 mmHg (lit.[21] 139-141 °C/10 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.11−7.16 (m, 2H), 6.65−6.67 (m, 1H), 6.58−6.61 (m, 2H), 3.54 (brs, 1H), 3.22−3.29 (m, 1H), 2.04−2.08 (m, 2H), 1.73−1.77 (m, 2H), 1.62−1.66 (m, 1H), 1.35−1.42 (m, 2H), 1.27−1.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 147.4, 129.3, 116.8, 113.2, 51.6, 33.5, 26.0, 25.1; GC−MS (EI, *m/z*): 175 [M+].

***N*-Allylaniline (11a).** Colorless oil, bp 105−108 °C/15 mmHg (lit.[22] 102−110 °C/15 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.18 (t, *J* 7.6 Hz, 2H), 6.73 (t, *J* 7.6 Hz, 1H), 6.65 (d, *J* 7.6 Hz, 2H), 5.92−6.01 (m, 1H), 5.29 (dd, *J* 17.2 Hz, 1.6 Hz, 1H), 5.16 (dd, *J* 10.4 Hz, 1.2 Hz, 1H), 4.04 (brs, 1H), 3.79 (d, *J* 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 147.8, 135.2, 128.7, 117.1, 115.6, 112.6, 46.3; GC−MS (EI, *m/z*):

133 [M^+].

***N*-Benzylaniline (12a).** Colorless oil, bp 165−169 °C/10 mmHg (lit.[23] 169−172 °C/10 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.31−7.38 (m, 4H), 7.27 (d, *J* 7.2 Hz, 1H), 7.18 (t, *J* 7.6 Hz, 2H), 6.72 (t, *J* 7.2 Hz, 1H), 6.65 (d, *J* 8.0 Hz, 2H), 4.45 (brs, 1H), 4.33 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 148.1, 139.5, 129.4, 128.7, 127.7, 127.3, 117.7, 112.9, 48.5; GC−MS (EI, *m/z*): 183 [M+].

***N*-Heptylaniline (13a).** Colorless oil, bp 160−162 °C/20 mmHg (lit.[24] 160−161 °C/20 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.18 (t, *J* 8.0 Hz, 2H), 6.69 (t, *J* 7.2 Hz, 1H), 6.61 (d, *J* 8.0 Hz, 2H), 3.61 (brs, 1H), 3.11 (t, *J* 7.2 Hz, 2H), 1.57−1.65 (m, 2H), 1.26−1.44 (m, 8H), 0.89 (t, *J* 6.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 148.7, 129.4, 117.2, 112.9, 44.1, 32.0, 29.8, 29.4, 27.4, 22.8, 14.4; GC−MS (EI, *m/z*): 191 [M^+].

***N*-Methyl-*N*-(2-naphthyl)amine (14a).** Colorless oil, bp 180−185 °C/20 mmHg (lit.[25] 180 °C/25 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.71−7.80 (m, 3H), 7.49 (t, *J* 7.2 Hz, 1H), 7.33 (t, *J* 7.2 Hz, 1H), 6.92 (d, *J* 8.8 Hz, 1H), 6.88 (s, 1H), 3.82 (brs, 1H), 2.97 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 147.2, 135.5, 128.9, 127.9, 127.6, 126.6, 126.1, 122.1, 118.1, 103.8, 30.7; GC−MS (EI, *m/z*): 157 [M+].

Diphenylamine (15a). White solid, mp 53−54 °C (lit.[26] 52−54 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.25−7.29 (m, 4H), 7.08 (d, *J* 7.6 Hz, 4H), 6.92 (t, *J* 7.2 Hz, 2H), 5.72 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 143.4, 129.5, 121.2, 118.1; GC−MS (EI, *m/z*): 169 [M+].

4-Methylaniline (17a). Analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.01 (d, *J* = 7.6 Hz, 2H), 6.52 (d, *J* = 7.6 Hz, 2H), 6.18 (s, 2H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 142.3, 131.1, 130.6, 116.1, 20.5; GC−MS (EI, m/z): 107 [M+], identical with commercial sample.

Benzylamine (18b). Analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.25−7.30 (m, 3H), 7.16−7.21 (m, 2H), 3.73 (s, 2H), 1.73 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 143.3, 128.4, 127.1, 126.6, 46.5; GC−MS (EI, m/z): 107 [M+], identical with commercial sample.

***N*-Methylaniline (19a).** Analyzed by ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.17 (t, *J* 7.2 Hz, 2H), 6.70 (t, *J* 7.2 Hz, 1H), 6.61 (d, *J* 8.0 Hz, 2H), 3.57 (brs, 1H), 2.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 149.3, 129.3, 117.2, 112.5, 30.7; GC−MS (EI, *m/z*): 107 [M^+], identical with commercial sample.

Benzamide (23a). White solid, mp 125−126 °C (lit.[27] 125−128 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.81 (d, *J* 7.6 Hz, 2H), 7.52 (t, *J* 7.6 Hz, 1H), 7.45 (t, *J* 8.0 Hz, 1H), 6.12 (brs, 1H), 5.93 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 169.3, 135.0, 132.0, 128.8, 128.2; GC-MS (EI, *m/z*): 121 [M^+].

Acetamide (24b). White solid, mp 78−80 °C (lit.[28] 78−80 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 5.79−6.01 (br, 2H), 2.01 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 171.5, 15.6; GC−MS (EI, *m/z*): 59 [M^+].

Benzyl carbamate (26b). White solid, mp 87−89 °C (lit.[29] 86−89 °C); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ (ppm): 7.33−7.38 (m, 5H), 5.12 (s, 2H), 4.78 (brs, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS) δ (ppm): 157.3, 136.2, 128.5, 128.3, 128.2, 67.2; GC−MS (EI, *m/z*): 151 [M^+].

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