

Supplementary Material

Reduction of hydrazines to amines with low-valent titanium reagent

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Contents	page
Preparation of hydrazines	S2
Characterization data of products	S3-S4
References	S5

Preparation of hydrazines

Monosubstituted arylhydrazines were prepared from corresponding amines.¹ *N*-Alkyl-*N*-arylhydrazines were prepared from corresponding monosubstituted arylhydrazines.² *N,N*-Diarylhydrazines³ and *N,N*-dialkylhydrazines⁴ 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 NaNO₂ (25%, 5.6 g) slowly. After cooling to -20 °C, a mixture of SnCl₂ (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%), extracted 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 °C, 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 °C and the reaction mixture was stirred for additional 2 h. Then H₂O (20 mL) was added to remove superfluous sodium amide. To the resulting mixture was extracted with CH₂Cl₂ three times. The extracts were dried over MgSO₄. 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 CH₂Cl₂ and Et₂O (250 mL, 4:1 v/v), was added TiCl₄ (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*-nitrosodialkylamine (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 Et₂O 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 CH₂Cl₂ 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 ^1H 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); ^1H 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-Methoxyaniline (3a). Yellow oil, bp 105–106 °C/15 mmHg (lit.¹⁷ 103–104 °C/12 mmHg); ^1H 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-Choloroaniline (4a). Analyzed by ^1H 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), ^1H 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); ^1H 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 ^1H 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); ^1H 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 ^1H 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); ^1H 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); ^1H 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); ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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); ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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); ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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); ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 143.4, 129.5, 121.2, 118.1; GC–MS (EI, *m/z*): 169 [M⁺].

4-Methylaniline (17a). Analyzed by ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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 ¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm): 7.25–7.30 (m, 3H), 7.16–7.21 (m, 2H), 3.73 (s, 2H), 1.73 (s, 2H); ¹³C NMR (100 MHz, CDCl₃, 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 ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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); ¹H NMR (400 MHz, CDCl₃, 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); ¹³C NMR (100 MHz, CDCl₃, 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); ¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm): 5.79–6.01 (br, 2H), 2.01 (s, 3H). ¹³C NMR (100 MHz, CDCl₃, 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); ¹H NMR (400 MHz, CDCl₃, TMS) δ (ppm): 7.33–7.38 (m, 5H), 5.12 (s, 2H), 4.78 (brs, 2H); ¹³C NMR (100 MHz, CDCl₃, 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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