SUPPORTING INFORMATION

Synthesis of Mono- and Symmetrical Di- *N*- Hydroxy- and *N*-Amino- Guanidines.

Alan R. Katritzky, * Niveen M. Khashab, Sergey Bobrov and Megumi Yoshioka

Center for Heterocyclic Compounds, University of Florida, Department of Chemistry,

Gainesville, Florida 32611-7200, USA

e-mail: Katritzky@chem.ufl.edu

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General. Melting points were determined on a hot-stage apparatus and are uncorrected. NMR spectra were recorded in CDCl_3 , or $\text{DMSO}-d_6$ with TMS as the internal standard for ^1H (300 MHz) or a solvent as the internal standard for ^{13}C NMR (75 MHz). Column chromatography was conducted on silica gel (200–425 mesh) or on basic alumina (60–325 mesh). Microwave heating was carried out with a single-mode cavity Discover Microwave Synthesizer (CEM Corporation, NC).

***N'*-Isopropyl-*N*-hydroxy-*N*-methyl-*N''*-(4-methylphenyl)guanidine (13b).** oil (72%); ^1H NMR δ 7.08 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 8.0 Hz, 2H), 6.68 (br s, 1H), 4.87 (d, J = 8.1 Hz, 1H), 3.94–3.87 (m, 1H), 2.22 (s, 3H), 1.68 (br s, 1H), 1.06 (d, J = 6.3 Hz, 6H); ^{13}C NMR δ 155.6, 136.1, 129.7, 128.7, 121.4, 42.0, 23.2, 20.8. Anal. Calcd for $\text{C}_{11}\text{H}_{17}\text{N}_3\text{O}$: C, 69.54; H, 10.21; N, 20.27. Found: C, 69.86; H, 10.22; N, 20.14.

***N*-(4-Chlorophenyl)-*N'*-cyclohexyl-*N''*-hydroxyguanidine (13c).** oil (56%); ^1H NMR δ 7.38 (d, J = 8.6 Hz, 2H), 7.16 (d, J = 8.6 Hz, 2H), 3.66–3.65 (m, 3H), 2.00–1.96 (m, 2H), 1.79–1.70 (m, 2H), 1.62–1.50 (m, 2H), 1.43–1.26 (m, 5H); ^{13}C NMR δ 129.1, 128.9, 120.8, 116.2, 33.9, 33.6, 32.2, 25.5, 24.8, 24.3. Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{ClN}_3\text{O}$: C, 58.31; H, 6.78. Found: C, 58.26; H, 6.47.

***N*-Butyl-*N*-hydroxy-*N''*-mesitylguanidine (13d).** oil (87%); ^1H NMR δ 6.86 (s, 2H), 5.67 (br s, 1H), 4.20 (br s, 1H), 4.19 (br s, 1H), 3.10 (q, J = 6.7 Hz, 2H), 2.22 (s, 3H), 2.17 (s, 6H), 1.36–1.28 (m, 2H), 1.25–1.15 (m, 2H), 0.80 (t, J = 7.1 Hz, 3H); ^{13}C NMR δ 157.1, 137.7, 137.1, 131.2, 129.4, 39.9, 32.5, 20.9, 19.9, 18.1, 13.8. Anal. Calcd for $\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}$: C, 66.43; H, 9.30; N, 11.55. Found: C, 66.22; H, 9.25; N, 11.29.

***N''*-Benzoyl-*N,N*-diethyl-*N'*-hydroxyguanidine (13e).** oil (71%); ^1H NMR δ 7.77–7.56 (m, 5H), 3.15 (q, $J = 7.4$ Hz, 2H), 3.04 (q, $J = 7.4$ Hz, 2H), 1.48 (t, $J = 7.3$ Hz, 3H), 1.42 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR δ 168.2, 143.5, 134.2, 131.5, 128.5, 127.0, 36.2, 29.8. Anal. Calcd for $\text{C}_{12}\text{H}_{17}\text{N}_3\text{O}_2$: C, 61.26; H, 7.28. Found: C, 61.28; H, 7.55.

***N*-[(*E*)-(Hydroxyamino)(morpholino)methylidene]benzamide (13f).** oil (74%); ^1H NMR δ 8.12–8.09 (m, 2H), 7.61–7.54 (m, 3H), 3.88–3.84 (m, 4H), 3.58–3.55 (m, 4H), 1.73 (br s, 1H); ^{13}C NMR δ 159.9, 146.0, 132.5, 129.3, 128.9, 127.9, 66.2, 46.3. Anal. Calcd for $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_3$: C, 57.42; H, 6.07; N, 18.86. Found: C, 57.12; H, 6.08; N, 18.53.

***N''*-(Benzyloxy)-*N*-isopropyl-*N'*-(4-methylphenyl)guanidine (13g).** Oil (41%); ^1H NMR δ 7.31–7.26 (m, 5H), 6.96 (d, $J = 8.3$ Hz, 2H), 6.82 (d, $J = 8.3$ Hz, 2H), 4.83 (s, 2H), 3.45 (br s, 1H), 2.19 (s, 3H), 0.98 (d, $J = 6.3$ Hz, 6H); ^{13}C NMR δ 152.4, 138.0, 129.7, 128.5, 128.4, 128.3, 128.1, 127.9, 127.6, 75.4, 23.1, 43.5, 20.6. Anal. Calcd for $\text{C}_{18}\text{H}_{23}\text{N}_3\text{O}$: C, 72.70; H, 7.80. Found: C, 72.60; H, 7.66.

***N*-Benzyl-*N*-methoxyguanidinehydrochloride (13h).** oil (67%); ^1H NMR δ 7.27–7.18 (m, 5H), 5.17 (br s, 2H), 3.60 (s, 2H), 2.08 (s, 3H); ^{13}C NMR δ 147.61, 128.9, 128.7, 127.6, 126.2, 48.2, 30.9. Anal. Calcd for $\text{C}_9\text{H}_{14}\text{ClN}_3\text{O}$: C, 50.12; H, 6.54; N, 10.48. Found: C, 50.02; H, 6.94; N, 10.21.

***N'*-Benzyl-*N*-hydroxy-*N*-methyl-*N''*-(4-methylphenyl)guanidine (13i).** oil (53%); ^1H NMR δ 7.68 (br s, 1H), 7.33–7.26 (m, 5H), 7.20 (d, $J = 8.1$ Hz, 2H), 7.09 (d, $J = 7.3$ Hz, 2H), 6.18 (brs, 1H), 4.87 (d, $J = 5.4$ Hz, 2H), 2.33 (s, 3H), 1.61 (br s, 3H); ^{13}C NMR δ

137.8, 137.3, 132.9, 130.9, 128.8, 127.7, 127.6, 125.6, 49.5, 21.0. Anal. Calcd for $C_{16}H_{19}N_3O$: C, 71.35; H, 7.08; N, 13.60. Found: C, 71.20; H, 7.90; N, 13.55.

***N'*-Butyl-*N*-methoxy-*N*-methylguanidine (13j).** oil (22%); 1H NMR δ 6.92 (br s, 2H), 3.62 (s, 3H), 3.25 (t, $J = 7.1$ Hz, 2H), 3.20 (s, 3H), 1.60–1.52 (m, 2H), 1.36–1.29 (m, 2H), 0.88 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR δ 152.6, 31.6, 31.2, 29.7, 22.6, 19.9, 14.1. HRMS (EI) Calcd for $C_7H_{17}N_3O$ ($M+1$): 160.1444. Found: 160.1445.

***N*-Butyl-2-(4-methoxyphenyl)-1-hydrazinecarboximidamide (14b).** oil (91%); 1H NMR δ 7.73 (d, $J = 9.1$ Hz, 2H), 6.97 (d, $J = 9.1$ Hz, 2H), 3.88–3.81 (m, 5H), 2.17 (s, 1H), 1.57 (s, 3H), 1.32–1.26 (m, 4H), 0.88 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR δ 145.0, 129.3, 124.2, 114.0, 113.7, 55.4, 54.9, 30.7, 21.8, 14.0. Anal. Calcd for $C_{12}H_{20}N_4O$: C, 60.99; H, 8.53; N, 23.71. Found: C, 61.39; H, 7.22; N, 23.64.

***N*-Benzyl-2,2-dimethyl-*N'*-(4-methylphenyl)-1-hydrazinecarboximidamide (14d).** oil (82%); 1H NMR δ 7.34–7.26 (m, 5H), 7.07 (d, $J = 8.1$ Hz, 2H), 6.72 (d, $J = 8.1$ Hz, 2H), 4.33 (s, 2H), 2.80 (s, 6H), 2.26 (s, 3H); ^{13}C NMR δ 157.6, 138.2, 129.9, 128.7, 127.5, 127.3, 124.3, 121.8, 115.4, 49.8, 48.7, 39.4. Anal. Calcd for $C_{17}H_{22}N_4$: C, 72.31; H, 7.85; N, 19.84. Found: C, 72.05; H, 7.89; N, 19.48.

Ethyl-4-[(butylamino)(2,2-dimethylhydrazino)methylene]amino}benzoate (14e). oil (84%); 1H NMR δ 7.85 (d, $J = 8.4$ Hz, 2H), 6.84 (d, $J = 8.4$ Hz, 2H), 5.60 (br s, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 3.25–3.20 (m, 2H), 2.37 (s, 6H), 1.57–1.45 (m, 2H), 1.35–1.28 (m, 5H), 0.89 (t, $J = 7.4$ Hz, 3H); ^{13}C NMR δ 166.8, 154.5, 150.1, 131.5, 130.9, 122.9, 60.4,

47.9, 40.6, 31.8, 20.2, 14.4, 13.9. Anal. Calcd for $C_{16}H_{26}N_4O_2$: C, 62.72; H, 8.55; N, 16.28. Found: C, 62.90; H, 8.65; N, 16.00.

***N*-(2,2-Dimethylhydrazino)(morpholino)methylene]benzamide (14f).** oil (84%); 1H NMR δ 8.1–8.06 (m, 2H), 7.37–7.31 (m, 3H), 4.72 (s, 1H), 3.86–3.83 (m, 4H), 3.72–3.68 (m, 4H), 2.50 (s, 6H); ^{13}C NMR δ 176.3, 161.0, 138.4, 131.1, 129.0, 127.8, 66.9, 48.0, 47.6. Anal. Calcd for $C_{14}H_{20}N_4O_2$: C, 61.25; H, 7.29; N, 19.17. Found: C, 61.59; H, 7.57; N, 19.20.

***N*-Butyl-2-methyl-2-phenyl-1-hydrazinecarboximidamide (14g).** oil (85%); 1H NMR δ 7.29–7.24 (m, 2H), 7.02–6.99 (m, 2H), 6.84–6.78 (m, 2H), 4.34 (br s, 1H), 3.73 (br s, 2H), 3.10 (s, 3H), 3.03 (t, J = 7.0 Hz, 2H), 1.59–1.51 (m, 2H), 1.41–1.34 (m, 2H), 0.93 (t, J = 7.3 Hz, 3H); ^{13}C NMR δ 152.5, 128.8, 118.5, 116.7, 113.4, 45.6, 44.4, 31.5, 19.3, 13.4. HRMS calcd for $C_{12}H_{20}N_4$ ($M+1$): 221.1761. Found: 221.1756.

***N'*-(4-Chlorophenyl)-*N*-isopropyl-1,2-dimethyl-1-hydrazinecarboximidamide**

hydrate (14h) oil (30%); 1H NMR δ 8.16 (br s, 1H), 7.20 (br s, 2H), 7.04 (br s, 2H), 4.55–4.46 (m, 1H), 1.94 (s, 3H), 1.81 (s, 3H), 1.22 (d, J = 6.6 Hz, 6H); ^{13}C NMR δ 148.7, 129.5, 129.0, 124.5, 116.2, 46.3, 29.7, 25.1, 22.5. Anal. Calcd for $C_{12}H_{19}ClN_4$: C, 51.57; H, 8.52; N, 16.99. Found: C, 51.40; H, 8.42; N, 16.81.