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New approach to *N,N*-dialkoxy-*N′*-arylureas and *N,N*-dialkoxycarbamates

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Experimental

N-*Chloro*-N-*(3-methylbutoxy)*-N′-*(4-nitrophenyl)urea* **1c** was obtained by chlorination of *N*-(3-methylbutoxy)-*N′*-(4-nitrophenyl)urea, yield 94 %, white crystals, mp 88–89 ˚C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.00 (d, 6H, CH*Me*$_2$, ^3J 6.6 Hz), 1.67 (q, 2H, OCH_2CH_2CH, ^3J 6.6 Hz), 1.74 (non, 1H, CH_2CHMe_2, ^3J 6.6 Hz), 4.19 (t, 2H, $NOCH_2CH_2$, ^3J 6.6 Hz), 7.69 [d, 2H, C(2)H, C(6)H, ^3J 9.3 Hz], 8.26 [d, 2H, C(3)H, C(5)H, ^3J 9.3 Hz], 8.28 (br. s, 1H, NH). Found (%): N, 14.05; Cl, 11.65. Calc. for $C_{12}H_{16}N_3O_4Cl$ (%): N, 13.93; Cl, 11.75.

N-*Chloro*-N-*ethoxy*-N′-*(2-nitrophenyl)urea* **1d** was synthesized by chlorination of *N*-ethox*y*-*N′*-(2-nitrophenyl)urea, yield 67 %, yellow crystals, mp 65–66 ˚C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.48 (t, 3H, OCH_2Me, ^3J 7.2 Hz), 4.27 (q, 2H, OCH_2Me, ^3J 7.2 Hz), 7.29 [t, 1H, C(4)H, ^3J 8.4 Hz], 7.74 [t, 1H, C(5)H, ^3J 8.4 Hz], 8.30 [d, 1H, C(6)H, ^3J 8.4 Hz], 8,74 [d, 1H, C(3)H, ^3J 8.4 Hz]; 11.41 (br. s, 1H, NH). Found (%): N, 16.08; Cl, 13.43. Calc. for $C_9H_{10}N_3O_4Cl$ (%): N, 16.18; Cl, 13.65.

N-*Chloro*-N-*ethoxy*-N′-*(4-bromophenyl)urea* **1f** was synthesized by chlorination of *N*-ethox*y*-*N′*-(4-bromophenyl)urea, yield 89 %, white crystals, mp 75–75.5 ˚C (decomp.). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.40 (t, 3H, OCH_2Me, ^3J 6.9 Hz), 4.20 (q, 2H, OCH_2Me, ^3J 6.9 Hz), 7.41 [d, 2H, C(2)H, C(6)H, ^3J 9.3 Hz], 7.48 [d, 2H, C(3)H, C(3)H, ^3J 9.3 Hz], 7.95 (br. s, 1 H, NH). EI MS, *m/z* (%): 296 M^+ (2), 294 M^+ (8), 292 M^+ (6), 61(100). FAB MS, *m/z* (%): 297 $[M + H]^+$ (7), 295 $[M + H]^+$ (29), 293 $[M + H]^+$ (23), 259 (100). Found (%): C, 36.50; H, 3.62. Calc. for $C_9H_{10}N_2O_2BrCl$ (%): C, 36.83; H, 3.43.

N-*Benzyloxy*-N-*methoxy*-N′-*(4-nitrophenyl)urea* **2b**, yield 99 %, pale yellow solid after long storing at 5˚C, mp 65–67 ˚C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.85 (s, 3H, NOMe), 5.12 (s, 2H, $NOCH_2$), 7.40–7.50 (m, 5H, CH_2Ph), 7,56 [d, 2H, C(2)H, C(6)H, ^3J 9.3 Hz], 7.96 (br. s, 1H, NH), 8.20 [d, 2H, C(3)H, C(5)H, ^3J 9.3 Hz]. IR (ν, cm^{-1}): 3313 (NH), 1700 (C=O), 1580 (NO_2), 1332 (NO_2). FAB MS, *m/z* (%): 318 $[M + H]^+$ (14), 91 Bn^+ (100). Found (%): C, 56.58; H, 4.72; N, 13.02. Calc. for $C_{15}H_{15}N_3O_5$ (%): C, 56.78; H, 4.77; N, 13.24.

N-*(3-Methylbutoxy)*-N-*methoxy*-N′-*(4-nitrophenyl)urea* **2c**, yield 91 %, pale yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.00 (d, 6H, CH*Me$_2$,* ^3J 6.6 Hz), 1.67 (q, 2H, OCH_2CH_2CH, ^3J 6.6 Hz), 1.78 (non, 1H, CH_2CHMe_2, ^3J 6.6 Hz), 3.94 (s, 3H, NOMe), 4.19 (t, 2H, $NOCH_2CH_2$, ^3J 6.6 Hz), 7.71 [d, 2H, C(2)H, C(6)H, ^3J 9.0 Hz], 8.18 (br. s, 1H, NH), 8.26 [d, 2H, C(3)H, C(5)H, ^3J 9.0 Hz]. FAB MS, *m/z* (%): 336 $[M + K]^+$ (81); 298 $[M + H]^+$ (16); 71 (100). Found (%): C, 52.31; H, 6.68; N, 14.03. Calc. for $C_{13}H_{19}N_3O_5$ (%): C, 52.52; H, 6.44; N, 14.13.

N-*Ethoxy*-N-*methoxy*-N′-*(2-nitrophenyl)urea* **2d,** yield 95 %, yellow viscous oil, n_D^{21} 1.5641. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.45 (t, 3H, OCH_2Me, ^3J 6.9 Hz), 3.96 (s, 3H, NOMe), 4.25 (q, 2H, OCH_2Me, ^3J 6.9 Hz), 7.23 [t, 1H, C(4)H, ^3J 8.4 Hz], 7.71 [t, 1H, C(5)H, ^3J 8.4 Hz], 8.28 [d, 1H, C(6)H, ^3J 8.4 Hz], 8.76 [d, 1H, C(3)H, ^3J 8.4 Hz], 11.19 (br. s, 1H, NH). FAB MS, *m/z* (%): 256 $[M + H]^+$ (17); 224 $[M + H - MeOH]^+$ (100). Found (%): N, 16.32. Calc. for $C_{10}H_{13}N_3O_5$ (%): N, 16.46.

N-*Ethoxy*-N-*methoxy*-N′-*(4-chlorophenyl)urea* **2e,** yield 62 %, yellowish viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.37 (t, 3H, OCH_2Me, ^3J 7.2 Hz), 3.90 (s, 3H, NOMe), 4.18 (q, 2H, OCH_2Me, ^3J 7.2 Hz), 7.30 [d, 2H, C(2)H, C(6)H, ^3J 9.3 Hz], 7.46 [d, 2H, C(3)H, C(5)H, ^3J 9.3 Hz], 7.90 (br. s, 1H, NH). FAB MS, *m/z* (%): 247 $[M + H]^+$ (5), 245 $[M + H]^+$ (13), 215 $[M - MeO]^+$ (40), 213 $[M - MeO]^+$ (100), 201 (8), 199 (33), 156 (18), 154 (37). Found (%): N, 11.40. Calc. for $C_{10}H_{13}N_2O_3Cl$ (%): N, 11.45.

N-*Ethoxy*-N-*methoxy*-N′-*(4-bromophenyl)urea* **2f,** yield 92%, yellowish viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.39 (t, 3H, OCH_2Me, ^3J 7.2 Hz), 3.92 (s, 3H, NOMe), 4.21 (q, 2H, OCH_2Me, ^3J 7.2 Hz), 7.43 [d, 2H, C(2)H, C(6)H, ^3J 9.0 Hz], 7.48 [d, 2H, C(3)H, C(5)H, ^3J 9.0 Hz], 7.91 (br. s, 1H, NH). Found (%): N, 9.78. Calc. for $C_{10}H_{13}N_2O_3Br$ (%): N, 9.69.