Supporting Information

Amidinoquinoxaline N-oxides as novel spin traps

Nadia Gruber, a,b,c Lidia L. Piehl, b Emilio Rubin de Celis, b Jimena E. Díaz, a María B. García, a Pierluigi Stipa, c and Liliana R. Orelli*a

c S.I.M.A.U. Department - Chemistry Division, Università Politecnica delle Marche, via Brecce Bianche 12, I-60131 Ancona, Italy.

Contents

1. Synthesis of nitrones 1 p. 2
2. Synthesis of N-(2-nitroaryl)-1, 3-propanediamines 3 p. 2
3. Synthesis of N-arylacetyl-N´-(2-nitroaryl)-1,3-propanediamines 4 p. 2
4. References p. 3
5. Copies of 1H and 13C spectra of nitrones 1e,g-i p. 4
1. Scheme. Synthesis of nitrones 1

![Scheme Image]

2. Synthesis of \(N\)-(2-nitroaryl)-1, 3-propanediamines 3

\(N\)-(2-Nitrophenyl)-1,3-propanediamine was described in the literature.\(^1\)

\(N\)-(3-Nitropyridin-2-yl)-1,3-propanediamine\(^2\) was obtained as a yellow solid (0.175 g, 89%). \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta= 8.44\) (1H, bs, ex), 8.39-8.41 (2H, m), 6.61-6.64 (1H, m), 3.72-3.75 (2H, m), 2.84 (2H, t, \(J=6.7\)), 1.83 (2H, p, \(J=6.7\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 25 °C): \(\delta= 155.7, 152.7, 135.3, 111.5, 39.6, 38.9, 32.9.\)


The acyl chloride (1 mmol) was added to a chloroformic solution of the corresponding \(N\)-(o-nitrophenyl)-1,\(n\)-diamine 3 (1 mmol), followed by aq 4% NaOH (1 mL). The mixture was shaken for 15 min, after which the organic layer was separated, washed with H\(_2\)O, dried (Na\(_2\)SO\(_4\)) and filtered. The solvent was removed in vacuo. The crude product was purified by flash chromatography on silica gel using mixtures of chloroform:ethyl acetate as eluent. Yields and analytical data of new compounds are as follows.

\(N\)-(2-Methoxyphenyl)acetyl-\(N\''-(2-nitrophenyl)-1,3-propanediamine 4e\)

This compound was obtained as a yellow solid (0.343 g, 100%), mp 125-127°C (from ethanol/water). \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta= 8.17\) (1H, dd, \(J=8.6, 1.5\)), 8.00 (1H, bs ex), 7.40-7.44 (1H, m), 7.22-7.31 (2H, m), 6.86-6.98 (2H, m), 6.77 (1H, d, \(J=8.5\)), 6.64-6.67 (1H, m), 5.90 (1H, bs ex), 3.85 (3H, s), 3.60 (2H, s), 3.34-3.38 (2H, m), 3.27-3.30 (2H, m), 1.86 (2H, p, \(J=6.9\)). \(^{13}\)C NMR (125 MHz, CDCl\(_3\), 25 °C): \(\delta=171.8, 157.1, 145.3, 136.2, 131.9, 131.3, 128.9, 126.9, 123.5, 121.2, 115.3, 113.6, 110.8, 55.5, 40.3, 38.7, 37.1, 29.1.\) Anal. Calcd for C\(_{18}\)H\(_{21}\)N\(_3\)O\(_4\): C, 63.0; H, 6.2; N, 12.2. Found: C, 63.2; H, 6.3; N, 12.0%.

\(N\)-(2-Iodophenyl)acetyl-\(N\''-(2-nitrophenyl)-1,3-propanediamine 4g\)

This compound was obtained as a yellow solid (0.422 g, 96%), mp 126-128 °C (from hexane/chloroform). \(^1\)H NMR (500 MHz, CDCl\(_3\), 25 °C, TMS): \(\delta= 8.18\) (1H, dd, \(J= 8.5, 1.5\)), 8.06 (1H, bs ex), 7.87-7.89 (1H, m), 7.44 (1H, ddd, \(J= 8.7, 7.0, 1.5\)), 7.37–7.38 (2H,
N-(3-Thienyl)acetyl-N’-(2-nitrophenyl)-1,3-propanediamine 4h
This compound was obtained as a yellow solid (0.238 g, 87%), mp 104-106°C. (from hexane/chloroform). $^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta$= 8.14 (1H, dd, J=8.5, 1.5), 8.05 (1H, bs ex), 7.42 (1H, ddd, J=8.6, 7.0, 1.5), 7.32 (1H, dd, J=4.8, 3.0), 7.14-7.15 (1H, m), 7.00 (1H, dd, J=4.8, 1.1), 6.78 (1H, d, J=8.6), 6.64 (1H, ddd, J=8.6, 7.0, 1.0), 3.61 (2H, s), 5.85 (1H, bs ex), 3.37 (2H, q, J=6.7), 3.28-3.32 (2H, m), 1.88 (2H, p, J=6.7). $^{13}$C NMR (125 MHz, CDCl$_3$, 25 °C): $\delta$= 170.9, 155.2, 136.2, 134.7, 131.8, 128.3, 126.9, 126.7, 123.4, 115.4, 113.6, 40.5, 38.1, 37.3, 29.0. Anal. Calcd for C$_{15}$H$_{18}$N$_2$O$_3$: C, 65.7; H, 6.6; N, 10.2. Found: C, 65.5; H, 6.7; N, 10.2%.

N-Phenylacetyl-N’-(3-Nitropyridine-2-yl)-1,3-propanediamine 4i
This compound was obtained as a yellow solid (0.292 g, 93%), mp 116-118°C (from hexane/chloroform). $^1$H NMR (500 MHz, CDCl$_3$, 25 °C, TMS): $\delta$= 8.39 (1H, dd, J=8.4, 1.7), 8.35 (1H, bs ex), 8.04 (1H, dd, J=4.5, 1.7), 7.36-7.39 (2H, m), 7.29-7.33 (3H, m), 6.59 (1H, dd, J=8.4, 4.5), 6.08 (1H, bs ex), 3.63 (2H, q, J=6.4), 3.63 (2H, s), 3.29 (2H, q, J=6.4), 1.79 (2H, p, J=6.4). $^{13}$C NMR (125 MHz, CDCl$_3$, 25 °C): $\delta$= 171.3, 155.5, 152.8, 135.4, 135.0, 129.6, 129.0, 128.0, 127.3, 111.6, 44.0, 38.0, 36.5, 30.0. Anal. Calcd for C$_{16}$H$_{18}$N$_4$O$_3$: C, 61.1; H, 5.8; N, 17.8. Found: C, 60.9; H, 5.9; N, 17.6%.

References
$^1$H and $^{13}$C NMR (500 MHz, CDCl$_3$) of compound 1e
$^1$H and $^{13}$C NMR (500 MHz, CDCl$_3$) of compound 1g
$^1$H and $^{13}$C NMR (500 MHz, CDCl$_3$) of compound 1h
$^1$H and $^{13}$C NMR (500 MHz, CDCl$_3$) of compound II