Electronic supplementary materials *Mendeleev Commun*., 2009, **19**, 161–162

Vicarious nucleophilic substitution in nitro derivatives of imidazo[1,2-*a*]pyridine

Mohammad Rahimizadeh, Mehdi Pordel, Mehdi Bakavoli,* Hossein Eshghi and Ali Shiri

Characteristics for compounds:

2-Ethyl-2-(3-nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)butanenitrile* **4b** was passed through silica gel column ($CHCl_3$–MeOH, 19:1) to give analytical sample of **4b** as a colourless crystal (MeOH), yield 52%, mp 107–109 °C. ^{1}H NMR ($CDCl_3$) δ: 1.05 (t, 6H, *J* 7.4 Hz), 1.98–2.74 (m, 4H), 7.35 (dd, 1H, H-6, $J_{6,5}$ 7.0 Hz, $J_{6,7}$ 6.1 Hz), 7.71 (dd, 1H, H-7, $J_{7,8}$ 7.1 Hz, $J_{7,6}$ 6.1 Hz), 7.89 (d, 1H, H-8, $J_{8,7}$ 7.1 Hz), 9.54 (d, 1H, H-5, $J_{5,}$6 7.0 Hz). IR (KBr, ν/cm^{-1}): 2250 (CN). MS, *m*/*z*: 258 (M^+). Found (%): C, 60.35; H, 5.35; N, 21.56. Calc. for $C_{13}H_{14}N_4O_2$ (258.3) (%): C, 60.46; H, 5.46; N, 21.69.

2-Benzyl-2-(3-nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)-3-phenylpropane*-nitrile **4c**: yellow crystals (EtOH), yield 85%, mp 160–162 °C. ^{1}H NMR ($CDCl_3$) δ: 3.45 (d, 2H, *J* 13.7 Hz), 3.91 (d, 2H, *J* 13.7 Hz), 7.03–7.39 (m, 11H), 7.62 (dd, 1H, H-7, $J_{7,8}$ 7.1 Hz, $J_{7,6}$ 6.1 Hz), 7.75 (d, 1H, H-8, $J_{8,7}$ 7.1 Hz), 9.49 (d, 1H, H-5, $J_{5,6}$ 7.0 Hz). IR (KBr, ν /cm^{-1}): 2250 (CN). MS, *m*/*z*: 382 (M^+). Found (%): C, 71.93; H, 4.68; N, 14.55. Calc. for $C_{23}H_{18}N_4O_2$ (382.2) (%): C, 72.24; H, 4.74; N, 14.65.

2-Allyl-2-(3-nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)-4-pentenenitrile* **4d**: colourless crystals (EtOH), yield 86%, mp 127–129 °C. ^{1}H NMR ($CDCl_3$) δ: 2.80–3.39 (m, 4H), 5.60–6.08 (m, 2H), 7.30 (dd, 1H, H-6, $J_{6,5}$ 7.0 Hz, $J_{6,7}$ 6.1 Hz), 7.65 (dd, 1H, H-7, $J_{7,8}$ 7.1 Hz, $J_{7,6}$ 6.1 Hz), 7.84 (d, 1H, H-8, $J_{8,7}$ 7.1 Hz), 9.52 (d, 1H, H-5, $J_{5,6}$ 7.0 Hz). IR (KBr, ν/cm^{-1}): 2250 (CN). MS, *m*/*z*: 282 (M^+). Found (%): C, 63.71; H, 4.89; N, 19.73. Calc. for $C_{15}H_{14}N_4O_2$ (282.3) (%): C, 63.82; H, 5.00; N, 19.85.

2-(3-Nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)-4-oxo-2-(2-oxopropyl)pentane-nitrile* **4e**: colourless crystals (EtOH), yield 65%, mp 189–191 °C. ^{1}H NMR ($CDCl_3$) δ: 2.25 (s, 6H), 3.53 (d, 2H, *J* 17.7 Hz), 3.83 (d, 2H, *J* 17.7 Hz), 7.31 (dd, 1H, H-6, $J_{6,5}$ 7.0 Hz, $J_{6,7}$ 6.1 Hz),

7.67 (dd, $J_{7,8}$ 7.1 Hz, $J_{7,6}$ 6.1 Hz), 7.75 (d, 1H, H-8, $J_{8,7}$ 7.1 Hz), 9.42 (d, 1H, H-5, $J_{5,6}$ 7.0 Hz), IR (KBr, ν/cm^{-1}): 2250 (CN). MS (*m*/*z*) 314 (M^+). Found (%): C, 57.12; H, 4.35; N, 17.51. Calc. for $C_{15}H_{14}N_4O_4$ (314.3) (%): C, 57.32; H, 4.49; N, 17.83.

2-(3-Nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)-1,2,3-propanetricarbonitrile* **4f**: colourless crystals (EtOH), yield 70%, mp 215–217 °C. ^{1}H NMR ([$^2H_6$]acetone) δ: 3.75 (d, 2H, *J* 17.1 Hz), 3.99 (d, 2H, *J* 17.1 Hz), 7.65 (dd, 1H, H-6, $J_{6,5}$ 7.0 Hz, $J_{6,7}$ 6.1 Hz), 7.90 (dd, 1H, H-7, $J_{7,8}$ 7.1 Hz, $J_{7,6}$ 6.1 Hz), 8.05 (d, 1H, H-8, $J_{8,7}$ 7.1 Hz), 9.55 (d, 1H, H-5, $J_{5,6}$ 7.0 Hz). IR (KBr, ν/cm^{-1}): 2250 (CN). MS, *m*/*z*: 280 (M^+). Found (%): C, 55.31; H, 2.73; N, 29.86. Calc. for $C_{13}H_8N_6O_2$ (280.2) (%): C, 55.72; H, 2.88; N, 29.99.

2-(3-Nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)hexanenitrile* **5b** was passed through silica gel column ($CHCl_3$–MeOH, 19:2) to give **5b** as a yellow crystal, yield 35%, mp 70–72 °C. ^{1}H NMR ($CDCl_3$) δ: 0.99 (t, 3H, *J* 7.4 Hz), 1.28–2.3 (m, 6H), 4.42 (t, 1H, *J* 7.1 Hz), 7.35 (dd, 1H, H-6, $J_{6,5}$ 7.3 Hz, $J_{6,7}$ 6.3 Hz), 7.68 (dd, 1H, H-7, $J_{7,8}$ 8.9 Hz, $J_{7,6}$ 6.3 Hz), 7.90 (d, 1H, H-8, $J_{8,7}$ 8.9 Hz), 9.38 (d, 1H, H-5, $J_{5,6}$ 7.3 Hz). IR (KBr, ν/cm^{-1}): 2250 (CN). MS, *m*/*z*: 258 (M^+). Found (%): C, 60.25; H, 5.35; N, 21.53. Calc. for $C_{13}H_{14}N_4O_2$ (258.3) (%): C, 60.46; H, 5.46; N, 21.69.

2-(3-Nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)-3-phenylpropanenitrile* **5c**: yellow crystals (MeOH), yield 55%, mp 173–175 °C. ^{1}H NMR ($CDCl_3$) δ: 3.31–3.45 (m, 2H), 5.18 (dd, 1H, *J* 8.0 Hz, *J′* 4.0 Hz), 7.30–7.49 (m, 6H), 7.72 (dd, 1H, H-7, $J_{7,8}$ 8.9 Hz, $J_{7,6}$ 6.3 Hz), 7.95 (d, 1H, H-8, $J_{8,7}$ 8.9 Hz), 9.50 (d, 1H, H-5, $J_{5,6}$ 7.3 Hz). IR (KBr, ν/cm^{-1}): 2250 (CN). MS, *m*/*z*: 292 (M^+). Found (%): C, 65.53; H, 3.98; N, 18.83. Calc. for $C_{16}H_{12}N_4O_2$ (292.3) (%): C, 65.75; H, 4.14; N, 19.17.

2-(3-Nitro-H-*imidazo[1,2*-a*]pyridin-2-yl)-4-pentenenitrile* **5d**: yellow crystals (MeOH), yield 37%, mp 145–147 °C. ^{1}H NMR ($CDCl_3$) δ: 2.85–3.38 (m, 2H), 4.96–5.39 (m, 3H), 5.64–6.18 (m, 1H), 7.40 (dd, 1H, H-6, $J_{6,5}$ 7.3 Hz, $J_{6,7}$ 6.3 Hz), 7.78 (dd, 1H, H-7, $J_{7,8}$ 8.9 Hz, $J_{7,6}$ 6.3 Hz), 7.95 (d, 1H, H-8, $J_{8,7}$ 8.9 Hz), 9.54 (d, 1H, H-5, $J_{5,6}$ 7.3 Hz). IR (KBr, ν/cm^{-1}): 2250 (CN). MS, *m*/*z*: 242 (M^+). Found (%): C, 59.37; H, 4.02; N, 22.96. Calc. for $C_{12}H_{10}N_4O_2$ (242.3) (%): C, 59.50; H, 4.16; N, 23.13.

3-Nitro-H-*imidazo[1,2*-a*]pyridin-2-amine* **6a**: bright yellow crystals (DMF–EtOH), yield 80%, mp 277–279 °C. ^{1}H NMR ([$^2H_6$]DMSO) δ: 7.18 (dd, 1H, H-6, $J_{6,5}$ 6.8 Hz, $J_{6,7}$ 6.5 Hz), 7.46 (d, 1H, H-8, $J_{8,7}$ 9.1 Hz), 7.73 (dd, 1H, H-7, $J_{7,8}$ 9.1 Hz, $J_{7,6}$ 6.5 Hz), 7.81 (br. s, 2H), 9.26 (d, 1H, H-5, $J_{5,6}$ 6.8 Hz). IR (KBr, ν/cm^{-1}): 1350, 1525 (NO_2), 3380 (NH_2). MS (*m*/z): 178 (M^+). Found (%): C, 46.95; H, 3.27; N, 31.32. Calc. for $C_7H_6N_4O_2$ (178.1) (%): C, 47.19; H, 3.39; N, 31.45.

6-Chloro-3-nitro-H-*imidazo[1,2*-a*]pyridin-2-amine* **6b**: bright yellow crystals (EtOH), yield 65%, mp 250–253 °C. ^{1}H NMR ([$_2H_6$]DMSO) δ: 7.45 (d, 1H, H-8, $J_{8,7}$ 9.4 Hz), 7.77 (dd, 1H, H-7, $J_{7,8}$ 9.4 Hz, $J_{7,5}$ 2.1 Hz), 7.83 (br. s, 2H), 9.21 (d, 1H, H-5, $J_{5,7}$ 2.1 Hz). IR (KBr, ν/cm^{-1}): 1350, 1525 (NO_2), 3380 (NH_2). MS, *m*/*z*: 214 ($M^+ + 2$). Found (%): C, 39.23; H, 2.29; N, 26.14. Calc. for $C_7H_5ClN_4O_2$ (212.6) (%): C, 39.55; H, 2.37; N, 26.35.