Electronic supplementary materials *Mendeleev Commun*., 2013, **23**, 209−211

Unexpected reduction of the nitro group in (3-nitrophenyl)-1,2,4-triazines during their aza-Diels−Alder reaction with 1-morpholinocyclopentene

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General. All common reagents and solvents were used as purchased. Melting points were measured on the instrument Boetius. NMR spectra were acquired on a Bruker Avance-400 spectrometer, 298 K, digital resolution ± 0.01 ppm, using TMS as internal standard. Mass-spectra were recorded on MicrOTOF-Q II (Bruker Daltonics), electrospray as a method of ionization. Microanalyses (C, H, N) were performed using a Perkin–Elmer 2400 elemental analyzer.

Synthesis

Hydrazones **3** [1]**,** triazine **5e** [2]**,** 3-nitrophenylglyoxale **11** [3], amidrazone **13** [4] were synthesized in accordance with literature methods.

Typical experimental procedure for the synthesis of triazines 5 and 8.

Mixture of the corresponding 2-bromoacetophenone **1** or **12** (8.2 mmol), acid hydrazide **2** or **14** (16.4 mmol) and sodium acetate (0.81 g, 9.84 mmol) was stirred on refluxing under argon atmosphere in ethanol-acetic acid solution (3:1, 150 ml) for 12 h. Afterwards the reaction mixture was cooled to r.t., the product precipitated and it was separated by filtration, washed with ethanol and dried. Analytical sample was recrystallized from ethanol.

6-(3-Nitrophenyl)-3-phenyl-1,2,4-triazine (**5a**). Yield 1.03 g (3.69 mmol, 45%). Mp 226-228 °C. **NMR ^{1}H** (DMSO-d_6, δ, ppm): 7.61 (m, 3H, Ph), 7.91 (dd, J = 8.0 Hz, 1H, H-5 (3-NO_2Ph)), 8.42 (m, 1H, H-6 (3-NO_2Ph)), 8.54 (m, 2H, Ph), 8.72 (m, 1H, H-4 (3-NO_2Ph)), 9.11 (dd, J = 2.0 Hz, 1H, H-2 (3-NO_2Ph)), 9.62 (s, 1H, H-5). **ESI-MS**, *m/z*: found 279.09, required 297.09 $(M+H)^+$. Calcd for $C_{15}H_{10}N_4O_2$: C 64.74; H 3.62; N 20.13. Found: C 64.58; H 3.49; N 20.01.

3-(4-Methoxyphenyl)-6-(3-nitrophenyl)-1,2,4-triazine (5b). Yield 1.06 g (3.44 mmol, 42%). Mp 215-217 °C. **NMR ^{1}H** (DMSO-d_6, δ, ppm): 3.90 (s, 3H, OMe), 7.08 (m, 2H (4-MeOPh)), 7.88 (dd, *J* = 8.0 Hz, 1H, H-5 (3-NO_2Ph)), 8.39 (m, 1H, H-6 (3-NO_2Ph)), 8.48 (m, 2H (4-MeOPh)), 8.68 (m, 1H, H-4 (3-NO_2Ph)), 9.08 (dd, *J* = 2.0 Hz, 1H, H-2 (3-NO_2Ph)), 9.49 (s, 1H, H-5). **ESI-MS**, *m/z*: found 309.10, required 309.10 $(M+H)^+$. Calcd for $C_{16}H_{12}N_4O_3$: C 62.34; H 3.92; N 18.17. Found: C 62.21; H 3.80; N 17.97.

6-(3-Nitrophenyl)-3-(2-thienyl)-1,2,4-triazine (5c). Yield 0.88 g (3.12 mmol, 38%). Mp 226-228 °C. **NMR ^{1}H** (DMSO-d_6, δ, ppm): 7.27 (dd, *J* = 3.2, 5.2 Hz, 1H, H-4 (thiophene)), 7.82 (d, *J* = 5.2 Hz, 1H, H-5 (thiophene)), 7.88 (dd, *J* = 8.0 Hz, 1H, H-5 (3-NO_2Ph)), 8.15 (d, *J* = 3.2 Hz, 1H, H-3 (thiophene)), 8.40 (m, 1H, H-6 (3-NO_2Ph)), 8.67 (m, 1H, H-4 (3-NO_2Ph)), 9.08 (dd, *J* = 2.0 Hz, 1H, H-2 (3-NO_2Ph)), 9.50 (s, 1H, H-5). **ESI-MS**, *m/z*: found 285.05, required 285.04 $(M+H)^+$. Calcd for $C_{13}H_8N_4O_2S$: C 54.92; H 2.84; N 19.71. Found: C 54.77; H 2.72; N 19.46.

3-(3-Nitrophenyl)-6-(4-methylphenyl)-1,2,4-triazine (8). Yield 1.03 g (3.53 mmol, 43%). Mp 207-209 °C. **NMR ^{1}H** (DMSO-d_6, δ, ppm): 2.46 (s, 1H, Me), 7.41 (m, 2H, Tol), 7.90 (dd, *J* = 8.0 Hz, 1H, H-5 (3-NO_2Ph)), 8.18 (m, 2H, Tol), 8.43 (m, 1H, H-6 (3-NO_2Ph)), 8.91 (m, 1H, H-4 (3-NO_2Ph)), 9.25 (dd, *J* = 2.0 Hz, 1H, H-2 (3-NO_2Ph)), 9.46 (s, 1H, H-6). **ESI-MS**, *m/z*: found 293.10, required 293.10 $(M+H)^+$. Calcd for $C_{16}H_{12}N_4O_2$: C 65.75; H 4.14; N 19.17. Found: C 65.61; H 3.98; N 18.92.

6-(3-Nitrophenyl)-3-(2-pyridyl)-1,2,4-triazine (5d). Hydrazone **3a** (1.3 g, 6.24 mmol) was dissolved in ethanol (25 ml), aldehyde **4** (0.6 ml, 6.24 mmol) was added and the resulting mixture was kept at r.t. for 10 h. The precipitate formed was filtered off, washed with ethanol and suspended in acetic acid (30 ml). The resulting mixture was several times brought to boiling and cooled to r.t. Acetic acid was removed under reduced pressure. The residue was treated with ethanol, the precipitate was filtered off, washed with ethanol and dried. Analytical sample was recrystallized from ethanol. Yield 1.19 g (4.26 mmol, 68%). Mp 178-180 °C. **NMR ^{1}H** (DMSO-d_6, δ, ppm): 7.59 (ddd, *J* 4.8, 7.7, 1.0 Hz, 1H, H-5 (Py)), 7.92 (dd, *J* = 8.0 Hz, 1H, H-5 (3-NO_2Ph)), 8.04 (ddd, *J* 7.7, 7.7, 2.0 Hz, 1H, H-4 (Py)), 8.44 (m, 1H, H-6 (3-NO_2Ph)), 8.57 (m, 1H, H-4 (3-NO_2Ph)), 8.77 (dd, *J* 7.7, 1.0 Hz, 1H, H-3 (Py)), 8.84 (dd, *J* = 4.8, 2.0 Hz, 1H, H-6 (Py)), 9.17 (dd, *J* = 2.0 Hz, 1H, H-2 (3-NO_2Ph)), 9.70 (s, 1H, H-5). **NMR ^{13}C** (DMSO-d_6, δ, ppm): 122.1, 124.4, 125.9, 126.3, 131.4, 133.8, 135.3, 137.9, 148.8, 149.2, 150.7, 152.8, 154.5, 162.5. **ESI-MS**, *m/z*: found 280.08, required 280.08 $(M+H)^+$. Calcd for $C_{14}H_9N_5O_2$: C 60.21; H 3.25; N 25.08. Found: C 59.98; H 3.11; N 24.81.

5-(3-Nitrophenyl)-3-(2-pyridyl)-1,2,4-triazine (7). 3-Nitrophenylglyoxal **11** (3.22 g, 18 mmol) was dissolved in ethanol (50 ml). Solution of amidrazone **13** (2.45 g, 18 mmol) in ethanol (10 ml) was added and the resulting mixture was stirred under reflux for 2 h. The precipitate formed was filtered, washed with ethanol and dried. Analytical sample was obtained by recrystallizaton from ethanol. Yield 3.1 g (11.1 mmol, 62%). Mp 211-213 °C. **NMR ^{1}H** (DMSO-d_6, δ, ppm): 7.61 (ddd, *J* 4.8, 7.7, 1.0 Hz, 1H, H-5 (Py)), 7.93 (dd, *J* = 8.0 Hz, 1H, H-5 (3-NO_2Ph)), 8.05 (ddd, *J* 7.7, 7.7, 2.0 Hz, 1H, H-4 (Py)), 8.49 (m, 1H, H-6 (3-NO_2Ph)), 8.60 (m, 1H, H-4 (3-NO_2Ph)), 8.86 (dd, *J* = 4.8, 2.0 Hz, 1H, H-6 (Py)), 8.91 (dd, *J* 7.7, 1.0 Hz, 1H, H-3 (Py)), 9.26 (dd, *J* = 2.0 Hz, 1H, H-2 (3-NO_2Ph)), 10.27 (s, 1H, H-6). **NMR ^{13}C** (DMSO-d_6, δ, ppm): 122.9, 124.5, 126.4, 127.3, 131.5, 134.6, 135.7, 137.9, 145.5, 149.1, 150.7, 153.0, 153.6, 162.8. **ESI-MS**, *m/z*: found 280.08, required 280.08 $(M+H)^+$. Calcd for $C_{14}H_9N_5O_2$: C 60.21; H 3.25; N 25.08. Found: C 60.10; H 3.08; N 24.93.

4-(3-Aminophenyl)-1-(4-methoxyphenyl)-6,7-dihydro-5*H*-cyclopenteno[*c*]pyridine (6b). Yield 340 mg (1.0 mmol, 54%). Mp 140-142 °C. **NMR ^{1}H** ($CDCl_3$, δ, ppm): 2.06 (m, 2H, 6-CH_2), 3.04 (t, *J* = 7.2 Hz, 2H, 7-CH_2), 3.15 (t, 2H, *J* = 7.2 Hz, 5-CH_2), 3.75 (br. s., 2H, NH_2), 3.87 (s, 3H, OMe), 6.71 (m, 1H, H-4 (3-NH_2Ph)), 6.79 (dd, *J* = 1.8 Hz, 1H, H-2 (3-NH_2Ph)), 6.87 (m, 1H, H-6 (3-NH_2Ph)), 7.00 (m, 2H, H (4-MeOPh)), 7.26 (dd, *J* = 8.0 Hz, 1H, H-5 (3-NH_2Ph)), 7.76 (m, 2H, H (4-MeOPh)), 8.51 (s, 1H, H-3). **NMR ^{13}C** ($CDCl_3$, δ, ppm): 25.9, 33.0, 33.2, 55.3, 113.7, 114.3, 115.1, 119.0, 129.5, 129.8, 132.3, 132.7, 136.9, 139.1, 146.6, 147.0, 152.4, 152.5, 159.7. **ESI-MS**, *m/z*: found 317.17, required 317.16 $(M+H)^+$. Calcd for $C_{21}H_{20}N_2O$: C 79.72; H 6.37; N 8.85. Found, %: C 79.51; H 6.22; N 8.44.

4-(3-Aminophenyl)-1-(2-thienyl)-6,7-dihydro-5*H*-cyclopentene[*c*]pyridine (6c). Yield 290 mg (1 mmol, 50%). Mp 172-174 °C. **NMR ^{1}H** ($CDCl_3$, δ, ppm): 2.12 (m, 2H, 6-CH_2), 3.02 (t, *J* = 7.6 Hz, 2H, 7-CH_2), 3.21 (t, *J* = 7.6 Hz, 2H, 5-CH_2), 3.78 (br. s., 2H, NH_2), 6.69 (m, 1H, H-4 (3-NH_2Ph)), 6.73 (dd, *J* = 1.8 Hz, 1H, H-2 (3-NH_2Ph)), 6.83 (m, 1H, H-6 (3-NH_2Ph)), 7.14 (dd, *J* = 3.6, 4.8 Hz, 1H, H-4 (thiophene)), 7.23 (dd, *J* = 8.0 Hz, 1H, H-5 (3-NH_2Ph)), 7.41 (d, *J* = 4.8 Hz, 1H, H-5 (thiophene)), 7.50 (d, *J* = 3.6 Hz, 1H, H-3 (thiophene)), 8.42 (s, 1H, H-3). **NMR ^{13}C** ($CDCl_3$, δ, ppm): 25.0, 32.7, 33.2, 114.4, 115.0, 118.9, 126.0, 127.1, 128.0, 129.5, 132.5, 135.2, 138.9, 145.4, 146.7, 146.8, 147.0, 152.7. **2D COSY (^{1}H – ^{15}N)** experiment spectra is shown in Fig. 1. **ESI-MS**, *m/z*: found 293.11, required 293.11 $(M+H)^+$. Calcd for $C_{18}H_{16}N_2S$: C 73.94; H 5.52; N 9.58. Found: C 73.61; H 5.30; N 9.22.

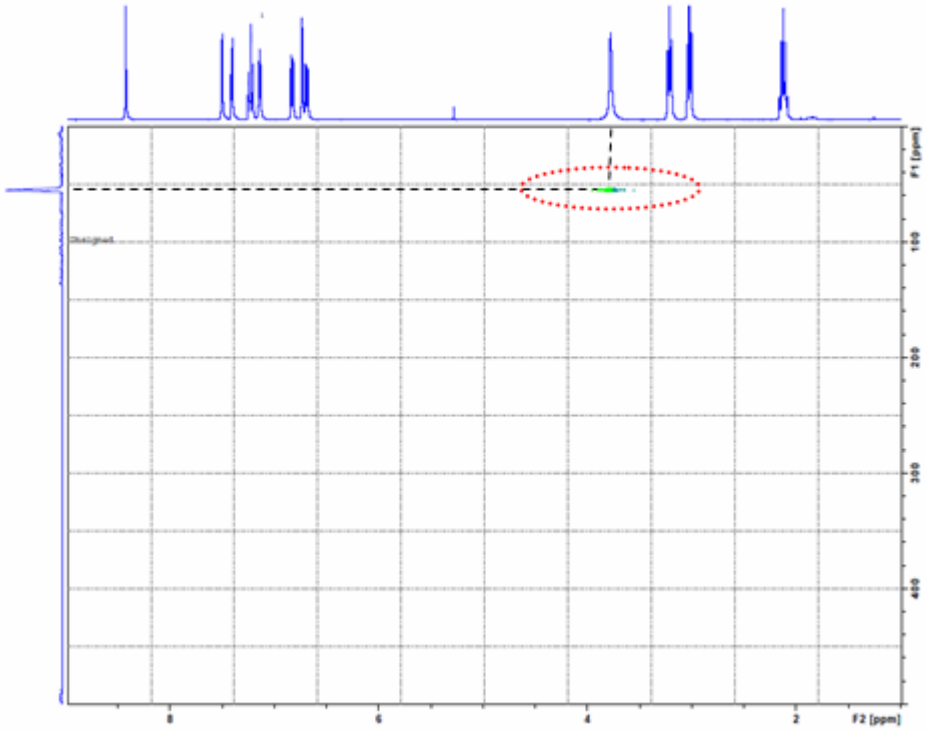

Figure S1 2D COSY (^{1}H – ^{15}N) experiment spectra for product **6c**: an interaction of nitrogen atom (54 ppm) with hydrogens (3.78 ppm) can be observed.

4-(3-Aminophenyl)-1-(2-pyridyl)-6,7-dihydro-5*H*-cyclopenteno[*c*]pyridine (6d). Yield 260 mg (0.9 mmol, 45%). Mp 113-115 °C. **NMR ^{1}H** ($CDCl_3$, δ, ppm): 2.07 (m, 2H, 6-CH_2), 3.03 (t, *J* = 7.6 Hz, 2H, 7-CH_2), 3.44 (t, *J* = 7.2 Hz, 2H, 5-CH_2), 3.73 (br. s., 2H, NH_2), 6.73 (m, 1H, H-4 (3-NH_2Ph)), 6.79 (dd, *J* = 2.0 Hz, 1H, H-2 (3-NH_2Ph)), 6.88 (m, 1H, H-6 (3-NH_2Ph)), 7.26 (m, 2H, H-5 (3-NH_2Ph), H-5 (Py)), 7.80 (ddd, *J* 7.8, 7.8, 2.0 Hz, 1H, H-4 (Py)), 8.18 (dd, *J* 7.8, 1.0 Hz, 1H, H-3 (Py)), 8.52 (s, 1H, H-3), 8.70 (dd, *J* = 4.8, 2.0 Hz, 1H, H-6 (Py)). **NMR ^{13}C** ($CDCl_3$, δ, ppm): 25.5, 32.7, 33.4, 114.4, 115.1, 119.0, 122.7, 123.0, 128.4, 129.5, 133.9, 136.4, 139.0, 139.2, 146.7, 148.7, 150.8, 153.2, 158.3. **ESI-MS**, *m/z*: found 288.15, required 288.15 $(M+H)^+$. Calcd for $C_{19}H_{17}N_3$: C 79.41; H 5.96; N 14.62. Found: C 79.03; H 5.65; N 14.34.

1-(3-Aminophenyl)-4-(4-methylphenyl)-6,7-dihydro-5*H*-cyclopenteno[*c*]pyridine (10). Yield 310 mg (1.04 mmol, 52%). Mp 118-120 °C. **NMR ^{1}H** ($CDCl_3$, δ, ppm): 2.06 (m, 2H, 6-CH_2), 2.42 (s, 3H, Me), 3.04 (t, *J* = 7.2 Hz, 2H, 7-CH_2), 3.16 (t, 2H, *J* = 7.2 Hz, 5-CH_2), 3.70 (br. s., 2H, NH_2), 6.73 (m, 1H, H-4 (3-NH_2Ph)), 7.15 (m, 2H, H-2,6 (3-NH_2Ph)), 7.28 (m, 3H, Tol, H-5 (3-NH_2Ph)), 7.39 (m, 2H, Tol), 8.52 (s, 1H, H-3). **NMR ^{13}C** ($CDCl_3$, δ, ppm): 21.2, 25.9, 33.0, 33.2, 115.1, 115.2, 118.9, 128.4, 129.1, 129.3, 129.5, 132.5, 135.0, 137.4, 141.2, 146.5, 147.0, 152.3, 152.8. **ESI-MS**, *m/z*: found 301.17, required 301.17 $(M+H)^+$. Calcd for $C_{21}H_{20}N_2$: C 83.96; H 6.71; N 9.33. Found, %: C 84.79; H 6.55; N 9.22.

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