

Metathesis of azomethine imines in reaction of 6-aryl-1,5-diazabicyclo[3.1.0]hexanes with (het)arylidene malononitriles

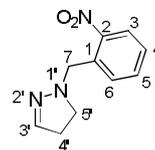
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General remarks

Elemental analysis was performed by the CHN Analyzer Perkin–Elmer 2400. Mass spectra were measured using a Finnigan MAT INCOS-50 instrument. HRMS were measured on an MicrOTOF II (Bruker Daltonics) of the method ESI. The NMR spectra of all compounds were recorded using a Bruker AM-300 spectrometer at 300 MHz for ^1H and 75.47 MHz for ^{13}C spectra as well as Bruker AV-600 instrument with the frequencies 600.13 and 150.90 for ^1H and ^{13}C , respectively, in CDCl_3 . The chemical shifts of the signals of CDCl_3 residual proton (7.27 ppm) and carbon (77.0 ppm) were used as the internal standard. The spectra were measured at 30 °C. Aluminum TLC plates with silica gel QF 254 (Merck) were used for analytical thin-layer chromatography. New compounds were purified by column chromatography on Silica gel, 0.060–0.200 mm, 60 Å (ACROS) with AcOEt–light petroleum as eluent. Quantum chemical calculations were performed within the framework of density functional theory (DFT) (Gaussian 98 program package).¹

Characterization of products

Compounds **4a–c** were characterized in refs. 2, 3, 4, respectively.



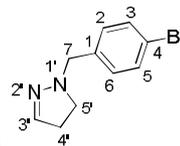
1-(2-Nitrobenzyl)-4,5-dihydro-1H-pyrazole **4d** (method ii).

^1H NMR (300 MHz, CDCl_3 , 30 °C): δ 7.92 (d, $^3J_{\text{H,H}} = 8.1$ Hz, 1 H, H-3), 7.76 (d, $^3J_{\text{H,H}} = 7.3$ Hz, 1 H, H-6), 7.59 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 1 H, H-5), 7.41 (t, $^3J_{\text{H,H}} = 8.1$ Hz, 1 H, H-4), 6.83 (s, 1 H, H-3'), 4.44 (s, 2 H, H-7), 3.08 – 3.02 (m, $^3J_{\text{H,H}} = 9.3$ Hz, 2 H, H-5'), 2.70 – 2.64 (m, $^3J_{\text{H,H}} = 9.2$ Hz, 9.3 Hz, 2 H, H-4').

^{13}C NMR (75 MHz, CDCl_3 , 30 °C): δ 144.18 (C-3'), 149.18, 133.77, 133.45, 131.28, 128.02, 124.56 (Ar), 56.86 (C-7), 53.06 (C-5'), 34.31 (C-4').

MS (EI, 70 eV), m/z (I, %): 205 $[M]^+$ (8), 83 $[M - 2\text{-nitrophenyl}]^+$ (19), 69 $[M - 2\text{-nitrobenzyl}]^+$ (40).

Found (%): C, 58.57; H, 5.36; N, 20.43. Calc. for $C_{10}H_{11}N_3O_2$ (%): C, 58.53; H, 5.40; N, 20.48.



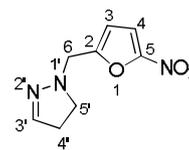
1-(4-Bromobenzyl)-4,5-dihydro-1H-pyrazole 4e (method iii).

^1H NMR (300 MHz, CDCl_3 , 30 °C): δ 7.46 (d, $^3J_{\text{H,H}} = 8.0$ Hz, 2 H, H-3,5), 7.26 (d, $^3J_{\text{H,H}} = 7.9$ Hz, 2 H, H-2,6), 6.82 (s, 1 H, H-3'), 4.14 (s, 2 H, H-7), 2.96 – 2.89 (m, $^3J_{\text{H,H}} = 9.3$ Hz, 2 H, H-5'), 2.68 – 2.62 (m, $^3J_{\text{H,H}} = 9.2$ Hz, 9.1 Hz, 2 H, H-4').

^{13}C NMR (75 MHz, CDCl_3 , 30 °C): δ 143.59 (C-3'), 136.79, 131.51, 130.70, 121.23 (Ar), 59.93 (C-7), 52.18 (C-5'), 34.24 (C-4').

MS (EI, 70 eV), m/z (I, %): 238 $[M]^+$ (24), 169 $[M - \text{pyrazoline ring}]^+$ (100), 90 $[M - \text{pyrazoline ring} - \text{Br}]^+$ (65).

Found (%): C, 50.25; H, 4.61; Br, 33.38; N, 11.73. Calc. for $C_{10}H_{11}\text{BrN}_2$ (%): C, 50.23; H, 4.64; Br, 33.42; N, 11.72.



1-[(5-Nitrofuran-2-yl)methyl]-4,5-dihydro-1H-pyrazole 4f (method iv).

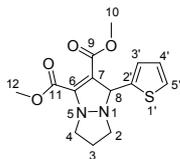
^1H NMR (300 MHz, CDCl_3 , 30 °C): δ 7.29 (d, $^3J_{\text{H,H}} = 3.6$ Hz, 1 H, H-4), 6.87 (s, 1 H, H-3'), 6.55 (d, $^3J_{\text{H,H}} = 3.6$ Hz, 1 H, H-3), 4.27 (s, 2 H, H-6), 3.12 – 3.06 (m, $^3J_{\text{H,H}} = 9.4$ Hz, 2 H, H-5'), 2.74 – 2.68 (m, $^3J_{\text{H,H}} = 9.4$ Hz, 9.2 Hz, 2 H, H-4').

^{13}C NMR (75 MHz, CDCl_3 , 30 °C): $\delta =$ 143.59 (C-3'), 155.88, 148.34, 112.62, 111.90 (furyl), 52.35 (C-6), 52.24 (C-5'), 34.61 (C-4').

MS (EI, 70 eV), m/z (I, %): 195 $[M]^+$ (28), 149 $[M - \text{NO}_2]^+$ (37), 83 $[M - \text{nitrofuryl}]^+$ (18).

Found (%): C, 49.19; H, 4.60; N, 21.58. Calc. for $C_8H_9N_3O_3$ (%): C, 49.23; H, 4.65; N, 21.53.

Dimethyl 3,5,6,7-tetrahydro-3-(thiophen-2-yl)pyrazolo[1,2-a]pyrazole-1,2-dicarboxylate 13a.

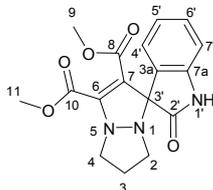


^1H NMR (300 MHz, CDCl_3 , 30 °C): δ 7.19 (d, $^3J_{\text{H,H}} = 5.0$ Hz, 1 H, H-5'), 7.06 (d, $^3J_{\text{H,H}} = 3.3$ Hz, 1 H, H-3'), 6.94 (t, $^3J_{\text{H,H}} = 4.0$ Hz, 4.5 Hz, 1 H, H-4'), 5.50 (s, 1 H, H-8), 3.93 (s, 3 H, H-12), 3.68 (s, 3 H, H-10), 3.54 – 3.45, 3.39 – 3.31 (both m, 2 H, H-4), 3.22 – 3.15 (m, 1 H, H-2b), 2.87 (q, $^3J_{\text{H,H}} = 8.9$ Hz, 9.1 Hz, 1 H, H-2a), 2.18 – 2.09 (m, 2 H, H-3).

^{13}C NMR (75 MHz, CDCl_3 , 30 °C): δ 163.78 (C-9), 162.75 (C-11), 150.34 (C-6), 144.42 (C-2'), 126.82 (C-4'), 124.64 (C-3'), 124.43 (C-5'), 106.70 (C-7), 65.91 (C-8), 53.11 (C-12), 51.44 (C-10), 51.36 (C-2), 46.23 (C-4), 24.93 (C-3).

HRMS (ESI): calc. for $\text{C}_{14}\text{H}_{16}\text{N}_2\text{O}_4\text{S}$ $[\text{M} + \text{Na}]^+$ 331.0723; found 331.0721.

Dimethyl 2-oxo-6',7'-dihydro-5'H-spiro[indoline-3,1'-pyrazolo[1,2-a]pyrazole]-2',3'-dicarboxylate 13b, mp 83–84 °C (decomp.).

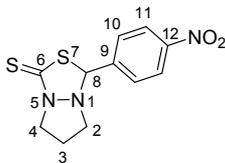


^1H NMR (600 MHz, CDCl_3 , 30 °C): δ 7.75 (br s, 1 H, H-1'), 7.33 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, H-4'), 7.24 (t, $^3J_{\text{H,H}} = 7.8$ Hz, 7.2 Hz, 1 H, H-5'), 7.03 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 7.8 Hz, 1 H, H-6'), 6.85 (d, $^3J_{\text{H,H}} = 7.8$ Hz, 1 H, H-7'), 3.96 (s, 3 H, H-9), 3.52 (s, 3 H, H-11), 3.49 – 3.46, 3.45 – 3.41 (both m, 2 H, H-4), 3.25 (q, $^3J_{\text{H,H}} = 9.6$ Hz, 7.2 Hz, 1 H, H-2b), 2.99 – 2.96 (m, 1 H, H-2a), 2.27 – 2.22, 2.20 – 2.14 (both m, 2 H, H-3).

^{13}C NMR (150 MHz, CDCl_3 , 30 °C): δ 174.58 (C-2'), 162.64 (C-10), 162.14 (C-8), 151.94 (C-6), 140.46 (C-3a), 129.77 (C-5'), 128.96 (C-7a), 125.21 (C-4'), 122.97 (C-6'), 110.06 (C-7'), 104.35 (C-7), 73.44 (C-3'), 53.26 (C-9), 51.41 (C-11), 47.91 (C-2), 46.13 (C-4), 26.26 (C-3).

HRMS (ESI): calc. for $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}_5$ $[\text{M} + \text{Na}]^+$ 366.1060; found 366.1060.

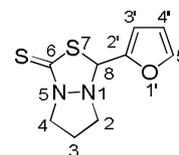
Dihydro-3-(4-nitrophenyl)-3H-pyrazolo[1,2-c][1,3,4]thiadiazole-1(5H)-thione 14a.



^1H NMR (300 MHz, CDCl_3 , 30 °C): δ 8.26 (d, $^3J_{\text{H,H}} = 8.7$ Hz, 2 H, H-11), 7.72 (d, $^3J_{\text{H,H}} = 8.7$ Hz, 2 H, H-10), 5.88 (s, 1 H, H-8), 4.21 – 4.11, 3.74 – 3.65 (both m, 2 H, H-4), 3.26 – 3.20 (m, 1 H, H-2b), 2.91 (q, $^3J_{\text{H,H}} = 8.3$ Hz, 9.7 Hz, 1 H, H-2a), 2.63 – 2.49 (m, 2 H, H-3).

^{13}C NMR (75 MHz, CDCl_3 , 30 °C): δ 185.05 (C-6), 148.52 (C-12), 143.60 (C-9), 128.33 (C-10), 124.29 (C-11), 72.08 (C-8), 51.21 (C-2), 46.50 (C-4), 27.00 (C-3).

HRMS (ESI): calc. for $\text{C}_{11}\text{H}_{11}\text{N}_3\text{O}_2\text{S}_2$ $[\text{M} - \text{H}]^+$ 280.0209; found 280.0216.



3-(Furan-2-yl)tetrahydro-1H-pyrazolo[1,2-c][1,3,4]thiadiazole-1-thione 14b.

^1H NMR (300 MHz, CDCl_3 , 30 °C): δ 7.46 (d, $^3J_{\text{H,H}} = 1.1$ Hz, 1 H, H-5'), 6.54 (d, $^3J_{\text{H,H}} = 3.3$ Hz, 1.9 Hz, 1 H, H-3'), 6.39 (m, 1 H, H-4'), 5.89 (s, 1 H, H-8), 4.06 – 3.97, 3.76 – 3.67 (both m, 2 H, H-4), 3.21 – 3.15 (m, 1 H, H-2b), 2.90 (q, $^3J_{\text{H,H}} = 8.2$ Hz, 1 H, H-2a), 2.53 – 2.40 (m, 2 H, H-3).

^{13}C NMR (75 MHz, CDCl_3 , 30 °C): δ 185.08 (C-6), 148.22 (C-2'), 143.91 (C-5'), 110.85 (C-4'), 110.16 (C-3'), 65.61 (C-8), 50.40 (C-2), 46.28 (C-4), 26.84 (C-3).

HRMS (ESI): calc. for $\text{C}_9\text{H}_{10}\text{N}_2\text{OS}_2$ $[\text{M} - \text{H}]^+$ 225.0151; found 225.0159.

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