2-Aryl-5-imino-2,5-dihydro-1,2,3-thiadiazoles: new examples of 1,3-dipolar compounds

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Some heterocycles with an exocyclic imino or thioxo group in the α-position relative to the ring S (or N) atom can exhibit properties of latent dipoles and react with dienophiles as 1,3-dipolar compounds.[1—5] In particular, a series of studies[3—5] have been devoted to reactions of thiatriazolinimines with alkynes and heterocumulenes.

We studied for the first time reactions of [5-imino-2-(4-methoxyphenyl)-2,5-dihydro-1,2,3-thiadiazol-4-yl]pyrrolidinomethanone **1** with *N*-methyl- and *N*-phenylmaleimides **2a,b** and with dimethyl acetylenedicarboxylate (DMAD). The products obtained, which were identified by mass spectrometry, ^{1}H and ^{13}C NMR spectroscopy, and elemental analysis, suggested that the reaction mechanism is 1,3-dipolar cycloaddition yielding hydrogenated pyrrolo[3,4-*d*]thiazolediones **3a,b** and thiazole **4** (Scheme 1).

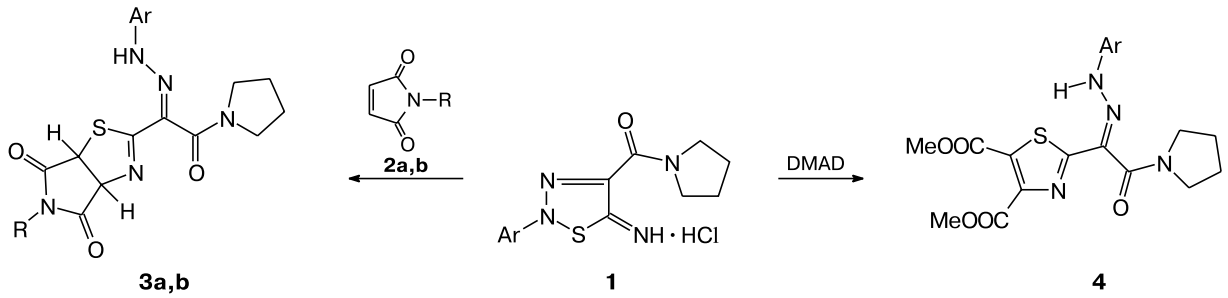
The most characteristic signals in the ^{1}H NMR spectra of heterocyclic derivatives **3** and **4** are signals for the methyl protons of two methoxycarbonyl groups in thiazole **4** at δ 3.73—3.95 and signals for the protons of the hydrogenated pyrrolo[3,4-*d*]thiazole system at δ 4.6—6.6 in compounds **3a,b** as an AB system with J = 8.9 Hz. Some signals are doubled because compounds **3** and **4a,b** exist as the *E*- and *Z*-isomers.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WM-250 spectrometer (250.13 and 100 MHz, respectively) in DMSO-d_6. Mass spectra were recorded on a Varian MAT 311A instrument (EI, 70 eV).

2-[1-(4-Methoxyphenylhydrazono)-2-oxo-2-pyrrolidinoethyl]-5-methyl-3a*H*-pyrrolo[3,4-*d*]thiazole-4,6(5*H*,6a*H*)-dione (3a). *N*-Methylmaleimide (0.167 g, 1.5 mmol) was added to a solution of 2-aryl-1,2,3-thiadiazole **1** (0.1 g, 0.3 mmol) in toluene (20 mL) and the reaction mixture was refluxed for 3 h. After the solvent was removed, the product was purified by chromatography with chloroform—acetone (2 : 1) as an eluent. The yield of compound **3a** was 0.105 g (86%), m.p. 234—235 °C. Found (%): C, 54.65; H, 4.63; N, 16.72. $C_{19}H_{21}N_5O_4S$. Calculated (%): C, 54.93; H, 5.09; N, 16.86. ^{1}H NMR, δ: 1.84—1.90 (m, 4 H, CH_2); 2.91 (s, 3 H, Me); 3.24—3.26 (m, 1 H, CH_2); 3.47—3.53 (m, 2 H, CH_2); 3.74, 3.77 (both s, 3 H, OMe); 3.79—3.82 (m, 1 H, CH_2); 4.57 and 5.71; 4.73 and 5.67 (AA´BB´, 2 H, 2 CH, J = 8.9 Hz); 6.82, 6.89 (both d, 2 H each, Ar, J = 8.9 Hz); 7.19 (d, 2 H, Ar, J = 8.9 Hz); 10.55, 14.37 (both s, 1 H each, NH) (a mixture of the *E*- and *Z*-isomers in the ratio 3 : 7). ^{13}C NMR, δ: 23.35, 23.78, 24.91, 24.95, 25.17, 26.40, 45.00, 46.09, 46.55, 47.11, 47.78, 49.58 (d, CH, J = 156.1 Hz); 55.25, 55.35, 78.89, 82.14 (d, CH, J = 156.1 Hz); 114.58, 115.08, 115.16, 116.4, 122.93, 131.22, 135.44, 136.84, 154.85, 156.27, 160.28, 163,21, 163.57, 165,76, 173.33, 173.61, 175.54, 175.71. MS, m/z (I_{rel} (%)): 415 $[M]^+$ (4.6).

2-[1-(4-Methoxyphenylhydrazono)-2-oxo-2-pyrrolidinoethyl]-5-phenyl-3a*H*-pyrrolo[3,4-*d*]thiazole-4,6(5*H*,6a*H*)-dione (3b) was obtained analogously. The yield was 0.125 g (89%), m.p. 175—176 °C. Found (%): C, 60.42; H, 4.98; N, 14.83. $C_{24}H_{23}N_5O_4S$. Calculated (%): C, 60.36; H, 4.85; N, 14.67. ^{1}H NMR, δ: 1.86—1.90 (m, 4 H, CH_2); 3.28—3.30 (m, 1 H,

Scheme 1



3a,b **1** **4**

Ar = 4-MeO—C_6H_4 (**1**, **3**, **4**); R = Me (**a**), Ph (**b**)

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 5, pp. 912—913, May, 2006.

CH_2); 3.49—3.54 (m, 2 H, CH_2); 3.74, 3.76 (both s, 3 H each, OMe); 3.84—3.87 (m, 1 H, CH_2); 4.74 and 5.87; 4.89 and 5.82 (AB, 1 H, CH, J = 8.9 Hz); 6.83, 6.91 (both d, 1 H each, Ar, J = 8.9 Hz); 6.99—7.08 (m, 2 H, Ar); 7.19—7.32 (m, 3 H, Ar); 7.39—7.48 (m, 3 H, Ar); 10.62, 14.44 (both s, 1 H each, NH) (a mixture of the *E*- and *Z*-isomers in the ratio 1 : 1). MS, m/z (I_{rel} (%)): 477 $[M]^+$ (2.1).

Dimethyl 2-[1-(4-methoxyphenylhydrazono)-2-oxo-2-pyrrolidinoethyl]thiazole-4,5-dicarboxylate (4) was obtained analogously. The yield was 0.079 g (60%), m.p. 169—170 °C. Found (%): C, 53.87; H, 4.68; N, 12.29. $C_{20}H_{22}N_4O_6S$. Calculated (%): C, 53.80; H, 4.97; N, 12.55. ^{1}H NMR, δ: 1.83—1.96 (m, 4 H, CH_2); 3.52—3.55 (m, 2 H, CH_2); 3.73, 3.77 (both s, 3 H each, OMe); 3.85, 3.88 (both s, 3 H each, OMe); 3.92, 3.95 (both s, 3 H each, OMe); 3.92—3.94 (m, 2 H, CH_2); 6.94, 7.03 (both d, 2 H each, Ar, J = 9.1 Hz); 7.29 (d, 2 H, Ar, J = 9.1 Hz); 10.81, 14.16 (both s, 1 H each, NH) (a mixture of the *E*- and *Z*-isomers in the ratio 1 : 9). MS, m/z (I_{rel} (%)): 446 $[M]^+$ (16.4).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 04-03-32926a) and the Ministry of Education and Science of the Russian Federation.

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Received February 1, 2006;
in revised form April 13, 2006