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SHORT COMMUNICATIONS

Oxidation of 4-Amino-5-aryl-4*H*-1,2,4-triazole-3-thiols

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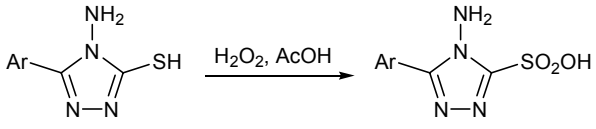
Heterocyclic thiols of the 1,2,4-triazole series, in particular 4-amino-5-aryl-4*H*-1,2,4-triazole-3-thiols **I** exhibit a broad spectrum of biological activity, such as antibacterial, antifungal, etc. [1–4]. Transformation of thiols into the corresponding sulfones and sulfonic acids usually enhances their biological activity [5]. Triazoles **I** are widely used as starting compounds for the synthesis of fused heterocycles [6, 7]. On the other hand, published data on the oxidation of triazoles **I** to sulfonic acids are very few in number, and the reported oxidation procedures are characterized by low efficiency. The corresponding oxidation products are formed in ~30% yield [8].

We propose a simple and efficient procedure for the preparation of triazolesulfonic acids. Oxidation of 4-amino-5-aryl-4*H*-1,2,4-triazole-3-thiols with 30% hydrogen peroxide in acetic acid at room temperature afforded 65–80% of the corresponding sulfonic acids **II**. The product structure was confirmed by the ^{1}H and ^{13}C NMR and IR spectra and elemental analyses.



Ia–Id **IIa–IId**

Ar = 3-MeOC$_6$H$_4$ (**a**), 2-ClC$_6$H$_4$ (**b**), 3-FC$_6$H$_4$ (**c**), 4-BrC$_6$H$_4$ (**d**).

Unlike initial thiols **Ia–Id**, the ^{1}H NMR spectra of sulfonic acids **IIIa–IIId** lack signal at δ 14–16 ppm typical of SH proton but contain a signal at δ 9–10 ppm due to proton of the SO_3H group. In addition, the NH_2 signal becomes broadened and shifts toward weaker field (δ 6.0–8.5 ppm). In the IR spectra of **IIIa–IIId**, absorption bands corresponding to stretching vibrations of the SO_2 fragment are observed at 1000–1300 cm^{-1}.

General procedure for the oxidation of 4-amino-5-aryl-4*H*-1,2,4-triazole-3-thiols Ia–Id. A mixture of 0.5 g of 4-amino-5-aryl-4*H*-1,2,4-triazole-3-thiol **Ia–Id** and 5 ml of glacial acetic acid was cooled to room temperature, 1.5 ml of 30% hydrogen peroxide was added, and the mixture was kept for 1 h on a cold water bath. The bath was removed, the mixture was left to stand for a week, and the precipitate was filtered off and dried.

4-Amino-5-(3-methoxyphenyl)-4*H*-1,2,4-triazole-3-sulfonic acid (IIa). Yield 80%, mp 120–121°C. IR spectrum, ν, cm^{-1}: 1220, 1030 (SO_2). ^{1}H NMR spectrum, δ, ppm: 3.84 s (3H, OCH_3), 7.16–7.18 d (1H, H_{arom}), 7.46–7.51 t (1H, H_{arom}), 7.62–7.64 s (2H, H_{arom}), 8.0 br.s (2H, NH_2), 9.29 s (1H, SO_3H). ^{13}C NMR spectrum, δ_C, ppm: 55.5, 114.3, 117.5, 121.2, 123.9, 130.0, 145.9, 151.4, 159.3. Found, %: C 39.95, 38.99; H 3.85, 3.78; N 19.95, 19.84; S 10.73, 11.96. $C_9H_{10}N_4O_4S$. Calculated, %: C 40.00; H 3.73; N 20.73; S 11.86.

4-Amino-5-(2-chlorophenyl)-4*H*-1,2,4-triazole-3-sulfonic acid (IIb). Yield 65%, mp 104–105°C (decomp.). IR spectrum, ν, cm^{-1}: 1180, 1100 (SO_2). ^{1}H NMR spectrum, δ, ppm: 6.60 br.s (2H, NH_2), 7.43–7.47 t (1H, H_{arom}), 7.50–7.63 m (3H, H_{arom}), 9.67 s (1H, SO_3H). ^{13}C NMR spectrum, δ_C, ppm: 122.2, 127.4, 129.9, 133.1, 133.4, 145.2. Found, %: C 33.98, 34.00; H 3.11, 2.48; N 19.84, 19.94; S 11.73, 11.56. $C_8H_7ClN_4O_3S$. Calculated, %: C 34.98; H 2.57; N 20.40; S 11.67.

4-Amino-5-(3-fluorophenyl)-4*H*-1,2,4-triazole-3-sulfonic acid (IIc). Yield 78%, mp 159–160°C (decomp.). IR spectrum, ν, cm^{-1}: 1200, 1090 (SO_2). ^{1}H NMR spectrum, δ, ppm: 6.10 br.s (2H, NH_2), 7.39–7.42 t (1H, H_{arom}), 7.59–7.64 q (1H, H_{arom}), 7.90–7.94 d.d (2H, H_{arom}), 9.29 s (1H, SO_3H). ^{13}C NMR spectrum, δ_C, ppm: 115.4, 118.4, 124.9, 125.9, 130.9, 146.1, 150.8. Found, %: C 36.95, 37.15; H 2.87, 2.56;

N 20.84, 21.67; S 11.83, 12.56. $C_8H_7FN_4O_3S$. Calculated, %: C 37.21; H 2.73; N 21.70; S 12.42.

4-Amino-5-(4-bromophenyl)-4*H*-1,2,4-triazole-3-sulfonic acid (IId). Yield 89%, mp 175–176°C (decomp.). IR spectrum, ν, cm^{-1}: 1160, 1095 (SO_2). ^1H NMR spectrum, δ, ppm: 7.76–7.78 d (2H, H_{arom}), 8.02–8.04 d (2H, H_{arom}), 8.22 br.s (2H, NH_2), 9.47 s (1H, SO_3H). ^{13}C NMR spectrum, δ_C, ppm: 122.1, 125.8, 131.0, 131.9, 145.9, 151.1. Found, %: C 30.16, 29.85; H 2.37, 2.28; N 17.56, 16.79; S 11.00, 10.11. $C_8H_7FN_4O_3S$. Calculated, %: C 30.11; H 2.21; N 17.56; S 10.05.

The IR spectra were recorded in KBr on an FSM 1201 spectrometer with Fourier transform. The ^1H and ^{13}C NMR spectra were obtained on a Bruker AM-500 instrument at 500.13 and 50.32 MHz, respectively, using DMSO-d_6 as solvent.

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