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ARYLAMINATION OF 1,2,5-THIADIAZOL-3-YL TRIFLUOROMETHANESULFONATE

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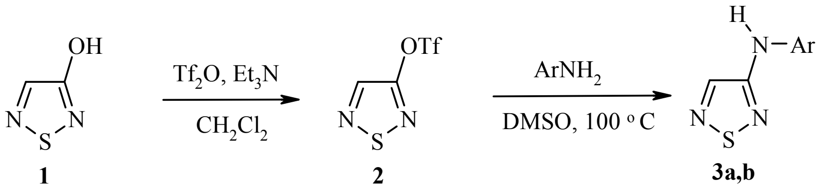
At the present time, there is no convenient method for synthesis of 3-arylamino derivatives of 1,2,5-thiadiazole.

We have discovered that triflate **2**, obtained from 3-hydroxy-1,2,5-thiadiazole **1**, smoothly reacts with aromatic amines to form the previously not easily accessible [1] 3-arylamino derivatives of 1,2,5-thiadiazole **3**.



3 a Ar = Ph, **b** Ar = 4-MeC_6H_4

The only known example of such a reaction between hetaryl triflates and aromatic amines without using catalysts [2] is the reaction of quinolin-2-yl trifluoromethanesulfonate and aniline.

The ^1H and ^{19}F NMR spectra were taken on a Varian VXR-300, internal standard TMS (^1H) and $FCCl_3$ (^{19}F).

1,2,5-Thiadiazol-3-yl Trifluoromethanesulfonate (2). Yield 85%; mp 50-52°C (15 torr), n_D^{15} 1.4368, d_4^{15} 1.6. ^1H NMR spectrum (299 MHz, $CDCl_3$), δ, ppm: 8.45 (1H, s, H-4). ^{19}F NMR spectrum (282 MHz, $CDCl_3$), δ, ppm: -72.0 (3F, s, CF_3). Found, %: C 15.28; H 0.39; F 24.11; N 11.85; S 27.1. $C_3HF_3N_2O_3S_2$. Calculated, %: C 15.39; H 0.43; F 24.34; N 11.96; S 27.38.

N-Phenyl-1,2,5-thiadiazole-3-amine (3a). Yield 64%; mp 80-82°C; according to data in [1], mp 80°C. ^1H NMR spectrum (299 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 6.99 (1H, br. s, NH); 7.07 (1H, t, $J = 7.2$, C_6H_5); 7.36 (2H, dd, $J = 7.2$, $J = 8.1$, C_6H_5); 7.5 (2H, t, $J = 8.1$, C_6H_5); 8.08 (1H, s, H-4).

N-(4-Methylphenyl)-1,2,5-thiadiazole-3-amine (3b). Yield 52%; mp 96-98°C. ^1H NMR spectrum (299 MHz, $CDCl_3$), δ, ppm (*J*, Hz): 2.33 (3H, s, CH_3); 6.9 (1H, br. s, NH); 7.17 (2H, d, $J = 8.2$, Ar); 7.37 (2H, d, $J = 8.2$, Ar); 8.05 (1H, s, H-4). Found, %: C 56.52; H 4.74; N 21.97; S 16.76. $C_9H_9N_3S$. Calculated, %: C 56.38; H 4.78; N 21.71; S 16.89.

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REFERENCES

1. J. Rokach, P. Hamel, Y. Girard, and G. Reader, *J. Org. Chem.*, **44**, 1118 (1979).
2. S. Cacchi, A. Carangio, G. Fabrizi, L. Moro, and P. Pace, *Synlett*, **12**, 1400 (1997).