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UNUSUAL DIMERIZATION OF 2-AMINO-5-TRIFLUOROMETHYL-1,3,4-THIADIAZOLE

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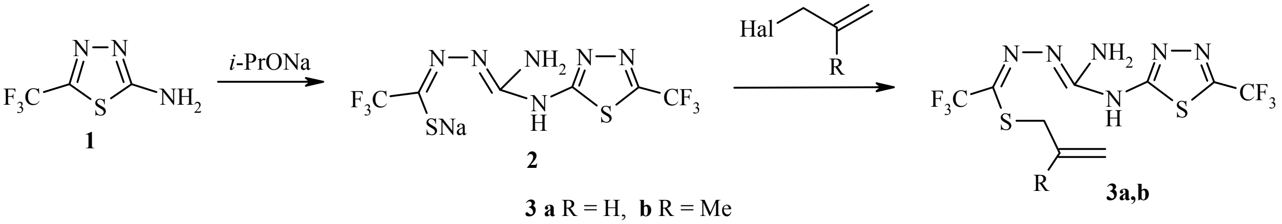
Keywords: 2-(5-allylthio-2-amino- and 2-(2-amino-6,6,6-trifluoro-5-methallylthio-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole, 2-(2-amino-6,6,6-trifluoro-5-mercapto-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole, 2-amino-5-trifluoromethyl-1,3,4-thiadiazole.

1,3,4-Thiadiazoles convert to the corresponding 1,2,4-triazole-3-thiones by the action of amines [1] or upon heating [2].

We have found that 2-amino-5-trifluoromethyl-1,3,4-thiadiazole (**1**) undergoes an unusual dimerization reaction with opening of a thiadiazole ring and formation of the S-sodium salt of 2-(2-amino-6,6,6-trifluoro-5-mercapto-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole (**2**) upon the action of sodium isopropylate. The structure of compound **2** was demonstrated by the alkylation by allyl bromide and methallyl chloride, which yielded 2-(5-allylthio-2-amino- (**3a**) and 2-(2-amino-6,6,6-trifluoro-5-methallylthio-1,3,4-triaza-2,4-hexa-dien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazoles (**3b**), respectively. The structures of these products were supported by GC/MS, IR and ^1H NMR spectroscopy.



3 a R = H, **b** R = Me

The ^1H NMR spectra were taken on a Bruker DRX-400 spectrometer at 400 MHz in DMSO-d_6 with TMS as the internal standard. The IR spectra were taken on a Varian 800FT-IR. The electron impact mass spectra were taken an Agilent GC/MS-PC at 70 eV using a 6890N gas chromatograph and 5975 mass selective detector.

Thiadiazole **1** was obtained according to Boechat et al. [3].

S-Sodium Salt of 2-(2-Amino-6,6,6-trifluoro-5-mercapto-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole (2). Thiadiazole **1** (1.014 g, 6 mmol) was added to a solution of sodium (0.138 g, 6 mmol) in 2-propanol (5 ml) and heated at reflux for 3 h. The solvent was distilled off. Water was added to the

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residue and the mixture was filtered. The filtrate was evaporated to give 0.734 g (34%) thiadiazole **2**; mp 192°C. IR spectrum, ν, cm^{-1}: 748 (CF_3), 3104, 3290 and 3458 (NH). Found, %: C 19.87; H 0.87; N 23.12; S 17.57. $C_6H_3F_6N_6NaS_2$. Calculated, %: C 20.00; H 0.84; N 23.33; S 17.80.

Preparation of Compounds 3a,b (General Method). Allyl halide (1 mmol) was added dropwise to a solution of thiadiazole **2** (0.180 g, 0.5 mmol) in 2-propanol (5 ml), heated at reflux for 1 h, and filtered. 2-Propanol was distilled off. The residue was treated with chloroform and filtered. The solvent was distilled off to give compounds **3a**,**b**.

2-(5-Allylthio-2-amino-6,6,6-trifluoro-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole (3a) was obtained in 82% yield (0.155 g); mp 110°C (ethanol). IR spectrum, ν, cm^{-1}: 745 (CF_3), 3283, 3391, and 3502 (NH). ^1H NMR spectrum, δ, ppm (*J*, Hz): 3.78 (2H, d, *J* = 6.86, SCH_2); 5.16 (1H, d, *J* = 10.15, $CH{=}C\underline{H_2}$); 5.23 (1H, d, *J* = 16.99, $CH{=}C\underline{H_2}$); 5.86 (1H, m, $C\underline{H}{=}CH_2$); 6.77 (2H, br. s, NH_2); 11.91 (1H, br. s, NH). Mass spectrum, *m/z* (I_{rel}, %): 378 $[M]^+$ (7), 195 (100). Found, %: C 28.13; H 2.17; N 22.10; S 16.73. $C_9H_8F_6N_6S_2$. Calculated, %: C 28.57; H 2.13; N 22.21; S 16.95.

2-(2-Amino-6,6,6-trifluoro-5-methallylthio-1,3,4-triaza-2,4-hexadien-1-yl)-5-trifluoromethyl-1,3,4-thiadiazole (3b) was obtained in 50% yield (0.097 g); mp 100°C (ethanol). ^1H NMR spectrum, δ, ppm (*J*, Hz): 1.80 (1H, s, CH_3); 3.75 (2H, s, SCH_2); 4.90 (2H, d, *J* = 1.43, $C(CH_3){=}C\underline{H_2}$); 6.78 (2H, br. s, NH_2), 11.92 (1H, br. s, NH). Mass spectrum, *m/z* ($I_{rel,}$ %): 392 $[M]^+$ (4), 195 (100). Found, %: C 30.42; H 2.64; N 21.36; S 16.21. $C_{10}H_{10}F_6N_6S_2$. Calculated, %: C 30.61; H 2.57; N 21.42; S 16.35.

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