Chemistry of Heterocyclic Compounds, Vol. 40, No. 9, 2004

UNEXPECTED REACTION OF THIOSEMICARBAZIDE WITH 3,6-BIS(VINYLSULFONYL)-1,2,4,5-TETRAFLUOROBENZENE

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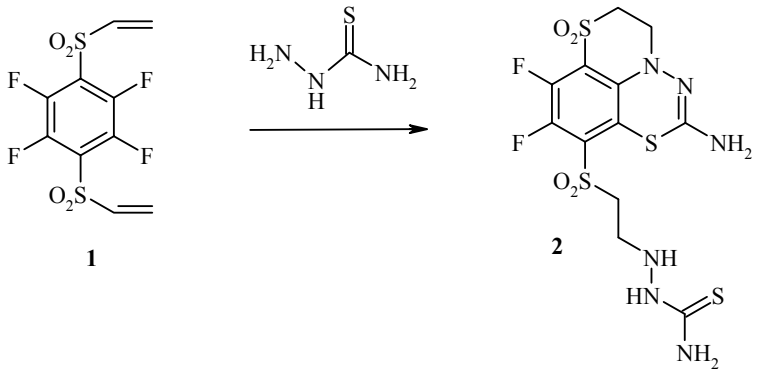
Keywords: 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene, thiosemicarbazide, nucleophilic addition and nucleophilic intramolecular substitution.

We have observed an unexpected direction for the reaction of thiosemicarbazide with 3,6-bis(vinylsulfonyl)-1,2,4,5-tetrafluorobenzene (**1**), leading to formation of the fluorinated derivative of a condensed nitrogen- and sulfur-containing heterocyclic compound: 2-amino-8,9-difluoro-10-(2-thiosemicarbazidoethylsulfonyl)-5,6-dihydrobenzo[*h,i*]-1,4-thiazino[4,3-*d*]-1,3,4-thiadiazine-7,7-dioxide (**2**).



1 **2**

Compound **2** was obtained as a result of nucleophilic addition of thiosemicarbazide to the activated vinyl group of sulfone **1** and subsequent intramolecular substitutions of the fluorine atoms of the benzene ring in the *ortho* position with participation of the NH group, and in the *meta* position with participation of the second nucleophilic center of the thiosemicarbazide, the sulfur atom. We described examples of simultaneous participation of the NH_2 group of amines in nucleophilic addition and substitution reactions [1,2].

The reaction proceeds with a four-fold molar excess of thiosemicarbazide in DMF at 70°C.

The structure of compound **2** was proven by IR and NMR (^1H, ^{13}C, ^{19}F, and ^{15}N) spectroscopy. The ^1H, ^{13}C, ^{19}F, and ^{15}N NMR spectra were recorded on a Bruker DPX 400. Operating frequencies: ^1H 400.13 MHz, ^{13}C 100.61 MHz, ^{19}F 376.50 MHz, and ^{15}N 40.54 MHz. The ^{15}N NMR spectrum, obtained by the DEPT technique with ^{15}N-H spin-spin coupling constants of 90 Hz, contains only the chemical shifts for the nitrogen atoms directly bonded to protons.

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2-Amino-8,9-difluoro-10-(2-thiosemicarbazidoethylsulfonyl)-5,6-dihydrobenzo[*h*,*i*]-1,4-thiazino-[4,3-*d*]-1,3,4-thiadiazine 7,7-Dioxide (2). Yield 54%; mp 235°C (decomposition). IR spectrum, ν, cm^{-1}: 1134 and 1326 (SO_2), 3314 (NH), 3454 (NH_2). ^1H NMR spectrum (DMF-d_7), δ, ppm: 3.38 (2H, m, CH_2SO_2); 3.85 [2H, m, CH_2SO_2 (ring)]; 3.89 (2H, m, CH_2N); 4.15 [2H, m, CH_2N (ring)]; 5.40 (1H, br. s, CH_2NH); 6.77 (2H, br. s, NH_2C=N); 7.81, 7.50 (2H, br. s, NH_2C=S); 8.85 (1H, s, NHC=S). ^{13}C NMR spectrum, δ, ppm (*J*, Hz): 43.84 (CH_2NH); 47.75 [CH_2N (ring)]; 49.38 [CH_2SO_2 (ring)]; 53.05 (CH_2SO_2); 119.90 ($C_{(4)}$, Ar, d, $^2J_{C,F\text{-}8}$ = 12.93); 122.23 ($C_{(6)}$, Ar); 128.45 ($C_{(1)}$, d, $^2J_{C_{(1)},F\text{-}9}$ = 10.78); 138.87 ($C_{(5)}$, Ar); 143.51 ($C_{(2)}$, dd, $^1J_{C_{(2)},F\text{-}9}$ = 260; $^2J_{C_{(2)},F\text{-}8}$ = 17.7); 146.74 ($C_{(3)}$, dd, $^1J_{C_{(3)},F\text{-}8}$ = 256, $^2J_{C_{(3)},F\text{-}9}$ = 16); 148.62 (C=N); 181.33 (C=S). ^{19}F NMR spectrum, δ, ppm (*J*, Hz): -138.63 (1F, d, $^3J_{F\text{-}8,F\text{-}9}$ = 23.5, F-9); -142.75 (1F, d, $^3J_{F\text{-}8,F\text{-}9}$ = 23.5, F-8). ^{15}N NMR spectrum (internal standard, $MeNO_2$), δ, ppm: -308.8 (NH_2C=N); 307.44 [NHNHC(S)]; 276.33 (NH_2C=S); -243.78 (NHC=S). Found, %: C 29.89; H 3.12; F 8.52; N 17.08; S 27.13. $C_{12}H_{14}F_2N_6O_4S_4$. Calculated, %: C 30.50; H 2.99; F 8.04; N 17.78; S 27.14.

This research was done with the financial support of the Russian Foundation for Basic Research (project No. 02-03-32844).

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