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REACTION OF 7-METHYL-5-OXO-2-THIOCYANATO-5H-1,3,4-THIADIAZOLO[3,2-*a*]PYRIMIDINE WITH THIOSEMICARBAZIDE

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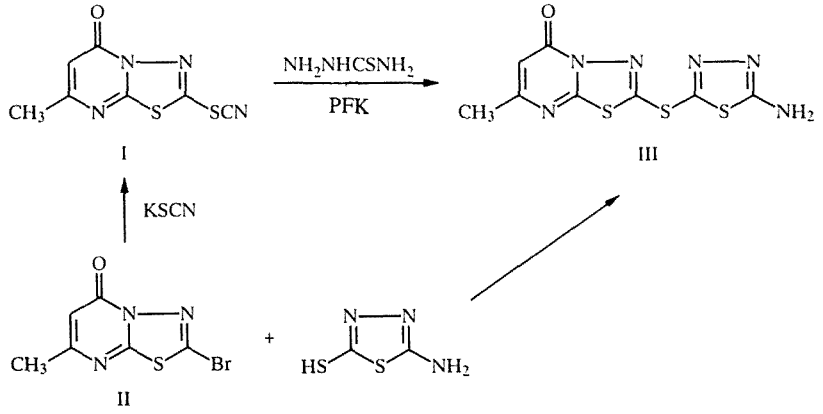
It is known that thiosemicarbazide reacts with alkyl(aryl) thiocyanates to form 2-amino-5-alkyl(aryl)thio-1,3,4-thiadiazoles [1]. However it has been noted that heterocyclic thiocyanates, e.g., 2-thiocyanatobenzothiazole, behave anomalously and are converted to the isomeric isothiocyanates in boiling methanol [2].

We have found that 7-methyl-5-oxo-2-thiocyanato-5H-1,3,4-thiadiazolo[3,2-*a*]pyrimidine (I), synthesized from 2-bromo-7-methyl-5-oxo-5H-1,3,4-thiadiazolo[3,2-*a*]pyrimidine (II) and potassium thiocyanate, does not isomerize in PFK but reacts with thiosemicarbazide at 90-100°C to give 2-(2-amino-1,3,4-thiadiazol-5-yl)thio-7-methyl-5-oxo-5H-1,3,4-thiadiazolo[3,2-*a*]pyrimidine (III).



Compound III was synthesized directly by the reaction of compound II with 2-amino-5-mercapto-1,3,4-thiadiazole.

The elemental analyses of compounds I and III agreed with the calculated figures.

Compound I ($C_7H_4N_4OS_2$). A mixture of potassium thiocyanate (0.03 mole) and II (0.02 mole) [3] in 50% aqueous ethanol (25 cm^3) was stirred for 5-6 h at 40-50°C. The precipitate was filtered off, washed with water and air dried, m.p. 255-256°C (1:1 dioxane-water). IR spectrum (thin layer): 1670 (C=O), 1510 (C=N), 2070 cm^{-1} (SCN). ^1H NMR spectrum (DMSO): 6.00 (H, s, CH), 2.35 ppm (3H, s, CH_3). Yield 89%.

Compound III ($C_8H_6N_6OS_3$). A. Thiosemicarbazide (0.02 mole) was dissolved with heating in PFK (15-20 g) and I (0.02 mole) was added in portions. The reaction mixture was stirred for 3-4 h at 90-100°C, then cooled, diluted with water (100 cm^3) and the solution adjust to pH 5-7 by addition of 40% NaOH. The precipitate was filtered off, washed with water and air dried, m.p. 239-240°C (5:1 dioxane−water). IR spectrum (thin layer): 1680 (C=O), 1509, 1568 (C=N), 3280 cm^{-1} (NH). ^1H NMR spectrum (DMSO): 7.87 (2H, s, NH_2), 6.17 (H, s, CH), 2.17 ppm (3H, s, CH_3). Yield 61%.

B. A mixture of 2-amino-5-mercapto-1,3,4-thiadiazole (0.011 mole) and NaOH (0.011 mole) in 50% aqueous ethanol (20 cm^3) was stirred for 0.5 h and II (0.01 mole) was then added. After stirring for a further 3-4 h, the precipitate was filtered off, washed with water and air dried. M.p. 239-240°C. Yield 93%.

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