REACTION OF ETHYL CYANOACETATE WITH 4-AMINO-3-MERCAPTO-5R-1,2,4-TRIAZOLE

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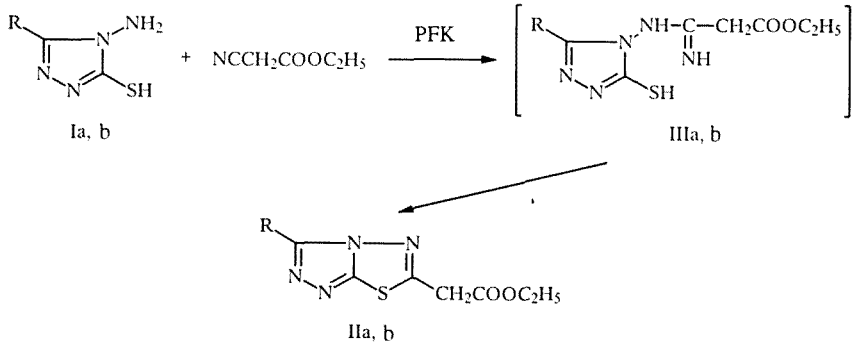
The traditional route for heterocyclization with the introduction of alkoxycarbonylmethyl group is based on ethyl cyanoacetate [1, 2]. Recently a relatively simple method for the construction of heterocycles by interaction of thiosemicarbazide with ethyl cyanoacetate and ethyl acetoacaetate in PFK was proposed for the preparation of 7-methyl-5-oxo-2-ethoxycarbonylmethyl-5H-1,3,4-thiadiazolo[3,2-*a*]pyrimidine [3]. To investigate the scope of this method the reaction of the 4-amino-3-mercapto-5R-1,2,4-triazoles (Ia, b) with ethyl cyanoacetate was studied. The reaction products were the 2-ethoxycarbonylmethyl-5R-1,2,4-triazolo[3,4-*b*]1,3,4-thiadiazoles (IIa,b).



I—III a R = CH_3, b R = C_2H_5

The products II are evidently formed by addition of the cyano group of ethyl cyanoacetate to the amino group of the triazole I to give the intermediate (III) which subsequently cyclizes. To obtain compounds IIa,b a mixture of 0.01 mole ethyl cyanoacetate, 0.01 mole of triazole Ia,b and 10 g PFK was stirred on a boiling water bath for 3-4 h, then cooled, diluted with 100 cm^3 of water and the reaction product extracted with chloroform (3 × 20 cm^3).

Compound IIa ($C_8H_{10}N_4O_2S$), m.p. 115-116°C (1:2 chloroform–hexane). IR spectrum (thin layer): 1719 (C=O), 1590 cm^{-1} (C=N). ^1H NMR spectrum ($CDCl_3$): 1.2 (3H, t, CH_3), 2.6 (3H, q, CH_3), 4.05 (2H, s, CH_2), 4.13 ppm (2H, q, CH_2). Yield 50%.

Compound IIb ($C_{19}H_{12}N_4O_2S$). M.p. 46-47°C (1:3 chloroform–hexane). IR spectrum (thin film): 1720 (C=O), 1590 cm^{-1}. ^1H NMR spectrum ($CDCl_3$): 1.15 (3H, t, CH_3), 1.22 (3H, t, CH_3), 2.9 (2H, q, CH_2), 3.95 (2H, s, CH_2), 4.1 ppm (2H, q, CH_2). Yield 62%.

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