EFFECT OF BASES ON 1,3,4-THIADAZOLO[3,2-a]PYRIMIDINIUM SALTS

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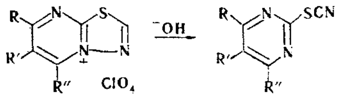
1,3,4-Thiadiazolo[3,2-a]pyrimidinium salts are converted by the action of bases to 2-thiocyanopyrimidines, which were also obtained from 2-amino-1,3,4-thiadiazole and β-diketones, thus bypassing the step involving the isolation of the pyrimidinum salts.

The formation of 2-thiocyanopyrimidines by the action of alkali on 1,3,4-thiadiazolo[3,2-a]pyrimidones and their derivatives was described in a recently published paper [1]; Tsuji and Kamo assume that the indicated transformation occurs through thiadiazolopyrimidinium salts with a positively charged bridge nitrogen atom in one of the mesomeric structures. The reaction occurs by the action of 5% NaOH, whereas weaker bases (aqueous sodium carbonate solution) are incapable of cleaving the thiadiazole ring.

In the present paper we used genuine thiadiazolopyrimidinium salts in which the positive charge is located on the bridge nitrogen atom in the ground structure; we were the first to obtain these compounds [2], after which they were prepared by German [3] and Japanese [4] chemists. In this case, the thiadiazole ring is cleaved not only by alkali but also by ammonium hydroxide.



I a, c, d IIa, c, d

I, IIa R = R″ = CH_3, R′ = H; c R = R″ = CH_3, R′ = C_2H_5; d R = CH_3, R″ = cyclopropyl R′ = H

Moreover, we showed that 2-thiacyanopyrimidines IIa, IIb (R = R′ = R″ = CH_3), and IIe (R = CH_3, R′ = H, and R″ = C_6H_5) are formed in the reaction of 2-amino-1,3,4-thiadiazole with β-diketones in acetic acid and

TABLE 1. 2-Thiocyanopyrimidines (II)

Compound	Method	mp, °C (recrystallization solvent)	Empirical formula	S, %		ν_{SCN}, cm^{-1}	δ, ppm			Yield, %
				found	calc.		R	R′	R″	
a	A	68[a] (octane)	$C_7H_7N_3S$	19,3	19,4	2164	2,57	7,08	2,57	56
	D									75
b	C	54—55 (hexane)	$C_8H_9N_3S$	17,6	17,9	2167	2,60	2,35	2,60	21
c	A	115—120 (2 mm)[c]	$C_9H_{11}N_3S$	16,6	16,6	2167	2,58	1,18[b] 2,4—2,8[d]	2,58	40
d	B	84 (heptane)	$C_9H_9N_3S$	16,6	16,8	—	—	—	—	96
e	C	70—72 (octane)	$C_{12}H_9N_3S$	14,1	14,1	—	2,58	7,4—7,5[e]	7,4 (м, 2H) 8,0 (м, 3H)	60

[a] According to [5], this compound has mp 65°.

[b] $-CH_2CH_3$, t, J = 7.5 Hz.

[c] This is the boiling point of the product with n_D^{16} 1.5530.

[d] CH_2CH_3, q, J = 7.5 Hz.

[e] Superimposed on the signal of the phenyl ring.

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subsequent neutralization with ammonia or alkali and even by reaction of the aminothiadiazole with acetylacetone in aqueous media without alkalization. In both cases, the reaction probably proceeds through thiadiazolopyrimidinium salts; in the second case, water or the β-diketone act as acids and bases.

EXPERIMENTAL

The PMR spectra of CCl_4 solutions were recorded with a ZKR 60 spectrometer and are presented on the δ scale with respect to tetramethylsilane. The IR spectra of KBr pellets or of the pure liquids were recorded with a UR-10 spectrometer.

Preparation of 2-Thiocyanopyrimidines. A) A suspension of 0.005 mole of I in 20 ml of water was shaken with 7 ml of 5% NaOH for 20-30 min. The precipitated product was removed by filtration, washed with water, and air dried. In the case of IIc, the product was extracted with ether and vacuum distilled after drying and removal of the solvent.

B) The reaction was carried out similarly, but ammonium hydroxide was used in place of alkali and the mixture was shaken for 40 min.

C) A solution of 0.01 mole of 2-amino-1,3,4-thiadiazole and 0.011 mole of β-diketone in 1 ml of acetic acid was refluxed for 30 min. It was then cooled, excess 5% NaOH was added, and the mixture was stirred for 30 min. The reaction product was removed by filtration or extracted with chloroform, which was washed with a weak solution of alkali and water. The extract was dried, and the solvent was removed to give the reaction product.

D) A mixture of 3.7 g (37 mmole) of 2-amino-1,3,4-thiadiazole and 12.4 g (124 mmole) of acetylacetone was refluxed for 2 h. It was then cooled, 450 ml of water was added, and the mixture was filtered to give 4.5 g of 2-thiocyano-4,6-dimethylpyrimidine.

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