According to the results of gas—liquid chromatography (GLC), the principal product of the reaction of methylthiirane with acetone hydrazone isolated by distillation [bp 82-83°C (11 mm) and n_D^{20} 1.5058] is an individual compound, but the presence in its mass spectrum of a fragment ion with m/e 99 ($[M - 47]^+$) and the considerably more intense ion with m/e 85 ($[M - 61]^+$), which corresponds to hydrazone Ib, do not exclude the fact that partial mercaptoalkylation takes place with alternative opening of the thiirane ring.

The principal products of the reaction of acetone hydrazone with thiiranes are tautomeric mixtures. Thus singlets of CH_3 groups of the chain (C_2Cl_4, 1.70 and 1.85 ppm) and cyclic (1.46 ppm) forms are observed in the PMR spectrum of the Ia $\rightleftarrows$ IIa mixture; the Ia: IIa ratio is 4:1 at 30°C and 16:1 at 90°C. The intensities of the singlet signals of the CH_3 groups of the chain (1.68 and 1.83 ppm) and cyclic (1.30 and 1.57 ppm) forms correspond to Ib:IIb ratios of 1:1 and 6:1 at 30 and 90°C, respectively. The oxygen analogs of Ia, b do not undergo cyclization (for example, see [1]).

The reaction of thiirane with isobutyraldehyde hydrazone gives mainly aminothiazolidine IIIc (60% according to GLC) with bp 87-88°C (8 mm) and n_D^{20} 1.5172. PMR spectrum (CCl_4), δ: 0.95 and 1.04 (d, J = 6.5 Hz, diastereotopic CH_3 groups), 1.73 (m, α-H), 2.5-3.4 (m, 4- and 5-H), and 3.76 ppm (d, J = 10 Hz, 2-H). The structure was proved by conversion to IVc with bp 98-99°C (7 mm), n_D^{20} 1.5081, and a C=N band at 1637 cm^{-1}. The PMR spectrum of IVc differs from the spectrum of thiazolidine IIIc primarily with respect to the presence of two singlets at 1.90 and 2.04 ppm ($Me_2C{=}N$). The formation of aminothiazolidines III is probably the first example of the addition of thiiranes to the C=N bond; however, a similar reaction with nitriles in the presence of acids, which leads to thiazolines, is known [2].

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REPLACEMENT OF THE CHLORINE ATOM IN 3-CHLORO-6-HYDRAZINOPYRIDAZINE AND 5(8)-CHLORO-8(5)-HYDRAZINOPYRIDO[2,3-d]PYRIDAZINES BY AN SH GROUP BY REACTION WITH CARBON DISULFIDE

I. B. Lundina, N. N. Vereshchagina,
G. S. Melkozerova, and D. V. Kiryaeva

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We have observed that replacement of the chlorine atom by a mercapto group takes place along with the expected formation of a triazole ring in the reaction of 3-chloro-6-hydrazinopyridazine (I) with CS_2 in pyridine solution to give 6-mercapto-3(2H)-sym-triazolo[4,3-b]pyridazinethione (II).

5(8)-Chloro-8(5)-hydrazinopyrido[2,3-d]pyridazines (III, V) also react similarly: (See scheme at top of next page).

We assumed that this unusual replacement of a chlorine atom by a mercapto group in the reaction with carbon disulfide occurs due to the hydrogen sulfide evolved during the reaction. The formation of, for example, 5-hydrazino-8(7H)-pyrido[2,3-d]pyridazinethione (VII), when hydrogen sulfide is passed through a pyridine solution of chloride V serves as a confirmation of this assumption. We note that VII cannot be obtained by reaction of chloride V with thiourea: the starting compound is recovered. The structure of VII is confirmed by its conversion by the action of carbon disulfide to a compound identical to 6-mercapto-3(2H)-pyrido[3,2-d]-sym-triazolo[4,3-b]pyridazinethione (VI) and by the absence in its IR spectrum of an absorption band at 2500-2600 cm^{-1}. The IR spectra of II, IV, and VI contain bands at 2533, 2558, and 2550 cm^{-1}, which, respectively, are related to the vibrations of an SH group, and at 3000-3300 cm^{-1}, which corresponds to the NH vibrations of a thioamide group. Taking

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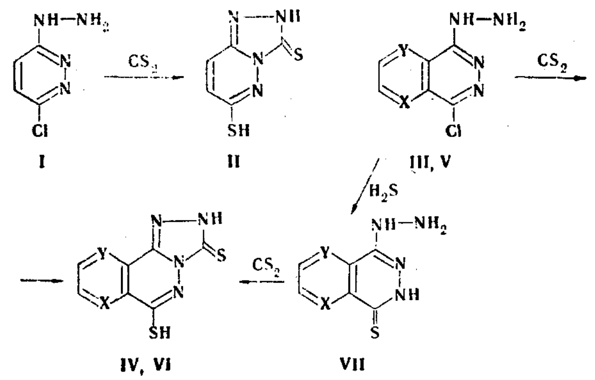
I II III, V IV, VI VII

III, IV X=CH, Y=N; V–VII X=N, Y=CH

into account the fact that mercapto derivatives of triazole generally exist in the thione form, the structures indicated in the reaction scheme above can be assigned to II, IV, and VI.

The compounds obtained had the following melting points and were obtained in the indicated yields (in percent): 6-mercapto-3(2H)-sym-triazolo[4,3-d]pyridazinethione (II), 278-281°C, 70; 6-mercapto-3(2H)-pyrido[2,3-d]-sym-triazolo[4,3-d] pyridazinethione (IV), > 300°C, 60; 6-mercapto-3(2H)-pyrido[3,2-d]-sym-triazolo[4,3-b]pyridazinethione (VI), >300°C, 50; 5-chloro-8-hydrazinopyrido[2,3-d]pyridazine (VII), 279-280° (dec.), 85.

The results of complete elementary analysis of the compounds obtained are in agreement with the calculated values.