CD_3OD) for II, $\Delta G_{253K}^{\neq} = 12.3$ for III, and $\Delta G_{257K}^{\neq} = 11.9$ (±0.5) kcal/mole for IV. The same value of the barrier to conversion (12.7 kcal/mole) was recently found also for 3,4-dimethyl derivative VI [3]. Thus the presence of substituents at both the nitrogen and carbon atoms does not have a substantial effect on the barrier to ring conversion.

LITERATURE CITED

1. S. M. Shevchenko, T. Ya. Vakhitov, and A. A. Potekhin, Khim. Geterotsikl. Soedin., No. 10, 1427 (1978).
2. S. M. Shevchenko and A. A. Potekhin, Khim. Geterotsikl. Soedin., No. 11, 1569 (1978).
3. A. R. Katritzky, R. C. Patel, and D. M. Read, Tetrahedron Lett., No. 43, 3803 (1977).

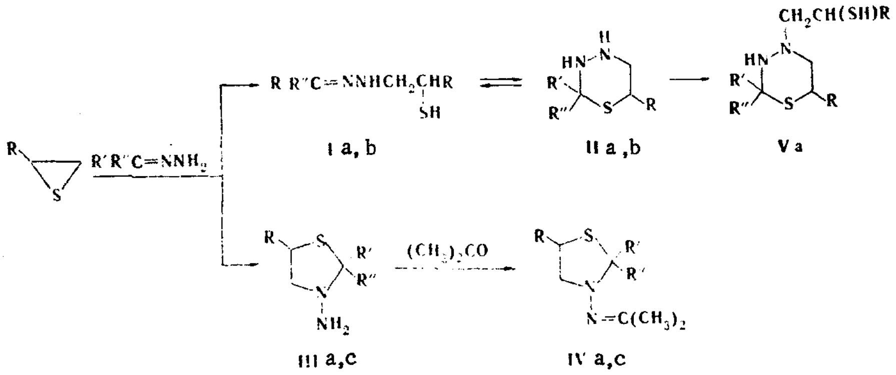
REACTION OF THIIRANES WITH HYDRAZONES

S. M. Shevchenko and A. A. Potekhin

UDC 547.789.1'876

We have found that the reaction of thiiranes with unsubstituted hydrazones (with a fourfold excess of the hydrazone in benzene at 60°C) leads to (2-mercaptoalkyl)hydrazones I, which undergo reversible cyclization to perhydro-1,3-thiadiazines II or to thiazolidine derivatives III.

The synthesis of II from aldehydes or ketones and the corresponding heretofore unknown hydrazino thiols seems more convenient; however attempts to obtain the latter by mercaptoalkylation of hydrazine were unsuccessful because of polymerization of the thiiranes.



I–V a R=H, R′=R″=Me; Ib IIb R=R′=R″=Me; IIIc IVc R=R′=H, R″=*i*-Pr

The formation of I ⇄ II (in 30-40% yields) is complicated by side and secondary processes. Thus distillation of the products of the reaction of acetone hydrazone with thiirane yielded, in addition to perhydrothiadiazine IIa [bp 77-78°C (8 mm) and n_D^{20} 1.5190], 2-hydrazinoethanethiol (8%), with mp 63-64°C (from CCl_4), which is converted to IIa by the action of acetone. The hydrazino thiol is formed simultaneously with acetone azine, evidently as a result of an exchange reaction of hydrazone Ia with the starting hydrazone. The principal reaction product (Ia ⇄ IIa) contained only ~10% of the impurity, to which the singlet at 1.50 ppm (CCl_4) in the PMR spectrum corresponded. The assumption that the impurity has aminothiazolidine structure IIIa that was made on the basis of this is confirmed by the formation of isopropylidene derivative IVa on treatment with acetone; the structure of the latter is in agreement with the mass-spectrometric data and with the presence in the PMR spectrum (CCl_4) of singlet signals of CH_3 groups at 1.42, 1.92, and 1.99 ppm. An adduct involving one molecule of hydrazone and two molecules of thiirane, with bp 124-127°C (11 mm) and n_D^{20} 1.5440, was isolated in 9% yield from the same reaction mixture. The signlet signal of both CH_3 groups observed in the PMR spectrum of the adduct at 30°C (1.50 ppm, $CDCl_3$) is converted below −14°C to two singlets (1.39 and 1.65 ppm), which indicates the relatively high barrier to ring conversion and is more likely in agreement with a six-membered structure (Va) rather than a five-membered structure.

A. A. Zhdanov Leningrad State University, Leningrad 199164. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1569-1570, November, 1978. Original article submitted May 23, 1978.

0009-3122/78/1411-1282$07.50

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].

LITERATURE CITED

1. A. A. Potekhin and B. D. Zaitsev, Khim. Geterotsikl. Soedin., No. 3, 301 (1971).
2. G. K. Helmkamp, D. J. Pettitt, and J. R. Loweil, J. Am. Chem. Soc., 88, 1030 (1966).

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

UDC 547.852.859

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

---

S. M. Kirov Ural Polytechnic Institute, Sverdlovsk 620002. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, p. 1571, November, 1978. Original article submitted October 31, 1977.