

FORMATION AND RECYCLIZATION OF HETEROCYCLES

V.* REACTION OF HYDRAZINE WITH SOME AZOLIDONES

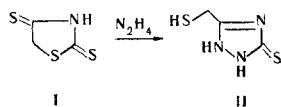
O. P. Shvaika, V. N. Artemov,
and S. N. Baranov

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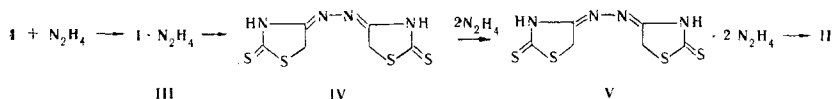
Thiorhodanine is recycled to 1,2,4-triazole-3-thione by reaction with hydrazine. The intermediate recyclization products were identified. 4-Iminothiazolidone is recycled to 1,2,4-triazol-3-one by reaction with hydrazine. 1,3-oxazolid-4-one-2-thione forms 2-hydrazono-oxazolid-4-one by reaction with hydrazine in neutral solvents. The intermediate transformation products were isolated and indicate that the reaction proceeds as a recyclization of the starting oxazolidone under the influence of hydrazine.

In previous communications we examined the reaction of rhodanines, isorhodanines, and oxa- and thiazolidinediones with hydrazine [1-3]. In this communication we will deal with the reactions of hydrazine with thiorhodanines, 4-iminothiazolidones, oxazolidonethiones, and the associated recyclization reactions.

We have found that thiorhodanines, on reaction with hydrazine, are recycled to triazolethiones [4], which we previously described in [1].

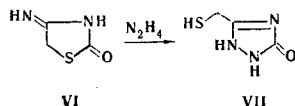


The intermediate products through which this reaction probably occurs can be isolated by a gradual change in the temperature conditions of the process. A salt of I with hydrazine (III) is initially formed and is an extremely unstable compound which can be identified in anhydrous media at -10° and readily evolves hydrogen sulfide with increasing temperature to give azine IV. The latter, with excess hydrazine, forms a salt-like substance (V), which is converted to II on further heating. Only II and IV can be isolated in aqueous media. Thus, the course of the recyclization of thiorhodanine with hydrazine can be expressed by the scheme



The salt structure of V follows from its chemical properties. With benzaldehyde it forms a benzalazine and IV, while hydrazine hydrochloride and IV are formed by reaction with hydrochloric acid. In addition, V dissolves in water and is insoluble in organic solvents.

4-Iminothiazolid-2-one (VI), on reaction with hydrazine, is recycled to triazolone VII, which is identical to the compound we synthesized in [2, 3].



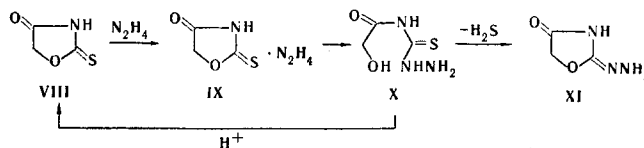
*See [1] for communication IV.

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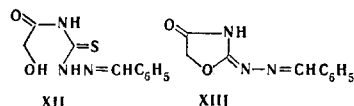
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The mechanism for the recyclization of VI is probably analogous to the mechanism for the recyclization of isorhodanines described in [3, 5].

A ring-opening product (X) was identified in the reaction of 1,3-oxazolid-4-one-2-thione (VIII) with hydrazine (a similar reaction is known for rhodanine [1]) which is converted to 2-hydrazoneoxazolid-4-one (XI) on heating. The latter can also be obtained by direct reaction of oxazolidonethione with an equivalent amount of hydrazine. Thus, the recyclization of oxazolidonethione on reaction with hydrazine can be expressed by the scheme



X and XI form N-benzylidene derivatives (XII and XIII) and give a positive reaction for a hydrazine group with Fehling's solution.



Like the rhodanine derivatives [1], X in acid media is again converted to starting oxazolidonethione; the ring is destroyed on refluxing the oxazolidonethione with excess hydrazine to give glycolic acid and thiosemicarbazide.

EXPERIMENTAL

Hydrazinium Thiorhodanide (III). Thiorhodanine was suspended in a methanol-ether mixture (1:1), and an equimolecular amount of hydrazine hydrate was added to the suspension at -15 to -10° ; III precipitated in the process. The yield of III with mp $\sim 40^\circ$ (at the thermometer bulb) was almost quantitative. The reaction of III with benzaldehyde gave benzalazine with mp 92° , which did not depress the melting point of an authentic sample.

4,4'-Azinobis-1,3-thiazolidine-2-thione (IV). A) III evolved hydrogen sulfide at room temperature and formed a yellow substance with mp 194 – 196° (dec.). Found %: N 21.5; S 48.5. $C_6H_6N_4S_4$. Calc. %: N 21.4; S 48.8.

B) Thiorhodanine [1.5 g (10 mmole)] was added in portions with stirring to a solution of 0.5 ml (10 mmole) of hydrazine hydrate in methanol at room temperature. A homogeneous solution formed with hydrogen sulfide evolution. A yellow precipitate of IV formed after some time and was filtered and washed with methanol and ether to give 0.9 g (68%) of a product with mp 194° (dec.) which did not depress the melting point of the previous sample.

Dihydrazinium 4,4'-Azinobis-1,3-thiazolidine-2-thionide (V). A) Thiorhodanine [1.5 g (10 mmole)] was sprinkled in small portions with stirring into a solution of 0.75 ml (15 mmole) of hydrazine hydrate in 10 ml of methanol. After 30 min the yellow precipitate of V was filtered and thoroughly squeezed on filter paper to give 1.5 g (94%) of a product with mp $\sim 88^\circ$. An equimolecular amount of benzaldehyde was added to a suspension of V in ether to give IV with mp 194° (dec.) which did not depress the melting point of the above-described sample. Benzalazine with mp 92° was isolated from the mother liquor and did not depress the melting point of an authentic sample. Found %: N 34.6; S 39.0. $C_6H_{14}N_8S_4$. Calc. %: N 34.3; S 39.3.

B) Hydrazine hydrate [0.5 ml (10 mmole)] was added to a suspension of 1.3 g (5 mmole) of IV and 10 ml of methanol to give 1.5 g (93%) of a bright-yellow precipitate of V with mp 88° ; this product did not depress the melting point of the previous sample.

5-(α -Mercaptomethyl)-1,2,4-triazole-3-thione (II). A) An equimolecular amount of hydrazine hydrate was added gradually with stirring to a solution of thiorhodanine in alcohol, and after 0.5 h of stirring (during which hydrazine sulfide evolution was observed) the alcohol solution was diluted with a twofold volume of water, and another half equivalent of hydrazine hydrate was added. The reaction mixture was refluxed for 10 min, cooled, and the resulting precipitate was filtered and washed with alcohol and ether to give 50% of

a product with mp 220° (dec.) which did not depress the melting point of a sample obtained by the method in [1].

B) Hydrazine hydrate [0.25 ml (5 mmole)] was added to a suspension of 1.3 g (5 mmole) of IV in 10 ml of water. The resulting solution was cooled, acidified with hydrochloric acid until it gave an acid reaction to Congo red, and 0.8 g (60%) of a precipitate of II with mp 220° (from water) was removed by filtration; this product did not depress the melting point of a sample obtained according to [1].

5-(α -Mercaptomethyl)-1,2,4-triazol-3-one (VII). Hydrazine hydrate [0.5 ml (10 mmole)] was added to a suspension of 1.16 g (10 mmole) of 4-iminothiazolidone in water, and the mixture was refluxed for 20 min (during which ammonia was evolved). Cooling of this mixture precipitated 1.1 g (84%) of white crystals of VII with mp 218° (from water) which did not depress the melting point of an authentic sample obtained according to [2, 3].

4-Glycolylthiosemicarbazide (X). 1,3-Oxazolid-4-one-2-thione [1.17 g (10 mmole)] was suspended in 2 ml of methanol, the suspension was cooled to -10°, and 0.5 ml (10 mmole) of hydrazine hydrate was added with stirring. A homogeneous solution was formed, from which oily product IX was isolated after the addition of 3 ml of ether. White crystals of X [0.9 g (60%)] formed on raising the temperature to room temperature and had mp 116°. Found %: C 24.3; H 4.8; N 28.4; S 21.3. $C_3H_7N_3O_2S$. Calc. %: C 24.2; H 4.7; N 28.2; S 21.5.

In a similar experiment in an aqueous medium a thiosemicarbazide with mp 180° was isolated in 83% yield; this did not depress the melting point of an authentic sample.

Benzaldehyde 4-Glycolylthiosemicarbazone (XII). X [0.75 g (5 mmole)] was suspended in 5 ml of methanol, 0.53 g (5 mmole) of benzaldehyde was added, and the mixture was heated until everything had completely dissolved (~5 min). Cooling of this mixture precipitated 1.1 g (93%) of white crystals of II with mp 152° (from alcohol) which were soluble in dioxane and slightly soluble in alcohol. Found %: N 17.5; S 13.5. $C_{10}H_{11}N_3O_2S$. Calc. %: N 17.3; S 13.5.

2-Benzoylidenehydrazono-1,3-oxazolid-4-one (XIII). 1,3-Oxazolid-4-one-2-thione [1.17 g (10 mmole)] was dissolved in 4 ml of methanol, and 0.48 ml (9.6 mmole) of hydrazine hydrate was added to the solution. The solution was refluxed for 5 min until hydrogen sulfide evolution ceased, 0.6 ml (5.7 mmole) of benzaldehyde was added, and the mixture was cooled. The resulting crystals were filtered and washed with ether to give 0.7 g (36%) of XIII with mp 230° (from dioxane). Found %: C 59.2; H 4.6; N 20.5. $C_{10}H_9N_3O_2$. Calc. %: C 59.1; H 4.5; N 20.7.

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