STUDIES ON AZOLIDONES AND THEIR DERIVATIVES

I. Preparation and Properties of 4-Iminothiazolid-2-one

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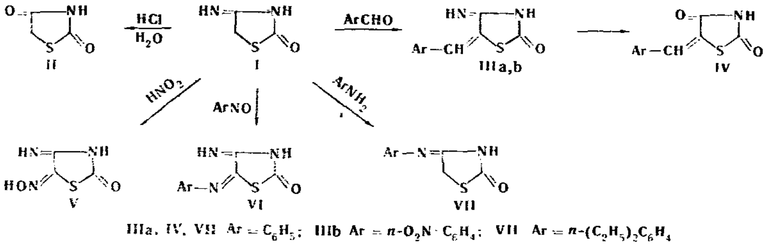
The action of a concentrated aqueous solution of ammonia on 4-thioxothiazolid-2-one has given an isomer of pseudothiohydantoin, 4-iminothiazolid-2-one (I). 5-Substituted derivatives of I have been obtained by the condensation of I with carbonyl and nitroso compounds and 4-substituted derivatives by condensation with amino compounds.

In the isomer of rhodanine that we have previously obtained [1], 4-thioxothiazolid-2-one, not only the methylene group but also the thioketone group > C=S proved to be extremely active, readily reacting with amino compounds [2]. In view of this, we became interested in the reaction of isorhodanine with ammonia as a method of obtaining unsubstituted 4-iminothiazolid-2-one (I), an isomer of pseudothiohydantoin. The synthesis of this compound from thiocyanoacetamide was reported in 1893 by Miolati [3], who called it "isothiohydantoin". However, it was impossible to repeat this synthesis. At the same time, by the reaction of isorhodanine with concentrated ammonia solution a product was obtained in high yield all the properties of which corresponded to the imino compound I but differed markedly from those of Miolati's "isothiohydantoin".

The I that we synthesized readily condenses with carbonyl and nitroso compounds with the formation of the corresponding derivatives III, V, and VI, which shows the high reactivity of the hydrogen atoms of the methylene group. The structure of III was shown by its conversion into IV by acid hydrolysis. I also reacts with amines, forming the 4-imino-substituted derivative VII, which have been described previously [2].



IIIa, IV, VII Ar = C_6H_5; IIIb Ar = n-$O_2N \cdot C_6H_4$; VII Ar = n-$(C_2H_5)_2C_6H_4$

EXPERIMENTAL

4-Iminothiazolid-2-one (I). A mixture of 3.3 g (0.025 mole) of isorhodanine and 15 ml of 25% aqueous ammonia was heated at 80° C in a flask with a reflux condenser for 15 min. The white crystalline precipitate that had deposited was filtered off, washed with 50 ml of water and a small amount of methanol, and dried at 60° C. Yield 2.3 g (80%). After recrystallization from water it formed colorless lamellar plates; it did not melt below 325° C. Sparingly soluble in water and organic solvents. UV spectrum: λ_{max} 250 nm, log ε 3.77; λ_{min} 290 nm, log ε 1.91 (in ethanol). Found, %: C 31.28, 31.31; H 3.53, 3.46; N 24.20; 24.02; S 27.34, 27.59. Calculated for $C_3H_4N_2OS$ %: C 31.03; H 3.47; N 24.14; S 27.61.

Acid hydrolysis of I. A mixture of 0.58 g (0.005 mole) of I and 2 ml of concentrated hydrochloric acid was boiled for 15 min. The white crystalline precipitate that deposited on cooling was filtered off, washed with water, and dried. Yield 0.46 g. After recrystallization from water, mp 124–125° C, with no depression in admixture with authentic thiazolidine-2,4-dione (II) [4].

5-Benzylidene-4-iminothiazolid-2-one (IIIa). A mixture of 0.58 g (0.005 mole) of I, 0.54 g (0.005 mole) of benzaldehyde, 0.5 g of anhydrous sodium acetate, and 5 ml of glacial acetic acid was boiled under reflux for 15 min and was then cooled and poured into 30 ml of water. The precipitate was filtered off, washed with water and ethanol, and dried at 60° C. Yield 0.92 g (90%). Mp 266–267° C (decomp., from ethanol). Small light yellow crystals sparingly soluble in water and the usual organic solvents. Found, %: N 13.59, 13.63; S 15.55, 15.55. Calculated for $C_{10}H_8N_2OS$, %: N13.71; S 15.70.

Acid hydrolysis of IIIa. A mixture of 0.2 g (0.001 mole) of IIIa and 5 ml of 10% hydrochloric acid was boiled under reflux for 6 hr. After cooling, the precipitate was filtered off, washed with water, and dried; mp 242–243° C (from acetic acid) with no depression in admixture with authentic 5-benzylidene-thiazolidine-2,4-dione [5].

5-(p-Nitrobenzylidene)-4-iminothiazolid-2-one (IIIb). A mixture of 1.16 g (0.01 mole) of I, 1.51 g (0.01 mole) of p-nitrobenzaldehyde, 1 g of anhydrous sodium acetate, and 15 ml of glacial acetic acid was heated in the water bath for 30 min. The cooled reaction mixture was poured into 50 ml of water, and the precipitate was filtered off, washed with water and with methanol, and dried at 60° C. Yield 2.4 g (96%), mp 258–259° C (from methanol). Yellow needles, sparingly soluble in water and the usual organic solvents. Found, %: N 17.01, 16.94; S 12.72, 12.68. Calculated for $C_{10}H_8N_3O_3S$, %: N 16.86; S 12.87.

5-(p-Diethylaminophenylimino)-4-iminothiazolid-2-one (VI). A mixture of 0.58 g (0.005 mole) of I, 0.89 g (0.005 mole) of p-nitrosodiethylaniline, and 5 ml of acetic anhydride was prepared with cooling and was left for 20 hr. Then 20 ml of water was added and the mixture was left for 4 hr. The precipitate was filtered off, washed with water, and dried over sulfuric acid. Yield 0.58 g (42%); mp 198–200° C (decomp. from butanol). Dark brown lustrous plates, sparingly soluble in organic solvents, insoluble in water. Found, %: N 20.14, 20.17; S 11.70, 11.55. Calculated for $C_{13}H_{16}N_4OS$, %: N 20.27; S 11.60.

5-Isonitroso-4-iminothiazolid-2-one (V). To 50 ml of 5% hydrochloric acid cooled to 0° C 5.8 g (0.05 mole) of I was added and to this mixture, with stirring and cooling, a solution of 10.5 g of sodium nitrite in 20 ml of water was added dropwise over 3 hr. The resulting mixture was left at room temperature for 12 hr. The precipitate was filtered off, washed with water and with acetone, and dried at 60° C. Yield 5.1 g (70%). Mp 198–200° C (from water). Colorless prisms, sparingly soluble in water and in organic solvents. Found, %: N 10.04; 9.96; S 11.57, 11.32%. Calculated for $C_3H_3N_3OS$, %: N 9.99; S 11.44.

4-Phenyliminothiazolid-2-one (VII). A mixture of 1.1 g (0.01 mole) of I, 0.93 g (0.01 mole) of aniline, 0.5 g of anhydrous sodium acetate, and 5 ml of glacial acetic acid was boiled under reflux for 15 min. After cooling, 50 ml of water was added and the precipitate was filtered off, washed with water and methanol, and dried at 60° C. Yield 1.5 g (78%); mp 227° C (from methanol), with no depression in admixture with authentic 4-phenyliminothiazolid-2-one [2].

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