INVESTIGATIONS IN THE FIELD OF 2, 1, 3-THIADIAZOLE AND 2, 1, 3-SELENADIAZOLE

LV. Reduction of o-Aminonitrobenzo-2,1,3-thiadiazoles with Ferrous Hydrate*

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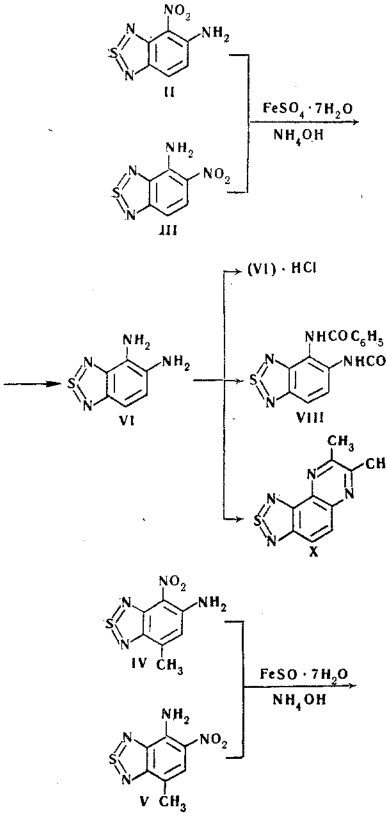
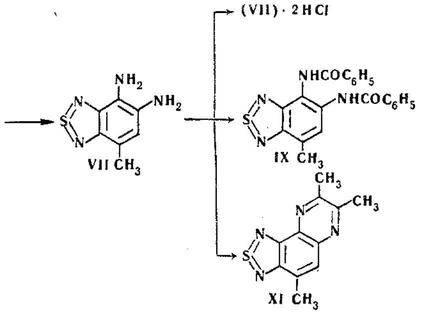
The action of ferrous hydrate on o-aminonitrobenzo-2,1,3-thiadiazoles forms the corresponding o-diamines in good yield.

The instability of the thiadiazole ring to reducing agents creates serious difficulties in the study of the chemical properties of derivatives of this heterocycle connected with the use of substances possessing reducing properties. It has been shown previously [2–4] that the thiadiazole ring is fairly stable to certain mild reducing agents: iron in the presence of 2% acetic acid; aqueous solutions of sodium disulfide, sulfide, or hydrosulfide; aqueous or alkaline solutions of sodium dithionite; and hydrogen sulfide in 25% ammonia. This has enabled many derivatives of benzo-2, 1, 3-thiadiazole (I)—for example, nitro, nitroso, and azo derivatives—to be converted into the corresponding amino derivatives of compound I, and the various reactions of the latter to be studied. It must be mentioned that sodium sulfides and dithionite react differently with derivatives of I according to the nature and position of the substituent [2].





In the present paper we give the results of a study of the reaction of some o-aminonitrobenzothiazoles with ferrous hydrate. The action of ferrous sulfate in the presence of 10% ammonia solution on 5-amino-4-nitro- (II), 4-amino-5-nitro- (III), 5-amino-7-methyl-4-nitro- (IV), and 4-amino-7-methyl-5-nitrobenzo- (V) -2, 1, 3-thiadiazoles gave good yields of 4, 5-diaminobenzo-2, 1, 3-thiadiazole (VI) and 4, 5-diamino-7-methylbenzo-2, 1, 3-thiadiazole (VII). The diamides VI and VII were converted into the hydrochlorides, into 4, 5-dibenzoylamino-2, 1, 3-thiadiazole (VIII) and 4, 5-dibenzoylamino-7-methylbenzo-2, 1, 3-thiadiazole (IX), and into the pyrazine derivatives X and XI.

EXPERIMENTAL

Reduction of the o-aminonitrobenzo-2, 1, 3-thiadiazoles with ferrous hydroxide. A suspension of 0.01 mole of II, III, IV, or V in 10 ml of 10% ammonia solution was added in a thin stream with stirring into a hot solution of 20 g of $FeSO_4 \cdot 7\ H_2O$ in 20 ml of water, and then 100 ml of 10% ammonia solution was added, and the mixture was heated to the boil and filtered hot. After cooling, the crystals that separated out were rapidly filtered off and washed with water. Yield 70–80%; the melting points of the o-diamines obtained correspond to literature figures.

4, 5-Diaminobenzo-2, 1, 3-thiadiazole, hydrochloride. A current of hydrogen chloride was passed into a solution of VI in benzene to saturation (the color changed from red to light yellow), and the precipitate that separated out was filtered off and washed with benzene. Yellow crystals, readily soluble in water, with mp 218° C (decomp.). Found, %: N 28.45, 29.11; S 15.20, 16.11; Cl 16.15, 16.62. Calculated for $C_6H_6N_4S \cdot HCl$, %: N 27.65; S 15.80; Cl 27.53.

4, 5-Diamino-7-methylbenzo-2, 1, 3-thiadiazole dihydrochloride. This was obtained similarly. Mp 240° C (decomp.). Yield, quantitative. The crystals were readily soluble in water. Found, %: S 14.39, 14.61; Cl 15.93, 15.98. Calculated for $C_7H_8N_4S \cdot 2HCl$, %: S 14.78; Cl 16.39.

4, 5-Dibenzoylamino-7-methylbenzo-2, 1, 3-thiadiazole (IX). A 2.4 g (0.017 mole) quantity of benzoyl chloride was added to 0.9 g (0.005 mole) of VII in 40 ml of water and the mixture was heated to the boil, cooled, acidified with 10% caustic soda solution, and filtered. The residue consisted of colorless crystals with mp 221–223° C (from ethylene glycol with subsequent washing with ethanol). Yield 1.75 g (90%). Found, %: S 8.22, 8.29. Calculated for $C_{21}H_{16}N_4O_2S$, %: S 8.25.

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*For part LIV, see [1].

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4, 5-Dibenzoylaminobenzo-2, 1, 3-thiadiazole (VIII). This was obtained similarly. Colorless crystals with mp 228–230° C (from ethylene glycol with subsequent washing with ethanol). Yield 1.68 g (90%). Found, %: N 14.79; S 8.92. Calculated for $C_{20}H_{14}N_4O_2S$, %: N 14.98; S 8.56.

4, 5-(2', 3'-Dimethyl-5', 6'-pyrazino)benzo-2, 1, 3-thiadiazole (X). With stirring, 1.8 g (0.021 mole) of biacetyl was added to a solution of 3.32 g (0.02 mole) of VI in 60 ml of ethanol and the mixture was heated to the boil and evaporated to dryness on the water bath; the residue was dissolved in benzene and the solution was filtered through activated alumina. After the elimination of the benzene, the filtrate yielded colorless crystals with mp 148–150° C. Yield 4.2 g (97.2%). Found, %: N 26.28, 26.31; S 14.61, 14.67. Calculated for $C_{10}H_8N_4S$, %: N 25.93; S 14.81.

4, 5-(2', 3'-Dimethyl-5', 6'-pyrazino)-7-methylbenzo-2, 1, 3-thiadiazole (XI). This was obtained similarly from VII. Yield quantitative. Colorless crystals with mp 190–192° C, giving a yellow coloration with H_2SO_4 which disappeared on dilution with water. Found, %: N 24.75, 25.10; S 14.08, 14.60. Calculated for $C_{11}H_{10}N_4S$, %: N 24.35; S 13.91.

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