SYNTHESIS OF CENTROSYMMETRIC DIMETHYLBENZODITHIAZOLE

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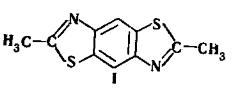
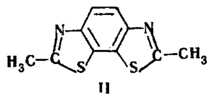
UDC 547.789.6.07

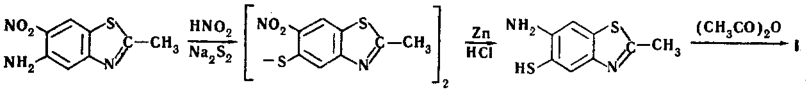
In 1967 we pointed out [1] that 1,4-diaminobenzene-2,3-dithiosulfuric acid rather than 1,4-diaminobenzene-2,5-dithiosulfuric acid is formed by reaction of p-phenylenediamine with sodium thiosulfate, sodium bichromate, and sulfuric acid, and that reaction of this acid with acetic anhydride gives the angular isomer 2,7-dimethylbenzo[1,2-d:4,3-d']dithiazole (II) rather than the linear, centrosymmetric 2,6-dimethylbenzo[1,2-d:4,5-d']dithiazole (I), as supposed by Green and Perkin [2] and a number of other investigators [3-6].


I

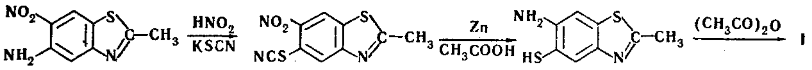

II

Others [7-9] arrived at this conclusion somewhat later.

In the same paper [1] we first described the synthesis of I via the scheme

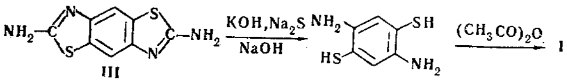


In 1968, Grandolini et al. [10] described the synthesis of I via a scheme extremely similar to ours in low (like ours) yields:



While referring to [1] in connection with the structure of the diaminobenzenedithiosulfuric acid, they did not deem it necessary to mention the fact that the synthesis of I is also presented in the same paper.

In this communication we propose a new, more convenient method for obtaining I by alkaline fusion of 2,6-diaminobenzo[1,2-d:4,5-d']dithiazole III, the synthesis of which was recently described [7, 9].



2,6-Dimethylbenzo[1,2-d:4,5-d']dithiazole (I). A mixture of 12 g of potassium hydroxide, 12 g of sodium hydroxide, and 6 g of crystalline sodium sulfide was heated in a copper vessel until water evolution ceased. Compound III [5 g (0.022 mole], obtained via the method in [9] and recrystallized from acetic acid, was added with stirring under nitrogen in 10 min to the melt at 200° (225° in a silicone oil bath). The mixture was held at this temperature for 15 min, cooled, and dissolved in 200 ml of water. Acetic anhydride (100 ml) was added in small portions to the solution, the solution was cooled, and water was added twice, and the precipitate was

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Institute of Organic Chemistry, Academy of Sciences of the Ukrainian SSR, Kiev. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1435-1436, October, 1970. Original article submitted January 27, 1970.

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filtered and boiled for 5 min with 170 ml of 50% sulfuric acid. The solution was filtered, and the base was precipitated with ammonia. The precipitate was filtered, dried, dissolved in chloroform, and the solution was passed through a small layer of aluminum oxide. Evaporation of the chloroform yielded 2.0 g (40%) of I with mp 227° (from benzene or by sublimation in vacuo).

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