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Abstract

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STUDIES IN THE CHEMISTRY OF PIAZTHIOLE

(3,4-BENZ-1,2,5-THIODIAZOLE)

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In previous communications ([1]) we presented data characterizing the aromatic properties of benz-2,1,3-thiodiazole. Of the several possible structures, the latter is most consistent with structure (I) or (II):

(I) (II)

The synthesis of benz-2,1,3-thiodiazole from *o*-phenylenediamine and thionyl chloride (or sulfurous anhydride) ([2]) indicates structure (I); the clearly expressed aromatic character and the high stability of piazthiole toward various chemical agents (oxidants, acids, alkalis) can be explained by either structure ([2], [3]). Data from physical studies ([4]) likewise give no definite indication as to the structure of this heterocycle. The dipole moments of benz-2,1,3-thiodiazole and its 5-chloro derivative, as well as of benz-2,1,3-selenadiazole and its 5-chloro derivative, studied by Hill and Sutton ([5]), permit structure (II) for the first two substances and, for the second two, both structure (II) and (I). Measurement of interatomic distances carried out by Luccati ([4]) also permits acceptance of both structures.

It would seem that, if benz-2,1,3-thiodiazole has structure (II), it should possess a known degree of unsaturation. Elucidation of the unsaturated character of this heterocycle appeared all the more important because the available experimental data indicated only the aromatic nature of the latter. As for chemical properties that might indicate the presence of a quinoid structure, such data had not been confirmed by anyone; on the contrary, according to recently published data ([3]), piazthiole is not capable of addition reactions.

Our investigations, however, showed that piazthiole vigorously (with evolution of heat) adds both chlorine and bromine; the reaction proceeds both in the melt and in organic solvents (chloroform, dichloroethane, etc.), in the presence or absence of catalysts (iron filings). The reaction products are, respectively, tetrachloro- or tetrabromotetrahydrobenz-2,1,3-thiodiazoles, formed as a mixture of stereoisomers.

By fractional crystallization of the tetrachlorotetrahydrobenz-2,1,3-thiodiazoles we isolated from the above-mentioned mixture two isomers with melting points 123–124° and 82°. On treatment of the tetrahalogenotetrahydro derivatives with an alcoholic solution of caustic potash, dihalogenopiazthioles were isolated, the structure of which was proved by independent synthesis from the corresponding dihalogeno-*o*-diamines and thionylaniline.

The data obtained thus make it possible to assume that, in the interaction of piazthiol with chlorine (or bromine), addition of four halogen atoms occurs, with formation of tetrahalotetrahydro derivatives, which, on interaction with an alcoholic solution of alkali, eliminate two molecules of hydrogen halide (HCl or HBr), with formation of dihalogen derivatives according to the scheme:

[benz-2,1,3-thiodiazole] $\xrightarrow{2Cl_2}$ [tetrachlorotetrahydrobenz-2,1,3-thiodiazole] $\xrightarrow[-2HCl]{2KOH}$ [dichlorobenz-2,1,3-thiodi

L. S. Efros and R. M. Levit, who recently studied the reaction of piazthiol with chlorine, found that in this process (only in the presence of iron filings) dichloropiazthiol of the structure shown above is most probably formed.

Of the four isomers synthesized by us—all those predicted by structural theory for dichloropiazthiols—not one corresponded to the substance with m.p. 57.5°, described by the authors. It is therefore not excluded that the latter is a product of partial addition of chlorine to piazthiol, of the structure:

[partially chlorinated piazthiol structure] or [alternative partially chlorinated piazthiol structure]

In order to test this assumption, the chlorination of piazthiol was carried out by us with stoichiometric quantities of chlorine (by weight, corresponding to two chlorine atoms). After distillation in vacuo, apart from benz-2,1,3-thiodiazole that had not entered into reaction, only tetrachlorotetrahydrobenz-2,1,3-thiodiazole was found; on treatment of the latter with an alcoholic solution of caustic potash, 4,7-dichlorobenz-2,1,3-thiodiazole was isolated.

In further investigations in the field of halogenation of piazthiol derivatives, we established that 5-methyl-, 5-bromo-, and other piazthiol derivatives also enter into the reaction of interaction with chlorine (or bromine); it was also shown that 1′,2′-naphtho-2,1,3-thiodiazole likewise enters into the reaction of addition of chlorine (or bromine). The experimental data obtained in this way show that piazthiol (as well as 1′,2′-naphtho-2,1,3-thiodiazole) and its derivatives, along with aromatic properties, possess properties characteristic of unsaturated compounds.

Experimental Part

Chlorination of benz-2,1,3-thiodiazole. Into a melt of 13.6 g of benz-2,1,3-thiodiazole at 60°, chlorine was passed until an increase in weight of 7.1 g was reached (corresponding to two chlorine atoms). On distillation, four fractions were obtained. Fraction I: b.p. up to 140° (20-30 mm)—5 g, m.p. 42-44°; it showed no depression in a mixed-melting-point test with piazthiol. Fraction II: b.p. 141-150° (20-30 mm)—2 g; a transparent oily liquid, not crystallizing on storage. On treatment of the latter with an alcoholic solution of caustic potash, a substance with m.p. 175-178° was isolated; it showed no depression in a mixed-melting-point test with 4,7-dichlorobenz-2,1,3-thiodiazole. Fraction III: b.p. 151-185° (20-30 mm)—3.5 g, an oily liquid which crystallized on storage; after recrystallization from alcohol, m.p. 75-82°. A mixed-melting-point test with tetrachlorotetrahydrobenz-2,1,3-thiodiazole (m.p. 82°) showed no depression. Fraction IV: b.p. 186-195°

(20-30 mm)—4 g; an oily liquid, which quickly crystallized. After recrystallization from alcohol, m.p. 175-178°; a mixed melting test with 4,7-dichlorobenz-2,1,3-thiodiazole showed no depression.

The investigation of chlorinated benz-2,1,3-thiodiazole was also carried out by another route: 35 g of the substance were mixed with 50 ml of alcohol while heating; upon cooling with ice and salt, the alcoholic solution, separated from the oily liquid, deposited, after repeated recrystallization from alcohol, 3.5 g of substance (22% of theory), m.p. 120-124°. It consists of white needles, soluble in alcohol, chloroform, dichloroethane, and benzene, sparingly soluble in petroleum ether, and insoluble in water.

Found, %: C 25.95; 26.10; H 1.45; 1.62; N 10.38; 10.05; S 11.30; 11.63
Cl 51.44; 51.68

$C_6H_4N_2SCl_4$. Calculated, %: C 25.90; H 1.44; N 10.07; S 11.51;
Cl 51.08

The oily liquid, after heating with 50 ml of alcohol and subsequent cooling, as a result of repeated fractional crystallization yielded 1.4 g of crystalline substance, m.p. 82°, soluble in alcohol, chloroform, and benzene, sparingly soluble in petroleum ether, insoluble in water.

Found, %: C 26.68; 25.90; H 1.66; 1.47; N 10.23; 10.06; S 11.87; 11.76;
Cl 52.02; 51.90

$C_6H_4N_2SCl_4$. Calculated, %: C 25.90; H 1.44; N 10.07; S 11.51;
Cl 51.08

4,7-Dichlorobenz-2,1,3-thiodiazole. a) To a suspension of 3,6-dichloro-1,2-phenylenediamine, m.p. 95-97°, in 5 ml of benzene, 3.8 g of thionylaniline, b.p. 198-200°, was gradually added with constant stirring. After heating on a water bath for 30 min, the reaction mass was cooled, and the filtered precipitate, after washing with benzene, was recrystallized from alcohol. 2.05 g of substance was

obtained, m.p. 181–182.5° (88.7% of theory). It consists of colorless acicular crystals, insoluble in water, sparingly soluble in alcohol (more readily in hot alcohol), and soluble in chloroform and dichloroethane.

Found, %: C 35.43; 35.81; H 1.22; 1.35; N 13.52; 13.82; S 15.21; 15.68
Cl 35.01; 34.80

$C_6H_2N_2SCl_2$. Calculated, %: C 35.12; H 0.97; N 13.66; S 15.68;
Cl 34.63

b) The remaining three isomers were synthesized from the corresponding dichloro-*o*-diamines and thionylaniline, analogously to the preceding.

Bromination of benz-2,1,3-thiodiazole. To 9 g of molten piazthiol, m.p. 42°, 32 g of bromine was added over 25 min with constant stirring, after which the reaction mixture was heated to boiling for 1 hour, and the solid mass formed on cooling was left in air until the excess bromine had evaporated. 28.85 g of a yellow substance was obtained (95.55% of theory); after recrystallization from alcohol, the latter consists of white crystals, m.p. 142°, readily soluble in benzene, carbon tetrachloride, acetone, and acetic acid, less soluble in alcohol.

Found, %: N 6.19; 6.29
$C_6H_4N_2Br_4S$. Calculated, %: N 6.14

4,7-Dibromobenz-2,1,3-thiodiazole. a) 1 g of tetrabromotetrahydrobenz-2,1,3-thiodiazole, m.p. 142°, 20 ml of alcohol, and a solution of 0.32 g of caustic potash in 1 ml of water were heated to boiling for 1 hour; after cooling and dilution with water, 0.42 g of substance was obtained (65% of theory), melting after recrystallization from alcohol at 184–185°. A mixed melting test with 4,7-dibromobenz-2,1,3-thiodiazole showed no depression.

b) **Synthesis of 4,7-dibromobenzo-2,1,3-thiodiazole.**
1 g of 3,6-dibromo-1,2-diaminobenzene, m.p. 92–94°, and 1.2 g of thionylaniline, b.p. 198–200°, were heated with 3 ml of benzene to boiling for 30 min. After cooling, the precipitate that separated was filtered off, washed with benzene, and recrystallized from alcohol. Yield: 1 g of 4,7-dibromobenzo-2,1,3-thiodiazole, m.p. 184–185°.

$C_6H_2Br_2N_2S$

Found, %: N 9.88; 9.61
Calculated, %: N 9.52

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Note: Figure translations are in progress. See original paper for figures.