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Abstract

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STUDIES IN THE CHEMISTRY OF PIAZTHIOLE

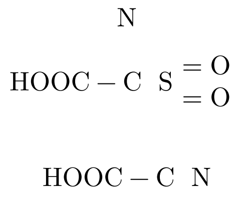
OXIDATION OF 3,4-BENZ-1,2,5-THIODIAZOLE AND ITS DERIVATIVES

(Presented by Academician I. N. Nazarov, March 12, 1957)

It was shown earlier that piazthiole and its derivatives, as well as 1′,2′-naphthopiazthiole ($^{1-3}$), possess, along with aromatic properties, a certain degree of unsaturation; the unsaturated character of these compounds, however, is not devoid of a certain specificity. Thus, some reactions characteristic of ethylenic compounds cannot be carried out with piazthiole (addition of HCl, diene synthesis). Moreover, it was found that the unsaturation established for piazthiole itself is weakened in its 1,4-dichloro derivative, while, on the contrary, the aromatic character in the latter is intensified. In this connection it was of interest to undertake a further investigation of the unsaturated properties of piazthiole and its derivatives, and for this purpose we used oxidation.

On oxidation of piazthiole, 2-methyl-, 2-chloro-, and 1,4-dichloropiazthiole with peracetic acid, predominantly destruction of the entire organic part of the molecule was observed (sulfur was detected only in the form of ammonium sulfate). In the oxidation of 2-chloropiazthiole, along with ammonium sulfate, a small amount of the 2,4-dinitrophenylhydrazone, presumably of glycolaldehyde, was isolated, while in the oxidation of piazthiole only a qualitative indication of the presence of an aldehyde group was obtained. Thus, peracetic acid, which promotes the formation of N-oxides of heterocyclic compounds, in its interaction with piazthiole and its derivatives led predominantly to destruction of the organic part of the molecule. It is interesting to note in this connection that, on heating 2-methylpiazthiole with 30% hydrogen peroxide in glacial acetic acid, no noticeable changes were observed (^{4}).

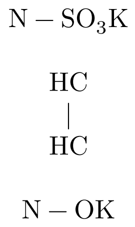
On oxidation of piazthiole with potassium permanganate, however, we isolated two products; one, judging from the analytical data and from its ability to form a dimetallic derivative, is most likely S-dioxide 2,1,3-thiadiazole-4,5-dicarboxylic acid, of the structure:



$$\begin{array}{c} \mathrm{N} \\ \mathrm{HOOC-C\ \ S}\begin{smallmatrix}=\mathrm{O}\\=\mathrm{O}\end{smallmatrix} \\ \\ \mathrm{HOOC-C\ \ N} \end{array}$$

I

the other, less thoroughly studied, according to the analytical data corresponds to the composition $C_2H_2N_2O_4SK_2$, and its structure may tentatively be represented by the formula:



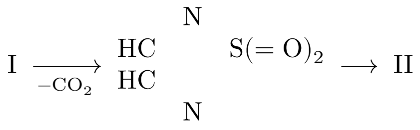
$$\begin{array}{c} \mathrm{N-SO_3K} \\ \\ \mathrm{HC} \\ | \\ \mathrm{HC} \\ \\ \mathrm{N-OK} \end{array}$$

II

The formation of these substances can be explained if it is assumed that oxidation with potassium permanganate proceeds through preliminary addition of the elements of hydrogen peroxide (according to Wagner):

$$\text{III} \longrightarrow \text{hexahydroxy intermediate} \longrightarrow \text{2,1,3-thiodiazole-4,5-dicarboxylic acid} \longrightarrow \text{I (A)}$$

At the same time, further oxidation of the 2,1,3-thiodiazole-4,5-dicarboxylic acid formed also takes place according to the scheme:



$$\mathrm{I} \xrightarrow[-\mathrm{CO_2}]{} \begin{array}{c} \mathrm{N} \\ \mathrm{HC} \qquad \mathrm{S(=O)_2} \\ \mathrm{HC} \\ \mathrm{N} \end{array} \longrightarrow \mathrm{II}$$

The oxidation reaction of 2-methyl- and $1', 2'$-naphthopiazthioles proceeds in the same way.

The views expressed concerning the mechanism of the oxidation reaction of piazthiol with potassium permanganate are apparently confirmed by the oxidation of 1,4-dichloropiazthiol, which, in comparison with piazthiol, exhibits considerably less unsaturation; the latter is in agreement with the halogenation reaction.

Whereas piazthiol readily adds chlorine or bromine, 1,4-dichloropiazthiol under analogous conditions does not add halogens.

In the oxidation of 1,4-dichloropiazthiol with potassium permanganate, the latter enters into reaction less vigorously than with piazthiol; therefore the interaction of 1,4-dichloropiazthiol with potassium permanganate had to be carried out under somewhat more severe conditions. It is possible that in this case process (B) predominated over process (A), as a result of which compound II was formed predominantly.

On ozonization of piazthiol* an ozonide with m.p. 60° was isolated, which after decomposition was a mixture of 2,1,3-thiodiazole-4,5-dicarboxylic acid, 2,1,3-thiodiazole-4,5-dialdehyde, and glyoxal; in this case the reaction mechanism may be represented as follows:

$$\mathrm{III} \xrightarrow{O_3} \text{ozonide} \longrightarrow \left\{\begin{array}{l} \text{2,1,3-thiodiazole-4,5-dialdehyde,} \\ \text{2,1,3-thiodiazole-4,5-dicarboxylic acid,} \\ \text{glyoxal} \end{array}\right. \qquad \text{(B)}$$

The last two substances were isolated in the form of the corresponding semicarbazones; in addition, a certain amount of ammonium sulfate was also obtained.

On the basis of the data obtained for the oxidation of piazthiol and some of its derivatives with potassium permanganate and ozone, it follows that piazthiol has an indeterminate character, as previously established in examples of halogenation.

Experimental Part

Oxidation of piazthiol with peracetic acid.

10 g of piazthiol, m.p. 40–42°, and 135 ml of acetic acid containing 11% peracetic acid were heated on a boiling water bath for 48 hours, after which the reaction mixture was diluted with water. The precipitate that separated (1.3 g of piazthiol that had not entered into reaction) was filtered off, the filtrate was concentrated (in the process a considerable amount of piazthiol was distilled off), and the residue was washed with alcohol and ether; 0.75 g of ammonium sulfate was obtained.

Found, %: S 23.75; 23.98
$(NH_4)_2SO_4$. Calculated, %: S 24.24

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* We take this opportunity to express our gratitude to Prof. A. I. Yakubchik and N. G. Kasatkina for assistance in carrying out the work at LSU and for valuable suggestions.

Oxidation of piazthiol with potassium permanganate.

To a mixture of 4 g of piazthiol, m.p. 40-42°, and 40 ml of water, 30 g of potassium permanganate (as an 8% solution) was added in portions at 50° with stirring until a faint pink coloration appeared. The manganese dioxide that separated was filtered off, washed with hot water, and the combined filtrates were concentrated in vacuo at 50-60°, after which the crystals that separated were filtered off. 2.42 g of a potassium-containing substance was obtained, readily soluble in water, sparingly soluble in alcohol, and insoluble in organic solvents. From the filtrate, after neutralization with hydrochloric acid, 2.86 g of a substance, m.p. 268° (with decomposition), was isolated; after recrystallization from water it was sparingly soluble in alcohol and insoluble in organic solvents.

Found, %: C 23.70; 23.39; H 1.11; 0.86; N 13.62; 13.68; S 15.23; 15.20
$C_4H_2N_2O_6S$. Calculated, %: C 23.30; H 0.97; N 13.59; S 15.52

Analysis of the same product as the Ag derivative (by gravimetry):
Analysis of the potassium-containing product

Found, %: Ag 51.80; 51.77
$C_4N_2O_6SAg_2$. Calculated, %: Ag 51.43

Analysis of the potassium-containing product

Found, %: C 10.79; 10.66; H 1.01; 1.19; N 12.12; 12.18
$C_2H_2O_4N_2SK_2$. Calculated, %: C 10.53; H 0.89; N 12.28

Oxidation of 1,4-dichloropiazthiol with potassium permanganate.

A mixture of 3 g of 1,4-dichloropiazthiol, m.p. 178-179.5°, and 40 ml of 4% sodium hydroxide solution was heated to boiling, and at this temperature, with stirring, a solution of 20 g of potassium permanganate in 250 ml of water was gradually added until a faint pink coloration appeared. After removal of the manganese dioxide and concentration of the filtrate (in vacuo), 2.32 g of substance was isolated.

Found, %: C 10.96; 10.61; H 1.12; 1.05; N 11.93; 12.04
$C_2H_2O_4N_2SK_2$. Calculated, %: C 10.53; H 0.887; N 12.28

Ozonization of piazthiol.

Ozone (ozone concentration ~7%) was passed into a solution of 4 g of piazthiol, m.p. 42°, in 65 ml of chloroform at −10, −15°. 5 g of white crystals were isolated, m.p. 60° (with decomposition in a sealed capillary); yield 73.2% of theory.

1.45 g of the ozonide was decomposed with water, the solution was neutralized with barium carbonate, the precipitate (barium sulfate with an excess of barium carbonate) was filtered off, washed with hot water, and the combined filtrates were concentrated in vacuo at 50°. The white precipitate that separated was filtered—

was washed and recrystallized from water; 0.5 g of the barium salt of 2,1,3-thiodiazole-4,5-dicarboxylic acid was obtained.

$C_4H_4N_2SBa$.	Found, %:	C 15.77; 15.48
	Calculated, %:	C 15.55

The filtrate was diluted with 50° alcohol, and 1 g of semicarbazide hydrochloride and 1.5 g of sodium acetate were added to the solution; 1 g of the semicarbazone was obtained, m.p. 193–195°; after recrystallization from dilute alcohol, m.p. 196.5–197°.

$C_6H_8O_2N_8S$.	Found, %:	C 28.09; 28.21;	H 3.23; 3.31;	N 43.73; 43.41;	S 12.40; 12.75
	Calculated, %:	C 28.13;	H 3.12;	N 43.75;	S 12.50

According to the analytical data, the substance corresponds in composition to the disemicarbazone of 2,1,3-thiodiazole-4,5-dialdehyde.

An aqueous solution of the barium salt (0.5 g) of 2,1,3-thiodiazole-4,5-dicarboxylic acid was treated with sulfuric acid until barium sulfate had completely precipitated; the free acid was isolated, m.p. 172–173°.

$C_4H_2O_4N_2S$.	Found, %:	N 15.73; 15.90
	Calculated, %:	N 16.09

This corresponds to 2,1,3-thiodiazole-4,5-dicarboxylic acid. In another experiment (the decomposition products of 6.4 g of ozonide were examined), 0.28 g of ammonium sulfate and glyoxal dialdehyde in the form of its semicarbazone were isolated.

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