(characteristic for azoles), and 1590–1600 cm^{-1} (CH) (aromatic). Found: C 78.0; H 4.7; N 12.1%. $C_{22}H_{15}N_3O$. Calculated: C 78.0; H 4.7; N 12.1%.

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FORMATION OF 1-PYRAZOLINE 1,2-DIOXIDES BY OXIDATION OF 1,3-HYDROXYLAMINO OXIMES

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Cyclization with the formation of an N–N bond and simultaneous bromination, which lead to 3-bromo-1-pyrazoline 1,2-dioxides, apparently through a step involving the dinitroso derivative, occur in the reaction of sodium hypobromite with 1,3-hydroxylamino oximes. Dehydrobromination of the bromopyrazoline leads to the corresponding 3H-pyrazole. The same treatment of acetylacetone dioxime gives 4H-dibromo-3,5-dimethyl-4H-pyrazole 1,2-dioxide, which is readily hydrolyzed to the corresponding 4-oxo derivative. Data from the IR, UV, and PMR spectra are presented.

We have previously shown that the reaction of tertiary 1,2-hydroxylamino oximes with sodium hypobromite leads to 3-bromo-1,2-diazetine 1,2-dioxide [1]. In the present research we examine the possibility of the synthesis of 1-pyrazoline 1,2-dioxides from 1,3-hydroxylamino oximes.

A colorless crystalline compound (IIa) with the composition $C_6H_{11}BrN_2O_2$ is formed by treatment of N-(4-oximino-2-methyl-2-pentyl)hydroxylamine (Ia) with excess sodium hypobromite. Absorption with λ_{max} 286 nm (log ε 3.88) is observed in the UV spectrum of IIa, and its IR spectrum contains two intense bands at 1380 and 1490 cm^{-1}, which is characteristic for cis-dimeric nitroso compounds [2], and an intense band at

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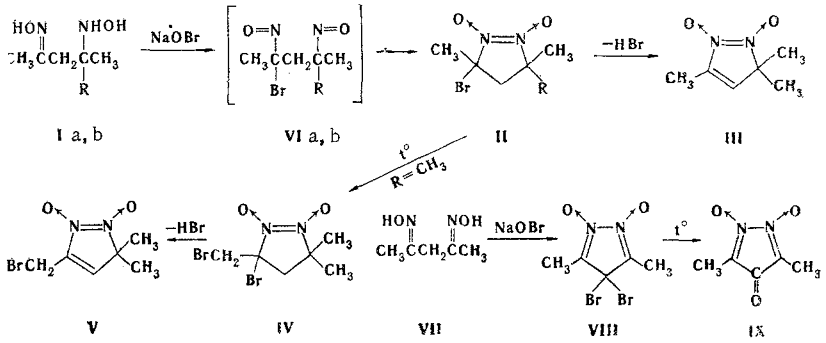
TABLE 1. Data from the IR, UV, and PMR Spectra

Compound	IR spectrum, cm^{-1}	UV spectrum, λ_{max}, nm (log ε)	PMR spectrum (in $CDCl_3$), δ, ppm
IIa	1380, 1430, 1485	286 (3,88)	1,59 (5-CH_3); 1,73 (5-CH_3); 2,29 (3-CH_3); 2,69 and 3,29 (4-H, $J=15$ Hz)
IIb	1380, 1440, 1495	288 (3,86)	1,68 (5-CH_3, d, $J=6,5$ Hz); 2,21 (3-CH_3); 2,43 and 3,40 (4-H, $J_{AB}=14,5$; $J_{AX}=10$, $J_{BX}=6$ Hz); 4,45 (5-H_X, $J_{AX}=10$, $J_{BX}=6$, $J_{X\,CH_3}=6,5$ Hz)
III	1375, 1440, 1480	216 (4,00) 311 (3,65)	1,55 (5-CH_3); 2,23 (3-CH_3, d, $J=2,0$ Hz); 6,39 (4-H, m)
IV	1380, 1410, 1430, 1495	290 (3,86)	1,60 (5-CH_3); 1,71 (5-CH_3); 3,11 and 3,29 (4-H, $J_{AB}=15$ Hz); 3,99 and 4,45 (3-H, $J_{AB}=12$ Hz)
V	1380, 1435, 1480	223 (3,86) 302 (4,16)	1,64 (5-CH_3); 3,06 (3-CH_2, d, $J=2,5$ Hz); 7,29 (4-H, t, $J=2,5$ Hz)
VIII	1330, 1350, 1680	272 (3,58)	2,37 (3,5-CH_3)
IX	1335, 1360, 1635—1660 1695	281 (4,07)	2,06 (3,5-CH_3)*

*In CCl_4.

1485 cm^{-1}, which can be assigned to the stretching vibrations of the $N=N\rightarrow O$ group [3, 4]. On the basis of these data, we assigned the 3-bromo-3,5,5-trimethyl-1-pyrazoline 1,2-dioxide structure to IIa. The PMR spectrum of IIa (Table 1) contains 5-CH_3 singlets and 1.73 and 1.59 ppm, a 3-CH_3 singlet at 2.29 ppm, and 4-H signals at 3.29 and 2.69 ppm (an AB system). The spectral characteristics of IIa (Table 1) are close to those observed for the known 3,4-dibromo-3,5,5-trimethyl-1-pyrazoline 1,2-dioxide [5]. A confirmation of the structure of pyrazoline IIa is also its ability to readily split out hydrogen halide on treatment with alcoholic alkali to give the known [5] 3,3,5-trimethyl-3H-pyrazole 1,2-dioxide (III).



I, II, VI a R=CH_3; b R=H

Heating 1-pyrazoline 1,2-dioxide IIa in benzene leads to destruction of the ring, and a compound with the composition $C_6H_{10}Br_2N_2O_2$ was isolated from the reaction products; the spectral characteristics of this compound are close to the spectral characteristics of IIa (Table 1), on the basis of which the 3-bromo-3-bromomethyl-5,5-dimethyl-1-pyrazoline 1,2-dioxide (IV) structure was assigned to it. Treatment of IV with alcoholic alkali leads to splitting out of hydrogen halide and the formation of pyrazole V, the spectral characteristics of which are close to the characteristics of III (Table 1).

Treatment of 1,3-hydroxylamino oxime Ib with excess sodium hypobromite also leads to pyrazoline 1,2-dioxide IIb, the spectral characteristics of which are close to those of IIa (Table 1). The formation of 3-bromo-1-pyrazoline 1,2-dioxides II from tertiary and secondary 1,3-hydroxylamino oximes IIa, b can be represented by a scheme in which the reaction commences with oxidation of the hydroxylamino group and subsequent reaction of halogen with the ketoxime group to give 1,3-dinitroso derivative VI. The subsequent reaction of the two nitroso groups, like the dimerization of nitroso compounds, leads to pyrazoline 1,2-dioxides II.

It has previously been shown that the oxidation of secondary 1,2-hydroxylamino oximes leads to dioximes [1]. The formation of 1,3-dioxime VII also cannot be excluded in the oxidation of secondary 1,3-hydroxylamino oxime Ib. It was observed that the oxidation of acetylacetone VII with sodium hypobromite in weakly alkaline media gives VIII with the composition $C_5H_6Br_2N_2O_2$, in the PMR spectrum of which one observes a singlet at 2.37 ppm corresponding to six protons of two methyl groups; its UV spectrum contains absorption at 272 nm (log ε 3.59), and its IR spectrum contains an intense band at 1680 cm^{-1}. On the basis of these data we assigned the 4,4-dibromo-3,5-dimethyl-4H-pyrazole 1,2-dioxide structure to VIII. Compound VIII is unstable and readily undergoes hydrolysis to give the known [6] 4-oxo-3,5-dimethyl-4H-pyrazole 1,2-dioxide (IX). It should be noted that the oxidation of 1,3-dioxime VII in alkaline media leads either to a mixture of VIII and IX or only to IX. Consequently, 4H-pyrazole derivatives rather than 1-pyrazoline 1,2-dioxides are formed in the oxidation of 1,3-dioxime VII with sodium hypobromite. The fact that the final product in the reaction of 1,3-hydroxylamino oxime Ib with sodium hypobromite is pyrazoline 1,2-dioxide IIb can be explained by the fact that dimerization of the two nitroso groups occurs at a higher rate than isomerization of the nitroso group to an oxime.

Thus the reaction of 1,3-hydroxylamino oximes I with sodium hypobromite makes it possible to obtain 3-bromo-1-pyrazoline 1,2-dioxide derivatives II.

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds (0.25%) were recorded with a UR-20 spectrometer. The UV spectra of alcohol solutions of the compounds were recorded with a Specord spectrometer. The PMR spectra of 5-7% solutions of the compounds in $CDCl_3$ and CCl_4 were recorded with a Varian A-56-60A spectrometer with hexamethyldisiloxane as the internal standard. The melting points, results of elementary analysis, yields, and spectral characteristics of the compounds are presented in Tables 1 and 2.

N-(4-Oximino-2-methyl-2-pentyl)- (Ia) and N-(4-Oximino-2-pentyl)hydroxylamine (Ib) were obtained by the method in [7, 8]; acetylacetone dioxime VII was obtained by the method in [9].

3-Bromo-3,5,5-trimethyl-1-pyrazoline 1,2-Dioxide (IIa). A cold solution of 1.2 g (7.5 mmole) of bromine in 6 ml of 10% sodium hydroxide was added dropwise with stirring to a cooled (to ~−5°) mixture of 5 ml of chloroform and a solution of 0.575 g (3 mmole) of oxalate Ia in 10 ml of water, after which the chloroform solution was separated, and the aqueous solution was extracted with chloroform. The chloroform solutions were combined and washed with 1% potassium carbonate solution and water and dried with magnesium sulfate. The solvent was evaporated, the residue was treated with diethyl ether, and the precipitate was removed by filtration.

3-Bromo-3,5-dimethyl-1-pyrazoline 1,2-Dioxide (IIb). A solution of 1.06 g (8 mmole) of Ib in 10 ml of water was added dropwise with stirring to a cooled (to −5°) mixture of 10 ml of chloroform and a solution of 3.2 g (20 mmole) of bromine in 16 ml of 10% sodium hydroxide solution. Compound IIb was isolated under the conditions indicated above.

3,3,5-Trimethyl-3H-pyrazole 1,2-Dioxide (III). An alcohol solution of 0.14 g (2.4 mmole) of potassium hydroxide was added in small portions at 20° to an alcohol solution of 0.45 g (2 mmole) of pyrazoline IIa, and the mixture was allowed to stand for 3 h. The solvent was evaporated, and the residue was treated with the minimum amount of water and extracted thoroughly with chloroform. The extract was dried with magneiusm sulfate, and the solvent was evaporated; the residue began to crystallize when it was treated with diethyl ether. The solid was removed by filtration to give 0.18 g (62%) of a product with mp 138-140° (from alcohol) (mp 138-140° [5]).

3-Bromo-3-bromomethyl-5,5-dimethyl-1-pyrazoline 1,2-Dioxide (IV). A suspension of 2 g (9 mmole) of pyrazoline IIa in 20 ml of dry benzene was refluxed until the starting material vanished [monitored by thin-layer chromatography (TLC)]. The solvent was evaporated, the residue was triturated with diethyl ether, and the resulting solid was removed by filtration and washed with cold alcohol.

5-Bromomethyl-3,3-dimethyl-3H-pyrazole 1,2-Dioxide (V). This compound was obtained under the conditions of the synthesis of III.

TABLE 2. Synthesized Compounds

Compound	mp, °C	Found, %				Empirical formula	Calculated, %				Yield, %
		C	H	Br	N		C	H	Br	N	
IIa	110—112[a]	32,1	5,2	35,4	12,6	$C_6H_{11}BrN_2O_2$	32,2	4,9	35,8	12,5	40
IIb	82—84[b]	28,7	4,3	38,6	13,1	$C_5H_9BrN_2O_2$	28,7	4,3	38,2	13,3	15
IV	158—160[c]	24,1	3,5	52,5	9,3	$C_6H_{10}Br_2N_2O_2$	23,8	3,3	53,0	9,3	9
V	145—146[c]	32,2	4,2	35,9	12,6	$C_6H_9BrN_2O_2$	32,5	4,1	36,2	12,7	80
VIII	87—89[b]	21,0	2,2	56,4	9,6	$C_5H_6Br_2N_2O_2$	20,9	2,1	56,0	9,8	39

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[a] From ethyl acetate.

[b] From chloroform−petroleum ether.

[c] From alcohol.

4,4-Dibromo-3,5-dimethyl-4H-pyrazole 1,2-Dioxide (VIII). An aqueous solution of 3.0 g (23.4 mmole) of dioxime VII was added dropwise with stirring to a cooled (to −5°) solution of 15.9 g (93 mmole) of bromine in 75 ml of 10% sodium hydroxide solution. The resulting precipitate was removed by filtration and washed with water and petroleum ether.

4-Oxo-3,5-dimethyl-4H-pyrazole 1,2-Dioxide (IX). A suspension of 0.2 g (0.7 mmole) of VIII in 5 ml of alcohol was heated to the boiling point, after which the solvent was evaporated, the residue was triturated with a small amount of cold water, and the solid material was removed by filtration to give 0.053 g (52%) of a product with mp 108-110° [from alcohol−ether (1 : 10)] (mp 109-110° [6]).

Oxidation of 1,3-Dioxime VII under Alkaline Conditions. An alkaline solution of VII was added under the conditions of the preparation of VIII, and the precipitated VIII was removed rapidly by filtration and washed with cold water and petroleum ether to give the product in 12% yield. The aqueous filtrate was neutralized to pH ~4 and extracted with chloroform. The extract was washed with water and dried with magnesium sulfate, and the solvent was evaporated. The residue began to crystallize when it was treated with diethyl ether, and the precipitated IX (11% yield) was removed by filtration.

Only IX was obtained in 5% yield under the same conditions after the addition of an alkaline solution of dioxime VII, except that the mixture was allowed to stand at 0° for 20 min.

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REACTION OF 1,3-HYDROXYLAMINO OXIMES WITH FORMALDEHYDE, ACETALDEHYDE, AND ACETONE

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The products of condensation of 1,3-hydroxylamino oximes with formaldehyde have 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxide (cyclic form) structures, the products of condensation with acetone have N-(3-oximino-substituted)-α,α-dimethylnitrone (open form) structures, and the products of condensation with acetaldehyde exist in solution in the form of a tautomeric mixture of the open and cyclic forms. The products of condensation of alkyl-aromatic 1,3-hydroxylamino oximes with acetaldehyde have N-(3-oximino-substituted)-α-nitrone (open form) structures.

It is known that the reaction of 1,2-hydroxylamino oximes with aliphatic aldehydes and ketones leads to the formation of aliphatic N-(2-oximino-substituted)nitrones, 1-hydroxy-3-imidazoline 3-oxides, or their

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