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.

LITERATURE CITED

1. L. B. Volodarskii and L. A. Tikhonova, Khim. Geterotsikl. Soedin., No. 6, 748 (1975).
2. H. Feuer (editor), The Chemistry of Nitro and Nitroso Groups [Russian translation], Vol. 1, Mir, Moscow (1972), pp. 103, 108.
3. J. P. Freeman and J. J. Gannon, J. Org. Chem., 34, 194 (1969).
4. K. A. Ogloblin and D. M. Kunovskaya, Zh. Org. Khim., 9, 1547 (1973).
5. J. P. Freeman, J. Org. Chem., 27, 1309 (1962).
6. J. P. Freeman, J. J. Gannon, and D. L. Surbev, J. Org. Chem., 34, 187 (1969).
7. A. Ya. Tikhonov and L. B. Volodarskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 10, 2372 (1973).
8. A. Ya. Tikhonov and L. B. Volodarskii, Zh. Org. Khim., 9, 770 (1973).
9. C. Harries and T. Haga, Ber., 32, 1191 (1899).

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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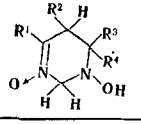
TABLE 1. Products of Condensation of 1,3-Hydroxylamino Oximes with Aldehydes and Acetone

Compound	R^1	R^2	R^3	R^4	R^5	R^6	mp, °C	Crystallization solvent	Found, % C	Found, % H	Found, % N	Empirical formula	Calculated, % C	Calculated, % H	Calculated, % N	$\nu_{(C=N)}$*, cm^{-1}	λ_{max}, nm (lg ε)	Yield, %
VIII	H	H	H	H	H	H	114—116	Methanol	41,1	6,9	—	$C_4H_8N_2O_2$	41,4	6,9	—	1639	237 (4,06)	80
IX	CH_3	H	H	H	H	H	141—143	Alcohol	46,2	7,7	21,8	$C_5H_{10}N_2O_2$	46,2	7,8	21,5	1640	234 (3,97)	90
X	CH_3	H	H	H	CH_3	CH_3	102—104	Acetone	53,3	8,9	17,8	$C_7H_{14}N_2O_2$	53,1	8,9	17,7	1625	238 (3,97)	87
XI	CH_3	CH_3	H	H	H	H	122—124	Dioxane	49,9	8,4	19,6	$C_6H_{12}N_2O_2$	50,0	8,4	19,4	1626	234 (3,97)	75
XII	CH_3	CH_3	H	H	H	CH_3	107—109	Dioxane	53,3	8,9	17,7	$C_7H_{14}N_2O_2$	53,1	8,9	17,7	1628	233 (3,94)	71
XIII	CH_3	CH_3	H	H	CH_3	CH_3	104—106	Acetone	55,8	9,1	16,5	$C_8H_{16}N_2O_2$	55,8	9,4	16,3	1624	239 (3,96)	77
XIV	CH_3	H	CH_3	H	H	H	148—150	Absolute alcohol	49,7	8,5	19,3	$C_6H_{12}N_2O_2$	50,0	8,4	19,4	1651	233 (3,96)	93
XV	CH_3	H	CH_3	H	H	CH_3	Oil	By chromatography	52,9	9,0	17,5	$C_7H_{14}N_2O_2$	53,1	8,9	17,7	1612	234 (3,90)	84
XVI	CH_3	H	CH_3	H	CH_3	CH_3	116—119	Acetone	55,8	9,5	16,3	$C_8H_{16}N_2O_2$	55,8	9,4	16,3	1606	239 (3,95)	80
XVII	CH_3	H	CH_3	CH_3	H	H	149—151	Dioxane	53,1	8,9	17,7	$C_7H_{14}N_2O_2$	53,1	8,9	17,7	1635	232 (3,95)	72
XVIII	CH_3	H	CH_3	CH_3	H	CH_3	105—107	Ethyl acetate	56,0	9,3	16,4	$C_8H_{16}N_2O_2$	55,8	9,4	16,3	1612	234 (3,98)	69
XIX	C_6H_5	H	H	H	H	H	160—162	Alcohol	62,8	6,4	14,8	$C_{10}H_{12}N_2O_2$	62,5	6,3	14,6	1608	282 (3,96)	60
XX	C_6H_5	H	H	H	H	CH_3	106—108	Alcohol	64,2	7,0	13,9	$C_{11}H_{14}N_2O_2$	64,0	6,8	13,6	1631	238 (4,19)	86
XXI	C_6H_5	H	H	H	CH_3	CH_3	147—148	Alcohol	65,2	7,2	12,9	$C_{12}H_{16}N_2O_2$	65,4	7,3	12,7	1627	242 (4,28)	95
XXII	C_6H_5	CH_3	H	H	H	H	149—151	Ethyl acetate— alcohol	64,2	6,8	13,5	$C_{11}H_{14}N_2O_2$	64,0	6,8	13,6	1595	267 (3,86)	60
XXIII	C_6H_5	CH_3	H	H	H	CH_3	119—121	Dioxane	65,5	7,3	12,8	$C_{12}H_{16}N_2O_2$	65,4	7,3	12,7	1628	231 (4,12)	88
XXIV	C_6H_5	CH_3	H	H	CH_3	CH_3	171—173	Alcohol	66,5	7,8	12,1	$C_{13}H_{18}N_2O_2$	66,6	7,7	12,0	1620	239 (4,21)	97

*This is the absorption band of the nitrone group. In the case of X, XII, XIII, and XVI, the $\nu_{C=N}$ band of the oxime group is found, respectively at 1655, 1662, 1662, and 1657 cm^{-1}. The spectrum of XV was obtained from a solution in chloroform, whereas the spectra of the remaining compounds were obtained from KBr pellets.

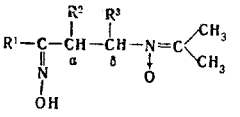
TABLE 2. Data from the PMR Spectra [δ, ppm (J, Hz)] of Products of Condensation with Formaldehyde



Compound[a]	R^1	R^2	5-H	R^3	R^4	2-H_2	OH
IX	CH_3 2,15	H 2,5 — 3,1		$R^3=R^4=H$ 3,28		4,56[b]	—
XI	CH_3 2,17	CH_3 1,16 (6,2)		$R^3=R^4=H$ 2,6—3,5		4,65	—
XIV	CH_3 2,12	H 2,61 (7,0)		CH_3 1,19 (6,4)	H 3,41 (6,4; 7,0)	4,26; 4,60 (15,5)[c]	8.48[c]
XVII	CH_3 1,94	H 2,47		$R^3=R^4=CH_3$ 1,09		4,46	8.82
XIX	C_6H_5 7,3—7,6 8,2—8,5	H 2,92		$R^3=R^4=H$ 3,29		4,67	8.79

[a] The spectra of IX and XIV in D_2O, of XI in $CDCl_3$, and of XVII and XIX in $(CD_3)_2SO$ were recorded.
[b] In CD_3OD.
[c] In $(CD_3)_2SO$.

TABLE 3. Data from the PMR Spectra [δ, ppm (J, Hz)] of the Products of Condensation with Acetone[a]



Compound	R^1	R^2	α-H	β-H	R^3	$=(CH_3)_2$
X	CH_3 1,87	H 2,78 (7,6)		R^3=H 4,14 (7,6)		2,14
XIII	CH_3 1,83	CH_3 1,09 (7,0)	H_X 3,22 (7,0)	H_A 3,87	H_B 4,07	2,13, 2,15
			J_{AX}=8,0; J_{BX}=6,5; J_{AB}=12,0			
XVI[b] syn	CH_3 1,83	H 2,72 (7,0)		4,97 (6,5; 7,0)	CH_3 1,37 (6,5)	2,14
XVI[b] anti	CH_3 1,83	H_A 2,41	H_B 2,93	H_X 4,71 (6,5)	CH_3 1,37 (6,5)	2,14
		J_{AB}=15,5; J_{AX}=5,0; J_{BX}=8,0				
XXI	C_6H_5 7,3—7,9	H 3,32 (7,2)		R^3=H 4,19 (7,2)		2,01, 2,09
XXIV	C_6H_5 7,2—7,6	CH_3[c] 1,09 (6,4) 1,37 (6,0)	R^3=H	3,6—4,7		2,06, 2,12

[a] The spectra of X, XIII, XVI, and XXIV in $CDCl_3$ and of XXI in CD_3OD were recorded.

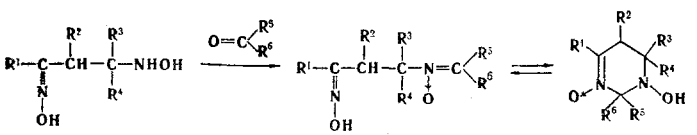
[b] The assigned chemical shifts and constants were obtained from analysis of the nuclear magnetic double resonance (NMDR) spectra; the syn/anti ratio was ~2 : 3.

[c] The constants correspond to two isomeric oximes (syn and anti) in a ratio of ~1 : 1.

tautomeric mixture [1]. In the case of 1,3-hydroxylamino oximes [2, 3] this sort of reaction has made it possible to obtain 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxides, which are of interest as starting compounds for the synthesis of difficult-to-obtain pyrimidine N,N'-dioxides.*

The reaction of 1,3-dihydroxylamino oximes I-VII with formaldehyde, acetaldehyde, and acetone leads to substances whose compositions correspond to products of condensation involving the splitting out of a water molecule (VIII-XXIV). An intense band at 1595-1651 cm^{-1} (Table 1) corresponding to the stretching vibrations of the C=N bond in nitrones [5, 6] is observed in the IR spectra of these compounds. Absorption with λ_{max} 282 and 267 nm, respectively, is observed in the UV spectra of the products of condensation (XIX and XXII) of alkyl-aromatic 1,3-hydroxylamino oximes VI and VII with formaldehyde (Table 1); this indicates the presence of a phenylnitrone grouping [5] and makes it possible to assume 1-hydroxy-4-phenyl- and 1-hydroxy-5-methyl-4-phenyl-1,2,5,6-tetrahydropyrimidine 3-oxide structures for XIX and XXII. The PMR spectrum of XIX (Table 2) is in agreement with a tetrahydropyrimidine structure.

The UV spectra of VIII-XVIII are very similar to one another [λ_{max} 232-239 nm (log ε 3.90-4.06), Table 1] and similar to the UV spectra of aliphatic nitrones [5, 7]; this does not make it possible to choose between the open structure of the aliphatic N-(3-oximino-substituted)nitrone (VIIIA-XVIIIA) and the cyclic structure of 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxide (VIIIB-XVIIIB).

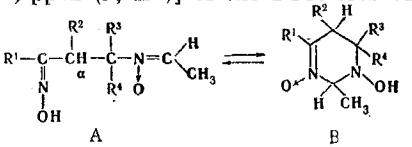


I-VII A VIII-XXIV B

II R^1=CH_3; III R^1=R^2=CH_3; IV R^1=R^3=CH_3; V R^1=R^3=R^4=CH_3; VI R^1=C_6H_5; VII R^1=C_6H_5, R^2=CH_3; unspecified R=H. See Table 1 for R=VIII-XXIV.

*See [4] for our preliminary communication.

TABLE 4. Data from the PMR Spectra [δ, ppm (J, Hz)] of the Products of Condensation with Acetaldehyde[a]



A B

Compound	Form A						
	R^1	R^2	α-H	R^3	R^4	$=CHCH_3$	$=CHCH_3$
XII	CH_3 1,86	CH_3 1,10 (6,8)	H_X 3,21 (6,8)	H_A 3,70	H_B 4,12	6,87 (5,8)	2,02 (5,8)
			$J_{AX}=7,5$; $J_{BX}=7,0$; $J_{AB}=11,8$				
XV	CH_3 1,82	H_A 2,41	H_B 2,84	CH_3 1,41 (6,5)	H_X 4,26 (6,5)	6,94 (5,8)	1,97 (5,8)
		$J_{AB}=15,0$; $J_{AX}=5,8$; $J_{BX}=7,8$					
XVIII	CH_3 1,82	H 2,74		$R^3=R^4=CH_3$ 1,49		7,45 (6,0)	2,02 (6,0)
XX[b]	C_6H_5 7,3—7,8	H 3,34 (7,2)		$R^3=R^4=H$ 4,09 (7,2)		7,07 (6,0)	1,84 (6,0)
XXIII[b]	C_6H_5 7,29	CH_3 1,01 (6,2)		$R^3=R^4=H$ 3,3—4,4		6,67 (5,6)	1,93 (5,6)

Compound	Form B							K_T in $CDCl_3$
	R^1	R^2	5-H	R^3	R^4	2-CH_3	2-H	
XII	CH_3 2,17	CH_3[c]	H[c]	H[c]	H[c]	1,56 (6,8)	4,77 (6,8)	5,6
XV	CH_3 2,11	H[c]	H[c]	CH_3 1,22 (6,3)	H[c]	1,55 (7,0)	4,78 (7,0)	1,4
XVIII	CH_3 2,13	H_A 2,49 (20,0), H_B 2,97 (20,0)		$R^3=R^4=CH_3$ 1,20, 1,27		1,62 (6,3)	4,87 (6,3)	0,6

[a] The spectra of XII, XV, and XXIII in $CDCl_3$, of XVIII in D_2O, and of XX in CD_3OD were recorded.
[b] The signals of the cyclic form are not observed.
[c] These signals coincide with the signals of the open form.

Signals whose positions indicate that these compounds have a 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxide structure (cyclic form B) are observed in the PMR spectra of the products of condensation of 1,3-hydroxylamino oximes II-VI with formaldehyde (IX, XI, XIV, XVII, and XIX) (Table 2). The signals of the protons of the methylene group in the 2 position of the heteroring are observed at 4.2-4.7 ppm, but signals for the protons of the methylenenitrone group of open form A ($O\leftarrow N=CH_2$, $R^5=R^6=H$), which might have been expected at 6.0-7.0 ppm [8], are absent.

On the other hand, the products of condensation of 1,3-hydroxylamino oximes II-IV, VI, and VII with acetone have an N-(3-oximino-substituted-α,α-dimethylnitrone structure (form A). In the PMR spectra of these compounds (X, XIII, XVI, XXI, and XXIV, Table 3) the signals of the protons of an α,α-dimethylnitrone group are observed at 2.0-2.2 ppm, and signals of protons of methyl groups for cyclic form B ($R^5=R^6=CH_3$), which might have been expected at 1.4-1.6 ppm [9, 10], are absent. A band at 1655-1662 cm^{-1} (Table 1, X, XIII, and XVI) corresponding to the stretching vibrations of the C=N bond in oximes [11] is observed in the IR spectra of the products of condensation of aliphatic 1,3-hydroxylamino oximes with acetone; this is in conformity with a structure of the A type proposed for these compounds. The UV spectra of XXI and XXIV are similar to the UV spectra of aliphatic nitrones X, XIII, and XVI (Table 1); this is also in agreement with their existence in open form A.

Signals that attest to the presence in solution of both the open form – the N-(3-oximino-substituted)-α-methylnitrone (form A) – and the cyclic form – the 1-hydroxy-2-methyl-1,2,5,6-tetrahydropyrimidine 3-oxide (form B) – are observed in the PMR spectra of the products of condensation of aliphatic 1,3-hydroxylamino oximes III-V with acetaldehyde (Table 4, XII, XV, and XVIII). The ratio of the cyclic and open forms depends on both the numbers and positions of the substituents and on the solvent [12] (Table 4). For example, the tautomeric equilibrium constant ($K_T=[A][B]$) for XII in $CDCl_3$ is 5.6, as compared with 3.3 in D_2O; K_T for XVIII in $(CD_3)_2SO$ and D_2O is, respectively, 1.9 and 0.3. An increase in the number of substituents leads to a shift in the equilibrium to favor the cyclic form. Thus passing from XV to XVIII leads to a decrease in the tautomeric equilibrium constant in $CDCl_3$ from 1.4 to 0.6.

According to the PMR (Table 4) and UV (Table 1) spectra, the products of condensation of alkyl-aromatic 1,3-hydroxylamino oximes VI and VII with acetaldehyde have N-(1-oximino-2-phenyl-3-propyl)- and N-(1-oximino-2-methyl-1-phenyl-3-propyl)-α-methylnitrone structures (XXA and XXIIIA, respectively).

It should be noted that during recording of the PMR spectrum of XII in $CDCl_3$, signals of only the open form (XIIA) are observed immediately after the compound is dissolved. It might be assumed that XII exists in the crystalline state in the N-(3-oximino-2-methyl-1-butyl)-α-methylnitrone form (XIIA). This is confirmed by the fact that the IR spectrum of a KBr pellet of this compound (Table 1) contains, in addition to stretching vibrations of the C=N bond of a nitrone grouping at 1628 cm^{-1}, a band at 1662 cm^{-1}, which can be ascribed to the stretching vibrations of the C=N bond of an oxime group [11]. The absence of this band in the IR spectrum of a KBr pellet of XVIII, on the other hand, makes it possible to assume that in the cyrstalline state it has a 1-hydroxy-2,4,6-tetramethyl-1,2,5,6-tetrahydropyrimidine 3-oxide structure (XVIIIB).

Two forms of the cyclic tautomer – the cis and trans forms relative to the hydrogen atoms in the 2 and 5 positions (XIIB) and the 2 and 6 positions (XVB) of the heteroring – can participate in the ring-chain tautomeric equilibrium; this has been observed for five-membered and six-membered heterorings [13]. However, signals of only one form of the heteroring are observed in the PMR spectra of XII and XV. This may be explained by the low concentration of cyclic form B in the tautomeric mixture, the complex character of the spectrum, and the coincidence of the chemical shifts for the cis and trans isomers of the heteroring.

Thus an examination of the PMR spectra and other spectral characteristics shows that the products of condensation of 1,3-hydroxylamino oximes with formaldehyde have a 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxide structure and that the products of condensation with acetone have an N-(3-oximino-substituted)-α,α-dimethylnitrone structure. The products of condensation of aliphatic 1,3-hydroxylamino oximes with acetaldehyde exist in solution in the form of a tautomeric mixture of open and cyclic forms ($A \rightleftarrows B$). Ring-chain tautomerism evidently occurs in all cases, but the equilibrium is shifted to favor the cyclic form in the case of the products of condensation with formaldehyde and to favor the open form in the case of the products of condensation with acetone.

EXPERIMENTAL

The IR spectra of the compounds were recorded with a UR-20 spectrometer. The UV spectra of alcohol solutions of the compounds were recorded with a Specord spectrophotometer. The PMR spectra of the com-

pounds were recorded with Varian A-56/60A and Varian HA-100 spectrometers with hexamethyldisiloxane (0.04 ppm) and tert-butyl alcohol (1.22 ppm) (aqueous solutions) as the internal standards.

1,3-Hydroxylamino Oximes III and VII. These compounds were obtained from the appropriate α-phenylnitrones (XXV and XXVI) by the method in [2].

N-(3-Oxo-2-methyl-1-butyl)-α-phenylnitrone (XXV). This compound, with mp 75-76° (from ether–methanol), was obtained in 80% yield. Found: C 70.1; H 7.4; N 7.1%. $C_{12}H_{15}NO_2$. Calculated: C 70.2; H 7.4; N 6.8%.

N-(1-Oxo-2-methyl-1-phenyl-3-propyl)-α-phenylnitrone (XXVI). This compound, with mp 67-69° (from ether), was obtained in 76% yield. Found: C 76.4; H 6.4; N 5.4%. $C_{17}H_{17}NO_2$. Calculated: C 76.4; H 6.4; N 5.2%.

N-(3-Oximino-2-methyl-1-butyl)hydroxylamine (III). This compound, the oxalate of which had mp 179-181° (from 50% alcohol), was obtained in 73% yield. Found: C 40.6; H 7.5; N 15.7%. $C_5H_{12}N_2O_2 \cdot 1/2(COOH)_2$. Calculated: C 40.7; H 7.4; N 15.8%.

N-(1-Oximino-2-methyl-1-phenyl-3-propyl)hydroxylamine (VII). This compound, with mp 117-119° (from ethyl acetate), was obtained in 73% yield. Found: C 61.7; H 7.4; N 14.4%. $C_{10}H_{14}N_2O_2$. Calculated: C 61.8; H 7.3; N 14.4%.

Compounds VI and V, which have previously been described in the form of the hydrochloride [2] and oxalate [3], respectively, were obtained as crystalline substances, VI with mp 79-81° (from ethyl acetate), and V with mp 68-70° (from ethyl acetate). PMR spectrum of V in $CDCl_3$, δ, ppm: anti isomer: 1.11 [gem-$(CH_3)_2$], 1.90 (CH_3), and 2.37 (CH_2); syn isomer: 1.17 [gem-$(CH_3)_2$], 1.90 (CH_3), and 2.53 (CH_2); the anti : syn isomer ratio was 6 : 1 (see [14]).

Condensation of 1,3-Hydroxylamino Oximes with Formaldehyde. A 0.012-mole sample of formaldehyde (~30% aqueous solution) was added with stirring to a solution of 0.01 mole of the 1,3-hydroxylamino oxime (II-V) in 15 ml of alcohol. After 1 h, the solvent was evaporated, the oily residue was triturated in ether or ethyl acetate, and the resulting solid material (IX, XI, XIV, or XVII) was removed by filtration.

1-Hydroxy-1,2,5,6-tetrahydropyrimidine 3-Oxide (VIII). A solution of 5.0 g (0.048 mole) of I in 90 ml of absolute alcohol was added with stirring in the course of 15 min to a solution of 5 ml of a 27% (0.048 mole) solution of formaldehyde in 70 ml of absolute alcohol. After 1 h, the solvent was vacuum evaporated at 35°, the oily residue was triturated in ethyl acetate, and the precipitated VIII (4.5 g) was removed by filtration. Oxide VIII was difficult to purify, apparently because of its tendency to undergo polymerization (see [15]).

1-Hydroxy-4-phenyl-5-R^2-1,2,5,6-tetrahydropyrimidine 3-Oxides (XIX and XXII). A 0.008-mole sample of acetic acid was added to a solution of 0.015 mole of 1,3-hydroxylamino oxime VI or VII in 30 ml of alcohol, after which 0.018 mole of an aqueous solution of formaldehyde (27-35%) was added with stirring. After 3 days, the solvent was evaporated, the oily residue was triturated in ether, and the precipitated XIX or XXII was removed by filtration.

Condensation of 1,3-Hydroxylamino Oximes with Acetaldehyde. A solution of 0.012 mole of acetaldehyde in 5 ml of alcohol was added with stirring to a solution of 0.01 mole of the appropriate 1,3-hydroxylamino oxime in 10 ml of alcohol. After 1 h, the solvent was evaporated, the residue was triturated in ether, and the precipitated XII, XVIII, XX, or XXIII was removed by filtration. Compound XV was isolated by preparative thin-layer chromatography on silica gel in an ether-methanol system (4 : 1).

Condensation of 1,3-Hydroxylamino Oximes with Acetone. The hydroxylamino oxime (II, III, VI, or VII) was dissolved in a 20-fold excess of acetone, and the solution was allowed to stand at room temperature for 2 h. The precipitated condensation products (XXI or XXIV) were removed by filtration. Compounds X and XIII were isolated by evaporation of the solvent and crystallization of the residue by trituration in ether. In the condensation of IV with acetone, the solution was refluxed for 7 h, after which the acetone was evaporated, and the residue was crystallized by trituration in ether. The precipitated XVI was removed by filtration.

LITERATURE CITED

1. L. B. Volodarskii, Khim. Geterotskil. Soedin., No. 10, 1299 (1973).
2. A. Ya. Tikhonov and L. B. Volodarskii, Zh. Org. Khim., 9, 770 (1973).
3. A. Ya. Tikhonov and L. B. Volodarskii, Izv. Akad. Nauk SSSR, Ser. Khim., 2372 (1973).
4. A. Ya. Tikhonov and L. B. Volodarskii (Volodarsky), Tetrahedron Lett., 2721 (1975).

5. J. Hamer and A. Macaluso, Chem. Rev., 64, 474 (1964).
6. G. R. Delpierre and M. Lamchen, Quart. Rev., 19, 329 (1965).
7. L. S. Kaminsky and M. Lamchen, J. Chem. Soc., B, 1085 (1968).
8. J. E. Baldwin, A. K. Qureshi, and B. Sklarz, Chem. Commun., 373 (1968).
9. R. Z. Sagdeev, Yu. N. Molin, G. A. Kutikova, and L. B. Volodarskii, Teor. i Éksp. Khim., 6, 220 (1970).
10. L. B. Volodarskii and A. Ya. Tikhonov, Zh. Org. Khim., 6, 307 (1970).
11. L. Bellamy, New Data on the IR Spectra of Complex Molecules [Russian translation], Mir, Moscow (1971), p. 58.
12. R. É. Valter, Usp. Khim., 43, 1417 (1974).
13. Yu. G. Putsykin and L. B. Volodarskii, Izv. Sibirsk, Otd. Akad. Nauk SSSR, Ser. Khim., 9, 4, 86 (1969).
14. A. Belly, F. Petrus, and J. Verducci, Bull. Soc. Chim. France, 1395 (1973).
15. J. F. Elsworth and M. Lamchen, J. Chem. Soc., C, 2423 (1968).

PREPARATION AND SOME PROPERTIES OF PYRIMIDINE 1,3-DIOXIDES

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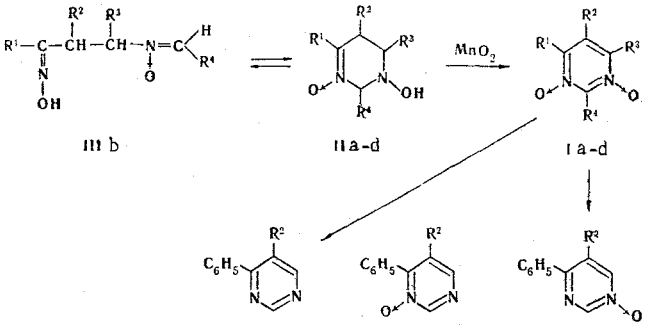
Oxidation of 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxides with active manganese dioxide leads to pyrimidine 1,3-dioxides. Depending on the conditions, pyrimidines or isomeric pyrimidine N-monoxides are formed by deoxygenation of pyrimidine 1,3-dioxides with triethyl phosphite.

There is very little available information regarding pyrimidine 1,3-dioxides (I); the only example we know of is 5-nitro-2,4,6-triaminopyrimidine 1,3-dioxide [1].

In a previous paper [2] we showed that the reaction of 1,3-hydroxylamino oximes with carbonyl compounds leads to the formation of 1-hydroxy-1,2,5,6-tetrahydropyrimidine 3-oxides (II), aliphatic N-(3-oximino-substituted)nitrones (III) or a tautomeric mixture of them (II ⇄ III). During a study of the properties of the condensation products we examined the possibility of their use for the synthesis of pyrimidine 1,3-dioxides (I). In the case of compounds existing in a ring–chain tautomeric equilibrium (II ⇄ III) this would correspond to fixing of the pyrimidine ring (see [3]). We found that active manganese dioxide [5] oxidizes II to give pyrimidine 1,3-dioxides I.*



I—IIa R^1=H, R^2=H, R^3=H, R^4=H; I—IIIb R^1=CH_3, R^2=H, R^3=CH_3, R^4=CH_3; I—IIc, IV—VIc R^1=C_6H_5, R^2=H, R^3=H, R^4=H; I—IId, IV—VId R^1=C_6H_5, R^2=CH_3, R^3=H, R^4=H

*See [4] for our preliminary communication.

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