

A. A. Potekhin and B. D. Zaitsev

UDC 541.623:547.875

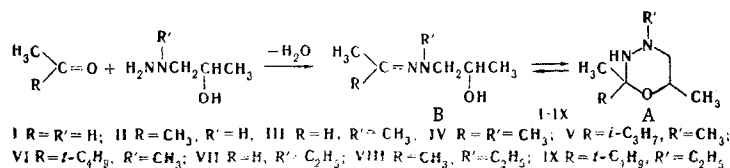
1-Hydrazino-2-propanol reacts with aliphatic carbonyl compounds to form the corresponding (2-hydroxypropyl)hydrazones. 1-(N-Alkylhydrazino)-2-propanols, on the other hand, give tautomeric mixtures of alkyl-substituted perhydro-1,3,4-oxadiazines and N-alkyl-N-(2-hydroxypropyl)hydrazones. As compared with derivatives of 2-(N-alkylhydrazino)ethanols, the position of the equilibrium in the investigated cases is shifted to favor the cyclic forms.

It was established in [1] that the products of the condensation of 2-(N-alkylhydrazino)ethanols with aliphatic carbonyl compounds are tautomeric mixtures of alkylperhydro-1,3,4-oxadiazines and the corresponding hydrazones. We investigated derivatives of (2-hydroxypropyl)-substituted hydrazines for a further study of the effect of the structure of the starting hydrazine on the equilibrium position in this tautomeric system.

The starting 1-hydrazino-, 1-(N-methylhydrazino)-, and 1-(N-ethylhydrazino)-2-propanols were obtained by the reaction of hydrazine hydrate and, respectively, alkylhydrazines with propylene oxide. It turned out that the properties of the products of condensation of these hydrazinoalcohols with acetaldehyde and saturated ketones are basically similar to the properties of preparations obtained from 2-hydrazino-substituted ethanols [1], although there are some differences in the behavior of individual representatives of these two groups of compounds. The characteristics of the twice-distilled reaction products are presented in Table 1.

1-Hydrazino-2-propanol reacts with acetaldehyde and acetone to give 2-hydroxypropyl-substituted hydrazones IB and IIB. The hydrazone structure of these compounds is confirmed by their refractometric constants (exaltation of the molecular refraction peculiar to monosubstituted hydrazones and high dispersions) and the data of IR and PMR spectroscopy (see Table 2). The IR spectra of both preparations contain bands of medium intensity from the valence vibrations of the C=N bonds ( $1615-1630\text{ cm}^{-1}$ ) and broad, intense bands from the valence vibrations of the O-H and N-H bonds ( $3170-3500\text{ cm}^{-1}$ ). In the PMR spectra the signals of the methyl groups are observed at  $\tau$  8.20-8.40 ppm, which is characteristic for the  $\text{CH}_3-\text{C}=\text{N}$  grouping. According to the PMR spectrum, the hydrazone of acetaldehyde (I) is a mixture of syn and anti isomers (57:43). The corresponding cyclic tautomers cannot be detected by means of spectral methods, and hydrazones IB and IIB are consequently completely analogous to 2-hydrazinoethanol derivatives, which also do not manifest any tendency for cyclization [1].

However, in the case of the products of condensation (III-IX) of 1-(N-alkylhydrazino)-2-propanols with aldehydes and ketones this tendency is more appreciably manifested than for derivatives of 2-hydroxyethyl-substituted hydrazines:



\*See [1] for communication I.

A. A. Zhdanov Leningrad State University. Translated from *Khimiya Geterotsiklicheskikh Soedinenii*, No. 3, pp. 301-308, March, 1971. Original article submitted September 29, 1970.

© 1973 Consultants Bureau, a division of Plenum Publishing Corporation, 227 West 17th Street, New York, N. Y. 10011. All rights reserved. This article cannot be reproduced for any purpose whatsoever without permission of the publisher. A copy of this article is available from the publisher for \$15.00.

TABLE 1. Products of the Condensation of  $\text{RCOCH}_3$  with 2-Hydroxypropyl-Substituted Hydrazines  $\text{H}_2\text{NNR}'\text{CH}_2\text{CH}(\text{OH})\text{CH}_3$

Reaction prod- uct	R	R'	Structure	bp, °C (pressure, mm)	$d_4^{20}$	$n_D^{20}$	$n_D^{25}$	$\Delta_{FC}$	$\omega_{FCD}$	MR <sub>D</sub>		Empirical formula	Found		Calc.		Yield, %
										found	calc.		N, %	M	N, %	M	
I	H	H	B	102—104 (14)	0.9794	1.4748	1.4715	114.6	24.2	33.38	32.93	32.93	24.1 23.8	124 125	24.1	116	73
II	CH <sub>3</sub>	H	B	98—99 (9)	0.9586	1.4719	1.4687	112.6	24.0	38.02	37.58	37.58	21.6 21.8	129 128	21.5	130	88
III	H	CH <sub>3</sub>	A A ⇌ B	71—72 (55)	0.9377 0.9394	1.4431 1.4460	1.4407 1.4434	86.8 90.3	19.6 20.3	36.82 36.96	37.06	37.77	21.1 21.5	127 127	21.5	130	73
IV	CH <sub>3</sub>	CH <sub>3</sub>	A A ⇌ B	66—67 (40)	0.9175 0.9172	1.4393 1.4424	1.4369 1.4399	83.7 87.9	19.5 19.9	41.36 41.64	41.70	42.41	19.3 19.3	147 148	19.4	144	87
V	<i>i</i> -C <sub>3</sub> H <sub>7</sub>	CH <sub>3</sub>	A ⇌ B	75—77 (12)	0.9027	1.4472	1.4446	91.1	20.4	51.01	51.00	51.71	16.3 15.8	170 170	16.3	172	75
VI	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	B *	93—94 (14)	0.8828	1.4485	1.4458	95.7	21.3	56.55	55.65	56.36	14.7 14.6	187 188	15.0	186	60
VII	H	C <sub>2</sub> H <sub>5</sub>	A A ⇌ B	82—83 (60)	0.9226 0.9230	1.4432 1.4436	1.4407 1.4412	85.7 86.3	19.3 19.5	41.43 41.47	41.70	42.41	19.0 18.9	139 143	19.4	144	83
VIII	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	A ⇌ B	82—84 (53)	0.9036 0.9037	1.4392 1.4394	1.4367 1.4369	84.4 84.6	19.2 19.3	46.08 46.10	46.35	47.06	17.7 17.9	157 160	17.7	158	78
IX	<i>t</i> -C <sub>4</sub> H <sub>9</sub>	C <sub>2</sub> H <sub>5</sub>	B A ⇌ B	94—95 (8)	0.8774 0.8784	1.4480 1.4473	1.4455 1.4448	93.3 91.8	20.7 20.3	61.12 60.97	60.30	61.01	13.9 14.1	197 204	14.0	200	69

\*Contains a trace of the second tautomer.

TABLE 2. PMR Spectra of the Products of Condensation of Carbonyl Compounds with 2-Hydroxypropylhydrazines\*

Compound	T, ppm (J, Hz)										
	A					B					
2-CH <sub>5</sub>	2-R	R'	5-CH <sub>2</sub>	6-CH	6-CH <sub>2</sub>	CH <sub>2</sub> C=N	R	R'	CH <sub>2</sub> -N	CH-O	CH <sub>2</sub> -O
I	—	—	—	—	—	8,36 d (5,5) 8,22 d (5,0)	3,17 q (5,5) 3,68 q (5,0)	—	7,23 d (5,0) 7,07 d (5,0)	6,31 m	8,96 d (5,5)
II	—	—	—	—	—	8,37 s	8,24 s	—	7,16 d (5,0)	6,31 m	8,95 d (5,0)
III	8,94 d (5,0)	5,82 q (5,0)	7,77 s	8,52 dd ( $J_{aa}^{vic} = J_{ad}^{gem} = 10,5$ ) 7,40 dd ( $J_{ae}^{vic} = 2,5$ , $J_{ae}^{gem} = 10,5$ )	6,54 m	8,29 d (5,0)	3,81 q (5,0)	7,46 s	7,46 d (5,0)	6,5 m	9,0 d
IV	8,88 s	8,68 s	7,80 s	8,43 dd ( $J_{aa}^{vic} = J_{ae}^{gem} = 10,0$ ) 7,43 dd ( $J_{ae}^{vic} = 2,5$ , $J_{ae}^{gem} = 10,0$ )	6,20 m	8,28 s	8,34 s	7,80 s	7,43 d (5,0)	6,20 m	8,97 d (6,0)
V	8,65 s 8,76 s	9,02 d	...	...	...	8,20 s	9,02 d (6,0)	7,80 s	7,45 d (5,0)	6,20 m	9,05 d (6,5)
VI	8,68 s	...	...	...	...	8,18 s	8,95 s	7,81 s	7,45 d (5,0)	6,43 m	9,02 d (5,5)
VII	8,91 d (5,5)	5,77 q (5,5)	9,00 t (6,0)	8,55 dd ( $J_{aa}^{vic} = 9,5$ , $J_{ae}^{gem} = 10,5$ ) 7,35 dd ( $J_{ae}^{gem} = 10,5$ , $J_{ae}^{vic} = 2,5$ )	6,37 m	—	—	—	—	—	—
VIII	8,84 s	8,68 s	9,07 d (6,0)	8,34 dd ( $J_{aa}^{vic} = J_{ae}^{gem} = 10,5$ ) 7,40 dd ( $J_{ae}^{vic} = 2,5$ , $J_{ae}^{gem} = 10,5$ )	6,23 m	8,20 s	8,17 s	...	...	...	...
IX	8,67 s	...	...	...	...	8,16 s	8,97 s	9,08 d (7,0) 7,45 q (7,0)	7,44 d (5,0)	6,45 m	9,03 d (5,0)

\* d - doublet, s - singlet, t - triplet, q - quartet, m - multiplet, dd - double doublet, gem - geminal, vic - vicinal.

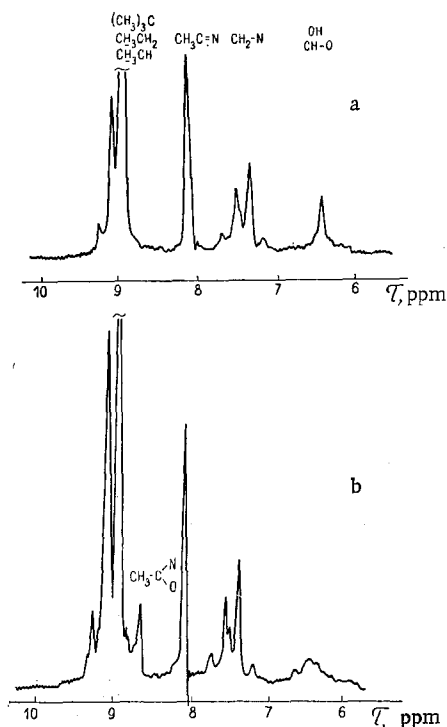


Fig. 1. PMR spectra: 1) N-ethyl-N-(2-hydroxypropyl)hydrazone of pinacolone (IXB); 2) equilibrium mixture of IXB and 2-tert-butyl-2,6-dimethyl-4-ethylperhydro-1,3,4-oxadiazine (IXA).

TABLE 3. Composition of Equilibrium Mixtures of (2-Hydroxypropyl)-hydrazone (B) and Perhydro-1,3,4-oxadiazine (A)

Mixture	A : B form from	
	MR <sub>D</sub> (20°)	PMR (~25°)
I	0 : 100	0 : 100
II	0 : 100	0 : 100
III	90 : 10*	88 : 12
IV	73 : 27	76 : 24
V	—	40 : 60
VI	0 : 100	5 : 95
VII	97 : 3*	100 : 0
VIII	—	80 : 20
IX	—	9 : 91

\* Allowing for exaltation of the molecular refraction (0.4) [1].

spectrum. (A weak singlet is observed at  $\tau$  8.67 ppm, which is characteristic for an axial methyl group in the 2-position of cyclic form VIA.)

The product of the condensation of pinacolone with 2-(N-ethylhydrazino)-2-propanol behaves anomalously. Its constants and IR and PMR spectra (Fig. 1, curve a) immediately after distillation indicate the pinacolone N-ethyl-N-(2-hydroxypropyl)hydrazone structure (IXB). However, its molecular refraction and dispersion decrease rather than increase with time, as was observed until now for all labile products of the reaction of carbonyl compounds with hydroxyalkyl-substituted hydrazines (Table 1). A singlet at 8.67 ppm simultaneously appears in its PMR spectrum (Fig. 1b); this singlet should be ascribed to the 2-methyl group in 2-tert-butyl-2-methyl-4-ethylperhydro-1,3,4-oxadiazine (IXA). Thus, for the first time it was here possible to observe the formation of an equilibrium mixture from the chain tautomer rather than from the cyclic tautomer. The point is that in vapors at about 100° the equilibrium is apparently shifted to favor

Thus, in preparation III, obtained from acetaldehyde and 1-(N-methylhydrazino)-2-propanol, the percentage of hydrazone IIIB reaches only about 10% after achieving equilibrium, while the analogous 2-(N-methylhydrazino)ethanol derivative contains about 50% of the chain form [1]. The concentration of the hydrazone tautomer was also depressed in the products of condensation of acetone with both 1-(N-alkylhydrazino)-2-propanols.

In contrast to the hydrazinoethanol derivatives the refractometric method was not suitable enough to study the interconversion of the ring and chain forms in a number of the cases investigated here. The reason for this consists in the higher rate of establishment of equilibrium between the tautomers. In the preparation obtained, for example, from acetone and 1-(N-ethylhydrazino)-2-propanol the concentration of hydrazone VIII B is close to the equilibrium concentration immediately after distillation, and the refractometric characteristics of the compound remain virtually constant. The characteristic band of the C=N bond ( $1630\text{ cm}^{-1}$ ) is present in the IR spectrum of a freshly distilled sample, and signals of methyl groups attached to the azomethine carbon atom ( $\tau$  8.17 and 8.20 ppm) are observed in its PMR spectrum. The refractive index and density of the product of reaction of methyl isopropyl ketone with 1-(N-methylhydrazino)-2-propanol also remain virtually constant, but it is erroneous to conclude that there is a low concentration of the chain form (VB) in the equilibrium mixture on the basis of this. The PMR spectrum of equilibrium preparation V indicates the predominance of precisely the chain form (VB): there are an intense singlet at 8.16 ppm ( $\text{CH}_3\text{C}=\text{N}$ ) and two singlets of considerably lower intensity at 8.76 and 8.65 ppm (2- $\text{CH}_3$  in stereoisomeric cyclic forms VA).

The refractometric characteristics of the product of condensation of pinacolone with 1-(N-methylhydrazino)-2-propanol also remain absolutely unchanged. However, here the equilibrium is almost completely shifted to favor hydrazone tautomer VIB, and only an insignificant trace of perhydro-1,3,4-oxadiazine VIA can be detected by means of the PMR

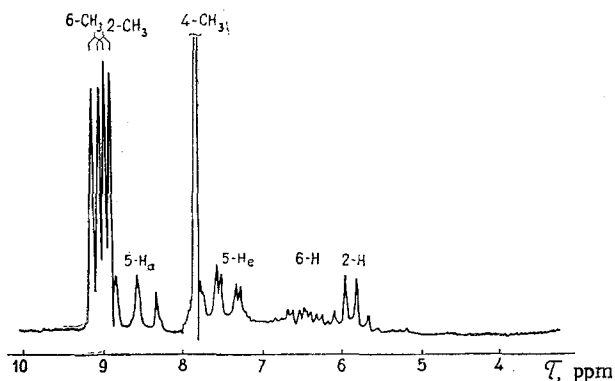


Fig. 2. PMR spectrum of 2,4,6-trimethylperhydro-1,3,4-oxadiazine.

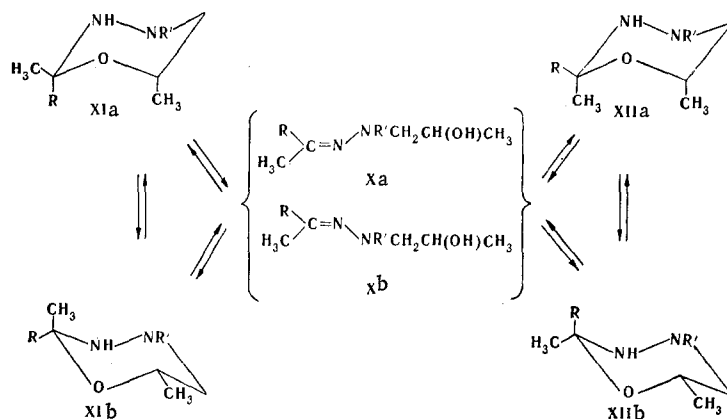
the hydrazone, while in the liquid phase at 20° the equilibrium preparation contains an appreciable amount of the cyclic form. Even by changing the distillation conditions we still could not isolate the low-boiling cyclic form, apparently as a consequence of the high rate of conversion of it to the hydrazone.

The approximate composition of equilibrium tautomeric mixtures, determined from molecular refraction data [1] (in those cases where the freshly distilled preparation was virtually free of the second tautomer) and from PMR spectra, is presented in Table 3. It is apparent from Table 3 that all of the regularities previously observed for derivatives of 2-hydroxyethyl-substituted hydrazines [1] are preserved in this series of compounds (the increase in the equilibrium concentration of the hydrazone on passing from aldehyde derivatives to ketone derivatives, on increasing the bulk of the substituents attached to the azomethine carbon atom, and on decreasing the bulk of the substituent in the hydrazine fragment). A comparison with the data in [1] leads to the conclusion that the introduction of a methyl group into the  $\beta$  position of the  $\beta$ -hydroxyethyl group promotes stabilization of the ring tautomer. A general property of ring-chain tautomeric systems, which is expressed in a shift in the equilibrium to favor the cyclic form on increasing the number of ring substituents [2], is apparently manifested here.

In considering the tautomeric conversion of the 2-hydroxypropylhydrazone to 6-methylperhydro-1,3,4-oxadiazine, the equilibrium between two stereoisomeric chain forms, on the one hand, and two stereoisomeric cyclic forms, on the other, should be taken into account in the general case. Each of the latter in turn can exist as a pair of conformers.

In the case of disubstituted hydrazones of aldehydes (X, R = H), only one configuration, viz., the syn configuration (Xa), is realized; the stability of Xa is due to the fact that only here is it possible to preserve the  $p-\pi$  conjugation chain in the system of C=N-N bonds [3]. In fact, signals of only one chain form (III and VII, Table 2) are observed in the PMR spectra of acetaldehyde derivatives. As for the corresponding cyclic forms (IIIA and VIIA), conformer XIIa with two axial methyl groups in the 2- and 6-positions should surely be excluded from consideration, and only conformation XIIb is consequently peculiar to the cis isomer. Moreover, the PMR spectra of 2,6-dimethylperhydrohydroxydiazines IIIA and VIIA suggest the absence of both conformations of trans isomer XI in the tautomeric system. The latter, having either a 2- (XIb) or 6-methyl group (XIa) in the axial position, is naturally thermodynamically less stable than diequatorial conformer XIIb. Excluding a rapid isomerization ( $XI \rightleftharpoons XII$ ), the signals of three cyclic forms should have been observed in the PMR spectra of IIIA and VIIA. The PMR spectra, however, indicate the presence of only one form (Table 2 and Fig. 2). As seen from a comparison of the chemical shifts of the 2-methyl group in 2-mono- and 2,2-disubstituted perhydrooxadiazines, in the first case this group is found exclusively in the equatorial position. A comparison with the data for 2,4-disubstituted perhydro-1,3,4-oxadiazines [1] confirms the validity of the assumption of the practically complete absence of the conformer with an axial 2-methyl group in previously investigated tautomeric mixtures.

The C-5 and C-6 protons in the PMR spectra of 2,4,6-trisubstituted perhydrooxadiazines IIIA and VIIA give three groups of signals; this made it possible to estimate the spin-spin splitting constants. As seen from Table 2, the vicinal interaction constants amount to approximately 10 and 2.5 Hz, which also indicates the existence of cyclic tautomers in the chair form. These values are close to the analogous constants in perhydro-1,3-oxazines [4] for which the chair conformation was also determined by other methods.



In the general case the disubstituted hydrazones of ketones are formed as a mixture of geometrical isomers, the ratio between which depends on the nature of the substituents attached to the azomethine carbon atom. In the PMR spectra of the compounds that we obtained, however, we were able to identify the signals of only one of these, apparently the syn isomer (Xb). The concentration of anti form Xa is probably extremely insignificant. A rapid, direct isomerization ( $Xa \rightleftharpoons Xb$ ), which would lead to averaging of the spectrum, is excluded on the basis of the fact that the PMR spectra of acetone derivatives IVB and VIII B contain the signals of two nonequivalent methyl groups in the isopropylidene radical.

Of the four possible conformers of the 2,2-disubstituted perhydrooxadiazines (XIa, b and XIIa, b), two — with an axial methyl group attached to C-6 — can be disregarded as a consequence of their thermodynamic instability due to the diaxial interaction of the two alkyl groups. Both of the remaining conformers in the case of 2,2-dimethyl derivatives XIb and XIIb ( $R = CH_3$ ) turn out to be identical. It might have been expected that in these cases the cyclic form would exist as one conformer in the tautomeric mixture. In fact, only two signals of equal intensity, which correspond to both methyl groups attached to C-2 (equatorial at 8.85 ppm and axial at 8.68 ppm), are observed in the PMR spectra of preparations IVA and VIII. The signal of only the axial methyl group in 2-tert-butyl-2-methylperhydrooxadiazines (8.65–8.70 ppm) can be observed in the PMR spectra of pinacolone derivatives VI and IX, which should have been expected, considering the considerably higher conformational energy of the tert-butyl substituent. On the other hand, 2-isopropyl-2,4,6-trimethylperhydro-1,3,4-oxadiazine (VA) is present in the tautomeric mixture as both stereoisomers (XIb and XIIb), and the major isomer is naturally the trans-2,6-dimethyl isomer (XIIb).

The spin-spin interaction constants for the C-5 and C-6 protons in 2,2-dimethylperhydrooxadiazines IVA and VIII A remain at the same order of magnitude as in the 2-monosubstituted compounds, which once more confirms their stereochemical affinity. These constants could not be determined for the remaining 2,2-dialkylperhydrooxadiazines because of the low equilibrium concentration of the cyclic form.

## EXPERIMENTAL

The PMR spectra were obtained with a YaMR-5535 spectrometer (40 MHz) with hexamethyldisiloxane as the internal standard. In the case of viscous hydrazones IB and IIB, their solutions (25–30%) in  $CCl_4$  were investigated; the spectra of the remaining compounds were obtained without a solvent. The IR spectra (thin layer) were obtained with a UR-10 spectrometer.

**1-Hydrazino-2-propanol.** Propylene oxide (1 mole) was added with stirring at  $0^\circ$  to 10 moles of a 25% solution of hydrazine hydrate, and the reaction mixture was held at room temperature for 12 h and vacuum distilled to give 76% of a product with bp  $95-97^\circ$  (4 mm),  $d_4^{20}$  1.0433,  $n_D^{20}$  1.4774,  $n_C^{20}$  1.4747,  $\Delta_{FC}$  70.8, and  $\omega_{FCD}$  14.8 (bp  $92-93^\circ$  (2 mm) [5]).

**1-(N-Methylhydrazino)-2-propanol.** An aqueous solution of methylhydrazine sulfate [6] was made alkaline with a fivefold excess of solid potassium hydroxide and distilled almost to dryness. The methylhydrazine concentration in the distillate was determined by titration with hydrochloric acid, after which propylene oxide (90% of the calculated amount) was added dropwise with stirring and ice cooling. The mixture was worked up as described for the synthesis of 1-hydrazino-2-propanol to give 44% of a product with bp  $90-92^\circ$  (25 mm),  $d_4^{20}$  0.9528,  $n_D^{20}$  1.4511,  $n_C^{20}$  1.4485,  $\Delta_{FC}$  89.9, and  $\omega_{FCD}$  19.9. IR spectrum:  $1610\text{ cm}^{-1}$

(medium,  $\delta_{\text{NH}_2}$ ), 3260-3360  $\text{cm}^{-1}$  (strong,  $\nu_{\text{OH}}$ ,  $\nu_{\text{NH}_2}$ ). Found %: N 26.7, 26.8; mol. wt. 102, 106;  $\text{MR}_D$  29.44.  $\text{C}_4\text{H}_{12}\text{N}_2\text{O}$ . Calculated %: N 26.9; mol. wt. 104;  $\text{MR}_D$  29.53.

1-(N-Ethylhydrazino)-2-propanol. Propylene oxide (0.95 mole) was added dropwise with stirring and ice cooling to a solution of 1 mole of ethylhydrazine in an equal volume of ethanol. The mixture was allowed to stand for 24 h, heated for 2 h at 50°, and vacuum distilled to give 60% of the hydrazinoalcohol with bp 86-87° (14 mm),  $d_4^{20}$  0.9360,  $n_D^{20}$  1.4512,  $n_C^{20}$  1.4487,  $\Delta_{\text{FC}}$  88.1, and  $\omega_{\text{FCD}}$  19.5. IR spectrum: 1610  $\text{cm}^{-1}$  ( $\delta_{\text{NH}_2}$ ), 3280-3360  $\text{cm}^{-1}$  ( $\nu_{\text{OH}}$ ,  $\nu_{\text{NH}_2}$ ). Found %: N 23.7, 23.4; mol. wt. 119, 121;  $\text{MR}_D$  34.02.  $\text{C}_5\text{H}_{14}\text{N}_2\text{O}$ . Calculated %: N 23.7; mol. wt. 118;  $\text{MR}_D$  34.17.

(2-Hydroxypropyl)hydrazone of Acetaldehyde (IB). Acetaldehyde [13.5 g (0.31 mole)] was added dropwise with vigorous stirring and ice cooling to 27 g (0.3 mole) of 1-hydrazino-2-propanol. The reaction mixture was heated at 75° for 1 h, and the reaction product was isolated by vacuum distillation.

Acetone hydrazone IIB (see Table 1) was similarly obtained.

2,4,6-Trimethylperhydro-1,3,4-oxadiazine (IIIA). The reaction of acetaldehyde with 1-(N-methylhydrazino)-2-propanol was carried out as described for the synthesis of hydrazone IB. The reaction mixture was saturated with solid potassium hydroxide, and the organic layer was dried with solid alkali and distilled.

Perhydrooxadiazines IVA, VIIA, and VIIIA (Table 1) were similarly obtained.

N-Methyl-N-(2-hydroxypropyl)hydrazone of Pinacolone (VIB). A solution of 26 g (0.26 mole) of pinacolone and 26 g (0.25 mole) of 1-(N-methylhydrazino)-2-propanol in 50 ml of benzene was refluxed in a flask equipped with a Dean-Stark trap until the distillation of water ceased. The benzene was removed by distillation at atmospheric pressure, and the residue was vacuum distilled.

Pinacolone N-ethyl-N-(2-hydroxypropyl)hydrazone (IXB) and a mixture of 2-isopropyl-2,4,6-trimethylperhydro-1,3,4-oxadiazine (VA) and methyl isopropyl ketone N-methyl-N-(2-hydroxypropyl)hydrazone (VB) (Table 1) were similarly obtained.

#### LITERATURE CITED

1. A. A. Potekhin, *Zh. Organ. Khim.*, 7, 16 (1971).
2. P. R. Jones, *Usp. Khim.*, 35, 1589 (1966).
3. B. V. Ioffe, O. V. Sverdlova, and L. M. Korzhikova, *Teor. i Éksperim. Khim.*, 119 (1967).
4. Y. Ablingham, R. C. Cookson, T. A. Crabb, and S. Vary, *Tetrahedron*, 24, 4625 (1968).
5. G. Gever, *J. Am. Chem. Soc.*, 76, 1284 (1954).
6. *Synthesis of Organic Preparations*, Vol. 2 [Russian translation], IL, Moscow (1949), p. 323.