RING-CHAIN TAUTOMERISM OF SUBSTITUTED HYDRAZONES

VII.* SUBSTITUTED 4-tert-BUTYLPERHYDRO-1,3,4-OXADIAZINES

A. A. Potekhin and E. A. Bogan'kova

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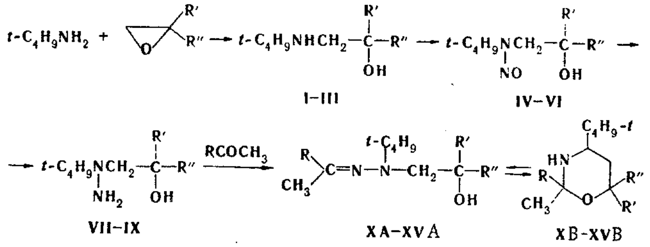
The reaction of β-(N-tert-butylhydrazino)alcohols with acetone and acetaldehyde leads to the formation of 4-tert-butylperhydro-1,3,4-oxadiazines. The tautomeric equilibrium between the latter and the corresponding N-tert-butyl-N-(β-hydroxyalkyl)hydrazones is displaced strongly in the direction of the cyclic form. The PMR spectra of the majority of the perhydrooxadiazines obtained show that they exist in the chair conformation with practically no deformation in the N—C—C—O region. However, for the 2,2,6,6-tetramethyl derivative two nonchair (probably twist) conformations are preferred.

The position of the equilibrium in the tautomeric system formed by an N-alkyl-N-(β-hydroxyalkyl)-hydrazone and the corresponding 4-alkylperhydro-1,3,4-oxadiazine depends fundamentally on the structure of the alkyl radical [2]. Since the tert-butyl group, which has a high spatial demand, may exert a great influence on the relative stabilities of the chain and cyclic forms, it appeared of definite interest to study the products of the condensation of carbonyl compounds with β-(N-tert-butylhydrazino)-substituted alcohols.

The initial hydrazino alcohols (VII-IX) were obtained by the usual method of synthesizing unsymmetrically disubstituted hydrazines: nitrosation of the amino alcohols (I-III) with the subsequent reduction of the nitrosamines (IV-VI) with zinc amalgam in hydrochloric acid. The reaction of acetaldehyde and acetone with the hydrazino alcohols (VII-IX) takes place with somewhat greater difficulty than with the homologs having smaller alkyl groups on the nitrogen atom, leading to the condensation products (X-XV) (Table 1).



I, IV, VII $R'=R''=H$; II, V, VIII $R'=H$, $R''=CH_3$; III, VI, IX $R'=R''=CH_3$
X $R=R'=R''=H$; XI $R=CH_3$, $R'=R''=H$; XII $R=R''=H$, $R'=CH_3$; XIII $R=R'=CH_3$,
$R''=H$; XIV $R=H$, $R'=R''=CH_3$; XV $R=R'=R''=CH_3$

As in the majority of preceding cases [1-3], all the freshly prepared compounds had the cyclic structure B, as was shown by means of refractometry (Table 1) and also by IR and PMR spectroscopy. Their IR spectra lacked the $\nu_{C=N}$ band (1600-1700 cm^{-1}) and showed a comparatively narrow ν_{N-H} band (3160-3180 cm^{-1}) of medium intensity.

The PMR spectra of compounds (X-XV) (Table 2) are similar to the spectra of the perhydro-1,3,4-oxadiazines described previously [1-3]. In the first place they permit the conclusion that in the majority of cases the preferred conformation of the perhydrooxadiazine ring is the chair conformation. Thus, in the spectrum of the 2,6-dimethyl derivative (XIIB) the values of the vicinal constants of $J_{5a6a} = 10.0$ Hz and

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*For Communication VI, see [1].

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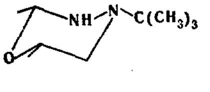
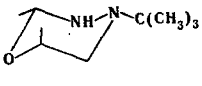
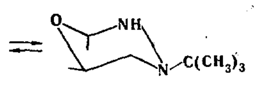
TABLE 1. 4-tert-Butylperhydro-1,3,4-oxadiazines (XB-XVB) and Equilibrium Mixtures of Them with the Corresponding Hydrazones

Reaction product	R	R′	R″	Structure	bp, °C (pressure, mm)	mp, °C	d_4^{20}	n_D^{20}	MR_D		A/B ratio	Empirical formula	Found		Calc.,		Yield, %
									found	calc., A/B			N, %	equiv.	N, %	equiv.	
X	H	H	H	B $A \rightleftarrows B$	69—71 (13)		0,9247 0,9253	1,4461 1,4474	45,66 45,73	47,06/46,35	3 : 97	$C_8H_{18}N_2O$	17,7 18,0	154 152	17,7	158	67
XI	CH_3	H	H	B $A \rightleftarrows B$	70,5—72 (13)		0,9096 0,9096	1,4420 1,4432	50,12 50,23	51,71/51,00	7 : 93	$C_9H_{20}N_2O$	16,6 16,6	167 165	16,3	172	56
XII	H	CH_3	H	B $A \rightleftarrows B$	65—68 (10)		0,9108 0,9103	1,4450 1,4454	50,35 50,42	51,71/51,00	4 : 96	$C_9H_{20}N_2O$	15,9 16,0	172 171	16,3	172	75
XIII	CH_3	CH_3	H	B	84—85 (20)	28—28,5		1,4411				$C_{10}H_{22}N_2O$	15,0 15,0	186 185	15,1	186	52
XIV	H	CH_3	CH_3	B	72—75 (13)		0,8960 0,8960	1,4409 1,4415	54,91 54,98	56,35/55,66	4 : 96	$C_{10}H_{22}N_2O$	15,0 15,1	185 187	15,1	186	72
XV	CH_3	CH_3	CH_3	B	94—95 (32)	~22		1,4410				$C_{11}H_{24}N_2O$	13,6 14,0	202 202	14,0	200	50

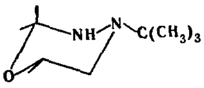
$J_{5e6e} = 2.7$ Hz show the axial arrangement of the 6-H proton and, consequently, the equatorial arrangement of the 6-CH_3 group. On the other hand, the protons of the methyl groups resonate in the comparatively high-field region (Table 2), which is also characteristic of equatorial groupings [1, 2]. Compound (XIIB) therefore has the cis configuration with the diequatorial position of the 2- and 6-CH_3 substituents (XVI). The trans isomer which, as might be expected, should exist in the form of a mixture of the conformers (XVII) ⇄ (XVIII) was not detected in the condensation product (XIIB).

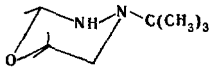

XVI


XVII


XVIII

The cis-diequatorial structure (XVI) is also confirmed by a comparison of the spectrum of (XIIB) with the spectra of the 2,2,6- and 2,6,6-trimethyl derivatives (XIIIB and XIVB, respectively). For both the latter compounds only the conformation with the equatorial 6- or 2-methyl group (XIX and XX, respectively) is acceptable. A comparison of the chemical shifts of the methyl groups in the spectra of the perhydrooxadiazines (XIIB-XIVB) (Table 2) leads to the unambiguous conclusion that the signal of an axial substituent is found in a weaker field than that of an equatorial substituent, and the signal of a substituent in position 2 is in weaker field than that of a substituent in position 6 (when they have the same orientation). Furthermore, it can be seen from the comparison of the spectra of compounds (XIIB) and (XIIIB) that the introduction of an axial methyl group into position 2 does not lead to any appreciable change in the vicinal constant J_{56} whatever and, consequently, scarcely changes the geometry of the $-CH_2CH(R)O-$ fragment.


XIX


XX

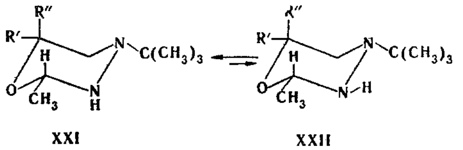
The parameters of the PMR spectrum of 4-tert-butyl-2-methylperhydro-1,3,4-oxadiazine (XB) were established by using double resonance ("decoupling" with the axial and equatorial 5-H protons). The axial protons in positions 5 and 6 of compound (XB) are shielded more strongly than the corresponding equatorial protons (Table 2). However, the differences in the shifts $\Delta\delta_{5e5a}$ and $\Delta\delta_{6e6a}$ [for (XB) 0.5 and 0.05 ppm, respectively] depend fundamentally on the structure of the substituents in the ring, in the general case. According to the information available to us, the 2,4-dimethyl and 2(4)-ethyl-4(2)-methyl derivatives show an inversion of the shifts of the 6-H protons $\Delta\delta_{6e6a}$ approximately -0.05 ppm), which may be connected with the increase in the proportion of the 2- or 4-axially substituted conformers in these cases. The hypothesis of the deshielding of the axial 6-H proton by the syn-axial 2-CH_3 group is confirmed by a consideration of the spectra of the 2,2-dimethyl derivatives (XIB) and (XIIIB): for (XIB), $\Delta\delta_{6e6a} = -0.3$ ppm (see below), and in (XIIIB) the 6-H signal is shifted downfield by 0.2 ppm as compared with the 2-monomethyl derivative (XIIB). A particularly large influence on the difference $\Delta\delta_{5e5a}$ is exerted by the neighboring equatorial group: thus, when an equatorial 6-CH_3 group is present [compounds (XIIB) and (XIIIB)], δ_{5e5a} rises to 1-1.2 ppm.

TABLE 2. PMR Spectra of the Perhydrooxadiazines (XB-XVB)[a]

Compound	R	R′	R″	Chemical shifts, δ, ppm (J, Hz)							
				2-CH_3 (e)	2-R_a	3-H	$(CH_3)_3C$	5-H_a	5-H_e	6-R''_a	6-R'_e
XB	H	H	H	1,10 d	4,32 m (6,0)	1,89 d (12,0)	0,98 s	2,27 m ($J_{5a5e}=-10,9$, $J_{5a6e}=3,4$, $J_{5a6a}=10,4$, $J_{5e6a}=3,0$, $J_{5e6e}=1,6$, $J_{6a6e}=-10,7$)	2,73 m	3,72 m	3,78 m
XIB[b]	CH_3	H	H	1,27 s		1,95 s	0,97 s	2,49 m		3,75 m	
XIIB	H	CH_3	H	1,12 d	4,31 m (6,3)	~1,7[c] (11,0)	1,00 s	1,73 dd ($J_{5a5e}=-10,6$, $J_{5a6a}=10,0$, $J_{5e6a}=2,7$, $J_{6\text{-H},6\text{-}CH_3}=6,8$)	2,78 dd	3,68 m	1,06 d
XIIIB	CH_3	CH_3	H	1,17 s	1,37 s	1,87 s	0,98 s	1,63 dd ($J_{5a5e}=-10,5$, $J_{5a6a}=10,3$, $J_{5e6a}=2,8$, $J_{6\text{-H},6\text{-}CH_3}=6,3$)	2,82 dd	3,88 m	0,98 d
XIVB	H	CH_3	CH_3	d′	4,47 m (6,2)	1,56 d (10,5)	0,99 s	1,83 dd (−10,6)	2,63 dd	1,25 s	1,06 s
XVB[e]	CH_3	CH_3	CH_3	1,28 s		1,73 s	1,03 s	2,20 s		1,17 s	

a) Abbreviations: s — singlet; d — doublet; dd — doublet of doublets; m — multiplet. b) In the spectrum of the equilibrium mixtures, weak signals of the hydrazone (XIA) are also observed: singlets at 2.02 and 1.94 ppm [$(CH_3)_2C=N$] and triplets (J ~ 6 Hz) at 3.50 ppm (OCH_2) and 2.61 ppm (NCH_2). c) Superposed on the 5-H_a signal. d′) Masked by the signals of the $(CH_3)_3C$ and the equatorial 6-CH_3 groups. e) The spectrum of the equilibrium mixture also shows weak singlet signals of the hydrazone (XVA): δ 1.90 and 2.00 ppm [$(CH_3)_2C=N$] and 2.64 ppm (NCH_2).

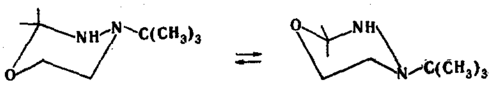
We have established that in 1 M solutions in tetrachloroethylene the intermolecular exchange of the proton of the NH group in the 2-methyl derivatives (XB, XIIB, and XIVB) is greatly retarded even at room temperature, so that the 2-H signal in compound (XB), for example, is observed in the form of a "sextet" with J_{H,CH_3} ~ 6 Hz and $J_{H,NH} \approx 12$ Hz, and the NH signal is split into a doublet ($J \approx 12$ Hz). The high value of the $J_{H,NH}$ constant shows the diaxial orientation of the interacting protons and the pronounced shift of the conformational equilibrium (XXI) ⇌ (XXII) caused by the inversion of the N-3 nitrogen atom in the direction of the conformer (XXI) with an axial N—H bond.



XXI XXII

The predominance of a conformer of the type of (XXI) has been suggested by us previously [2], although this was not proved because of the rapid NH exchange connected with the presence of considerable amounts of the chain tautomer with a hydroxy group. Recently, by means of PMR [4], IR spectroscopy, and dipole moments [5], it has been shown that in analogous six-membered saturated heterocycles — hexahydropyrimidines and tetrahydro-1,3-oxazines —, as well, the N—H bond is oriented axially. The axial position of the NH proton could be assumed by considering, on the one hand, the possibility of the appearance of a "generalized anomeric effect" [6] and, on the other hand, the presence of a hydrazine fragment in the perhydrooxadiazines. A preference for the location of the lone electron pairs at an angle close to 90° has been established for a number of hydrazine derivatives [7, 8]. Since, in the perhydrooxadiazines investigated, the lone pair at N-4 must be predominantly axial because of the high conformational energy of the tert-butyl group, the lone pair of the neighboring nitrogen atom occupies the equatorial position. However, it must be stated that these two effects (the anomeric effect and the specific effect for a hydrazine fragment) are probably of the same nature and the axial orientation of the 3-H proton is due mainly to the interaction of the polar bonds (gauche effect [9]).

The PMR spectrum of 4-tert-butyl-2,2-dimethylperhydro-1,3,4-oxadiazine (XIB), taken in tetrachloroethylene at 25°C (Table 2) shows the stereochemical equivalence of the geminal methyl groups in position 2 and of the pairs of methylene protons in positions 5 and 6, which is undoubtedly a consequence of the rapid inversion of the conformers (XXIII ⇌ (XXIV) (d*l* pair).



XXIII XXIV

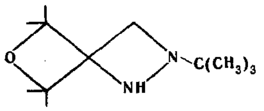
However, the spectrum of compound (XIB) taken at −40°C in methylene chloride is characteristic for a fixed noninverting conformation. Two singlets of methyl groups correspond to axial (δ 1.41 ppm) and equatorial (δ 1.19 ppm) substituents. For the methylene protons a spectrum of the AMXY type is observed, an analysis of which in the first-order approximation gives δ_{5a} 2.27, δ_{5c} 2.81, δ_{6a} 3.98, δ_{6e} 3.66 ppm; $J_{5a5e} = J_{6a6e} = -11.0$, $J_{5a6a} = 11.0$, $J_{5a6e} = 3.5$, $J_{5e6a} = 2.9$, and $J_{5e6e} = 1.4$ Hz. The values of the chemical shifts and the spin−spin coupling constants are, thus, close to those found for the 2-monomethyl derivative (XB) (Table 2), with the exception of the fact that the axial 6-H proton is deshielded as compared with the equatorial proton.

According to the literature [10, 11], the value of the interior torsional angle Ψ in saturated six-membered cyclic systems is connected with the vicinal spin−spin coupling constant by the relation

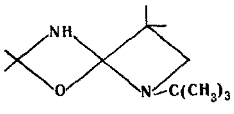
$$\cos\Psi = \left(\frac{3}{2+4R}\right)^{1/2}, \text{ where } R = \frac{J_{aa}+J_{ee}}{J_{ae}+J_{ea}}.$$

This method of evaluating Ψ can be applied to the 2-methyl derivative (XB), for which the conformational equilibrium is strongly displaced in the direction of the conformer with the equatorial methyl group (the parameters of the spectrum scarcely change when the temperature is lowered to −60°C) and to the 2,2-dimethyl derivative (XIB), which exists in the form of a mixture of two thermodynamically equivalent conformers [10, 11]. In both cases, the use of the values of J_{56} leads to the same value of the torsional angle N−C−C−O of 56°. Another method of evaluating Ψ [12] that can also be applied to the 6-methyl derivatives (XIIB and XIIIB) since it requires a knowledge of only two vicinal constants, gives approximately the same results. These results, which have a semiquantitative nature, permit the conclusion that in the N−C−C−O region the perhydrooxadiazine ring is practically undeformed (in cyclohexane [13], Ψ = 56°).

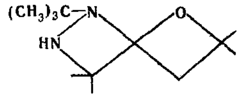
Like compound (XIB), 4-tert-butyl-2,2,6,6-tetramethylperhydro-1,3,4-oxadiazine (XVB) has a PMR spectrum showing the spatial equivalence at ordinary temperatures of the geminal methyl groups and the geminal protons. However, the chair conformation is unacceptable for the tetramethyl derivative (XVB) because of the strong repulsion of the axial 2- and 6-CH_3 groups. Drawing an analogy between compounds (XVB) and some polymethyl-1,3-dioxanes [14] it is necessary to adopt as the preferential conformations for (XVB) nonchair conformations rapidly interconverting at room temperature. The main conformations of this type are, probably, the 1,4- 2,5-, and 3,6-twist forms (XXV-XXVII).



XXV



XXVI



XXVII

In the PMR spectrum of (XVB) taken at −70°C in methylene chloride, the signals can be divided into two groups according to their intensities: to the singlets of methyl substituents with δ 1.41, 1.16, 1.29, and 1.06 ppm corresponds a quadruplet of the 5-H methylene protons with δ 1.91 and 1.94 ppm (J = −9.0 Hz), and to the singlets at 1.26, 1.13, 1.10, and 1.08 ppm a quadruplet with δ 2.72 and 2.59 ppm (J = −11.0 Hz). Attention is attracted by the marked decrease, as compared with the other perhydrooxadiazines, of the difference $\Delta\delta_{5a5e}$, which is connected primarily with approximately the same shielding of the 5-H protons by the vicinal methyl groups and, possibly, with a change in the relative orientation of the free pair of electrons of the N-4 nitrogen atom [15]. Thus, at a low temperature only two nonchair conformations of the perhydrooxadiazine (XVB) are comparatively stable. The amount of one of them is approximately three times that of the other, which corresponds to a value of $\Delta G^0_{-70°C}$ of about −0.45 kcal/mole. The complexity of the evaluation of the torsional and angular strain of the nonbound and the dipole−dipole interactions in the twist forms (XXV-XXVII) does not permit us to predict their relative stabilities. Nevertheless, since the shifts of the methyl groups of the more stable form are close to the shifts of the corresponding equatorial and axial substituents (Table 2), it may be assumed that it has the 1,4-twist conformation (XXV) with pseudoaxial and pseudoequatorial CH_3 groups. In this conformation the 4-t-C_4H_9 in the "stern" position does not have unfavorable interactions with the other substituents. The second conformer, with very similar 6-CH_3 shifts, apparently exists in the 3,6-twist form (XXVII), although it is not clear why this is more stable than (XXVI).

As was expected, the tert-butyl group exerts a considerable influence on the position of the equilibrium between the tautomeric ring (B) and chain (A) forms. At room temperature, the refractometric characteristics of the liquid perhydrooxadiazines change somewhat (Table 1), reaching constant values after a day for the 2,2-dimethyl derivative (XIB) and after several days for the 2-monomethyl derivatives (XB, XIIB, and XIVB). An estimate of the position of the equilibrium from the magnitude of the molecular refraction gives an equilibrium concentration of the hydrazones of from 3 to 7% (Table 1). In 1 M solutions in tetrachloroethylene, the concentration of the chain form is still smaller because of the absence of polarity of the solvent [16], and the hydrazone was detected in the PMR spectrum for only two of the products of condensation with acetone, (XI) and (XV) (A : B ratios 91 : 9 and 93 : 7, respectively).

Thus, the effects of a tert-butyl group in positions 2 and 4 of perhydro-1,3,4-oxadiazines are markedly different: in position 2 the substituent destabilizes [2, 3, 16] and in position 4 it stabilizes the cyclic form as compared with the chain form. In this connection, the product of the condensation of the hydrazino alcohol (VIII) with acetone (XV) is particularly striking. A homolog of compound (XVB) having a methyl group in position 4 could not be isolated at all, and in the equilibrium mixture (for the pure liquid) its concentration was only about 5% [1]. In the case of the tert-butyl derivative (XV), the equilibrium is displaced in the opposite direction.

In the perhydrooxadiazines (XB-XVB), the nonbound interactions of the 4-tert-butyl substituent with the axial 3-H and 5-H protons should destabilize the cyclic form relative to the hydrazone form to a greater extent than for the simplest 4-alkyl derivatives. However, in our opinion a more considerable role is played by the relative destabilization of the N-tert-butyl-N-(β-hydroxyalkyl) hydrazones, one of the important reasons for which is a decrease in the entropy of rotation of the chain form with the introduction of a substituent onto the "amine" nitrogen atom. The role of the entropy factor is large for ring-chain conversions in general [17], and it must be particularly pronounced in the case of substituents with high spatial demands, i.e., in the case of branched N-alkyl and N-(β-hydroxyalkyl) groups in substituted hydrazones. Another, less general, cause of the decrease in the relative stability of the hydrazone form is the weakening of the intramolecular hydrogen bond between the alcoholic hydroxy group and the "amine" nitrogen atom. A consideration of Dreiding models shows that with an increase in the branching in the alkyl and β-hydroxyalkyl radical the conditions for the formation of an intramolecular hydrogen bond become ever less favorable, so that in the case of the hydrazone (XVA) it becomes quite impossible. Apparently, it is just this latter circumstance that is responsible for the marked difference between the stabilities of the hydrazone (XVA) and its N-methyl homolog [1].

EXPERIMENTAL

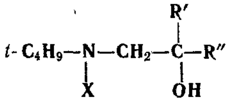
The PMR spectra were obtained on a Varian H-100 D-15 instrument using 1 M solutions in tetrachloroethylene (at a working temperature of 25-30°C) or in methylene chloride (at low temperatures; HMDS was used as internal standard.

The β-tert-Butylamino Alcohols (I-III; Table 3). With ice cooling and stirring, 0.5 mole of an alkene oxide was slowly added to a solution of 0.5 mole of tert-butylamine in 80 ml of ethanol. The mixture was kept at room temperature for 12 h and was then heated at 50°C for 2 h, and distilled.

The β-tert-Butylnitrosamino Alcohols (IV-VI). In small portions, 1 mole of an amino alcohol (I-III) was dissolved in 250 ml of cold 20% hydrochloric acid. To the resulting solution was gradually added 1.1 mole of sodium nitrite and the mixture was carefully boiled for 30 min. The upper layer of nitrosamine was separated off after the addition of 50 ml of benzene. The aqueous layer was made strongly alkaline with caustic soda and extracted with benzene (3 × 50 ml). The benzene solution was dried with potassium carbonate and the solvent was distilled off in vacuum. The liquid nitrosamines (V and VI) and also the crystalline (IV) (Table 3) were used for subsequent reduction without additional purification.

The β-(N-tert-Butylhydrazino) Alcohols (VII-IX; Table 3). With vigorous stirring, 290 ml of concentrated hydrochloric acid was added to a mixture of 86 g (1.3 g-atom) of granulated zinc, 10 ml of mercury, and 325 g of ice, and then 0.65 mole of one of the nitrosamines (IV-VI) was added in small portions over 4 h. The mixture was stirred at room temperature for 2 h, the layer of mercury was separated off, and 190 g of caustic potash was added. The precipitate was filtered off and washed with 300 ml of ether. The aqueous filtrate was made strongly alkaline with caustic potash and the hydrazino alcohol was extracted with ether. The combined ethereal extracts were dried with potassium carbonate, and the hydrazino alcohol was isolated by distillation. In all cases, the denitrosation of the nitrosamine took place in parallel with its reduction, so that about 20% of the initial amino alcohol (I-III) was recovered.

TABLE 3


$$t\text{-}C_4H_9\text{—}\underset{X}{N}\text{—}CH_2\text{—}\overset{R'}{\underset{OH}{C}}\text{—}R''$$

Compound	R′	R″	X	bp, °C (pressure, mm)	mp, °C	Empirical formula	Found		Calc.		Yield, %
							N, %	equiv.	N, %	equiv.	
I	H	H	H	71—75 (11)a	43	$C_6H_{15}NO$	—	—	—	—	55
II	H	CH_3	H	70—71 (20)b	~17	$C_7H_{17}NO$	—	—	—	—	73
III	CH_3	CH_3	H	68—69 (17)c	—	$C_8H_{19}NO$	9,5; 9,9	147; 148	9,7	145	50
IV	H	H	NO	—	60d	$C_6H_{14}N_2O_2$	19,2; 19,3	—	19,2	—	87
VII	H	H	NH_2	85—89 (12)e	42	$C_6H_{16}N_2O$	20,9; 21,0	138; 139	21,0	138	20
VIII	H	CH_3	NH_2	103—108 (21)f	—	$C_7H_{18}N_2O$	19,0; 19,2	144; 146	19,2	146	41
IX	CH_3	CH_3	NH_2	103—107 (15)	44	$C_8H_{20}N_2O$	17,0; 17,1	161; 162	17,5	160	51

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a) Literature data [18]: bp 72°C (14 mm); mp 43-45°C. b) n_D^{20} 1.4375. Literature data [19]: bp 58°C (2.5 mm). c) d_4^{20} 0.8445; n_D^{20} 1.4272. Found MR_D 44.19. Calculated: MR_D 44.37. d) From cyclohexane. e) n_D^{20} 1.4620. f) d_4^{20} 0.9196; n_D^{20} 1.4537. Found: MR_D 43.04. Calculated: MR_D 43.47.

4-tert-Butyl-2-methylperhydro-1,3,4-oxadiazines (XB, XIIB, and XIVB) (Table 1). With ice cooling and stirring, 0.23 mole of acetaldehyde was added in an atmosphere of nitrogen over 30 min to a solution of 0.25 mole of one of the hydrazino alcohols (I-III) in 20 ml of benzene. Then the mixture was heated at 60°C for 40 min and was distilled through a column.

4-tert-Butyl-2,2-dimethylperhydro-1,3,4-oxadiazines (XIB, XIIIB, and XVB) (Table 1). A few drops of acetic acid was added to a mixture of 0.13 mole of one of the hydrazino alcohols (I-III) and 0.14 mole of acetone, and the mixture was stirred at 75°C in a current of nitrogen for 3 h. The reaction product was dissolved in 50 ml of ether, and the solution was dried with potassium carbonate and distilled.

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