LITERATURE CITED

1. V. P. Kruglenko, A. A. Timoshin, N. N. Kobets, and M. V. Povstyanoi, Ukr. Khim. Zh., 53, 1095 (1987).
2. V. P. Kruglenko, N. S. Patalakha, P. B. Kurapov, N. A. Klyuev, V. A. Idzikovskii, I. I. Grandberg, and M. V. Povstyanoi, Khim. Geterotsikl. Soedin., No. 5, 694 (1985).
3. T. V. Sycheva, O. S. Anisimova, and L. N. Yakhontov, Khim. Geterotsikl. Soedin., No. 1, 91 (1986).
4. K. Nakanishi, Infrared Absorption Spectroscopy, Holden-Day, San Francisco (1962).
5. A. N. Kost, P. A. Sharbatyan, P. B. Terent'ev, Z. F. Solomko, V. S. Tkachenko, and L. G. Gergel', Zh. Org. Khim., 8, 2113 (1972).
6. I. P. Lavergne, Ph. Viallefont, and I. Daunis, Org. Mass Spectrom., 11, 752 (1976).
7. A. Bernardini, Ph. Viallefont, and R. Zieber, Org. Mass Spectrom., 13, 344 (1978).
8. N. S. Vul'fson, V. G. Zaikin, and A. I. Mikaya, Mass Spectrometry of Organic Compounds [in Russian], Khimiya, Moscow (1986), pp. 224, 158.
9. N. A. Klyuev, M. V. Povstyanoi, G. G. Aleksandrov, and V. P. Gumennyi, Khim. Geterotsikl. Soedin., No. 1, 88 (1983).

HYDROXY-, ALKOXY-, AMINOMETHYLATION OF NH-OXAZIRIDINES*

S. V. Varlamov, G. K. Kadorkina, and R. G. Kostyanovskii

UDC 541.63:547.717.07

3,3-Dimethyloxaziridine reacts with chloral and acetaldehyde to give crystalline N-(α-hydroxyalkyl)oxaziridines; the reaction with acetaldehyde is reversible. The N-aminomethylation of NH-oxaziridines is not realized, evidently because of the tendency of oxaziridines to iminate nucleophiles. The weakly nucleophilic chloromethylphthalimide and chloromethyl methyl ether give imidomethyl- and methoxymethyloxaziridines. 3,3-Dimethyldiaziridine reacts with excess chloromethyl methyl ether to give the N-monomethoxymethyl derivative. It is shown that α-hydroxyalkyloxaziridines and methoxymethyl-substituted oxaziridine and dizaridine do not enter into the aminomethylation of compounds with a labile hydrogen.

The products of the reaction of secondary amines with carbonyl compounds – aminocarbinols – and alkoxymethylamines are active α-aminoalkylating reagents. However, their reactivities decrease markedly when a nitrogen atom is included in the strained three-membered ring. Thus, aziridines and diaziridines react with carbonyl compounds to give stable aminocarbinols [3-5], which do not give symmetrical aminals with excess starting amine [4, 6], while alkoxymethylamines are formed in the presence of alcohol [4, 7]. Stable adducts with chloral are used for the isolation and identification of aziridines [3, 8] and diaziridines [5].

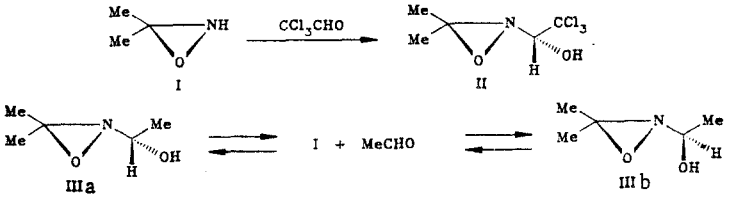
In the present research the reaction of NH-oxaziridines with aldehydes was studied for the first time. It is shown that 3,3-dimethyloxaziridine (I) reacts with chloral or chloral hydrate to give adduct II in the form of one diastereomer† (according to PMR), which is a stable crystalline compound that does not react with excess starting oxaziridine. In contrast to chloral, acetaldehyde reacts with oxaziridine I reversibly. The formation of oxaziridinocarbonyl III in the form of a mixture of diastereomers IIIa and IIIb is observed from the PMR

*Communication 54 of the series "Asymmetric Nitrogen" (see [1] for communication 53); communication 35 of the series "Geminal Systems" (see [2] for communications 34).
†Here and subsequently, the absolute configurations of the diastereomeric oxaziridines are shown conventionally.

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow 117,977. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 24, No. 3, pp. 390-395, March, 1988. Original article submitted July 16, 1986; revision submitted February 17, 1987.

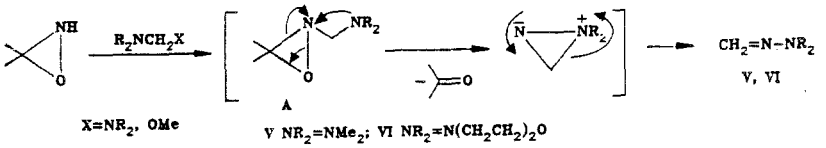
 0009-3122/88/2403-0320$12.50

spectrum of the reaction mixture in toluene at 20°C. Crystalline adduct IIIa is obtained by carrying out the reaction in excess acetaldehyde as the solvent with subsequent removal of it in vacuo with cooling. When the crystals are dissolved (in d_8-toluene at 20°C), signals of only one diastereomer IIIa are initially observed in the PMR spectra, after which signals of the starting compounds appear, followed, finally, by signals of the second diastereomer IIIb. It hence follows that dissociation of the adduct into acetaldehyde and the NH-oxaziridine precedes the formation of IIIb. The equilibrium is shifted to favor the formation of the adduct with a decrease in temperature, during which the ratio of the diastereomers remains constant at 1:1.

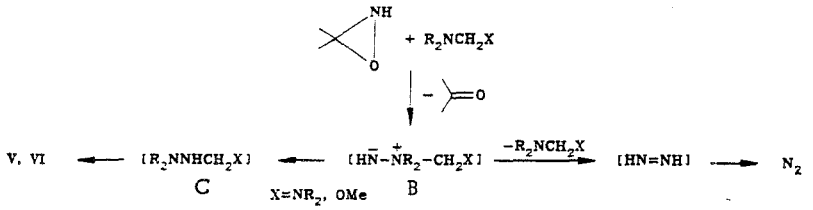


It should be noted that oxaziridinocarbinol III and oxaziridine I are simultaneously present in solution at 20°C. However, in contrast to ordinary secondary amines, the formation of a symmetrical aminal is not observed. This can be explained by the inability of oxaziridinocarbinols, like aziridino- and diaziridinocarbinols [3, 7, 9], to undergo aminomethylation.

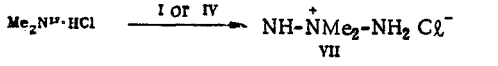
It is known that NH-aziridines are readily aminomethylated by ordinary aminocarbinols and alkoxymethylamines, while NH-diaziridines are also readily aminomethylated by diaminomethanes. In this connection we studied the reactions of NH-oxaziridines with aminomethylating reagents. We found that the expected aminomethyloxaziridines are not formed in the reaction of 3,3-dimethyl- and 3-methyl-3-ethyloxaziridines (I and IV) with bis(dimethylamino)-methane and methoxymethylmorpholine, which readily aminomethylate diaziridines [10], as well as with bis(morpholino)methane (CH_2Cl_2 or C_6H_6 at 20°C). In all of these cases the liberation of a gas from the reaction mixtures and the disappearance of their oxidizing activity are observed; this constitutes evidence for opening of the oxaziridine ring. The formation of hydrazones V (from the PMR and UV spectra of the reaction mixture) and VI (from the PMR spectra of the residue after removal of the solvent) was detected in the reactions of oxaziridine I. Hydrazone VI is also obtained as a result of the reaction of oxaziridine IV with methoxymethylmorpholine. A possible pathway to the hydrazones is through intermediate aminomethyloxaziridines A via the scheme of intramolecular amination proposed for the formation of diaziridine [11]:



Moreover, the low yields of hydrazones V and VI and the liberation of a gas during the reactions make it possible to propose that, with respect to NH-oxaziridines, the tertiary amines R_2NCH_2X act not as aminomethylating reagents but rather as, chiefly, N nucleophiles. According to [12], the formation of intermediate ylids B, which evidently decompose with the formation of diimide and, subsequently, nitrogen, is possible in this case. In addition, rearrangement of ylids B to the corresponding hydrazines C – precursors of the hydrazones V and VI obtained – is possible.

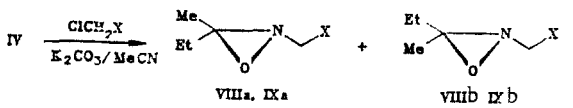


Methyleneiminium salts have been used as aminomethylating reagents to hinder direct imination under the influence of oxaziridines. However, in the reactions of oxaziridines I and IV with $Me_2\overset{+}{N}{=}CH_2\overset{-}{Cl}$ (in MeCN at 20°C), instead of the expected salts of Mannich bases, we obtained, in 15-20% yields, dimethyltriazanium chloride (VII), which was identical to the compound described in [13]. Its formation can be explained by double amination of dimethylamine, which is liberated in the hydrolysis of the methyleneiminium salt under the influence of traces of water in the reaction mixture,* by the NH-oxaziridines, which are active aminating reagents with respect to amines [14]:



The reactions of oxaziridines I and IV with $O(CH_2CH_2)_2\overset{+}{N}{=}CH_2\overset{-}{Cl}$ in the presence of an acid acceptor lead to a mixture of hydrazone VI and bis(morpholino)methane. The formation of the latter is explained by hydrolysis of the methyleneiminium salt. As in the case described above, hydrazone VI can be obtained through intermediate aminomethyloxaziridine A or via amination of the morpholine formed in the hydrolysis of the methyleneiminium salt and subsequent condensation with CH_2O. The presence of traces of moisture is sufficient for transformation via the latter pathway. One therefore cannot make an unequivocal choice between these possible schemes.

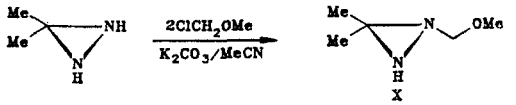
To eliminate hydrolysis and hypothetical intramolecular amination in the step involving aminomethyl derivative A we used weakly nucleophilic imidomethylating and alkoxymethylating reagents, under the influence of which the desired derivatives are formed smoothly from oxaziridine IV:



VIIIa, IXa VIIIb IXb

VIII X=phthalimido IX X=OMe

The previously unknown N-methoxymethyldiaziridine (X) was similarly obtained; only monoalkylation occurs even under the influence of excess chloromethyl methyl ether:



In the case of IX and X it was shown that alkoxymethyl-substituted oxaziridines and diaziridines do not undergo aminomethylation. Oxaziridine IX does not react with phthalimide (in MeOH for 3 days at 20°C) and diaziridine X does not react with imidazole (in MeCN, refluxing for 2 h followed by maintenance at 20°C for 12 h); these compounds react readily with ordinary alkoxymethylamines. Thus, for example, methoxymethylmorpholine reacts with phthalimide to give N-morpholinomethylphthalimide (XI) in 84% yield. It is known that exchange of the alkoxy group occurs when alkoxymethylamines are heated with alcohols [15]. However, exchange with CD_3OD is not observed for IX and X (5 days at 20°C for oxaziridine IX; in the presence of CD_3COOD, refluxing for 6 h followed by maintenance at 20°C for 12 h, for diaziridine X). Thus the ban on aminomethylation is extended to all three-membered nitrogen heterocycles – aziridines, diaziridines, and oxaziridines.

EXPERIMENTAL

The PMR spectra were measured with a Bruker WM-400 spectrometer with tetramethylsilane as the internal standard. The melting points were determined with a Boetius PNMK 0.5 stage.

*The synthesis of the oxaziridines was carried out in a water–organic solvent heterophase system [14], and the solutions of the reaction products were dried with $MgSO_4$, which does not ensure complete drying.

3,3-Dimethyloxaziridine (I) and 3-Methyl-3-ethyloxaziridine (IV). These compounds were obtained from the corresponding ketones by the method in [14]. The solutions of the products in CH_2Cl_2 or Et_2O were dried with $MgSO_4$. The percentages of the oxaziridines here and subsequently were determined by iodometric titration. PMR spectrum of oxaziridine I (d_8-toluene): 0.86 and 1.02 (broad s, Me); 3.0 ppm (broad s, NH). PMR spectrum of oxaziridines IV ($CDCl_3$) (1:1 mixture of diastereomers): 0.94 and 0.98 (t, β-Me, ^3J = 7.5 Hz); 1.40 and 1.56 (s, 3-Me); 1.66 (m, CH_2, $^2J_{AB}$ = 11.0 Hz); 1.79 (q, CH_2, $^2J_{AB}$ = 0.4 Hz); 3.51 and 3.63 ppm (broad s, NH).

3,3-Dimethyl-2-(1-hydroxy-2,2,2-trichloroethyl)oxaziridine (II). A solution of oxaziridine I in 125 ml of CH_2Cl_2 was evaporated to a volume of 2 ml, and the concentrate was diluted with 20 ml of absolute Et_2O. A solution of 1.2 g (8.1 mmole) of chloral or 1.34 g (8.1 mmole) of chloral hydrate in 5 ml of absolute Et_2O was added to the resulting solution, which contained 8.05 mmole of the oxaziridine, and the resulting mixture was maintained at −10°C for 2 days. The ether was then removed in vacuo, and the residue – a clear greenish oil – was evacuated with periodic cooling until complete crystallization occurred. This procedure gave 1.1 g (62%) of a product with mp 63-65°C (from hexane). PMR spectrum (C_6D_6) (one diastereomer): 1.08 and 1.12 (s, Me); 1.63 (broad s, OH); 4.78 ppm (s, CH). Found, %: C 27.3, H 3.5, N 6.3. $C_5H_8Cl_3NO_2$. Calculated, %: C 27.2, H 3.4, N 6.4.

3,3-Dimethyl-2-(1-hydroxyethyl)oxaziridine (III). A solution of 12 mmole of oxaziridine I in 125 ml of CH_2Cl_2 was evaporated to a volume of 1 ml, and the concentrate was added at 0°C to 1.8 g (40 mmole) of freshly distilled acetaldehyde. The mixture was cooled to −78°C and maintained at this temperature for 2 h, after which it was dried at −10°C. The adduct crystallized in the form of colorless crystals. The excess acetaldehyde was removed in vacuo at −70°C to −50°C, after which the temperature was gradually raised to 20°C without allowing melting. This procedure gave 0.8 g (56%) of a product with mp 28-30°C in the form of one diastereomer IIIa. The product was characterized from the PMR spectrum (d_8-toluene, −40°C: 0.85 and 1.11 (q, 3-Me, ^4J = 0.6 Hz); 1.14 (d, β-Me, ^3J = 5.9 Hz); 4.01 (q, CH); 5.68 ppm (broad s, OH). Signals of the second diastereomer (IIIb) appeared after establishment of the equilibrium IIIa ⇄ IIIb (1:1): 1.28 and 1.29 (q, 3-Me, ^4J = 0.6 Hz); 1.54 (d, β-Me, ^3J = 5.9 Hz); 4.05 (q, CH); 5.65 ppm (broad s, OH).

Reaction of Oxaziridine I with Bis(dimethylamino)methane. A 0.03-g (0.3 mmole) sample of bis(dimethylamino)methane was added at 20°C to a solution of 0.27 mmole of oxaziridine I in 3 ml of CD_2Cl_2. After stirring, the liberation of a gas from the reaction mixture began. After 3 h, signals of hydrazone V [2.75 (s, Me_2N); 6.06 ppm (broad s, CH_2)] and starting bis-(dimethylamino)methane in a molar ratio of 1:3 were observed in the PMR spectrum. A band with λ_{max} 242 nm was observed in the UV spectrum after dilution of the reaction mixture with 50 ml of heptane. According to the PMR and UV spectra, the reaction product was identical to a genuine sample of the hydrazone.

Reaction of Oxaziridine I with Bis(morpholino)methane. A 0.056-g (0.3 mmole) sample of bis(morpholino)methane was added to a solution of 0.27 mmole of oxaziridine I in 3 ml of CH_2Cl_2. After stirring, a gas was liberated from the reaction mixture. After 5 h, the solvent was removed in vacuo, and the residue was dissolved in $CDCl_3$. Signals of hydrazone VI (see below) and starting bis(morpholino)methane in a ratio of 1:6 were observed in the PMR spectrum of the solution obtained.

Reaction of Oxaziridine I with Methoxymethylmorpholine. This reaction was carried out as in the preceding experiment. Signals of hydrazone VI, methoxymethylmorpholine, and bis-(morpholino)methane in a molar ratio of 1:3:1 were observed in the PMR spectrum of a solution of the residue in $CDCl_3$.

Reaction of Oxaziridine IV with Methoxymethylmorpholine. A solution of oxaziridine IV in 50 ml of Et_2O was evaporated to a volume of 1 ml, and the concentrate was diluted with 10 ml of absolute C_6H_6. A 0.4-g (3 mmole) sample of methoxymethylmorpholine was added with stirring to the resulting solution, which contained 3.5 mmole of oxaziridine IV, and the mixture was maintained at 10°C for 24 h. The benzene was removed in vacuo. A gas was liberated from the residue (a yellow oil). After additional maintenance at −10°C for a week and evacuation until the evolution of a gas ceased, the residue contained (according to the PMR spectrum of a solution in $CDCl_3$) hydrazone VI and bis(morpholino)methane in a molar ratio of 2:3.

Reaction of Oxaziridine I with N,N-Dimethylmethyleneiminium Chloride. A solution of oxaziridine I in 100 ml of CH_2Cl_2 was evaporated to a volume of 2 ml, and the concentrate

was diluted with 10 ml of absolute MeCN. The resulting solution, which contained 6.75 mmole of the oxaziridine, was added with stirring and cooling (to 0°C) to a suspension of 0.3 g (3.2 mmole) of the methyleneiminium salt in 20 ml of absolute MeCN. After 3 min, all of the salt had dissolved; after 5-7 min, a crystalline precipitate formed. Stirring was continued for 2 h, and the precipitate was removed by filtration and crystallized from acetone–alcohol (4:1) to give 0.07 g (20% based on the salt) of triazanium chloride VII, which decomposed at 132-135°C (see [13]). According to iodometric titration, the percentage of the principal substance was no less than 97%. PMR spectrum (CD_3OD): 3.48 (s, Me_2N); 6.37 ppm (broad s, NH_2) (see [13]). Found, %: C 21.5, H 9.3, N 37.7. $C_2H_{10}ClN_3$. Calculated, %: C 21.5, H 9.0, N 37.6.

Reaction of Oxaziridine IV with N,N-Dimethylmethyleneiminium Chloride. This reaction was carried out as in the preceding experiment. The reaction of 8 mmole of oxaziridine IV and 0.3 g (3.2 mmole) of the methyleneiminium salt gave 0.04 g (11% based on the salt) of triazanium chloride VII, which decomposed at 130-132°C.

Reaction of Oxaziridine IV with Methylenemorpholinium Chloride. A solution of 10 mmole of the oxaziridine in 150 ml of CH_2Cl_2 was added dropwise with stirring to a suspension of 2.2 g (16 mmole) of the methyleneiminium salt and 2.2 g (16 mmole) of K_2CO_3 in 30 ml of absolute CH_2Cl_2, after which stirring was continued for 5 h. The mixture was then filtered, the solvent was removed in vacuo, and the residue was distilled to give 0.6 g (93% based on the oxaziridine) of hydrazone VI with bp 45-46°C (5 mm) (see [16]) [PMR spectrum ($CDCl_3$): 3.03 (t, NCH_2, ^3J = 5.0 Hz); 3.85 (t, OCH_2); 6.53 and 6.37 ppm (AB, CH_2, $^2J_{AB}$ = 11.0 Hz] and 0.7 g of bis(morpholino)methane with bp 103-105°C (5 mm).

3-Methyl-2-(N-phthalimidomethyl)-3-ethyloxaziridine (VIIIa,b). A mixture of 6.8 mmole of oxaziridine IV, 1.0 g (5.1 mmole) of chloromethylphthalimide, and 0.8 g (6.8 mmole) of K_2CO_3 in 50 ml of absolute MeCN was stirred at 20°C for 2 days, after which the solution was filtered, and the solvent was removed in vacuo to give 1.05 g (60%) of a product with mp 150-160°C, which was identified as a mixture of diastereomers. PMR spectrum ($CDCl_3$): diastereomer VIIIa: 0.96 (t, β-Me, ^3J = 7.9 Hz); 1.64 and 1.71 (m, CCH_2, $^2J_{AB}$ = 14.0 Hz); 1.73 (s, 3-Me); 4.55 and 4.93 (AB, NCH_2, $^2J_{AB}$ = 13.4 Hz); 7.8 ppm (m, C_6H_4); diastereomer VIIIb: 1.23 (t, β-Me, ^3J = 7.9 Hz); 1.98 and 2.02 (m, CCH_2, $^2J_{AB}$ = 14.0 Hz); 1.44 (s, 3-Me); 4.55 and 4.84 (AB, NCH_2, $^2J_{AB}$ = 13.4 Hz); 7.8 ppm (m, C_6H_4). The VIIIa:VIIIb ratio was ~2:1. Found, %: C 63.5, H 5.6, N 11.3. $C_{13}H_4N_2O_3$. Calculated, %: C 63.4, H 5.7, N 11.4.

3-Methyl-2-methoxymethyl-3-ethyloxaziridine (IXa,b). A mixture of 11 mmole of oxaziridine IV, 0.95 g (12 mmole) of chloromethyl methyl ether, and 1.8 g (12 mmole) of K_2CO_3 in 50 ml of absolute MeCN was stirred at 20°C for 10 h, after which the solution was filtered, the solvent was removed in vacuo, and the residue was distilled to give 0.95 g (66%) of a product with bp 55-56°C (10 mm), which was identified as a mixture of diastereomers. PMR spectrum ($CDCl_3$): diastereomer IXa: 0.97 (t, β-Me, ^3J = 7.6 Hz); 1.66 and 1.75 (m, CCH_2, $^2J_{AB}$ = 13.9 Hz); 1.51 (s, 3-Me); 3.99 and 4.51 (AB, NCH_2, $^2J_{AB}$ = 11.0 Hz); 3.53 ppm (s, MeO); diastereomer IXb: 1.12 (t, β-Me, ^3J = 7.6 Hz); 1.77 and 1.84 (m, CCH_2, $^2J_{AB}$ = 13.9 Hz); 1.45 (s, 3-Me); 4.01 and 4.58 (AB, NCH_2, $^2J_{AB}$ = 11.0 Hz); 3.53 ppm (s, MeO). The IXa:IXb ratio was ~5:4. Found, %: C 55.2, H 10.2, N 9.7. $C_6H_{11}NO_2$. Calculated, %: C 55.0, H 10.0, N 10.7.

3,3-Dimethyl-1-(methoxymethyl)diaziridine (X).* A solution of 2.27 g (28 mmole) of chloromethyl methyl ether in 10 ml of absolute MeCN was added dropwise with cooling (to 13°C) and stirring to a solution of 1.01 g (14 mmole) of 3,3-dimethyldiaziridine and 3.9 g (28 mmole) of K_2CO_3 in 40 ml of absolute MeCN, after which the mixture was stirred for 4 h and then allowed to stand at 20°C for 12 h. It was filtered, the solvent was removed in vacuo, and the residue was distilled to give 0.88 g (54%) of a product with bp 47-48°C (12 mm). PMR spectrum (CD_3OD): 1.34 and 1.38 (s, 3-Me); 3.45 (s, MeO); 3.84 and 4.21 ppm (AB, NCH_2, $^2J_{AB}$ = 9.0 Hz). Found, %: C 52.3, H 9.8, N 24.2. $C_5H_{12}N_2O$. Calculated, %: C 52.2, H 9.6, N 24.3.

N-(Morpholinomethyl)phthalimide (XI). A 0.27-g (2 mmole) sample of methoxymethylmorpholine was added to a solution of 0.3 g (2 mmole) of phthalimide in 15 ml of absolute MeOH, and the mixture was maintained at 20°C for 24 h. The solvent was removed in vacuo, and the residue was recrystallized from acetone to give 0.42 g (84%) of a product with mp 117-119°C (see [16]).

*The synthesis was accomplished by O. G. Nabiev.

LITERATURE CITED

1. A. B. Zolotoi, O. A. D'yachenko, L. O. Atovmyan, G. V. Shustov, S. N. Denisenko, and R. G. Kostyanovskii, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2441 (1986).
2. R. G. Kostyanovskii, R. K. Alekperov, G. K. Kadorkina, and I. I. Chervin, Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2523 (1987).
3. R. G. Kostyanovskii, Dokl. Akad. Nauk SSSR, 139, 877 (1961).
4. R. G. Kostyanovskii and B. F. Bystrov, Izv. Akad. Nauk SSSR, Otd. Khim. Nauk, No. 8, 1488 (1962).
5. E. Schmitz, Three-Membered Rings with Two Heteroatoms [Russian translation], Mir, Leningrad (1970), p. 152.
6. A. A. Dudinskaya, A. E. Bova, L. I. Khmel'nitskii, and S. S. Novikov, Izv. Akad. Nauk SSSR, Ser. Khim., No. 7, 1523 (1971).
7. R. G. Kostyanovskii, K. S. Zakharov, M. Zaripova, and V. F. Rudchenko, Izv. Akad. Nauk SSSR, Ser. Khim., No. 4, 875 (1975).
8. P. T. Trapentsier, I. Ya. Kalvin'sh, É. É. Liepin'sh, É. Ya. Lukevits, G. A. Bremanis, and A. V. Eremeev, Khim. Geterotsikl. Soedin., No. 6, 774 (1985).
9. R. G. Kostyanovskii, O. A. Pan'shin, and T. Z. Papoyan, Dokl. Akad. Nauk SSSR, 177, 1099 (1967).
10. O. G. Naviev, M. A. Shakhgel'diev, I. I. Chervin, and R. G. Kostyanovskii, Dokl. Akad. Nauk SSSR, 284, 872 (1985).
11. E. Schmitz and R. Ohme, Tetrahedron Lett., No. 23, 1857 (1965).
12. Y. Hata and M. Watanabe, J. Am. Chem. Soc., 101, 6671 (1979).
13. T. J. Giordano, G. T. Palenik, and H. N. Sisler, Inorg. Chem., 15, 751 (1976).
14. E. Schmitz, R. Ohme, and S. Schramm, Chem. Ber., 97, 2521 (1964).
15. K. G. Mizuch and R. A. Lapina, Zh. Org. Khim., 23, 1512 (1953).
16. G. Zinner, H. Böhlke, and W. Klegel, Arch. Pharm., 299, 245 (1966).

STEREOCHEMISTRY AND CONFIGURATIONAL STABILITY OF CYCLIC NH- AND N-DIMETHYLCARBAMOYLDIALKOXYAMINES*

I. I. Chervin, V. S. Nosova, V. F. Rudchenko, V. I. Shevchenko, and R. G. Kostyanovskii

UDS 547.875'793.6:541. 63:543.422.25

On the basis of the data from the ^{1}H, ^{13}C, and ^{15}N NMR spectra it was established that perhydro-1,3,2-dioxazine has the chair conformation with the equatorial orientation of the NH proton; the barrier to inversion at the N atom is $\Delta G^{\neq}$ = 21.9 kcal/mole. The preferred conformer of its 4-methyl derivative has the 2e,4e configuration. Stereospecific spin–spin coupling constants $^{4}J_{e\text{-}HCONH\text{-}e}$, $^{3}J_{^{13}CONH\text{-}e}$, and $^{3}J_{^{15}NOCH\text{-}e}$ were obtained for these compounds. 1,3,2-Dioxazolidine has a "bent envelope" conformation with the axial orientation of the NH proton; a stereospecific spin–spin coupling constant $^{4}J_{e\text{-}HCONH\text{-}e}$ was obtained, and the invariability of the PMR spectrum at 170°C was demonstrated.

Earlier it was shown that the configurational stability of the nitrogen atom in 2-tert-alkyl-1,3,2-dioxazolidines [3] and perhydro-1,3,2-dioxazines [4] is increased in comparison with the acyclic dialkoxyamines [5]. In this connection there was the prospect of finding

*Communication 58 of the Series "Asymmetric Nitrogen," for Communication 57 see [1]; Communication 35 of the Series "Geminal Systems," for Communication 34, see [2].

Institute of Chemical Physics, Academy of Sciences of the USSR, Moscow 117,977. Translated from Khimiya Geterotsiklicheskikh Soedinenii, Vol. 24, No. 3, pp. 396-402, March, 1988. Original article submitted September 24, 1986.

0009-3122/88/2403-0325$12.50