

of anhydrous pyridine, and the mixture was heated to 100°C and allowed to stand for 1 h. It was then diluted with 100 ml of water, and the precipitate was removed by filtration, dried, and dissolved in 20 ml of chloroform and chromatographed on silica gel (100-250 μm) by elution with chloroform. The first (green) fraction was collected, and the eluent was evaporated to give 0.3 g (64%) of dark acicular crystals. The characteristics of VI are presented in Table 1.

LITERATURE CITED

1. E. V. Tsoi, G. B. Afanas'eva, and O. N. Chupakhin, *Khim. Geterotsikl. Soedin.*, No. 3, 330 (1984).
2. B. Boduszek and J. L. Kice, *J. Org. Chem.*, **47**, 2055 (1982).
3. P. Muller, T. Venakis, and C. H. Eugster, *Helv. Chem. Acta*, **62**, 2350 (1979).
4. G. B. Afanas'eva, V. I. Vysokov, T. K. Pashkevich, and O. N. Chupakhin, *Khim. Geterotsikl. Soedin.*, No. 2, 214 (1983).
5. W. A. Spitzer, T. Goodson, S. R. Lammert, and S. Kukolja, *J. Org. Chem.*, **46**, 3570 (1981).
6. Y. Ueno, *Ann.*, No. 7, 1403 (1982).
7. A. Blackhall and R. H. Thomsom, *J. Chem. Soc.*, 1138 (1953).
8. Y. Ueno, Y. Takeuchi, J. Koshitani, and T. Yoshida, *J. Heterocycl. Chem.*, **18**, 645 (1981).
9. T. K. Pashkevich, G. B. Afanas'eva, I. Ya. Postovskii, and K. I. Pashkevich, *Khim. Geterotsikl. Soedin.*, No. 3, 353 (1975).
10. T. K. Pashkevich, G. B. Afanas'eva, I. Ya. Postovskii, and L. P. Anan'ina, *Khim. Geterotsikl. Soedin.*, No. 10, 1430 (1975).
11. K. I. Pashkevich, G. B. Afanas'eva, and I. Ya. Postovskii, *Khim. Geterotsokl. Soedin.*, No. 6, 746 (1971).

1-ACYLOXYAZIRIDINE-2,2-DICARBOXYLIC ACID ESTERS

A. I. Mishchenko, A. V. Prosyaniuk, P. N. Belov,
V. A. Romanchenko, E. G. Belova, and V. I. Markov

UDC 547.717'791.6'26.07:
542.924.5:543.422

The reaction of diazomethane and O-acylisonitrosomalones gave Δ^2 -1,2,3-triazoline-5,5-dicarboxylic acid esters, the rates of formation and thermal stabilities of which are determined by the character of the substituent attached to the oxygen atom. Thermolysis of the triazolines leads to mixtures of 1-acyloxiaziridine-2,2-dicarboxylic acid esters and isomeric dialkyl O-acylisonitrososuccinates; acidolysis with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ makes it possible to obtain exclusively aziridines. The acidic decompositions of dimethyl 4-methyl- Δ^2 -1,2,3-triazoline-5,5-dicarboxylate, which was obtained from the reaction of diazoethane and dimethyl O-tosylisonitrosomalone, leads to dimethyl α -tosyloxiamino- α -vinylmalonate. A dependence of the spin-spin coupling constants (SSCC) of the protons of the aziridine ring on the electronegativities of the substituents attached to the oxygen atom was observed.

Owing to the high pyramidal stability of the nitrogen atom, derivatives of 1-hydroxyaziridine-2,2-dicarboxylic acid esters are ideal subjects for the investigation of the stereochemistry of nitrogen [1]. Enantiomerically pure compounds that have a chiral center only at the nitrogen atom were obtained for the first time in this series [2], and the maximally high barrier to inversion of the nitrogen atom was determined experimentally (31.3 kcal/mole [3]). The principal method for the synthesis of compounds of this class is the reaction of diazomethane with O-substituted derivatives of isonitrosomalonic ester [4].

1-Acyloxiaziridine-2,2-dicarboxylic acid esters are of particular interest. Up until now, only one representative of this series, viz., 1-tosyloxiaziridine, which was obtained by thermolysis or acidolysis (with trifluoroacetic acid) of 1-tosyloxy- Δ^2 -1,2,3-triazoline-5,5-dicarboxylic acid ester, was known [4]. However, decomposition of the triazoline in

F. É. Dzerzhinskii Dnepropetrovsk Institute of Chemical Technology, Dnepropetrovsk 320640. Translated from *Khimiya Geterotsiklicheskih Soedinenii*, No. 3, pp. 338-342, March, 1984. Original article submitted November 17, 1982; revision submitted April 19, 1983.

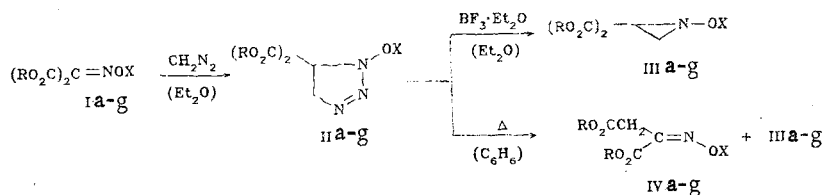
TABLE I. Characteristics of the Synthesized Compounds

Com- pound	mp, °C	n_D^{20}	Found, %			Empirical formula	Calculated, %			Yield, %
			C	H	N		C	H	N	
Ia	49-50	—	30,0	3,9	5,6	C ₆ H ₉ NO ₇ S	30,1	3,8	5,9	68
Ib	65	—	38,5	4,1	6,5	C ₇ H ₉ NO ₇	38,8	4,1	6,4	46
Ic	— ^a	1,4624	41,0	5,1	11,8	C ₈ H ₁₂ N ₂ O ₆	41,4	5,2	12,1	78
Id	73-74	—	36,0	3,6	4,9	C ₈ H ₁₃ NO ₇ S	36,0	3,9	5,2	71
Ie	62-63 ^b	—	—	—	—	C ₁₄ H ₁₇ NO ₇ S	—	—	—	75
If	191-192 (1,5) ^c	1,4480	58,9	5,6	4,8	C ₁₄ H ₁₅ NO ₆	58,6	5,6	4,6	69
Ig	125-126 (2) ^c	1,4440	46,4	5,3	5,8	C ₉ H ₁₃ NO ₆	46,8	5,7	6,1	89
Ih	94-95 ^d	—	—	—	—	C ₁₂ H ₁₃ NO ₇ S	—	—	—	70
IIa	65 (dec.)	—	29,7	3,7	15,1	C ₇ H ₁₁ N ₃ O ₇ S	29,9	3,9	14,9	96
IIb	83 (dec.)	—	36,5	4,3	15,9	C ₈ H ₁₁ N ₃ O ₇	36,8	4,2	16,1	73
IIc	82 (dec.)	—	—	—	—	C ₉ H ₁₄ N ₂ O ₆	—	—	—	57
IId	68 (dec.)	—	—	—	—	C ₉ H ₁₅ N ₃ O ₇ S	—	—	—	93
IIe	47 (dec.)	—	—	—	—	C ₁₅ H ₁₉ N ₃ O ₇ S	—	—	—	96
IIf	50 (dec.)	—	—	—	—	C ₁₅ H ₁₇ N ₃ O ₆	—	—	—	89
IIg	54 (dec.)	—	—	—	—	C ₁₀ H ₁₅ N ₃ O ₆	—	—	—	69
IIh	59 (dec.)	—	—	—	—	C ₁₄ H ₁₇ N ₃ O ₇ S	—	—	—	79
IIIa	82	—	33,0	4,2	5,5	C ₇ H ₁₁ NO ₇ S	33,2	4,4	5,5	67
IIIb	125-126 (0,5) ^c	1,4541	41,1	4,5	6,2	C ₆ H ₁₁ NO ₇	41,2	4,8	6,0	71
IIIc	—	1,4684	43,6	5,9	11,4	C ₉ H ₁₄ N ₂ O ₆	43,9	5,7	11,4	69
IIIe	52-53	—	38,3	5,2	5,5	C ₉ H ₁₅ NO ₇ S	38,4	5,0	5,4	84
IIIe	52	—	50,6	5,1	4,1	C ₁₅ H ₁₉ NO ₇ S	50,4	5,4	3,9	69
IIIf	—	1,4994	58,9	5,5	4,5	C ₁₅ H ₁₇ NO ₆	58,6	5,6	4,6	77
IIIg	125-126 (0,5) ^c	1,4508	48,9	6,0	5,8	C ₁₀ H ₁₅ NO ₆	49,0	6,2	5,7	86
IVe	69-70	—	50,6	5,4	4,0	C ₁₅ H ₁₉ NO ₇ S	50,4	5,4	3,9	46
VIII	75	—	49,0	4,9	4,3	C ₁₄ H ₁₇ NO ₇ S	48,8	5,2	4,1	56

^aIsolated by column chromatography [silica gel (100/160 μ m), CHCl₃]. ^bThis compound has mp 63.5°C in [5]. ^cBoiling point (mm). ^dThis compound has mp 94-95°C in [4].

both cases leads to mixtures of compounds that are difficult to separate. The goal of the present research was the specific synthesis of 1-sulfonyl- and the previously unknown 1-acyloxiaziridine-2,2-dicarboxylic acid esters.

We found that the reaction of diazomethane with O-acylisonitrosomalones Ia-g in ether at 0-5°C (monitoring by means of the PMR spectra) leads to Δ^2 -1,2,3-triazolines IIa-g (Table 1):



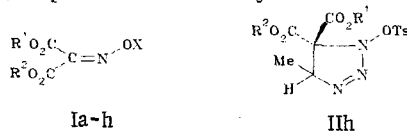
III, IVa R=Me, X=Ms; b R=Me, X=MeOCO; c R=Me, X=Me₂NCO; d R=Et, X=Ms; e R=Et, X=Ts; f R=Et, X=PhCO; g R=Et, X=MeCO

The reaction time increases (0.25 h for Ia,d, 1 h for Ie, 2 h for Ib, 20 h for Ic, 72 h for Ig, and 120 h for If) as the electron-acceptor properties of substituents X decrease in the order Ms > Ts > MeOCO > PhCO > Me₂NCO > MeCO, which was determined on the basis of the σ_m substituent constants [6]. The anomalously long reaction time in the case of O-benzoyloxime If is evidently explained by shielding of the C=N bond by the bulky phenyl group.

The individual triazolines and their solutions are relatively stable. For example, O-acetyltriazoline IIg remains unchanged for 3 months at 0-5°C, whereas O-methylsulfonyl analog IId decomposes appreciably in 3 weeks (monitoring by means of the PMR spectra). When the temperature of the solutions is raised to 20°C, these differences level out, and the decomposition of the triazolines goes to completion overnight. Consequently, intermediate triazolines could not be isolated or detected in the analogous synthesis of 1-alkoxylaziridine-2,2-dicarboxylic acid esters [4], since the reaction of CH₂N₂ with O-alkyl esters of isonitrosomalones proceeds at 20°C for 2 weeks.

Thermolysis of solutions of triazolines IIa-g in benzene at 20°C for 24 h leads to mixtures of the corresponding aziridines IIa-g and the isomeric isonitrososuccinates IVa-g

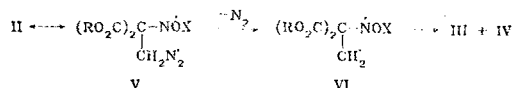
TABLE 2. Parameters of the IR (ν , cm^{-1}) and PMR (5% solutions in CHCl_3 , δ , ppm) Spectra of O-Acyloximes and Triazolines



Compound	IR spectrum ^a		PMR spectrum				
	C=O	C=N (N=N)	X	R ¹		R ²	
			Me	Me	CH ₂	Me	CH ₂
Ia	1715, 1738	1638	3,11 ^b	3,90	—	3,91	—
Ib	1754, 1807	1628	3,27 ^c	3,15	—	3,17	—
Ic	1755, 1768	1621	2,93 ^b	3,88	—	3,90	—
Id	1718, 1750	1635	3,25	1,34	4,55	1,34	4,58
Ie	1719, 1748	1625	2,38 ^{b,d}	1,25	4,21	1,28	4,33
If	1728, 1745	1624	— ^{d,e}	1,34	4,29	1,34	4,34
Ig	1725, 1745	1625	2,11 ^b	1,30	4,36	1,33	4,36
Ih	1732, 1752	1629	2,37 ^b	3,74	—	3,80	—
IIa	1710, 1729	(1529)	3,31	3,78	—	—	4,88 ^f
IIb	1718, 1765	(1534)	3,80	3,95	—	—	4,87 ^f
IIc	1758, 1771	(1551)	3,00	3,83	—	—	4,98 ^f
IId	1709, 1730	(1529)	3,31	1,25	4,23	—	4,85 ^f
IIe	1720, 1735	(1557)	2,35	1,21	4,21	—	4,66 ^f
IIf	1743, 1764, 1782	(1550)	—	1,23	4,30	—	5,05 ^f
IIg	1740, 1803	(1549)	2,26	1,30	4,33	—	4,91 ^f
IIh	1719, 1731	(1532)	1,75	3,09	1,10 ^g	3,53	4,70 ^f

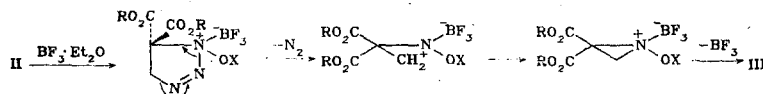
^aObtained from KBr pellets of solid samples and thin layers of liquid samples. ^bIn CCl_4 . ^cIn C_6H_6 . ^d $\delta_{\text{H}}(\text{aryl}) = 7.60$ ppm, $\Delta\nu = 0.51$ ppm, $J_{\text{HH}} = 8.8$ Hz. ^ePh, multiplet at 7.18–7.90 ppm. ^fRing CH_2 . ^g5-Me.

(Tables 1–3). In the case of O-tosyl derivative IIe methyl tosylate is formed in addition to III and IV. The ratios of the isomers were determined from the PMR spectra of the reaction mixtures: a, d 17/83; c 31/69; e 24/44; f 22/78; g 30/70. An increase in the electron-acceptor properties of the O-substituents leads to a decrease in the thermal stabilities of the triazolines in the order IIIf, g > IIb > IIc > IIa, d; this is evidently due to an increase in the stabilities of intermediate diradicals V and VI [4].



It should be noted that O-dimethylcarbamoyl derivatives Ic and IIIc decompose with CO_2 evolution during storage. The relatively low stability of triazoline IIc is evidently also due to radical decomposition of the Me_2NCOON group, which initiates decomposition of the triazoline.

In contrast to thermolysis and the previously used decomposition with an equimolar amount of $\text{CF}_3\text{CO}_2\text{H}$ [4], the decomposition of triazolines IIa–g with a catalytic amount of $\text{BF}_3 \cdot \text{Et}_2\text{O}$ leads exclusively to aziridines IIIa–g (Table 1):



The acidic decomposition of triazoline IIh, obtained by the reaction of O-tosyloxime Ih with diazomethane, evidently also proceeds similarly. However, in this case stabilization with splitting out of a proton is preferable for the intermediately formed cation as a consequence of the steric and thermodynamic factors:

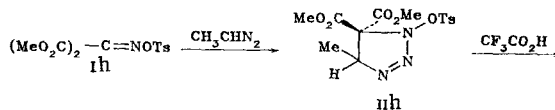
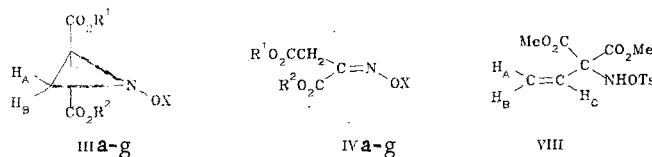


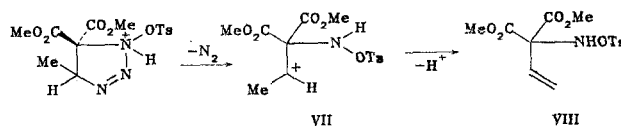
TABLE 3. Parameters of the IR (ν , cm^{-1}) and PMR (5% solutions in CCl_4 , δ , ppm) Spectra of O-Acylaziridines and Their Isomers



Compound	IR spectrum ^a		PMR spectrum							
	C=O	CH ₂	X	R ¹		R ²		H _A	H _B	J _{AB} ^b
			Me	Me	CH ₂	Me	CH ₂			
IIIa	1735, 1740	3115	3,16 ^c	3,75	—	3,81	—	2,77	3,20	-4,20
IIIb	1732, 1765	3108	3,74	3,73	—	3,73	—	2,67	2,88	-3,75
IIIc	1735, 1753	3112	2,78	3,79	—	3,84	—	2,74	2,93	-3,60
IIId	1732, 1752	3106	3,14	1,28	4,23	1,29	4,31	2,73	3,11	-4,20
IIIe	1729	3108	2,38 ^d	1,17	4,11	1,22	4,21	2,55	3,06	-3,80
III _f	1755	3106	— ^e	1,18	4,25	1,30	4,30	2,88	3,11	-3,75
IIIg	1745, 1752	3120	1,95	1,28	4,28	1,28	4,31	2,70	2,88	-3,15
IVb	—	—	3,79	3,71	—	3,70	—	3,80	—	—
IVc	—	—	2,78	3,79	—	3,83	—	3,76	—	—
IVd	—	—	3,11	1,28	4,21	1,28	4,36	3,75	—	—
IVe	1715, 1723	1629 ^f	2,36 ^e	1,17	4,11	1,22	4,21	3,75	—	—
IV _f	—	—	—	1,20	4,26	1,31	4,32	3,78	—	—
IVg	—	—	2,05	1,26	4,25	1,26	4,28	3,82	—	—
VIII	1725	3240 ^g	2,62 ^h	3,67	—	—	5,19 ⁱ	5,0 ^g	5,12	0,5

^aObtained from KBr pellets of solid samples and thin layers of liquid samples. ^bThe sign of J was taken as in [4]. ^cIn CDCl_3 . ^d $\delta_{\text{H}}(\text{aryl}) = 7.54$ ppm, $\Delta\nu = 0.55$ ppm, $J_{\text{HH}_h} = 8.0$ Hz.

^ePh, multiplet at 7.75–8.13 ppm. ^f $\nu_{\text{C}=\text{N}}$. ^g ν_{NH} . ^h $\delta_{\text{H}}(\text{aryl}) = 7.53$ ppm, $\Delta\nu = 0.5$ ppm, $J_{\text{HH}} = 8.0$ Hz. ⁱ δ_{C} , $J_{\text{AC}} = 9.13$, $J_{\text{BC}} = 5.63$ Hz.



The structure of VIII was proved by the IR spectrum, which displays a narrow absorption band of an NH group at 3240 cm^{-1} [7] [which excludes the alternative $\text{H}_2\text{C}=\text{CHN}(\text{OTs})\text{CH}(\text{CO}_2\text{Me})_2$ structure], and by the PMR spectrum, in which the characteristic subspectrum of a vinyl group is observed; the assignment of the signals of the protons was realized on the basis of the known relationship of the spin-spin coupling constants (SSCC) for vinyl systems: $|J_{\text{trans}}| > |J_{\text{cis}}| > |J_{\text{gem}}|$ [8].

The structures of the remaining synthesized compounds were also confirmed by the PMR and IR spectra (Tables 1-3). Except for IVE, O-acylisonitrososuccinates IV were not isolated in the individual state but were characterized from the PMR spectra, which display a singlet of a CH_2 group at 3.7–3.8 ppm [4] (Table 3). The IR spectra of triazolines IIA-g contain an absorption band of an $\text{N}=\text{N}$ bond at $1529\text{--}1551 \text{ cm}^{-1}$ [7] (Table 2), and the PMR spectra contain a singlet of a CH_2 group of a triazolone ring at 4.4–5.1 ppm [9] (Table 2). The formation of O-acylisonitrososuccinates IVA-g from triazolines IIA-g proves their $\Delta^2\text{-1,2,3}$ -triazolone structure. The assignment of the signals of the protons of ester groups and of the ring protons in the PMR spectra of O-acyloximes IA-h (Table 2) and aziridines IIIA-g (Table 3) was made on the basis of the shielding effect of the unshared pair of electrons of the nitrogen atom as compared with the XON group [4]. The decrease in absolute value of the geminal SSCC of the protons of the aziridine ring from 4.20 to 3.15 Hz in the order IIIA, d > IIIe > IIIb, f > IIIc > IIIg is due to the decrease in the electronegativities of the O-acyl substituents; this is confirmed by the decrease in the $|^2J_{\text{AB}}|$ values to 2.8–2.3 Hz in 1-alkoxyaziridine-2,2-dicarboxylic acid esters [4].

EXPERIMENTAL

The PMR spectra of 5% solutions of the compounds were recorded with Tesla BS-487C (80 MHz) and RYa-2305 (60 MHz) spectrometers with hexamethyldisiloxane as the internal standard. The IR spectra were obtained with a UR-20 spectrometer.

Dimethyl Mesoxalate O-Methylsulfonyloxime (Ia). This compound was obtained in 68% yield by mesylation of dimethyl mesoxalate oxime by the method in [5] (Table 1). O-Acylisomalonates Ic-h were similarly obtained (Table 1).

Dimethyl Mesoxalate O-Methoxycarbonyloxime (Ib). A solution of 13 g (0.13 mole) of triethylamine in 100 ml of absolute ether was added with cooling (0°C) and stirring to a solution of 16.1 g (0.1 mole) of dimethyl mesoxalate oxime and 12.3 g (0.13 mole) of MeOCCl in 100 ml of absolute ether, after which stirring was continued at 20°C for 4 h, and the mixture was allowed to stand overnight. The precipitate was removed by filtration, the solvent was removed, and the residue was distilled in vacuo to give 10.1 g (46%) of Ib (Table 1).

1-Methoxysulfonyl-5,5-bis(carbomethoxy)- Δ^2 -1,2,3-triazoline (IIa). An ether solution (200 ml) of diazomethane [4.2 g (0.1 mole)] was added dropwise with stirring and cooling from -15 to -10°C to a solution of 11.2 g (0.05 mole) of Ia in 100 ml of CH₂Cl₂, after which stirring was continued at 0 to -5°C for 1 h. The solvent was removed in vacuo to give 12.7 g of triazoline IIa, which was recrystallized from CH₂Cl₂-Et₂O-C₅H₁₂ (1:4:1) (Table 1). Triazolines IIb-g were similarly obtained, except that the reactions were carried out in ether solutions (Table 1).

Dimethyl 1-(Methylsulfonyloxy)aziridine-2,2-dicarboxylate (IIIa). Three to five drops of BF₃·Et₂O were added with cooling at 0°C to a solution of 10.6 g (0.04 mole) of IIa in 50 ml of CH₂Cl₂, and the mixture was allowed to stand overnight at 0°C. The solvent was removed in vacuo, and the residue was crystallized from isopropyl alcohol to give 6.3 g (6.7%) of ester IIIa (Table 1). Aziridines IIb-g were similarly obtained, except that the reactions were carried out in ether solutions (Table 1).

Diethyl Z-O-Tosylisonitrososuccinate (IVe). A 19.27-g (0.05 mole) sample of triazoline IIe was maintained at room temperature for 3 days, after which the solid reaction mixture, which, judging from the PMR spectrum, contained 20.5% aziridine IIIe and 79.5% ester IVd, was crystallized twice from the minimum amount of CCl₄ to give 8.2 g (46%) of isonitrososuccinate IVe (Table 1).

1-Tosyloxy-4-methyl-5,5-bis(carbomethoxy)- Δ^2 -1,2,3-triazoline (IIh). This compound was obtained in 70% yield (Table 1) by the reaction of Ih with diazoethane in solution in C₆H₆-Et₂O (1:5) by a procedure similar to that used to prepare triazoline IIa.

Dimethyl α -Tosyloxyamino- α -vinylmalonate (VIII). A solution of 3.4 g of trifluoroacetic acid in 5 ml of absolute methanol was added slowly to 0 to -10°C to a solution of 5.0 g (0.013 mole) of triazoline IIh in 20 ml of CH₂Cl₂, and the mixture was allowed to stand overnight at 0°C. The precipitated crystals of p-toluenesulfonic acid were removed by filtration, and the residue remaining after removal of the solvent was crystallized from MeOH-Et₂O-C₆H₁₄ (1:10:10) at -78°C to give 2.5 g (56%) of ester VIII (Table 1).

LITERATURE CITED

1. R. G. Kostyanovskii, V. F. Rudchenko, A. V. Prosyaniuk, M. D. Isobaev, I. I. Chervin, and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 3, 628 (1977).
2. R. G. Kostyanovskii and V. F. Rudchenko, *Dokl. Akad. Nauk SSSR*, **231**, 878 (1976).
3. G. V. Shustov, N. B. Tavakalyan, N. L. Zaichenko, and R. G. Kostyanovskii, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 9, 2183 (1980).
4. R. G. Kostyanovskii, A. V. Prosyaniuk, A. I. Mishchenko, G. V. Shustov, I. I. Chervin, N. L. Zaichenko, A. P. Pleshkova, P. N. Belov, and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 8, 1780 (1979).
5. J.-M. Biehler, J. Perchais, and J.-P. Fleury, *Bull. Soc. Chim. Fr.*, No. 19, 2711 (1971).
6. A. Gordon and R. Ford, *The Chemist's Companion*, Wiley (1973).
7. A. A. Kazitsina and N. B. Kuplet-skaya, *Application of UV, IR, and NMR Spectroscopy in Organic Chemistry [in Russian]*, Vysshaya Shkola, Moscow (1971), p. 35.
8. J. W. Emsley, J. Feeney, and L. H. Sutcliffe, *High-Resolution NMR Spectroscopy*, Pergamon, Oxford (1965).
9. R. G. Kostyanovskii, G. I. Kadorkina, G. V. Shustov, and K. S. Zakharov, *Dokl. Akad. Nauk SSSR*, **221**, 370 (1975).