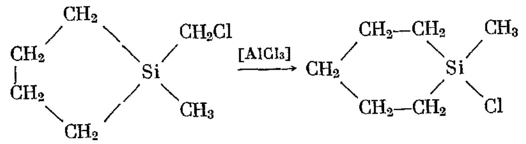
TRANSFORMATIONS OF (CHLOROMETHYL)SILACYCLOALKANES UNDER THE INFLUENCE OF ALUMINUM CHLORIDE

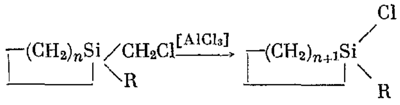
N. S. Nametkin, V. M. Vdovin,
K. S. Pushchevaya, and A. N. Egorochkin

UDC 542.97 + 546.287

Previously we had established [1] that 1-chloromethyl-1-methyl-1-silacyclopentane undergoes skeletal rearrangement under the influence of $AlCl_3$, as a result of which 1-chloro-1-methyl-1-silacyclohexane is formed.

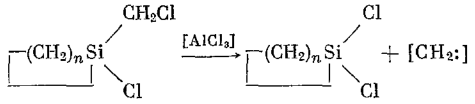


A study of this reaction was continued in the present paper. It proved that the manifested rearrangement of the rings bears a general character: 1-chloromethyl-1-methyl-1-silacyclohexane is isomerized to 1-chloro-1-methyl-1-silacycloheptane, while 1-chloromethyl-1-chloro-1-silacyclopentane and —hexane are isomerized to 1,1-dichloro-1-silacyclohexane and —heptane, respectively.



$R = CH_3—, Cl—, n = 4,5$

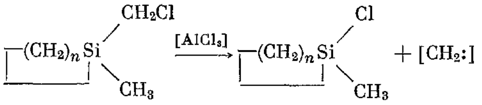
The indicated transformations testify to the specificity of the reaction for expansion of the heterocycle, inasmuch as chloromethylchlorosilane derivatives are not active in the Whitmore — Sommer rearrangement [2, 3]. The yield of the isomerization product in the case of 1-chloromethyl-1-methyl-1-silacyclohexane reached approximately 90%, whereas in the case of 1-chloromethyl-1-chloro-1-silacyclopentane and —hexane it reached approximately 80 and 65%, respectively. A reduction in the yields in the last two cases is explained by the fact that the rearrangement is accompanied by the reaction of α-decomposition.



As evidence of this is the fact that dichlorosilacycloalkanes, containing the same number of carbon atoms in the ring as the starting compound, are found to be present in the reaction mixture.*

---

* A careful study of the main fractions of the rearrangement products obtained from the (chloromethyl)methylsilacycloalkanes, made employing the gas-liquid chromatography method (GLC), revealed that also in the case of these compounds the rearrangement is accompanied by α-decomposition. However, the products confirming this were detected only in traces. The reaction for the α-decomposition of the (chloromethyl)methylsilacycloalkanes can be depicted by the scheme:



A. V. Topchiev Institute of Petrochemical Synthesis, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2530-2537, November, 1967. Original article submitted December 17, 1964. Additions made June 14, 1967.

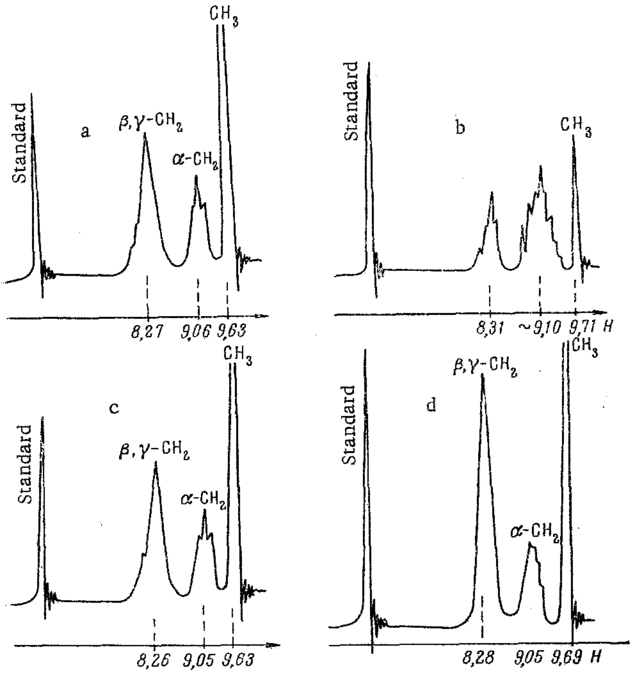


Fig. 1. NMR spectra: a) 1,1-dimethyl-1-silacyclohexane; b) 1-methyl-1-ethyl-1-silacyclohexane; c) methylated rearrangement product of 1-chloromethyl-1-chloro-1-silacyclopentane; d) methylated rearrangement product of 1-chloromethyl-1-methyl-1-silacyclohexane.

We postulated that the α-decomposition takes place by the carbene mechanism. We observed that the amount of α-decomposition products decreases, and the yield of isomerization products correspondingly increases, with increase in the amount of catalyst taken for reaction (the amount of $AlCl_3$ was varied between 5 and 10 mole %). The boiling point, density, refractive index and infrared spectrum of the 1,1-dichloro-1-silacyclohexane obtained by rearrangement all coincided with the indicated properties of this product, synthesized in known manner [4, 5].

$$\mathrm{BrMg(CH_2)_5MgBr + SiCl_4 \xrightarrow{\text{abs. ether}} (CH_2)_5SiCl_2 + 2MgClBr}$$

After methylation the rearrangement product proved to be identical with the known 1,1-dimethyl-1-silacyclohexane [4-6]. The product of the α-decomposition of 1-chloromethyl-1-chloro-1-silacyclopentane was also isolated and identified, which in all of its principal constants coincided with the known 1,1-dichloro-1-silacyclopentane [5, 7].

From the reaction mixture, obtained as a result of reacting 1-chloromethyl-1-chloro-1-silacyclohexane with $AlCl_3$, taken in an amount of 5 and 10 mole %, we were able to isolate and identify 1,1-dichloro-1-silacyclohexane [4, 5] in a yield of 25-30 and 10-15% respectively, and also the rearrangement product in a yield of 60 and 75%. The amount of hydrolyzable chlorine and the MR_D of the latter compound enabled us to assign it the structure of 1,1-dichloro-1-silacycloheptane. Its Raman spectrum does not contain lines at 800 and 910-915 cm^{-1}, characteristic for the silacyclohexanes [6]. However, the constants of this compound did not agree with the literature data [5]. Our attempts to synthesize 1,1-dichloro-1-silacycloheptane as described in [5] proved unsuccessful. The desired compound was isolated in very low yield (~5%) and, in addition, based on the GLC data it contained up to 40% of a difficultly separable impurity.

In the case of 1-chloromethyl-1-methyl-1-silacyclohexane, being an unstrained and stable heterocycle, it could be expected that it is not the reaction for expansion of the ring that takes place, but rather a rearrangement of the radicals along the lines of a Whitmore — Sommer reaction [3], with the formation of 1-chloro-1-ethyl-1-silacyclohexane.

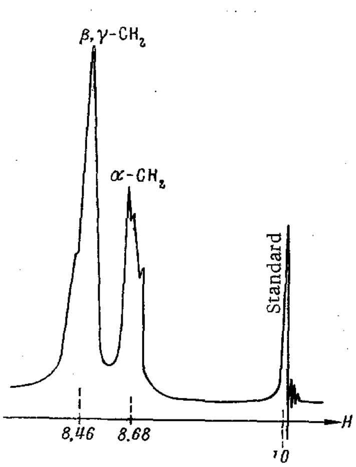
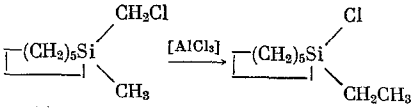


Fig. 2. NMR spectrum of 1,1-dichloro-1-silacycloheptane.



This compound as a standard was synthesized by us according to the scheme:

$$BrMg(CH_2)_5MgBr + C_2H_5SiCl_3 \rightarrow (C_2H_5)Cl\underline{Si(CH_2)_5} + 2MgBrCl$$

A comparison of the properties of the rearrangement product and the standard compound revealed that their boiling points, n_D^{20} and d_4^{20} were very close, but their infrared spectra were completely different. The infrared and Raman spectra of the methylation products of the two compounds were also different. We obtained conclusive proof regarding the structure of the rearrangement products on the basis of studying their NMR spectra.

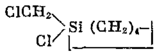
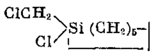
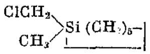
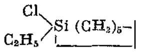
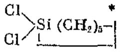
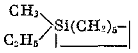
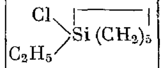
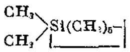
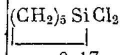
Previous study of the NMR spectra of a number of silacycloalkanes of general formula $RR'\underline{Si(CH_2)_n}$ (n = 3, 4, 5, R = R' = CH_3, R_1 = H) revealed that the signals of the chemical shifts of the protons of the groups CH_3, α-CH_2, common signal, β,γ-CH_2, and also Si—H, are well resolved in the spectra of all of these compounds, if the ring contains the silane group. The difference in the values of the chemical shifts for the different rings is slight (with the exception of the silacyclobutanes), and only different is the ratio in the intensities of the signals from the protons of the α-CH_2 and β,γ-CH_2 groups. The protons of the CH_3 group give a shift with $\tau \sim 9.7$ p.p.m., the α-protons of the ring give a shift with $\tau_1 \sim 9$ p.p.m., the β,γ-protons of the ring give a shift with $\tau_2 \sim 8.2$-8.3, and the Si—H protons give a shift with $\tau_3 \sim 5.1$ p.p.m. The ratio in the intensities of the signals $\tau_1 : \tau_2$ in the case of the silacyclobutanes is ~ 4 : 2, in the case of the silacyclopentanes it is ~ 4 : 4, and in the case of the silacyclohexanes it is ~ 4 : 6.

The NMR spectra of 1-methyl-1-ethyl-1-silacyclopentane and —hexane differed from all of the preceding by the contour of the signal with $\tau \sim 9$ p.p.m; in the case of the ethyl derivatives this signal represents a complex multiplet as a result of the superimposition of the signals of the ethyl radical on the signal of the α-protons of the ring, which is in agreement with the literature data [8]. The NMR spectra of the methylated rearrangement products of 1-chloromethyl-1-chloro- and 1-chloromethyl-1-methyl-1-silacyclopentane [1] proved to be the same, and coincided completely with the NMR spectrum of the standard 1,1-dimethyl-1-silacyclohexane. The spectra of the methylated rearrangement products of the 1-chloromethyl-1-chloro- and 1-chloromethyl-1-methyl-1-silacyclohexanes also proved to be the same, and they differed from the spectra of the 1,1-dimethyl-1-silacycloalkanes only in the ratio of the intensities of the signals $\tau_1 : \tau_2$, which in the given case corresponded to ~ 4 : 8.

The NMR spectra of the methylated rearrangement products and of the corresponding standard compounds are shown in Fig. 1. The NMR spectrum of the rearrangement product of 1-chloromethyl-1-chloro-1-silacyclohexane, which is assigned the structure of 1,1-dichloro-1-silacycloheptane, is characterized by two signals — from the protons of the α-CH_2 and β,γ-CH_2 groups. The ratio in the intensities of these signals corresponds to ~ 4 : 8 (Fig. 2). As a result, the NMR spectra confirm the fact that the rearrangement takes place with an expansion of five-membered rings to six-membered rings, and of six-membered rings to seven-membered rings.

As chemical proof for the formation of the seven-membered ring can serve its polymerization under the influence of $AlCl_3$ [9]. The results of the study make it possible to conclude that the discovered by us skeletal rearrangement of silacycloalkanes, containing a chloromethyl radical attached to the silicon atom, is general for at least the five- and six-membered rings. In conclusion we will mention that the reaction for the expansion of six-membered rings to seven-membered rings can possess preparative interest, since the known organometallic method for the synthesis of silacycloheptanes [5] leads, as we proved to ourselves, to very low yields of the desired products. In this connection the constants given in [5] are far from the true values due to the presence of substantial amounts (30-40%) of difficultly separable impurities.

TABLE 1

No.	Obtained silacycloalkane	Amount of starting alkyl halide, M	Amount of starting silane chloride, M	Amount		Yield, %	bp, °C (p, mm Hg)	n_D^{20}	d_4^{20}	MR found / calculated	Found / Calculated, %
				Mg, M	absolute diethyl ether, ml						
1		Br $(CH_2)_4$ Br 1.8	$ClCH_2SiCl_3$ 1.8	4.2	2500	40	182	1.4880	1.1783	$\frac{41.37}{41.8}$	Cl $\frac{21.7}{20.9}$
2		Br $(CH_2)_5$ Br 0.51	$ClCH_2SiCl_3$ 0.4	1.2	1500	45	93.5—94 (20)	1.4890	1.1450	$\frac{46.38}{46.51}$	Cl $\frac{19.4}{19.28}$
3		Br $(CH_2)_5$ Br 0.56	$ClCH_2SiCl_2CH_3$ 0.5	1.54	1500	53	188—189	1.4770	0.9863	$\frac{46.62}{46.88}$	$\frac{\text{Si 17.06; C 51.4; H 9.20}}{\text{Si 17.22; C 51.6; H 9.28}}$
4		Br $(CH_2)_5$ Br 0.25	$Cl_3SiC_2H_5$ 0.25	0.87	750	52	55—57 (5)	1.4712	0.9876	$\frac{46.08}{46.18}$	Cl $\frac{20.8}{21.8}$
5	*	Br $(CH_2)_5$ Br 0.5	$SiCl_4$ 0.40	1.5	1500	56	170	1.4702	1.1520	—	—
6		CH_3Br	 0.06	0.12	150	83	161—161.5	1.4520	0.8250	$\frac{46.32}{46.55}$	$\frac{\text{Si 19.82; C 67.98; H 12.52}}{\text{Si 19.78; C 67.5; H 12.74}}$
7		CH_3Br	 0.17	0.6	500	80	131—131.5	1.4429	0.8127	$\frac{41.82}{41.92}$	

---

* The literature data [4] coincide with the obtained.

† The literature data [10] coincide with the obtained.

‡ The literature data [11] coincide with the obtained.

EXPERIMENTAL

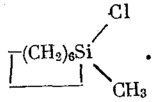
1. Synthesis of Starting and Standard Silacycloalkanes. The compounds, obtained in the present study from the corresponding alkyl halides and silane chlorides by the Grignard reaction, using the procedures described in [1, 4-7], and also their methylation products, are given in Table 1.

2. Transformation of 1-Chloromethyl-1-chloro-1-silacyclopentane in the Presence of Aluminum Chloride. In a 50-ml three-necked flask, fitted with a thermometer, dropping funnel and a reflux condenser, was placed 0.4 g of $AlCl_3$. The flask was cooled and 10 g of 1-chloromethyl-1-chloro-1-silacyclopentane was added carefully from the dropping funnel. The flask contents were brought up to room temperature and then careful heating was started. Vigorous exothermic reaction began at approximately 60-70°. At the end of reaction the mixture was treated with fused NaCl, and the liquid portion was decanted and fractionally distilled, having first added decalin to it to act as a high-boiling cushion. The following fractions were obtained from the fractional distillation: I) 0.8 g of 1,1-dichloro-1-salacyclopentane with bp 139-142° and n_D^{20} 1.4610, which agrees with the literature data [4, 6]. II) 7.8 g of 1,1-dichloro-1-silacyclohexane with bp 168-170°; n_D^{20} 1.4700; d_4^{20} 1.1531; found %: Cl 41.25; calculated for $\underline{Cl_2Si(CH_2)_5}$. Cl 41.78%. Literature data [5]: bp 170°; n_D^{20} 1.4679. The constants of the 1,1-dichloro-1-silacyclohexane synthesized by us are given in Table 1. III) 0.5 g of residue with bp > 170°.

Analysis of fractions I and II by the GLC method, using the standards, also confirmed the structure assigned to them. The methylation of fraction II with twice the theoretical amount of CH_3MgBr led to the formation of $\underline{(CH_3)_2Si(CH_2)_5}$ (89% yield) with bp 131.5°; n_D^{20} 1.4430; d_4^{20} 0.8119. Its NMR spectrum is shown in Fig. 1c.

The properties of the 1,1-dimethyl-1-silacyclohexane synthesized by us are given in Table 1, while its NMR spectrum is shown in Fig. 1a. Literature data [6]: bp 131.2-131.3° (740 mm); n_D^{20} 1.4428; d_4^{20} 0.8111.

3. Transformation of 1-Chloromethyl-1-methyl-1-salacyclohexane under the Influence of Aluminum Chloride. In a 100-ml four-necked flask, fitted with a stirrer, reflux condenser, dropping funnel and a thermometer, was placed 1.2 g of $AlCl_3$. The flask was cooled and from the dropping funnel, with stirring, was carefully added a solution of 15 g of 1-chloromethyl-1-methyl-1-silacyclohexane in an equal volume of n-hexane, previously fractionally distilled from sodium. The mixture was carefully heated up to 60°, after which the heating was terminated, but the temperature spontaneously rose up to 82° and the mixture frothed stormily. After exothermic reaction had ceased, 0.5 g of fused $AlCl_3$ was added and the stirred flask contents were heated for 20 min. The liquid portion was carefully decanted and fractionally distilled. We obtained 13.5 g (90% yield) of product with bp 55.5-57° (5 mm); n_D^{20} 1.4712; d_4^{20} 0.9876. Found %: Cl (hydrolyzable) 20.8; MR 46.05.



$\underline{(CH_2)_6Si}(Cl)(CH_3)$

. Calculated %: Cl (hydrolyzable) 21.7; MR 46.30.

When the reaction of 1-chloromethyl-1-methyl-1-silacyclohexane with 5 mole % of $AlCl_3$ was run without a solvent, a stormy exothermic reaction began just as soon as the components were mixed (at 20°), similar to the reaction of 1-chloromethyl-1-methyl-1-silacyclopentane with $AlCl_3$ [1]. A foamlike polymeric product was formed as a result, which, based on the titration data and the infrared spectra, contained the Si—Cl bond. Apparently, the formed 1-chloro-1-methyl-1-silacycloheptane, at the high temperature developed during the rearrangement process, is polymerized at the Si—C bond of the ring [9]. The possibility of this occurring was confirmed by the control polymerization of 1-chloro-1-methyl-1-silacycloheptane with 10 mole % of aluminum chloride at 150-200°.

Methylation of the rearrangement product with excess CH_3MgBr led to the formation of 10 g of 1,1-dimethyl-1-silacycloheptane with bp 163.5°; n_D^{20} 1.4532; d_4^{20} 0.8270. Found %: C 67.35; H 12.57; Si 20.00; MR 46.52. $(CH_3)_2\underline{Si(CH_2)_6}$. Calculated %: C 67.51; H 12.74; Si 19.78; MR 46.56.

The principal characteristic line of a six-membered ring containing silicon (800 cm^{-1}) [6] was not detected in the Raman spectrum. The NMR spectrum is shown in Fig. 1d.

4. Transformation of 1-Chloromethyl-1-chloro-1-silacyclohexane under the Influence of Aluminum Chloride. The reaction was run as described in Expt. 2. A mixture of 8.44 g of the silacyclane and 0.67 g of $AlCl_3$ was taken for reaction. Exothermic reaction began at a mixture temperature of approximately 65-70°. After the appropriate workup and a double fractional distillation of the mixture we isolated the following fractions: I) 0.4 g of a mixture with bp < 167°; II) 1.2 g of 1,1-dichloro-1-silacyclohexane with bp 167-168°; n_D^{20} 1.4700; d_4^{20} 1.1530. III) 4.5 g of a product with bp 203-204° (760 mm) and 95° (30 mm); n_D^{20} 1.4802; d_4^{20} 1.1443. Found %: Cl 39.0; MR 45.51. $Cl_2\underline{Si(CH_2)_6}$. Calculated %: Cl 38.7; MR 45.93. The Raman spectrum does not contain the main line, characteristic for silacyclohexane (800 cm^{-1}). The NMR spectrum is shown in Fig. 2. IV) Polymeric residue ~ 2 g, formed due to polymerization of the 1,1-dichloro-1-silacycloheptane at high temperature.

The methylation of fraction III gave 1.5 g of substance with bp 163°, n_D^{20} 1.4532; d_4^{20} 0.8268. Both GLC and the infrared spectra disclosed that this compound is identical with the product described in Expt. 3.

5. Preparation of 1,1-Dimethyl-1-silacycloheptane by the West Method [5]. The Grignard reagent was obtained from 50 g of Mg and 186 g of 1,6-dibromohexane in 500 ml of ether. To a solution of 170 g of $SiCl_4$ in 700 ml of absolute ether, with stirring and cooling, was slowly added the obtained Grignard reagent. The reaction mixture was heated for 2 h on the water bath. The formed mass was filtered on a Buchner funnel, and the filtrate was fractionally distilled. We obtained 7 g of a fraction with bp 200-205°; n_D^{20} 1.4683; d_4^{20} 1.1198. Found %: Cl 36.7. $Cl_2SiC_6H_{12}$. Calculated %: Cl 38.7.* Literature data [5]: bp 201°; n_D^{25} 1.4520; d_4^{25} 1.065.

All of the obtained chloride was methylated with excess methylmagnesium bromide. As a result we isolated 2.5 g (1.2%) of substance with bp 159-162°; n_D^{20} 1.4400; d_4^{20} 0.8140. Found %: MR 46.07; $\underline{(CH_3)_2Si(CH_2)_6}$. Calculated %: MR 46.5.

Analysis of the substance by GLC revealed that it consists 60% of a compound, having the same retention time as $(CH_3)_2\underline{Si(CH_2)_6}$, obtained by rearrangement and then methylated. Literature data for $(CH_3)_2\underline{Si(CH_2)_6}$ [5]: bp 161°, n_D^{25} 1.4335; d_4^{25} 0.780; found %: MR 47.45; calculated %: MR 45.56.

The NMR spectra were obtained on a JNM-3 spectrometer (40 MHz) using dioxane as the internal standard, mixed with the sample in a volume ratio of 1:5. The chemical shifts τ were determined by the method of side bands, taking $\tau = 10$ for tetramethylsilane, and 6.43 p.p.m. for dioxane. The accuracy of determining the chemical shifts was ± 0.03 p.p.m. The NMR spectrum of $Cl_2\underline{Si(CH_2)_6}$ could not be taken on the indicated apparatus, since its resolving capacity proved to be inadequate and the protons of all of the methylene groups gave no common signal. For this reason its spectrum was taken on a more sensitive instrument (100 MHz) (internal standard HMDS).

The Raman spectra were taken on an ISP-51 instrument with a medium chamber. The infrared spectra were taken on a UR-10 instrument. The authors wish to thank I. I. Leshcheva, L. A. Leites and V. D. Oppengeim for taking the spectra.

CONCLUSIONS

1. Five- and six-membered silacycloalkanes of type $R(CH_2Cl)\underline{Si(CH_2)_n}$ (R = CH_3, Cl) undergo rearrangement under the influence of catalytic amounts of aluminum chloride, with an expansion of the ring and the formation of products of type $RCl\underline{Si(CH_2)_{n+1}}$.

2. The indicated new transformation can serve as a method for the preparation of silacycloheptanes.

LITERATURE CITED

1. V. M. Vdovin, N. S. Nametkin, K. S. Pushchevaya, and A. V. Topchiev, Izv. AN SSSR, Otd. Khim. Nauk, 1963, 274.

---

* Our attempts to increase the yield by changing the order of mixing the reagents, their ratio, or the reaction temperature, all proved unsuccessful.

2. L. H. Sommer, D. L. Bailey, J. R. Gould, and E. C. Whitmore, J. Amer. Chem. Soc., 76, 801 (1954).
3. J. C. Whitmore, L. H. Sommer, and J. R. Gould, J. Amer. Chem. Soc., 69, 1976 (1947).
4. Ch. Tamborski and H. Rosenberg, J. Org. Chem., 25, 246 (1960).
5. R. West, J. Amer. Chem. Soc., 76, 6012 (1954).
6. A. F. Plate, N. A. Belikova, and Yu. P. Egorov, Izv. AN SSSR, Otd. Khim. Nauk, 1956, 1085.
7. A. F. Plate, N. A. Momma, and Yu. P. Egorov, Dokl. AN SSSR, 97, 847 (1954).
8. A. N. Egorochkin, M. L. Khidekkel, V. A. Ponomarenko, and N. A. Zadorozhnyi, Izv. AN SSSR, Ser. Khim., 1963, 1868.
9. N. S. Nametkin, V. M. Vdovin, and K. S. Pushchevaya, Izv. AN SSSR, Ser. Khim., 1967, 2537.
10. C. D. Nenitzescu and I. Necsoiu, J. Amer. Chem. Soc., 72, 3485 (1950).
11. N. A. Belikova, Dissertation [in Russian], Moscow (1954).