CONDENSATION OF DICHLORODIMETHYLSILANE IN SILENT DISCHARGES

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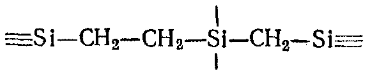
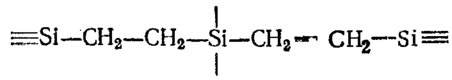
It was reported in previous communications [1, 2] that under the action of silent discharges trichloromethylsilane forms a mixture of linear polymers in which silicon and carbon atoms alternate in the main chain, in particular, 1,1,1,3,3-pentachloro-1,3-disilabutane, 1,1,1,4,4-pentachloro-1,4-disilapentane, and isomeric compounds of composition $C_3H_7Cl_3Si_3$ and $C_4H_9Cl_7Si_3$, containing the following groupings in the main chains:



$$\equiv Si-CH_2-CH_2-\overset{|}{\underset{|}{Si}}-CH_2-Si\equiv$$

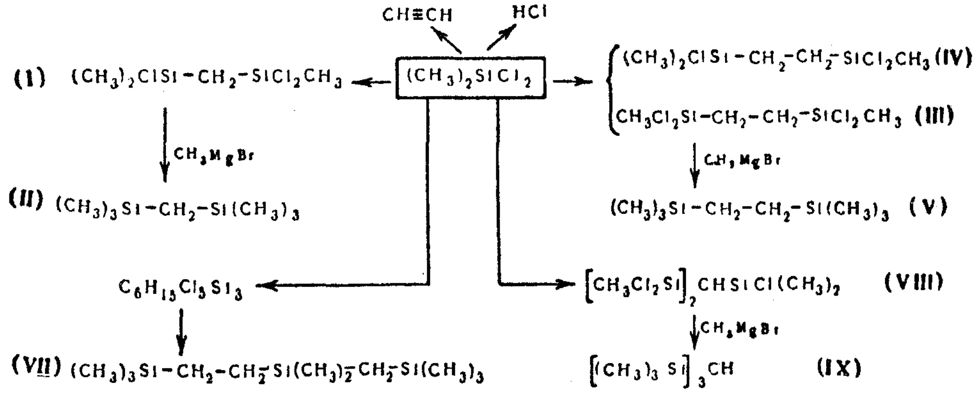
and



$$\equiv Si-CH_2-CH_2-\overset{|}{\underset{|}{Si}}-CH_2-CH_2-Si\equiv$$

In continuation of our investigations on the condensation of various organosilicon compounds in silent discharges, we have carried out the condensation of dichlorodimethylsilane and investigated the compositions of the compounds formed. The results are reported in the present communication.

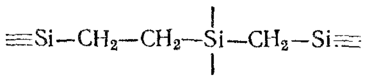
Experiments on the condensation of $(CH_3)_2SiCl_2$ were carried out in the previously described apparatus and under the conditions used previously [2]. We started with 1290 g of dichlorodimethylsilane and obtained 1050 g of condensate, the fractionation of which yielded 305 g of condensation products of b.p. above 100° (about 70% yield on the dichlorodimethylsilane that reacted and 29-30% yield on the dichlorodimethylsilane originally taken). To determine the compositions and structures of the products, the condensate was fractionated and the isolated compounds were investigated. To confirm the structures of the chloro sila-hydrocarbons obtained, they were converted into unsubstituted sila-hydrocarbons by the action of CH_3MgBr.



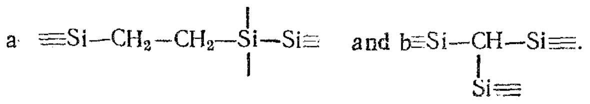
As will be seen from the scheme, the main condensation products obtained from dichlorodimethylsilane were formed by the condensation of two or three $(CH_3)_2SiCl_2$ molecules, and also of HCl. Also, the formation of small amounts of acetylene was noted. All the polymers obtained were of linear structure, had a main chain of alternating silicon and carbon atoms, and were therefore compounds of the same type as those obtained previously by the condensation of CH_3SiCl_3. The isolated 2,2,4-trichloro-4-methyl-2,4-disilapentane (I) had constants close to those of the compound described previously by Clark [3], and under the action of CH_3MgBr it gave 2,2,4,4-tetramethyl-2,4-disilapentane (II).

By the methylation of the fractions of b.p. 87-88° and 88-91° (9 mm), we obtained 2,2,5,5-tetramethyl-2,5-disilahexane (V), which indicates that these fractions contained compounds in which the hydrocarbon bridge $-CH_2-CH_2-$ occurred between silicon atoms in the main chain. Comparison of the constants of these fractions with data in the literature showed that the fractions probably contained a mixture of 2,2,5,5-tetrachloro-2,5-disilahexane (III) and 2,2,5-trichloro-5-methyl-2,5-disilahexane (IV). The densities and refractive indices of the fractions isolated were lower than those of pure (III), described by Shostakovskii and Kochkin [4], but higher than those of compounds of the composition $C_5H_{13}Cl_3Si_2$, e.g., 1,1,1-trichloro-4,4-dimethyl-1,4-disilapentane [5]. The analytical data also indicated a mixture of (III) and (IV).

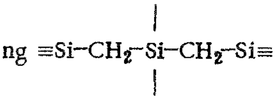
The formation of (III) can be readily explained by the recombination of two $CH_3Cl_2SiCH_2$. As regards (IV) –this compound was probably formed by the methylation of (III) by free CH_3 radicals. The possibility of the occurence of alkylation and arylation reactions of this sort under the action of silent discharges was shown by us earlier in the case of the formation of 1,1,1,4,4-pentachloro-1,4-disilapentane from CH_3SiCl_3 [1, 2] and trichloro (phenyl)- or trichloro (cyclohexyl)-silanes from $SiCl_4$ and benzene or cyclohexane [6].

In the methylation of chloro sila-hydrocarbons containing three silicon atoms we obtained two sila-hydrocarbons: 2,2,5,5,7,7-hexamethyl-2,5,7-trisilaoctane (VII) and tristrimethylsilylmethane (IX). For chloro sila-hydrocarbons of composition $C_6H_{15}Cl_5Si_3$ (VI), containing the grouping  $\equiv Si-CH_2-CH_2-\overset{|}{\underset{|}{Si}}-CH_2-Si\equiv$ in the main chain, nine isomers are possible; these differ in the distribution of five chlorine atoms and three methyl groups in the side chains. It is most probable that (VI) was a mixture of two isomers, 2,2,5,7,7-pentachloro-5-methyl-2,5,7-trisilaoctane and 2,2,5,5,7-pentachloro-7-methyl-2,5,7-trisilaoctane, which can be readily formed by chain processes from (III) and (IV). The presence of other isomers containing the groupings $(CH_3)_3Si-$, Cl_3Si-, $-CH_2-Si(CH_3)_2CH_2-$ and others is less probable because their formation requires the occurence of various secondary reactions, e.g. isomerization.

Chloro sila-hydrocarbons of composition $C_5H_{13}Cl_5Si_3$ (VIII) may have main chains with the following two structures:

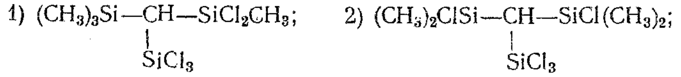


$$a\ \ \equiv Si-CH_2-CH_2-\overset{|}{\underset{|}{Si}}-Si\equiv \quad \text{and } b \equiv Si-\underset{Si\equiv}{\underset{|}{CH}}-Si\equiv.$$

The presence of compounds containing the grouping  $\equiv Si-CH_2-\overset{|}{\underset{|}{Si}}-CH_2-Si\equiv$ in their main chains is excluded because the sila-hydrocarbon (IX) obtained by the methylation of (VIII) differs considerably in its constants from 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane, which has been described in the literature [7].

Comparison of the molecular refractions given in the table leads to the conclusion that compounds (VIII) and(IX) must have the structure (b).

Three isomers are possible for chloro sila-hydrocarbons having this structure:



$$1)\ (CH_3)_3Si-\underset{SiCl_3}{\underset{|}{CH}}-SiCl_2CH_3; \quad 2)\ (CH_3)_2ClSi-\underset{SiCl_3}{\underset{|}{CH}}-SiCl(CH_3)_2;$$

3) $(CH_3)_2ClSi-CH(SiCl_2CH_3)_2$;

The presence of the first two isomers is not very probable, because they both contain the $SiCl_3$ (and the first contains also the $Si(CH_3)_3$ group), which is absent in the original dichlorodimethylsilane molecule. The occurence of various complex secondary reactions must be assumed for their formation. It is most probable that (VIII) has the last structure, which is that of (chlorodimethylsilyl)bis(dichloromethylsilyl)methane. On methylation it will give tristrimethylsilylmethane (IX).

In a recently published paper by Muller and Seitz [8] a compound was described which these authors consider to have the structure tristrimethylsilylmethane. However, the constants of this compound are greatly different from those which we obtained for (IX). This compound was obtained by Muller and Seitz by the action of CH_3MgBr on tristrichlorosilylmethane. This last compound was isolated from a condensate obtained by passing chloroform over a mixture of metallic silicon and copper at 300°. From the values of density and refractive index given in Muller and Seitz's paper, we have calculated the molecular refraction of the compound that they obtained. Below, for comparison purposes, we give the molecular refraction calculated for tristri-methylsilylmethane from Warrick's data [9] and values calculated from Muller and Seitz's and our experimental results:

	Chloro sila-hydrocarbons $C_5H_{13}Cl_5Si_3$ MR_D	Sila-hydrocarbons $C_{10}H_{28}Si_3$ MR_D
Calculated for compounds having:		
Structure (a)	77,37	79,46
" (b)	75,47	77,32
Found for (VIII)	75,54	—
" " (IX)	—	77,95

Calculated for tristrimethylsilymethane $MR_D = 77.32$
Found from Muller and Seitz's data $MR_D = 76.63$
Found from our data $MR_D = 77.95$

Comparison of these values shows that the molecular refractions of the compounds obtained by Muller and Seitz and by us differ from the theoretically calculated value by equal amounts (± 0.63-0.69) so that it is not possible by this means to decide which of the two compounds really has the structure of tristrimethylsilymethane. It would appear that this question could be resolved by the preparation of tristrimethylsilylmethane by some synthetic method which insured the preparation of a compound of this structure.

The chloro sila-hydrocarbons which we identified were undoubtedly formed by chain processes proceeding with the participation of hydrogen atoms and various free radicals. The close resemblance in type and structure between the compounds obtained in the present experiments and in those on the condensation of CH_3SiCl_3 [1, 2] gives us reason to suppose that the mechanism by which they are formed is the same in the two cases. The structures of the compounds isolated indicate that the main condensation reactions undergone by chloromethylsilanes under the action of silent discharges are 1) reactions in which new C–C bonds are formed, and 2) reactions in which new Si–C bonds are formed. The predominance in condensates obtained from CH_3SiCl_3 and $(CH_3)_2SiCl_2$ of compounds containing two and three silicon atoms, i.e., of relatively low molecular weight, indicates that the chain condensation process is accompanied by chain termination probably due mainly to the recombination of radicals in the bulk phase. These recombination processes were favored by our experimental conditons: atmospheric pressure in the reactor and a short distance between the walls of the reactor.

The primary process will be the cleavage of the $Si–CH_3$ in $(CH_3)_2SiCl_2$ with formation of the free radicals Cl_2CH_3Si and CH_3, which are initiators for chain reactions:

$$(CH_3)_2SiCl_2 \xrightarrow{e} Cl_2CH_3\dot{S}i + \dot{C}H_3$$

The formation of the compounds that we identified can be explained by the occurrence of the following chain reactions:

$$2CH_3 \rightarrow CH{\equiv}CH + 4\dot{H}$$

$$(CH_3)_2SiCl_2 + \dot{H} \rightarrow H_2 + CH_3Cl_2Si\dot{C}H_2$$

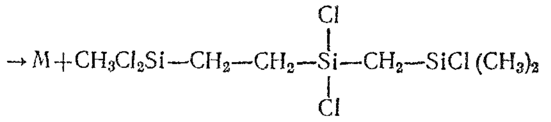
$$(CH_3)_2SiCl_2 + \dot{H} \rightarrow HCl + (CH_3)_2Cl\dot{S}i$$

$$2CH_3Cl_2Si\dot{C}H_2 + M \rightarrow M + CH_3Cl_2Si{-}CH_2{-}CH_2{-}SiCl_2CH_3 \qquad (III)$$

$$CH_3Cl_2SiCH_2 + (CH_3)_2Cl\dot{S}i + M \rightarrow M + (CH_3)_2ClSi{-}CH_2{-}SiCl_2CH_3 \qquad (I)$$

$$(III) + \dot{H} \rightarrow H_2 + CH_3Cl_2Si{-}CH_2{-}CH_2{-}SiCl_2\dot{C}H_2$$

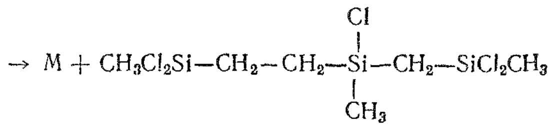
$$CH_3Cl_2Si{-}CH_2{-}CH_2{-}SiCl_2\dot{C}H_2 + (CH_3)_2Cl\dot{S}i + M \rightarrow$$



$$\rightarrow M + CH_3Cl_2Si{-}CH_2{-}CH_2{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{Si}}{-}CH_2{-}SiCl(CH_3)_2 \qquad (VI)$$

$$(III) + \dot{H} \rightarrow HCl + CH_3Cl_2Si{-}CH_2{-}CH_2{-}\dot{S}iClCH_3$$

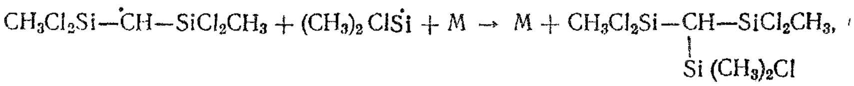
$$CH_3Cl_2Si{-}CH_2{-}CH_2{-}\dot{S}iClCH_3 + \dot{C}H_2SiCl_2CH_3 + M \rightarrow$$



$$\rightarrow M + CH_3Cl_2Si{-}CH_2{-}CH_2{-}\overset{\displaystyle Cl}{\underset{\displaystyle CH_3}{Si}}{-}CH_2{-}SiCl_2CH_3 \qquad (VI)$$

$$CH_3Cl_2Si\dot{C}H_2 + Cl_2CH_3\dot{S}i + M \rightarrow M + CH_3Cl_2Si{-}CH_2{-}SiCl_2CH_3$$

$$CH_3Cl_2Si{-}CH_2{-}SiCl_2CH_3 + \dot{H} \rightarrow H_2 + CH_3Cl_2Si{-}\dot{C}H{-}SiCl_2CH_3$$



$$CH_3Cl_2Si{-}\dot{C}H{-}SiCl_2CH_3 + (CH_3)_2Cl\dot{S}i + M \rightarrow M + CH_3Cl_2Si{-}\underset{\displaystyle Si(CH_3)_2Cl}{CH}{-}SiCl_2CH_3, \qquad (VIII)$$

in which M is a third particle that can accept excess of energy.

EXPERIMENTAL

The condensation of dichlorodimethylsilane in silent discharges was carried out under conditions analogous to those for the experiments with trichloromethylsilane [2, 3]. The discharge tube had the following principal dimensions: internal diameter of external electrode 22 mm, external diameter of internal electrode 12 mm, length of discharge zone 300 mm, volume of reaction (discharge) space 80 ml. The high-tension current of frequency 50 cycles/second was obtained from a single-phase 60-kv oil transformer. The experiments were carried out at 24.5 kv and 2.25 ma. The power of the discharge was 55 w, and the mean specific power was 0.68 w/cc (the measurements were made in a secondary circuit).

To accumulate condensation products, six experiments were carried out under standard conditions: a charge of 215 g of dichlorodimethylsilane and a reaction time of 60 hours. As a result of these experiments 1290 g of dichlorodimethylsilane gave 1050 g of a yellow condensate, which was fractionated through a column of 10-12 theoretical plates. We isolated 305 g of condensation products of b.p. above 100°; these were refractionated, first at atmospheric pressure and then under reduced pressure for the higher-boiling products. All the fractions isolated were clear colorless liquids which decomposed rapidly under the action of atmospheric moisture.

Investigation of Individual Fractions of the Condensate

Fraction VIII: b.p. 184-186°; n_D^{20} 1.4602; d_4^{20} 1.1421. Found: Si 25.30; Cl 46.73%. MR 53.18. $C_4H_{11}Cl_3Si_2$. Calculated: Si 25.33; Cl 47.98%. MR 52.69. For 2,2,4-trichloro-4-methyl-2,4-disilapentane the literature [3] gives m.p. 186° and d_{25} 1.160.

Hence, Fraction VIII, and also VII, which has similar constants (b.p. 180-184°, n_D^{20} 1.4583; d_4^{20} 1.1309), is 2,2,4-trichloro-4-methyl-2,4-disilapentane (I). Yield 10%.

Fraction I': b.p. 86-87° (9 mm); n_D^{20} 1.4658; d_4^{20} 1.2142. Found: Si 22.47; Cl 48.9%. $C_4H_{10}Cl_4Si_2$. Calculated: Si 21.92; Cl 55.38%. $C_5H_{13}Cl_3Si_2$. Calculated: Si 23.83; Cl 45.13%. This fraction, and also the neighboring factions II' and III' (b.p. 87-88° and 88-91°; n_D^{20} 1.4660; d_4^{20} 1.2145-1.2178) contains a mixture of 2,2,5-trichloro-5-methyl-2,5-disilahexane (IV) and 2,2,5,5-tetrachloro-2,5-disilahexane (III). Yield 14%.

Fraction V': b.p. 115-125° (9 mm); n_D^{20} 1.4832; d_4^{20} 1.2463. Found: Si 24.43; Cl 49.96%; MR 79.92. $C_6H_{15}Cl_5Si_3$. Calculated: Si 24.18; Cl 50.84%, MR 80.10.

This fraction is probably a mixture of two isomers of composition $C_6H_{15}Cl_5Si_3$(VI); namely 2,2,5,7,7-penta-chloro-5-methyl-2,5,7-trisilaoctane and 2,2,5,5,7-pentachloro-7-methyl-2,5,7-trisilaoctane. Yield 5.6%.

Fraction VII': b.p. 135-145° (9 mm); n_D^{20} 1.4897; d_4^{20} 1.2803. Found: Si 24.81, Cl 53.35%. MR 75.54. $C_5H_{13}Cl_5Si_3$. Calculated: Si 25.17; Cl 52.97%, MR 75.47. This fraction contains (chlorodimethylsilyl)bis(dichloromethylsilyl) methane (VIII). Yield 3.0%.

Investigation of Fractions VII-X, B.P. 180-199°

A Grignard reagent was prepared from 24.3 g (1 g-atom) of magnesium and methyl bromide in 400 ml of dry ether, and an ethereal solution of 32 g of the combined Fractions VII-X was added. We obtained 20.4 g of methylated products, the fractionation of which gave 12 g of a substance of b.p. 132-134°; n_D^{20} 1.4180; d_4^{20} 0.7522. found: MR 53.80; calculated: MR 53.73. For 2,2,4,4-tetramethyl-2,4-disilapentane the literature gives: b.p. 134°, n_D^{20} 1.4172; d_4^{20} 0.7520 (7); o.p. 134°; n_D^{20} 1.4178, and d_4^{20} 0.7516 [10]. Hence, the substance isolated (II) is 2,2,4,4-tetramethyl-2,4-disilapentane.

Investigation of Fractions I'-IV', B.P. 86-115° (9 mm)

A Grignard reagent was prepared from 24.3 g (1 g-atom) of magnesium and methyl bromide in 400 ml of dry ether, and an ethereal solution of 42.2 g of the combined Fractions I'-IV' was added. We obtained 24.5 g of methylation products, the fractionation of which gave 10.3 g of a substance of b.p. 151-153°; n_D^{20} 1.4200; d_2^{40} 0.7538; found MR 58.56; calculated MR 58.36. For 2,2,5,5-tetramethyl-2,5-disilahexane the literature gives: b.p. 150-151°, n_D^{20} 1.4204; d_4^{20} 0.7536 [11]; b.p. 150°, n_D^{20} 1.4200, and d_4^{20} 0.7566 [12]. Hence, the substance isolated (V) is 2,2,5,5-tetramethyl-2,5-disilahexane.

Investigation of Fractions V'-IX', B.P. 115-180° (9 mm)

A Grignard reagent was prepared from 36.5 g (1.5 g-atoms) of magnesium and methyl bromide in 500 ml of dry ether, and an ethereal solution of 40 g of the combined Fractions V'-IX' was added. We obtained 25.7 g of methylation products, refractionation of which gave two sila-hydrocarbons 1) and 2) in amounts of 5.0 g and 4.1 g, respectively.

1) B.p. 195-196°; n_D^{20} 1.4418; d_4^{20} 0.7892; found MR 77.95; calculated MR 77.32. Found: Si 36.11; 36.38; C 51.49; 51.28; H 12.19; 12.36%. $C_{10}H_{28}Si_3$. Calculated: Si 36.22; C 51.64; H 12.18%.

2) B.p. 214-218°; n_D^{20} 1.4482; d_4^{20} 0.8048; found MR 82.06; calculated MR 81.95. Found: Si 33.79; 33.74; C 53.79; 53.86; H 12.39; 12.19%. $C_{11}H_{30}Si_3$. Calculated: Si 34.26; C 53.57; H 12.26%.

The compound 1) has the composition $C_{10}H_{28}Si_3$; however, its boiling point and other constants differ from those of 2,2,4,4,6,6-hexamethyl-2,4,6-trisilaheptane (b.p. 206°; n_D^{20} 1.4420; d_4^{20} 0.7987), as described in the literature [7]. It is probable that this compound is an isomer of the above compound and is tristrimethylsilylmethane (IX). In composition and constants compound (2) corresponds to 2,2,5,5,7,7-hexamethyl-2,5,7-trisilaoctane (VII) [b.p. 87-92° (10 mm); n_D^{20} 1.4470; d_4^{20} 0.8051], which has been described previously [2].

SUMMARY

1. Dichlorodimethylsilane has been condensed under the action of silent discharges, and the composition of the condensate has been investigated. The main reaction products were chloro sila-hydrocarbons in which silicon and carbon atoms alternate in the main chain, which were formed by the condensation of two or three $(CH_3)_2SiCl_2$ molecules. The yield of condensation products was 68-70% on the amount of dichlorodimethylsilane that reacted.

2. The formation of the following compounds was proved: 2,2,4-trichloro-4-methyl-2,4-disilapentane, 2,2,5-trichloro-5-methyl-2,5-disilahexane, 2,2,5,5-tetrachloro-2,5-disilahexane, isomers of composition $C_6H_{15}Cl_5Si_3$ (probably 2,2,5,7,7-pentachloro-5-methyl-2,5,7-trisilaoctane and 2,2,5,5,7-pentachloro-7-methyl-2,5,7-trisilaoctane), and (chlorodimethylsilyl)bis(dichloromethylsilyl)methane.

3. The experiments proved that the main chemical processes occurring under the action of silent discharges are the creation of new Si–C and C–C bonds as the result of chain processes.

LITERATURE CITED

1. D. N. Andreev, Doklady Akad. Nauk SSSR 100, 697 (1955).
2. D. N. Andreev, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 818 (1957).*
3. H. A. Clark, British Pat. 672825; Chem. Abs. 47, 3869 (1953).
4. M. F. Shostakovskii and D. A. Kochkin, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 1150 (1956).
5. M. Kanazashi, Bull. Chem. Soc. Japan 28, 44 (1955).
6. D. H. Andreev, Doklady Akad. Nauk SSSR 100, 263 (1955).
7. L. H. Sommer, F. A. Mitch, and G. M. Goldberg, J. Amer. Chem. Soc. 71, 2746 (1949).
8. R. Müller and G. Seitz, Chem. Ber. 91, 22 (1958).
9. E. Warrick, J. Amer. Chem. Soc. 68, 2455 (1946).
10. N. S. Nametkin, A. V. Topchiev, and F. F. Machus, Doklady Akad. Nauk SSSR 96, 1003 (1954).
11. A. V. Topchiev, N. S. Nametkin, and A. A. Shcherbakova, Doklady Akad. Nauk SSSR 86, 559 (1952).
12. A. D. Petrov, V. A. Ponomarenko, and V. I. Boikov, Izvest. Akad. Nauk SSSR, Otdel. Khim. Nauk 504 (1954).

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*Original Russian pagination. See C. B. translation.