

CONCLUSIONS

1. Mercury salts of carboxylic acids are readily added on to bis(trifluoromethyl) ketene and its N-phenylimine, forming mixed anhydrides or imides of α -mercuriobishexafluoroisobutyric acid.

2. The mixed anhydride of trifluoroacetic and α -mercuriobishexafluoroisobutyric acids is readily decomposed to bis(trifluoromethyl) ketene, trifluoroacetic anhydride, and the internal salt of α -mercuriohexafluoroisobutyric acid. On decarboxylation in pyridine this salt is converted to hexafluoroisopropylidenemercury.

LITERATURE CITED

1. E. M. Rokhlin, A. Yu. Volkonskii, and E. I. Mysov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1359 (1978).
2. B. L. Dyatkin, N. I. Delyagina, and S. R. Sterlin, *Usp. Khim.*, **45**, 1218 (1976).
3. B. L. Dyatkin, L. G. Zhuravkova, B. I. Martynov, E. I. Mysov, S. R. Sterlin, and I. L. Knunyants, *J. Organomet. Chem.*, **31**, C15 (1971).
4. V. R. Polishchuk, L. S. German, and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 620 (1971).

SYNTHESIS OF BIS[ORGANOCYCLOTRI(TETRA,PENTA)SILOXY]POLYDIMETHYLSILOXANES

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Organocyclosiloxanes with a functional group at the silicon atom are obtained by a double decomposition reaction between 1,5-disodiooxyhexamethyltrisiloxane and methyltrichlorosilane [1] and by heterofunctional condensation of organotrichlorosilanes with α,ω -dihydroxydimethylsiloxanes [2, 3]. In the present work the condensation of α,ω -dihydroxydimethylsiloxanes with organotrichlorosilanes and with the organocyclosiloxanes which form was investigated.

The optimum concentrations of the initial compounds for the synthesis of organocyclo-tri(tetra)siloxanes are 0.13-0.25 M. A common relationship between the yield of the organocyclo-trisiloxanes, organocyclo-tetrasiloxanes, and organocyclo-pentasiloxanes and the initial concentration of the dihydroxydimethylsiloxanes is not observed (Table 1). The formation of the organocyclosiloxanes is also affected by the rate of addition of the reagents, by the

*Deceased.

TABLE 1. The effect of the Reaction Conditions on the Yield of Organo(chloro)cyclosiloxanes (solvent ether)

Organo-(chloro)-cyclosiloxane	Concentration of diol, M	Yield of organo-(chloro)-cyclosiloxane, %	Time, h		Organo-(chloro)-cyclosiloxane	Concentration of diol, M	Yield of organo-(chloro)-cyclosiloxane, %	Time, h	
			reaction	heating				reaction	heating
(Ib)	0,17	53,6	7	7	(Ie)	0,19	63,0	48	4
(Ib)	0,18	34,6	72	2	(Ie)	0,25	58,6	48	5
(Ic)	0,25	50,5	48	3	(Ie)*	0,27	71,3	72	—
(Id)	0,24	67,3	48	1	(I g)	0,17	53,6	6	2
(Ie)*	0,13	58,3	36	—	(II)	0,19	66,8	6	2
(Ie)	0,13	54,0	5	5	(II)	0,22	68,9	20	2
(Ie)	0,19	45,0	8	5					

*Solvent benzene.

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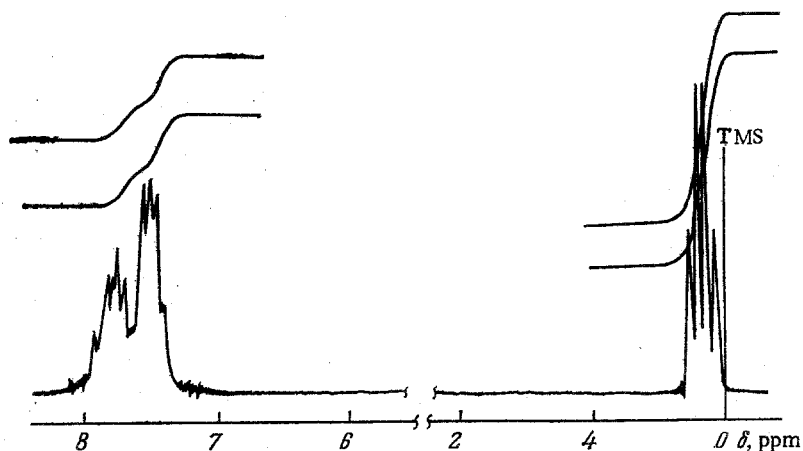


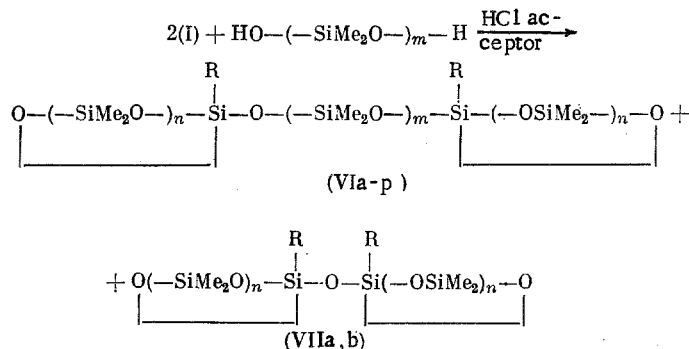
Fig. 1. The PMR spectrum of 1,7-dichloro-1,7-diphenyl-3,3,5,5,9,9,11,11-octamethylcyclohexasiloxane (IIa).

The presence of two signals of identical intensity at δ 0.20 and 0.30 ppm in the PMR spectrum of (Ia) and of four signals with intensity ratios 1:2:1:2 at δ 0.12, 0.15, 0.20, and 0.28 ppm in the spectrum of (Id) corresponds to the number of nonequivalent positions of the CH_3 groups in the rings. In the spectrum of the siloxane (If) three signals with intensity ratios 1:2:1 are observed at δ 0.08, 0.14, and 0.26 ppm as a result of the fact that the signals of the two types of CH_3 groups coincide. The siloxanes (I) with $\text{R} = \text{Ph}$ and ClPh have analogous PMR spectra.

From the PMR spectrum of 1,7-dichloro-1,7-diphenyl-3,3,5,5,9,9,11,11-octamethylcyclohexasiloxane (IIa), which contains four signals for CH_3 groups at δ 0.08, 0.15, 0.20, and 0.28 ppm (Fig. 1), it follows that there is a mixture of cis and trans isomers in a ratio of 1:2. The assignment was made with due regard to data on the screening of the protons of the CH_3 groups in the cyclosiloxanes by the Ph groups and Cl atoms [7].

From the siloxanes (Ia-g) we obtained bis[organocyclotri(tetra,penta)siloxy]polydimethylsiloxane (VI) (Tables 3 and 4) with a considerably higher yield (59-79%) than that of compound (VI) ($\text{R} = \text{Me}$) in [8] (25-30%).

Analysis of the products from the reaction of the siloxanes (I) with dihydroxydimethylsiloxane showed that the oxydi(organocyclosiloxane) (VII) is formed in addition to (VI), irrespective of the value of m in the dihydroxydimethylsiloxane:

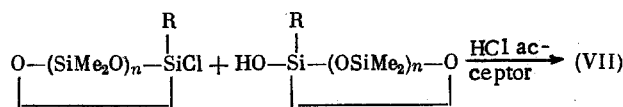


$m = 2, n = 3, \text{R} = \text{ClPh}$ (VIa), $m = n = 3, \text{R} = \text{Me}$ (VIb);
 $m = n = 3, \text{R} = \text{Ph}$ (VIc); $m = n = 3, \text{R} = \text{ClPh}$ (VI d);
 $m = 4, n = 3, \text{R} = \text{Ph}$ (VIe); $m = 4, n = 3, \text{R} = \text{ClPh}$ (VI f),
 $m = 6, n = 3, \text{R} = \text{Me}$ (VIg); $m = 6, n = 3, \text{R} = \text{Ph}$ (VIh); $m = 6,$
 $n = 3, \text{R} = \text{ClPh}$ (VI i); $m = 8, n = 3, \text{R} = \text{Me}$ (VI j);
 $m = 8, n = 3, \text{R} = \text{Ph}$ (VI k); $m = 3, n = 2, \text{R} = \text{ClPh}$ (VI l);
 $m = 2, n = 4, \text{R} = \text{ClPh}$ (VI m); $m = 3, n = 4, \text{R} = \text{ClPh}$ (VI n);
 $m = n = 4, \text{R} = \text{Ph}$ (VI o); $m = n = 4, \text{R} = \text{ClPh}$ (VI p).
 $m = 0, n = 3, \text{R} = \text{Ph}$ (VIIa); $m = 0, n = 3, \text{R} = \text{ClPh}$ (VIIb)

Compound (VII) was also obtained by the reaction

TABLE 3. The Properties of the Bis(organocyclotetrasiloxo)-polydimethylsiloxanes (VIa-k) and Oxydi(organocyclotetrasiloxanes) (VIIa, b)

Compound	Yield, %	bp, °C (torr)	n _D ²⁰	d ₄ ²⁰	Molecular formula	Found/calculated				
						MR	C, %	H, %	Si, %	Cl, %
(VIIa)	70,9	168-170 (1)	1,4601	1,0867	C ₂₄ H ₄₈ Si ₈ O ₉	177,29	41,12	6,59	32,29	-
						177,12	40,99	6,59	31,95	-
(VIIb)	80,6	198-201 (1)	1,4698	1,1400	C ₂₄ H ₄₄ Si ₈ Cl ₂ O ₉	188,92	37,40	5,80	28,81	9,50
						188,24	37,35	5,71	29,05	9,21
(VIa)	79,1	216-220 (1)	1,4588	1,1107	C ₂₈ H ₅₆ Si ₁₀ Cl ₂ O ₁₁	226,47	36,43	6,00	30,39	7,78
						225,84	36,56	6,09	30,47	7,73
(VIb)	59,7	140-142 (1)	1,4061	1,0197	C ₂₆ H ₆₀ Si ₁₁ O ₁₂	193,15	29,97	7,31	38,44	-
						193,40	30,00	7,50	38,50	-
(VIc)	53,2	191-193 (9·10 ⁻³)	1,4464	1,0642	C ₃₀ H ₆₄ Si ₁₁ O ₁₂	232,56	39,20	7,24	33,42	-
						233,04	38,96	6,93	33,33	-
(VI d)	63,6	217-220 (2·10 ⁻²)	1,4550	1,1020	C ₃₀ H ₆₂ Si ₁₁ Cl ₂ O ₁₂	244,88	37,20	6,20	30,36	7,49
						244,52	36,25	6,24	30,02	7,25
(VIe)	73,4	194-196 (8·10 ⁻³)	1,4431	1,0519	C ₃₂ H ₇₀ Si ₁₂ O ₁₃	252,06	38,64	7,03	33,36	-
						251,68	38,44	7,06	33,71	-
(VI f)	65,9	242-245 (1·10 ⁻²)	1,4502	1,0907	C ₃₂ H ₆₈ Si ₁₂ Cl ₂ O ₁₃	263,41	36,03	6,43	31,36	6,38
						263,36	35,99	6,37	31,49	6,65
(VI g)	67,5	132-135 (2·10 ⁻²)	1,4059	1,0133	C ₂₆ H ₇₈ Si ₁₄ O ₁₅	248,20	30,72	7,72	38,32	-
						249,32	30,49	7,68	38,40	-
(VI h)	55,1	217-222 (1·10 ⁻²)	1,4382	1,0466	C ₃₆ H ₈₂ Si ₁₄ O ₁₅	288,06	38,23	7,38	33,91	-
						288,96	37,66	7,20	34,25	-
(VI i)	61,5	234-236 (8·10 ⁻³)	1,4439	1,0722	C ₃₆ H ₈₀ Si ₁₄ Cl ₂ O ₁₅	301,46	35,67	6,51	32,48	6,10
						301,04	35,56	6,58	32,26	5,84
(VI j)	59,5	175-176 (8·10 ⁻³)	1,4055	1,0035	C ₃₀ H ₉₀ Si ₁₆ O ₁₇	286,67	30,63	7,62	38,11	-
						286,60	30,74	7,74	38,33	-
(VI k)	72,0	238-241 (2·10 ⁻⁴)	1,4337	1,0335	C ₄₀ H ₉₄ Si ₁₆ O ₁₇	326,51	37,18	7,15	34,74	-
						326,24	37,06	7,31	34,66	-



Compounds (VIa-p) and (VIIa, b) are transparent mobile liquids readily soluble in normal solvents. Their structures were confirmed by their PMR spectra (Fig. 2).

EXPERIMENTAL

The PMR spectra were recorded in carbon tetrachloride solution on a Hitachi-Perkin-Elmer R-20 spectrometer at 60 MHz with TMS as internal standard. The molecular weight of compound (IIa) was determined on an AEIMS-30 mass spectrometer with a DS-50 data processing system at an ionizing potential of 70 V and with the direct-inlet system at 25°C.

Tetramethyl(phenyl)(chloro)cyclotrisiloxane (Ia). To 100 ml of absolute ether, while stirring and cooling to -10°C, we added simultaneously from two dropping funnels 42.5 g (0.20 mole) of phenyltrichlorosilane in 250 ml of absolute ether and a solution of 30.0 g (0.18 mole) of 1,3-dihydroxytetramethyldisiloxane and 33.7 g (0.36 mole) of aniline in 250 ml of absolute ether. The mixture was stirred at 20°C for 72 h. The precipitated aniline hydrochloride was filtered off, and the solvent was distilled. By distillation of 51.2 g of the product we isolated 25.8 g (46.7%) of (Ia) (Table 2) and 6.1 g (11.1%) of 1,7-dichloro-1,7-diphenyl-3,3,5,5,9,9,11,11-octamethylcyclohexasiloxane (IIa); bp 175-177°C (1 mm Hg). Found, %: Si 26.96; Cl 12.67; M⁺ 609.1. Relative intensity H_{Me}:H_{Ph} = 2.36:1.00. C₂₀H₃₄Si₆O₆Cl₂. Calculated, %: Si 27.63; Cl 11.63. Mol. wt. 609.9. H_{Me}:H_{Ph} = 2.40:1.00.

Hexamethyl(phenyl)(chloro)cyclotetrasiloxane (Id). To 100 ml of absolute ether at -10°C we added simultaneously 39.6 g (0.187 mole) of phenyltrichlorosilane in 250 ml of absolute

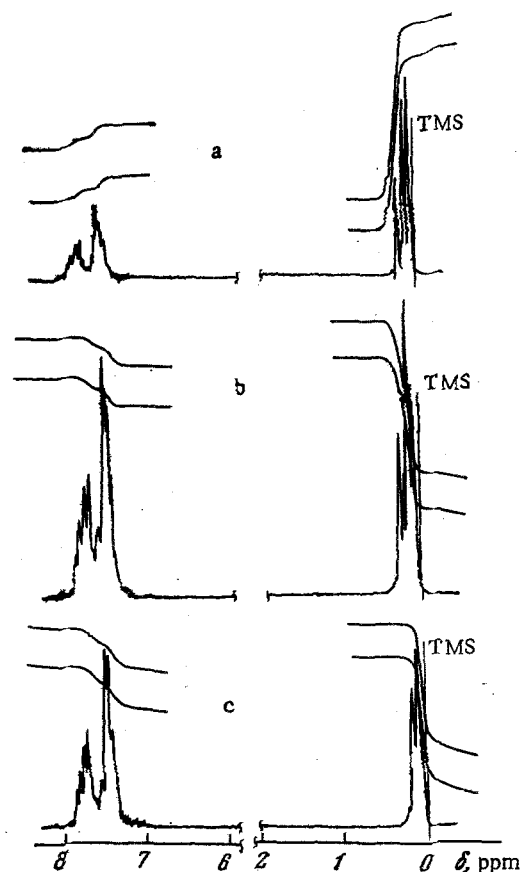


Fig. 2. The PMR spectra: c) Oxidi-[hexamethyl(phenyl)cyclotetrasiloxane] (VIIa); b) 1,7-bis[hexamethyl(phenyl)cyclotetrasiloxyl]octamethyltetrasiloxane (VIe); a) 1,7-bis[octamethyl(phenyl)cyclopentasiloxyl]octamethyltetrasiloxane (VI d).

TABLE 4. The Properties of the Bis[organocyclotri(penta)siloxyl]polydimethylsiloxanes (VII-p)

Compound	Yield, %	bp, °C	n_D^{20}	d_4^{20}	Molecular formula	Found/calculated				
						MR	C, %	H, %	Si, %	Cl, %
(VII)	57,2	227-228 (1,5)	1,4602	1,1179	$C_{26}H_{50}Si_5Cl_2O_{10}$	207,37	37,24	6,05	29,70	8,25
						206,84	36,92	5,92	29,82	8,40
(VI m)	55,7	203-207 (7·10 ⁻³)	1,4519	1,0940	$C_{33}H_{64}Si_{12}Cl_2O_{13}$	263,51	36,18	6,53	31,05	6,70
						263,44	35,99	6,37	31,49	6,65
(VI n)	58,7	202-204 (8·10 ⁻³)	1,4480	1,0847	$C_{34}H_{74}Si_{13}Cl_2O_{14}$	281,60	35,95	6,56	31,56	6,18
						282,24	35,76	6,49	31,90	6,22
(VI o)	51,2	215-217 (4·10 ⁻²)	1,4398	1,0487	$C_{36}H_{82}Si_{14}O_{15}$	288,45	38,23	7,30	33,73	-
						288,96	37,66	7,20	34,24	
(VI p)	53,4	220-222 (6·10 ⁻³)	1,4459	1,0804	$C_{36}H_{80}Si_{14}Cl_2O_{15}$	300,36	36,01	6,57	32,24	5,74
						301,04	35,56	6,58	32,26	5,84

ether and a solution of 40.0 g (0.167 mole) of 1,5-dihydroxyhexamethyltrisiloxane and 31.1 g (0.334 mole) of aniline in 250 ml of absolute ether. The mixture was stirred for 96 h. By distillation of 60.4 g of the product we isolated 39.8 g (66.2%) of compound (Id) (Table 2). By distillation of the residue (15.3 g) on a fractionating column we isolated 3.2 g (5.1%) of 1,3-dichloro-1,3-diphenyl-5,5,7,7,9,9-hexamethylcyclopentasiloxane (IIIa); bp 160-162°C

(1 mm Hg), n_D^{20} 1.4812, d_4^{20} 1.1508. Found, %: C 40.08; H 5.86; Si 26.33; Cl 13.14. MR 132.53 $H_{Me}:H_{Ph} = 2.03:1.00$. $C_{18}H_{28}Si_5O_5Cl_2$. Calculated, %: C 40.35; H 5.27; Si 26.21; Cl 13.23. MR 132.10, $H_{Me}:H_{Ph} = 1.80:1.00$. In addition to (IIIa), we isolated 2.8 g (4.6%) of 1,9-tetrachloro-1,9-diphenyl-3,3,5,5,7,7-hexamethylpentasiloxane (IVa); bp 180-182°C (1 mm Hg), n_D^{20} 1.4781, d_4^{20} 1.1595. Found, %: C 36.65; H 4.95; Si 24.48; Cl 20.80. MR 144-22, $H_{Me}:H_{Ph} = 2.06:1.00$. $C_{18}H_{28}Si_5O_4Cl_4$. Calculated, %: C 36.61; H 4.75; Si 23.73; Cl 24.08. MR 143.00, $H_{Me}:H_{Ph} = 1.80:1.00$.

Compounds (Ia-g) (Table 2) were synthesized similarly.

Hexamethyl(phenyl)(hydroxy)cyclotetrasiloxane (Vd). To 2.8 g (0.153 mole) of water, 9.6 g (0.103 mole) of aniline, and 1 g of acetone in 300 ml of ether at -5°C we added 39.0 g (0.103 mole) of (Id) in 200 ml of ether. The mixture was stirred at ~ 20°C for 1 h. The precipitated aniline hydrochloride was filtered off, and the ether solution was washed three times with an equal volume of water and dried over sodium sulfate. The ether was distilled. By distillation of the residue (35.1 g) we isolated 31.4 g (84.8%) of compound (Vd) (Table 2).

Compounds (Vc) and (Ve) were obtained similarly.

Oxydi[hexamethyl(phenyl)cyclotetrasiloxane] (VIIa). To 16.2 g (0.043 mole) of (Id) in 150 ml of absolute ether at -10°C we added 15.4 g (0.043 mole) of (Vd) and 4.3 g (0.043 mole) of triethylamine in 150 ml of absolute ether. The mixture was stirred at ~ 20°C for 5 days. The precipitated triethylamine hydrochloride was filtered off, and the ether was distilled. By distillation of the residue (28.2 g) we isolated 22.7 g (70.9%) of (VIIa) (Table 3).

Compound (VIIb) was obtained similarly.

1,7-Bis[hexamethyl(phenyl)cyclotetrasiloxyl]octamethyltetrasiloxane (VIe). To 22.7 g (0.06 mole) of (Id) in 250 ml of absolute ether at -10°C we added a solution of 9.4 g (0.03 mole) of 1,7-dihydroxyoctamethyltetrasiloxane and 6.1 g (0.06 mole) of triethylamine in 200 ml of absolute ether. The mixture was stirred at ~ 20°C for 5 days. By distillation (27.5 g) we isolated 20.2 g (73.4%) of (VIe) (Table 3). Compounds (VIa-p) were obtained similarly.

The authors thank B. D. Lavrukhin for interpreting and discussing the PMR spectra.

CONCLUSIONS

1. The heterofunctional condensation of organotrichlorosilanes with α,ω -dihydroxydimethylsiloxanes leads to condensation products, i.e., chlorine- and dichlorine-substituted organocyclosiloxanes and linear tetrachlorine-substituted organodimethylsiloxanes.

2. By the condensation of organo(chloro)cyclosiloxanes with α,ω -dihydroxydimethylsiloxanes 16 new bis(organocyclosiloxy)polydimethylsiloxanes were obtained. The oxydi(organocyclosiloxane) is also formed in this reaction, irrespective of the length of the diol.

LITERATURE CITED

1. K. A. Andrianov and L. M. Volkova, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **1962**, 264.
2. G. M. Omietanski and T. C. Williams, U. S. Patent No. 3358009, 1963; *Chem. Abstr.*, **68**, 39812 (1968).
3. K. A. Andrianov, A. B. Zachernyuk, and S. A. Danielov, *Khim. Geterotsikl. Soedin.*, **1972**, 893.
4. Yu. A. Yuzhelevskii, T. V. Kurilova, B. G. Kagan, and M. V. Suvorova, *Zh. Obshch. Khim.*, **42**, 2006 (1972).
5. N. F. Novikova, V. P. Mileshevich, A. V. Karlin, and V. F. Udot, *Collection: Investigations in the Physics and Chemistry of Rubbers [in Russian]*, Leningr. Tekhnol. Inst. im. Lensovetu (1975), p. 113.
6. M. Sakiyama, Y. Nishisawa, and R. Okawara, *Bull. Chem. Soc. Jpn.*, **38**, 2182 (1965).
7. D. E. Williams, G. M. Ronk, and D. Spielyogel, *J. Organomet. Chem.*, **69** (1974).
8. L. M. Volkova, K. A. Andrianov, and M. S. Obusheva, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1963**, 1986.