Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

THE HYDROLYSIS REACTION OF THE HIGHER ALKYL-METHYLDICHLOROSILANES

K. A. ANDRIANOV AND B. A. IZMAYLOV
Academy of Sciences, Department of Organo-Element Compounds, Moscow (U.S.S.R.)

(Received October 4th, 1966)

The hydrolytic poly-condensation reaction of the higher dialkyldichlorosilanes and the influence of the volume of the alkyl radicals at the silicon atom on the hydrolysis reaction and on the composition of the resulting products is of considerable interest. Therefore we aimed to study the hydrolysis reactions of hexylmethyldichlorosilane, octylmethyldichlorosilane, iso-nonylmethyldichlorosilane, and decylmethyldichlorosilane without hydrogen chloride as acceptor, and in 34.7% hydrogen chloride. It was found that the hydrolysis products of these compounds can be completely vacuum distilled. In the first case the cyclic and linear products are formed according to the reaction:

$$n\,RR'SiCl_2 + 2n\,H_2O \rightarrow (RR'SiO)_{m+2} + HO\text{–}\overset{\overset{R'}{|}}{\underset{\underset{R}{|}}{Si}}\text{–}(O\text{–}\overset{\overset{R'}{|}}{\underset{\underset{R}{|}}{Si}})_m\text{–}O\text{–}\overset{\overset{R'}{|}}{\underset{\underset{R}{|}}{Si}}\text{–}OH + 2n\,HCl$$

where m equals 1, 2, 3 ...

In the second case, only cyclic products are formed according to the reaction:

$$n\,RR'SiCl_2 + 2n\,H_2O \rightarrow (RR'SiO)_{m+2} + 2n\,HCl$$

where m equals 1, 2, 3...

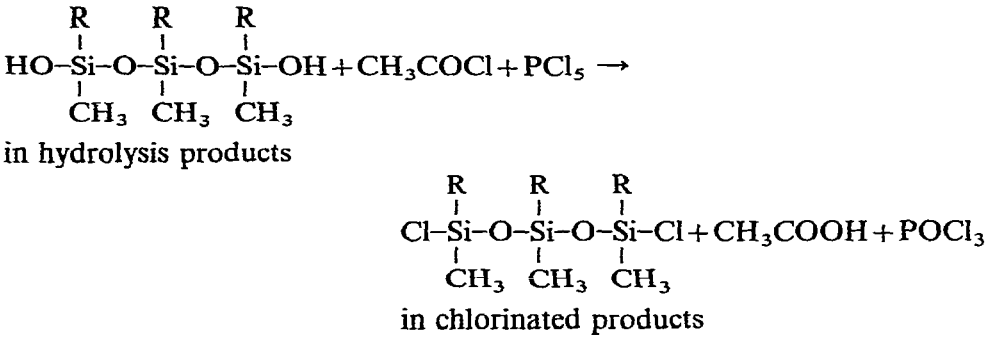
The physical constants of the products obtained are given in Table 1.

TABLE 1

PHYSICAL CONSTANTS OF THE PRODUCTS OF HYDROLYSIS OF ALKYLMETHYLDICHLOROSILANES AND CHLORINATED DERIVATIVES OF THE PRODUCTS OF HYDROLYSIS

No.	*Formula*	*B.p.* (°C/mm)	n_D^{20}	d_4^{20}	MR_D *found*	MR_D *calcd.*
I	$[(C_6H_{13})(CH_3)Si]_4O_3(OH)_2$	125–132/1.5·10^{-2}	1.4410	0.9125	170.9	171.204
II	$[(C_6H_{13})(CH_3)Si]_3O_2Cl_2$	103–110/1·10^{-2}	1.4430	0.9501	136.1	136.428
III	$[(C_6H_{13})(CH_3)Si]_4O_3Cl_2$	132–140/1·10^{-2}	1.4408	0.9373	178.0	178.364
IV	$[(iso\text{-}C_9H_{19})(CH_3)Si]_3O_2Cl_2$	175–182/3	1.4508	0.9289	177.92	178.26
V	$(CH_3\cdot C_6H_{13}SiO)_3$	154–159/2	1.4356	0.9007	125.52	125.808
VI	$(CH_3\cdot C_6H_{13}SiO)_4$	204–212/2	1.4383	0.9047	167.52	167.744
VII	$(CH_3\cdot C_8H_{17}SiO)_3$	204–210/1.5	1.4430	0.8930	153.45	153.696
VIII	$(CH_3\cdot C_8H_{17}SiO)_4$	250–256/1.5	1.4450	0.8953	204.83	204.928
IX	$(CH_3\cdot C_{10}H_{21}SiO)_3$	245–253/1	1.4495	0.8379	181.03	181.584
X	$(CH_3\cdot iso\text{-}C_9H_{19}SiO)_3$	202–208/2	1.4479	0.8936	167.42	167.64
XI	$(CH_3\cdot iso\text{-}C_9H_{19}SiO)_5$	254–260/2	1.4507	0.8980	279.20	279.40

The hydrolysis of higher dialkyldichlorosilanes, without the acceptor yields a mixture of cyclic and linear products. Their composition and structure were elucidated by chlorinating the hydrolysis products according to the reaction:

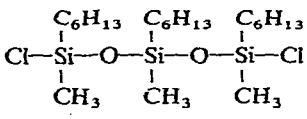
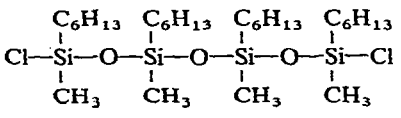
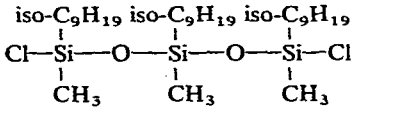


where R = C_6H_{13}, iso-C_9H_{19}.

The quantitative data on the yield of the individual compounds extracted after distillation of the chlorinated products of the hydrolysis of hexylmethyl- and iso-nonylmethyl-dichlorosilanes indicate that linear dialkyl siloxanes constitute about $\frac{1}{3}$ of the hydrolysate, their ratio increasing as the number of higher alkyl siloxane groups in a molecule increases, and depending on the size of the organic radicals at the silicon atom (Table 2).

TABLE 2

YIELD OF α,ω-DICHLOROALKYLMETHYLSILOXANES

Formula	*Yield* (%)
	9.63
	16.50
	14.80

The infrared spectra of (a) compounds (V, VII, IX and X, Table 1) showed the intensive absorption band at 1025–1015 cm^{-1} characteristic of the valency oscillations of the ≡Si–O–Si≡ bond in six-membered rings; (b) compounds (VI, VIII, Table 1)—at 1090–1085 cm^{-1}, characteristic of the same oscillations in eight-membered rings; (c) compound (XI, Table 1)—the intensive band at 1085–1045 cm^{-1} is to be attributed to the valency oscillations of the ≡Si–O–Si≡ bond characteristic for ten-membered rings. The intensive absorption bands at 810–785 and 1265–1263 cm^{-1} of compounds (I and V–XI, Table 1) indicate the presence of Si–CH_3. Compound (I, Table 1) has intensive absorption bands at 905–895 and 3410–3240 cm^{-1} indicating

the presence of OH-groups. The infrared spectrograms of the synthesized compounds, obtained with prisms of KBr, NaCl, and LiF, can be seen in Fig. 1.

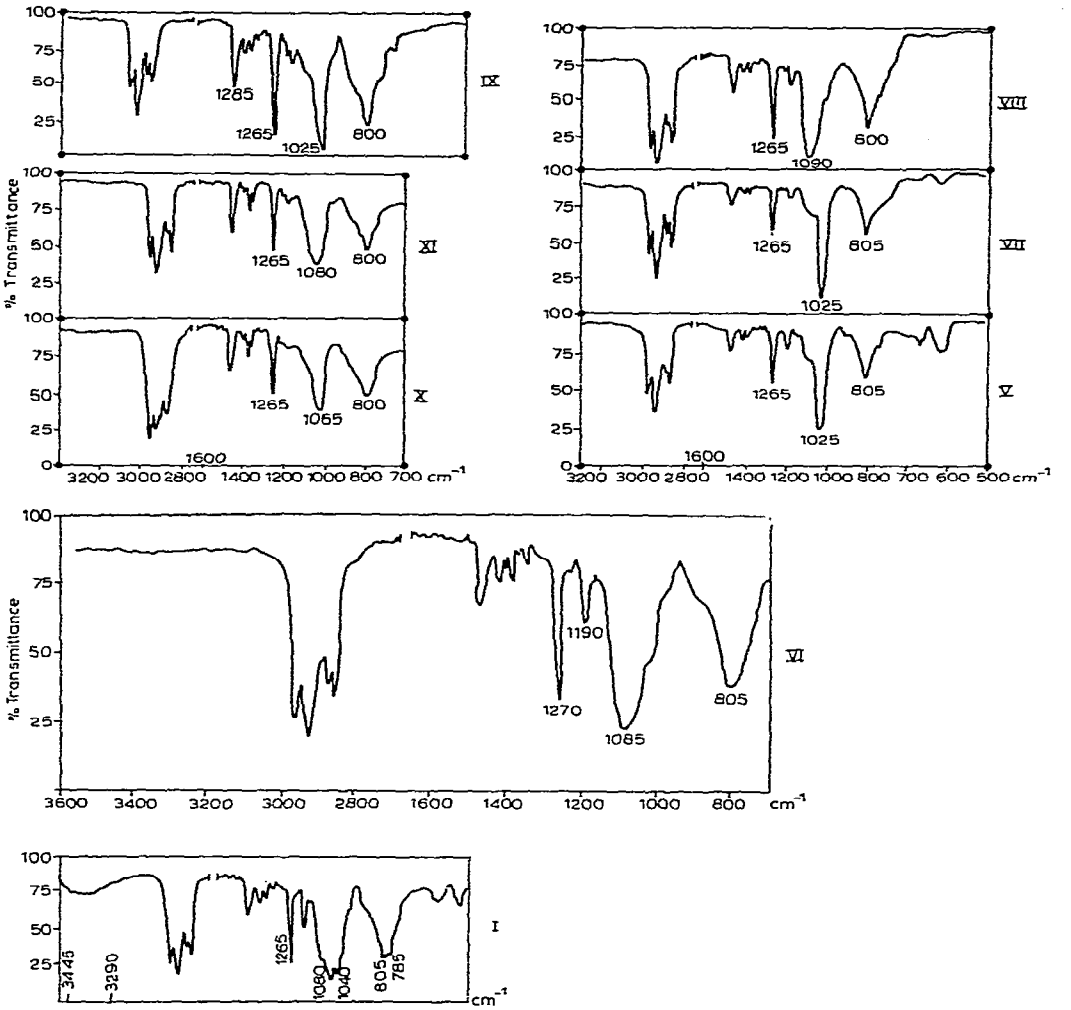


Fig. 1. The infra-red spectra of the synthesized compounds.

A study of the poly-condensation reaction of pure hexylmethyl-, decylmethyl-, and iso-nonylmethyl-dihydroxysilanes at 160° and of the products of hydrolysis, without acceptor, of hexylmethyl, octylmethyl, and iso-nonylmethyl-dichlorosilanes, demonstrated that only cyclic products are formed; these can be completely vacuum distilled. The maximum yield of six-membered dialkyl cyclosiloxanes is 43.2% and of eight-membered 20%. This shows the dependence of the yield of dialkyl cyclosiloxanes on the organic radical at the silicon atom. As the radicals increase in the series, $C_6H_{13} < C_8H_{17} < C_{10}H_{21}$, the yield of six-membered dialkyl cyclosiloxanes increases (Table 3); it is known that the hydrolysis of dimethyldichlorosilane yields, predominantly eight-membered dialkyl cyclosiloxanes; the yield of six-membered dialkyl cyclosiloxanes is insignificant.

TABLE 3

YIELD OF ALKYLMETHYLCYCLOSILOXANES

Formula	*Yield (%)*
$(CH_3 \cdot C_6H_{13}SiO)_3$	31.0
$(CH_3 \cdot C_6H_{13}SiO)_4$	20.0
$(CH_3 \cdot C_8H_{17}SiO)_3$	37.8
$(CH_3 \cdot C_8H_{17}SiO)_4$	17.6
$(CH_3 \cdot C_{10}H_{21}SiO)_3$	43.2
$(CH_3 \cdot iso\text{-}C_9H_{19}SiO)_3$	38.2
$(CH_3 \cdot iso\text{-}C_9H_{19}SiO)_5$	12.9

EXPERIMENTAL

Hydrolysis of hexylmethyldichlorosilane. 98.11 g of hexylmethyldichlorosilane (b. p. 46–50° at 3 mm Hg, n_D^{20} 1.4360; Cl, 35.9%) in 100 ml of ether was introduced into 100 ml of ether and double the quantity of distilled water at 18–20° and stirred for 10 min. The organic layer was separated, washed with water until neutral, dried over sodium sulfate, filtered, and the ether vacuum distilled at 15 mm Hg. 70.45 g of product was obtained, n_D^{20} 1.4380. (Found: C, 57.91; H, 11.3; Si, 18.45; OH, 4.71, 4.60%. $C_{28}H_{64}Si_4O_4$ calcd.: C, 58.27; H, 11.20; Si, 19.45%.)

(a) 9.38 g of this product was distilled at high vacuum. The following fractions were obtained:

No. of fraction	*B.p. (°C/mm)*	*Weight*	n_D^{20}	*OH (%)*
1	80–90/1.5·10^{-2}	0.96	1.4380	3.70
2	93–97/1.5·10^{-2}	2.78	1.4376	3.75
3	98–125/1.5·10^{-2}	1.94	1.4380	3.65
4	125–132/1.5·10^{-2}	1.16	1.4410	5.35
Still residue	>160/1.5·10^{-2}	1.32	1.4441	2.80

The 4th fraction is 1,3,5,7-tetrahexyl-1,3,5,7-tetramethyl-1,7-dihydroxytetrasiloxan, mol.wt. 586, 590 (calcd. 595.0). (Found: C, 56.20, 56.26; H, 11.08, 11.26; Si, 18.99, 19.00. $C_{28}H_{66}O_5Si_4$ calcd.: C, 56.51; H, 11.18; Si, 18.86; OH, 5.71%).

(b) Vacuum distillation of 32.32 g of the product, n_D^{20} 1.4398 (Found: C, 58.87; H, 11.33; Si, 18.91%. $C_{28}H_{64}Si_4O_4$ calcd.: C, 58.27; H, 11.20; Si, 19.45%) obtained by condensation at 160° of the product of hydrolysis of hexylmethyldichlorosilane yielded:

No. of fraction	*B.p. (°C/mm)*	*Weight*	n_D^{20}
1	40–152/2	0.30	1.4349
2	154–159/2	10.00	1.4356
3	164–202/2	6.82	1.4360
4	204–212/2	6.47	1.4383
5	280–298/2	5.20	1.4450
Still residue	>300/2	3.00	1.4450

The 2nd fraction is trihexyltrimethylcyclotrisiloxane, mol.wt. 430, 436 (calcd. 432.7). (Found: C, 58.18, 58.42; H, 11.22, 11.33; Si, 19.41, 19.25. $C_{21}H_{48}O_3Si_3$ calcd.: C, 58.27; H, 11.20; Si, 19.45%.)

The 4th fraction is tetrahexyltetramethylcyclotetrasiloxane, mol. wt. 568 (calcd. 577.00). (Found: C, 58.02; H, 11.20; Si, 19.75, 19.80. $C_{28}H_{64}O_4Si_4$ calcd.: C, 58.27; H, 11.20; Si, 19.45%.)

(c) 19.17 g of the hydrolysis product of hexylmethyldichlorosilane was chlorinated by boiling with 150 g of acetyl chloride for 1 h, adding 15 g of PCl_5 and then boiling again for 1 h; the acetyl chloride was then distilled.

Vacuum distillation of 12.5 g of the chlorinated product, n_D^{20} 1.4410 (Found: C, 55.38; H, 10.53; Si, 18.75; Cl, 13.5, 13.3%.) gave:

No. of fraction	*B.p. (°C/mm)*	*Weight (g)*	n_D^{20}	*Cl (%)*
1	80–100/1·10^{-2}	0.30	—	—
2	103–110/1·10^{-2}	1.20	1.4430	13.91
3	113–130/1·10^{-2}	1.37	—	—
4	132–140/1·10^{-2}	2.06	1.4408	10.89
5	145–167/1·10^{-2}	2.39	1.4450	4.0
Still residue	>180/1·10^{-2}	5.22	1.4470	0.22

The 2nd fraction is 1,3,5-trihexyl-1,3,5-trimethyl-1,5-dichlorotrisiloxane, mol. wt. 480 (calcd. 487.7). (Found: C, 52.00, 52.16; H, 9.99, 9.77; Si, 17.61, 17.60; Cl, 13.91, 13.98. $C_{21}H_{48}O_2Si_3Cl_2$ calcd.: C, 51.70; H, 9.91; Si, 17.25; Cl, 14.55%.)

The 4th fraction is 1,3,5,7-tetrahexyl-1,3,5,7-tetramethyl-1,7-dichlorotetrasiloxane, mol. wt. 625 (calcd. 632). (Found: C, 52.82, 52.95; H, 10.15, 10.00; Si, 17.85, 17.90; Cl, 10.89, 10.98. $C_{28}H_{64}O_3Si_4Cl_2$ calcd.: C, 53.20; H, 10.20; Si, 17.76; Cl, 11.23%.)

Hydrolysis of octylmethyldichlorosilane. 54.19 g of octylmethyldichlorosilane (b.p. 45–50° at 1 mm Hg; n_D^{20} 1.4455; Cl, 31.65%) yielded 40.48 g of product, n_D^{20} 1.4440 (Found: C, 62.08; H, 11.68; Si, 15.67; OH, 4.20%. Calcd.: C, 62.81; H, 11.69; Si, 16.28%.)

Vacuum distillation of 37.92 g of the product, n_D^{20} 1.4458 (Found: C, 62.48; H, 11.59; Si, 16.65. $C_{36}H_{30}Si_4O_4$ calcd.: C, 62.81; H, 11.69; Si, 16.28%) obtained by condensation at 160° of the hydrolysis product of octylmethyldichlorosilane produced:

No.	*B.p. (°C/mm)*	*Weight (g)*	n_D^{20}
1	115–200/1.5	1.50	1.4425
2	204–210/1.5	14.30	1.4430
3	216–250/1.5	12.00	1.4448
4	250–256/1.5	6.66	1.4450
Still residue	>270/1.5	2.70	1.4500

The 2nd fraction is trioctyltrimethylcyclotrisiloxane, mol. wt. 505 (calcd. 516.9). (Found: C, 62.89, 62.87; H, 11.67, 11.96; Si, 16.47, 16.43. $C_{27}H_{60}O_3Si_3$ calcd.: C, 62.81; H, 11.69; Si, 16.28%.)

The 4th fraction is tetraoctyltetramethylcyclotetrasiloxane, mol. wt. 680 (calcd. 689.2). (Found: C, 62.48; H, 11.59; Si, 16.55. $C_{36}H_{80}O_4Si_4$ calcd.: C, 62.81; H, 11.69; Si, 16.28%.)

Hydrolysis of iso-nonylmethyldichlorosilane. 113 g of iso-nonylmethyldichorosilane (b.p. 68–72° at 1.5 mm Hg; n_D^{20} 1.4480; Cl, 30.0%), yielded 88.94 g of product, n_D^{20} 1.4490. (Found: C, 63.92; H, 11.45; Si, 14.28; OH, 5.80%. Calcd.: C, 64.45; H, 11.90; Si, 15.05%.)

(a) Vacuum distillation of 19.98 g produced:

No. of fraction	*B.p. (°C/mm)*	*Weight (g)*	n_D^{20}	*OH (%)*
1	165–185/1	6.12	1.4519	5.60
2	195–240/1	5.68	1.4495	1.30
3	244–250/1	2.58	1.4507	no
Still residue	>270/1	2.76	1.4520	no

The 3rd fraction is penta-iso-nonylpentamethylcyclopentasiloxane, mol. wt. 924 (calcd. 931.6). (Found: C, 64.27, 64.46; H, 12.07, 12.23; Si, 14.98, 14.91. $C_{50}H_{110}O_5Si_5$ calcd.: C, 64.45; H, 11.90; Si, 15.05%.)

(b) Vacuum distillation of 28.11 g of the product, n_D^{20} 1.4428 (Found: C, 64.58; H, 11.98; Si, 14.96%. Calcd.: C, 64.45; H, 11.90; Si, 15.05%) obtained by condensation at 160° of the product of hydrolysis of iso-nonylmethyldichlorosilane yielded:

No. of fraction	*B.p. (°C/mm)*	*Weight (g)*	n_D^{20}
1	179–200/2	2.80	1.4455
2	202–208/2	10.75	1.4479
3	214–252/2	6.68	1.4480
4	254–260/2	3.62	1.4507
Still residue	>278/2	3.29	1.4520

The 2nd fraction is tri-iso-nonyltrimethylcyclotrisiloxane, mol. wt. 551, 559.00). (Found: C, 64.08; H, 11.75; Si, 15.35. $C_{30}H_{66}O_3Si_3$, calcd.: C, 64.45; H, 11.90; Si, 15.05%.)

The 4th fraction is penta-iso-nonylpentamethylcyclopentasiloxane.

(c) Vacuum distillation of 21.28 g of product, n_D^{20} 1.4592 (Found: C, 61. 05; H, 11.07; Si, 14.72; Cl, 9.98, 9.89%) obtained by chlorination of 18.4 g of the hydrolysis product of iso-nonylmethyldichlorosilane with 135 g of acetyl chloride and 13.5 g PCl_5 as described above, yielded:

No. of fraction	*B.p.* (°C/mm)	*Weight* (g)	n_D^{20}	*Cl* (%)
1	104–173/3	1.20	1.4590	9.89
2	175–182/3	3.15	1.4508	11.35
3	189–226/3	8.00	1.4487	4.70
4	232–274/3	3.57	1.4494	1.20
Still residue	>280/3	3.06	1.4508	0.20

The 2nd fraction is 1,3,5-tri-iso-nonyl-1,3,5-trimethyl-1,5-dichlorotrisiloxane, mol.wt. 598, 600 (calcd. 614.0). (Found: C, 58.78, 58.55; H, 10.43, 10.43; Si, 13.28, 12.98; Cl, 11.35, 11.55. $C_{30}H_{66}O_2Si_3Cl_2$, calcd.: C, 58.68; H, 10.83; Si, 13.70; Cl, 11.56%.) By double distillation of the 3rd and 4th fractions 6.65 g of tri-iso-nonyltrimethylcyclotrisiloxane was obtained, mol. wt. 550.

The hydrolysis in concentrated hydrochloric acid was carried out in a different manner from that described above. A mixture of the dialkyldichlorosilane, toluol, and hydrochloric acid (34.7%) in the ratio 1 : 1 : 1 by volume was vigorously stirred at 800 rev./min by a turbine stirrer for 15 h, and at 1500 rev./min for 7 h at 20–22°. The end of hydrolysis was controlled by a determination of chlorine ion in the organic layer after complete stratification of the mixture. Gaseous hydrogen chloride was collected and titrated. The organic layer when washed forms a stable emulsion. Toluol was distilled at 10-mm vacuum until a constant weight of product was obtained.

(a) 16.24 g of hexylmethyldichlorosilane, 12.7 g of toluol, and 15.44 g of hydrochloric acid (34.7%) produced 10 g of hydrolysis product (Table 4) and 6.04 g of hydrogen chloride.

TABLE 4

Hydrolysis products in 34.7% hydrochloric acid	*B.p.* (°C/mm)	n_D^{20}	*Found* (%)		
			C	*H*	*Si*
(a) of hexamethyldichlorosilane	153–296/2	1.4350	58.20	11.12	19.24
(b) of iso-nonylmethyldichlorosilane	185–298/2	1.4475	63.79	11.96	15.10

Vacuum distillation of this product produced 3.13 g of trihexyltrimethylcyclotrisiloxane and 1.85 g of tetrahexyltetramethylcyclosiloxane.

(b) 12.45 g of iso-nonylmethyldichlorosilane, 12.4 g of toluol, and 12.50 g of 34.7% hydrochloric acid produced 8.72 g of hydrolysis product and 3.87 g of hydrogen chloride. Vacuum distillation of this product yielded 3.32 g of tri-iso-nonyltrimethylcyclotrisiloxane.

Poly-condensation of higher alkylmethyldihydroxysilanes. Vacuum distillation of 10 g of the condensation product of hexylmethylhydroxysilane (Table 5(a)) gave 3.1 g of trihexyltrimethylcyclotrisiloxane.

TABLE 5

Products of condensation of dialkyl dihydroxysilanes at 160°	*B.p. (°C/mm)*	*Found (%)*		
		C	*H*	*Si*
(a) of hexylmethyldihydroxysilane	148–290/2	58.48	11.28	19.15
(b) of decylmethyldihydroxysilane	230–310/1	63.59	12.78	15.01
(c) of iso-nonylmethyldihydroxysilane	179–280/2	64.58	11.98	14.96

Vacuum distillation of 10 g of the condensation product of decylmethyldihydroxysilane (Table 5(b)) gave 4.32 g of tridecyltrimethylcyclotrisiloxane, mol. wt. 558 (calcd. 565). (Found: C, 63.45; H, 12.65; Si, 15.12. $C_{33}H_{72}O_3Si_3$, calcd.: C, 63.76; H, 12.84; Si, 14.89%.)

Vacuum distillation of 8.5 g of the condensation product of iso-nonylmethyldihydroxysilane (Table 5(b)) produced 2.72 g of tri-iso-nonyltrimethylcyclotrisiloxane.

SUMMARY

1. A study of the hydrolysis reaction of the higher alkylmethyldichlorosilanes shows that this reaction results in the formation of a mixture of cyclic and linear compounds. The hydrolysis in concentrated hydrochloric acid produces only cyclic compounds; these can be vacuum distilled.

2. It is demonstrated that condensation of the hydrolysis products of the higher alkylmethyldichlorosilanes results in the formation of a mixture of six-, eight-, and ten-membered dialkyl cyclosiloxanes.

3. It is shown that in the chlorination of the dialkyl α,ω-dihydroxysiloxanes in the hydrolysis products of the higher alkylmethyldichlorosilanes, hydroxyl groups are replaced by chlorine atoms.