SOME ORGANOSILICON COMPOUNDS CONTAINING SILOXANE-CARBON, SILTHIANE-CARBON, AND SILAZANE-CARBON GROUPINGS IN THE CHAIN

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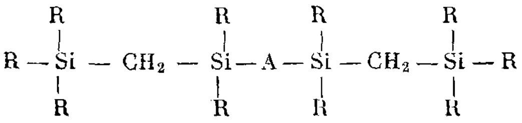
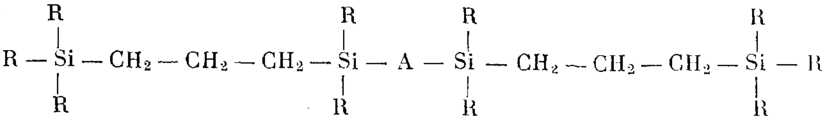
We have shown that it is possible, on the basis of the products of the reaction of methylene chloride with silicon, to prepare compounds containing siloxane-carbon, silthiane-carbon, and silazane-carbon groupings [1-5] of general formula



$$R-\underset{R}{\overset{R}{Si}}-CH_2-\underset{R}{\overset{R}{Si}}-A-\underset{R}{\overset{R}{Si}}-CH_2-\underset{R}{\overset{R}{Si}}-R$$

in which A = O, NH, or S

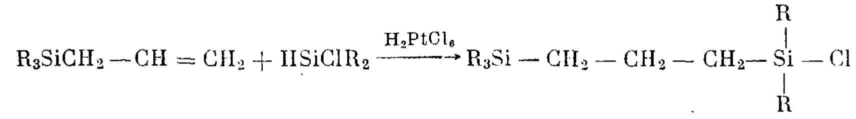
In the present communication we describe the synthesis of compounds having the following general formula



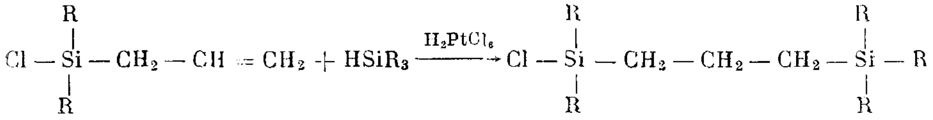
$$R-\underset{R}{\overset{R}{Si}}-CH_2-CH_2-CH_2-\underset{R}{\overset{R}{Si}}-A-\underset{R}{\overset{R}{Si}}-CH_2-CH_2-CH_2-\underset{R}{\overset{R}{Si}}-R$$

in which A = O, NH, or S.

These compounds were prepared from dialkyl[3-(trialkylsilyl)propyl]silyl chlorides, which in their turn were prepared by the addition of various hydride silanes to allylsilanes in presence of chloroplatinic acid by the following reactions:



$$R_3SiCH_2-CH=CH_2+HSiClR_2\xrightarrow{H_2PtCl_6}R_3Si-CH_2-CH_2-CH_2-\underset{R}{\overset{R}{Si}}-Cl \qquad (1)$$



$$Cl-\underset{R}{\overset{R}{Si}}-CH_2-CH=CH_2+HSiR_3\xrightarrow{H_2PtCl_6}Cl-\underset{R}{\overset{R}{Si}}-CH_2-CH_2-CH_2-\underset{R}{\overset{R}{Si}}-R \qquad (2)$$

In accordance with the scheme (1) we carried out the addition of chloromethylphenylsilane to allyltrimethylsilane, of chloroethylphenylsilane and of chlorodiethylsilane to allyltriethylsilane, and of chlorodipropylsilane to allyltripropylsilane at molar ratios of 1 : 1; the yields of addition product ranged from 60% to 70%. In accordance with scheme (2) we carried out the addition of tripropylsilane to allylchlorodipropylsilane, but even with a 100% excess of the hydride silane we obtained only a 30% yield of the addition product, i.e., only one half of the yield obtained by carrying out the addition in accordance with scheme (1).

Physical and chemical properties of dialkyl- and alkylphenyl-[3-(trialkylsilyl)propyl]silyl chlorides are presented in Table 1.

Tetraalkyl- and dialkyldiphenyl-1,3-bis[3-(trialkylsilyl)propyl]disiloxanes, whose properties are presented in Table 2, were prepared by the hydrolysis of the corresponding dialkyl-or alkylphenyl- [3-(trialkylsilyl)propyl]silyl chlorides.

TABLE 1

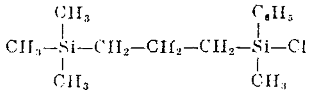
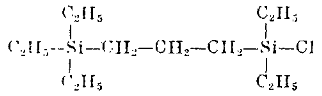
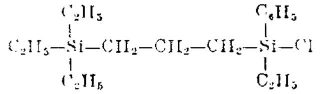
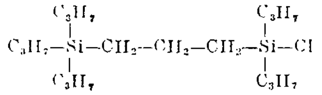
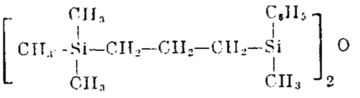
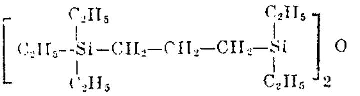
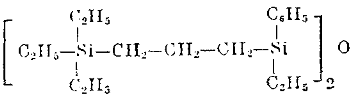
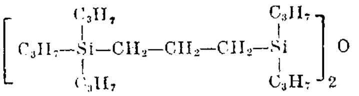
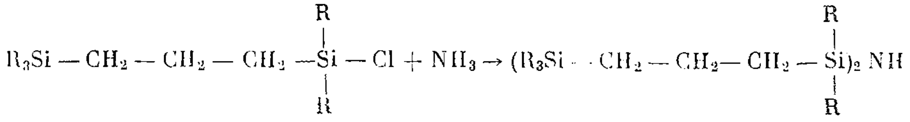
Formula	B.p., °C (p. mm)	Yield, %	Cl content, %	
			found	calculated
 $CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2-CH_2-CH_2-\underset{CH_3}{\overset{C_6H_5}{Si}}-Cl$	140—145 (2)	69,3	13,16 12,74	13,12
 $C_2H_5-\underset{C_2H_5}{\overset{C_2H_5}{Si}}-CH_2-CH_2-CH_2-\underset{C_2H_5}{\overset{C_2H_5}{Si}}-Cl$	139—144 (2)	74,7	12,81 13,66	12,75
 $C_2H_5-\underset{C_2H_5}{\overset{C_2H_5}{Si}}-CH_2-CH_2-CH_2-\underset{C_2H_5}{\overset{C_6H_5}{Si}}-Cl$	168—170 (2)	62,8	10,38 10,68	10,87
 $C_3H_7-\underset{C_3H_7}{\overset{C_3H_7}{Si}}-CH_2-CH_2-CH_2-\underset{C_3H_7}{\overset{C_3H_7}{Si}}-Cl$	160—162 (2)	61	10,21 10,25	10,18

TABLE 2

Formula	B.p., °C (p, mm)	Yield, %	n_D^{20}	d_4^{20}	MR	
					found	calculated
 $\left[CH_3-\underset{CH_3}{\overset{CH_3}{Si}}-CH_2-CH_2-CH_2-\underset{CH_3}{\overset{C_6H_5}{Si}}\right]_2O$	220—225 (2)	14	1,5000	0,9292	153,82	154,00
 $\left[C_2H_5-\underset{C_2H_5}{\overset{C_2H_5}{Si}}-CH_2-CH_2-CH_2-\underset{C_2H_5}{\overset{C_2H_5}{Si}}\right]_2O$	200—205 (2)	44,5	1,4638	0,8751	158,60	159,58
 $\left[C_2H_5-\underset{C_2H_5}{\overset{C_2H_5}{Si}}-CH_2-CH_2-CH_2-\underset{C_2H_5}{\overset{C_6H_5}{Si}}\right]_2O$	255—260 (2)	52,2	1,5035	0,9372	189,40	190,20
 $\left[C_3H_7-\underset{C_3H_7}{\overset{C_3H_7}{Si}}-CH_2-CH_2-CH_2-\underset{C_3H_7}{\overset{C_3H_7}{Si}}\right]_2O$	230—235 (2)	51,6	1,4641	0,8589	206,30	207,08

Tetrallkyl- and dialkyldiphenyl-1,3-bis[3-(trialkylsilyl)propyl]disilazanes were prepared by the reaction of dialkyl- and alkylphenyl-[3-(trialkylsilyl)propyl]silyl chlorides with ammonia by the scheme:



$$R_3Si-CH_2-CH_2-CH_2-\underset{R}{\overset{R}{Si}}-Cl+NH_3\rightarrow(R_3Si-CH_2-CH_2-CH_2-\underset{R}{\overset{R}{Si}})_2NH$$

Properties of tetraalkyl- and dialkyldiphenyl-1,3-[3-(trialkylsilyl)propyl]disilazanes are presented in Table 3.

By the reaction of methylphenyl[3-(trimethylsilyl)propyl]silyl chloride and of ethylphenyl[3-(triethylsilyl)propyl]silyl chloride with hydrogen sulfide we obtained compounds containing a silthiane-carbon grouping; their properties are presented in Table 4.

TABLE 3

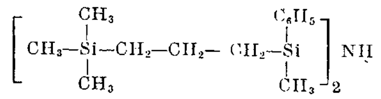
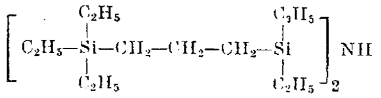
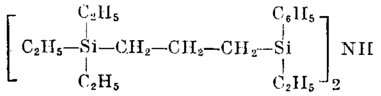
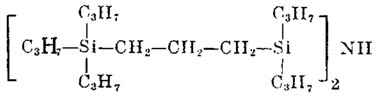
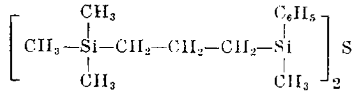
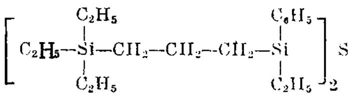
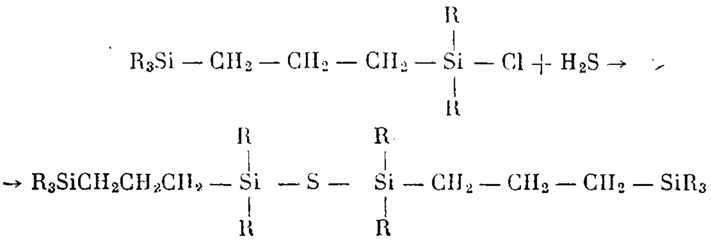
Formula	B.p., °C (p, mm)	Yield, %	d_4^{20}	n_D^{20}	MR	
					found	calculated
 $\left[CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2-CH_2-CH_2-\overset{C_6H_5}{\underset{CH_3}{Si}}\right]_2NH$	220 (2)	72,1	0,9304	1,5121	156,40	156,43
 $\left[C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{Si}}-CH_2-CH_2-CH_2-\overset{C_2H_5}{\underset{C_2H_5}{Si}}\right]_2NH$	250—252 (2)	32,0	0,8716	1,4699	160,60	161,89
 $\left[C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{Si}}-CH_2-CH_2-CH_2-\overset{C_6H_5}{\underset{C_2H_5}{Si}}\right]_2NH$	270—272 (2)	42,0	0,9401	1,5131	191,30	192,51
 $\left[C_3H_7-\overset{C_3H_7}{\underset{C_3H_7}{Si}}-CH_2-CH_2-CH_2-\overset{C_3H_7}{\underset{C_3H_7}{Si}}\right]_2NH$	270—272 (2)	30,0	0,8582	1,4694	208,60	209,39

TABLE 4

Formula	B.p., °C (p, mm)	Yield, %	n_D^{20}	d_4^{20}	MR	
					found	calculated
 $\left[CH_3-\overset{CH_3}{\underset{CH_3}{Si}}-CH_2-CH_2-CH_2-\overset{C_6H_5}{\underset{CH_3}{Si}}\right]_2S$	275—280 (2)	31,0	1,5165	0,9426	161,3	162,8
 $\left[C_2H_5-\overset{C_2H_5}{\underset{C_2H_5}{Si}}-CH_2-CH_2-CH_2-\overset{C_6H_5}{\underset{C_2H_5}{Si}}\right]_2S$	300 (2)	20,3	—	—	—	—



$$R_3Si-CH_2-CH_2-CH_2-\overset{R}{\underset{R}{Si}}-Cl + H_2S \rightarrow$$

$$\rightarrow R_3SiCH_2CH_2CH_2-\overset{R}{\underset{R}{Si}}-S-\overset{R}{\underset{R}{Si}}-CH_2-CH_2-CH_2-SiR_3$$

EXPERIMENTAL

Dialkyl-and alkylphenyl-[3-(trialkylsilyl)propyl]silyl chlorides were prepared by the addition of hydride silanes to allylsilanes in presence of a 10% solution of chloroplatinic acid in absolute isopropyl alcohol. The reaction was carried out in a three-necked flask. After the dropwise addition of the hydride silane to the allylsilane, the reaction mixture was heated for ten hours at 100°.

The properties of the compounds obtained are presented in Table 1.

Methylphenyl[3-(trimethylsilyl)propyl]silyl Chloride. From 85.5 g of allyltrimethylsilane and 117 g of chloromethylphenylsilane in presence of 1 ml of 10% chloroplatinic acid solution we obtained 139.5 g (69.3%) of methylphenyl[3-(trimethylsilyl)propyl]silyl chloride, b.p. 140-145° (2 mm).

Ethylphenyl[3-(triethylsilyl)propyl]silyl Chloride. From 100 g of allyltriethylsilane and 110 g of chloroethylphenylsilane in presence of 1 ml of 10% chloroplatinic acid solution we obtained 132 g (62.8%) of ethylphenyl[3-(triethylsilyl)propyl]silyl chloride, b.p. 168-170° (2 mm).

Dipropyl[3-(tripropylsilyl)propyl]silyl Chloride. From 100 g of allyltripropylsilane and 75.5 g of chlorodipropylsilane in presence of 10% chloroplatinic acid solution we obtained 107 g (61.1%) of dipropyl[3-(tripropylsilyl)propyl]silyl chloride, b.p. 160-162° (2 mm).

From 74.5 g of allylchlorodipropylsilane and 114 g of tripropylsilane in presence of 1 ml of 10% chloroplatinic acid solution we obtained 40 g (30.5%) of dipropyl[3-(tripropylsilyl)propyl]silyl chloride, b.p. 160-164° (2 mm).

Diethyl[3-(triethylsilyl)propyl]silyl Chloride. From 100 g of allyltriethylsilane and 78 g of chlorodiethylsilane in presence of 1 ml of 10% chloroplatinic acid solution we obtained 133 g (74.7%) of diethyl[3-(triethylsilyl)propyl]silyl chloride, b.p. 139-144° (2 mm).

Preparation of Organosilicon Compounds Containing Siloxane-, Silthiane-, and Silazane-Carbon Groupings

Tetraalkyl- and dialkyldiphenyl-1,3-bis[3-(trialkylsilyl)propyl]disiloxanes were prepared by the hydrolysis of dialkyl- and alkylphenyl-[3-(trialkylsilyl)propyl]silyl chlorides; their properties are presented in Table 2. The hydrolysis was carried out with dilute hydrochloric acid.

Dimethyldiphenyl-1,3-bis[3-(trimethylsilyl)propyl]disiloxane. By the hydrolysis of 30 g of methylphenyl[3-(trimethylsilyl)propyl]silyl chloride we obtained 20 g (74%) of dimethyldiphenyl-1,3-bis[3-(trimethylsilyl)propyl]disiloxane, b.p. 220-225° (2 mm). Found: C 64.22; 64.19; H 9.37; 9.36%. $C_{26}H_{46}Si_4O$. Calculated: C 64.18; H 9.46%.

Diethyldiphenyl-1,3-bis[3-(triethylsilyl)propyl]disiloxane. By the hydrolysis of 50 g of ethylphenyl[3-(triethylsilyl)propyl]silyl chloride we obtained 24 g (52.4%) of diethyldiphenyl-1,3-bis[3-(triethylsilyl)propyl]disiloxane, b.p. 255-260° (2 mm). Found: C 68.20; 68.14; H 10.63; 10.51; Si 18.51; 18.51%. $C_{34}H_{62}Si_4O$. Calculated: C 68.17; H 10.43; Si 18.69%.

Tetrapropyl-1,3-bis[3-(tripropylsilyl)propyl]disiloxane. By the hydrolysis of 25.4 g of dipropyl[3-(tripropylsilyl)propyl]silyl chloride we obtained 11.8 g (51.6%) of tetrapropyl-1,3-bis[3-(tripropylsilyl)propyl]disiloxane, b.p. 230-235° (2 mm). Found: C 67.63; 67.65; H 13.05; 12.99; Si 16.83; 16.82%. $C_{36}H_{82}Si_4O$. Calculated: C 67.28; H 12.78; Si 17.44%.

Tetraethyl-1,3-bis[3-(triethylsilyl)propyl]disiloxane. By the hydrolysis of 57.4 g of diethyl[3-(triethylsilyl)propyl]silyl chloride we obtained 22.5 g (44.5%) of tetraethyl-1,3-bis[3-(triethylsilyl)propyl]disiloxane, b.p. 220-225° (2 mm). Found: C 61.97; 61.99; H 12.51; 12.48; Si 22.32; 22.29%. $C_{26}H_{62}Si_4O$. Calculated: C 62.08; H 12.42; Si 22.31%.

Organosilicon compounds containing silazane-carbon groupings were prepared by the reaction of dialkyl- and alkylphenyl-[3-(trialkylsilyl)propyl]silyl chlorides with ammonia in a medium of dry toluene or ether. The reaction was carried out in a two-necked round-bottomed flask fitted with reflux condenser and tube for the passage of ammonia. Ammonia, dried with solid caustic alkali, was passed over the surface of the solution at the boiling point of the reaction mixture for 20 hours. The ammonium chloride formed was then filtered off. The product was vacuum-fractionated. The constants of the compounds obtained are presented in Table 3.

Dimethyldiphenyl-1,3-bis[3-(trimethylsilyl)propyl]disilazane. Ammonia was passed for 20 hours over a solution of 47.5 g of methylphenyl[3-(trimethylsilyl)propyl]silyl chloride in 200 ml of ether. We obtained 31.5 g (72.1%) of dimethyldiphenyl-1,3-bis[3-(trimethylsilyl)propyl]disilazane, b.p. 220° (2 mm). Found: C 64.48; 64.40; H 9.78; 9.81; Si 22.67%. $C_{26}H_{47}Si_4N$. Calculated: C 64.29; H 9.74; Si 23.10%.

Diethyldiphenyl-1,3-bis[3-(triethylsilyl)propyl]disilazane. Ammonia was passed for 20 hours over a solution of 49 g of ethylphenyl[3-(triethylsilyl)propyl]silyl chloride in 200 ml of dry toluene. We obtained 25 g (42.09%) of diethyldiphenyl-1,3-bis[3-(triethylsilyl)propyl]disilazane, b.p. 270-272° (2 mm). Found: C 68.52; 68.44; H 10.74; 10.74; Si 18.79; 19.61%. $C_{34}H_{62}Si_4N$. Calculated: C 68.34; H 10.72; Si 18.76%.

Tetraethyl-1,3-bis[3-(triethylsilyl)propyl]disilazane. Ammonia was passed for 25 hours over a solution of 69.5 g of diethyl[3-(triethylsilyl)propyl]silyl chloride in 200 ml of dry toluene. We obtained 20 g (32%) of tetraethyl-1,3-bis[3-(triethylsilyl)propyl]disilazane, b.p. 250-252° (2 mm). Found: C 62.23; 62.04; H 12.51; 12.56; Si 21.74; 21.99%. $C_{26}H_{63}Si_4N$. Calculated: 62.27; H 12.57; Si 22.35%.

Tetrapropyl-1,3-bis[3-(tripropylsilyl)propyl]disilazane. Ammonia was passed for 25 hours over a solution of 69.6 g of dipropyl[3-(tripropylsilyl)propyl]silyl chloride in 200 ml of toluene. We obtained 20.5 g (30%) of tetrapropyl-1,3-bis[3-(tripropylsilyl)propyl]disilazane, b.p. 270-272% (2 mm). Found: C 67.45; 67.34; H 12.79; 12.99; Si 16.85; 16.77%. $C_{36}H_{83}Si_4N$. Calculated: C 67.39; H 12.94; Si 17.48%

Organosilicon compounds containing a silthiane-carbon grouping were prepared by the reaction of dialkyl- and alkylphenyl-[3-(trialkylsilyl)propyl]silyl chlorides with hydrogen sulfide in a dry toluene medium. The reaction was carried out in a three-necked flask fitted with stirrer, reflux condenser, dropping funnel, and tube for the passage of hydrogen sulfide. Pyridine was used to bind the hydrogen chloride liberated in the reation. The reaction was carried out at the boiling point of toluene.

A mixture of toluene and pyridine was prepared in the reaction flask, and over a period of 30 minutes it was saturated with hydrogen sulfide. The dialkyl- or alkylphenyl-[3-(trialkylsilyl)propyl]silyl chloride was then added from the dropping funnel. At the end of the reaction pyridine hydrochloride was filtered off. Toluene was distilled off, and the reaction product was vacuum-fractionated in an atmosphere of nitrogen. The properties of the compounds obtained are presented in Table 4.

Dimethyldiphenyl-1,3-bis[3-(trimethylsilyl)propyl]disilthiane. Hydrogen sulfide was passed into a solution of 17.4 g of pyridine and 60 g of methylphenyl[3-(trimethylsilyl)propyl]silyl chloride 100 ml of dry toluene for 19 hours at the boiling point of toluene. We obtained 17.2 g (31%) of dimethyldiphenyl-1,3-bis[3-(trimethylsilyl)propyl] disilthiane, b.p. 275-280° (2 mm). Found: C 62.12; 62.06; H 9.21; 9.27; Si 22.41%. $C_{26}H_{46}Si_4S$. Calculated: C 62.15; H 9.16; Si 22.31%.

Diethyldiphenyl-1,3-bis[3-(triethylsilyl)propyl]disilthiane. Hydrogen sulfide was passed into a solution of 18.5 g of pyridine and 75 g of ethylphenyl[3-(triethylsilyl)propyl]silyl chloride in 200 ml of dry toluene for 30 hours at the boiling point of toluene. We obtained 14.4 g (20.3%) of diethyldiphenyl-1,3-bis[3-(triethylsilyl)propyl]disilthiane, b.p. 290-300° (2 mm). Found: C 66.54; 66.40; H 10.30; 10.16; Si 18.40; 18.38%. $C_{34}H_{62}Si_4S$. Calculated: C 66.56; H 10.16; Si 18.23%.

SUMMARY

Some organosilicon compounds containing siloxane-carbon, silthiane-carbon, and silazane-carbon groupings in their main chains were synthesized, and their physical and chemical properties were determined.

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