4-SILALACTONES AND 4-SILALACTAMS

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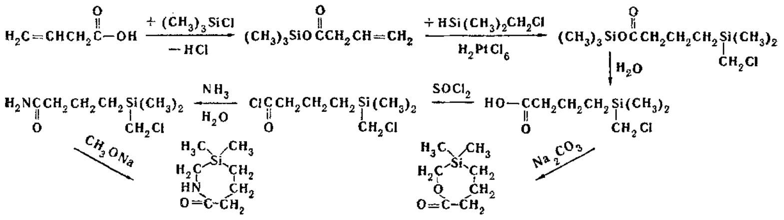
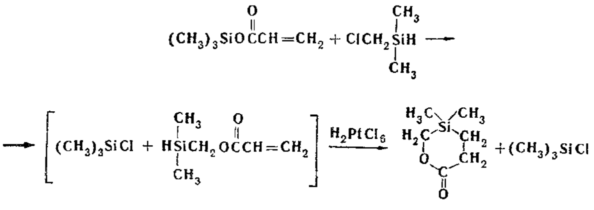
A general method for the preparation of organosilicon lactones and lactams in which a silicon atom attached to two carbon atoms is present in the β-position to the heteroatom O or N has been developed. A new reaction with acyloxysilanes has been observed for a number of silicon compounds containing a chloromethyl radical, which consists in the replacement of the chlorine by the acyl radical.

In a preliminary communication [1], we recently described a method for preparing six-membered silalactones and silalactams starting from methacrylic acid. It has also proved suitable for the synthesis of seven-membered silalactones and silalactams starting from vinylacetic acid:

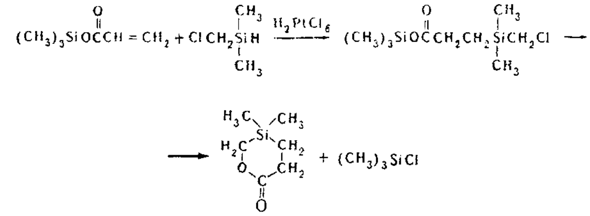


In all the stages of this scheme except the last, the reactions with vinylacetic acid derivatives, like those with methacrylic acid derivatives, take place readily and with high yields.

However, in the cyclization stage, the seven-membered 4-silalactone, unlike the six-membered compound, is formed in low yield (21%). This is due to the fact that under the reaction conditions the partial dimerization and polymerization of the silalactone takes place. At the same time, the seven-membered silalactam is formed in good yield (70%). When acrylic acid was used in the scheme given above, in the first stage a reaction unexpectedly took place which led directly to the formation of a six-membered 3-silalactone.



Since when this reaction was carried out in the absence of Speier's catalyst the bulk of the starting materials was recovered and $(CH_3)_3SiCl$ and $H(CH_3)_2SiCH_2O_2CCH{=}CH_2$ were formed in very small amounts, the synthesis of the 4-silalactones may also take place by a different route.



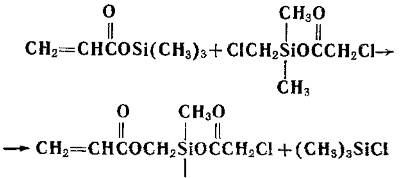
However, whatever may be the route for the formation of this silalactone, it includes the previously unknown reaction of the displacement of $(CH_3)_3SiCl$ from the trimethylsilyl ester of the corresponding acid with cleavage of the C—Cl bond in the α-chloromethylsilane and formation of the $\rangle SiCH_2O-\overset{O}{\overset{\|}{C}}-C\langle$ grouping. This reaction somewhat resembles the transsilylation reaction which we recently observed for silyl ethers and esters [2, 3].

$$R_3SiOR' + ClSiR_3'' \rightleftarrows R_3SiCl + R'OSiR_3'',$$

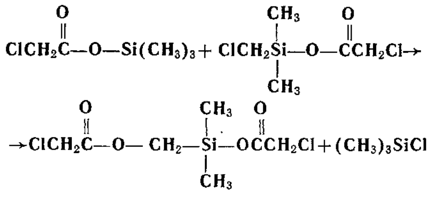
where R' = alkyl or RCO.

However, while the transsilylation reaction takes place with the cleavage of the Si—Cl bond and is reversible, the new reaction takes place with the participation of the C—Cl bond and is probably irreversible.

We have also observed other examples of the occurrence of this reaction:

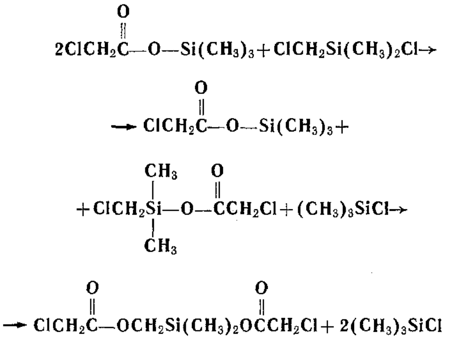


$$CH_2{=}CH\overset{O}{\overset{\|}{C}}OSi(CH_3)_3 + ClCH_2\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}O\overset{O}{\overset{\|}{C}}CH_2Cl \rightarrow CH_2{=}CH\overset{O}{\overset{\|}{C}}OCH_2\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}O\overset{O}{\overset{\|}{C}}CH_2Cl + (CH_3)_3SiCl$$



$$ClCH_2\overset{O}{\overset{\|}{C}}-O-Si(CH_3)_3 + ClCH_2\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}-O-\overset{O}{\overset{\|}{C}}CH_2Cl \rightarrow ClCH_2\overset{O}{\overset{\|}{C}}-O-CH_2-\underset{CH_3}{\underset{|}{\overset{CH_3}{\overset{|}{Si}}}}-O\overset{O}{\overset{\|}{C}}CH_2Cl + (CH_3)_3SiCl$$

The latter reaction also takes place with other starting materials.

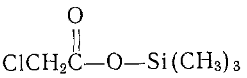
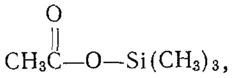


$$2ClCH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-Si(CH_3)_3+ClCH_2Si(CH_3)_2Cl\rightarrow$$

$$\rightarrow ClCH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-Si(CH_3)_3+$$

$$+ClCH_2\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{Si}}-O-\overset{\overset{\displaystyle O}{\|}}{C}CH_2Cl+(CH_3)_3SiCl\rightarrow$$

$$\rightarrow ClCH_2\overset{\overset{\displaystyle O}{\|}}{C}-OCH_2Si(CH_3)_2O\overset{\overset{\displaystyle O}{\|}}{C}CH_2Cl+2(CH_3)_3SiCl$$

In this case, a reaction first takes place at the Si—Cl bond and then at the C—Cl bond. However, the replacement in the last two schemes of the second component by $ClCH_2Si(CH_3)_3$ or by $ClCH_2Si(CH_3)_2H$, and of  $ClCH_2\overset{\overset{\displaystyle O}{\|}}{C}-O-Si(CH_3)_3$ by  $CH_3\overset{\overset{\displaystyle O}{\|}}{C}-O-Si(CH_3)_3$, under otherwise the same conditions, is accompanied by no reaction of any kind. Likewise, there is no reaction between $(CH_3)_3SiO_2CC_2H_5$ and $ClCH_2Si(CH_3)_2O_2CC_2H_5$.

Thus, while the transsilylation reaction is a general one, the possibility of the occurrence of the new reaction depends strongly on the structure of the features of the starting materials.

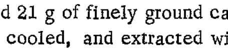
In conclusion, so far as concerns the properties of the lactones, it must be nöted that the six-membered lactone obtained from acrylic acid, in contrast to the lactone synthesized from methacrylic acid, is capable of dimerizing on standing. This capacity for dimerizing is shown by the seven-membered lactone to an even greater extent.

EXPERIMENTAL

A description of the synthesis of six-membered silalactones from methacrylic acid has been published previously [1]. The spectra of these compounds and those described below are given in Figs. 1 and 2.

Trimethylsilyl γ-(chloromethyldimethylsilyl)butyrate $ClCH_2(CH_3)_2Si(CH_2)_3COOSi(CH_3)_3$ (I). Over 2 hr, 26 g (0.16 mole) of $(CH_3)_3SiO_2CCH_2CH{=}CH_2$ was added to a boiling mixture of 18 g (0.16 mole) of $ClCH_2(CH_3)_2SiH$ and 0.2 ml of a 0.1 M solution of H_2PtCl_6 in isopropanol. The temperature of the reaction mixture rose to 160° C. Vacuum distillation yielded 35.5 g (81%) of I with bp 81–82° C (1 mm); n_D^{20} 1.4451; d_4^{20} 0.9777. Found, %: C 45.37, 45.32; H 8.56, 8.72; Si 21.02, 21.01; Cl 13.23, 13.36; MR_D 72.81. Calculated for $C_{10}H_{23}Si_2O_2Cl$, %: C 44.98; H 8.68; Si 21.04; Cl 13.29; MR_D 73.24.

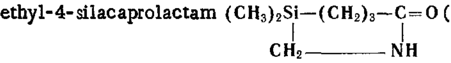
γ-(Chloromethyldimethylsilyl)butyric acid $ClCH_2(CH_3)_2Si(CH_2)_3COOH$ (II). A mixture of 44 g (0.16 mole) of I and 50 ml of water was stirred vigorously with heating to 60° C for 2 hr. The organic layer was separated off, dried, and distilled in vacuum to give 30.7 g (95.6%) of II with bp 116–117° C (1 mm); n_D^{20} 1.4629; d_4^{20} 1.0646. Found, %: C 42.89, 43.34; H 7.85, 7.61; Si 14.42, 14.50; Cl 18.02, 18.28; MR_D 50.6. Calculated for $C_7H_{15}SiO_2Cl$, %: C 43.16; H 7.76; Si 14.42; Cl 18.23; MR_D 50.38.

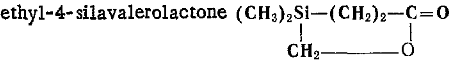
Si, Si-Dimethyl-4-silacaprolactone  $\begin{array}{l}(CH_3)_2Si-(CH_2)_3-C=O\\ \qquad\;|\qquad\qquad\qquad|\\ \quad\; CH_2\text{————}O\end{array}$ **(III).** A mixture of 33 g (0.17 mole) of II and 21 g of finely ground calcined sodium carbonate was heated for 1 hr, cooled, and extracted with ether. The ether was driven off from the extracts and the residue was distilled in vacuum. The yield of III was 5.7 g (21.2%). Bp 82–84° C (2 mm); n_D^{20} 1.4728; d_4^{20} 1.0238. Found, %: C 52.85, 52.94; H 9.00, 8.89; Si 17.48, 17.91; MR_D 43.30. Calculated for $C_7H_{14}SiO_2$, %: C 53.13; H 8.92; Si 17.70; MR_D 43.83.

We also obtained 2 g (7.5%) of dimer III with bp 160–162° C (2.5 mm), solidifying in the receiver into a colorless crystalline mass; mp 96–97° C. Found, %: C 53.18, 53.14; H 8.95, 8.79, Si 18.02, 18.16, mol. wt. 274. Calculated for $C_{14}H_{28}Si_2O_2$, %: C 53.13; H 8.91; Si 17.70; mol. wt. 316.53.

γ-(Chloromethyldimethylsilyl)butyroyl chloride $ClCH_2(CH_3)_2Si(CH_2)_3COCl$ (IV). A mixture of 8 g (0.04 mole) of **II** and 4.9 g (0.04 mole) of thionyl chloride was heated in the water bath for 1 hr and then distilled in vacuum. This gave 8.3 g (94%) of IV with bp 99–100° C (4 mm); n_D^{20} 1.4700; d_4^{20} 1.0971. Found, %: C 39.84, 39.52; H 6.67, 7.04; Si 12.89; Cl 33.05; 32.86; MR_D 53.77. Calculated for $C_7H_{14}SiCl_2O$, %: C 39.42; H 6.61; Si 13.17; Cl 33.29; MR_D 54.28.

γ-(Chloromethyldimethylsilyl)butyramide $ClCH_2(CH_3)_2Si(CH_2)_3CONH_2$ (V). Over 1 hr, 53 g (0.25 mole) of IV was added to 500 ml of a saturated aqueous solution of ammonia. The yield of V was 34.25 g (71%), bp 146–148° C (2 mm). Colorless liquid crystallizing on standing (mp 26–27° C). Found, %: C 43.16, 43.20; H 8.11, 8.35; Si 14.33, 14.03; Cl 17.71, 17.70. Calculated for $C_7H_{16}SiONCl$, %: C 43.39; H 8.32; Si 14.49; Cl 18.3.

Si, Si-Dimethyl-4-silacaprolactam  $\begin{array}{l}(CH_3)_2Si-(CH_2)_3-C=O\\ \qquad\;|\qquad\qquad\qquad|\\ \quad\; CH_2\text{————}NH\end{array}$ **(VI).** A solution of 2.06 g of sodium methoxide in 10 ml of absolute methanol was added to 7.4 g of V. The reaction mixture was boiled for 2 hr. The precipitate of sodium chloride that separated out was filtered off, and the methanol was distilled off from the filtrate. Vacuum distillation of the residue yielded 4.07 g (70%) of VI with bp 134–138° C (2 mm); n_D^{20} 1.4761; d_4^{20} 0.9938. Found, %: C 52.90, 52.90; H 10.09, 10.03; N 7.99, 8.00; MR_D 44.77. Calculated for $C_7H_{15}SiNO$, %: C 53.45; H 9.61; Si 17.85; N 8.9; MR_D 45.55.

Si, Si-Dimethyl-4-silavalerolactone  $\begin{array}{l}(CH_3)_2Si-(CH_2)_2-C=O\\ \qquad\;|\qquad\qquad\quad|\\ \quad\; CH_2\text{———}O\end{array}$ **(VII).** Over 1 hr 30 min, 27 g (0.05 mole) of $(CH_3)_3SiO_2CCH{=}CH_2$ was added to a boiling mixture of 21 g (0.05 mole) of $ClCH_2(CH_3)_2SiH$ and 0.2 ml of a 0.1 M solution of H_2PtCl_6 in isopropanol. The temperature of the reaction mixture first rose to 120° C and then fell to 110° C. It was boiled at 110° C for another 2 hr and was then distilled in vacuum. The yield of VII was 10 g (50%). Bp 66–68° C (3 mm); n_D^{20} 1.4555; d_4^{20} 1.0157. (The substance was subjected to additional purification by redistillation over a small amount of Na_2CO_3.) Found, %: C 49.77, 50.16; H 8.28, 8.49; Si 19.91, 19.69; MR_D 38.5. Calculated for $C_6H_{12}SiO_2$, %: C 49.99; H 8.39; Si 19.48; MR_D 39.20.

The substance obtained dimerized on standing (mp 76–77.5° C; mol. wt. 288.28, found mol. wt. 313.32). A 9.6-g quantity (48%) of $(CH_3)_3SiCl$ condensed in a trap. We also obtained 11.6 g of a fraction with bp 85–104° C (3 mm), probably containing $ClCH_2Si(CH_3)_2CH_2CH_2COOSi(CH_3)_3$ and a small amount of the lactone. Found, %: Cl 12.2, 12.3. Calculated for $C_9H_{21}Si_2O_2Cl$, %: Cl 14.05.

Chloroacetoxy(chloroacetoxymethyl)dimethylsilane—$ClCH_2COOCH_2(CH_3)_2SiO_2CCH_2CL$ (VIII). a) A 250-ml Claisen flask was charged with 100.4 g (0.7 mole) of $ClCH_2Si(CH_3)_2Cl$ and 115 g (0.7 mole) of $(CH_3)_3SiO_2CCH_2Cl$. On boiling, 67.6 g (91%) of $(CH_3)_3SiCl$ distilled off from the reaction mixture over 4 hr. Vacuum distillation of the residue yielded: 1) 76 g (54%) of $ClCH_2(CH_3)_2SiO_2CCH_2Cl$ with bp 109° C (6 mm); n_D^{20} 1.4549; d_4^{20} 1.2103. Found, %: C 29.69, 29.38; H 5.10, 4.87; Si 14.08, Cl 35.45; MR_D 45.29. Calculated for $C_5H_{10}SiO_2Cl_2$, %: C 29.58; H 5.03; Si 13.95; Cl 35.25; MR_D 45.07. 2) A 39.2 g quantity (22.2%) of **VIII** with bp 129° C (1 mm), n_D^{20} 1.4650; d_4^{20} 1.2844. Found, %: C 32.12, 32.21; H 4.66, 4.77; Si 10.63, Cl 27.23, 27.13; MR_D 55.83. Calculated for $C_7H_{12}SiO_4Cl_2$, %: C 32.45; H 4.63; Si 10.83; Cl 27.37; MR_D 56.33.

b) Under the conditions of the preceding experiment, when 8.5 g (0.05 mole) of $(CH_3)_3SiO_2CCH_2Cl$ and 10 g (0.05 mole) of $ClCH_2(CH_3)_2SiO_2CCH_2Cl$ were boiled, 4.4 g of $(CH_3)_3SiCl$ and 9.2 g (79.5%) of **VIII** with bp 129° C (1 mm), n_D^{20} 1.4642, were obtained.

1, 2-Bis(chloroacetoxymethyl)tetramethyldisiloxane $[ClCH_2COOCH_2Si(CH_3)_2]_2O$ (IX). Hydrolysis of VIII. A mixture of 29.7 g

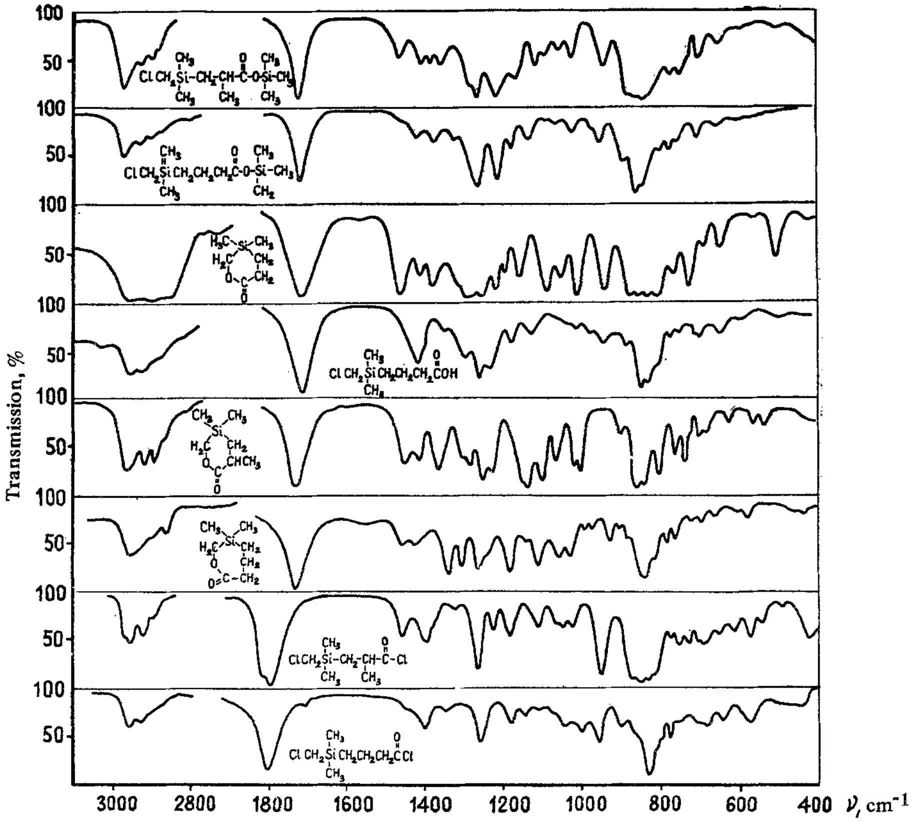

100
50
Transmission, %
3000
2800
1800
1600
1400
1200
1000
800
600
400
ν, cm⁻¹
ClCH₂Si(CH₃)₂-CH₂-CH(CH₃)-C(O)-O-Si(CH₃)₃
ClCH₂Si(CH₃)₂CH₂CH₂CH₂C(O)-O-Si(CH₃)₃
ClCH₂Si(CH₃)₂CH₂CH₂CH₂C(O)OH
ClCH₂Si(CH₃)₂-CH₂-CH(CH₃)-C(O)-Cl
ClCH₂Si(CH₃)₂CH₂CH₂CH₂C(O)Cl

Fig. 1

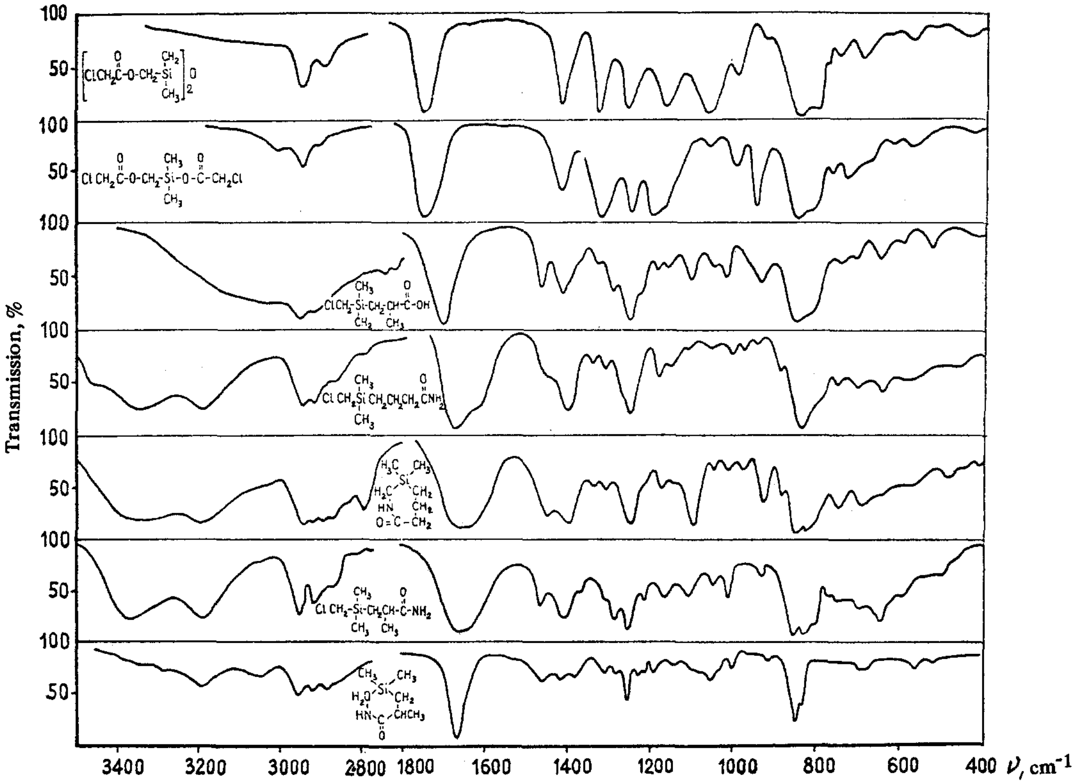

Transmission, %
100
50
[ClCH₂C(O)-O-CH₂-Si(CH₂)(CH₃)]₂O
ClCH₂C(O)-O-CH₂-Si(CH₃)₂-O-C(O)-CH₂Cl
ClCH₂-Si(CH₃)(CH₂)-CH₂-CH(CH₃)-C(O)-OH
ClCH₂Si(CH₃)₂CH₂CH₂CH₂C(O)NH₂
H₃C, CH₃, Si, H₂C, CH₂, HN, CH₂, O=C-CH₂
ClCH₂-Si(CH₃)₂-CH₂CH(CH₃)-C(O)-NH₂
CH₃, CH₃, Si, H₂C, CH₂, HN-C(O)-CHCH₃
3400
3200
3000
2800
1800
1600
1400
1200
1000
800
600
400
ν, cm⁻¹

Fig. 2

(0.116 mole) of **VIII** and 50 ml of water was stirred vigorously with heating to 80° C for 2 hr. The organic layer was separated off, dried, and distilled in vacuum to give 15.2 g (75%) of **IX** with bp 132.5–133° C (1 mm); n_D^{20} 1.4549, d_4^{20} 1.1764. Found, %: C 34.65, 34.67; H 5.71, 5.79; Si 16.50; Cl 20.7, 20.6; MR_D 79.60. Calculated for $C_{10}H_{20}Si_2O_5Cl_2$, %: C 34.58; H 5.80; Si 16.17; Cl 20.44; MR_D 79.65.

The aqueous layer yielded 5.3 g of chloroacetic acid with mp 56° C.

REFERENCES

1. V. F. Mironov and N. S. Fedotov, KhGS [Chemistry of Heterocyclic Compounds], 2, 453, 1966.
2. V. F. Mironov and N. S. Fedotov, KhGS [Chemistry of Heterocyclic Compounds], 3, 179, 1967.
3. V. F. Mironov, N. S. Fedotov, and V. L. Kozlikov, KhGS [Chemistry of Heterocyclic Compounds], 4, 354, 1968.

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