2-SILALACTONES

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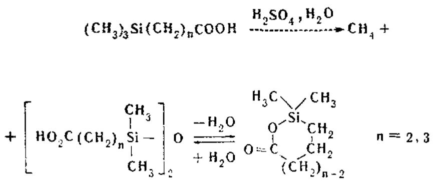
Several methods have been developed for the synthesis of 2-silalactones in which the silicon atom is bound to an oxygen atom. Some chemical reactions of these compounds have been studied.

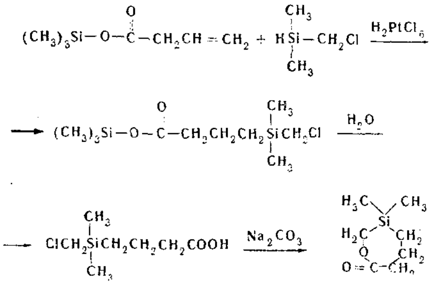
Silalactones of the type $(CH_3)_2\overline{SiO_2C(CH_2)_nCH_2}$ (n = = 1, 2) have been obtained by the action of concentrated sulfuric acid on trimethylsilylpropionic and trimethylsilylbutyric acids, respectively [1–3]:


(1)

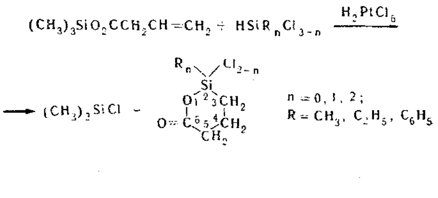
When these acids were vinylated under severe conditions over ZnO_2, a methyl group split out to a small degree, leading to the formation of similar lactones [4].

In all cases, the initial trialkylsilyl-substituted carboxylic acids were obtained by a multistage organometallic synthesis and were therefore comparatively poorly accessible substances [5–7].

We have recently reported [8, 9] methods for the synthesis of organosilicon compounds of a new type (3-silalactones) containing in the ring a silicon atom bound to carbon atoms:


(2)

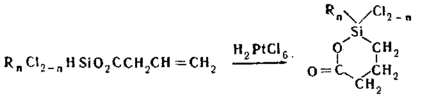
We subsequently observed (see the preliminary communications [10–12]) that the replacement of $ClCH_2SiH(CH_3)_2$ in this scheme by any other hydrosilane containing even a single chlorine atom attached to the silicon atom leads directly to the formation of 2-silalactones, in which the silicon atom is bound to an oxygen atom.


(3)

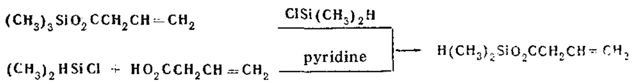
It may be assumed that the formation of the 2-silalactone takes place in two stages: first there is a previously unknown transsilylation reaction*

$$(CH_3)_3SiO_2CCH_2CH=CH_2 + HSiR_nCl_{3-n} \rightleftharpoons HR_nCl_{2-n}SiO_2CCH_2CH=CH_2 + (CH_3)_3SiCl$$

and then the hydrosilyl vinylacetate formed cyclizes in the presence of H_2PtCl_6 to form the silalactone:


(4)

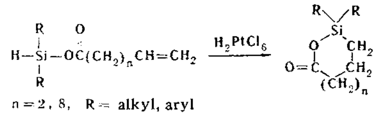
In actual fact, we have succeeded in carrying out the reaction separately. We have established that the transsilylation is an equilibrium reaction that takes place when the starting materials are boiled. The formation under these conditions of dimethylsilyl vinylacetate was shown by its independent synthesis.



$$\left.\begin{array}{l}(CH_3)_3SiO_2CCH_2CH=CH_2 \xrightarrow{ClSi(CH_3)_2H} \\ (CH_3)_2HSiCl + HO_2CCH_2CH=CH_2 \xrightarrow{\text{pyridine}}\end{array}\right] \rightarrow H(CH_3)_2SiO_2CCH_2CH=CH_2$$

In the presence of H_2PtCl_6, the dimethylsilyl vinylacetate obtained by either method cyclizes into Si-dimethyl-2-silavalerolactone (see reaction 4).

The cyclization of other hydrosilyl esters of unsaturated acids in the presence of Speier's catalyst is a fairly simple and general method for obtaining 2-silalactones [11, 12].


(5)

For example, we have succeeded in cyclizing dimethylsilyl undecylenate to give a 13-membered silalactone (n = 8).

At the same time, it has been found that it is impossible to effect the cyclization of dimethylsilyl acry-

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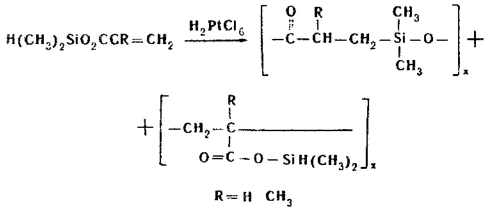
*The transsilylation reaction takes place readily in the absence of any catalysts whatever and is general for various silyl esters of carboxylic acids. We have established that the transsilylation reaction also takes place in a number is silyl ethers [10, 11, 13].

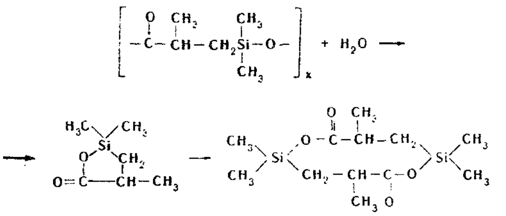
$$R_3SiO_2CR' + ClSiR''_3 \rightleftharpoons R''_3SiO_2CR' + R_3SiCl$$
$$R_3SiOR + ClSiR''_3 \rightleftharpoons R''_3SiOR' + R_3SiCl$$

late and methacrylate (n = 0), since under the reaction conditions they readily polymerize.



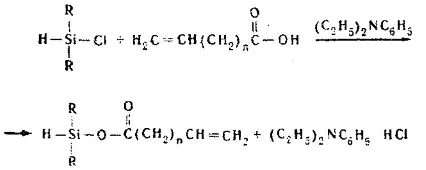
(6)

However, the hydrolysis of the polymeric products formed in the attempted cyclization of dimethylsilyl methacrylate leads to a five-membered lactone which rapidly changes into a ten-membered dilactone.



(7)

All the initial dialkylsilyl esters of unsaturated acids were obtained readily and in high yields by the reaction of dialkylchlorosilanes and the corresponding unsaturated acids in the presence of a hydrogen chloride acceptor [10,11].

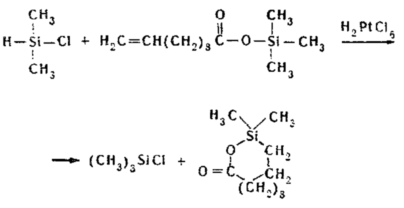


$$H-\underset{R}{\overset{R}{Si}}-Cl + H_2C{=}CH(CH_2)_n\overset{O}{\overset{\|}{C}}-OH \xrightarrow{(C_2H_5)_2NC_6H_5} H-\underset{R}{\overset{R}{Si}}-O-\overset{O}{\overset{\|}{C}}(CH_2)_nCH{=}CH_2 + (C_2H_5)_2NC_6H_5\ HCl$$

(8)

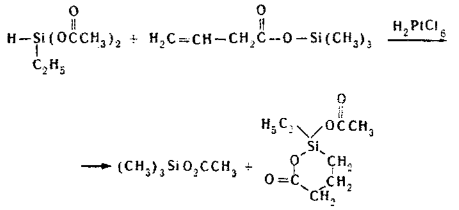
However, this method does not make it possible to obtain chlorohydrosilyl esters of unsaturated acids, since all the chlorine atoms bound to silicon are replaced by acyl groups.

A more universal method for obtaining silalactones proved to be reaction (3). Its performance in the presence of H_2PtCl_6 leads to an almost quantitative yield of the 2-silalactone, since the equilibrium in the transsilylation reaction is shifted almost completely to the right as a consequence of the cyclization of the hydrosilyl ester of the unsaturated acid to the 2-silalactone. This route has enabled us to obtain six-membered 2-silalactones with any substituents on the silicon atom, including halogen atoms (see Eq. 3). We have also succeeded in synthesizing a 13-membered lactone by this method in good yield.



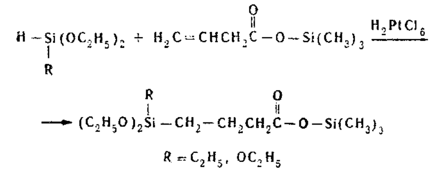
(9)

The use of diacetoxyethylsilane in this reaction has enabled us to obtain a silalactone with an acetoxy group on the silicon atom.



(10)

However, the addition of triethoxy- and alkyldiethoxysilanes to trimethylsilyl vinylacetate is not accompanied by the formation of silalactones, addition products being formed exclusively.

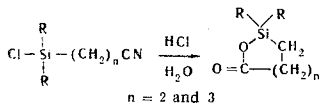


$$H-\underset{R}{Si}(OC_2H_5)_2 + H_2C{=}CHCH_2\overset{O}{\overset{\|}{C}}-O-Si(CH_3)_3 \xrightarrow{H_2PtCl_6} (C_2H_5O)_2\overset{R}{Si}-CH_2-CH_2CH_2\overset{O}{\overset{\|}{C}}-O-Si(CH_3)_3$$

$R = C_2H_5, OC_2H_5$

(11)

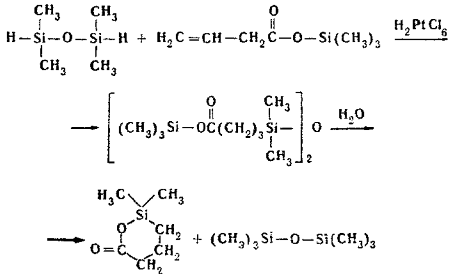
We have found yet another route to the 2-silalactones—the hydrochloric acid hydrolysis of cyanoalkyl-containing chlorosilanes. Thus, the hydrolysis of dialkyl(cyanoalkyl)chlorosilanes forms the corresponding 2-silalactones.



(12)

However, this method permits the preparation only of 2-silalactones containing alkyl radicals on the silicon atom, since the hydrochloric acid hydrolysis of alkyl(cyanoalkyl)dichloro- and (cyanoalkyl)trichlorosilanes leads to the formation of polymeric products.

Finally, we have obtained 2-silalactones by the addition of tetramethyldisiloxane to trimethylsilyl vinylacetate in the presence of Speier's catalyst with subsequent hydrolysis of the hydrosilylation product.

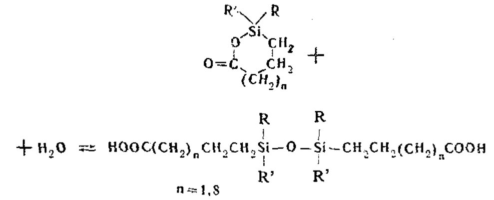


(13)

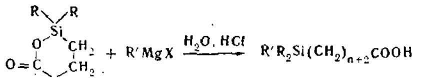
Of the chemical properties of the silalactones, only their capacity for undergoing hydrolysis to siloxanedicarboxylic acids has been reported in the literature [2,14].

The 2-silalactones that we synthesized also undergo hydrolysis unusually readily at the Si—O bond, forming the corresponding dicarboxylic acids in high yields;

on vacuum distillation, these dicarboxylic acids readily lose water again and are reconverted into the initial silalactones.

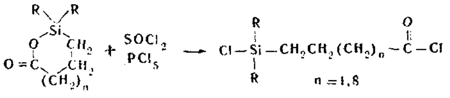

(14)

The 2-silalactones react with Grignard reagents at the Si—O bond, forming high yields of trialkylsilyl-substituted acids:


(15)

This method of synthesis of these acids is shorter than those previously known.

The action on the 2-silalactones of thionyl chloride or other chlorinating agents forms the chlorides of silyl-substituted carboxylic acids in high yields.


(16)

These acid chlorides, in their turn, readily undergo hydrolysis, with the formation of the corresponding dicarboxylic acids.

The 2-silalactones are viscous transparent liquids with molecular weights varying with time (they readily dimerize, trimerize, etc.). In their IR spectra, the stretching vibrations of the carbonyl group appear in the 1710–1750-cm^{-1} region and those of the Si—O bond in the 1080–1100-cm^{-1} region.

EXPERIMENTAL

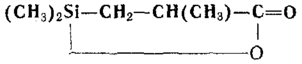
Trimethylsilyl undecylenate $(CH_3)_3SiOOC(CH_2)_8CH{=}CH_2$ (I). Over 3 hr, with stirring, 58.1 g (0.31 mole) of undecylenic acid was added to a mixture of 34.2 g (0.31 mole) of trimethylchlorosilane, 38.3 g (0.31 mole) of dimethylaniline, and 500 ml of absolute ether. The precipitate of dimethylaniline hydrochloride was filtered off and washed with absolute ether. The solvent was driven off from the ethereal mother solution, and the residue was distilled in vacuum. The yield of I was 57.9 g (71.2%); bp 96–100° C (2 mm); n_D^{20} 1.4364; d_4^{20} 0.8754. Found, %: C 65.63, 66.02; H 10.96, 10.93; Si 11.35, 11.56; MR_D 76.58. Calculated for $C_{14}H_{28}SiO_2$, %: C 65.56; H 11.00; Si 10.95; MR_D 76.98.

Dimethylsilyl undecylenate $H(CH_3)_2SiOOC(CH_2)_8CH{=}CH_2$ (II). Under the conditions of the preceding experiment, 21.6 g of dimethylchlorosilane, 27.1 g of dimethylaniline, and 41.1 g of undecylenic acid yielded 35.3 g (65.5%) of II with bp 94–95° C (2 mm); n_D^{20} 1.4391; d_4^{20} 0.8821. Found, %: Si 10.5, 10.73; MR_D 72.60. Calculated for $C_{13}H_{26}SiO_2$, %: Si 11.58; MR_D 72.20.

Si-Dimethyl-2-silalaurolactone $(CH_3)_2\overset{\text{—O—}}{Si{-}(CH_2)_{10}C{=}O}$ (III). A. A 600-ml two-necked flask fitted with a reflux condenser and dropping funnel was charged with 300 ml of dry benzene and 0.2 ml of a 0.1 M solution of H_2PtCl_6 in isopropanol. Over 2 hr 30 min, 33 g (0.136 mole) of dimethylsilyl undecylenate was added to the benzene solution heated to the boil. The benzene was driven off and the residue was distilled in vacuum. The yield of III with bp 148–149° C (3 mm) was 21.5 g (65%). Viscous colorless oil, n_D^{20} 1.4656; d_4^{20} 0.9559. Found, %: C 64.49, 64.29; H 10.97, 10.79; Si 10.95, 11.01; MR_D 70.20. Calculated for $C_{13}H_{26}SiO_2$, %: C 64.40; H 10.81; Si 11.58; MR_D 70.94.

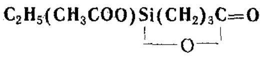
B. A 50-ml three-necked flask fitted with a reflux condenser, dropping funnel, and thermometer was charged with 7.3 g (0.075 mole) of dimethylchlorosilane, and 2–3 drops of a 0.1 M solution of H_2PtCl_6 in isopropanol was added. Over 2 hr 30 min, 20 g (0.075 mole) of I was added to the boiling solution. Vacuum distillation yielded 8.5 g (45%) of III with bp 134–137° C (1.5 mm); n_D^{20} 1.4652. Other substances isolated were $(CH_3)_3SiCl$, the initial dimethylchlorosilane, and the ester I. Reactions A and B with derivatives of vinylacetic acid have been described previously [10].

2, 2, 3-Trimethyl-2-silabutyrolactone


$$(CH_3)_2Si{-}CH_2{-}CH(CH_3){-}C{=}O \quad \text{(ring closed through O)}$$
(IV)

A 1-*l* two-necked flask fitted with a reflux condenser and dropping funnel was charged with 500 ml of dry benzene and 0.2 ml of a 0.1 M solution of H_2PtCl_6 in isopropanol. Over 3 hr, 65 g (0.45 mole) of dimethylsilyl methacrylate [10] was added to the solution heated to the boil. The bulk of the benzene was distilled off from the reaction mixture, 300 ml of water was added, and then it was boiled for 2 hr. The benzene layer was separated from the aqueous layer and dried. The benzene was driven off and the residue was distilled in vacuu. The yield of IV with bp 77–78° C (1 mm) was 37.2 g (57.2%). Colorless viscous oil with n_D^{20} 1.4540, crystallizing on standing; mp 67–67.5° C. Found, %: C 49.95, 50.14; H 8.60, 8.60; Si 19.55, 19.82. Calculated for $C_6H_{12}SiO_2$, %: C 49.96; H 8.38; Si 19.47.

2-Acetoxy-2-ethyl-2-silavalerolactone


$$C_2H_5(CH_3COO)\underbrace{Si(CH_2)_3C}_{O}{=}O$$
(V)

A 50-ml three-necked flask fitted with a reflux condenser, thermometer, and dropping funnel was charged with 2–3 drops of H_2PtCl_6 solution and 5 ml of a mixture obtained from 18 g (0.1 mole) of diacetoxyethylsilane and 16 g (0.1 mole) of trimethylsilyl vinylacetate. The remainder of this mixture was added to the reaction mixture, heated to the boil, over 1 hr. Distillation of the reaction product gave 14.1 g (70%) of V in the form of a colorless viscous oil with bp 123–125° C (2 mm); n_D^{20} 1.4610; d_4^{20} 1.1493. Found, %: C 47.37, 47.08; H 7.89, 7.41; Si 13.09, 13.51; MR_D 48.30. Calculated for $C_8H_{14}SiO_4$, %: C 47.49; H 6.97; Si 13.88; MR_D 48.29.

Trimethylsilyl γ-(diethoxyethylsilyl)-n-butyrate

$$C_2H_5(C_2H_5O)_2Si(CH_2)_3COOSi(CH_3)_3 \qquad \text{(VI)}$$

Fifteen grams (0.1 mole) of diethoxyethylsilane heated to 90° C was treated with 0.1 ml of a 0.1 M solution of H_2PtCl_6 in isopropanol and then 16 g (0.1 mole) of trimethylsilyl vinylacetate was added dropwise over 2 hr. The reaction mixture was boiled for another 1 hr at 174° C and was then distilled in vacuum. The yield of VI with bp 110–115° C (3 mm), n_D^{20} 1.4249, d_4^{20} 0.9438, was 22.3 g (73%). Found, %: C 50.69, 50.63; H 9.95, 9.89; Si 17.87; MR_D 83.01. Calculated for $C_{13}H_{30}Si_2O_2$, %: C 51.06; H 9.86; Si 18.32; MR_D 83.99.

Trimethylsilyl γ-(triethoxysilyl)-n-butyrate

$$(C_2H_5O)_3Si(CH_2)_3COSi(CH_3)_3 \qquad \text{(VII)}$$

To 10.5 g (0.064 mole) of triethoxysilane heated to the boil was added 0.1 ml of a 0.1 M solution of H_2PtCl_6 in isopropanol, and then 10 g (0.064 mole) of trimethylsilyl vinylacetate was run in over 1 hr 30 min. At the end of this process the temperature had risen to 150° C. Vacuum distillation yielded 17.5 g (85.5%) of VII with bp 105–107° C (2 mm); n_D^{20} 1.4179; d_4^{20} 0.9615. Found, %: C 48.55, 48.64; H 9.45, 9.48; Si 17.08, 16.86; MR_D 84.51. Calculated for $C_{13}H_{30}Si_2O_4$, %: C 48.41; H 9.37; Si 17.41; MR_D 84.81.

Bis(trimethylsilyl) ester of 1, 1, 3, 3-tetramethyl-1, 3-bis(3-carboxypropyl)disiloxane $\{(CH_3)_2[(CH_3)_3SiOOC(CH_2)_3]Si\}_2O$ (VIII). A 50-ml three-necked flask fitted with a reflux condenser, thermometer, and dropping funnel was charged with 13 g (0.1 mole) of tetramethyldisiloxane and 0.1 ml of a 0.1 M solution of H_2PtCl_6 in isopropanol. Over 2 hr, 31.6 g (0.2 mole) of trimethylsilyl vinylacetate was added to the mixture heated to the boil. The temperature at the end of the addition was 206° C. Vacuum distillation yielded 32.7 g (73%) of VIII with bp 126–128° C (1 mm); n_D^{20} 1.4320; d_4^{20} 0.9384. Found, %: C 47.89, 48.10; H 9.57, 9.55; Si 24.32, 24.43; MR_D 124.6. Calculated for $C_{18}H_{42}Si_4O_5$, %: C 47.84; H 9.37; Si 24.86; MR_D 125.3.

Hydrolysis of VIII. A 100-ml three-necked flask fitted with a stirrer, condenser, and dropping funnel was charged with 50 ml of water and 20 g (0.044 mole) of **VIII**. With heating and stirring, 5 ml of concentrated H_2SO_4 was added to the reaction mixture over 3 hr. The organic layer was separated off, and the acidic aqueous layer was extracted with ether. The ethereal extracts were combined with the organic layer and dried over $MgSO_4$. The ether was driven off and the residue was distilled in vacuum. The yield of Si-dimethyl-2-silavalerolactone with bp 77–79° C (2 mm), n_D^{20} 1.4630, was 11.5 g (84.3%). Literature data [10]: bp 69–70° C (1.5 mm); n_D^{20} 1.4640; d_4^{20} 1.0496.

1,3-Bis(10-carboxydecyl)-1,1,3,3-tetramethyldisiloxane

$$\{(CH_3)_2[HOOC(CH_2)_{10}]Si\}_2O \qquad (IX)$$

A mixture of 5.8 g (0.024 mole) of Si-dimethyl-2-silalaurolactone and 20 ml of water was stirred vigorously. After two days, the crystals that had deposited were filtered off and dried. The yield of **IX** with mp 55–56° C was 5 g (83.3%). Found, %: H_{act} 0.42, 0.39. Acid No.: 217.35, 221.6. Calculated, %: H_{act} 0.41; acid No. 222.

1,3-Bis(3-carboxypyropyl)-1,1,3,3-tetramethyldisiloxane

$$[(CH_3)_2(HOOCCH_2CH_2CH_2)Si]_2O \qquad (X)$$

A mixture of 15 g (0.1 mole) of Si-dimethyl-2-silavalerolactone and 40 ml of water was vigorously stirred. On standing, the liquid organic layer crystallized. The crystals were filtered off and dried. This gave 12 g (79%) of X with mp 46–47° C. Found, %: H_{act} 0.65, 0.66. Acid No. 356.6, 358.8. Calculated, %: H_{act} 0.68; acid No. 365.8. Literature data [3]: mp 49–49.5° C.

γ-(Ethyldimethylsilyl)-n-butyric acid $(CH_3)_2C_2H_5Si(CH_2)_3COOH$ (XI). A 2-*l* three-necked flask fitted with a stirrer, reflux condenser, and dropping funnel was charged with a solution of 92.4 g (0.64 mole) of Si-dimethyl-2-silavalerolactone in 200 ml of absolute ether and, with stirring, an ethereal solution of ethylmagnesium bromide (prepared from 19.1 g (0.79 g-atom) of magnesium, 85.6 g (0.79 mole) of ethyl bromide, and 480 ml of absolute ether) was added over 1 hr 30 min. The reaction mixture was boiled in the water bath for half an hour, and then 500 ml of 17% hydrochloric acid was added. The ethereal layer was separated off, and the acid layer was thrice extracted with ether. The ethereal extracts were combined with the ethereal layer and dried over calcium chloride. The ether was distilled off, and the residue was distilled in vacuum to give 92.7 g (83.1%) of **XI** with bp 98–100° C (2 mm); n_D^{20} 1.4478; d_4^{20} 0.9176; MR_D 50.83; calc. 50.41. Acid No.: 321.45; calc.: 321.88.

Acid hydrolysis of γ-cyanopropyl(dimethyl)chlorosilane. A 200-ml three-necked flask fitted with a reflux condenser, thermometer, and dropping funnel was charged with 61 g (0.38 mole) of γ-cyanopropyl-(dimethyl)chlorosilane and 47 ml of concentrated HCl. The reaction mixture was heated for an hour at 50–80° C with periodic stirring. A white precipitate deposited which rapidly dissolved when 50 ml of water was added. The solution was extracted with ether. The ethereal extracts were combined, washed with water, and dried over $MgSO_4$. The ether was driven off and the residue was distilled in vacuum to give 36.6 g (67.5%) of Si-dimethyl-2-silavalerolactone with bp 98° C (3 mm); n_D^{20} 1.4630; d_4^{20} 1.0515. Literature data [10]: bp 69–70° C (1.5 mm); n_D^{20} 1.4640; d_4^{20} 1.0495.

4-Dimethyldichlorosilyl-n-butyryl chloride $Cl(CH_3)_2Si(CH_2)_3COCl$ (XII). A 100-ml two-necked flask fitted with a reflux condenser and dropping funnel was charged with 50.8 g (0.34 mole) of Si-dimethyl-2-silavalerolactone, and 41.3 g (0.34 mole) of thionyl chloride was added over 1 hr. The reaction mixture was heated at 60–80° C for 2 hr and was then distilled in vacuum to give 58.4 g (85.6%) of **XII** with bp 95–97° C (21 mm); n_D^{20} 1.4592; d_4^{20} 1.1268. Found, %: C 36.68, 36.34; H 6.18, 5.89; Cl 35.80, 35.80; MR_D 48.50. Calculated for $C_6H_{12}SiOCl_2$, %: C 36.19; H 6.07; Si 14.10; Cl 35.60; MR_D 48.33.

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