Synthesis of Mono- and Di-Functional Silicon Containing Derivatives of Long Chain Fatty Acid Esters

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ABSTRACT

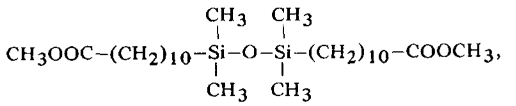
The addition products of some monochlorosilanes to methyl oleate and undecanoate were hydrolyzed and condensed to yield the corresponding difunctional disiloxanes, which were, in turn, transformed by alkaline hydrolysis or reduction to the corresponding diacids or diols. The addition products of dichlorosilanes gave on hydrolysis and condensation cyclosiloxanes but not linear polymers, as shown by mol wt data and IR spectra, while the corresponding addiiton products of trichlorosilances gave on similar treatment rubbery cross-linked polymers. In contrast to the silanol intermediates, obtained on hydrolysis of methylchlorosilanes, which condensed easily to the corresponding disiloxanes, the corresponding bulkier phenyl chlorosilanes gave stable silanols which showed a lower tendency to condense. Some mono- and di-alkoxy, phenoxy, and acetoxy silyl derivatives of the long chain fatty acid esters also were synthesized.

INTRODUCTION

Recently, we have investigated the addition reaction of various chlorosilanes to esters of long chain unsaturated fatty acids (1), such as oleic and linoleic, which are major constituents of various vegetable oils, as well as 10-undecenoic acid. Silicon containing long chain fatty acid derivatives are, thereby, obtained which contain one or more reactive silicone-chlorine bond, e.g.:

$$CH_2{=}CH{-}(CH_2)_8{-}COOCH_3 + Me_2ClSiH \xrightarrow{cat} Me_2ClSi{-}C_{10}H_{20}COOCH_3$$

In this work, we describe some reactions of the above mentioned compounds leading to synthesis of various long chain di-functional disiloxanes, e.g.:



$$CH_3OOC{-}(CH_2)_{10}{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}O{-}\underset{CH_3}{\overset{CH_3}{Si}}{-}(CH_2)_{10}{-}COOCH_3,$$

as well as the corresponding diacids, dichlorides, and diols.

In the literature, only a few such di-functional derivatives were reported such as tetramethyl-1,3-bis(p-carboxyphenyl), disiloxane (2), and some analogues (3).

The di-functional disiloxanes are suitable monomers which may enter polycondensation reactions. They also may have some use as plasticizers and additives to polymers. In this manner, the possibilities of utilization of some vegetable oil derivatives are broadened.

EXPERIMENTAL PROCEDURES

IR spectra were taken on a 257 Perkin-Elmer instrument. In the analytical results for carbon, hydrogen, the observed values differed from the calculated values by not more than ±0.4%.

The starting chlorosilyl derivatives were prepared as before (1). The new di-functional disiloxanes synthesized are listed in Table I. Some typical procedures for their synthesis are given below.

1,3-Bis(10-carbomethoxydecyl)Tetramethyldisiloxane

A mixture of methyl 11-(methyldichlorosilyl) undecanoate (4.0 g, 0.014 mole) and water (50 ml) was stirred for 1 hr at 25 C. The oily product was extracted with ether; the ethereal extract was washed thoroughly with water and dried over magnesium sulfate. The ether was evaporated and the oily diester (I in Table I) was obtained in 94% yield (Table I). IR: 1750(C=O), 1250(Si–CH3), and 1030-1070cm^{-1} (Si–O–Si). Analysis calculated for

TABLE I

Di-Functional Disiloxanes

Formula	Symbol	Yield (%)	n_D^{25}[a]
$[CH_3OOC{-}C_{10}H_{20}Si(CH_3)_2{-}]_2O$	I	94	1.4490
$[HOCH_2{-}C_{10}H_{20}Si(CH_3)_2{-}]_2O$	II	93	1.4590
$[HOOC{-}C_{10}H_{20}Si(CH_3)_2{-}]_2O$	III	90	b
$[ClOC{-}C_{10}H_{20}Si(CH_3)_2{-}]_2O$	IV	100	1.4630
$[CH_3OOC{-}C_{17}H_{34}Si(CH_3)_2{-}]_2O$	V	93	1.4570
$[HOCH_2{-}C_{17}H_{34}Si(CH_3)_2{-}]_2O$	VI	90	1.4650
$[HOOC{-}C_{17}H_{34}Si(CH_3)_2{-}]_2O$	VII	82	c
$[CH_3OOC{-}C_{10}H_{20}Si(CH_3)(C_6H_5){-}]_2O$	VIII	97	1.4975
$[HOCH_2{-}C_{10}H_{20}Si(CH_3)(C_6H_5){-}]_2O$	IX	96	1.5065
$[HOOC{-}C_{10}H_{20}Si(CH_3)(C_6H_5){-}]_2O$	X	92	1.5050
$[CH_3OCOCH_2{-}C_{10}H_{20}Si(CH_3)_2{-}]_2O$	XI	87	1.5010
$[CH_3OOC{-}C_{17}H_{32}Si(CH_3)_2{-}]_2O$	XII	85	1.4630
$[HOCH_2{-}C_{17}H_{32}Si(CH_3)_2{-}]_2O$	XIII	85	1.4710
$[HOOC{-}C_{17}H_{32}Si(CH_3)_2{-}]_2O$	XIV	80	1.4720
$[CH_3OCOCH_2{-}C_{10}H_{20}Si(CH_3)(C_6H_5){-}]_2O$	XV	88	1.4950

[a] Unless otherwise indicated all of the products were high boiling oils.

[b] Mp, 44 C.

[c] Mp, 30 C.

TABLE II

Silanol Derivatives of Long Chain Fatty Acid Esters

Formula	Yield (%)	n_D^{25}
$CH_3(OH)_2Si{-}C_{10}H_{20}COOCH_3$[a]	82	---
$(CH_3)_2(OH)Si{-}C_{10}H_{20}COOCH_3$	80	1.4503
$Ph(CH_3)(OH)Si{-}C_{10}H_{20}COOCH_3$[b]	91	1.4965
$CH_3(OH)_2Si{-}C_{17}H_{34}COOCH_3$[c]	82	---
$(CH_3)_2(OH)Si{-}C_{17}H_{34}COOCH_3$	79	1.4610
$Ph(CH_3)(OH)Si{-}C_{17}H_{34}COOCH_3$[b]	92	1.4878

[a] Recrystallized from hexane, mp, 40 C.

[b] Prepared by direct hydrolysis with water

[c] Recrystallized from hexane, mp, 74 C.

$C_{28}H_{58}Si_2O_5$: C, 63.15; H, 10.90. Found: C, 63.26; H, 10.77.

1,3-Bis(11-hydroxyundecyl)Tetramethyldisiloxane

A solution of I (in Table I) (2.66 g, 0.005 mole), in dry ether (100 ml) was added dropwise with stirring, to a suspension of lithium aluminum hydride (0.76 g, 0.02 mole) in dry ether (200 ml). The reaction mixture was stirred and heated under reflux for 4 hr and then cooled to O C. Cold water was added dropwise, followed by cold 10% sulfuric acid until 2 clear layers formed. The ethereal layer was separated and the aqueous layer extracted with ether. The combined ethereal solutions were washed with water and dried over magnesium sulfate. The ether was evaporated to yield the product II (Table I). IR: 3100-3400 (hydroxyl), 1260 ($Si{-}CH_3$), and 1040-1070cm^{-1} (Si–O–Si). Analysis calculated for $C_{26}H_{58}Si_2O_3$: C, 65.82; H, 12.24. Found: C, 65.90; H, 12.03.

1,3-Bis(10-Carboxydecyl)Tetramethyldisiloxane

To a 10% solution of sodium hydroxide (excess), the diester I (in Table I) (5.32 g, 0.01 mole) was added, and the mixture was heated under reflux for 8 hr. The reaction mixture was cooled, acidified with hydrochloric acid (10%) to pH 1, and extracted thoroughly with ether. The organic diacid was dissolved in ether, dried over $MgSO_4$, and the ether was evaporated to yield the product III (Table I). IR: 2700-3300 (–COOH), 1720 (C=O), 1260 ($Si{-}CH_3$), and 1040-1060cm^{-1} (Si–O–Si). Analysis calculated for $C_{26}H_{54}Si_2O_5$: C, 62.15; H, 10.76. Found: C, 62.34; H, 10.71.

1,3-Bis(10-Chlorocarbonyldecyl)Tetramethyldisiloxane

To a stirred solution of III (Table I) (5.02 g, 0.01 mole) in dry benzene (10 ml) containing anhydrous $CaCO_3$ (15 g), freshly distilled thionyl chloride (20 ml) was added, and the mixture was refluxed for 2 hr. After cooling, it was filtered, and the filtrate was concentrated under reduced pressure to give the product IV (Table I). IR: 1805 (C=O), 1260 ($Si{-}CH_3$), and 1040-1060cm^{-1} (Si–O–Si). Analysis calculated for $C_{26}H_{52}Si_2O_3Cl_2$: C, 57.88; H. 9.64; Cl, 13.17. Found: C, 58.06; H, 9.63; Cl, 12.15.

Disodium Salt of 1,3-Bis(10-Carboxydecyl) Tetramethyldisiloxane

To a solution of sodium metal (0.46 g, 0.02 mole) in absolute ethanol (40 ml), the diester I (Table I) (5.32 g, 0.01 mole) was added followed by water (ca. 0.5-1 ml). The mixture was heated to boiling for 1 hr to hydrolyze the diester. The disodium salt separated as a heavy precipitate in 92% yield. IR: 1560 (CO_2^-), 1260 ($Si{-}CH_3$), and 1040-1060cm^{-1} (Si–O–Si).

A typical procedure for synthesis of silanols (Table II) is given below.

TABLE III

Hydrolysis of Methyl 11-(Methyldichlorosilyl)Undecanoate[a]

Hydrolysis medium	Cyclosiloxane[b]	
	Trimer (%)	Tetramer (%)
Water (100 ml)	67	33
6N HCl (100 ml)	61	39
6N NH_4OH (100 ml)	57	43
Ether (50 ml) – water (50 ml)	54	46
n-Heptane (50 ml) – water (50 ml)	50	50
Chloroform (50 ml) – water (50 ml)	55	45
1,4-Dioxane (50 ml) – water (50 ml)	53	47

[a] Methyl 11-(methyldichlorosilyl)undecanoate (3.13 g, 0.01 mole) was stirred in the solvents given for 1 hr at room temperature.

[b] The cyclic siloxane oligomers were separated using a column packed with activated alumina, neutral (20%) water; the cyclic trimer (mp 30 C) was eluted by petroleum ether (40-60 C), and the cyclic tetramer eluted by chloroform was an oil. The two isomers differed in their IR spectra in regards to the Si–O–Si absorption; the trimer was at 1010-1020 and the tetramer at 1080-1090cm^{-1}.

Synthesis of 10-Carbomethoxydecylmethylsilane Diol

A solution of methyl 11-(methyldichlorosilyl)undecanoate (1.565 g, 0.005 mole) in ether (100 ml) was added dropwise, with vigorous stirring to a cooled (O C) solution of aniline (0.93 g, 0.01 mole) in ether (50 ml) and water (0.18 g, 0.01 mole). The rate of dropping was 2 ml/min, and the reaction temperature was maintained below 2 C during the addition. After 1 hr, the precipitated aniline hydrochloride was filtered off, and the filtrate was concentrated under reduced pressure. The white crystalline derivative was recrystallized from hexane (Table II). IR: 3100-3400 (hydroxyl), 1750 (C=O), and 1260cm^{-1} ($Si{-}CH_3$). Analysis calculated for $C_{13}H_{28}SiO_4$: C, 56.52; H, 10.14. Found: C, 55.18; H, 9.34.

Hydrolysis of Methyl-11-(Methyldichlorosilyl)-Undecanoate

A solution of methyl 11-(methyldichlorosilyl)undecanoate (3.13 g, 0.01 mole) in ether (50 ml) was added slowly, with vigorous stirring, to water (50 ml). The reaction mixture was stirred for 1 hr at room temperature. The organic layer was separated and washed with water until neutral. The ether was distilled off leaving a mixture of cyclosiloxanes (Table III). Average mol wt 880 (vapor pressure osmometer). Analysis calculated for $(C_{13}H_{26}SiO_3)_{3\text{-}4}$: C, 60.46: H, 10.08. Found: C, 59.78; H, 9.74.

Hydrolysis of Methyl 11-Trichlorosilyl Undecanoate

Methyl-11-trichlorosilyl undecanoate (3.33 g, 0.01 mole) was added gradually to water (50 ml). The reaction mixture was stirred for 1 hr at 0-2 C. The rubber-like cross-linked polysiloxane was filtered, washed with water, and dried over P_2O_5 under reduced pressure. The yield was nearly quantitative. Analysis calculated for $(C_{12}H_{23}SiO_{3.5})_n$: C, 57.37; H. 9.16. Found: C, 56.07; H, 8.91.

The alkoxide, phenoxide, and acyloxy silyl derivatives (Table IV) were synthesized according to the procedure described below.

Methyl 9(10)-(Methyldibutyoxysilyl)Stearate

A mixture of methyl 9(10)-(methyldichlorosilyl)stearate (2.0 g, 0.005 mole) was heated under reflux with an excess of n-butanol (50 ml) for 5 hr. Excess n-butanol was distilled off under reduced pressure, leaving behind the di-n-butoxy derivative (Table IV). IR: 1750 (C=O), 1260($Si{-}CH_3$), and 1080cm^{-1} (Si–O–C). Analysis calculated for $C_{28}H_{58}SiO_4$:C, 69.14; H, 11.94. Found: C, 69.40; H, 11.60.

Methyl 9(10)-(Methyldiethoxysilyl)Stearate

To a mixture of methyl 9(10)-(methyldichlorosilyl) stearate (4.0 g, 0.01 mole) and freshly distilled ethyl

TABLE IV

Alkoxide, Phenoxide, and Acetoxy Derivatives of Long Chain Fatty Acid Esters

Formula[a]	n_D^{25}	Bp, C (pressure in torr)
$CH_3(OCH_3)_2Si-R_1$[b]	1.4372	121/0.1
$CH_3(OC_2H_5)_2Si-R_1$[b]	1.4351	140/0.2
$CH_3(OC_6H_5)_2Si-R_1$[c]	1.5038	140/0.1
$(CH_3)_2(OC_6H_5)\ Si-R_1$[c]	1.4778	---
$CH_3(OCH_3)_2Si-R_2$[b]	1.4484	170-172/0.05
$CH_3(OC_2H_5)_2Si-R_2$[b]	1.4456	190/0.2
$CH_3(OC_4H_9)_2Si-R_2$[d]	1.4550	---
$CH_3(OC_6H_{11})_2Si-R_2$[d]	1.4706	---
$CH_3(OC_6H_5)_2Si-R_2$[c]	1.5031	---
$(CH_3)_2(OC_6H_5)Si-R_2$[c]	1.4740	---
$CH_3(OCOCH_3)_2Si-R_1$[e]	1.4378	130-135/0.1
$C_6H_5(OCOCH_3)_2Si-R_1$[e]	1.4830	160/0.2
$(CH_3)_2(OCOCH_3)Si-R_1$[e]	1.4409	138/0.2
$(C_6H_5)(CH_3)(OCOCH_3)Si-R_1$	1.4852	163/0.1
$CH_3(OCOCH_3)_2Si-R_2$[e]	1.4507	180-185/0.1
$(CH_3)_2(OCOCH_3)Si-R_2$[e]	1.4520	---
$CH_3(OCOCH_3)_2Si-R_3$[e]	1.4531	---
$CH_3(OCOCH_3)_2Si-R_4$	1.4618	180/0.1

[a] $R_1=C_{10}H_{20}$; $R_2=C_{17}H_{34}$, $R_3=C_{17}H_{32}$; and $R_4=C_{17}H_{30}$.

[b] Prepared by orthoformate method.

[c] Prepared by reaction of phenol with the chlorosilyl derivatives.

[d] Prepared by reaction of the alcohols with the chlorosilyl derivatives.

[e] The chlorosilyl derivative of the fatty acid methyl ester was heated in benzene with silver acetate (excess).

orthoformate (7.40 g, 0.05 mole), anhydrous aluminum chloride (0.1 g) was added. The mixture was heated under reflux for 6 hr, then distilled. The methyl 9(10)-(methyldiethoxysilyl)stearate passed at 190 C/0.2 mm (Table IV). Analysis calculated for $C_{24}H_{50}SiO_4$: C, 66.97; H, 11.63. Found: C, 67.00; H, 11.32.

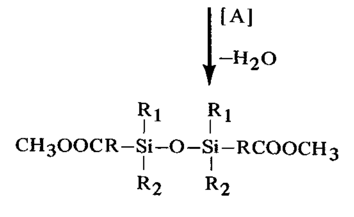
Methyl 9(10) Methyldiacetoxysilyl)Stearate

A mixture of methyl 9(10)-(methyldichlorosilyl)stearate (3.0 g, 0.0075 mole), silver acetate (3.73 g, 0.022 mole), and dry benzene (25 ml) was heated under reflux for 2 hr. The precipitated AgCl was filtered off, and the filtrate was distilled fractionally. The pure diacetoxy derivative passed at 183-188 C/0.05 mm (Table IV). IR: 1750(CO, ester), 1720(CO, acetoxy), 1260(Si–CH_3), and 1020cm^{-1} (Si–O–C). Analysis calculated for $C_{24}H_{46}SiO_6$: C, 62.88; H, 10.04. Found: C, 62.62; H, 10.18.

RESULTS AND DISCUSSION

The addition products of chlorosilanes to methyl oleate, linoleate, 10-undecenoate, and 1-undecen-11-yl-acetate (1), which contain one or two Si–Cl reactive bonds, were utilized for the synthesis of various mono- and di-functional derivatives, as well as cyclic siloxanes.

Silicon-chlorine bonds are very reactive and hydrolyze in the presence of moisture to give the stable siloxane bond. We made use of this fact to convert the addition products which have only one Si–Cl bond into di-functional disiloxane monomers (Table I) as follows:



$$2R_1R_2ClSi-RCOOCH_3 \xrightarrow[-HCl]{H_2O} 2\,[R_2R_2Si(OH)-RCOOCH_3]$$

$$\downarrow [A]\ -H_2O$$

$$CH_3OOCR-\overset{R_1}{\underset{R_2}{Si}}-O-\overset{R_1}{\underset{R_2}{Si}}-RCOOCH_3$$

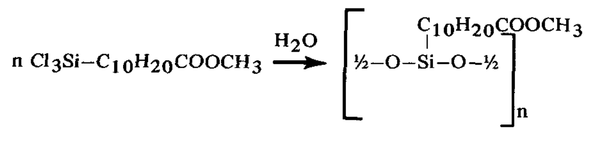
The hydrolysis is especially rapid when the substituents on the silicon are methyl groups ($R_1=R_2=CH_3$). In this case, the hydrolysis proceeds in the presence of water at room temperature, and the silanol intermediate [A] condenses readily and cannot be isolated. It was possible to isolate this intermediate only when the hydrolysis was carried out in ether, using an equivalent amount of water, in the presence of aniline as hydrogen chloride acceptor (4) (Table II).

When one of the methyl groups was replaced by a bulkier phenyl group, the condensation of the silanol to disiloxane was more difficult. Thus, with the silyl-undecanoate derivative, this took place only on heating the intermediate [A] ($R_1=C_6H_5$) with dilute hydrogen chloride at 60 C and with the silyl-stearate derivative, which has a bulkier long chain alkyl group; the condensation to the disiloxane derivative did not occur even on boiling with dilute hydrogen chloride, and only the silanol derivative could be isolated (Table II).

We also investigated the hydrolysis of the dichloro silyl derivatives of the long chain fatty acid esters. It is known that, with nonbulky dichlorosilanes, such as dimethyldichlorosilane, both linear and cyclic polysiloxanes are obtained on hydrolysis. With bulkier substituted dichlorosilanes, such as diphenyldichlorosilanes, hydrolysis under mild conditions proceeds only to the diphenylsilane diol stage (5), and cyclic siloxanes are only obtained on using more drastic conditions. With still more sterically hindered silane diols, such as di-t-butylsilane diol, even treatment with hot concentrated hydrochloric or sulfuric acids has failed to condense this compound (6).

In the case of methyl 11-(methyldichlorosilyl)undecanoate and methyl 9(10)-dichloromethylsilyl-stearate, we found that, on carrying out the hydrolysis under various conditions (Table III), only mixtures of cyclic siloxanes were obtained and no polymers. This was seen from IR spectra, which showed the absence of hydroxyl absorption at 3100-3400cm^{-1}, and from mol wt data which indicated the formation of a mixture of cyclic trimer and tetramer. The cyclic siloxanes derived from undecenoic acid were isolated using a column packed with activated aluminium oxide, neutral (20% water); the cyclic trimer which was a solid (mp/30 C) was eluted with petroleum-ether (40-60 C) and the cyclic tetramer which was an oil eluted with chloroform. The two isomers differed in their IR spectra in regard to the Si–O–Si absorption; the trimer had it at 1010-1020 and the tetramer at 1080-1090cm^{-1}.

Hydrolysis of the trichlorosilyl derivatives, such as methyl 11-trichlorosilyl undecanoate and methyl 9(10)-trichlorosilyl stearate, led to the formation of tridimensional cross-linked polysiloxanes as follows:

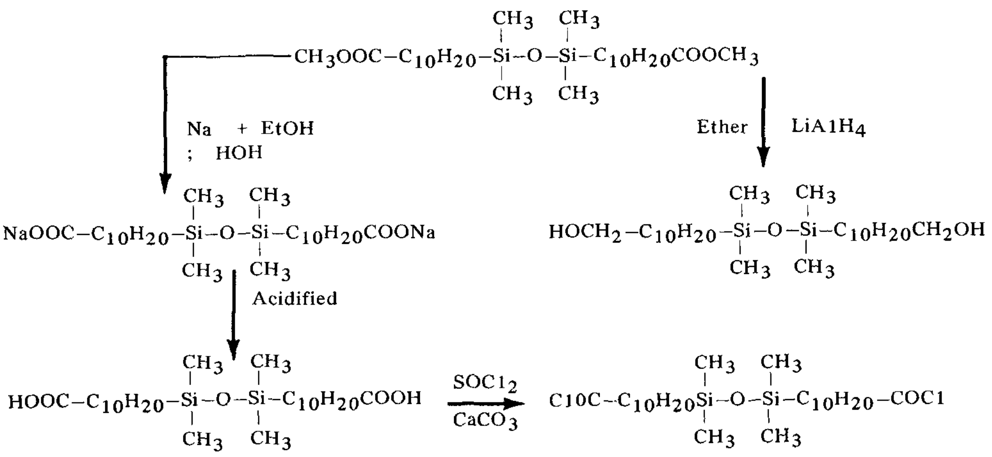


$$n\ Cl_3Si-C_{10}H_{20}COOCH_3 \xrightarrow{H_2O} \left[\tfrac{1}{2}-O-\overset{C_{10}H_{20}COOCH_3}{Si}-O-\tfrac{1}{2}\right]_n$$

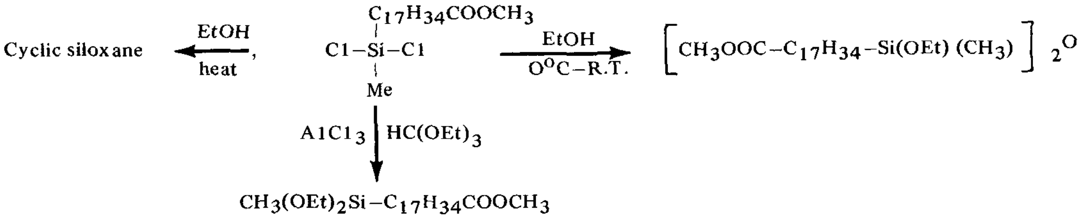
These rubber like cross-linked polymers were not soluble in organic solvents.

The diesters containing siloxane linkages were converted into the corresponding diacids by alkaline hydrolysis (Table I), from which, by reaction with $SOCl_2$ in the presence of $CaCO_3$, the diacid chloride derivatives were synthesized (Table I). The disodium salts of the diacids showed surfactant properties. The diesters also were reduced to the diols with lithium aluminum hydride (Table I). All these bi-functional monomers were oils. A typical synthesis of these diols, dichlorides, and diacid containing siloxane linkages is summarized in Scheme 1.

The above mentioned diols were synthesized by an alternative route, in which Me_2ClSiH was added to the long

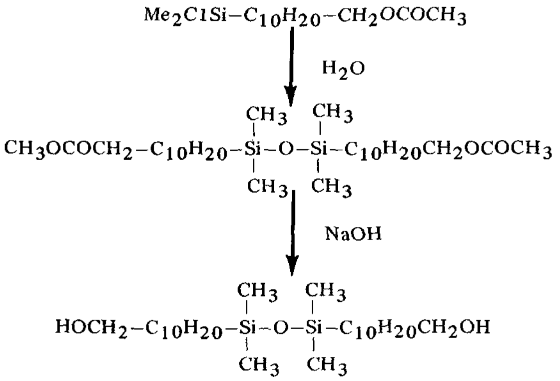


Scheme 1



Scheme 2

chain alkenyl acetate (1) and the hydrolysis of the product was carried out in one stage as follows:



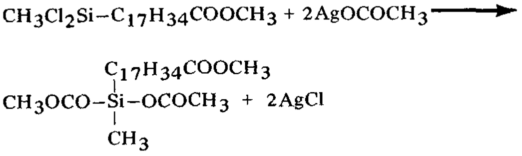
$$\mathrm{Me_2ClSi{-}C_{10}H_{20}{-}CH_2OCOCH_3} \xrightarrow{H_2O} \mathrm{CH_3OCOCH_2{-}C_{10}H_{20}{-}}\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}\mathrm{{-}O{-}}\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}\mathrm{{-}C_{10}H_{20}CH_2OCOCH_3} \xrightarrow{NaOH} \mathrm{HOCH_2{-}C_{10}H_{20}{-}}\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}\mathrm{{-}O{-}}\overset{CH_3}{\underset{CH_3}{\mathrm{Si}}}\mathrm{{-}C_{10}H_{20}CH_2OH}$$

We investigated the synthesis of alkoxide and phenoxide derivatives of the long chain fatty acid esters containing silicon. It was found that reacting methanol and ethanol with the dichlorosilyl derivatives under mild conditions (OC-room temperature), led to formation of dimers having siloxane linkages, while, on heating with methanol or ethanol, cyclic siloxanes were obtained and not the corresponding alkoxides. The best way to synthesize the dimethoxide and diethoxide derivatives was using methyl or ethyl orthoformate in the presence of anhydrous aluminum chloride. A typical synthesis is summarized in Scheme 2.

The reaction of higher alcohols or phenol with the chlorosilyl derivatives proceeded smoothly to give the alkoxide or phenoxide derivatives (7). Thus, the di-n-butoxide; diphenoxide, dicyclohexyloxide, and the monophenoxide derivatives were synthesized (Table IV).

These alkoxy and phenoxy-silyl derivatives are more stable than the corresponding chlorosilyl derivatives and can be stored for longer periods without undergoing polymerization.

We also synthesized the acetyloxy-silyl derivatives by reaction of acetic anhydride (8) or silver acetate (9) with the chlorosilyl derivatives (Table IV):



$$\mathrm{CH_3Cl_2Si{-}C_{17}H_{34}COOCH_3 + 2AgOCOCH_3} \longrightarrow \mathrm{CH_3OCO{-}}\overset{C_{17}H_{34}COOCH_3}{\underset{CH_3}{\mathrm{Si}}}\mathrm{{-}OCOCH_3 + 2AgCl}$$

Although more stable than the corresponding chlorosilyl derivatives these derivaties polymerized on long standing.

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