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Preparation of Tetraalkylsilanes from Trichloromethylsilane and Trioctylaluminum

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The synthesis of methyltrioctylsilane has been achieved in a single-step from commercially available trichloromethylsilane and trioctylaluminum. Co-products resulting from alkyl group redistribution are minimized by addition of sodium or lithium halides. Use of potassium or rubidium halides drastically changes the course of the reaction to produce methyldioctylsilane as the major product.

Silicon derivatives of hydrocarbons have great potential as high-performance lubricants and hydraulic fluids because of their excellent thermal stability. Tetraalkylsilanes with one short chain and three long chains are of particular interest because they exhibit excellent viscosity characteristics over a wide temperature range and have low pour points. Previously, such compounds have been prepared using Grignard or alkyllithium reagents with chlorosilanes,[1,2] or via hydrosilation of 1-alkenes.[3] The Griganard procedure is cumbersome and not suited to large scale production. The hydrosilation procedure is more elegant, but methylsilane, the required starting material, is not available in commercial quantities and would require a difficult reduction step. Therefore, we sought a route based on commercially available starting materials.

Methyltrioctylsilane was selected as the initial target. We considered the reaction of trioctylborane with trichloromethylsilane (Eqs. 1 and 2).

$$6\,RCH{=}CH_2 + B_2H_6 \longrightarrow 2\,(RCH_2CH_2)_3B \qquad (1)$$

$$CH_3SiCl_3 + (RCH_2CH_2)_3B \longrightarrow CH_3Si(CH_2CH_2R)_3 + BCl_3 \qquad (2)$$

Serveral attempts at this sequence confirmed that step 2 was not feasible as predicted by thermodynamic calculations.[4] We then turned to the reaction of trialkylaluminums with chlorosilanes, a thermodynamically favored process (Eq. 3).[4]

The reaction of trichloromethylsilane with trialkylaluminum compounds is best represented by a series of equilibria (Eq. 4).

$$CH_3SiCl_3 + Al(C_8H_{17})_3 \longrightarrow CH_3Si(C_8H_{17})_3 + AlCl_3 \qquad (3)$$

$$\begin{aligned} CH_3SiCl_3 + R_3Al &\rightleftarrows CH_3RSiCl_2 + R_2AlCl \\ &\rightleftarrows CH_3R_2SiCl + RAlCl_2 \\ &\rightleftarrows CH_3R_3Si + AlCl_3 \qquad (4) \end{aligned}$$

The reaction of trialkylaluminum compounds with chlorosilanes was first reported by Jenkner who also noted that the addition of one mole of alkali metal chloride per mole of aluminum shifted the equilibrium to the right by formation of metal tetrachloroaluminates.[5] Russell approached the equilibrium from the right by reacting aluminum chloride with tetraalkylsilanes.[6] Hungarian and Russian researchers studied the equilibria starting with alkylaluminum chlorides or sesquichlorides trying to maximize the intermediate products.[7–9] In all the previous studies, only results with methyl or ethyl groups were reported. When methyl and ethyl compounds were used simultaneously, some alkyl–alkyl interchange was noted in addition to the alkyl–chloro exchange.[9]

We now report the results of our use of longer alkylaluminums. The chemistry is much more complex than indicated by Eq. 4. In addition to the intermediates depicted above, the following types of co-products were observed:

1. Products from silicon to silicon alkyl transfer.
2. Products containing silicon–hydrogen bonds.
3. Dimers of the initial alkyl group.
4. Silanes containing alkyl groups derived from dimers.
5. Silanes containing alkyl groups derived from impurities in trioctylaluminum.
6. Products with silicon–oxygen bonds.

Experimental

Chromatographic analyses were performed on a Hewlett-Packard 5880A (FID) instrument using a 25 m, 2% OV-101, fused silica capillary column programmed from 50 to 300 °C at 8 °C min^{-1}. The IR spectra were recorded on a Perkin-Elmer Model 597 spectrometer. GC/MS data were obtained on a Finnigan 4510 system with an electron impact source at 70 eV. Trioctylaluminum (Ethyl Corp.) and alkylchlorosilanes (Aldrich and Petrarch) were used as received.

General Procedure. Reactions were carried out in a thick-walled glass reactor connected to a nitrogen pressure manifold with Fisher–Porter compression fittings. Similar fittings connected a side arm to a wide-bore Hoke valve and a rubber septum. Heat was supplied with a heating mantle and controlled with a West-800 controller. An egg-shaped magnetic stirrer supplied adequate agitation.

The reactor was charged with alkali metal halide and connected to the nitrogen system. The system was purged by pressuring to 30 psig and venting ten times. Trioctylaluminum was added via syringe followed by trichloromethylsilane. Stirring and heating were started. Approximately 25—35 minutes were required to attain temperature. Reaction time was measured as the time at temperature. When the reaction was terminated, the vessel was allowed to cool to room temperature and vented. At this point, the reaction mixture was not pyrophoric. The reactor was disconnected from the nitrogen system and an equal volume of heptane was added. Methanol was added to quench unreacted alkylaluminum and to convert any remaining chlorosilanes to methoxysilanes. The mixture was transferred to a separatory funnel. Water was added to facilitate separation of the layers. The organic layer was dried over magnesium sulfate, filtered, and stripped on a rotary evaporator. The crude product was analyzed by gas chromatography.

Results and Discussion

Physical Aspects of the Reaction. Previous work had been performed in metal autoclaves. Our initial work has employed a thick-walled glass reactor. While the pressure limitations of the glass undoubtedly reduced yields and possibly rates because a significant portion of the volatile trichloromethylsilane remained in the vapor space, the system proved excellent for observing the physical state of the reaction mixture. In a typical run, as the mixture of salt, trichloromethylsilane and trioctylaluminum is heated the following sequence of events occurs:

1. As the boiling points of the volatile components are exceeded the pressure rises and refluxing occurs. The salt remains as a discrete solid until a minimum reaction temperature, characteristic of the particular salt, is attained.
2. At reaction temperature the salt dissolves. The pressure starts to drop.
3. The liquid phase becomes cloudy. If the stirrer is stopped two liquid phases separate rapidly.
4. With time the upper phase diminishes while the lower phase grows.

During this period the pressure remains relatively constant.

5. The upper phase reaches a minimum. The pressure once again begins to drop as the upper phase begins to increase again. When the amount of upper phase stabilizes, the reaction is terminated.
6. Upon cooling, the lower layer solidifies.

Figure 1 gives a graphical representation of this behavior. The relative time periods for the various parts of the sequence vary with reaction temperature and the type and amount of salt employed.

The lower liquid phase obviously is some sort of complex between the salt and the other constituents. It does not appear to be a simple complex of trioctylaluminum and salt, since heating trioctylaluminum and sodium chloride for one hour at 180 °C showed no evidence of dissolution of the salt. Since alkylaluminum chlorides are much stronger Lewis acids than trialkylaluminum and are well-know to form complexes with alkali metal halides,[10] it would appear that initial exchange of alkyl and chloro groups are required before the complex can form. The cause of the period of static pressure during the growth of the complex is not understood at this time. If the reaction is terminated at the maximum complex formation (minimum upper layer), the product distribution is similar to that for a typical longer run; but yield is lower.

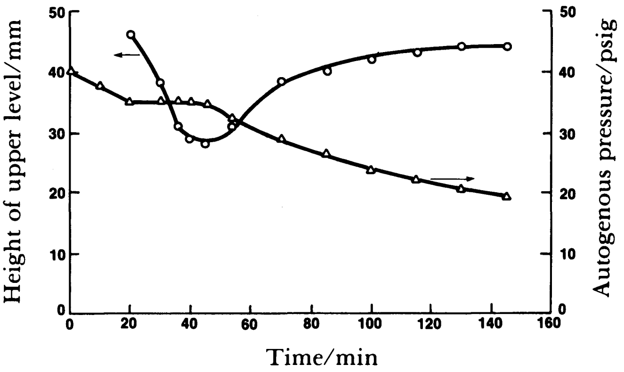

Fig. 1. Profile of autogenous pressure (Δ) and height (O) of product containing layer with time.

Effect of Amount of Salt. Runs listed in Table 1 illustrate the effect of the amount of added sodium chloride. Only those reaction products which are severely altered are shown. With no added sodium chloride, extensive transfer of alkyl groups from silicon to silicon occurs. Addition of 0.5 mol of salt per mole of aluminum greatly improves the selectivity to methyltrioctylsilane. Lesser amounts have little effect. Larger amounts show no further improvement. Varying the reaction time between 1 and 6 hours produces no major change in the product distribution. The main effect of sodium chloride appears to be inhibition of alkyl group redistribution rather than shifting the equilibrium as suggested by Jenkner.[5]

Alkyl group redistribution could result from post-alkylation equilibrium (Eq. 5).

$$(CH_3)_4Si \rightleftarrows (CH_3)_3(C_8H_{17})Si \rightleftarrows (CH_3)_2(C_8H_{17})_2Si \rightleftarrows CH_3(C_8H_{17})_3Si \rightleftarrows (C_8H_{17})_4Si \quad (5)$$

Alternatively, a prealkylation equilibration of the chlorosilanes could cause the same product distribution (Eq. 6).

$$SiCl_4 \rightleftarrows CH_3SiCl_3 \rightleftarrows (CH_3)_2SiCl_2 \rightleftarrows (CH_3)_3SiCl \rightleftarrows (CH_3)_4Si \quad (6)$$

Aluminum chloride is a known catalyst for the equilibration depicted in Eq. 5.[6] To assess the magnitude of such a reaction, 50 mmol of methyltrioctylsilane and 10 mmol of aluminum chloride were heated to 160 °C for one hour. Gas chromatography revealed that the product contained only 59% of the initial silane. Repetition of the experiment with

Table 1. Effect of Sodium Chloride

Run	Molar ratio[a]	Time/h			Yield/mole percent[b]		
	TNOA/MTCS/NaCl		$(CH_3)_3(C_8H_{17})Si$	$(CH_3)_2(C_8H_{17})_2Si$	$CH_3(C_8H_{17})_3Si$	$(C_8H_{17})_4Si$	$CH_3(C_8H_{17})_2SiH$
1	1/0.8/0	6	3.4	8.7	26.1	27.1	—
2	1/0.8/0.25	2	2.6	13.0	33.3	21.3	—
3	1/0.8/0.5	6	—	5.6	63.4	3.9	—
4	1/0.8/1	1	—	3.2	58.5	0.6	0.7
5	1/0.8/1	3	—	3.4	61.3	3.0	2.4

a) TNOA=trioctylaluminum, MTCS=trichloromethylsilane, reaction conditions: 210 °C, autogenous pressure, 85 mmol TNOA, 70 mmol MTCS. b) Gas chromatographic yield based on MTCS as limiting reagent.

Table 2. Composition of Vapor Phase

Run	Sample	Timing				Mole percent[a]			
			Isobutene	$(CH_3)_2SiHCl$	CH_3SiHCl_2	$(CH_3)_3SiCl$	CH_3SiCl_3	1-Octene	Other C_8 hydrocarbons
6[b]	1	Upon reaching reaction temp	20.3	—	7.4	2.0	22.7	38.0	9.6
	2	Incipient molten phase	8.2	—	7.7	7.8	26.8	36.8	12.8
	3	Maximum lower phase	11.4	—	6.5	4.9	21.8	44.5	10.9
	4	1 h	12.0	7.6	5.0	6.2	21.3	35.7	12.3
	5	4 h	—	8.8	6.6	5.9	22.1	44.9	11.7
7[c]	1	Upon reaching reaction temp	9.0	—	3.6	1.5	17.7	51.2	17.0
	2	1 h	11.2	—	4.3	2.8	17.1	48.2	16.4
	3	3 h	24.8	—	4.5	—	18.2	3.1	49.4

a) Tentative assignments made by sequentially spiking a sample of 1-octene with the suspected components. $(CH_3)_2SiCl_2$ could not be separated from CH_3SiCl_3 under the conditions employed. b) 100 mmol $(C_8H_{17})_3Al$, 100 mmol NaCl, 89 mmol CH_3SiCl_3, reaction temperature 190 °C. c) 50 mmol $(C_8H_{17})_3Al$, 40 mmol CH_3SiCl_3, reaction temperature 190 °C.

10 mmol of added sodium chloride gave a product with 76% starting silane. This indicates that sodium chloride is indeed effective in stopping alkyl redistribution. Presumably, in a typical reaction, very little free aluminum chloride ever forms because of prior complexation with the alkali metal salt leading to the direct generation of the inactive tetrachloroaluminate.

To determine if Eq. 6 was of any importance, the composition of the vapor phase of runs with and without sodium chloride was determined by gas chromatography. Table 2 summarizes the results. Some other silicon compounds not present in the feed do form under the reaction conditions. The relative proportions are about the same, with or without sodium chloride, and remain roughly constant throughout the reaction. The isobutene present is derived from impurities in the trioctylaluminum. In the absence of sodium chloride the 1-octene in the vapor phase is gradually isomerized.

These experiments indicate that a small portion of the alkyl redistribution is due to prealkylation equilibria; but, major redistribution is the result of postalkylation equilibria when insufficient sodium chloride is present.

Effect of Type of Salt. While the literature indicated that the alkali metal halides were interchangeable,[5] the obvious importance of the complex to the reaction suggested that different salts should have some effect. The strength of the various alkali metal halides as complexing agents for alkylaluminums increases with the increasing radius of the cation and with the decreasing size of the halide ion.[11] This is usually manifested in a lower temperature of complex formation. If the reaction complex could be formed at lower temperature, the reaction might proceed with greater selectivity.

Based on this premise, reactions were carried out using sodium, potassium, or rubidium chloride with trioctylaluminum and trichloromethylsilane wherein the mixtures were heated at a uniform rate until the salt dissolved. At this point the temperature was stabilized and held. The dissolution temperature and the approximate time from dissolution to separation of the two liquid phases followed the expected trend (Table 3). However, analysis of the products of the potassium and rubidium runs revealed that methyltrioctylsilane was no longer the major product! Infrared showed a strong Si–H absorption at 2120 cm^{-1}. Co-injection with an authentic sample confirmed the major product as methyldioctylsilane.

A series of runs at constant temperature varying both the cation and the halide shows that both affect the product distribution (Table 4). The tendency to form methyldioctylsilane instead of methyltrioctylsilane increases in the sequence Li<Na<K<Rb and in the sequence I<Br<Cl. The fluoride run is somewhat out of line. However, fluoride frequently gives anomalous behavior when compared to the other halides. A decrease in the amount of alkyl redistribution also occurs in the same sequences. Mixtures of two salts gave product distributions intermediate between the individual salts.

Runs with potassium or rubidium chloride produce two to three times as much octene dimers (mainly 2-hexyl-1-decene by GC/MS) as the analogous runs with sodium or lithium chloride. Also, no traces of alkylation by the $C_{16}H_{33}$ group are found when potassium or rubidium salts were present. This suggests that these complexes prefer to expel dimeric molecules as the olefin at some stage of the reaction leaving aluminum hydride residue. Presumably, the hydride is then transferred to silicon in the same manner as an alkyl group. The relatively large loss of octyl groups to dimers probably accounts for larger amounts of partially alkylated silanes rather than inability of potassium to shift the equilibrium.

The relative distribution of the silicon compounds in the vapor phase for potassium runs was similar to that of a sodium run indicating no drastic change in the prealkylation equilibria. Only traces of 1-octene were found. Two closely spaced, unidentified peaks comprised approximately 45% of the vapor phase. Based on gas chromatography retention time, a crude estimate of the molecular weight would be ca. 140—150. Unfortunately, the materials were not stable. No trace could be found after work up.

Reactivity of Silicon-Hydrogen Bonds. The presence of silicon–hydrogen bonds in the vapor phase, even in the sodium chloride runs raised the question of the ability to replace the hydrogen with an alkyl group. Dichloromethylsilane produced predominantly methyltrioctylsilane (Eq. 7).

$$CH_3SiHCl_2 + Al(C_8H_{17})_3 \longrightarrow \underset{43\%}{CH_3(C_8H_{17})_3Si} + \underset{25\%}{CH_3(C_8H_{17})_2SiH} \quad (7)$$

Reaction of hexylsilane under similar conditions

Table 3. Relationship of Type of Salt to Minimum Temperature of Complex Formation[a]

Salt	Dissolution temperature/°C	Time from dissolution to separation of complex/min
NaCl	190—200	5—10
KCl	160—175	15—45
RbCl	140—150	30—60

a) 85 mmol trioctylaluminum, 75 mmol trichloromethylsilane, 85 mmol salt stirred at constant rate with constant heat input until dissolution occurred.

Table 4. Effect of Type of Salt on Product Distribution[a]

Run	Salt	Selectivity/mole percent $(CH_3)_3(C_8H_{17})Si$	$CH_3(C_8H_{17})_2SiH$	$(CH_3)_2(C_8H_{17})_2Si$	$CH_3(C_8H_{17})_2SiCl$	$CH_3(C_8H_{17})_3Si$	$(C_8H_{17})_4Si$
8	LiCl	0.8	—	8.4	3.8	50.4	7.8
9	LiBr	1.6	—	10.4	7.2	37.6	4.8
10	NaCl	0.9	2.4	3.8	2.1	63.2	2.1
11	NaBr	—	1.0	3.1	3.3	66.7	5.2
12	KF	—	30.3	0.6	7.1	13.9	0.2
13	KCl	—	47.2	0.9	12.2	8.3	0.2
14	KBr	—	18.8	2.0	8.6	47.6	0.6
15	KI	—	13.4	2.2	7.6	54.3	1.8
16	RbCl	—	47.4	2.1	2.1	21.5	0.2

a) Temperature: 180 °C; time: 4 h; mole ratio trioctylaluminum/trichloromethylsilane/salt: 1/1/1.

also produced some alkylation (Eq. 8); but, the reaction of Si–H bond is definitely much slower than the Si–Cl bond. In this case the sodium chloride never changes from its granular state and probably does not enter into the reaction.

$$C_6H_{13}SiH_3 + Al(C_8H_{17})_3 \longrightarrow \underset{31\%}{C_6H_{13}(C_8H_{17})SiH_2} + \underset{20\%}{C_6H_{13}(C_8H_{17})_2SiH} \quad (8)$$

Effect of Impurities in the Feed. The trichloromethylsilane used in this study was chromatographically pure. The vapor phase results indicate that a near steady state concentration of the disproportionation products is achieved very quickly. Since these same disproportionation products are the impurities usually found in technical grade trichloromethylsilane, its use would have no drastic effect.

In the case of trioctylaluminum the effect of impurities is much greater. Since each desired product molecule contains three octyl chains derived from trioctylaluminum, each non-desired alkyl chain can waste up to two octyl chains by its reaction, i.e. one mole percent impurity in the trioctylaluminum produces three mole percent impurities in the product. Preparation of trioctylaluminum is generally accomplished by displacement of isobutylene from triisobutylaluminum with 1-octene. Failure to displace all the isobutyl groups in the preparation of the trioctylaluminum can lead to silanes containing one or more isobutyl substituents. Coinjection with authentic diisobutylmethyloctylsilane and isobutylmethyldioctylsilane confirmed the presence of traces of the former and up to 2% of the latter in a typical run.

Vinylidene impurities present in 1-olefins represent another source of impurity in the trioctylaluminum. In the case of 1-octene this results in the introduction of 2-ethylhexyl substituents. The presence of 2-ethylhexyl-containing silanes was confirmed by independent synthesis and co-injection. Use of longer chain alkylaluminums would exacerbate this problem.

Oxygen Containing Co-Products. In this work any excess of unreacted alkylaluminum was generally quenched with water or methanol. This also hydrolyzes any partially converted chlorosilanes to disiloxanes or methoxysilanes.

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