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ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Recovery of Trimethylchlorosilane from Its Azeotropic Mixture with $SiCl_4$

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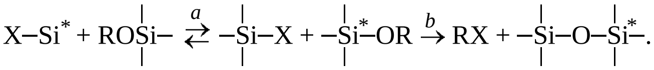
Abstract—Reaction of tetraethoxysilane with the azeotropic mixture $Me_3SiCl–SiCl_4$ in the presence of certain cyclic (tetrahydrofuran, dioxane) and acyclic (diethyl ether) ethers, ethanol, or dimethylformamide was studied with the aim of $SiMe_3Cl$ recovery.

Trimethylchlorosilane is one of the most important organosilicon monomers. It is used to incorporate inert terminal groups into oligoorganosiloxanes to be applied as heat- and frost-resistant oils, lubricants, liquid dielectrics, heat carriers, hydrophobizing components, lacquers, and enamels; also, it is widely used as trimethylsilylating agent in organic and organometallic chemistry [1].

Direct synthesis of methylchlorosilane by reaction of CH_3Cl with the Si–Cu contact mass yields up to 10% of the azeotropic mixture $Me_3SiCl–SiCl_4$ [2]. The majority of methods proposed for its separation [azeotropic distillation with acetonitrile; partial hydrolysis or alcoholysis; chemical binding of $SiCl_4$ in the form of solid complexes with tertiary aliphatic and aromatic amines, formamide, and dimethylformamide (DMF), insoluble in the reaction medium; fluorination in aqueous solution] have a number of drawbacks: low yield of Me_3SiCl, strongly corrosive medium, gelation, and formation of abundant by-products whose utilization requires sophisticated procedures [3–5].

Simple procedures for Me_3SiCl recovery from the azeotropic mixture $Me_3SiCl–SiCl_4$ have been developed only recently. They are based on binding of $SiCl_4$ with organylalkoxysilanes, ethyl silicate, and bottoms from its synthesis in the presence of alcohols, traces of moisture, metal salts, and acid catalysts [6, 7].

The reaction between alkoxy- and chlorosilanes occurs either as exchange of an alkoxy group for a halogen atom [scheme (1), *a*] or as heterofunctional condensation [scheme (1), *b*] [1]:



$$X{-}Si^* + RO\overset{|}{\underset{|}{Si}}{-} \overset{a}{\rightleftarrows} {-}\overset{|}{\underset{|}{Si}}{-}X + {-}\overset{|}{\underset{|}{Si^*}}{-}OR \xrightarrow{b} RX + {-}\overset{|}{\underset{|}{Si}}{-}O{-}\overset{|}{\underset{|}{Si^*}}{-}. \quad (1)$$

Both pathways, *a* and *b*, are accelerated in the presence of HCl. As a rule, the contribution of pathway *b* becomes appreciable at elevated temperatures.

Reaction of $SiCl_4$ with $Si(OEt)_4$ at 150–160°C yields a mixture of OEt–Cl exchange products [8–10]. In the presence of 0.24 wt % ethanol, this reaction is 76–97% complete in 20–70 h at molar ratio $SiCl_4 : Si(OEt)_4 = 1 : 3$ and 20–22°C [11].

A procedure has been developed for separation of a technical azeotropic mixture $Me_3SiCl–SiCl_4$ containing $MeSiHCl_2$ and $HSiCl_3$ impurities by binding $SiCl_4$ with tetraethoxysilane to form ethoxychlorosilanes in a selective reaction in the presence of initiators, with subsequent fractionation of the reaction mixture [12, 13].

To this end, a technical azeotropic mixture was brought into reaction with $Si(OEt)_4$ in the presence of 0.2–10 wt % DMF, tetrahydrofuran (THF), dioxane, diethyl ether, or ethanol. The reaction was performed at 20–25°C or at refluxing (60–65°C) for 2–72 h until conversion of $SiCl_4$ into ethoxychlorosilanes and -siloxanes was complete:

$$SiCl_4 + (EtO)_4Si \rightarrow Cl_{4-n}Si(OEt)_n + [Cl_mSi(OEt)_{3-m}O]_kSiCl_p(OEt)_{3-k-p}, \quad (2)$$

where $n, m, k, p = 1–3$.

With the above initiators, it was possible to recover 6–88% of Me_3SiCl from the reaction mixture. In the presence of DMF, the mixture undergoes partial tarring due to low thermal stability of $DMF–SiCl_4$ complexes [14].

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Conditions and isolated products of the reaction of $Si(OEt)_4$ with $SiCl_4$ in an industrial azeotropic mixture with Me_3SiCl

Reaction conditions					Yield of indicated exchange product, g					Yield of 99% Me_3SiCl, %
initiator, wt %	T, °C	τ, h	azeotrope	$(EtO)_4Si$	$EtOSiCl_3$	$(EtO)_2SiCl_2$	$(EtO)_3SiCl$	$(EtO)_4Si$	ethoxychloropolysiloxanes	
			g							
THF:										
1.0	60–65	10	10.15	15.6	3.4	4.7	8.9	5.1	0.6	66
1.0	60–65	15	10.15	15.6	–	4.5	15.6	1.8	0.6	70
1.0	25	72	10.15	15.6	1.1	1.8	14.9	3.6	0.6	80
2.0	60–65	5	5.08	7.8	0.5	3.9	4.6	1.5	0.5	80
2.0	25	72	5.08	7.8	2.0	3.1	3.6	1.8	0.2	88
Dioxane:										
1.0	60–65	15	10.15	15.6	2.2	6.2	6.3	6.8	0.6	78
1.0	25	72	10.15	15.6	1.0	6.3	11.7	2.4	1.2	68
2.0	60–65	5	5.08	7.8	1.5	1.4	3.9	3.6	0.3	84
2.0	25	72	5.08	7.8	1.0	2.3	5.0	2.6	0.2	72
Ethanol:										
0.2	60–65	10	10.15	15.6	1.0	4.2	12.8	3.1	1.2	68
0.2	60–65	15	10.15	15.6	0.75	3.95	13.8	1.5	2.25	71
DMF:										
5.0	60–65	18	25.00	11.5	0.9	1.6	4.4	2.9	3.5	72

Reaction (2) performed in the presence of 0.2 wt % ethanol, 1 wt % THF or dioxane, or 2 wt % diethyl ether mainly yields triethoxychlorosilanes, with relatively low content of siloxanes originating from heterofunctional condensation (see table). Raising the concentration of THF or dioxane to 2 wt % noticeably decreases the yield of ethoxychlorosilanes and favors formation of oligosiloxanes even at 20–25°C (see table). At THF content as high as 10 wt %, Me_3SiCl is also involved in the heterofunctional condensation.

Initiation of exchange between alkoxy groups and chlorine atoms in reactions of chlorosilanes with alkoxysilanes under the action of HCl (usually present in chlorosilanes because of their partial hydrolysis by atmospheric moisture) is believed to occur in two stages [1]:

$$-\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{OEt} + \mathrm{HCl} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}}}-\mathrm{Cl} + \mathrm{HOEt}, \quad (3a)$$

$$-\overset{|}{\underset{|}{\mathrm{Si}^*}}-\mathrm{Cl} + \mathrm{HOEt} \rightleftarrows -\overset{|}{\underset{|}{\mathrm{Si}^*}}-\mathrm{OEt} + \mathrm{HCl}. \quad (3b)$$

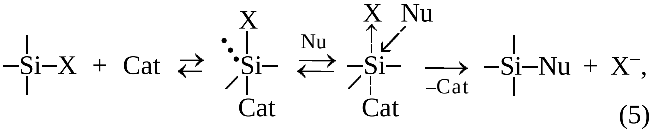
The initial rate of the reaction between trimethylmethoxysilane and $SiCl_4$ in the presence of HCl or hydroxyl-containing compounds ROH (R = H, MeO, PhCO, Et_3Si) releasing HCl in the reaction with $SiCl_4$, is proportional to squared HCl concentration [15].

In this connection, formation of intermediate associates like $Me_3SiOMe \cdot 2HCl$, decomposing with cleavage of the Si–O bond, was suggested:

$$Me_3SiOMe \cdot 2HCl \rightleftarrows Me_3SiCl + HOMe + HCl. \quad (4)$$

In a solvent forming associates with HCl, the equilibrium of reaction (4) is significantly shifted to the left. This fact is nicely consistent with the previously found [13] catalytic activity of ethanol in reaction (3). However, addition of acyclic (Et_2O) and cyclic (THF, dioxane) ethers, capable of forming oxonium complexes with HCl [16], must enhance the catalytic effect of HCl. In the case of THF, the oxonium complex can transform into 4-chloro-1-butanol whose capability for etherification of type (3b) is considerably lower than that of ethanol. This fact could decrease the content of HCl in the reaction mixture and hinder reaction (3). However, when THF is added in an amount as large as 10 wt %, the reaction is not inhibited; moreover, more inert Me_3SiCl is involved in the process.

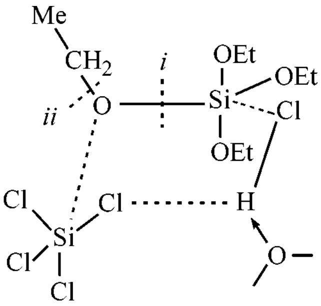
Nucleophilic substitution at the silicon atom is accelerated in the presence of strong nucleophiles (DMF, HMPA, F^-, $RCOO^-$, Cl^-) and is a first-order reaction with respect to the initial silane, alcohol, and activating nucleophile [17, 18]. The suggested reaction mechanism involves formation of an intermediate with a five-coordinate Si atom and its subsequent attack by a nucleophile (Nu):



$$-\mathrm{Si}-X + \mathrm{Cat} \rightleftarrows \overset{X}{\underset{\mathrm{Cat}}{-\mathrm{Si}-}} \xrightleftharpoons{\mathrm{Nu}} \overset{X\ \ \mathrm{Nu}}{\underset{\mathrm{Cat}}{-\mathrm{Si}-}} \xrightarrow[-\mathrm{Cat}]{} -\mathrm{Si}-\mathrm{Nu} + X^-, \qquad (5)$$

where X = H, OR, NR$_2$, Cl.

Presumably, DMF in reaction (2), forming a complex with SiCl$_4$, enhances the nucleophilicity of the Cl atoms. However, THF, dioxane, and diethyl ether are quite inert relative to SiCl$_4$ and Si(OEt)$_4$ [19, 20]. A common property of ethers (and alcohols) is their capability to form oxonium complexes with hydrogen halides. In such complexes, the nucleophilicity of chloride ions is enhanced, and their exchange with ethoxy groups is activated. Presumably, reaction (2) involves formation of a six-membered cyclic transition state in which cleavage of the Si–O bond (i) yields exchange products, and cleavage of the O–CH$_2$Me bond (ii), heterofunctional cyclization products:



EXPERIMENTAL

The azeotropic mixture SiCl$_4$–Me$_3$SiCl obtained from synthesis of chlorosilanes[1] contained 49.07% Me$_3$SiCl, 37.05% SiCl$_4$, 12.00% MeSiHCl$_2$, 0.77% SiH$_2$Cl$_2$, 0.74% SiHCl$_3$, and 0.21% Me$_3$SiOSiMe$_3$.

Chromatographic analysis was performed with a Hewlett–Packard HP 5890 device (EI, 70 eV, HP 5971 A mass-selective detector, 50-m Ultra-2 column coated with polymethylsilicone containing 5% phenyl groups, vaporizer temperature 250°C, column temperature 50–280°C).

Reaction of Si(OEt)$_4$ with SiCl$_4$ in azeotropic mixture with Me$_3$SiCl in the presence of initiator. (a) A mixture of 10.15 g of Me$_3$SiCl–SiCl$_4$ azeotrope, 15.6 g of Si(OEt)$_4$, and 1.0 wt % THF was heated for 10 h at 60–65°C and fractionated. Yield of Me$_3$SiCl 3.3 g (66%), purity 99%.

(b) A mixture of 25.0 g of Me$_3$SiCl–SiCl$_4$ azeotrope, 11.5 g of Si(OEt)$_4$, and 1.83 g (5.0 wt %) of DMF was heated to reflux for 18 h and cooled to room temperature; the liquid phase was separated by decanting and fractionated.

(c) A mixture of 17.9 g of Me$_3$SiCl–SiCl$_4$ azeotrope, 10.7 g of Si(OEt)$_4$, and 6.0 g of the complex SiCl$_4$ · 2H(O)CNMe$_2$ was heated to reflux for 4 h. After cooling to room temperature, the liquid phase was separated from the precipitate (4.9 g) by decanting and distilled to give 5.9 g (67%) of Me$_3$SiCl, bp 55–56°C; 4.9 g of (EtO)SiCl$_3$, bp 102–105°C; 3.7 g of (EtO)$_2$SiCl$_2$, bp 137–139°C; and 5.8 g of (EtO)$_3$ · SiCl, bp 156–158°C.

At other reaction times and temperatures and with other amounts of catalysts, the mixtures were worked up similarly. The experimental conditions and reaction products are listed in the table.

Reaction of Me$_3$SiCl–SiCl$_4$ azeotrope with Si(OEt)$_4$ in the presence of 10 wt % THF. A mixture of 5.08 g of Me$_3$SiCl–SiCl$_4$ azeotrope, 7.8 g of Si(OEt)$_4$, and 10 wt % THF was heated at 60–65°C for 10 h. The resulting mixture was analyzed by GC–MS. Component content, wt %: Me$_3$SiCl 7.7, THF 8.5, (EtO)$_2$SiCl$_2$ 5.5, (EtO)$_3$SiCl 58.5, Si(OEt)$_4$ 15.0, (EtO)$_3$SiOMe$_3$ 3.2, (EtO)$_2$Si(OSiMe$_3$)$_2$ 1.5, and EtOSi(OSiMe$_3$)$_3$ and unidentified products <0.5.

Reaction of SiCl$_4$ with Si(OEt)$_4$ in the presence of Et$_2$O. (a) A mixture of 4.25 g of SiCl$_4$, 5.2 g of Si(OEt)$_4$, and 2 wt % Et$_2$O was heated at 60–65°C for 10 h and then analyzed by GC–MS. Component content, wt %: Et$_2$O 0.2, EtOSiCl$_3$ 1.1, (EtO)$_2$SiCl$_2$ 14.9, (EtO)$_3$SiCl 76.7, Si(OEt)$_4$ 5.1, and ethoxychloropolysiloxanes 2.0.

(b) A mixture of 1.7 g of SiCl$_4$, 6.24 g of Si(OEt)$_4$, and 2 wt % Et$_2$O was heated at 60–65°C for 10 h and then analyzed by GC–MS. Component content, wt %: Et$_2$O 1.6, EtOSiCl$_3$ 22.4, (EtO)$_2$SiCl$_2$ 2.5, Si(OEt)$_4$ 69.0, Cl$_3$SiOSi(OEt)$_3$ 2.7, and unidentified compounds 1.8.

CONCLUSION

Treatment of the azeotropic mixture Me$_3$SiCl–SiCl$_4$ with Si(OEt)$_4$ at 25–65°C in the presence of 0.2–10 wt % cyclic (THF, dioxane) or acyclic (diethyl ether) ethers, ethanol, or dimethylformamide allows isolation of 99% pure trimethylchlorosilane in up to 88% yield.

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