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A Convenient Method for the Preparation of Hydrogensiloxanes

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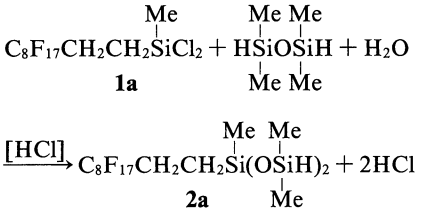
Synopsis. Chlorosilanes containing fluorinated organosubstituents are hydrolyzed in a stirred mixture of 1,1,3,3-tetramethyldisiloxane and hydrochloric acid to give the corresponding hydrogensiloxanes substituted with dimethylsiloxy groups in place of chlorine atoms.

Hydrogensiloxanes[1] are useful addtion reaction crosslinkers in the silicone industry. In general, siloxane compound such as 1,1,3,3,5,5-hexamethyl-1,3,5-trisiloxane has been prepared by equilibration reaction from 1,1,3,3,5,5,7,7-octamethyl-1,3,5,7-cyclotetrasiloxane and 1,1,3,3-tetramethyldisiloxane,[2] however, it is difficult to obtain the intended siloxanes selectively. To convert the chlorine atom of chlorosilane into the dimethylsiloxy group directly, cohydrolysis of chlorosilanes with dimethylchlorosilane has been frequently used.[3,4] In handling dimethylchlorosilane, however, care must be taken as it is volatile and stimulative and the reaction requires an excess of dimethylchlorosilane. The reaction of silanol with chlorosilane in the presence of amine is also well known.[5] But, preparation of the hydrogensiloxanes is restricted to the limited availability of silanols. In this paper, I wish to report the selective conversion of chlorosilanes **1** into the dimethylsiloxy-terminated siloxanes **2** by the hydrolysis of chlorosilanes in a stirred mixture of 1,1,3,3-tetramethyldisiloxane and hydrochloric acid.



$$\mathrm{C_8F_{17}CH_2CH_2\overset{Me}{Si}Cl_2} + \mathrm{H\underset{Me}{\overset{Me}{Si}}O\underset{Me}{\overset{Me}{Si}}H} + \mathrm{H_2O} \xrightarrow{[\mathrm{HCl}]} \mathrm{C_8F_{17}CH_2CH_2\overset{Me}{Si}(O\underset{Me}{\overset{Me}{Si}}H)_2} + 2\mathrm{HCl}$$

1a **2a**

Chlorosilanes **1a**—**1f** produced the corresponding hydrogensiloxanes **2a**—**2f** in high yields. The results are summarized in Table 1. Chlorosilanes **1g**—**1i** terminated with chlorosilyl group on both sides also gave hydrogensiloxanes **2g**—**2i** in high yields. It is worth to point out that a small excess amount of dimethylsiloxy groups against the chlorine atom was sufficient to yield the hydrogensiloxanes, and the formation of polysiloxane by-products was slight. Chlorosilanes containing comparatively bulky alkyl and aryl groups also gave the hydrogensiloxanes: *i*-BuMe$SiCl_2$, $C_5H_{11}SiCl_3$, MePh$SiCl_2$, Ph_2SiCl_2, and $PhSiCl_3$ gave corresponding siloxanes in a 76, 85, 84, 87, and 87% yield,[4] respectively.

In summary, I have demonstrated an effective method for converting the chlorine atom of chlorosilanes into a dimethylsiloxy group, from which hydrogensiloxanes can be readily synthesized.

Experimental

All boiling points were uncorrected. IR spectra were recorded on a JASCO IR-810 spectrophotometer. ^{1}H NMR spectra were measured on a JEOL PMX 60SI spectrometer using $CHCl_3$ as an internal standard.

General Procedure for Preparation of Hydrogensiloxanes. A four-necked flask was placed with 1,1,3,3-tetramethyldisiloxane (134 g, 1.0 mol), concentrated hydrochloric acid (90 g) and water (32 g), and the mixture was maintained at 5 to 10 °C by cooling with ice water. Under stirring, methyl(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro)decyldichlorosilane (**1a**) (505 g, 0.9 mol) was added into the mixture over a period of 3 h. After the addition, 200 ml of water was added so as to maintain the reaction mixture at a temperature of 20 °C or below. The organic layer was washed twice with water, twice with an aqueous 5% solution of $NaHCO_3$ and further 5 times with water, followed by drying over Na_2SO_4. Distillation under reduced pressure gave the siloxane **2a** (536 g, 93%); 92—94 °C/4 mmHg (1 mmHg=133.322 Pa).

Analytical data of products obtained are as follows.

2a: IR (neat) 2140 and 1070 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.23 (s, 3H), 0.33 (d, J=9 Hz, 12H), 0.67—1.10 (m, 2H), 1.67—2.70 (m, 2H), 4.70—5.00 (m, 2H). Anal. ($C_{15}H_{21}F_{17}O_2Si_3$) C, H.

2b: IR (neat) 2150 and 1070 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.35 (d, J=9 Hz, 18H), 0.70—1.07 (m, 2H), 1.67—2.70 (m, 2H), 4.67—5.00 (m, 3H). Anal. ($C_{16}H_{25}F_{17}O_3Si_4$) C, H.

2c: IR (neat) 2140 and 1070 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.27 (s, 6H), 0.30 (d, J=9 Hz, 6H), 0.70—1.10 (m, 2H), 1.63—2.67 (m, 2H), 4.63—4.93 (m, 1H). Anal. ($C_{14}H_{17}F_{17}OSi_2$) C, H.

2d: IR (neat) 2140 and 1070 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.23 (s, 3H), 0.30 (d, J=9 Hz, 12H), 0.70—1.10 (m, 2H), 1.63—2.67 (m, 2H), 4.70—5.00 (m, 2H). Anal. ($C_{11}H_{21}F_3O_2Si_3$) C, H.

2e: IR (neat) 2140 and 1070 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.20 (s, 3H), 0.33 (d, J=9 Hz, 12H), 0.57—1.03 (m, 2H), 1.90—2.60 (m, 2H), 4.63—4.97 (m, 2H). Anal. ($C_8H_{21}F_3O_2Si_3$) C, H.

2f: IR (neat) 2140 and 1050 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.20 (s, 3H), 0.30 (d, J=9 Hz, 12H), 0.63—1.07 (m, 2H), 1.70—2.53 (m, 2H), 4.63—4.97 (m, 2H). Anal. ($C_{15}H_{21}F_{17}O_4Si_3$) C, H.

2g was identified by comparison of its spectroscopic behavior with that prepared by the method described in Ref. 3.

2h: IR (neat) 2140 and 1070 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.13 (s, 6H), 0.23 (d, J=9 Hz, 24H), 0.50—0.97 (m, 4H), 1.83—2.57 (m, 4H), 4.60—4.90 (m, 4H). Anal. ($C_{23}H_{42}F_{18}O_7Si_6$) C, H.

2i: IR (neat) 2140 and 1070 cm^{-1}; ^{1}H NMR (CCl_4) δ=0.28 (d, J=9 Hz, 36H), 0.53—1.03 (m, 4H), 1.67—2.57 (m, 4H), 4.63—4.98 (m, 6H). Anal. ($C_{25}H_{50}F_{18}O_9Si_8$) C, H.

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Table 1. Synthesis of Hydrogensiloxanes from Chlorosilanes[a]

	Chlorosilane **1**	Addition time/h	Product **2**	Yield[b] %	Bp °C/mmHg
a	$C_8F_{17}CH_2CH_2\overset{Me}{Si}Cl_2$	4	$C_8F_{17}CH_2CH_2\overset{Me}{Si}(O\overset{Me}{\underset{Me}{Si}}H)_2$	93	92—94/4
b	$C_8F_{17}CH_2CH_2SiCl_3$	6	$C_8F_{17}CH_2CH_2Si(O\overset{Me}{\underset{Me}{Si}}H)_3$	85	103—104/4
c	$C_8F_{17}CH_2CH_2\overset{Me}{\underset{Me}{Si}}Cl$	4	$C_8F_{17}CH_2CH_2\overset{Me}{\underset{Me}{Si}}O\overset{Me}{\underset{Me}{Si}}H$	87	76—78/3
d	$C_4F_9CH_2CH_2\overset{Me}{Si}Cl_2$	3	$C_4F_9CH_2CH_2\overset{Me}{Si}(O\overset{Me}{\underset{Me}{Si}}H)_2$	87	65—66/5
e	$CF_3CH_2CH_2\overset{Me}{Si}Cl_2$	4	$CF_3CH_2CH_2\overset{Me}{Si}(O\overset{Me}{\underset{Me}{Si}}H)_2$	85	79—80/57
f	$F(\underset{CF_3}{C}FCF_2O)_2\underset{CF_3}{C}FCH_2CH_2\overset{Me}{Si}Cl_2$	4	$F(\underset{CF_3}{C}FCF_2O)_2\underset{CF_3}{C}FCH_2CH_2\overset{Me}{Si}(O\overset{Me}{\underset{Me}{Si}}H)_2$	91	72—74/2
g	$Cl_3SiCH_2CH_2C_6F_{12}CH_2CH_2SiCl_3$[c]	4	$(H\overset{Me}{\underset{Me}{Si}}O)_3SiCH_2CH_2C_6F_{12}CH_2CH_2Si(O\overset{Me}{\underset{Me}{Si}}H)_3$	92	147—150/1.2×10^{-5}
h	$Cl_2\overset{Me}{Si}CH_2CH_2\underset{CF_3}{C}FOCF_2CF_2O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}FCH_2CH_2\overset{Me}{Si}Cl_2$	3	$(H\overset{Me}{\underset{Me}{Si}}O)_2\overset{Me}{Si}CH_2CH_2\underset{CF_3}{C}FOCF_2CF_2O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}FCH_2CH_2\overset{Me}{Si}(O\overset{Me}{\underset{Me}{Si}}H)_2$	90	150—153/1.0×10^{-5}
i	$Cl_3SiCH_2CH_2\underset{CF_3}{C}FOCF_2CF_2O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}FCH_2CH_2SiCl_3$	4	$(H\overset{Me}{\underset{Me}{Si}}O)_3SiCH_2CH_2\underset{CF_3}{C}FOCF_2CF_2O\underset{CF_3}{C}FCF_2O\underset{CF_3}{C}FCH_2CH_2Si(O\overset{Me}{\underset{Me}{Si}}H)_3$	86	160—162/1.0×10^{-5}

a) 1,1,3,3-Tetramethyldisiloxane was used so that -OSi(Me)$_2$H moiety was 1.1 to 1.2 equivalent per Cl. b) Isolated yield. c) Chlorosilane was added as a solution of *m*-bis(trifluoromethyl)benzene because chlorosilane is solid.

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