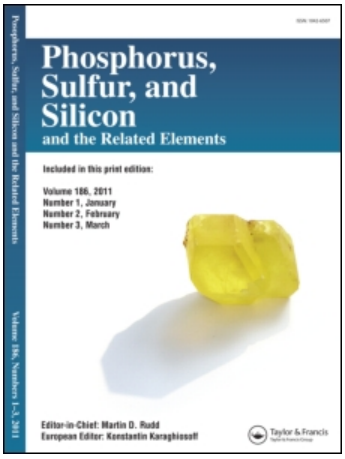


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

REDISTRIBUTION OF DICHLOROSILANES AND DIHYDRIDOSILANES. SYNTHESIS OF CHLORO HYDRIDOSILANES

A. Benouargha[a]; D. Boulahia[b]; B. Boutevin[b]; G. Caporiccio[c]; F. Guida-pietrasanta[b]; A. Ratsimihety[b]
[a] Laboratoire de Chimie Organique Hétérocyclique, Faculté des Sciences, Université Mohamed V, Rabat, Morocco [b] URA D 1193 CNRS, Laboratoire de Chimie Appliquée, Ecole Nationale Supérieure de Chimie de Montpellier, Montpellier Cedex 1, France [c] Dow Corning Corp, Midland, Michigan, USA

To cite this Article Benouargha, A. , Boulahia, D. , Boutevin, B. , Caporiccio, G. , Guida-pietrasanta, F. and Ratsimihety, A.(1996) 'REDISTRIBUTION OF DICHLOROSILANES AND DIHYDRIDOSILANES. SYNTHESIS OF CHLORO HYDRIDOSILANES', Phosphorus, Sulfur, and Silicon and the Related Elements, 113: 1, 79 — 87
To link to this Article: DOI: 10.1080/10426509608046380
URL: http://dx.doi.org/10.1080/10426509608046380

Phosphorus, Sulfur, and Silicon, 1996, Vol. 113, pp. 79–87
Reprints available directly from the publisher
Photocopying permitted by license only

REDISTRIBUTION OF DICHLOROSILANES AND DIHYDRIDOSILANES. SYNTHESIS OF CHLORO HYDRIDOSILANES

A. BENOUARGHA,† D. BOULAHIA,‡ B. BOUTEVIN,‡ G. CAPORICCIO,§ F. GUIDA-PIETRASANTA‡·¶ and A. RATSIMIHETY‡

†*Université Mohamed V, Laboratoire de Chimie Organique Hétérocyclique, Faculté des Sciences, Rabat, Morocco;* ‡*URA D 1193 CNRS, Laboratoire de Chimie Appliquée, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale, 34053 Montpellier, Cedex 1, France;* §*Dow Corning Corp, Midland, Michigan, USA*

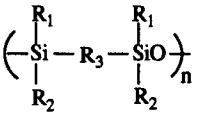
(Received November 14, 1995; in final form December 5, 1995)

The redistribution of dichlorosilanes $RSi(CH_3)Cl_2$ and dihydridosilanes $RSi(CH_3)H_2$, prepared by reduction of the homologues dichlorosilanes, in the presence of a quaternary ammonium salt is presented. The influence of the nature of R (fluoroalkyl chain $R_FCH_2CH_2$ with $R_F = CF_3$, C_4F_9, C_8F_{17}, alkyl chain $R = C_6H_{13}$ or aromatic $R = C_6H_5$) and of the temperature on the rate of the reaction is studied. The equilibrium constants and free enthalpies are calculated and discussed taking into account the nature of R. The new products described were characterized from I.R, ^1H, ^{19}F and ^{29}Si NMR spectroscopies.

Key words: Chlorosilanes, hydridosilanes, chlorohydridosilanes, redistribution.

INTRODUCTION

Chlorohydridosilanes $HSi(R_1)(R_2)Cl$ are very interesting compounds as they may be used either for their ≡Si—H or for their ≡Si—Cl functions. They may be considered as precursors of silicones, and particularly, via a hydrosilylation of α, ω-dienes, followed by hydrolysis and polycondensation, they may lead to silalkylene siloxanes, or hybrid silicones[1,2]:



These hybrid silicones are known to exhibit the advantage of retaining the positive properties of polysiloxanes —$[Si(R_1)(R_2)O]_n$— and lacking their drawbacks such as reversion. Depending on the nature of R_1, R_2, R_3 they may exhibit special properties.

In general, pure chlorohydridosilanes are not easy to obtain. Around the fifties, various synthetic routes have been described in the literature:

—direct synthesis from elemental silicium and halogenated organic products[3,4]
—use of Grignard reagents[5–7]

¶Author to whom correspondence should be addressed.
‖Present address: Via E. Filiberto 13, Milano, Italy.

—redistribution between a hydridosilane and a chlorosilane heated in the presence of Al Cl_3.[8,9]

These methods lead to complex mixtures and the yields are generally low. However, the redistribution reaction has been studied more in detail,[10-12] and it was possible to obtain a methylhydridochlorosilane $RSi(CH_3)(H)Cl$ in about 50% yield from a methyldichlorosilane $RSi(CH_3)Cl_2$ and a methyldihydridosilane $RSi(CH_3)H_2$ heated in the presence of quaternary ammonium or phosphonium salts (Bu_4NX or Bu_4PX).

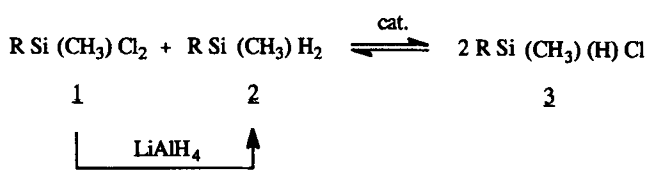
We have chosen to study this reaction with silanes bearing various R groups to evaluate the influence of the nature of R on the rate of the reaction. And we have been particularly interested in R = $R_FCH_2CH_2$ as this redistribution reaction could be a new method to synthesize fluoroalkyl substituted chlorohydridosilanes.

RESULTS AND DISCUSSION

The redistribution of methyl dichlorosilanes 1 and methyldihydridosilanes 2 was performed according to Scheme 1.

If chlorosilanes 1a and 1e were commercially available, chlorosilanes 1b, 1c and 1d had to be synthesized, and this was performed via the hydrosilylation of olefins R—CH=CH_2 (respectively R = C_4F_9, C_8F_{17}, C_4H_9) with methyl dichlorohydridosilane H $Si(CH_3)Cl_2$ in the presence of H_2PtCl_6 according to our usual method.[13]

Then, all hydridosilanes 2 were prepared by reduction of the corresponding chlorosilanes 1 with $LiAlH_4$. The structure of every new prepared product was confirmed by IR, and ^1H, ^{19}F and ^{29}Si NMR spectroscopies. The ^1H NMR spectrum of dichlorosilane 1b exhibited a singlet at 0.85 ppm for the methyl group and an AA'XX' system for the two methylene groups of the $C_4F_9CH_2CH_2Si$ chain, the XX' part being tripled by the α CF_2 group. This structure was checked by successive irradiations of the CH_2 attached to the Si atom, at 1.35 ppm, and of the CH_2 attached to C_4 F_9, at 2.25 ppm. The former irradiation induces a change in the complex system at 2.25 ppm which becomes a triplet [due to the adjacent CF_2, J(H—F) = 17.5 Hz]. The latter irradiation transforms the system at 1.35 ppm in a singlet, showing that this



a) R = $C_2H_4CF_3$
b) R = $C_2H_4C_4F_9$
c) R = $C_2H_4C_8F_{17}$
d) R = $C_2H_4C_4H_9$
e) R = C_6H_5

Scheme 1

system resulted only of the coupling with the adjacent CH_2. No change was observed on the AA'XX' system when the methyl protons at 0.85 ppm were irradiated.

The coupling constants were determined according to H. Günther,[14] J(A—A') = 12.8 Hz, J(X—X') = 10.9 Hz, J(A—X) = 16.2 Hz and J(A—X') = 0.65 Hz. A negative sign was attributed to J(AA') and J(XX') as, in this case, the two hydrogen atoms have geminal coupling constants. ^{1}H NMR spectrum of dichlorosilanes 1c was identical to that of 1b. For dichlorosilane 1a, the ^{1}H NMR is slightly different as the CH_2 forming the XX' part of the AA'XX' system is now adjacent to a CF_3 group and thus is quadrupled.

For dihydridosilanes 2a–c, ^{1}H NMR spectra exhibit again an AA'XX' system for the two CH_2 groups, the AA' parts being now upfield shifted (at 0.95 ppm) and being tripled by SiH_2 [^2J(H—H) = 4 Hz]. The SiH_2 protons exhibit a tripled quadruplet centered at 3.80 ppm. The CH_3 protons give triplets centered at 0.20 ppm [^2J(H—H) = 4 Hz]. ^{29}Si NMR spectra of dichlorosilanes 1a to 1d exhibit a singlet at +31 ppm, whereas 1e spectrum exhibits a singlet at +18.7 ppm, all in agreement with the values found in the literature for such compounds.[15] For dihydridosilanes 2a to 2d, ^{29}Si NMR spectra exhibit a singlet at −31 ppm when the protons are irradiated, and a triplet in the absence of protons irradiation [^1J(Si—H) = 195 Hz]. Likewise, 2e ^{29}Si NMR spectrum exhibits a singlet at −35.6 ppm when the protons are irradiated and a triplet, having the same coupling constant as previously, in the absence of protons irradiation.

All the hydridosilanes exhibit a strong absorption at 2145 cm^{-1} in I.R spectroscopy, which is characteristic for a Si—H.

As for the redistribution reaction (Scheme 1), it is noteworthy mentioning that such an equilibrium occurs only in the presence of a catalyst. The mainly used catalysts are Bu_4NX or Bu_4PX (X = Cl, Br). We have used 1% dry tetrabutyl ammonium bromide Bu_4NBr in all cases, and in one case, (1b + 2b), we have also used tetrabutyl phosphonium bromide Bu_4PBr to evaluate the influence of the catalyst.

The redistribution of 1e and 2e had already been studied in the presence of Bu_4NCl, in a sealed NMR tube heated at 100°C for 96 hours and an equilibrium constant of 8.5 had been determined.[11]

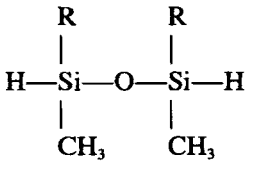
Our equilibria were performed in flasks, at various temperatures and under an inert atmosphere (Argon). In all cases, the maximum reaction temperature was fixed under the boiling point of the hydridosilane in order to avoid a displacement of the equilibrium. The boiling points of the different silanes present in the reaction mixture are in the order:

$$RSi(CH_3)H_2 < RSi(CH_3)(H)(Cl) < RSi(CH_3)Cl_2$$

Moreover, from a thermogravimetric analysis (TGA) we determined the decomposition temperature of the catalyst to be around 155°C, and even in the case where R = $C_2H_4C_8F_{17}$ [$RSi(CH_3)H_2$ boiling point being much higher than 155°C] the maximum temperature used was 140°C in order to be sure that the catalyst would not decompose during the reaction.

In each case, aliquots of the crude reaction mixture were taken at different times during the reaction and they were analysed, at room temperature, in ^{1}H NMR where the relative percentages of the methyl groups on the Si atom of the different com-

pounds in the mixture can be measured. As previously stated, the methyl in dichlorosilane 1 gives a singlet at 0.85 ppm and in dihydridosilane 2 it gives a triplet at 0.20 ppm, whereas the methyl of the hydridochlorosilane 3 formed, gives a doublet at 0.55 ppm. In some cases, the presence of a by-product, dihydridodisiloxane 4, can be observed:



4

issued from the hydrolysis of hydridochlorosilane 3. Its methyl groups are evidenced as a doublet at 0.25 ppm, easy to differentiate from the three other silanes.

In all cases, there was no change at all between the aliquots taken after 20 and 24 hours. So, we have considered that the equilibrium was reached after 24 hours, and it was not necessary to carry out the reaction any longer. We have checked that the values obtained from NMR spectra performed at room temperature were reliable. As a matter of fact, the aliquots taken after 24 hours were left for one week at room temperature, then were tested again in ^1H NMR and their spectra were identical to the previous ones. So, it seems that the equilibria were not modified at room temperatures. In two cases, (1a + 2a) and (1e + 2e), the reactions were also performed in sealed tubes for 24 hours, respectively at 56 and 105°C, and the results were similar to those obtained when the reactions were performed in flasks; the equilibria were slightly displaced to the right (higher percentage of 3).

However, when 1a and 2a were reacted at 105°C for 24 hours in a sealed tube, the equilibrium was highly displaced to the right as 63% of 3a were obtained, when only 33% were obtained at 56°C.

All our results are summarized in Table I, and the values of the equilibrium constant K are given for each compound and at each temperature, these values being deduced from the relative percentages of 3, 2 and 1 at the equilibrium.

In fact the equilibrium constant is given by:

$$K = \frac{[R(CH_3)Si(H)Cl]^2}{[R(CH_3)SiH_2][R(CH_3)SiCl_2]} = \frac{[3]^2}{[2][1]}$$

if the concentration of 1 and 2 at time zero is a_0, at time t (equilibrium), it will be $a_0(1 - x)$ and the concentration of 3 will be a_0x.

So,

$$K = \frac{(2a_0x)^2}{[a_0(1 - x)]^2} = \frac{4x^2}{(1 - x)^2}$$

at the equilibrium,

$$x = \frac{[3]}{[1] + [2] + [3]}$$

if A_1, A_2 and A_3 are the respective integrations of the methyl groups in 1, 2 and 3, we consider that

$$x = \frac{A_3}{A_1 + A_2 + A_3}$$

and K may be calculated in each case.

Table I also gives the values of free enthalpy $\Delta G°$, for at the equilibrium, $\Delta G° = -RT \ln K$, or $\ln K = -\Delta G°/RT$. And as we have the values of K at various temperatures, we may draw the curve $\ln K = f(1/T)$ where the slope will be $-\Delta G°/R$, from which we can determine the value of $\Delta G°$.

If we consider the values listed in Table I, we can say that:

- —in the case where R is an alkylfluorinated chain $C_2H_4R_F$ ($R_F = CF_3$, C_4F_9 and C_8F_{17}), the longer the fluorinated chain, the more difficult the formation of $HSi(CH_3)R(Cl)$. $\Delta G°$ decreases when the length of R_F increases.
- —comparing an alkyl chain C_6H_{13} and a fluoroalkyl chain $C_2H_4C_4F_9$ having the same length, but being more electron withdrawing, shows that $\Delta G°$ is higher for the fluoroalkyl chain. The formation of $HSi(CH_3)R(Cl)$ is easier. Likewise, when R is an aromatic, $\Delta G°$ is much higher than for an alkyl chain.
- —the use of Bu_4PBr as catalyst, instead of Bu_4NBr, in the case where R = $C_2H_4C_4F_9$, did not show a significant change [respectively 45% and 52% of $HSi(CH_3)(C_2H_4C_4F_9)Cl$ were formed, when the reaction was performed at 105°C]. This is in agreement with what had already been observed with Bu_4PCl compared to Bu_4NCl.[9]

Moreover, we also performed an experiment (1b + 2b) at 120°C with a higher amount of catalyst (5%) and we obtained the same amount of 3b as when the reaction was performed with 1% of catalyst. The amount of catalyst seemed to have no effect on the equilibrium, in this case.

We know that an equilibrium constant K = 8.5 had already been measured for R = C_6H_5,[11] when the reaction was performed in a sealed tube during 96 hours at 100°C and with Bu_4NCl as catalyst. When we carried out the reaction in a flask, under Argon, at 105°C during 24 hours and in the presence of Bu_4NBr, that is to say in different conditions, we obtained K = 2.1 which is slightly different but in the same range order of value.

As we have already stated, the redistribution reaction must be performed under an inert atmosphere in order to avoid any trace of moisture which would hydrolyse the chlorosilanes present in the mixture.

Thus, operating in these conditions, we have been able, after distillation of the crude reaction mixture, to isolate the pure hydridochlorosilanes 3a, 3b and 3e. The first fraction separated is the dihydridosilane 2 which is the more volatile. Then, the expected hydridochlorosilane 3 is obtained, and the remaining dichlorosilane may distill or stay as the residue.

But, on the contrary, if some traces of water are introduced in the reaction mixture, the hydridochlorosilane 3 is immediately hydrolysed in dihydridodisiloxane 4 which is also an interesting precursor for siloxanes as it may lead either to homopolymers or to copolymers if it is condensed with other kinds of silicone precursors.

On two examples, (1b + 2b) and (1e + 2e), we have hydrolysed the crude reaction mixture and we have thus been able to separate the dihydridodisiloxane 4b and 4e after distillation of the remaining dihydridosilane 2, and the products have been characterized as usual by I.R and NMR spectroscopies.

TABLE I

Equilibrium constants and $\Delta G°$ values

R	$C_2H_4CF_3$		$C_2H_4C_4F_9$		$C_2H_4C_8F_{17}$		C_6H_{13} ($C_2H_4C_4H_9$)		C_6H_5	
b.p.R(CH_3)SiH_2(°C)	59		113		31/2,5.10^{-3}		135		139	
T°C	% 3	K	% 3	K	% 3	K	% 3	K	% 3	K
30	18	0.19								
40			18	0.2	16	0.15				
50	27	0.55								
56	29	0.66								
	33	0.95								
80			38	1.5	21	0.28	23	0.36	24	0.4
105	63 (sealed tube)	11	45	2.7	27	0.55	24	0.4	42	2.1
			52*	4.69*					48 (sealed tube)	3.4
120			58.5	7.9	29	0.7	29	0.7	48	3.4
140					degradation					
$\Delta G°$ Kcal deg^{-1} $mole^{-1}$	11.6		10.59		4.74		3.83		16	

* cat = Bu_4 P Br

CONCLUSION

The redistribution of dichlorosilanes $RSi(CH_3)Cl_2$ and dihydridosilanes $RSi(CH_3)H_2$ catalysed by an ammonium salt has shown to be an interesting method to prepare hydridochlorosilanes which are important precursors in the synthesis of silicones, and it is particularly interesting for the synthesis of fluorinated hydridochlorosilanes. It may also be considered as a way to prepare dihydridodisiloxanes by hydrolysis of the crude reaction mixture.

The nature of R (alkyl, fluoroalkyl or aryl) plays a role on the rate of the reaction. But the nature of the catalyst (Bu_4NBr or Bu_4PBr) and its amount (1% or 5%) has little or no effect on the equilibrium reaction.

EXPERIMENTAL

IR spectra were recorded on a NICOLET 510P FTIR spectrometer. NMR spectra were recorded on BRUKER WP200 or WH250 spectrometers with TMS as reference for ^1H and ^{29}Si NMR and $CFCl_3$ as reference for ^{19}F NMR. Chemical shifts are reported in ppm: s = singlet, d = doublet, t = triplet, q = quadruplet and m = multiplet. All spectra were recorded for $CDCl_3$ solutions. $CF_3C_2H_4SiCl_2CH_3$ was supplied by Dow Corning Corp. $C_6H_5SiCl_2CH_3$ was purchased from Aldrich.

General Procedure for Hydrosilylation

A solution consisting of 0.1 mol methyldichlorosilane, 0.1 mol olefin and 200 ppm of H_2PtCl_6 relative to the amount of olefin (10% solution of H_2PtCl_6, $6H_2O$ in 2-propanol) was placed in a Carius type glass tube which was sealed and heated overnight at 110°C. After cooling, the black reaction mixture was filtered and distilled.

Nonafluorohexyl methyl dichlorosilane 1b: Hydrosilylation of $C_4F_9CH{=}CH_2$ according to the general procedure gave the corresponding dichloro methyl silane $C_4F_9C_2H_4SiCl_2CH_3$ 1b.
Yield = 88%, Bp = 170°C
^1H NMR: 0.85 (s, 3H, $SiC\underline{H}_3$); 1.3–1.45 (m, 2H, $SiC\underline{H}_2$); 2.15–2.45 (m, 2H, $SiCH_2C\underline{H}_2$)
^{19}F NMR: −82 (t, 3F, $C\underline{F}_3$); −117 (t, 2F, $CH_2C\underline{F}_2$); −125 (m, 2F, $CH_2CF_2C\underline{F}_2$); −126 (m, 2F, $CF_3C\underline{F}_2$)
29Si NMR: +31.4 (s, $\underline{Si}Cl$)

Heptadecafluorodecyl methyl dichlorosilane 1c: Hydrosilylation of $C_8F_{17}CH{=}CH_2$ according to the general procedure gave the corresponding dichloro methyl silane $C_8F_{17}C_2H_4SiCl_2CH_3$ 1c.
Yield = 82%, Bp = 62°C ($2\cdot10^{-3}$ mm Hg)
^1H NMR: 0.85 (s, 3H, $SiC\underline{H}_3$); 1.3–1.45 (m, 2H, $SiC\underline{H}_2$); 2.15–2.45 (m, 2H, $SiCH_2C\underline{H}_2$)
^{19}F NMR: −81.8 (t, 3F, $C\underline{F}_3$); −116.5 (t, 2F, $CH_2C\underline{F}_2$); −122.6 (m, 2F, $CH_2CF_2C\underline{F}_2$); −123.5 (m, 4F, $CH_2CF_2CF_2C\underline{F}_2C\underline{F}_2$); −123.9 (m, 2F, $CF_3CF_2CF_2C\underline{F}_2$); −124.3 (m, 2F, $CF_3CF_2C\underline{F}_2$); −127 (m, 2F, $CF_3C\underline{F}_2$)
^{29}Si NMR: + 31.6 (s, $\underline{Si}Cl$)

Hexyl methyl dichlorosilane 1d: Hydrosilylation of 1-hexene $C_4H_9CH{=}CH_2$ according to the general procedure gave the corresponding dichloro methyl silane $C_4H_9C_2H_4SiCl_2CH_3$ 1d.
Yield = 82%, Bp = 40°C (1 mm Hg)
^1H NMR: 0.8 (s, 3H, $SiC\underline{H}_3$); 0.9 (m, 2H, $SiC\underline{H}_2$); 1.1–1.2 (t, 3H, $CH_3C\underline{H}_2$); 1.3–1.6 (m, 8H, four internal $C\underline{H}_2$)
^{29}Si NMR: +31.5 (s, $\underline{Si}Cl$)

General Procedure for the Reduction of Dichlorosilanes into Dihydridosilanes

0.028 mol $LiAlH_4$ and 100 ml anhydrous ether were placed in a 250 ml flask equipped with a condenser, a dropping funnel and swept by Argon. 0.055 mol $RSiCl_2CH_3$ diluted in 50 ml anhydrous ether were dropwise added and the reaction mixture was refluxed for two hours. After cooling, the excess lithium aluminium hydride was treated with 10% hydrochloric acid. The organic layer was separated, washed until neutrality, dried over Na_2SO_4 and distilled.

Trifluoropropyl methyl dihydridosilane 2a: Reduction of $CF_3C_2H_4SiCl_2CH_3$ 1a according to the general procedure but using dibutylether (in order to separate easily the solvent from the product formed) at 40°C gave the corresponding dihydrido methyl silane $CF_3C_2H_4SiH_2CH_3$ 2a.
Yield = 82%, Bp = 60°C
^{1}H NMR: 0.2 (t, 3H, SiC$\underline{H}_3$); 0.85–1 (m, 2H, SiC$\underline{H}_2$); 2–2.25 (m, 2H, SiCH$_2$C$\underline{H}_2$); 3.8 (q, 2H, Si$\underline{H}_2$).
^{19}F NMR: −69 (t, C$\underline{F}_3$)
^{29}Si NMR: −31.9 (s when ^{1}H are irradiated, t without irradiation, $\underline{Si}H_2$); J(Si—H) = 195 Hz

Nonafluorohexyl methyl dihydridosilane 2b: Reduction of $C_4F_9C_2H_4SiCl_2CH_3$ according to the general procedure gave the corresponding dihydrido methyl silane $C_4F_9C_2H_4SiH_2CH_3$ 2b.
Yield = 83%, Bp = 113°C
^{1}H NMR: 0.2 (t, 3H, SiC$\underline{H}_3$); 0.9–1 (m, 2H, SiC$\underline{H}_2$); 2–2.3 (m, 2H, SiCH$_2$C$\underline{H}_2$); 3.8–3.9 (q, 2H, Si$\underline{H}_2$).
^{19}F NMR: −81.5 (t, 3F, C$\underline{F}_3$); −116.5 (t, 2F, CH$_2$C$\underline{F}_2$); −124.5 (m, 2F, CH$_2$CF$_2$C$\underline{F}_2$); −126.5 (m, 2F, CF$_3$C$\underline{F}_2$)
^{29}Si NMR: −31.30 (t, $\underline{Si}H_2$); J(Si—H) = 195 Hz

Heptadecafluorodecyl methyl dihydridosilane 2c: Reduction of $C_8F_{17}C_2H_4SiCl_2CH_3$ according to the general procedure gave the corresponding dihydrido methyl silane $C_8F_{17}C_2H_4SiH_2CH_3$ 2c.
Yield = 83%, Bp = 31°C ($2.5 \cdot 10^{-3}$ mm Hg)
^{1}H NMR: 0.15 (t, 3H, SiC$\underline{H}_3$); 0.85–1 (m, 2H, SiC$\underline{H}_2$); 2–2.25 (m, 2H, SiCH$_2$C$\underline{H}_2$); 3.8 (q, 2H, Si$\underline{H}_2$)
^{19}F NMR: −81.5 (t, 3F, C$\underline{F}_3$); −116.5 (t, 2F, CH$_2$C$\underline{F}_2$); −122.5 (m, 2F, CH$_2$CF$_2$C$\underline{F}_2$); −123 (m, 4F, CH$_2$CF$_2$CF$_2$C$\underline{F}_2$C$\underline{F}_2$); −123.5 (m, 2F, CF$_3$CF$_2$CF$_2$C$\underline{F}_2$); −124.5 (m, 2F, CF$_3$CF$_2$C$\underline{F}_2$); −127 (m, 2F, CF$_3$C$\underline{F}_2$)
^{29}Si NMR: −31.5 (t, $\underline{Si}H_2$); J(Si—H) = 195 Hz

Hexyl methyl dihydridosilane 2d: Reduction of $C_4H_9C_2H_4SiCl_2CH_3$ according to the general procedure gave the corresponding dihydrido methyl silane $C_4H_9C_2H_4SiH_2CH_3$ 2d.
Yield = 82%, Bp = 134–135°C
^{1}H NMR: 0.15 (t, 3H, SiC$\underline{H}_3$); 0.75 (m, 2H, SiC$\underline{H}_2$); 0.95 (t, 3H, C$\underline{H}_3$—CH$_2$); 1.2–1.5 (m, 8H, 4 internal C$\underline{H}_2$); 3.75 (q, 2H, Si$\underline{H}_2$)
^{29}Si NMR: −31.5 (t, $\underline{Si}H_2$); J(Si—H) = 195 Hz

Phenyl methyl dihydridosilane 2e: Reduction of $C_6H_5SiCl_2CH_3$ according to the general procedure gave the corresponding dihydrido methyl silane $C_6H_5SiH_2CH_3$ 2e.
Yield = 84%, Bp = 139–140°C
^{1}H NMR: 0.6 (t, 3H, SiC$\underline{H}_3$); 4.6 (q, 2H, Si$\underline{H}_2$); 7.5–7.8 (m, 5HC$_6\underline{H}_5$)
^{29}Si NMR: −35.6 (t, $\underline{Si}H_2$); J(Si—H) = 194 Hz

General Procedure for the Synthesis of Hydridochlorosilanes via Redistribution of Dichlorosilanes and Dihydridosilanes

0.01 mol $RSiCl_2CH_3$ 1 and 0.01 mol $RSiH_2CH_3$ 2 were placed in a two necked flask equipped with a condenser and a dropping funnel and swept by Argon. 10^{-4} mol tetrabutylammonium bromide were added. The reaction was performed during 24 hours at various temperatures, and in each case, aliquotes of the reaction mixture were taken and analysed in ^{1}H NMR to follow the evolution of the reaction and verify it has attained an equilibrium.

Trifluoropropyl methyl hydridochlorosilane 3a: 0.01 mol $CF_3C_2H_4SiCl_2(CH_3)$ 1a, 0.01 mol $CF_3C_2H_4SiH_2(CH_3)$ 2a and 10^{-4} mol Bu_4NBr were reacted for 24 hours at 105°C in a sealed tube. After cooling, the crude reaction mixture was distilled.

A first fraction was obtained. Bp = 60°C. It was identified as the starting dihydridosilane 2a. Yield = 25%.

Then, the expected hydridochlorosilane 3a was distilled. Bp = 98–100°C. Yield = 50%. It was identical to a sample of trifluoropropyl methyl hydridochlorosilane provided by Dow Corning Corp.

Nonafluorohexyl methyl hydridochlorosilane 3b: From an experiment performed with 1b + 2b, at 120°C, according to the general procedure, the crude reaction mixture was distilled.

The first fraction, Bp = 113°C, was the starting dihydridosilane 2b. Yield = 20%.

Then, the expected hydridochlorosilane 3b was distilled. Bp = 140°C. Yield = 50%.
^{1}H NMR: 0.55 (d, 3H, SiC$\underline{H}_3$); 1.15 (m, 2H, SiC$\underline{H}_2$); 2.1–2.3 (m, 2H, SiCH$_2$C$\underline{H}_2$); 4.9 (m, 1H, Si$\underline{H}$)
^{19}F NMR: −82 (t, 3F, C$\underline{F}_3$); −117 (t, 2F, CH$_2$C$\underline{F}_2$); −125 (m, 2F, CH$_2$CF$_2$ C$\underline{F}_2$); −126 (m, 2F, CF$_3$C$\underline{F}_2$)
^{29}Si NMR: +13.1 (d, $\underline{Si}H$); J(Si—H) = 190 Hz

Phenyl methyl hydridochlorosilane 3e: From an experiment performed with 1e + 2e, at 120°C, according to the general procedure, the crude reaction mixture was distilled.

The first fraction, Bp = 140°C, was the starting dihydridosilane 2e. Yield = 25%.

Then, the expected hydridochlorosilane 3e was distilled. Bp = 113°C (100 mm Hg). Yield = 42%.

^{1}H NMR: 0.8 (d, 3H, SiC$\underline{H}_3$); 5.4 (m, 1H, Si$\underline{H}$); 7.5–7.8 (m, 5HC$_6\underline{H}_5$)

^{29}Si NMR: +3.4 (d, $\underline{Si}$H); J(Si—H) = 220 Hz

Bis(nonafluorohexyl methyl hydrido)disiloxane 4b: From an experiment performed with 1b + 2b, at 120°C, according to the general procedure for redistribution, the crude reaction mixture was hydrolysed with 0.01 mol of water. The mixture was stirred for 15 minutes then distilled.

The first fraction was the unreacted dihydridosilane 2b.

Then, the expected bis(hydrido)disiloxane 4b was distilled. Bp = 120°C (20 mm Hg). Yield = 45%.

I.R: 2130 cm^{-1} (νSi—H)

^{1}H NMR: 0.25 (d, 3H, SiC$\underline{H}_3$); 0.8–1 (m, 2H, SiC$\underline{H}_2$); 1.9–2.2 (m, 2H, SiCH$_2$C$\underline{H}_2$); 4.7 (m, 1H, Si$\underline{H}$)

^{19}F NMR: −82 (t, 3F, C$\underline{F}_3$); −117 (t, 2F, CH$_2$C$\underline{F}_2$); −125 (m, 2F, CH$_2$CF$_2$C$\underline{F}_2$); −127 (m, 2F, CF$_3$C$\underline{F}_2$)

^{29}Si NMR: −2.25 (d, $\underline{Si}$H); J(Si—H) = 179 Hz

Bis(phenyl methyl hydrido)disiloxane 4e: From an experiment performed with 1e + 2e, at 120°C, according to the general procedure for redistribution, the crude reaction mixture was hydrolysed, as above, with 0.01 mol of water. The mixture was stirred for 15 minutes then distilled.

The first fraction was the unreacted dihydridosilane 2e.

Then, the expected bis(hydrido)disiloxane 4e was distilled. Bp = 120°C (2 mm Hg). Yield = 25%.

I.R: 2127 cm^{-1} (νSi—H)

^{1}H NMR: 0.6 (d, 3H, SiC$\underline{H}_3$); 5.4 (m, 1H, Si$\underline{H}$; 7.4–7.8 (m, 5H, aromatic protons)

^{29}Si NMR: −11.4 (d, $\underline{Si}$H); J(Si—H) = 195 Hz

ACKNOWLEDGEMENTS

We wish to thank the Dow Corning Corporation for supporting this work.

REFERENCES

1. M. O. Riley, Y. K. Kim and O. R. Pierce, *J. Fluorine Chem.*, **10,** 85 (1977).
2. B. Ameduri, B. Boutevin, F. Guida-Pietrasanta, A. Manseri, A. Ratsimihety and G. Caporiccio, submitted to publication.
3. E. G. Rochow, "An Introduction to the Chemistry of the Silicon," New York, John Wiley and Sons Inc., 1951, 2nd Ed., p. 36.
4. (a) K. A. Andrianov, S. A. Golubtsov, I. V. Trofimova, A. S. Denisova and R. A. Turetskaya, *Dokl. Akad. Nauk. SSSR*, **108,** 465 (1956); (b) K. A. Andrianov, S. A. Golubtsov, I. V. Trofimova and A. S. Denisova, *Zh. Prikl. Khim.*, **30,** 1277 (1957).
5. H. J. Emeleus and D. S. Payne, *J. Chem. Soc.*, 1590 (1947).
6. H. Gilman and R. N. Clark, *J. Amer. Chem. Soc.*, **69,** 1499 (1947).
7. A. J. Barry, Brit. Pat. n° 622,970 (1949) for Dow Chemical.
8. F. C. Whitmore, L. Pietrusa and L. H. Sommer, *J. Amer. Chem. Soc.*, **69,** 2108 (1947).
9. S. N. Borisov, M. G. Voronkov and B. N. Dolgov, *Dokl. Akad. Nauk.* USSR, 114 (1957); Chem. Abstr., **52,** 1057a (1958).
10. D. Weyenberg, A. Bey and P. Ellison, *J. Organomet. Chem.*, **3,** 489 (1965).
11. D. Weyenberg, A. Bey, H. Stewart and W. Atwell, *J. Organomet. Chem.*, **6,** 583 (1965).
12. (a) K. Moedritzer and J. R. Van Wazer, *J. Organomet. Chem.*, **12,** 69 (1968); (b) K. Moedritzer, in E. I. Becker and M. Tsutsui eds., "Organometallic Reactions," John Wiley, New York, 1970, Vol. 2, pp. 1–116.
13. B. Boutevin, G. Caporiccio, F. Guida-Pietrasanta and A. Ratsimihety, *J. Fluorine Chem.*, **68,** 71 (1994).
14. H. Günther, "La Spectroscopie de RMN," Ed. Masson, Paris, 1993, p. 187.
15. H. Marsmann, in P. Diehl, E. Fluck and R. Kosfeld, eds., "NMR Spectroscopy; Basic Principles and Progress," Springer-Verlag, Berlin, 1981, Vol. 17, pp. 65–235.
16. B. Ameduri, J. Balague, B. Boutevin and G. Caporiccio, *J. Fluorine Chem.*, **70,** 215 (1995).