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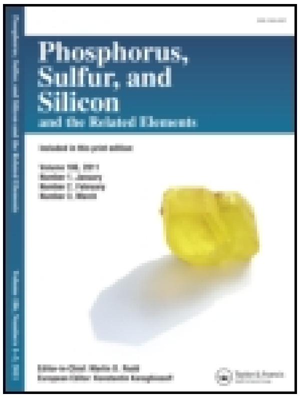

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A CONVENIENT ONE-POT SYNTHESIS OF STANNYLSILANES

Reinhard Hummeltenberg [a], Klaus Jurkschat [a] & Frank Uhlig [a]
[a] Lehrstuhl für Anorganische Chemie II, Universität Dortmund, Fachbereich Chemie Offo-Hahn-Straße 6, 44221, Dortmund

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A CONVENIENT ONE-POT SYNTHESIS OF STANNYLSILANES*

REINHARD HUMMELTENBERG, KLAUS JURKSCHAT
and FRANK UHLIG

*Lehrstuhl für Anorganische Chemie II, Universität Dortmund, Fachbereich Chemie
Otto-Hahn-Straße 6, 44221 Dortmund*

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Stannylsilanes were synthesized in high yields by reaction of organotinchlorides with organofluorosilanes and magnesium. The fluorosilanes were prepared in good yields and under mild conditions by reaction of the corresponding chlorosilanes with $[n\text{-}Bu_4N][Ph_3SnF_2]$. All products were characterized by ^{29}Si, ^{119}Sn NMR spectroscopy and elemental analysis.

Keywords: fluorosilanes; stannylsilanes; α, ω- distannyloligosilanes; ^{29}Si; ^{119}Sn NMR spectroscopy

INTRODUCTION

To the best of our knowledge there are only two general methods for the synthesis of compounds containing a tin-siliconbond, i.e., i) the metathesis reaction using either organotin or organosilicon metallates and organosilicon or organotin halides, respectively (Equation 1, 2) and ii) reactions under metal hydride elimination (Equation 3)[1].

$$R_3SnM \;+\; X\text{-}SiR_3 \;\longrightarrow\; \underset{\mathbf{1}}{R_3Sn\text{-}SiR_3} \;+\; M\text{-}X \qquad (1)$$

$$R_3SnX \;+\; MSiR_3 \;\longrightarrow\; \mathbf{1} \;+\; M\text{-}X \qquad (2)$$

$$M = Li, Na, K, MgX;\; X = Cl, Br$$

$$R_3Sn\text{-}H \;+\; LiSiR_3 \;\longrightarrow\; R_3Sn\text{-}SiR_3 \;+\; Li\text{-}H \qquad (3)$$

Attempts to apply the metathesis reaction for the synthesis of α, ω-distannylated oligosilanes resulted in formation of **2** in only moderate yields (Equation 4).

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* Dedicated to Professor R. Wolf on the occasion of his retirement

$$2\,Ph_3SnM + Cl\text{-}(SiMe_2)_n\text{-}Cl \longrightarrow \qquad (4)$$

$$Ph_3Sn\text{-}(SiMe_2)_n\text{-}SnPh_3 + 2\,MCl$$

$$\begin{array}{ll} \mathbf{2a}\ n = 4; & M = Li, Na, K \\ \mathbf{2b}\ n = 6 & \end{array}$$

Due to metal-halogen exchange considerable ammounts of dodecamethylcyclohexasilane $(SiMe_2)_6$ and hexaorganodistannanes $(R_3Sn)_2$were formed as byproducts. These were difficult to separate[2].

RESULTS AND DISCUSSION

In an attempt to synthesize 3-triphenylstannylpropyldimethylfluorosilane **3** we obtained both **3** and the functionalized stannylsilane **4a** (Equation 5).

$$2\,Me_2(F)Si(CH_2)_3Cl + 2\,ClSnPh_3 + 2\,Mg \xrightarrow[\substack{-Mg(F)Cl \\ -MgCl_2}]{\qquad\qquad} \qquad (5)$$

$$\begin{array}{cc} Me_2(F)Si(CH_2)_3SnPh_3 & + Cl(CH_2)_3SiMe_2SnPh_3 \\ \mathbf{3} & \mathbf{4a} \end{array}$$

There was no formation of corresponding disilanes and distannanes resulting from a Wurtz-type-coupling.

In absence of a halogen function in the silicon bonded organic group the formation of stannylsilanes is almost quantitative (Equation 6, 7).

$$\begin{array}{lllll} Ph_3SnCl + RMe_2SiF + Mg & \longrightarrow & Ph_3Sn\text{–}SiMe_2R + & Mg(F)Cl & (6) \\ \mathbf{5a} & & \mathbf{4b},\ R = n\text{–}C_8H_{17} & & \\ & & \mathbf{4c},\ R = \text{Vinyl} & & \\ & & \mathbf{4d},\ R = \text{Allyl} & & \\ & & \mathbf{4e},\ R = Ph & & \end{array}$$

$$\begin{array}{lll} Me_2SnCl_2 + n\,\text{Vinyl}Me_2SiF + n\,Mg \longrightarrow Z\text{–}Me_2Sn\text{–}SiMe_2\text{Vinyl} + n\,Mg(F)Cl & & (7) \\ \mathbf{5b} & \mathbf{6a},\ n = 1,\ Z = Cl & \\ & \mathbf{6b},\ n = 2,\ Z = SiMe_2\text{Vinyl} & \end{array}$$

$$\begin{array}{ll} 2\,\mathbf{5a} + F\text{–}(SiMe_2)_n\text{–}F + 2\,Mg \longrightarrow Ph_3Sn\text{–}(SiMe_2)_n\text{–}SnPh_3 + 2\,Mg(F)Cl & (8) \\ \qquad\qquad\qquad\qquad \mathbf{2a},\ n = 4 & \\ \qquad\qquad\qquad\qquad \mathbf{2b},\ n = 6 & \end{array}$$

Wurtz type coupling products are formed below 5 % (NMR) or are even absent.

Within our studies it was necessary to look for convenient methods for the synthesis of organofluorosilanes. A variety of such methods is described in the literature starting from organochlorosilanes and using HF^3, $ZnF_2{}^4$, $SbF_3{}^5$, $SbF_3/SbCl_5{}^6$, Me_3SnF^7, $CuCl_2/CuI/KF^8$ or $CuF_2/CCl_4{}^9$ as fluorinating agents. Not all of these methods are very convenient, especially when the resulting fluorosilanes have a high boiling point or when they show a limited thermal stability.

We found that tetrabutylammonium triphenyldifluorostannate[10] $[n\text{-}Bu_4N]^+[Ph_3SnF_2]^-$ **8** is an excellent fluorinating agent. It allows fluorination of organochlorosilanes in solution at room temperature (Equation 9).

$$\underset{\textbf{7}}{2\,RR^1{}_2SiCl} + \underset{\textbf{8}}{[n\text{-}Bu_4N][Ph_3SnF_2]} \longrightarrow \underset{\textbf{9}}{2\,RR^1{}_2SiF} + \underset{\textbf{10}}{[n\text{-}Bu_4N][Ph_3SnCl_2]} \qquad (9)$$

The organofluorosilanes **9** synthesized via this method are listed in Table I.

TABLE I Yields, boiling points and ^{29}Si NMR chemical shifts of fluorosilanes **9**

Fluorosilane	*yield [%]*	*b.p./mm Hg [°C]*	$\delta^{29}Si$ *NMR[ppm]* ($^1J(^{29}Si - ^{19}F)$*[Hz]*)
$ClCH_2CH_2CH_2Si(Me)_2F$	81	51/10	31.4 (281)
$CH_2{=}CHCH_2Si(Me)_2F$	79	95	28.4 (283)
$PhSi(Me)_2F$	89	58/8	19.9 (278)
$n\text{-}OctSi(Me)_2F$	92	79/9	33.7 (281)
$F(SiMe_2)_4F$	85	a)	35.7 (297) -50.4[b)]
$F(SiMe_2)_6F$	90	a)	36.9 (318) -40.1 -45.5[c)]

a) pure products, no purification was necessary
b) ^2J - ^{29}Si) 28 Hz
c) ^2J - ^{29}Si) 29 Hz

The resulting tetrabutylammonium triphenyldichlorostannate **10** can easily be separated from the reaction mixture. Furthermore, it can be recycled to tetrabutylammonium triphenyldifluorostannate **8** with aqueous potassium fluoride (Equation 10).

$$\underset{\textbf{10}}{[Bu_4N][Ph_3SnCl_2]} + 2\,KF \longrightarrow \underset{\textbf{8}}{[Bu_4N][Ph_3SnF_2]} + 2\,KCl \qquad (10)$$

EXPERIMENTAL

All manipulations were performed under nitrogen using Schlenk techniques. The solvents were dried by standard methods and distilled before use. The organochlorostannanes **5**, organochlorosilanes **7** and tetrabutylammonium triphenyldifluorostannate **8** were prepared by known methods[10,11].

The ^{29}Si and ^{119}Sn NMR spectra were recorded in $CDCl_3$ on Bruker DPX-300 and DRX-400 spectrometers at 59.63 MHz resp. 79.49 MHz for ^{29}Si and 111.92 MHz resp. 149.21 MHz for ^{119}Sn using Me_4Si and Me_4Sn as external references.

General procedure for the preparation of fluorosilanes 9 from organochlorosilanes and 8

The corresponding organochlorosilane and tetrabutylammonium triphenyldifluorostannate in the molar ratio 2:1 were dissolved in 50 ml of CH_2Cl_2 and stirred at room temperature for 2 hours. The CH_2Cl_2 was distilled off and diethyl ether was added. The resulting mixture was stirred for 60 min and the precipitate of $[n\text{-}Bu_4N][Ph_3SnCl_2]$ was filtered off. The ether was removed in vacuo. The fluorosilanes were obtained as colourless liquids in 80 - 95 % yield. Their boiling points, yields and ^{29}Si NMR spectroscopical data are given in Table I.

Conversion of $[Bu_4N][Ph_3SnCl_2]$ 10 into $[Bu_4N][Ph_3SnF_2]$ 8

50 g (75 mmol) of $[Bu_4N][Ph_3SnCl_2]$ were dissolved in 400 ml dichloromethane. A solution of 30 g (528 mmol) KF (seven-fold excess) in 300 ml of distilled water was added. The mixture was then stirred for 48 hours at room temperature.

The CH_2Cl_2 - phase was separated and the solvent was removed in vacuo. The residue was recrystallized from acetone/hexane (1.7:1) to yield 40.4 g (85%) of $[Bu_4N][Ph_3SnF_2]$ as colourless crystals, m.p.= 189-192°C (lit. 189-192°C[11]); δ ^{119}Sn: 344.1 ppm, $^{1}J(^{119}Sn\text{-}^{19}F)$ 1972 Hz.

General procedure for the reaction of organofluorosilanes and organochlorostannanes with magnesium

The corresponding amounts (see Table II) of organofluorosilane, organochlorostannane, magnesium turnings (50 % excess) and tetrahydrofuran (for example: for 30 mmol 50 ml thf) were placed in a Schlenk - tube with a magnetic stirrer. The reaction mixture was stirred for 72 h, followed by removal of the thf in vacuo. The residue was carefully extracted with diethylether. The ether layer was evaporated in vacuo and the residue was either distilled or recrystallized from diethylether/n-hexane. Yields are shown in Table II.

Physical data of the stannylsilanes 2, 4 and 6

a) triphenylstannyl-3-chloropropyldimethylsilane 4a

Found: C 56.4, H 5.55 $C_{23}H_{27}ClSiSn$. Calcd.: C 56.9, H 5.6 %.

TABLE II Amounts of educts and yields for the preparation of **2**, **4** and **6**

amounts [mmol][a]	*Fluorosilane*	*Cl–Sn< (Si : Sn)*	*reaction products*	*yield (g) [%]*
32.3	$Cl\text{-}(CH_2)_3\text{-}SiMe_2F$	**5a** (1:1)	$Cl\text{-}(CH_2)_3\text{-}SiMe_2\text{-}SnPh_3$	[41][b] (5.58)
28.8	$n\text{-}C_8H_{17}Me_2SiF$	**5a** (1:1)	$n\text{-}C_8H_{17}Me_2Si\text{-}SnPh_3$	[80] (12.2)
28.8	$CH_2{=}CH\text{-}SiMe_2F$	**5a** (1:1)	$CH_2{=}CH\text{-}SiMe_2\text{-}SnPh_3$	[81] (12.2)[e]
14.4	$CH_2{=}CH\text{-}SiMe_2F$	**5b** (2:1)	$[CH_2{=}CH\text{-}SiMe_2]_2SnMe_2$	[30] (0.69) [50][c]
			$CH_2{=}CH\text{-}SiMe_2\text{-}SnMe_2Cl$	[30][c]
5.1	$CH_2{=}CH\text{-}CH_2SiMe_2F$	**5a** (1:1)	$CH_2{=}CH\text{-}CH_2SiMe_2\text{-}SnPh_3$	[62] (1.42)
37.3	$PhMe_2SiF$	**5a** (1:1)	$PhMe_2Si\text{-}SnPh_3$	[93] (16.8)
1.6	$F\text{-}(SiMe_2)_4\text{-}F$	**5a** (1:2)	$Ph_3Sn\text{-}(SiMe_2)_4\text{-}SnPh_3$	[68] (1.02)
4.8	$F\text{-}(SiMe_2)_6\text{-}F$	**5a** (1:2)	$Ph_3Sn\text{-}(SiMe_2)_6\text{-}SnPh_3$	[75] (3.8)
15	$PhSiF_3$	**5a** (1:3)	fluorinated silanes Ph_6Sn_2 /Ph_3SnCl	c), d)

a) amounts of fluorosilane
b) "main product" s. eq. (5)
c) detected by NMR spectroscopy
d) Mg reacted completely
e) byproduct < 5% ; Ph_6Sn_2

b.p. = 150°C (10^{-4} Torr).
^{119}Sn NMR(149.21 MHz,δ): -171.2 ppm.
^{29}Si NMR(79.49 MHz, δ): -3.05 ppm; $^1J(^{117/119}Sn - {}^{29}Si)$ 623/651 Hz.

b) triphenylstannyl-n-octyldimethylsilane 4b

Found: C 64.26, H 7.31 $C_{28}H_{38}SiSn$. Calcd.: C 64.49, H 7.35 %.
b.p. = 125°C (2×10^{-3} Torr).
^{119}Sn NMR(111.92 MHz, δ): -169.3 ppm.
^{29}Si NMR(59.63 MHz, δ): -3.43 ppm; $^1J(^{117/119}Sn - {}^{29}Si)$ 618/648 Hz.

c) triphenylstannylvinyldimethylsilane 4c

Found: C 60.7, H 5.45 $C_{22}H_{24}SiSn$. Calcd.: C 60.71, H 5.56 %.

m.p. = 210°C.

^{119}Sn NMR(111.92 MHz, δ): -175.7 ppm.

^{29}Si NMR(59.63 MHz, δ): -13.6 ppm; $^{1}J(^{117/119}Sn - ^{29}Si)$ 641/672 Hz.

d) triphenylstannylallyldimethylsilane 4d

Found: C 61.3, H 5.72 $C_{23}H_{26}SiSn$. Calcd.: C 61.49, H 5.83 %.

m.p. = 176-178°C.

^{119}Sn NMR(149.21 MHz, δ): -170.2 ppm.

^{29}Si NMR(79.49 MHz, δ): -4.4 ppm; $^{1}J(^{117/119}Sn - ^{29}Si)$ 620/640 Hz.

e) triphenylstannylphenyldimethylsilane 4e

Found: C 64.0, H 5.5 $C_{26}H_{26}SiSn$. Calcd.: C 64.35, H 5.4 %.

m.p. = 64°C.

^{119}Sn NMR(111.92 MHz, δ): -176.5 ppm.

^{29}Si NMR(59.63 MHz, δ): -12.8 ppm; $^{1}J(^{117/119}Sn - ^{29}Si)$ 638/668 Hz.

f) bis(vinyldimethylsilanyl)dimethylstannane 6a

b.p. = 110°C (10^{-4} Torr, Kugelrohr distillation).

^{119}Sn NMR(111.92 MHz, δ): -275.4 ppm.

^{29}Si NMR(59.63 MHz, δ): -16.4 ppm; $^{1}J(^{117/119}Sn - ^{29}Si)$ 505/529 Hz.

g) chlorodimethylstannylvinyldimethylsilane 6b

^{119}Sn NMR(111.92 MHz, δ): -126.4 ppm.

^{29}Si NMR(59.63 MHz, δ): -14.1 ppm; $^{1}J(^{117/119}Sn - ^{29}Si)$ 621/644 Hz.

h) bis(triphenylstannyl)octamethyltetrasilane 2a

Found: C 58.4, H 5.5 $C_{44}H_{54}Si_4Sn_2$. Calcd.: C 57.7, H 5.8 %.

m.p. = 137-142°C.

^{119}Sn NMR(111.92 MHz, δ): -156.4 ppm.

^{29}Si NMR(59.63 MHz, δ): -36.7ppm; $^{2}J(^{117/119}Sn - ^{29}Si)$ 52/55 Hz; -29.6 ppm; $^{1}J(^{117/119}Sn - ^{29}Si)$ 451/472 Hz; $^{3}J(^{117,119}Sn - ^{29}Si)$ 39 Hz.

i) bis(triphenylstannyl)dodecamethylhexasilane 2b

Found: C 54.8, H 6.6 $C_{48}H_{66}Si_6Sn_2$. Calcd.: C 54.96, H 6.34 %.

m.p. = 120-122°C.

^{119}Sn NMR(111.92 MHz, δ): -156.5 ppm.

^{29}Si NMR(59.63 MHz, δ): -36.9 ppm; $^{2}J(^{117/119}Sn - ^{29}Si)$ 57/59 Hz; -29.3 ppm; $^{1}J(^{117/119}Sn - ^{29}Si)$ 454/475 Hz; -42.1 ppm; $^{3}J(^{117,119}Sn - ^{29}Si)$ 33 Hz.

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