Journal of Organometallic Chemistry, 142 (1977) 149—153

A CONVENIENT AND LARGE SCALE SYNTHESIS OF 1,1,2-TRIMETHYL-1,2,2-TRICHLORODISILANE AND 1,1,2,2-TETRAMETHYL-1,2-DICHLORODISILANE

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(Received June 22nd, 1977)

Summary

1,1,2-Trimethyl-1,2,2-trichlorodisilane and 1,1,2,2-tetramethyl-1,2-dichlorodisilane were prepared in large quantities by the dechlorinative methylation of a disilane mixture, $Me_nSi_2Cl_{6-n}$, with trimethylchlorosilane in the presence of aluminum chloride and methyldichlorosilane.

Introduction

In connection with our recent study [1], a facile and large scale synthesis of 1,1,2,2-tetramethyl-1,2-dichlorodisilane and 1,1,2-trimethyl-1,2,2-trichlorodisilane became highly desirable. Although several methods are available for the synthesis of these disilanes [2], we became particularly interested in a recent report of Ishikawa et al. [3] concerning aluminum chloride-catalyzed demethylative chlorination of hexamethyldisilane with trimethylchlorosilane. Reaction 1 is an equilibrium process and the reverse reaction is a dechlorinative methylation of a chlorodisilane with a methylmonosilane. Such reactions would furnish a convenient and economical route to $Me_4Si_2Cl_2$ or $Me_3Si_2Cl_3$, since large amounts of the "disilane residue" ($Me_nSi_2Cl_{6-n}$, n = ca. 2.5) are available from the direct synthesis of methylchlorodisilanes [4]. Such reactions would not require the use of Grignard reagents and therefore would be suitable for large scale application. The present paper describes results of an investigation of the dechlorinative methylation of the "disilane fraction" and of the separation of the desired disilanes from the resulting mixture.

$$Me_3SiSiMe_3 + 2Me_3SiCl \xrightarrow{AlCl_3} ClMe_2SiSiMe_2Cl + 2Me_4Si \qquad (1)$$

Results and discussion

The dechlorinative methylation of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane was examined first. The reaction was carried out in a stainless steel bomb which was kept at 200°C for 16 h, using 40 mmol of the disilane and 80 mmol of trimethylchlorosilane with 12 mmol of aluminum chloride. GLC analysis showed that the starting disilane was methylated to 1,1,2-trimethyl-1,2,2-trichlorodisilane and 1,1,2,2-tetramethyl-1,2-dichlorodisilane with 85% conversion (See Table 1).

$$Me_2Si_2Cl_4 \xrightarrow{Me_3SiCl} Me_3Si_2Cl_3 + Me_4Si_2Cl_2 \qquad (2)$$

Similarly, a sample of the disilane residue (b.p. 150—154°C, $Me_2Si_2Cl_4/Me_3Si_2Cl_3 = 7/3$) was methylated with varying amounts of trimethylchlorosilane. The results are summarized in Table 2, showing that extent of the methylation depends on the molar ratio of trimethylchlorosilane to starting disilanes. The best result was obtained when two equivalents of trimethylchlorosilane were used with respect to the disilane concentration. Low conversions associated with use of larger amounts of trimethylchlorosilane might not be unreasonable, since the reverse reaction, demethylative chlorination such as reactions 3 and 4 [3], would become important.

$$Me_3Si_2Cl_3 \xrightarrow{Me_3SiCl} Me_2Si_2Cl_4 \qquad (3)$$

$$Me_4Si_2Cl_2 \xrightarrow{Me_3SiCl} Me_3Si_2Cl_3 \qquad (4)$$

Next attention was turned to lowering the reaction temperature so as to make the reaction operative under milder conditions. This was achieved by adding $MeHSiCl_2$ as co-catalyst to the reaction mixture and results presented in Table 3 show that refluxing a mixture of $Me_2Si_2Cl_4$, Me_3SiCl, $AlCl_3$ and $MeHSiCl_2$ in a molar ratio of 1/2/0.3/0.1 led to almost complete consumption of the dimethyltetrachlorodisilane. It should be noted that such an effect of the hydrosilane on enhancing the ease of chlorine—methyl exchange has precedents [5,6].

An application of the methylation above to a "disilane residue" (b.p. 150—154°C, $Me_2Si_2Cl_4/Me_3Si_2Cl_3 = 7/3$) resulted in the formation of a disilane mixture containing 46% $Me_3Si_2Cl_3$ and 54% $Me_4Si_2Cl_2$. Since the tetramethyldichlorodisilane was conveniently converted to the trimethyltrichlorodisilane by passing

TABLE 1

DECHLORINATIVE METHYLATION OF 1,2-DIMETHYL-1,1,2,2-TETRACHLORODISILANE WITH TRIMETHYLCHLOROSILANE IN THE PRESENCE OF ALUMINUM CHLORIDE (12.0 mmol)[a]

Reactants (mmol)	Products[b] (mmol)
$Cl_2MeSiSiMeCl_2$ (40.0)	$ClMe_2SiSiMe_2Cl$ (13)
	$ClMe_2SiSiMeCl_2$ (24)
	$Cl_2MeSiSiMeCl_2$ (6)
Me_3SiCl (80.0)	Me_2SiCl_2 (54)
	Me_3SiCl (28)

[a] The reaction was carried out in a 50-ml stainless steel bomb at 200°C for 16 h. [b] Analysis was made by GLC.

TABLE 2

DECHLORINATIVE METHYLATION OF A DISILANE MIXTURE ($Me_2Si_2Cl_4/Me_3Si_2Cl_3$ = 7/3, b.p. 150–154°C) WITH TRIMETHYLCHLOROSILANE IN THE PRESENCE OF ALUMINUM CHLORIDE[a]

$[Me_3SiCl]$/[Disilanes]	Product distribution (%)[b]		
	$Cl_2MeSiSiMeCl_2$	$ClMe_2SiSiMeCl_2$	$ClMe_2SiSiMe_2Cl$
1	13	59	28
2	4	48	48
3	41	21	38
6	63	15	23

[a] The reaction was carried out in a 50-ml stainless steel bomb at 200°C for 16 h, using 11.1 g (50 mmol) of the disilane mixture and 2 g (15 mmol) of aluminum chloride. [b] Analysis was made by GLC.

anhydrous hydrogen chloride through the mixture in the presence of aluminum chloride [3], practically pure samples of 1,1,2-trimethyl-1,2,2-trichlorodisilane could easily be obtained (eq. 5). In a typical example, there was isolated 1010 g

$$ClMe_2SiSiMe_2Cl \xrightarrow[AlCl_3]{HCl} Cl_2MeSiSiMe_2Cl \qquad (5)$$

(82% yield) of the trimethyltrichlorodisilane starting from 1334 g of the "disilane fraction".

A large scale preparation of 1,1,2,2-tetramethyl-1,2-dichlorodisilane was similarly accomplished with some modifications. An extensive methylation of the "disilane residue" resulted in the collection of a disilane mixture comprising 25% $Me_3Si_2Cl_3$ and 75% $Me_4Si_2Cl_2$ from which the former compound was selectively removed by cleaving it with hydrogen chloride in the presence of $NiCl_2(PPh_3)_2$ [7]. Applying the cleavage reaction to the 25/75 mixture of the two disilanes, there was obtained 487 g (43% yield) of 1,1,2,2-tetramethyl-1,2-dichlorodisilane starting from 1334 g of the "disilane fraction".

$$Me_3Si_2Cl_3 \xrightarrow[NiCl_2(PPh_3)_2]{HCl} Me_2SiCl_2,\ MeHSiCl_2,\ Me_2HSiCl,\ MeSiCl_3 \qquad (6)$$

TABLE 3

EFFECT OF ADDED METHYLDICHLOROSILANE ON DECHLORINATIVE METHYLATION OF A DISILANE MIXTURE ($Me_2Si_2Cl_4/Me_3Si_2Cl_3$ = 7/3, b.p. 150–154°C) WITH TRIMETHYLCHLOROSILANE IN THE PRESENCE OF ALUMINUM CHLORIDE[a]

$[MeHSiCl_2]$ (mol. %)[b]	Product distribution (%)[c]			Conversion[d] (%)
	$Cl_2MeSiSiMeCl_2$	$ClMe_2SiSiMeCl_2$	$ClMe_2SiSiMe_2Cl$	
0	56	18	26	29
5	17	41	42	68
10	1	46	53	87

[a] A charge of 11.1 g (50 mmol) of the disilane mixture, 10.9 g (100 mmol) of trimethylchlorosilane and 2 g (15 mmol) of aluminum chloride were refluxed with an appropriate amount of methyldichlorosilane for 23 h. [b] Based on the starting disilane charged. [c] Determined by GLC. [d] The conversion is meant by 100 X (mol of the methyl group transferred to the starting disilane)/(mol of the methyl group which could be transferred to the starting disilane). An assumption was made that the starting disilanes can be methylated to 1,1,2,2-tetrachloro-1,2-dichlorodisilane, but not to pentamethylchlorodisilane under the conditions employed.

Experimental

NMR spectra were determined on a Varian A-60D spectrometer. IR spectra were recorded on a Hitachi EPI 3G. GLC analysis was performed with an Ohkura 802 GC using Teflon columns packed with 25% Silicone KF-96, 20% XF-1105 on 60/80 mesh Chromosorb W.

Reagent grade aluminum chloride and hydrogen chloride were used without further purification. Trimethylchlorosilane, methyldichlorosilane and the "disilane residue" were supplied by the Toshiba Silicone Co. Ltd. Dichlorobis(triphenylphosphine)nickel(II) was prepared according to the literature method [9]. Structural assignment for the products obtained was performed by comparing their physical properties (NMR, IR spectra, GLC retention times, etc) with authentic samples.

General procedure for the methylation

A. Reactions in a pressure vessel were carried out in a 50-ml stainless steel bomb containing a Teflon-covered stirring bar. The vessel was kept at 200°C with an oil bath for a stipulated period of time. After cooling, the bomb was opened and the reaction mixture was subjected to analysis.

B. In a 5-l round-bottomed flask equipped with a reflux condenser bearing a calcium chloride tube were placed a disilane (or a disilane mixture), trimethylchlorosilane, methyldichlorosilane and aluminum chloride. The mixture was then refluxed for an appropriate period of time. Product analysis was made as usual.

Preparation of 1,1,2-trimethyl-1,2,2-trichlorodisilane

A mixture of 1334 g (6 mol) of a disilane fraction (b.p. 150—154°C, $Me_2Si_2Cl_4/Me_3Si_2Cl_3 = 7/3$), 1304 g (12 mol) of trimethylchlorosilane and 72 g (0.6 mol) of methyldichlorosilane was heated under reflux in the presence of 240 g (1.6 mol) of aluminum chloride for 24 h. Most of the monosilanes present was removed by simple distillation and the remaining disilane mixture was shown by GLC analysis to contain 46% $Me_3Si_2Cl_3$ and 54% $Me_4Si_2Cl_2$. Anhydrous hydrogen chloride was passed through the mixture at room temperature until the GLC peak for $Me_4Si_2Cl_2$ virtually disappeared. Fractional distillation gave 1010 g (4.9 mol, 82% yield) of practically pure 1,1,2-trimethyl-1,2,2-trichlorodisilane (b.p. 60°C/40 mmHg).

Preparation of 1,1,2,2-tetramethyl-1,2-dichlorodisilane

A sample of 1334 g of the above "disilane residue" was treated with trimethylchlorosilane in essentially the same manner as above. After removal of the low boiling materials, the remaining mixture was again refluxed with 1304 g (12 mol) of trimethylchlorosilane and 72 g (0.6 mol) of methyldichlorosilane for 2 h. Distillation resulted in the collection of 748 g of a disilane mixture comprising 25% $Me_3Si_2Cl_3$ and 75% $Me_4Si_2Cl_2$, boiling at 144—149°C. The mixture through which anhydrous hydrogen chloride was bubbled at a rate of 50 ml/min for 10 h was kept at 130°C in the presence of 7.8 g (0.012 mol) of $NiCl_2(PPh_3)_2$. The resulting mixture was distilled under reduced pressure to give 483 g (2.6 mol, 43% yield) of pure 1,1,2,2-tetramethyl-1,2-dichlorodisilane (b.p. 62°C/30 mmHg).

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