

Preliminary communication

Extension of the Benkeser reaction to the reductive trichlorosilylation of main group element chlorides¹

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Abstract

Chlorophosphanes RR'PX **1** (**1a**: R, R' = *i*-propyl; **1b**: R = *t*-butyl, R' = *i*-propyl; **1c**: RR' = 3-methylphosphol-2-enyl) react with trichlorosilane and triethylamine to provide trichlorosilylphosphanes RR'PSiCl₃ **2a-c** and triethylammonium chloride in high yield. In the case of the reaction of dichlorophosphanes R₂PCl₂ **3** with trichlorosilane and triethylamine, double trichlorosilylation provides bis(trichlorosilyl)phosphanes RP(SiCl₃)₂ **4a-f** (a: R = *i*-Pr, b: R = *t*-Bu, c: R = 1-adamantyl, d: R = (Me₃Si)₂CH, e: R = NEt₂, f: R = N(*i*-Pr)₂). However, depending on the nature of R, reactions may also lead to cyclophosphanes (RP)_n **5** (thus **4a** and **4e** could not be isolated in a pure state) or to trichlorosilylphosphanes RP(H)SiCl₃ **6**. With **3g** (R = 2,4,6-*t*-Bu₃C₆H₂), mixtures of **6g** and 2,4,6-*t*-Bu₃C₆H₂PH₂ are formed. Chlorotrimethylstannane **7** reacts with trichlorosilane and triethylamine providing the trichlorosilylstannane R₃SnSiCl₃ (R = CH₃) **8**.

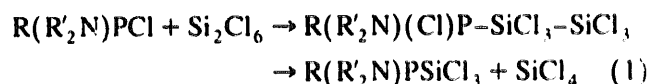
Keywords: Silyl stannane; Silyl phosphine; Group 14; Nuclear magnetic resonance; Group 15; Reductive silylation

1. Introduction

Trihalogenosilyl compounds are of general importance as trifunctional precursors for the synthesis of highly functionalised silicon compounds, like branched silicones and silasesquioxanes. Hexachlorodisilane is a useful reagent for the reductive trichlorosilylation of certain chlorophosphanes providing the corresponding trichlorosilylphosphanes [1–3]. The related cleavage of organotin phosphanes with hexachlorodisilane furnishes trichlorosilylphosphanes as well as the trichlorosilylstannanes [4]. Trichlorosilylstannanes and related germanes, being a kind of α -halogen(metal)silane, are most desirable precursors for further transformations. However, even on the "semi-catalytic" pathway according to Scheme 1 (including trichlorosilylphosphane recycling), the synthesis of Me₃SnSiCl₃ still requires Me₃SnCl, Si₂Cl₆ (which is quite expensive) and three equivalents of methyllithium [4] (Scheme 1).

The formation of trichlorosilylphosphanes from chlorophosphanes, and of trichlorosilylgermanes and -stannanes from germyl- and stannylphosphanes, with

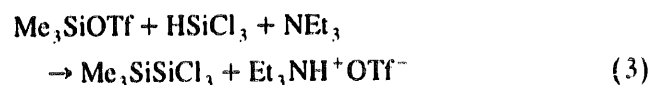
the help of hexachlorodisilane appears to be associated with latent trichlorosilyl anions. These latent trichlorosilyl anions are generated from one SiCl₃ group of Si₂Cl₆ when the other silicon atom is attacked by a phosphorus nucleophile [3]. By ³¹P and ²⁹Si NMR, a phosphane-hexachlorodisilane 1:1 adduct has been detected as intermediate in the course of such a trichlorosilylation reaction of an alkyl(dialkylamino)chlorophosphane with hexachlorodisilane [3]. Latent trichlorosilyl anions are also the key precursors in reactions of trichlorosilane/triethylamine mixtures with various organic halides leading to products of reductive C-trichlorosilylations [5,6].



[3]



[5,6]

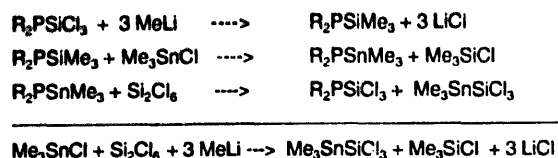


[7]

Therefore, it would be desirable to explore whether the easily accessible reagent of Benkeser's reactions

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¹ Dedicated to Professor R.J. Corriu on the occasion of his 62th birthday.



Scheme 1.

would also be useful as a synthetic alternative to hexachlorodisilane as precursor for various main group element trichlorosilyl compounds. By use of trimethylsilyltriflate as a starting material, the trichlorosilane/triethylamine reagent had been successfully used for Si–Si bond formation providing $Me_3SiSiCl_3$ [7]. The trichlorosilane/triethylamine reagent is known to reduce chlorophosphanes R_2PCl and $RPCl_2$ to phosphanes R_2PH and RPH_2 [8]. Recently, in the course of such a reaction, the formation of a trichlorosilylphosphane $Ph_3CP(SiCl_3)H$ had been recognised by ^{31}P NMR [9]; subsequently, alkyl(diorganylamino)chlorophosphanes were straightforwardly transformed into the corresponding trichlorosilylphosphanes with help of the trichlorosilane/triethylamine reagent [3].

As a probe for the generalisation of the Benkeser-type reductive trichlorosilylation of mono- and bifunctional main group element halides, we chose the reactions of various dialkylchlorophosphanes, alkylidichlorophosphanes, dialkylaminodichlorophosphanes and of chlorotrimethylstannane with the trichlorosilane/triethylamine reagent.

2. Results and discussion

The reactions of chlorophosphanes **1** and **3** with the trichlorosilane/triethylamine reagent in aprotic solvents were followed by ^{31}P NMR (Eqs. (4)–(7), Table 1). With moderately bulky di-*i*-propylchlorophosphane **1a** and *t*-butyl-*i*-propylchlorophosphane **1b** the trichlorosilane/triethylamine reagent provides, under mild conditions within a few hours, the trichlorosilylphosphanes **2a,b** in excellent yields. Depending on the reaction conditions, **2a** and **2b** are accompanied by small amounts of tetra-*i*-propyldiphosphane and 1,2-di-*t*-butyl-1,2-di-*i*-propyldiphosphane. Phospholene **1c** is also straightforwardly reduced by the trichlorosilane/triethylamine reagent; addition of the phospholene to a slight excess of the trichlorosilane/triethylamine reagent provides mainly the trichlorosilylphosphane **2c**; with half an equivalent of the trichlorosilane/triethylamine reagent, a mixture of diastereomers (*meso*/*rac*) of 3,3'-dimethyl-[1,1']-bisphosphol-2-en is formed. **2a-c** can be separated from the diphosphanes by distillation. The reactions of **1a** with **2a** or **1c** with **2c** can be used as simple syntheses of the diphosphanes.

Moderately bulky alkylidichlorophosphanes and dialkylaminodichlorophosphanes **3a-f** also react under

very mild conditions with the trichlorosilane/triethylamine reagent, furnishing alkyl- and dialkyl-bis(trichlorosilyl)phosphanes. The reaction is sometimes accompanied by cyclophosphane formation, but alkylbis(trichlorosilyl)phosphanes **4b-d** and dialkylaminodichlorophosphane **4f** could be isolated in fair yields from the reaction mixtures. Cyclophosphane formation in the course of the silylation reactions can be explained by decomposition of intermediate unstable chloro(silyl)phosphanes [10].

With *i*-propyldichlorophosphane **3a** as starting material, formation of tetra-*i*-propylcyclotetraphosphane and of cyclic silylphosphanes like $(^iPr_2P)_3(SiCl_2)_2$ and $(^iPr_2P)_4(SiCl_2)$ in the course of the distillation prevented the isolation of **4a** in a pure state. Using the extremely bulky arylidichlorophosphane 2,4,6- iBu_3C_6H_2PCl_2 **3g** as starting material, the trichlorosilane/triethylamine reagent led to a mixture of the mono-trichlorosilylphosphane **6g** and the primary phosphane 2,4,6- iBu_3C_6H_2PH_2 ; with increasing reaction time; the amount of **6g** in the reaction mixture decreases in favour of the primary phosphane (Eq. (7)). Protolytic cleavage of the P–Si bonds of **6g** (and of hypothetical **4g** [$2,4,6-^iBu_3C_6H_2P(SiCl_3)_2$]) might be due to the presence of triethylammonium chloride; this question is at present under investigation. Further small-scale experiments followed by ^{31}P NMR indicating the straightforward formation of $Ph_2CHP(SiCl_3)_2$ and $Ph(Me_3Si)CHP(SiCl_3)_2$ confirm that the bis-silylation of dihalogenophosphanes with $HSiCl_3/NEt_3$ is a synthetic method of wide applicability.

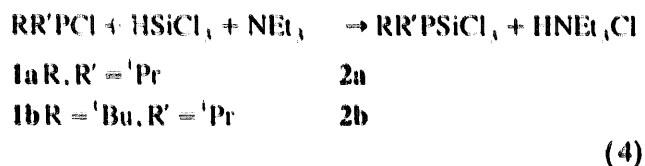



Table 1
 ^{31}P and ^{29}Si NMR data of trichlorosilylphosphanes

		$\delta^{31}P$ (ppm)	$\delta^{29}Si$ (ppm)	$ ^1J(^{31}P,^{29}Si) $ (Hz)
iPr_2PSiCl_3	2a [1]	–19.2	+16.7	104.3
$^iBu(^iPr)PSiCl_3$	2b	+6.5	+11.8	116.20
	2c	–32.2	+13.5	122.3
$^iPr_2P(SiCl_3)_2$	4a	–78.0	+8.0	72.7
$^iBuP(SiCl_3)_2$	4b [3]	–55.3	+7	77.3
1-AdaP(SiCl ₃) ₂	4c	–56.1	+7.2	79.8
$(Me_3Si)_2CHP(SiCl_3)_2$	4d	–82.8	+6.2	85.1
$Ph(Me_3Si)CHP(SiCl_3)_2$		–82.6		79.8
$Ph_2CHP(SiCl_3)_2$		–85.5		75.3
$Et_2NP(SiCl_3)_2$	4e	+11.7	+1.8	75
$^iPr_2NP(SiCl_3)_2$	4f	–9.3	+1.8	70.9
$2,4,6-^iBu_3C_6H_2P(H)SiCl_3$ 6g		–103.8	+14.8	88.5
				221.1 ^a

^a $^1J(PH)$.

