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A CONVENIENT SYNTHESIS OF (TRICHLOROMETHYL)CHLOROSILANES

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In the presence of a catalytic amount of triphenylphosphine, 1,1,2,2-tetrachloro-1,2-dimethyldisilane reacted smoothly under mild conditions with carbon tetrachloride to produce (trichloromethyl)-methyldichlorosilane $\underline{1}$ in good yield. (Trichloromethyl)dimethylchlorosilane was also readily prepared by the triphenylphosphine-promoted transfer of the trichloromethyl group from $\underline{1}$ to dimethyldichlorosilane.

It has been reported that (trichloromethyl)chlorosilanes of type $CCl_3SiMe_nCl_{3-n}$ are good dichloromethylene transfer agents[1] and also serve as precursors of polysiloxanes of improved flame resistance.[2] The most conventional routes to these important compounds are based on the chlorination of methylchlorosilanes with chlorine or sulfuryl chloride. Thus, (trichloromethyl)trichlorosilane can conveniently be prepared by the chlorination of methyltrichlorosilane.[1,3] However, the chlorination of dimethyldichlorosilane or trimethylchlorosilane gives a mixture of various chlorinated products[3] and therefore this method is not suitable for selective preparation of (trichlorometheyl)methyldichlorosilane or (trichloromethyl)dimethylchlorosilane. Thus, it has been reported by Lee and Roberts that the chlorination of dimethyldichlorosilane resulted in the isolation of only impure (trichloromethyl)methyldichlorosilane.[1c] We report herein a novel and convenient method for the synthesis of (trichloromethyl)chlorosilanes not including the chlorination procedure.

We found that, in the presence of a catalytic amount of triphenylphosphine, 1,1,2,2-tetrachloro-1,2-dimethyldisilane[4] reacted smoothly with carbon tetrachloride to produce (trichloromethyl)methyldichlorosilane $\underline{1}$. The reaction in

$$Cl_2MeSiSiMeCl_2 + CCl_4 \xrightarrow{PPh_3} \underset{\underline{1}}{CCl_3SiMeCl_2} + MeSiCl_3 \qquad (1)$$

the presence of 3 mol% of the phosphine reached completion within 2 h at reflux temperatures and produced a 1:1 mixture of $\underline{1}$ and methyltrichlorosilane.

Thus, a mixture of 1,1,2,2-tetrachloro-1,2-dimethyldisilane (16.0 g, 70 mmol), carbon tetrachloride (21.5 g, 140 mmol), and triphenylphosphine (0.55 g, 2.1 mmol) was refluxed under nitrogen for 2 h. GLC analysis of the resulting solution disclosed the quantitative formation of $\underline{1}$. Removal of excess carbon tetrachloride and the resulting methyltrichlorosilane by distillation and subsequent sublimation of the residue gave 10.1 g (62% yield) of the expected product as colorless crystals: mp. 101°C (lit.[3a] 99°C); IR (KBr) 1260 (m, SiMe) and 700-800 cm^{-1} (vs, CCl); NMR (CCl_4) δ 1.11 (s, SiMe).

Reaction 1 was also found to be effected by amines such as triethylamine and tri-n-propylamine, although their catalytic ability was lower compared to triphenylphosphine. For instance, refluxing a 1:2 mixture of 1,1,2,2-tetrachloro-1,2-dimethyldisilane and carbon tetrachloride in the presence of 3 mol% of triethylamine for 6 h gave $\underline{1}$ in only 31% yield. Group VIII metal-phosphine complexes, e.g., dichlorotris(triphenylphosphine)ruthenium(II), dichlorobis(triphenylphosphine)nickel(II), chlorotris(triphenylphosphine)rhodium(I), and tetrakis(triphenylphosphine)palladium(0), also effectively catalyzed this cleavage reaction. For instance, the reaction in the presence of 1 mol% of the ruthenium(II) complex afforded 94% yield of $\underline{1}$ after refluxing for 3 h. However, the catalytic ability of these complexes might be due to the phosphine ligand, because it is known that they liberate the ligand in organic solvents.[5]

In view of the known migratory attitude of the trichloromethyl group in (trichloromethyl)chlorosilanes,[3c,6] an attempt was made to prepare (trichloromethyl)-dimethylchlorosilane $\underline{2}$ from $\underline{1}$ by using $Si\text{-}CCl_3/Si\text{-}Cl$ interchange reaction (eqn. 2).

$$\underset{\underline{1}}{CCl_3SiMeCl_2} + Me_2SiCl_2 \rightleftharpoons MeSiCl_3 + \underset{\underline{2}}{CCl_3SiMe_2Cl} \qquad (2)$$

We found that triphenylphosphine effected the exchange reaction in this case also and that the use of large excess of dimethyldichlorosilane serves to shift the equilibrium almost completely towards the production of $\underline{2}$. Thus, refluxing a 1:10 mixture of $\underline{1}$ and dimethyldichlorosilane in the presence of 5 mol% of the phosphine for 1 h led to the formation of $\underline{2}$ in 95% yield.

These results indicate that the present reaction opens new route to practical preparation of (trichloromethyl)chlorosilanes 1 and 2. The method is advantageous because of the simplicity of the reaction mixture and ready availability of the starting materials as well as the catalyst.

Interestingly, the reaction of 1,1,2-trichloro-1,2,2-trimethyldisilane[7] with carbon tetrachloride (reflux, 2 h) gave a 1:1:1:1 mixture of 1, 2, dimethyldichlorosilane, and methyltrichlorosilane. The result is rather unexpected since

$$\mathrm{Cl_2MeSiSiMe_2Cl + CCl_4 \xrightarrow{PPh_3} \underset{1}{CCl_3SiMeCl_2} + \underset{2}{CCl_3SiMe_2Cl} + Me_2SiCl_2 + MeSiCl_3} \qquad (3)$$

the reaction of the disilane with allyl chloride in the presence of the Pd(0) catalyst gives a 98:2 mixture of allylmethyldichlorosilane and allyldimethylchlorosilane.[8] The present result might be explained by an assumption that the cleavage reaction of the disilane may be followed by the concurrent occurrence of Si-$\mathrm{CCl_3}$/Si-Cl interchange reactions between 1 and $\mathrm{Me_2SiCl_2}$ and/or between 2 and $\mathrm{MeSiCl_3}$ (cf. eqn. 2).

Further, 1,1,2,2-tetrachloro-1,2-dimethyldisilane reacted with chloroform to give (dichloromethyl)methyldichlorosilane 3, but vigorous conditions were required to achieve a reasonable yield of the product.

$$\mathrm{Cl_2MeSiSiMeCl_2 + CHCl_3 \xrightarrow{PPh_3} \underset{\substack{3\\(35\%\ yield)}}{CHCl_2SiMeCl_2} + MeSiCl_3} \qquad (4)$$

For the formation of 1, at least three mechanisms are possible : (a) nucleophilic displacement of chlorine in $\mathrm{CCl_4}$ by $\mathrm{SiMeCl_2^-}$ which is formed by the interaction between $\mathrm{PPh_3}$ and $\mathrm{Cl_2MeSiSiMeCl_2}$; (b) nucleophilic attack of a chlorophosphonium methanide salt, $\mathrm{Ph_3PCl^+CCl_3^-}$, at silicon ; (c) insertion of a silylene, SiMeCl, which is produced by the $\mathrm{PPh_3}$-catalyzed disproportionation of $\mathrm{Cl_2MeSiSiMeCl_2}$, into the C-Cl bond of $\mathrm{CCl_4}$.

A silyl anion mechanism has been proposed for a base-catalyzed cleavage or disproportionation of chlorodisilanes.[6,9] The intermediacy of a silyl anion has also been put forth for the trialkylamine-catalyzed reaction of CCl_4 with $HSiCl_3$ leading to CCl_3SiCl_3.[10] The second possibility is based on the fact that PPh_3 attacks CCl_4 to form $Ph_3PCl^+ CCl_3^-$.[11] The third possibility is related to precedents for the insertion of a silylene (e.g., $SiCl_2$) into the C-Cl bond of CCl_4.[12] However, no conclusive evidence is available at the present time and a mechanistic investigation is now under way.

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