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Conversion of Disilanes to Functional Monosilanes. IV.[1] Synthesis of Methyldichlorosilane and Dimethylchlorosilane by the Reaction of Methylchlorodisilanes with Hydrogen Chloride in the Presence of Tetrakis(triphenylphosphine)palladium(0)

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Synopsis. Methylchlorodisilanes such as 1,2-dimethyl-1,1,2,2-tetrachlorodisilane, 1,1,2-trimethyl-1,2,2-trichlorodisilane and 1,1,2,2-tetramethyl-1,2-dichlorodisilane were effectively cleaved by hydrogen chloride in the presence of tetrakis(triphenylphosphine)palladium(0) to give methylchlorohydrosilanes in good yields.

The cleavage of methylchlorodisilanes by hydrogen chloride constitutes one of the important routes to methyldichlorosilane and dimethylchlorosilane and considerable effort has been devoted to this reaction.[2] The transition metal-catalyzed cleavage, however, had been overlooked until 1973, when Atwell and Bokerman reported in a patent literature that the cleavage of a disilane mixture containing 1,2-dimethyl-1,1,2,2-tetrachlorodisilane, 1,1,2-trimethyl-1,2,2-trichlorodisilane and 1,1,2,2-tetramethyl-1,2-dichlorodisilane was effected by dichlorobis(phenyldimethylphosphine)palladium-(II).[3] In their experiment a low boiling mixture was obtained which consisted of methyldichlorosilane, dimethylchlorosilane, methyltrichlorosilane and dimethyldichlorosilane (yield was not given), indicating that all the disilanes had been cleaved to some extent.

During the course of our recent investigation on various cleavage reactions of methylchlorodisilanes,[1] we have found that disilanes such as 1,2-dimethyl-1,1,2,2-tetrachlorodisilane, 1,1,2-trimethyl-1,2,2-trichlorodisilane and 1,1,2,2-tetramethyl-1,2-dichlorodisilane were effectively cleaved by hydrogen chloride in the presence of tetrakis(triphenylphosphine)palladium-(0). The results are summarized in Table 1.

In the presence of this particular palladium catalyst, *sym*-dimethyltetrachlorodisilane was readily cleaved at 140 °C by hydrogen chloride to give a 1:1 mixture of methyldichlorosilane and methyltrichlorosilane in a 90% combined yield. It is apparent, therefore, that reaction 1

$$Cl_2MeSiSiMeCl_2 + HCl \xrightarrow{Pd(0)} MeSiHCl_2 + MeSiCl_3 \quad (50:50) \qquad (1)$$

provides a convenient method for preparation of methyldichlorosilane. The reaction of *sym*-tetramethyldichlorodisilane with hydrogen chloride was rather slow at 140 °C, but at 170 °C, the reaction with 0.4 mol% of the palladium(0) catalyst proceeded with a 32% conversion to afford a 1:1 mixture of dimethylchlorosilane and dimethyldichlorosilane in a 97% combined yield based on the disilane consumption. Thus, Reaction 2 is of some validity for the production of dimethylchlorosilane by a single route.

$$ClMe_2SiSiMe_2Cl + HCl \xrightarrow{Pd(0)} Me_2SiHCl + Me_2SiCl_2 \quad (50:50) \qquad (2)$$

1,1,2-Trimethyl-1,2,2-trichlorodisilane was found to be cleaved at 150 °C in two ways as shown below. The slightly preponderant occurrence of path A and path B suggests that attack of chlorine on the Me_2SiCl group in the disilane is somewhat favored over that on the $MeSiCl_2$ group.

$$Cl_2MeSiSiMe_2Cl + HCl \longrightarrow \begin{cases} MeSiHCl_2 + Me_2SiCl_2 \quad [\text{path A}] \\ (28:40) \\ Me_2SiHCl + MeSiCl_3 \quad [\text{path B}] \\ (8:24) \end{cases} \qquad (3)$$

Comparison of the reaction conditions for the cleavages 1, 2 and 3 finds the reactivity order of the disilanes to be $Me_2Si_2Cl_4 > Me_3Si_2Cl_3 > Me_4Si_2Cl_2$. This was further found to be the case by the competitive

TABLE 1. REACTION OF METHYLCHLORODISILANES WITH HYDROGEN CHLORIDE IN THE PRESENCE OF TETRAKIS(TRIPHENYLPHOSPHINE)PALLADIUM(0)[a]

Disilane	Conversion of disilane %[b]	Yield of monosilanes %[c]	Product distribution, %[d]			
			$MeSiHCl_2$	Me_2SiHCl	$MeSiCl_3$	Me_2SiCl_2
$Cl_2MeSiSiMeCl_2$[e]	100	90	50		50	
$ClMe_2SiSiMe_2Cl$[f]	32	97		50		50
$Cl_2MeSiSiMe_2Cl$[g]	100	80	28	8	24	40

a) The reactions were carried out by passing hydrogen chloride (50 ml/min) through a solution of a disilane (200 mmol), mesitylene (10 ml) and the Pd(0) complex. b) Conversion is meant by 100× (mol of the disilane consumed)/(mol of the disilane charged). c) Isolated yield based on the disilane consumption. d) Determined by GLC and NMR analyses. e) Carried out at 140 °C for 4 h. The catalyst concentration is 0.2 mol% based on the disilane charged. f) Carried out at 150 °C for 5 h. The catalyst concentration is 0.2 mol%. g) Carried out at 170 °C for 8 h. The catalyst concentration is 0.4 mol%.

cleavage of pairs of three disilanes at 150 °C in the presence of the palladium(0) catalyst which gave the relative rates $Me_2Si_2Cl_4$ 16, $Me_3Si_2Cl_3$ 10, and $Me_4Si_2Cl_2$ 1. The reactivity order thus found is in keeping with that for ammonium chloride-catalyzed cleavage reaction previously reported[4] and suggests that the present reaction is likely to involve the nucleophilic attack of chlorine atom in hydrogen chloride on the Si–Si bond for which the direct interaction with the Pd(0) complex is expected.[1c,5]

Finally, catalyst efficiency was tested briefly with other common Group VIII metal-phosphine complexes using the reaction of *sym*-dimethyltetrachlorodisilane with hydrogen chloride as standard (140 °C, 5 h, 0.2 mol% of the catalyst). For example, dichlorobis(triphenylphosphine)palladium(II) also was found to initiate the cleavage of the disilane, but the reaction gave a 34: 66 mixture of methyldichlorosilane and methyltrichlorosilane only in a 21% combined yield. Further, the reaction in the presence of dichlorobis(triphenylphosphine)nickel(II) gave only a 21% combined yield of methylchlorosilanes consisting of 3% methyldichlorosilane and 97% methyltrichlorosilane.

Experimental

1,2-Dimethyl-1,1,2,2-tetrachlorodisilane,[6] 1,1,2-trimethyl-1,2,3-trichlorodisilane,[7] and 1,1,2,2-tetramethyl-1,2-dichlorodisilane[7] were prepared by literature procedures. Commercial anhydrous hydrogen chloride was uesd without further purification. Authentic methylchlorosilanes (*e.g.*, $MeSiHCl_2$, Me_2SiHCl, Me_2SiCl_2, and $MeSiCl_3$) were obtained commercially. Reagent grade mesitylene was freshly distilled prior to use. The complexes $NiCl_2(PPh_3)_2$,[8] $Pd(PPh_3)_4$,[9] and $PdCl_2(PPh_3)_2$[10] were prepared according to literature directions. Structural assignment for the methylchlorosilanes obtained was performed by comparing their physical properties (*e.g.*, NMR and IR spectra and GLC retention times, *etc.*) with those of authentic samples.

General Procedure for the Cleavage Reactions. All cleavage reaction were carried out in an apparatus consisting of a 30 ml three-necked round-bottomed flask equipped with a magnetic stirrer, a thermometer and an inlet tube for hydrogen chloride and topped by a distillation column filled with glass helices. The upper part of this column was connecteed with an even pressure reflux regulator to which a 100 ml flask was attached for collection of methylchlorosilanes. Effluent gaseous materials were trapped in a tube immersed in a Dry Ice–acetone bath.

A typical procedure is exemplified by the cleavage of 1,2-dimethyl-1,1,2,2-tetrachlorodisilane in the presence of tetrakis(triphenylphosphine)palladium(0). To a mixture of 45.5 g (200 mmol) of the disilane and 10 ml of mesitylene was added 0.452 g (0.4 mmol) of the Pd(0) complex. The stirred mixture was kept at 140 °C, and hydrogen chloride was bubbled through the solution at a rate of 50 ml/min. The reaction was complete in 4 h and 47.6 g (90% yield based on the disilane charged) of methylchlorosilanes were collected. GLC and NMR analyses showed the product to be a 50: 50 mixture of methyldichlorosilane and methyltrichlorosilane.

Procedure for Competitive Experiments. Hydrogen chloride was bubbled through a mixture of two different disilanes, mesitylene and the palladium(0) complex (0.2 mol%) at 150 °C. After 30—70% completion, unconverted disilanes were analyzed by GLC. Relative rates were calculated using the Ingold-Shaw equation,[11] where A_i and B_i are the initial concentrations of two disilanes,

$$\frac{k_1}{k_2} = \frac{\log [A]_i/[A]_f}{\log [B]_i/[B]_f}$$

A_f and B_f final concentrations, and k_1/k_2 the ratio of rate constants for the attack of hydrogen chloride on the two species. Relative rates are expressed by taking that for 1,1,2,2-tetramethyl-1,2-dichlorodisilane as standard.

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