REDUCTION OF DIMETHYLDICHLOROSILANE WITH ETHYLDICHLOROSILANE IN PRESENCE OF ALUMINUM HALIDES

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The reduction of halosilanes $R_{4-n}SiX_n$ by hydrosilanes $R_{4-n}SiH_n$ is known from the middle of this century [1-7]. However, the preparative possibilities of this reaction are restricted by the fact that the $R_{4-n}SiH_n$ compounds (n = 1-3) are not commercial products.

The most readily available compounds, containing the Si–H bond, namely methyl- and ethyldichlorosilane, are the products of industrial direct synthesis. However, the possibility of their use for the reduction of alkylchlorosilanes has not been established up to now. In previous investigations [3] it was shown that when ethyldichlorosilane is heated with n-butyltrichlorosilane in the presence of anhydrous $AlCl_3$ the $C_4H_9SiCl_3$ is not reduced. At the same time, triethylsilane under these conditions smoothly reduces $C_4H_9SiCl_3$ to $C_4H_9SiH_3$ [3, 4]. An attempt to reduce methyltrichlorosilane with trichlorosilane proved unsuccessful [8]. The reduction of dimethylchlorosilane with methyldichlorosilane in the presence of tetrabutylammonium chloride [9] does not take place, and instead the methyldichlorosilane is reduced by the dimethylchlorosilane. All of this suggests that the accumulation of chlorine atoms on the silicon lowers the reducing ability of the Si–H bond, which decreases in the order: $R_3SiH > R_2SiHCl > RSiHCl_2 > HSiCl_3$.

Despite these data, which indicate the very low reducing ability of the alkyldichlorosilanes, we studied the possibility of reducing dimethyldichlorosilane with ethyldichlorosilane: $(CH_3)_2SiCl_2 + C_2H_5SiHCl_2 \rightarrow (CH_3)_2SiHCl + C_2H_5SiCl_3$.

The results that were obtained when either $AlCl_3$ (12 mole %) or $AlBr_3$ (4 mole %) was used as the catalyst are given in Table 1. The principal reaction product is dimethylchlorosilane, the amount of which in the volatile fraction with bp below 65° reaches 40-50%. The yield of $(CH_3)_2SiHCl$, based on starting dimethyldichlorosilane, when using $AlCl_3$ and $AlBr_3$ as the catalyst, is, respectively, 20 and 21%.

When $AlBr_3$ is used as the catalyst the reaction proceeds more rapidly and smoothly than in the case of $AlCl_3$. During reaction a substantial amount of the ethyldichlorosilane disproportionates to ethylchlorosilane and ethylsilane [1]. This reaction can be depicted by the following scheme:

$$5C_2H_5SiHCl_2 \xrightarrow{AlX_3} C_2H_5SiH_2Cl + C_2H_5SiH_3 + 3C_2H_5SiCl_3$$

The formation of methyldichlorosilane and methylchlorosilane is apparently due to the secondary process of demethylation of the dimethyldichlorosilane, or of its reduction products $(CH_3)_2SiHCl$ and $(CH_3)_2SiH_2$, by the aluminum halide [5], or of disproportionation reactions [10, 11]. The latter are less probable, since the expected disproportionation products, containing either the $(CH_3)_3Si-$ or $CH_3(C_2H_5)Si<$ fragments, were not found in the reaction mixture.

EXPERIMENTAL METHOD

The starting ethyldichlorosilane and dimethyldichlorosilane were commercial products, and after purification by distillation through an efficient column they, respectively, had bp 75.2° (760 mm) and 70.1° (760 mm).

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TABLE 1. Reaction Products of Reduction of Dimethyldichlorosilane with Ethyldichlorosilane (Mole ratio 1 : 1)

Reaction product	Amount in mixture of reaction products with bp < 65°, mole %*		Yield when based on starting $C_2H_5SiHCl_2$, %	
	$AlCl_3$	$AlBr_3$	$AlCl_3$	$AlBr_3$
CH_3SiHCl_2	8,2 (0,07)	8,2 (0,07)	—	—
CH_3SiH_2Cl	3,4 (0,04)	6,5 (0,08)	—	—
$(CH_3)_2SiHCl$	39,4 (0,42)	45,9 (0,48)	20,3	21,0
$(CH_3)_2SiCl_2$	17,7 (0,14)	16,1 (0,13)	—	—
$C_2H_5SiH_2Cl$	27,8 (0,29)	16,3 (0,17)	28,8	12,0
$C_2H_5SiH_3$	2,9 (0,05)	4,9 (0,08)	6,3	10,6

* The composition of the formed mixture of reaction products was determined by NMR.

Into the pot of a rectification column, packed with metal packing and having an efficiency of 25 theoretical plates, was charged a mixture of 168 g (1.3 moles) of $(CH_3)_2SiCl_2$, 168 g (1.3 moles) of $C_2H_5SiHCl_2$ and either 20 g of $AlCl_3$ or 16 g of $AlBr_3$, which was heated at reflux until the vapor temperature in the head of the column had dropped from 65 to 35-36°. After this the fraction with bp 35-65° was removed slowly (reflux ratio 10-15, removal rate 5-10 drops/min). The composition of this fraction was determined by NMR.

The NMR spectra were obtained on a Tesla BS-487B NMR spectrometer (80 MHz), using HMDS as the internal standard.

CONCLUSIONS

Ethyldichlorosilane in the presence of 4 mole % $AlBr_3$ or 12 mole % $AlCl_3$ reduces dimethyldichlorosilane to dimethylchlorosilane (21% yield). Here a substantial amount of the ethyldichlorosilane is converted to ethylchlorosilane and ethylsilane. CH_3SiHCl_2 and CH_3SiH_2Cl were also detected in the reaction products, the formation of which is apparently due to the demethylating action of the aluminum halides on either $(CH_3)_2SiCl_2$ or its reduction products.

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