REDUCTION OF ALKYLCHLOROSILANES WITH SODIUM HYDRIDE IN THE PRESENCE OF TRIETHYLALUMINUM

L. I. Zakharkin

Institute of Organoelemental Compounds, Academy of Sciences, USSR
Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 12, pp. 2244-2245, December, 1960
Original article submitted May 14, 1960

To reduce alkyl or aryl chlorosilanes, lithium aluminum hydride is used extensively in the laboratory. In a number of investigations [1-3] attempts have been made to use the cheap sodium hydride for reducing Si-Cl to Si-H. However, these attempts have not led to positive results. It has been found recently [4] that alkylchlorosilanes can be successfully reduced with sodium hydride if the alkylchlorosilane vapors are passed through a suspension of finely dispersed sodium hydride at 250°. At a lower temperature, for instance 200°, the reaction did not proceed well. We found in the work described in this instance that if a small quantity of triethylaluminum is added to a suspension of sodium hydride in an aromatic hydrocarbon (benzene, toluene, xylene, etc.), the reduction of chlorosilanes takes place readily at 60-80°. The part played by triethylaluminum in this reaction is as follows. Because of its low reactivity towards chlorosilanes at the temperatures involved, triethylaluminum reacts preferentially with the sodium hydride under formation of the complex $NaAl(C_2H_5)_3$, which is soluble in the hydrocarbon:

$$(C_2H_5)_3\,Al + NaH \rightarrow NaAl(C_2H_5)_3H$$

This complex functions as a reducing agent and converts Si-Cl into Si-H according to the following equation:

$$NaAl\,(C_2H_5)\,H + \begin{matrix}\diagdown\\ -Si-Cl\\ \diagup\end{matrix} \rightarrow \begin{matrix}\diagdown\\ -SiH\\ \diagup\end{matrix} + (C_2H_5)_3Al + NaCl$$

The triethylaluminum which is freed according to this equation reacts with a fresh portion of sodium hydride, bringing it into solution in the form of the complex, and so forth. The reduction is carried out in such a manner that the complex $NaAl(C_2H_5)_3$ is always present in the reaction mixture. By applying this method, we reduced trimethylchlorosilane, dimethylchlorosilane, diethyldichlorosilane, methyltrichlorosilane, methylbutyldichlorosilane, phenyltrichlorosilane, phenylmethyldichlorosilane, and γ-phenylpropyltrichlorosilane.

EXPERIMENTAL

Reduction of trimethylchlorosilane. To a suspension of 12 g of finely disintegrated sodium hydride in 60 ml of toluene, 5 ml of triethylaluminum were added; the mixture was kept under agitation at 80° for 10 min. At this temperature 42 g of trimethylchlorosilane were added gradually. The trimethylsilane which formed as a result of the reduction was collected in a cooled receiving vessel. On distillation 24.4 g (89% of theory) of trimethylsilane with a b.p. of 6-7° were obtained.

Reduction of dimethyldichlorosilane. To a suspension of 10 g of sodium hydride in 60 ml of toluene 6 ml of triethylaluminum were added. Reduction of 20 g of dimethyldichlorosilane was carried out as described above. In this manner, 7.8 g (84% of theory) of dimethylsilane with a b.p. of minus 20 – 18° were prepared.

Reduction of diethyldichlorosilane. To a suspension of 18 g of sodium hydride in 60 ml of toluene containing 5 ml of triethylaluminum, 40 g of diethyldichlorosilane were added at 85-90°. The diethylsilane which formed by reduction was distilled off from the reaction mixture. On distillation, 20.4 g (92% of theory) of diethylsilane with b.p. = 56-57°, n^{20} 1.3924, were obtained.

Reduction of methyl-n-butyldichlorosilane. To 15 g of sodium hydride in 60 ml of xylene and 6 ml of triethylaluminum, 38 g of methylbutyldichlorosilane were gradually added at 85-90°. After completion of the reduction the product was distilled out of the reaction flask together with a small quantity of xylene. On distillation with the use of a column 18.6 g (82% of theory) of methyl-n-butylsilane with a b.p. of 81-82° were obtained: $n^{20}D$ 1.3996; d^{20}_4 0.6992. Found: C 58.91; 58.94; H 13.75; 13.70; Si 27.40; 27.28%. $C_5H_{14}Si$. Calculated: C 58.76; H 13.61; Si 27.42%.

Reduction of methyltrichlorosilane. To 22 g of sodium hydride in 90 ml of toluene and 6 ml of triethylaluminum 25 g of methyltrichlorosilane were gradually added at 80-85°. The methylsilane that formed as a result of the reduction was collected in a cooled trap. The yield was 5.4 g (72% of theory) of methylsilane.

Reduction of phenylmethyldichlorosilane. To 9 g of sodium hydride in 50 ml of benzene and 5 ml of triethylaluminum 27 g of phenylmethyldichlorosilane were gradually added at 70-75°. After completion of the reduction all volatile products that had formed were distilled out of the reaction mixture, first at atmospheric pressure and finally in vacuum. On fractionation with the use of a column 12.2 g of phenylmethylsilane (71% of the theoretical yield) were obtained; b.p. 46-47° (20 mm), 139.5-140° (760 mm); $n^{20}D$ 1.5058; d^{20}_4 0.8895. Found: C 68.61; 68.64; H 8.24; 8.30; Si 23.21; 23.23%. $C_7H_{10}Si$. Calculated %: C 68.79; H 8.19; Si 23.01%.

Reduction of methyltrichlorosilane. To 8 g of sodium hydride in 40 ml of benzene and 5 ml of triethylaluminum 15.5 g of phenyltrichlorosilane were added at 70-75°. After cooling the reaction mixture was carefully poured into acidified ice water. The benzene solution was washed with water and dried over calcium chloride. On fractionation with the use of a column 5.8 g (74% of theory) of phenylsilane with a b.p. of 60-62° (100 mm) were obtained; $n^{20}D$ 1.5111; d^{20}_4 0.8817.

Reduction of γ-phenylpropyltrichlorosilane. To 18 g of sodium hydride in 55 ml of toluene and 6 ml of triethylaluminum 47.5 g of γ-phenylpropyltrichlorosilane were gradually added at 85-90°. After this all volatile pr products were distilled off in vacuum from the reaction mixture. On fractionation in vacuum 23 g (82% of theory) of γ-phenylpropylsilane with a b.p. of 76.5-77° (8 mm) were obtained; $n^{20}D$ 1.5051; d^{20}_4 0.8790. Found: C 72.09; 72.04; H 9.44; 9.48%. $C_9H_{14}Si$. Calculated: C 71.94; H 9.32%.

SUMMARY

It was found that alkylchlorosilanes and arylchlorosilanes can be reduced easily with sodium hydride in a hydrocarbon solution if a small quantity of triethylaluminum is present.

LITERATURE CITED

1. A. Finholt, A. Bond, K. Wilzbach, and H. Schlesinger, J. Am. Chem. Soc. 69, 2694 (1947).
2. E. Kipping and J. Short, J. Chem. Soc. 1930, 1029.
3. O. Ruff and K. Albert, Ber. 38, 2222 (1905).
4. A. Gilbert, G. Cooper and R. Shade, Ind. and Eng. Chem. 51, 665 (1959).
