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N. F. ORLOV

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## Abstract

## Full Text

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# NEW HALOGEN-CONTAINING ALUMINOSILICON ORGANIC COMPOUNDS OF THE TYPE $R_3SiOAlX_2$

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Compounds of the type $R_3SiOAlX_2$ (where X = Cl, Br) have not been described in the literature. In the work of M. G. Voronkov, B. N. Dolgov, and A. N. Dmitrieva ([1]) there is a suggestion of the possibility of formation of compounds of a similar type,

**Table 1**

Properties of hexaalkyldisiloxanes

| Compound | b.p., °C | Pressure, mm Hg | $d_4^{20}$ | $n_D^{20}$ | $MR_D$, calc. | $MR_D$, found |
|---|---|---|---|---|---|---|
| $(CH_3)_6Si_2O$ | 100.5 | 765 | 0.7625 | 1.3765 | 48.92 | 48.89 |
| $(CH_3)_4(C_2H_5)_2Si_2O$ | 156.5 | 750 | 0.7969 | 1.4012 | 58.18 | 58.09 |
| $(CH_3)_2(C_2H_5)_4Si_2O$ | 192 | 760 | 0.8199 | 1.4179 | 67.44 | 67.13 |
| $(C_2H_5)_6Si_2O$ | 231 | 760 | 0.8443 | 1.4330 | 76.70 | 75.87 |

**Table 2**

Properties of trialkylhalosilanes

| Compound | b.p., °C | Pressure, mm Hg | $d_4^{20}$ | $n_D^{20}$ | $MR_D$, calc. | $MR_D$, found |
|---|---|---|---|---|---|---|
| $(CH_3)_3SiCl$ | 58 | 760 | 0.8549 | 1.3870 | 29.91 | 29.93 |
| $C_2H_5(CH_3)_2SiCl$ | 90.5 | 745 | 0.8756 | 1.4050 | 34.54 | 34.34 |
| $CH_3(C_2H_5)_2SiCl$ | 119.5 | 732 | 0.882 | 1.4180 | 39.17 | 39.05 |
| $(C_2H_5)_3SiCl$ | 145.5 | 753 | 0.8963 | 1.4300 | 43.80 | 43.44 |
| $(CH_3)_3SiBr$ | 80 | 768 | 1.1725 | 1.422 | 32.91 | 33.18 |
| $C_2H_5(CH_3)_2SiBr$ | 111 | 750 | 1.1548 | 1.4345 | 37.54 | 37.72 |
| $CH_3(C_2H_5)_2SiBr$ | 138 | 760 | 1.1426 | 1.4460 | 42.17 | 42.27 |
| $(C_2H_5)_3SiBr$ | 163 | 760 | — | 1.4570 | — | — |

but they were not isolated. A brief communication on the isolation of $(CH_3)_3SiOAlCl_2$ in the reaction of trimethylethoxysilane with aluminum chloride was made by Zimmer ([2]), but the author gives neither constants of the compound nor analytical data, and indicates that the compound he isolated does not distill in vacuum.

We have developed a method for the synthesis of compounds of the above-indicated type by heating equimolecular amounts of hexaalkyldisiloxane with an aluminum halide while simultaneously distilling off the corresponding trialkyl-

Table 3

**Trialkylsiloxyaluminum dihalides**

| Compound | B.p., °C | Pressure, mm Hg | M.p., °C | Si, %, calcd. | Si, %, found | Al, %, calcd. | Al, %, found | Halogen, %, calcd. | Halogen, %, found |
|---|---|---|---|---|---|---|---|---|---|
| $(CH_3)_3SiOAlCl_2$ | 102 | 4 | 88 | 15.01 | 14.75; 14.64 | 14.42 | 14.58; 14.74 | 37.90 | 37.97; 37.60 |
| $C_2H_5(CH_3)_2SiOAlCl_2$ | 125 | 4 | 46.5 | 13.97 | 13.50; 13.26 | 13.41 | 13.70; 13.79 | 35.26 | 35.00; 35.00 |
| $CH_3(C_2H_5)_2SiOAlCl_2$ | 143 | 4 | 33* | 13.06 | 12.95; 12.93 | 12.54 | 12.52; 12.52 | 32.90 | 32.81; 33.25 |
| $(C_2H_5)_3SiOAlCl_2$ | 178 | 4 | 43* | 12.26 | 12.28; 12.33 | 11.77 | 11.74; 11.81 | 30.94 | 30.89; 31.02 |
| $C_2H_5(CH_3)_2SiOAlBr_2$ | 127 | 4 | 111.5<br>−143 | 10.17 | 9.96; 9.97 | 9.77 | 9.46; 9.70 | 57.91 | 57.6; 57.3 |
| $(CH_3)_3SiOAlBr_2$ | 105 | 2.5 | 65 | 9.67 | 9.67; 9.43 | 9.30 | 9.20; 9.43 | 55.41 | 55.55; 55.50 |
| $CH_3(C_2H_5)_2SiOAlBr_2$ | 173 | 3 | 55 | 9.24 | 9.22; 8.80 | 8.87 | 8.75; 8.77 | 52.57 | 52.52; 52.17 |
| $(C_2H_5)_3SiOAlBr_2$ | 181 | 3 | 73* | 8.83 | 8.58; 8.25 | 8.48 | 8.44; 8.04 | 50.25 | 50.12; 49.56 |

* M.p. of redistilled substances (without recrystallization).

halosilane. Heating of the reaction mixture is stopped when its temperature exceeds the boiling point of the starting hexaalkyldisiloxane by approximately 20–30°. The reaction proceeds in 70–85% yield according to the following scheme:

$$R_3SiOSiR_3 + AlX_3 \rightarrow R_3SiOAlX_2 + R_3SiX.$$

Trialkylsiloxyaluminum dihalides are colorless crystalline substances, distilling in vacuum, stable in dry air, and reacting vigorously with water. They dissolve readily in ether, benzene, carbon tetrachloride, and hexane.

In contrast to hexaalkyldisiloxanes, hexachlorodisiloxane does not react with aluminum chloride under analogous conditions.

## Experimental Part

The initial hexaalkyldisiloxanes, distilled over sodium, had the constants presented in Table 1. $AlBr_3$ was of chemically pure grade; $AlCl_3$ was sublimed in vacuum. All experiments were carried out in the absence of atmospheric moisture in a distillation flask with a 10-cm fir-tree dephlegmator connected to a Liebig condenser and a receiver. Two thermometers—in the flask and in the dephlegmator—made it possible to monitor the temperature of the reaction mixture in the flask and the temperature of the vapors of trialkylhalosilanes being evolved. The latter were redistilled, after which they had the constants indicated in Table 2.

The trialkylsiloxyaluminum dihalides were isolated either by recrystallization from hexane or by fractionation in vacuum.

The melting point was determined in sealed capillaries.

Analysis for halogen was carried out on separate weighed portions by titration of an aqueous dioxane solution of the substance according to Folgard. Silicon was determined by wet combustion of the substance with a mixture of oleum and nitric acid.

The precipitate of $SiO_2$, after ignition at 1000°, was treated, as a check, with a mixture of sulfuric and hydrofluoric acids. Aluminum was determined in the filtrate, after separation of silicic acid, by precipitation with ammonia in the presence of methyl red. The precipitate of aluminum hydroxide was ignited to $Al_2O_3$ at 1200°.

**Synthesis of $CH_3(C_2H_5)_2SiOAlCl_2$.** A mixture of 43.6 g (0.2 g-mole) of tetraethyldimethyldisiloxane and 26.6 g (0.2 g-mole) of aluminum chloride was gradually heated. At a temperature of 135° in the flask, methyldiethylchlorosilane began to distill off. Heating was continued for 1 hour and was stopped when the temperature in the flask reached 210° and the temperature of the departing vapors was 122°. In all, 24 g of $CH_3(C_2H_5)_2SiCl$ (87.5% of theory), b.p. 116–122°, was obtained. The residue in the flask was distilled in vacuo; 36 g of methyldiethylsiloxyaluminum dichloride was obtained, b.p. 143–147°/4 mm (83.5% of theory).

The constants listed in Table 3 were obtained after a second vacuum fractionation.

**Synthesis of $(CH_3)_3SiOAlBr_2$.** In a distillation flask containing 65 g (0.4 g-mole) of hexamethyldisiloxane, 80.0 g (0.3 g-mole) of $AlBr_3$ was placed. After 1 min the contents of the flask spontaneously warmed and boiled; all the $AlBr_3$ dissolved. The reaction mixture was heated, and trimethylbromosilane began to distill off. At a temperature of 115° in the flask, heating was stopped. There

were collected 36 g (67%) of $(CH_3)_3SiBr$, b.p. 79–81°, and 6 g of a mixture of trimethylbromosilane with hexamethyldisiloxane, b.p. 81–92°. On cooling to room temperature, the entire contents of the flask crystallized. Trimethylsiloxyaluminum dibromide, twice recrystallized from hexane, had the constants given in Table 3.

The yield of crude product was about 70%.

**Reaction of $AlCl_3$ with hexachlorodisiloxane.** A mixture of 28.5 g (0.1 g-mole) of hexachlorodisiloxane (b.p. 134°/760 mm) and 13.3 g (0.1 g-mole) of $AlCl_3$ was heated to boiling for 5 hours; during this time the temperature of the mixture remained 133–134°. On distillation, only unchanged hexachlorodisiloxane was obtained.

**Hydrolysis of $(CH_3)_3SiOAlCl_2$.** Into a separatory funnel containing 50 ml of water, 9.35 g (0.05 g-mole) of $(CH_3)_3SiOAlCl_2$ was added with stirring over 30 min. The organic layer, amounting to 3.3 g (81.5%), was separated and dried over potash. After distillation, hexamethyldisiloxane had the following constants: b.p. 100.0°, $d_4^{20}$ 0.7647, $n_D^{20}$ 1.3768. Literature data ([3]): b.p. 100.4°, $d_4^{20}$ 0.7637, $n_D^{20}$ 1.3774.

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Institute of Silicate Chemistry
Academy of Sciences of the USSR

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## CITED LITERATURE

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*Note: Figure translations are in progress. See original paper for figures.*