1011. *Reaction of Dichlorotrimethylsiloxyaluminium with Dialkylcyclosiloxanes.*

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The reaction between dichlorotrimethylsiloxyaluminium and four dialkylcyclosiloxanes has been studied. From methylsiloxanes, a crystalline substance $C_8H_{24}Al_3Cl_5O_6Si_4$ and an amorphous substance of formula $[Me_2Si{\cdot}O{\cdot}AlClO]_n$ have been isolated from ethylsiloxanes, only a crystalline substance $C_{16}H_{40}Al_3Cl_5O_6Si_4$ was found.

In the preparation of polyaluminium-organosiloxanes, we studied the reaction between dichlorotrimethylsiloxyaluminium and dialkylcyclosiloxanes. It is known [1] that dichlorotrimethylsiloxyaluminium decomposes when heated into chlorotrimethylsilane and

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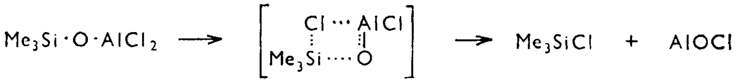
[1] M. G. Voronkov, B. N. Dolgov, and N. A. Dmitrieva, *Doklady Akad. Nauk S.S.S.R.*, 1952, **84**, 959.

aluminium oxide chloride: $Me_3SiO{\cdot}AlCl_2 \longrightarrow Me_3SiCl + AlOCl$, perhaps by the mechanism:[2]



We attempted to introduce the monomeric unit –AlCl·O– in dialkylcyclosiloxanes by direct reaction with aluminium oxide chloride, AlOCl, but always had negative results. Better results were obtained by decomposing dichlorotrimethylsiloxyaluminium directly in the presence of dialkylcyclosiloxanes. Thus, for example, in the reaction with octamethylcyclotetrasiloxane, we obtained trimethylchlorosilane, a crystalline product, $C_8H_{24}Al_3Cl_5O_6Si_4$ (I), and a solid amorphous polymeric residue (II) containing silicon and aluminium. This residue does not melt below 300°. Such products could arise on the basis of the following reactions:

$$3Me_3Si{\cdot}O{\cdot}AlCl_2 + [Me_2SiO]_4 \longrightarrow \underset{\text{(I)}}{C_8H_{24}Al_3Cl_5O_6Si_4} + Me_3SiCl + (Me_3Si)_2O \qquad (1)$$

$$4nMe_3Si{\cdot}O{\cdot}AlCl_2 + n[Me_2SiO]_4 \longrightarrow \underset{\text{(II)}}{[Me_2Si{\cdot}O{\cdot}AlCl{\cdot}O]_{4n}} + 4nMe_3SiCl \qquad (2)$$

Product (I) forms white crystals, m. p. 147—150° and is easily purified by sublimation at 160°/2 mm. In water it rapidly hydrolyses, the final products being liquid siloxanes and hydrated aluminium chloride.

We compared product (I) with that obtained from aluminium chloride and octamethylcyclotetrasiloxane by Zhdanov *et al.*;[3] they have the same empirical formula, and we found them identical. Product (II) is a solid, insoluble in hexane, soluble in hot benzene. It appears as a transparent glass when the benzene is boiled off from its solution. It is hydrolysed by atmospheric moisture and on complete hydrolysis gives liquid siloxanes and hydrated aluminium chloride. The relative quantities of reactants used (4 : 1 to 1 : 1 $Me_3Si{\cdot}O{\cdot}AlCl_2$: cyclosiloxane) do not affect the products. However, product (II) from several preparations contained aluminium and chlorine always in the ratio 1 : 1 whereas the aluminium–silicon ratio varied from 1 : 1 to 1·5 : 1. Thus the general formula given in reaction (2) can be considered correct for those samples in which chlorine, aluminium, and silicon are in atomic ratio 1 : 1 : 1, whereas when the Al : Si ratio favours aluminium we can suppose that the molecule contains Al–O–Si and Al–O–Al bonds.

The reaction between dichlorotrimethylsiloxyaluminium and hexamethylcyclotrisiloxane proceeds in the same way with the formation of chlorotrimethylsilane, as well as a crystalline product $C_8H_{24}Al_3Cl_5O_6Si_4$ (Ia, identical with product I), together with a solid amorphous residue (IIa) which does not melt below 300°.

The reaction between dichlorotrimethylsiloxyaluminium and octaethylcyclotetrasiloxane or hexaethylcyclotrisiloxane both gave chlorotrimethylsilane and a crystalline product (III) $C_{16}H_{40}Al_3Cl_5O_6Si_4$, which is structurally similar to product (I). Product (III) was also found to be identical with the substance produced, according to the method of A. A. Zhdanov, from aluminium chloride and the trimeric or tetrameric siloxane in which the methyl groups were replaced by ethyl. We did not observe the formation of substances analogous to product (II), as however did happen in the reactions with methylsiloxanes.

In all experiments, the quantity of chlorotrimethylsilane obtained was about equal to that theoretically possible from the dichlorotrimethylsiloxyaluminium taking part in the reaction.

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[2] C. Eaborn, " Organosilicon Compounds," Butterworths Scientific Publns., London, 1960, p. 266.

[3] A. A. Zhdanov, K. A. Andrianov, and A. A. Bogdanova, *Izvest. Akad. Nauk S.S.S.R., Otdel. khim. Nauk*, 1961, 1261.

EXPERIMENTAL

Reaction (A): Dichlorotrimethylsiloxyaluminium and Octamethylcyclotetrasiloxane.—Dichlorotrimethylsiloxyaluminium was prepared by Orlov's method[4] from hexamethyldisiloxane and anhydrous aluminium chloride and was distilled at 100°/4 mm. In a Claisen flask with a fractionating side-arm, dichlorotrimethylsiloxyaluminium (9·8 g., 0·052 mole) and octamethylcyclotetrasiloxane (3·9 g., 0·013 mole) were mixed and heated, in anhydrous conditions, for 24 hr. at 150—160°; the mixture of two products was then liquid and homogeneous. During the reaction the liquid distilled into a trap cooled by acetone–solid carbon dioxide; this liquid was fractionated and was found to be essentially chlorotrimethylsilane (95%) and hexamethyldisiloxane. At the end of the reaction, dichlorotrimethylsiloxyaluminium and the original tetramer were eliminated by distillation at 2 mm. At 160° a liquid (I) (3·8 g.) distilled which immediately crystallized in the side-arm. A solid residue (II) (2·1 g.) was obtained which did not melt below 300°. *Product* (I) was purified by sublimation at 160°/2 mm. or by crystallization from benzene (Found: C, 16·4; H, 4·2; Al, 13·7; Cl, 29·4; Si, 18·3%. $C_8H_{24}Al_3Cl_5O_6Si_4$ requires C, 16·4; H, 4·1; Al, 13·8; Cl, 30·2; Si, 19·1%). *Product* (II) was washed with hot dry hexane and dried [Found: C, 15·0; H, 4·4; Al, 17·6; Cl, 22·3; Si, 17·5. $(C_2H_6AlClO_2Si)_x$ requires C, 15·7; H, 3·9; Al, 17·7; Cl, 23·3; Si, 18·4%].

Reaction (B): Dichlorotrimethylsiloxyaluminium and Hexamethylcyclotrisiloxane.—The apparatus was similar to that used above. Dichlorotrimethylsiloxyaluminium (7·1 g., 0·0375 mole) and hexamethylcyclotrisiloxane (2·8 g., 0·0125 mole) were heated as above. This reaction also is homogeneous, and the distilled liquid was practically all chlorotrimethylsilane. By distillation at 2 mm. the initial reagents were eliminated. At 160° a liquid (Ia) distilled and solidified immediately on the walls of the apparatus (2·4 g.). An amorphous solid (IIa) (2·1 g.) remained in the flask.

Product (Ia) was purified by sublimation at 160°/2 mm. or by crystallization from benzene and was identical with product (I) of reaction (A) (Found: C, 16·4; H, 4·2; Al, 13·6; Cl, 29·8; Si, 18·6%). Product (IIa) was washed with hot dry hexane and dried (Found: C, 14·9; H, 4·1; Al, 18·8; Cl, 23·8; Si, 17·8%).

Reaction (C): Dichlorotrimethylsiloxyaluminium and Octaethylcyclotetrasiloxane.—Dichlorotrimethylsiloxyaluminium (9·5 g., 0·050 mole) and octaethylcyclotetrasiloxane (5·2 g., 0·0125 mole) were mixed and heated, in anhydrous conditions, for 24 hr. at 200°. Chlorotrimethylsilane continuously distilled during the reaction. The reaction mixture was fractionated at 2 mm. The two initial reactants distilled first, followed by a liquid (III) which crystallized (4·2 g.). *Product* (III) was dissolved in hot benzene, recovered, and sublimed at 180—190°/2 mm. (Found: C, 27·9; H, 5·5; Al, 10·9; Cl, 23·9; Si, 16·2. $C_{16}H_{40}Al_3Cl_5O_6Si_4$ requires C, 27·4; H, 5·3; Al, 11·6; Cl, 25·4; Si, 16·1%).

Reaction (D): Dichlorotrimethylsiloxyaluminium and Hexaethylcyclotrisiloxane.—Dichlorotrimethylsiloxyaluminium (10·5 g., 0·056 mole) and hexaethylcyclotrisiloxane (5·85 g., 0·019 mole) were heated as in reaction C. Chlorotrimethylsilane eliminated was almost pure. The excess of reactants having been distilled off at 180—190°/2 mm., a *product* (IIIa) crystallized in the fractionating arm. This product (4·0 g.) was purified by sublimation at 180—190°/2 mm. (Found: C, 28·2; H, 5·6; Al, 11·1; Cl, 24·8; Si, 16·5. $C_{16}H_{40}Al_3Cl_5O_6Si_4$ requires C, 27·4; H, 5·3; Al, 11·6; Cl, 25·4; Si, 16·1%).

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[4] N. F. Orlov, *Doklady Akad. Nauk S.S.S.R.*, 1957, **114**, 1033.