# *Alkylalkoxypolysiloxanes. II. Ethylisopropoxypolysiloxanes*

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The reaction of secondary alcohol and chlorosilanes has not been so well studied as that of primary alcohol and chlorosilanes. Recently we reported on the preparation of isopropoxypolysiloxanes[1] from isopropanol and corresponding chloropolysiloxanes with good yield. The reaction of isopropanol and diethyldichlorosilane in refluxing benzene was studied by McCusker and Green.[2]

Now we wish to report on the preparation and properties of ethylisopropoxydichlorosilane (I), ethyldiisopropoxychlorosilane (II) and ethylisopropoxypolysiloxanes including ethyltriisopropoxysilane (III). Ethylisopropoxychlorosilanes, i. e. (I) and (II), were prepared by partial isopropanolysis of ethyltrichlorosilane. Data on these materials are given in Table I. In the case of preparing ethylethoxypolysiloxanes[3], in which one ethyl group attaches to each silicon atom, ethylethoxychlorosilane and ethyltriethoxysilane were mixed in various mole ratios and refluxed. In this experiment, the ethylisopropoxypolysiloxanes having the similar structure were prepared by the same method. But in this case the mixture of ethyltrichlorosilane (1 mol.) and isopropanol in a different mole ratio (2.3 to 2.5 mol.) were refluxed. The chlorine content of the refluxing mixture was gradually decreased by a thermal reaction and there was obtained some amount of isopropylchloride in a cold trap. It may be supposed that the thermal reaction occurred at the refluxing temperature between Si-Cl and Si-$OC_3H_7$ with the result of the formation of siloxane bond and isopropylchloride as follows:

$$\text{Si-OC}_3\text{H}_7+\text{Si-Cl}=\text{Si-O-Si}+\text{C}_3\text{H}_7\text{Cl}. \qquad (1)$$

By fractional distillation, the chlorine-free mixture was separated into monomer, dimer and trimer fractions. By a rigorous redistillation of the polymer fractions, a small amount of cyclotrimer was obtained between the plateaus of dimer and linear trimer. Data on these polysiloxanes which belong to the linear-and cyclo-series as indicated by formula (A) and (B) are given in Table III.

$$\text{RO}\left(\begin{array}{l}\text{C}_2\text{H}_5\\|\\\text{SiO}\\|\\\text{OR}\end{array}\right)_n\text{R} \qquad \text{R}=\text{CH}(\text{CH}_3)_2 \quad n=1-3 \qquad (A)$$

$$\left(\begin{array}{l}\text{C}_2\text{H}_5\\|\\\text{SiO}\\|\\\text{OR}\end{array}\right)_n \qquad \text{R}=\text{CH}(\text{CH}_3)_2 \quad n=3 \qquad (B)$$

To obtain a series of compounds as indicated by formula (C) which have more isopropoxy groups in a molecule than the compounds of formula (A) have, the thermal reaction between (II) and tetraisopropoxysilane (IV) or (II)

1) R. Okawara, T. Tanaka and I. Ishimaru, This Bulletin, **27**, 45 (1954).
2) P. A. McCusker and C. E. Green, *J. Am. Chem. Soc.*, **70**, 2807 (1948).
3) R. Ōkawara, This Bulletin, **27**, 428 (1954).

$$C_2H_5\left(\begin{array}{c}OR\\|\\SiO\\|\\OR\end{array}\right)_n R \qquad R=CH(CH_3)_2\ n=2-3 \qquad (C)$$

and hexaisopropoxydisiloxane (V) was carried out.

On fractional distillation of the chlorine-free product, the constant boiling fraction which belongs to the series (C) was obtained. But there is a probability of the compound of the series (C) being contaminated by a small amount of the compound of series (A) or the isopropoxypolysiloxane of the same polymer size which may be formed by side reactions.

## Experimental

**Starting Materials.**—The ethyltrichlorosilane used in this experiment was prepared by the reaction of ethylchloride with copper-silicon and was purified by fractionation through a helices-packed column of about 20 plates. The redistilled fraction having the boiling point 98°–99°C (760mm Hg) was taken as a starting material. Found: Cl, 64.0. Calcd. for $C_2H_5SiCl_3$: Cl, 65.0%.

| Exp. No. | Ethyltrichlorosilane (a) (g.) | Isopropanol (b) (g.) | Mole Ratio (b)/(a) |
|---|---|---|---|
| 1 | 29.5 | 27 | 2.5 |
| 2 | 45.5 | 40 | 2.4 |
| 3 | 49 | 42 | 2.34 |

Isopropanol of Shell Chemicals (b.p. 82.2°C, $n_D^{20}$ 1.3776) was used without further purification. Tetraisopropoxysilane (IV) and hexaisopropoxydisiloxane (V) used for the preparation of the compounds of the series (C) were prepared as already described.[1]

Tetraisopropoxysilane (IV): b.p. 93°–4°C/28 mmHg, $n_D^{20}$1.3835, $d_4^{20}$0.8744. Found: Si, 10.59, Calcd. for $(C_3H_7O)_4Si$: Si, 10.62%.

Hexaisopropoxydisiloxane (V): b.p. 82°–3°C/1mmHg, $n_D^{20}$1.3921, $d_4^{20}$0.9236. Found: Si, 13.14, Calcd. for $(C_3H_7O)_6Si_2O$: Si, 13.17%.

**Preparation of Ethylisopropoxychlorosilanes.**—*Ethyldiisopropoxychlorosilane (II).* Ethyltrichlorosilane (41g.: 0.25 mol.) was placed in a 500 cc. three-necked flask equipped with an efficient stirrer, a reflux condenser and a dropping funnel. Isopropanol (30g.: 0.5 mol.) was added drop by drop for one hour with vigorous stirring. During the addition the temperature of the mixture was kept at 3° to 5°C. After the addition the mixture was aerated at room temperature (10°C) with dry air to bubble off the hydrogen chloride until the weight of the mixture attained the calculated value. After aerating for 40 minutes the weight of the mixture attained the calculated value (53g.) and the chlorine content of the mixture was 16.6% (calcd. 16.8%). The mixture was fractionated through a semi-micro stedman column of about 20 plates under reduced pressure.

The following fractions were obtained.

The first fraction: 4g., b.p. 70°–76°C/48 mmHg,

| "Refluxing Mixture" | | % Cl | |
|---|---|---|---|
| (g.) | (% theory) | Found | Calcd. |
| 41 | 102 | 7.9 | 8.0 |
| 61 | 100 | 9.8 | 9.7 |
| 65 | 100 | 10.3 | 10.8 |

Found Cl, 18.1%.

The second fraction: 27g., b.p. 76°C/48 mmHg, Found Cl, 16.7%.

The third fraction: 4g., b.p. 76°–78°C/48 mmHg, Found Cl, 13.6%.

The residue: 11g. Found: Cl, 2.1%.

The second fraction (yield: 50% theory) may be considered to be pure (II). (Calcd. for (II): Cl, 16.8%).

*Ethylisopropoxydichlorosilane (I).* From 41g. (0.25 mol.) of ethyltrichlorosilane and 15g. (0.25 mol.) of isopropanol treated in the same way as above, 44g. of the product (calcd. 47g.) of which the chlorine content is 36% (calcd. 37.9%) was obtained. By fractionating the product through the same semi-micro stedman column under 60 mmHg, 15g. of the fraction boiling at 67°C/60 mmHg was collected. Found Cl, 37.4 Calcd. for (I): Cl, 37.9%. The constants of ethylisopropoxychlorosilanes were determined by the redistilled product and are summarized in Table I.

TABLE I

ETHYLISOPROPOXYCHLOROSILANES

| Name | Boiling Point °C/mmHg | Refractive Index $n_D^{20}$ | Density $d_4^{20}$ | Molecular Refraction Found (Calcd.)* | % Cl Found (Calcd.) |
|---|---|---|---|---|---|
| Ethylisopropoxydichlorosilane (I) | 66–7/59 | 1.4115 | 1.0508 | 44.23 (44.19) | 37.4 (37.9) |
| Ethyldiisopropoxychlorosilane (II) | 74–6/48 | 1.4018 | 0.9361 | 54.73 (54.58) | 16.7 (16.8) |

* Calculated from bond refractivities by E. L. Warrick, *J. Am. Chem. Soc.*, 68, 2455 (1946).

**Preparation of the Ethylisopropoxypolysiloxanes of the Series (A) and (B)**; (Exp. 1 to 3 in Table II).—The "refluxing mixtures" of Exp. 1 to 3 were prepared by adding isopropanol to ethyltrichlorosilane with vigorous stirring and aerating the products at room temperature until the weight of the products attained the calculated value as described in the preparation of ethylisopropoxychlorosilanes. The amounts of the ethyltrichlorosilane, isopropanol and the product obtained were as follows.

The composition of the product which was used as the "refluxing mixture" was calculated from its chlorine content by assuming that only (II) and (III) were present in it and was given in Table II as "Refluxing Mixture".

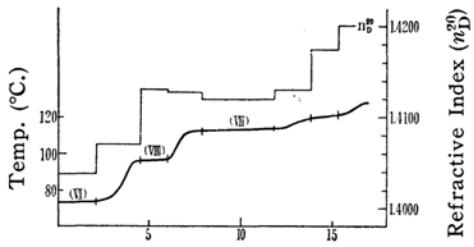


Fig. 1. Redistillation of the polymer fraction of ethylisopropoxypolysiloxanes. (VI): Dimer, (VII): Linear trimer, (VIII): Cyclotrimer

TABLE II

| Exp. No. | Refluxing Mixture Compds.* | | Mole Ratio | Time | Highest Temp. | Product | | Composition of the product | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | (A) (B) | (g.) | (A)/(B) | (hr.) | (°C) | (g.) | (% theory)** | Monomer (%) | Dimer (%) | Trimer (%) | Residue (%) |
| 1 | (II) | 18.8 | 1 | 64 | 205 | 29 | 87.8 | 60 | 12 | — | 28 |
| | (III) | 21.2 | | | | | | | | | |
| 2 | (II) | 35.5 | 1.5 | 64 | 205 | 43 | 91.5 | 47 | 8 | 13 | 32 |
| | (III) | 25.5 | | | | | | | | | |
| 3 | (II) | 41.4 | 2 | 112 | 205 | 47 | 96 | 31 | 14 | 7 | 48 |
| | (III) | 23.6 | | | | | | | | | |
| 4 | (II) | 4.5 | 0.5 | 144 | 210 | 9.8 | 86 | 12 | 11 | — | 77 |
| | (IV) | 8.6 | | | | | | | | | |
| 5 | (II) | 10.5 | 1 | 64 | 285 | 24.9 | 88.6 | 0 | 36 | 20 | 44 |
| | (V) | 21.4 | | | | | | | | | |

* (II): $C_2H_5Si(OC_3H_7)_2Cl$, (III): $C_2H_5Si(OC_3H_7)_3$,
(IV): $(C_3H_7O)_4Si$, (V): $(C_3H_7O)_6Si_2O$

** Ratio of the amount of the polysiloxane obtained to the calculated amount of the polysiloxane.

TABLE III

ETHYLISOPROPOXYPOLYSILOXANES

| Polymer Size | Name | Boiling Point °C/mmHg | Density $d_4^{20}$ | Refractive Index $n_D^{20}$ | Molecular Refraction Found (Calcd.)* | Molecular Weight Found** (Calcd.) | % Si Found (Calcd.) |
|---|---|---|---|---|---|---|---|
| | Series (A) and (B) | | | | | | |
| Monomer | Triisopropoxyethylsilane (III) | 65.4/8 | 0.8607 | 1.3938 | 65.12 (64.97) | 241 (234) | 11.84 (11.98) |
| Dimer | Tetraisopropoxy-1,3-diethyldisiloxane (VI) | 73/0.8 | 0.9091 | 1.4038 | 98.58 (98.26) | 362 (367) | 15.64 (15.32) |
| Linear Trimer | Pentaisopropoxy-1,3,5-triethyltrisiloxane (VII) | 112–3/0.8 | 0.9444 | 1.4120 | 131.38 (131.55) | 489 (499) | 17.14 (16.88) |
| Cyclotrimer | Triisopropoxy-1,3,5-triethylcyclotrisiloxane (VIII) | 96–7/0.8 | — | 1.4131 | — | 398 (397) | 20.75 (21.23) |
| | Series (C) | | | | | | |
| Dimer | Pentaisopropoxy-ethyldisiloxane (IX) | 82–3/0.8 | 0.9193 | 1.3962 | 103.71 (103.65) | 404 (397) | 13.67 (14.15) |
| Trimer | Heptaisopropoxy-1-ethyltrisiloxane (X) | 114–5/0.8 | 0.9570 | 1.4027 | 141.9 (142.3) | 563 (559) | 15.21 (15.06) |

* Calculated from bond refractivities (Table I footnote)

** Cryoscopic measurements in benzene

The mixture was refluxed until the chlorine could not be detected by Beilstein test. During the course of refluxing a small amount of liquid product was collected in a cold trap. Its boiling point (34.5°C) accorded well with that of isopropylchloride. The time required to produce the chlorine-free mixture and the highest refluxing temperature attained are cited in Table II.

The products were fractionated through a semimicro stedman column of about 30 theoretical plates under reduced pressure. Ethyltriisopropoxysilane (III) was distilled out at 65°C/8 mmHg. The disiloxane and trisiloxane fractions were the succeeding plateaus which were obtained at 73°C/0.8 mmHg and 112°C/0.8 mmHg. The amounts in percentage of these plateaus including the intermediate fractions cut on the distillation curve are also shown in Table II. As the amounts of disiloxane and trisiloxane fractions were small and fairly large amounts of the intermediate fraction was found between them, all the polysiloxane fractions were again fractionated rigorously through the same column. The distillation curve and the refractive index of the small portions are shown in Fig. 1.

Properties of these compounds are given in Table III.

In the preparation of ethylethoxypolysiloxanes[3] carried out by the same method, a smaller amount of cyclotrimer than in this experiment was supposed to be present between the plateaus of dimer and linear trimer, but it could not be isolated.

**Preparation of the Ethylisopropoxypolysiloxanes of the Series (C)**: (Exp. 4 and 5).—In experiments 4 and 5, ethyldiisopropoxychlorosilane (II) and tetraisopropoxysilane (IV) or hexaisopropoxydisiloxane (V) were refluxed until the mixture became chlorine free.

**Analysis of Silicon.**—Silicon was determined by decomposing the sample with concentrated sulfuric acid.

## Summary

(1) Ethylisopropoxychlorosilanes have been prepared and characterized.

(2) By the thermal reaction of partially isopropanolysis product of ethyltrichlorosilane, linear ethylisopropoxypolysiloxanes containing from 1 to 3 silicon atoms and cyclotrisiloxane have been prepared and characterized.

(3) Ethyldiisopropoxychlorosilane and isopropoxypolysiloxanes were refluxed and the two compounds of the series of linear ethylisopropoxypolysiloxanes in which one terminal group is the ethyl one have been synthesized and characterized.

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