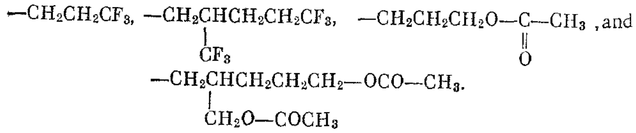
SYNTHESIS OF ORGANOCYCLOSILOXANES WITH POLAR SUBSTITUENTS IN THE ORGANIC GROUP

K. A. Andrianov and S. E. Yakushkina

UDC 542.91 + 546.287

We have shown that the cleavage of the Si — O — Si link in mixed organocyclosiloxanes and their ability to undergo polymerization in presence of bases depend on the nature of the group attached to the silicon atom [1-2].

It was of interest to investigate the polymerization of organocyclosiloxanes containing strongly polar groups such as CF_3 and $OCOCH_3$. For this purpose we synthesized octamethylcyclotetrasiloxanes in which on some of the silicon atoms one methyl group was replaced by one of the groups



$$-CH_2CH_2CF_3,\ -CH_2\underset{\displaystyle CF_3}{\underset{|}{C}}HCH_2CH_2CF_3,\ -CH_2CH_2CH_2O-\underset{\displaystyle O}{\underset{\|}{C}}-CH_3\text{ ,and}$$
$$-CH_2\underset{\displaystyle CH_2O-COCH_3}{\underset{|}{C}}HCH_2CH_2CH_2-OCO-CH_3.$$

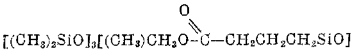
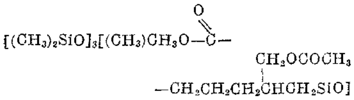
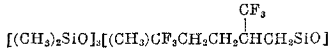
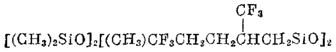
Organocyclosiloxanes with polar substituents in the organic group in the γ-position relative to the silicon atom were synthesized by the cohydrolysis of dichlorodimethylsilane with a dichloromethyl(trifluoroalkyl)silane or (3-acetoxypropyl)dichloromethylsilane by means of water in an acid medium in accordance with the scheme

$$n(CH_3)_2SiCl_2 + mRCH_3SiCl_2 + (n+m)H_2O$$
$$\rightarrow [(CH_3)_2SiO]_n[(CH_3)RSiO]_m + (m+n)HCl\ .$$

In this way we prepared some new organocyclosiloxanes, the properties of which are given in Table 1.

The last two compounds were prepared in 1963 [3] by the catalytic degradation of the moist cohydrolyzate of dichloromethyl(3,3,3-trifluoropropyl)silane with dichlorodimethylsilane in the molar ratio 1 : 1.

TABLE 1

Formula of compound	B. p., °C (p, mm)	n_D^{20}	d_4^{20}	Mol. wt.		MR	
				found	calcd.	found	calcd.
 $[(CH_3)_2SiO]_3[(CH_3)CH_3O-\overset{O}{\overset{\backslash\backslash}{C}}-CH_2CH_2CH_2SiO]$	113—120 (3)	1.4179	1.0171	382	384	95.26	95.12
 $[(CH_3)_2SiO]_3[(CH_3)CH_3O-\overset{O}{\overset{\backslash\backslash}{C}}-CH_2CH_2CH_2\overset{CH_2OCOCH_3}{\overset{|}{C}}HCH_2SiO]$	160—164 (2)	1.4308	1.0424	462	482	122.69	122.70
 $[(CH_3)_2SiO]_3[(CH_3)CF_3CH_2CH_2\overset{CF_3}{\overset{|}{C}}HCH_2SiO]$	105—107 (3)	1.3820	1.1058	479	474	98.64	98.28
 $[(CH_3)_2SiO]_2[(CH_3)CF_3CH_2CH_2\overset{CF_3}{\overset{|}{C}}HCH_2SiO]_2$	120—130 (3)	1.3789	1.2024	654	652	125.2	124.72
$[(CH_3)_2SiO]_3[(CH_3)CF_3CH_2CH_2SiO]$	85—86 (8)	1.3832	1.0432	368	378	84.04	84.21
$[(CH_3)_2SiO]_2[(CH_3)CF_3CH_2CH_2SiO]_2$	99—102 (5)	1.3781	1.1084	440	460	96.69	97.38

Institute of Heteroorganic Compounds, Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 1943-1946, November, 1966. Original article submitted June 23, 1964.

The organocyclotetrasiloxanes synthesized were identified by their elemental compositions, IR spectra, and molecular weights. The cyclotetrasiloxane containing a 3-acetoxypropyl group gave an intense absorption band at 1740 cm^{-1} characterizing the presence of an ester grouping, a band at 2960 cm^{-1} characterizing CH_3, bands at 800-814 and 1260 cm^{-1} for $Si — CH_3$, and a band in the region 1060-1090 cm^{-1} for the eight-membered ring. For cyclosiloxanes containing trifluoropropyl groups a diffuse band was observed in the region 1120-1350 cm^{-1}, and there was also a band at 2960 cm^{-1} for CH_2 groups.

Comparative experiments were conducted on the catalytic polymerization of heptamethyl(3,3,3-trifluoropropyl)cyclotetrasiloxanes and of octamethylcyclotetrasiloxane in presence of 0.5% of KOH (20% alcoholic solution). The changes in the specific viscosities of 1% solutions of the polymers in benzene showed that under the given conditions the rate of polymerization of heptamethyl(3,3,3-trifluoropropyl)cyclotetrasiloxane is greater than that of octamethylcyclotetrasiloxane. For example, after 30 min at 134° the specific viscosity of octamethylcyclotetrasiloxane had not changed and that of heptamethyl(3,3,3-trifluoropropyl)cyclotetrasiloxane was 0.03. After 60 min the specific viscosity of octamethylcyclotetrasiloxane had risen to 0.01, while that of heptamethyl(3,3,3-trifluoropropyl)cyclotetrasiloxane had risen to 0.065. When the yields of polymer were determined it was found that after 3 h of heating the yield of octamethylcyclotetrasiloxane polymer was 17.5%, whereas the yield of heptamethyl(3,3,3-trifluoropropyl)cyclotetrasiloxane polymer was 93%.

It may be supposed that this considerable change in the rate of polymerization is associated with the inductive effect of the polar CF_3 group. However, the absence of kinetic investigations does not allow us to a final conclusion. Work on the synthesis of cyclosiloxanes containing polar groups and on their polymerization continues.

EXPERIMENTAL

(3-Acetoxypropyl)dichloromethylsilane (b.p. 80° (4 mm); n_D^{20} 1.4455; d_4^{20} 1.16118),[5-acetoxy-2-(acetoxymethyl)pentyl]dichloromethylsilane (b.p. 115-118°; n_D^{20} 1.4623; d_4^{20} 1.1656),dichloromethyl(3,3,3-trifluoropropyl)silane (b.p. 122°), and dichloromethyl[5,5,5-trifluoro-2-(trifluoromethyl)pentyl]silane (b.p. 85° (30 mm); n_D^{20} 1.3850; d_4^{20} 1.3543),were prepared by the procedure described in [4].

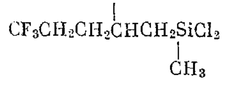
Synthesis of (3-Acetoxypropyl)heptamethylcyclotetrasiloxane. A mixture of 50 ml of water and 100 ml of ether was prepared in a round-bottom flask fitted with stirrer, dropping funnel, and reflux condenser, and a mixture of 0.05 mole of dichlorodimethylsilane and 0.011 mole of (3-acetoxypropyl)dichloromethylsilane was added slowly. Stirring was continued further for 1 h, after which the hydrolyzate was separated from the aqueous layer, washed with water, and dried over $CaCl_2$. Solvent was driven off, and the residue was vacuum-fractionated. The fraction isolated, which amounted to 20% by weight and had b.p. 113-120° (3 mm), was (3-acetoxypropyl)heptamethylcyclotetrasiloxane. Found: C 37.68; 37.50; H 7.52; 7.27; Si 29.60; 29.57%. $C_{12}H_{30}O_6Si_4$. Calculated: C 37.69; H 7.85; Si 29.31%.

In an analogous way by the cohydrolysis of dichlorodimethylsilane with [5-acetoxy-2-(acetoxymethyl) pentyl]dichloromethylsilane we isolated a 12.8% yield of [5-acetoxy-2-(acetoxymethyl)pentyl]heptamethylcyclotetrasiloxane. Found: C 41.16; 41.25; H 7.81; 7.80; Si 24.16; 24.19%; $C_{17}H_{38}O_8Si_4$. Calculated: C 42.32; H 7.87; Si 23.23%.

Synthesis of Heptamethyl(3,3,3-trifluoropropyl)cyclotetrasiloxane. In the analogous cohydrolysis of 0.1 mole of dichloromethyl(3,3,3-trifluoropropyl)silane (b.p. 122°, Cl 32.25%) with 0.3 mole of dichlorodimethylsilane by vacuum fractionation we isolated heptamethyl(3,3,3-trifluoropropyl)cyclotetrasiloxane in 22% yield. Found: C 31.76; 32.00; H 6.53; 6.34; F 15.82; 15.87%. $C_{10}H_{25}Si_4O_4F_3$. Calculated: C 31.72; H 6.61; F 15.08%.

We also obtained a 27.9% yield of a fraction of b.p. 99-102° corresponding to hexamethylbis(3,3,3-trifluoropropyl)cyclotetrasiloxane. Found: C 31.36; 31.50; H 6.17; 6.12; F 23.89; 27.77%. $C_{12}H_{26}Si_4O_4F_6$. Calculated: C 31.30; H 5.68; F 24.78%.

Synthesis of Heptamethyl[5,5,5-trifluoro-2-(trifluoromethyl)pentyl]cyclotetrasiloxane. In the cohydrolysis of 0.1 mole of



$$CF_3CH_2CH_2\overset{CF_3}{\overset{|}{C}}HCH_2\underset{\underset{CH_3}{|}}{Si}Cl_2$$

with 0.3 mole of dichlorodimethylsilane we isolated heptamethyl[5,5,5-trifluoro-2-(trifluoromethyl)pentyl] cyclotetrasiloxane in 10.5% yield by weight. Found: C 32.65; 32.65; H 6.14; 6.12; F 22.80; 22.87%. $C_{13}H_{28}Si_4O_4F_6$. Calculated: C 32.90; H 5.99; F 24.05%. Simultaneously we isolated hexamethylbis[5,5,5-trifluoro-2-(trifluoromethyl)pentyl]cyclotetrasiloxane in 10% yield. Found: C 32.83; 32.84; H 5.61; 5.57; F 32.13%. $C_{18}H_{32}Si_4O_4F_{12}$. Calculated: C 33.12; H 5.27; F 34.96%.

Polymerization. 3-4 g of the cyclotetrasiloxane was introduced into an ampule, and 0.5% of KOH was added as a 20% alcoholic solution. The ampule was sealed and placed in the vapor of boiling pentyl alcohol in a vessel with a reflux condenser. Polymerization proceeded at 134° for 3 h. The ampule was cooled and opened, and the polymer was dissolved in benzene. The benzene solution was washed with water to remove catalyst, and solvent was driven off. A vacuum was then applied, and monomer was driven off by bringing the temperature inside the flask to 200° at a residual pressure of 2-3 mm. Distillation of monomer was continued until the residue attained constant weight.

CONCLUSIONS

1. Six organocyclotetrasiloxanes were synthesized, and of these the following four are new: 3-acetoxypropyl)heptamethylcyclotetrasiloxane, [5-acetoxy-2-(acetoxymethyl)pentyl]heptamethylcyclotetrasiloxane, heptamethyl[5,5,5-trifluoro-2-(trifluoromethyl)pentyl]cyclotetrasiloxane, and hexamethylbis[5,5,5-trifluoro-2-(trifluoromethyl)pentyl]cyclotetrasiloxane.

2. The replacement of one methyl group in octamethylcyclotetrasiloxane by a 3,3,3-trifluoropropyl group leads to a great increase in the rate of polymerization.

LITERATURE CITED

1. K. A. Andrianov and S. E. Yakushkina, Vysokomolekul. Soed., 3, 1554 (1961).
2. K. A. Andrianov and S. E. Yakushkina, Vysokomolekul. Soed., 4, 1193 (1962).
3. Yu. A. Khilevskii, É. V. Kogan, and A. L. Klebanskii, Zh. Obshch. Khimii, 33, 3773 (1963).
4. R. Kh. Freidlina and E. Ts. Chukovskaya, Dokl. AN SSSR, 150, 1055 (1963).
