SYNTHESIS OF o-CARBORANESILOXANES AND STUDY OF THEIR REACTIVITY

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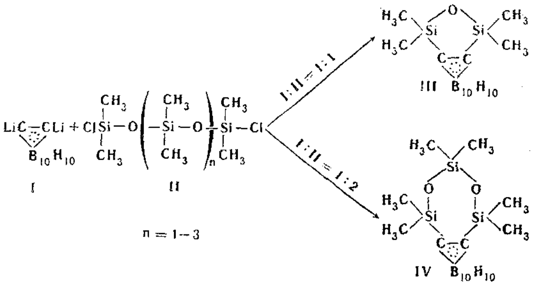
The coupling of dilithio-o-carborane with α,ω-dichlorooligodimethylsiloxanes of type $ClSi(CH_3)_2O[Si(CH_3)_2O]_nSi(CH_3)_2Cl$ with n from 1 to 3 has been performed. At a molar ratio of the reagent of 1 : 1, the products of the reaction are a five-membered ring compound, 1,3-o-carboranetetramethyldisiloxane and a cyclodimethylsiloxane, and at a ratio of the reagents of 1 : 2, a seven-membered ring compound, 1,5-o-carboranehexamethyltrisiloxane, and a cyclodimethylsiloxane. Attempts to open the seven-membered o-carboranesiloxane ring thermally or with the aid of acidic catalysts were unsuccessful. Under the influence of nucleophilic reagents, cleavage of the C—Si bond takes place with the splitting away of a silicon atom from the o-carborane nucleus and the formation of an o-carbonate and a cyclodimethylsiloxane.

The o-carboranesiloxane polymer possesses high thermal stability [1–9]. We have carried out the synthesis of bifunctional derivatives of o-carboranesiloxanes with the aim of obtaining polymers from them. The reaction of dilithio-o-carborane with α,ω-dichloropolydimethylsiloxanes were studied. The tendency of dilithio-o-carborane to form cyclic compounds with bifunctional silanes [10–12] and disiloxanes [11] has been reported in the literature.

In order to decrease the possibility of cyclization, we investigated the reaction of the α,ω-dichloropolydimethylsiloxanes with a longer chain (n = 1–3). As a result, it was found that at a molar ratio of the reactants I : II = 1 : 1, the reaction products are 1,3-o-carboranetetramethyldisiloxane, i. e., the five-membered ring compound III, which has been obtained previously [11, 12], and a cyclodimethylsiloxane containing about seven Si—O links. The length of the chain of the compound II used does not affect the size of the o-carboranesiloxane ring.

At a ratio I : II = 1 : 2, the reaction products are 1,5-o-carboranehexamethyltrisiloxane, i. e. , the seven-membered ring compound IV, which we have isolated for the first time, and a cyclodimethylsiloxane having about 11 Si—O linkages.



As in the preceding case, the length of the compound II chain used does not, with the given values of n, affect the size of the o-carboranesiloxane ring. It was also found that a change in the order of addition of the reactants and in the temperature of the reaction (from -70 to 0° C) does not affect the composition of the end-products. The structures of III and IV were confirmed by elementary analysis (Table 1) and also by their IR spectra. The IR spectrum of III has the following absorption bands: 2600, 1261, 1089, 968, 884, and 827 cm^{-1}, and the IR spectrum of IV 2600, 1262, 1083, 1020, and 865 cm^{-1}.

The content of o-carborane in compound IV (~41%) was determined from the B—H absorption band at a concentration of a solution of IV in CCl_4 of ~0.7 wt-% (in a cell 0.12 mm thick). This corresponds to the t theoretical value.

The oily cyclosiloxanes obtained in the process of synthesis are, it may be assumed, formed as a result of the cleavage of the siloxane chain under the action of the dilithium derivative of the o-carborane.

In order to obtain polymers, we studied the possibility of opening the ring of compound IV catalytically and thermally [12] (the possibility of opening the ring is greater for IV than for III). Compound IV was brought into reaction with the catalysts used for the polymerization of cyclodimethylsiloxanes. Ring opening could not be achieved by using acidic catalysts [conc H_2SO_4, conc $H_2SO_4 + Al_2(SO_4)_3$] (at low temperatures, IV remained unchanged). At high temperatures (up to 300° C), only slight resinification of IV took place.

We also studied the possibility of opening ring IV by means of nucleophilic catalysts (aqueous solutions of NaOH and LiOH, an ethereal suspension of dilithio-o-carborane, a n-heptane solution of $n\text{-}C_4H_9Li$). In all cases, however, the o-carborane and cyclodimethylsiloxanes were isolated. This shows that under the influence of these reactants a cleavage of the Si—C bond (with a C atom in the carborane nucleus) and the formation of the o-carborane take place, the latter, as may be assumed, being formed (in the case of aqueous solutions) through the addition to the o-carborane nucleus of the hydrogen of the water. However, in the case of a n-heptane solution of butyllithium and an ethereal suspension of lithiocarborane, the source of the hydrogen that adds to the carborane nucleus has not yet been elucidated.

It was impossible to open the ring of compound IV by heating it at 300° C for 24 hr (only the initial IV was isolated).

As already mentioned, in the reaction of I with II, o-carboranesiloxane rings with a smaller number of Si—O bonds than in the initial II are formed. This shows that the linear siloxanes split under the influence of the dilithio-o-carborane. On the basis of this hypothesis, we have attempted to open the ring of octamethylcyclotetrasiloxane by means of a suspension of dilithio-o-carborane in ether with heating to 300° C for 24 hr in

Table 1

Reaction of Dilithio-o-carborane (I) with α,ω-Dichlorooligodimethylsiloxanes (II)

Molar ratio of I : II	n	Crystalline reaction product	Empirical formula	Mp, °C	*M*		Found, %				Calculated, %				Oily cyclodimethylsiloxane	Molecular weight	
					found	calculated	B	Si	C	H	B	Si	C	H		found	calculated
1 : 1	1—3	III	$C_6H_{22}B_{10}OSi_2$	159—160*	258	274	39.40		26.80	8.00	39.41	20.43	26.27	8.03	~7	530	518
1 : 2	1—3	IV	$C_8H_{28}B_{10}O_2Si_3$	106—107	350	348	30.96	23.80	28.10	7.90	31.03	24.10	27.60	8.04	~11	825	814

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*According to the literature, mp 160° C.

Table 2

Results of the Experiments on the Opening of the Rings of Compounds IV

IV		Catalyst	Amount of catalyst			Reaction temperature C	Reaction time, hr	Reaction product	Mp, °C	Notes
g	mmole		g	*mM*	moles-% *of the IV* taken					
1.63	4.7	98% H_2SO_4	0.033	0.33	7.0	300	24	IV	106—107	A small part of the product is resinified.
1.66	4.8	98% $H_2SO_4+Al_2(SO_4)_3$	0.0025 0.0415	0.025 0.120	0.5 2.5	300	24	IV	106—107	
2.00	5.8	11.5% LiOH	0.007175	0.33	5.7	110—315	13.5	I	294—296	In all cases a cyclosiloxane containing no, or only traces of, boron was formed.
2.00	5.8	1.9% NaOH	0.0012	0.03	0.5	100—315	34.5	I	294—296	

order to obtain a polymer. However, no ring opening took place and the initial reactants remained unchanged.

EXPERIMENTAL

The o-carborane was obtained under the direction of A. F. Zhigach and was freed from impurities by recrystallization from petroleum ether and by distillation; mp 294–296° C. The α,ω-dichloro-oligodimethylsiloxanes [13] were obtained by the partial hydrolysis of dimethyldichlorosiloxane. The IR spectra were recorded on a Hilger H-800 spectrometer, with an NaCl prism in CCl_4 solution, in the region from 4000 to 800 cm^{-1}.

1,3-o-Carboranetetramethyldisiloxane (III). Dilithio-o-carborane [10,14,15] was obtained from 6.8 g (0.047 mole) of o-carborane and 3.6 g (0.095 mole) of n-butyllithium in ether. A 250-ml round-bottomed flask with three necks fitted with a bulb reflux condenser, a stirrer with a gas-tight seal, a dropping funnel, and an inlet for inert gas was first heated several times (with subsequent cooling in a current of argon). With ice cooling, the flask was charged with 20 g (0.047 mole) of 1,9-dichlorodecamethylpentasiloxane (II). Then, with careful stirring, a suspension of I in ether was added over 1.5 hr. After this, the reaction mixture was stirred for another 2 hr. The ethereal solution was separated from the LiCl that had precipitated during the reaction, the precipitate was washed three times with ether, and the extract was combined with the ethereal solution and separated from the LiCl. The ether was distilled off in vacuum. The crystals that deposited were separated from the oil formed and were recrystallized from n-hexane and sublimed, mp 159–160° C.

On standing, the oil formed in the process of distilling off the ether deposited crystals of III. It was impossible to achieve the complete separation of the oil from the crystals.

In order to establish the structure of the oil, the crystals of III were sublimed off from a small part of it in vacuum of 1 mm at 100–150° C for 30 hr. The residual oil had a mol. wt. = 530 and did not contain boron or OH groups.

Similarly, III was obtained at a ratio of I : II = 1 : 1 (n = 1,2).

1,5-o-Carboranehexamethyltrisiloxane (IV). Dilithio-o-carborane (I) was obtained from 17.7 g (0.123 mole) of o-carborane and 15.7 g (0.246 mole) of n-butyllithium in ether. The conditions of the synthesis were similar to those described for III.

From 86.5 g (0.246 mole) of 1,7-dichlorooctamethyltetrasiloxane was obtained 20 g of IV, mp 106–107° C. The oil formed in the process of distilling off the ether, when freed from IV, did not contain boron or OH groups, mol. wt. = 825. The same products were isolated at a molar ratio I : II = 1 : 2 (n = 1–3).

EXPERIMENTS ON THE OPENING OF THE RING OF IV

Acid Catalysts. a) A 25-ml flask fitted with a bulb reflux condenser, a stirrer, and a nitrogen inlet was charged with 1.63 g (4.7 mM) of IV, 0.033 g (0.33 mM) of 98% H_2SO_4, and 3 ml of n-heptane. The flask was purged with nitrogen. With careful stirring, the mixture was heated for a long time (Table 2), the n-heptane distilling off and the crystals of IV subliming off. A small part of the starting material blackened.

b) A mixture of 1.66 g (4.8 mM) of IV, 0.0415 g (0.121 mM) of aluminum sulfate, 0.00245 g (0.025 mM) of 98% H_2SO_4, and 3 ml of n-heptane was heated in an atmosphere of nitrogen. During this process, the n-heptane distilled off and the crystals of IV sublimed off. A small part of the product darkened.

Nucleophilic catalysts. A 25-ml flask fitted with a stirrer and nitrogen inlet was charged with 2.0 g (5.8 mM) of IV, and 0.0103 g of an 11.5% aqueous solution of LiOH was added at 100° C.

In view of the fact that no polymerization took place, a solution of LiOH was gradually added to the reaction flask with a simultaneous rise in the temperature. A total of 0.008 g (0.33 mM) of LiOH was added. At 270–300° C, crystals of o-carborane sublimed with mp 294–296° C. After sublimation, a small amount of a siloxane oil containing no boron remained.

Attempts to open the ring of compound IV under the action of 1.9% aqueous NaOH solution were carried out in the same way and led to similar results.

The results of the experiments on the catalytic opening of the ring of IV are given in Table 2.

Attempts at the thermal opening of the ring of IV. A tube with a capacity of 25 ml, previously heated in vacuum and purged with nitrogen, was charged with 1.0 g (2.87 mM) of IV. Then it was sealed and heated at 300° C for 24 hr. After this, the whole of the IV was recovered unchanged.

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