HYDROLYSIS AND ETHERIFICATION OF (o-CARBORANYLISOPROPYL)DICHLORO(METHYL)SILANE

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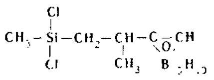
The behavior of (o-carboranylisopropyl)dichloro(methyl)silane in hydrolysis and etherification reactions has been studied. (o-Carboranylisopropyl)(methyl)silanediol and (o-carboranylisopropyl)diethoxy(methyl)silane have been obtained for the first time and characterized.

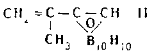
Carborane and its derivatives have recently attracted the attention of research workers to an ever-increasing extent [1]. Polymers based on carboranes are of particular interest [2–5], since they possess an increased thermal stability and do not require additional plasticization because of the plasticizing effect of the carborane nucleus.

The synthesis of carborane-siloxane polymers containing carborane rings both in the main chain and in side chains has been reported [2,5–7].

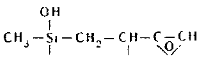
We have studied the reactivity of (o-carboranylisopropyl)dichloro(methyl)silane (I) as a compound from which a polymer with an o-carborane ring in the side chain can be obtained. In particular, we have studied the possibility of replacing the chlorine atoms attached to the silicon by other functionalgroups (HO—, RO—).


I

(o-Carboranylisopropyl)dichloro(methyl)silane (I) was obtained [8] by the addition of dichloro(methyl)silane (II) to isopropenyl-o-carborane in the presence of catalysts:

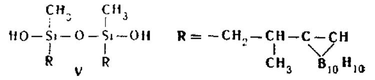

III $(H_2PtCl_6$ or $FeCl_3)$.

The hydrolysis of I was studied in order to obtain the corresponding dihydroxy derivative—(o-carboranylisopropyl)(methyl)silanediol (IV).

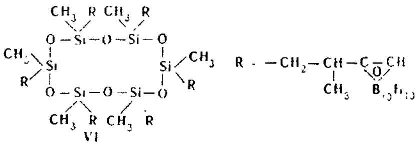

IV

When the hydrolysis was carried out with an excess of water in a solvent (ether, benzene, m-xylene) at −20–0° C in the presence of $NaHCO_3$ as hydrogen chloride acceptor, in all cases a dimer with a linear structure (V) was obtained.

On hydrolysis in a mixture of solvents (water + hexane + benzene, 1 : 1 : 1) without a hydrogen chloride acceptor at the boiling point of the reaction mixture, a hexamer with a cyclic structure was obtained, as was shown by the absence of OH groups and by the molecular weight determined by the ebullioscopic method in cyclohexane, of 1500 (calculated: 1464).


V

The structure of the ring can be shown by Formula VI:


VI

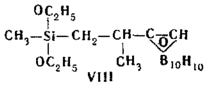
Monomeric (o-carboranylisopropyl)(methyl)silanediol (VI) was obtained from the hydrolysis of I with an excess of water in the presence of $NaHCO_3$ as hydrogen chloride acceptor. Compound IV exhibits a high tendency to undergo condensation in a solvent with the formation of a dimer similar to that obtained previously (V). This is shown in its molecular weight: by the cryoscopic method (in benzene) it was possible to determine only the first point because the condensation of the diol with the formation of the dimer took place after a few minutes and the molecular weight doubled. No further increase in the molecular weight took place either under the conditions of its determination or at room temperature.

At 180° C without a solvent, the condensation of (o-carboranylisopropyl)(methyl)silanediol takes place further with the formation of a cyclic compound (VII) with a molecular weight of 1200, which corresponds to a pentamer $(C_6H_{20}B_{10}OSi)_5$.

The etherification of I was carried out with absolute methanol or ethanol both in the presence of a hydrogen chloride acceptor (pyridine) and without it, at room temperature. In all cases the monomeric dialkoxy derivative could not be isolated, since condensation took place.

Since the aim of our investigation was the synthesis of monomeric bifunctional derivatives of (o-carboranylisopropyl)(methyl)silane, no detailed characterization of the products that we obtained on etherification was carried out.

The dialkoxy derivative VIII was obtained by the reaction of I with ethyl orthoformate (VI) by analogy with the preparation of other dialkoxy organosilicon derivatives [9,10].


VIII

Compound VIII was isolated and characterized (table).

Physical Constants and Results of the Analyses of Compounds IV–VIII

Compound	Name	Bp, °C (pressure, mm)	Mp, °C	d_4^{20}	n_D^{20}	Mol. wt.		Empirical formula	Found, %					Calculated, %					Yield, %
						found	calculated		C	H	B	Si	OH	C	H	B	Si	OH	
IV	(o-Carboranylisopropyl)-(methyl)silanediol	—	60—62	—	—	264	262	$C_6H_{22}B_{10}O_2Si$	27.3	8.37	41.3	10.2	12.4	27.46	8.4	41.22	10.7	12.98	90
V								$C_{12}H_{42}B_{20}O_3Si_2$	28.08	8.02	42.0	11.0	6.30	28.46	8.3	42.68	11.07	6.72	
VI								$C_{36}H_{120}B_{60}O_6Si_6$	29.75	8.6	44.0	11.63	0.0	29.50	8.19	44.26	11.48	0.00	
VII								$C_{30}H_{100}B_{50}O_5Si_5$	29.85	8.6	43.9	11.79	0.0	29.50	8.19	44.26	11.48	0.00	
VIII	(o-Carboranylisopropyl)diethoxy(methyl)silane	102—103 $(7 \cdot 10^{-2})$	—	0.9742	1.5070	309	318	$C_{10}H_{30}B_{10}O_2Si$	37.22	9.71	34.0	8.8	—	37.73	9.43	33.96	8.8	—	50

EXPERIMENTAL

STARTING MATERIALS

(o-Carboranylisopropyl)dichloro(methyl)silane (I), mp 52.5° C, bp 155–156° C (3 mm) [8].

Ethyl orthoformate was obtained by a published method [11], bp 144–146° C, n_D^{19} 1.3922, which corresponds to literature data [10].

(o-Carboranylisopropyl)(methyl)silanediol (IV). A 100-ml flask was charged with 5 g (16.7 M) of I and a solution of 3 g (35.7 mM) of $NaHCO_3$ in 50 ml of water. The reaction was carried out with cooling from 0 to −20° C (it was accompanied by pronounced foaming). The solid matter was filtered off, washed repeatedly with water to neutrality, and dried in a vacuum desiccator over P_2O_5. Compound IV formed a white powder with mp 60–62° C. Its elementary analysis is given in the table.

(o-Carboranylisopropyl)diethoxy(methyl)silane (VIII). A 100-ml flask fitted with a reflux condenser, a stirrer, an inlet for inert gas, and a dropping funnel was charged with 10 g (67.6 mM) of enthyl orthoformate, and then 10.1 g (3.38 mM) of I (dissolved in hexane or without a solvent) was gradually added at room temperature, whereupon the reaction mixture darkened. Then it was stirred at room temperature for 25 hr and after this at 120° C (1 mm) for 3 hr. Distillation yielded 12.8 g of a fraction boiling at 101–109° C (3.5×10^{-2} mm) containing 1.2% of Cl. In order to bring the reaction to completion this product was treated at room temperature with 0.9 g (6.08 mM) of orthoformate. After this, the VIII was isolated by distillation in the pure state (table).

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