dilute ammonium hydroxide. A solution of approximately 0.1 *M* sodium hydroxide was added slowly with stirring until a black precipitate formed which was filtered and recrystallized from 95% ethanol; yield 70%. *Anal.* Calcd.: Cu, 15.4; N, 6.8. Found: Cu, 15.2; N, 7.0.

(d) **Bis-(1-phenyl-3-amino-2-butene-1-one)-copper(II).**—A solution of ammoniacal copper(II) nitrate was added to a solution of 1.5 g. of 1-phenyl-3-amino-2-butene-1-one dissolved in 95% ethanol. The green solid which formed was recrystallized from acetone. *Anal.* Calcd.: Cu, 17.5; N, 7.3. Found: Cu, 16.8; N, 7.3.

Methods of Analysis.—Analysis for copper was made by decomposition with sulfuric acid followed by a potassium iodide–sodium thiosulfate titration to a starch indicator end-point. Nitrogen analysis was made by the Kjeldahl method.

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LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NOTRE DAME]

Reactions of Haloboranes with Organocyclosiloxanes. I. Boron Chloride with Methyl and Ethyl Trimer and Tetramer[1,2]

BY PATRICK A. MCCUSKER AND THOMAS OSTDICK, O.S.B.

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The reaction of boron chloride with hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane produces initially dialkylchlorosiloxydichloroboranes. These are thermally unstable and disproportionate rapidly to tris-(dialkylchlorosiloxy)-boranes and boron chloride on attempted distillation even at low pressures. Tris-(dialkylchlorosiloxy)-boranes on short refluxing at atmospheric pressure followed by fractional distillation disproportionate to *sym*-tetraalkyldichlorodisiloxanes and boric oxide. *sym*-Tetraalkyldichlorodisiloxanes are more stable to disproportionation than the siloxyboranes but on long heating and slow fractional distillation at atmospheric pressure they can be made to disproportionate completely into dialkyldichlorosilanes and hexaalkylcyclotrisiloxanes. No linear or higher cyclosiloxanes are formed in this disproportionation reaction. The rate of the initial boron chloride–cyclosiloxane reaction is affected strongly by a steric factor involving the availability of the oxygen atoms of the cyclosiloxanes.

The reaction of boron chloride with trialkylboroxines has been shown by work in these laboratories[3] to yield alkyldichloroboranes along with a semi-solid residue which on hydrolysis gave boric acid and alkylboronic acid. No products intermediate to the starting materials and the final products were observed in the boroxine reaction. The analogous reaction of boron chloride with alkylcyclosiloxanes has now been investigated and found to be similar to the boroxine reaction except that with the alkylcyclosiloxanes a number of intermediate products have been isolated. The results of this study are reported in the present paper. A similar reaction between boron halides and linear trialkylsiloxanes has been reported by Wiberg and Krüerke[4] and the related reaction of aluminum chloride with organocyclosiloxanes has been reported by Hyde.[5]

Experimental

Reagents.—Boron chloride was obtained in technical grade from the Matheson Company. A practical grade of hexamethylcyclotrisiloxane and octamethylcyclotetrasiloxane as well as diethyldichlorosilane were obtained from the Anderson Laboratories, Inc., Weston, Michigan. The methyl trimer was recrystallized three times from ethyl ether before use and the methyl tetramer was purified by fractional distillation, b.p. 175.5–176° at 750 mm., $n^{20}\text{D}$ 1.3962, d^{20} 0.9563. Hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane[6] were prepared by the hydrolysis of diethyldichlorosilane according to the methods reported by Hyde and DeLong[7] and Patnode and Wilcock[8] for the methyl compounds. Ethyl trimer: b.p. 88.7–89.0° at 1.9 mm., $n^{20}\text{D}$ 1.4305, d^{20} 0.9567; ethyl tetramer: b.p. 139.5–140.5° at 3 mm., $n^{20}\text{D}$ 1.4340, d^{20} 0.9590.

Reaction Apparatus.—The apparatus consisted of a 3-necked 300-ml. flask fitted with a thermometer, a reflux condenser and a glass tube drawn out to a capillary tip to facilitate bubbling the boron chloride into the cyclosiloxanes. Boron chloride was bubbled through mercury and then passed through a mercury safety release at the beginning of the reaction set-up. The condenser was connected to sulfuric acid bubbling bottles to which a stopcock was attached.

Purification and Characterization of Products.—The products were purified by fractional distillation either through a 12 × 500 mm. Vigreux column or through a 12 × 1500 mm. total reflux, partial take-off glass-helix packed column. Solid carbon dioxide–acetone and liquid nitrogen traps were provided.

Analysis for chlorine was made by titration of aqueous suspensions of the products under an ether layer with standard base using methyl orange as indicator. The same aqueous suspensions were analyzed for boron by adding mannitol and phenolphthalein and continuing the titration with standard base. Densities were determined with calibrated 0.5-ml. or 5.0-ml. Lipkin pycnometers and refractive indices were measured with an Abbe refractometer at 20.0 ± 0.1°. Molar refractions were calculated from the data for silicon compounds given by Warrick.[9] A value of 1.67 for the boron–oxygen bond refraction was calculated from Otto's data[10] on *n*-butyl and *n*-amyl borate. A value of 6.98 for the boron–chlorine bond refraction was derived from the data on *n*-amyl- and *n*-hexyldichloroborane given by McCusker, Ashby and Makowski.[3] Molecular weights were obtained from cryoscopic measurements in benzene.

Reaction of Boron Chloride with Methyl Trimer.—Boron chloride was passed into 18.5 g. (0.083 mole) of solid methyl trimer at room temperature. Boron chloride was absorbed and the solid partially liquefied. After 10 minutes the

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[1] Presented at the New York Meeting of the American Chemical Society, September, 1957.

[2] Work supported under AEC Contract AT (11-1)-38, Radiation Project of the University of Notre Dame.

[3] P. A. McCusker, E. C. Ashby and H. S. Makowski, THIS JOURNAL, **79**, 5182 (1957).

[4] E. Wiberg and U. Krüerke, *Z. Naturforschg.*, **8b**, 608 (1953).

[5] J. F. Hyde, U. S. Patent 2,645,654 (July 14, 1953); *C. A.*, **48**, 7050a (1954). British Patent 685,183 (Dec. 31, 1952); *C. A.*, **48**, 2761b (1954).

[6] Hexamethylcyclotrisiloxane, octamethylcyclotetrasiloxane, hexaethylcyclotrisiloxane and octaethylcyclotetrasiloxane will be referred to as the methyl trimer, methyl tetramer, ethyl trimer and ethyl tetramer, respectively.

[7] J. F. Hyde and R. C. DeLong, THIS JOURNAL, **63**, 1194 (1941).

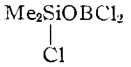
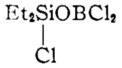
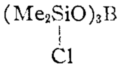
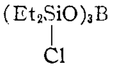
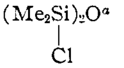
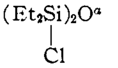
[8] W. Patnode and D. F. Wilcock, *ibid.*, **68**, 358 (1946).

[9] E. L. Warrick, *ibid.*, **68**, 2455 (1946).

[10] M. M. Otto, *ibid.*, **57**, 1476 (1935).

TABLE I

PHYSICAL CONSTANTS OF PRODUCTS

Compound	B.p. °C.	B.p. Mm.	$n^{20}D$	d^{20}	*MR*D Calcd.	*MR*D Obsd.	Mol. wt. Calcd.	Mol. wt. Obsd.	Boron, % Calcd.	Boron, % Obsd.	Cl, % Calcd.	Cl, % Obsd.
 $\underset{\mathrm{Cl}}{\mathrm{Me_2Si}}\mathrm{OBCl_2}$	.....	..	1.4210	1.1999	39.76	40.43	191.3	195.0	5.62	5.65	55.20	55.60
 $\underset{\mathrm{Cl}}{\mathrm{Et_2Si}}\mathrm{OBCl_2}$	67.5–68	18	1.4333	1.1721	49.02	48.67	219.4	227.2	4.93	4.95	48.47	48.57
 $(\underset{\mathrm{Cl}}{\mathrm{Me_2Si}}\mathrm{O})_3\mathrm{B}$	98.0–98.5 81.5–82.0	11 2	1.4130	1.0966	77.28	77.21	339.6	345.4	3.18	3.35	31.20	31.00
 $(\underset{\mathrm{Cl}}{\mathrm{Et_2Si}}\mathrm{O})_3\mathrm{B}$	137.5–138.0	2	1.4401	1.0665	105.06	104.64	423.3	420.0	2.55	2.58	25.10	25.20
 $(\underset{\mathrm{Cl}}{\mathrm{Me_2Si}})_2\mathrm{O}^a$	133.0	750	1.4054	1.0387	48.18	48.21	204.1	195.1	..	..	34.74	34.63
 $(\underset{\mathrm{Cl}}{\mathrm{Et_2Si}})_2\mathrm{O}^a$	106.0–107.0	20	1.4430	1.0301	66.70	66.72	259.3	250.1	..	..	27.34	27.31

[a] Previously reported; further characterized.

temperature rose to 45° and remained there until the reaction mixture was completely liquid. At this time 28.9 g. (0.249 mole) of boron chloride had been absorbed making the mole ratio of methyl trimer to boron chloride 1:3. The density, refractive index and molecular weight of the liquid, which was clear and colorless, were determined as recorded in Table I. It was concluded from these data that this reaction mixture was dimethylchlorosiloxydichloroborane, $(CH_3)_2SiClOBCl_2$. The dimethylchlorosiloxydichloroborane was heated at 2 mm. in a flask connected to the Vigreux column. Boron chloride (19.2 g.) was given off and collected in the liquid nitrogen trap and 0.5 g. of a liquid was collected in the solid carbon dioxide–acetone trap. Analyses for boron and chlorine and physical constants of the trap liquid established that it was dimethylchlorosiloxydichloroborane. The main fraction (22.8 g., 81% yield) was collected at 81.5–82° and identified by analysis and physical constants as tris-(dimethylchlorosiloxy)-borane, $[(CH_3)_2SiClO]_3B$. Data on this compound are listed in Table I.

Reaction of Boron Chloride with Methyl Tetramer.—The reaction was repeated as above using 29.5 g. (0.100 mole) of methyl tetramer and 12.0 g. (0.402 mole) of boron chloride. The maximum reaction temperature was 50° and the absorption of boron chloride required 6 hours. The resulting undistilled liquid was dimethylchlorosiloxydichloroborane as identified by physical constants listed in Table I. Upon distillation at 2 mm., the reaction mixture yielded 0.6 g. of dimethylchlorosiloxydichloroborane and a 40.0-g. fraction boiling at 81.7–81.9°, identified by the physical constants in Table I as tris-(dimethylchlorosiloxy)-borane (89% yield).

In a similar experiment 12.0 g. of boron chloride was added to 15.2 g. of methyl tetramer (methyl tetramer–boron chloride ratio, 1:2). The molecular weight of the undistilled reaction mixture was 181.7. This corresponds quite closely to the apparent molecular weight of 171 calculated for a mixture of 2 moles of dimethylchlorosiloxydichloroborane and $^1/_2$ mole of methyl tetramer. Distillation of the reaction mixture at 8 mm. gave 9.1 g. of tris-(dimethylchlorosiloxy)-borane (39.1% yield based on total amount of tetramer). Half of the tetramer was recovered unreacted and $^2/_3$ of the boron chloride was obtained in the liquid nitrogen trap.

Disproportionation of Tris-(dimethylchlorosiloxy)-borane and *sym*-Tetramethyldichlorodisiloxane.—Tris-(dimethylchlorosiloxy)-borane (18.9 g.) was refluxed at 160° for 2 hours and then distilled in the Vigreux column at 750 mm. A small forerun (2 g.) distilled at 68.5–68.7° (identified as dimethyldichlorosilane by boiling point and analysis for chlorine) and 14.0 g. distilled at 133.0–133.5°. The physical data for the latter fraction were obtained and are recorded in Table I. These identify the compound as *sym*-tetramethyldichlorodisiloxane (82% yield). The residue in the flask was a white solid. This was washed with ethyl ether and left 1.6 g. of a residue identified as boric oxide by analysis for boron.

sym-Tetramethyldichlorodisiloxane (10.2 g.) was heated at temperatures not exceeding 175° for 30 hours in the Vigreux column during which time 5.5 g. of a low boiling product was distilled over. This product was redistilled. Its physical constants indicate that the product was dimethyldichlorosilane (86% yield). The purified dimethyldichlorosilane had the following properties: b.p. 68.5–68.7° at 750 mm.; $n^{20}D$ 1.4108; d^{20} 1.0885; *MR*D calcd. 29.54, obsd. 29.43; % Cl calcd. for $C_2H_6SiCl_2$ 54.96, obsd. 54.78; mol. wt. calcd. 129.1, obsd. 124.9. In the flask were left 3.2 g. of pure methyl trimer identified by melting point (87% yield).

Reaction of Boron Chloride with Ethyl Trimer.—Boron chloride was passed into 14.4 g. (0.047 mole) of ethyl trimer at 10–13° until 16.6 g. had been added and the mole ratio of trimer to boron chloride was 1:3. From physical constants, the product in the undistilled reaction mixture was identified as diethylchlorosiloxydichloroborane, $(C_2H_5)_2SiClOBCl_2$. The diethylchlorosiloxydichloroborane was distilled at 10 mm. in the glass-packed column. Boron chloride (11.0 g.) was evolved and collected in the liquid nitrogen trap and about $^1/_2$ ml. of unchanged diethylchlorosiloxydichloroborane ($n^{20}D$ 1.4333) distilled at 67.5–68°. Fractionation was continued at 2 mm. and there resulted 14.4 g. of a substance (0.034 mole; 71.9% yield) identified as tris-(diethylchlorosiloxy)-borane, $[(C_2H_5)_2SiClO]_3B$, by physical constants as listed in Table I.

When boron chloride was added at room temperature to ethyl trimer until the ethyl trimer–boron chloride ratio was 1:1, a 30.1% yield of tris-(diethylchlorosiloxy)-borane was obtained. The reaction was repeated using a 1:2.07 mole ratio of trimer to boron chloride. The molecular weight of the undistilled reaction mixture was found to be 209.8. This compares to a value of 230 calculated for a mixture of 2 moles of diethylchlorosiloxydichloroborane and $^1/_3$ mole of unreacted ethyl trimer. The reaction mixture was distilled at 3.5 mm. and a 50.4% yield of tris-(diethylchlorosiloxy)-borane was obtained.

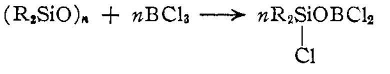
Reaction of Boron Chloride with Ethyl Tetramer.—Into 24.1 g. of ethyl tetramer at room temperature was bubbled 27.7 g. of boron chloride which corresponds to a mole ratio of the ethyl tetramer to boron chloride of 1:4.01. This required 16.5 hours during which time the temperature rose to 27°. The molecular weight of the reaction mixture before distillation was determined to be 210.3. This mixture was then distilled at 8 mm. using the glass-packed column. The major fraction had these properties: b.p. 175.0–175.5°, $n^{20}D$ 1.4351, d^{20} 0.9808, mol. wt. 427.5, % Cl 5.10, % B 0.596. When this fraction was refluxed for 3 hours and distilled at atmospheric pressure, boric oxide and *sym*-tetraethyldichlorodisiloxane (4.8 g., 8.1% yield), identified by its physical constants, were obtained, as well as ethyl trimer and diethyldichlorosilane (2.9 g., 8.0% yield), also identified by physical constants.

Disproportionation of Tris-(diethylchlorosiloxy)-borane and *sym*-Tetraethyldichlorodisiloxane.—Tris-(diethylchlorosiloxy)-borane (10.9 g.) was refluxed with a Vigreux column at 20 mm. for 4 hours at temperatures below 150°. A clear substance (7.4 g.) boiling at 106–107° was obtained and 0.5 g. of a liquid was collected in the solid carbon dioxide–acetone trap. Analysis of the material in the trap showed it to be diethyldichlorosilane (8.2% yield). The physical data for the 106–107° fraction, listed in Table I, identify the product as *sym*-tetraethyldichlorodisiloxane (73.9% yield). The residue in the flask was a white solid which, when washed with ethyl ether, left a residue of 0.3 g. of boric oxide.

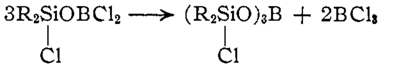
sym-Tetraethyldichlorodisiloxane (11.2 g.) was heated at temperatures less than 175° for 35 hours with the Vigreux column during which time 6.5 g. of a lower boiling product was collected. This distillate on redistillation was identified as diethyldichlorosilane by its boiling point and refractive index (b.p. 128.0–128.4° at 752 mm., $n^{20}D$ 1.4453; lit.[11] b.p. 129° at 760 mm., $n^{20}D$ 1.4452; yield 96%). Ethyl trimer (4.5 g.), identified by boiling point and refractive index, was left as a residue.

Results and Discussion

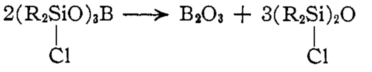
The following sequence of reactions has been established for the interaction of boron chloride with the methyl and ethyl trimers and tetramers and the stepwise disproportionation of the products.



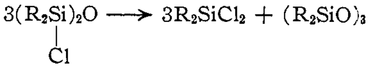
$$(R_2SiO)_n + nBCl_3 \longrightarrow nR_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Si}}}OBCl_2 \qquad (I)$$



$$3R_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Si}}}OBCl_2 \longrightarrow (R_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Si}}}O)_3B + 2BCl_3 \qquad (II)$$



$$2(R_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Si}}}O)_3B \longrightarrow B_2O_3 + 3(R_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Si}}})_2O \qquad (III)$$



$$3(R_2\underset{\mathrm{Cl}}{\underset{|}{\mathrm{Si}}})_2O \longrightarrow 3R_2SiCl_2 + (R_2SiO)_3 \qquad (IV)$$

Physical properties for all of these reaction products are listed in Table I. Identification of compounds was made on the basis of analysis for chlorine and boron, molecular weight measurements and agreement of the calculated and observed molar refractions. The dialkylchlorosiloxydichloroboranes and tris-(dialkylchlorosiloxy)-boranes are new types of compounds. The *sym*-tetraalkyldichlorodisiloxanes are mentioned in the literature[12] but complete physical data are not given for them.

The relative rates of the initial reaction were found to be strongly affected by steric factors involving the availability of the oxygen atoms of the cyclosiloxanes. Fisher–Hirschfelder–Taylor molecular models of the cyclosiloxanes were constructed. These models indicate that in the methylcyclosiloxanes the oxygen atoms are more sterically accessible to the boron chloride molecule than in the ethylcyclosiloxanes. In all cases the methylcyclosiloxanes reacted more rapidly than the ethylcyclosiloxanes. The models also indicate that the oxygen atoms in the trimers are more accessible than in the tetramers. Our observed relative rates were more rapid in all cases for the reactions of the trimers. In the extreme case of the sterically least accessible oxygen atoms of the ethyl tetramer, reaction was very slow and incomplete. With a large excess of boron chloride, only 16% of the ethyl tetramer reacted with boron chloride. The separation of tris-(diethylchlorosiloxy)-borane from ethyl tetramer was impossible because their boiling points at 8 mm. lie only 4° apart. However, the physical constants for the main fraction in the vacuum distillation of the reaction mixture indicate the presence of both tris-(diethylchlorosiloxy)-borane and unreacted ethyl tetramer. Distillation at atmospheric pressure caused the disproportionation of the tris-(diethylchlorosiloxy)-borane in the fraction. This resulted in an 8.1% yield of *sym*-tetraethyldichlorodisiloxane and an 8.0% yield of the disproportionation products of *sym*-tetraethyldichlorodisiloxane. This is equivalent to a 16% reaction of boron chloride and ethyl tetramer. In all other cases the reaction occurred quite readily on simply bubbling boron chloride into the cyclosiloxane, and gave yields of 80 to 90% of products.

The initial step in the reactions between boron chloride and the cyclosiloxanes is exothermic. And it appears from our results to involve the interaction of one molecule of boron chloride with each oxygen atom of the cyclosiloxane according to reaction I. This conclusion rests on an analysis of the results obtained when less than the amount of boron chloride called for in reaction I was used. Specifically, when one mole of boron chloride was added to one mole of cyclic trimer and the reaction mixture distilled, $^2/_3$ of a mole of boron chloride was evolved and $^2/_3$ of the cyclic trimer was left unreacted. Similarly when two moles of boron chloride were used for one mole of trimer, the reaction mixture gave up on distillation $1^1/_3$ moles of boron chloride and $^1/_3$ of the cyclic trimer was left unreacted. Again when 2 moles of boron chloride were added to 1 mole of tetramer, the reaction mixture yielded on distillation $1^1/_3$ moles of boron chloride and $^1/_2$ of the tetramer was recovered unreacted. The yields of final products in all these cases, however, were 70 to 80% when calculated on the basis of the amount of cyclosiloxane consumed and using the over-all equation, illustrated by the reaction with the trimer, $2(R_2SiO)_3 + 6BCl_3 \rightarrow 3R_2SiCl_2 + (R_2SiO)_3 + 4BCl_3 + B_2O_3$. Thus it seems clearly established that in the initial reaction each oxygen atom of the cyclosiloxanes interacts with one molecule of boron chloride.

It might be expected that this initial step in the reactions of boron chloride with the cyclosiloxanes would involve the coördination of each of the oxygen atoms in the cyclosiloxane molecule with a molecule of boron chloride. However, molecular weight determinations on the reaction mixtures did not support this expectation. The molecular weight of a 1:3 molar mixture of ethyl trimer and boron chloride which had been kept below 13° was determined immediately after the addition of boron chloride and gave a value of 227.2. This compares quite closely to the value of 219.4 calculated for the cleavage product, diethylchlorosiloxydichloroborane. It thus appears that if coördination takes place cleavage occurs too rapidly for experimental detection of the coördination compound to be successful.

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(11) T. Alfrey, F. J. Horn and H. Mark, *J. Polymer Sci.*, **1**, 102 (1946).

(12) R. A. Sauer, U. S. Patent 2,534,149 (Dec. 12, 1950); *C. A.*, **45**, 4739c (1951); P. D. George, L. H. Sommer and F. C. Whitmore, THIS JOURNAL, **75**, 1585 (1953).

The cleavage products, dialkylchlorosiloxydichloroboranes, fume strongly in air. The Si–O–B bond in these compounds is readily cleaved hydrolytically. On distillation the compounds were found to be thermally unstable. They can be obtained only in small yields (3–5%) when the reaction mixture is distilled at low pressures (2–10 mm.) through a packed column. The remainder of the dialkylchlorosiloxydichloroborane (95–97%) disproportionates to boron chloride and a product identified as tris-(dialkylchlorosiloxy)-borane according to reaction II.

That the product in reaction II is tris-(dialkylchlorosiloxy)-borane rather than $(R_2SiO)_3 \cdot BCl_3$ is not shown definitely by its physical properties alone. However, the fact that a compound of exactly the same physical properties is obtained from both trimer and tetramer eliminates the coördination compound as a possible product.

The tris-(dialkylchlorosiloxy)-boranes formed in reaction II are also fuming liquids and on standing exposed to the air for one hour they become tacky. When allowed to stand open to the air for 12 hours a rather soft, clear plastic substance is formed. The Si–O–B bonds in tris-(dialkylchlorosiloxy)-boranes are readily cleaved hydrolytically with the formation of cyclosiloxanes and boric acid. Tris-(dialkylchlorosiloxy)-boranes can be distilled at 2–11 mm. pressure and at temperatures below 150° with no detectable disproportionation. However, as described in reaction III, tris-(dimethylchlorosiloxy)-borane is disproportionated to *sym*-tetramethyldichlorodisiloxane and boric oxide by refluxing for 2 hours at 200° and then distilling at atmospheric pressure in a Vigreux column. When tris-(diethylchlorosiloxy)-borane is refluxed for 4 hours at 20 mm. pressure and at a temperature of 150° in a Vigreux column and then distilled, it undergoes a similar disproportionation. Under the conditions used for the disproportionation of both tris-(dialkylchlorosiloxy)-boranes with the consequent formation of the *sym*-tetraalkyldichlorodisiloxanes and boric oxide, about 5% of the *sym*-tetraalkyldichlorodisiloxanes formed underwent further disproportionation according to reaction IV.

sym-Tetraalkyldichlorodisiloxanes, however, are much more resistant to disproportionation than are the tris-(dialkylchlorosiloxy)-boranes. Long heating (about 30 hours for a 10-g. sample) of *sym*-tetraalkyldichlorodisiloxanes at atmospheric pressure and temperatures up to 175° along with slow fractional distillation using a Vigreux column is necessary to effect complete disproportionation of *sym*-tetraalkyldichlorodisiloxanes into cyclic trimers and dialkyldichlorosilanes, as in reaction IV. That the disproportionation of *sym*-tetraalkyldichlorodisiloxanes can be made quantitative by bleeding off the dialkyldichlorosilane as it is formed suggests that the disproportionation reaction involves an equilibrium which is fairly rapidly attained at distillation temperatures. Emeléus and Payne[13] and Patnode[14] reported the preparation of *sym*-tetraalkyldichlorodisiloxanes by methods other than those reported here but apparently did not observe the disproportionation reaction. The quantitative thermal disproportionation of an organosilicon compound, such as observed here for the *sym*-tetraalkyldichlorodisiloxanes, apparently has not been reported previously although partial thermal disproportionation,[15] catalytic disproportionation,[16] and some redistribution reactions[17] of organosilicon compounds have been reported.

In the reaction of boron chloride with trialkylboroxines previously reported from these laboratories[3] no intermediate products analogous to those found in the reactions with cyclosiloxanes were isolated. The fact, however, that the reaction of boron chloride with trialkylboroxines did not result in the immediate precipitation of boric oxide (or mixed polymer) suggests that soluble intermediate products may have been formed. On the basis of the work with cyclosiloxanes it also appears probable that the appearance of large amounts of apparently unreacted trialkylboroxine in the reaction of boron chloride with trialkylboroxines may be due at least in part to the disproportionation of unisolated intermediate products by a series of reactions similar to those given here for the reaction of boron chloride with cyclosiloxanes. Also the fact that boric oxide and no mixed polymeric material was found among the products of the cyclosiloxane reactions suggests the probability that only boric oxide and not a mixed polymer of boric oxide and trialkylboroxine was formed in the trialkylboroxine reactions.

In all cases the disproportionation of *sym*-tetraalkyldichlorodisiloxanes resulted in the formation of only trimeric siloxanes. No tetramer or higher boiling polymer was formed. This result is quite unexpected in view of the fact that in the preparation of trimers and tetramers by hydrolysis of dialkyldichlorosilanes and other methods a mixture of products always results. The exclusive formation of trimer in the disproportionation of *sym*-tetraalkyldichlorodisiloxane cannot result from catalytic action of any kind since no observable impurity was present in the compounds disproportionated. Indeed, the absence of any possible catalyst such as water, acid, or base may be responsible for the exclusive formation of trimer. In the disproportionation of *sym*-tetraalkyldichlorodisiloxane, R_2–Si–O units are probably first formed. Under our experimental conditions such units appear to join together to form only trimer.

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