

**ORGANOSILOXANE POLYMERS CONTAINING
POLAR GROUPS IN THE SIDE CHAINS**

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FOREWORD

This report was prepared by Harvard University, Cambridge, Massachusetts under U.S.A.F. Contract No. AF 33(616)-479. The contract was initiated under Project 7340, "Rubber, Plastic and Composite Materials," Task 73404, "Synthesis and Evaluation of New Polymers" (formerly under Research and Development Order No. 617-11) and was administered under the Direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Capt. J. F. O'Brien acting as project engineer.

This report covers the period of work from January 1955 to September 1955.

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WADC TR 54-102 Pt 2

Contracts

Abstract

In accordance with the proposed objectives of this research a study of the synthesis of polymerizable organosilicon monomers containing organoboron groups was made. Such monomers are intended to be used in conjunction with nitrogen-containing monomers to increase inter-chain attraction in the polymer.

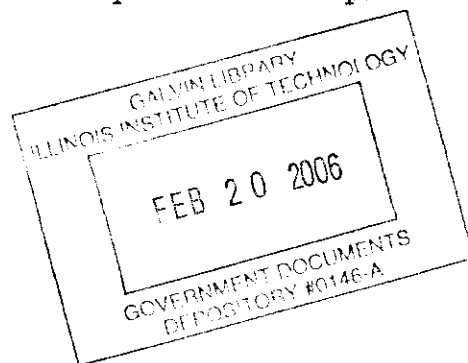
A high-vacuum system was built and by this means large quantities of dimethylboron bromide were prepared.

Side-chain chlorination of methylsilanes were carried out by photochemical reactions. In particular, methyl(chloromethyl)dichlorosilane was prepared by this method and was converted to methyl(chloromethyl)bis(*o*-cresoxy)silane, a hitherto unknown compound.

A method was found to convert chlorosilanes to silanes, using lithium aluminum hydride, without reducing chloromethyl groups attached to silicon. Methyl(chloromethyl)silane was prepared for the first time by this process.

Attempts to prepare a Grignard reagent from methyl(chloromethyl)bis(*o*-cresoxy)silane failed, probably because of steric hindrance of the two bulky *o*-cresoxy groups. However, by replacing the *o*-cresoxy groups with hydrogen atoms the preparation of the Grignard reagent was successful.

The reaction of dimethylboron bromide with the Grignard reagent of methyl(chloromethyl)silane appeared to proceed satisfactorily. The product was separated as an adduct of dimethylamine. Many attempts were made to find a suitable solvent for purification of this compound. Although the product contained boron, silicon, hydrogen, and nitrogen, the results of the analyses indicate presence of impurities. The synthesis of polymerizable silane monomers containing organoboron groups thus appears feasible by the methods developed under this project, but further improvements in separation are



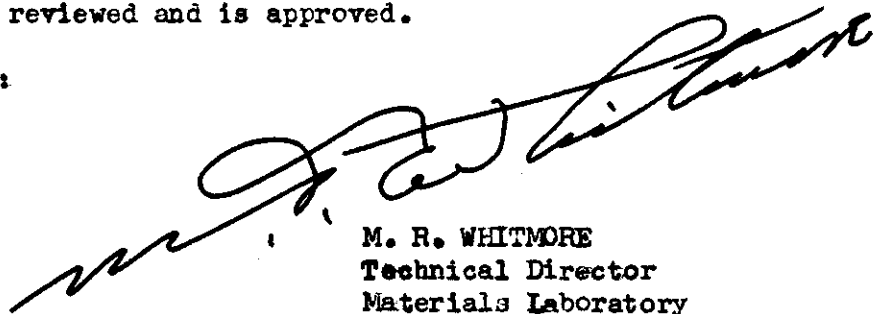
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necessary in order readily to prepare considerable amounts of polymer for evaluation.

PUBLICATION REVIEW

This report has been reviewed and is approved.

FOR THE COMMANDER:



**M. R. WHITMORE
Technical Director
Materials Laboratory
Directorate of Research**

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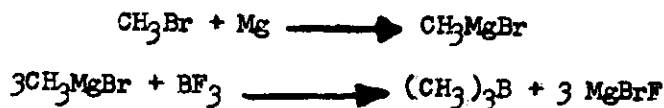
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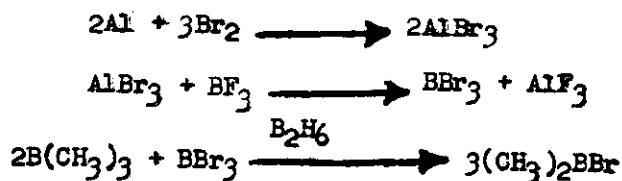
The object of the research covered by the present report was the syntheses of polymerizable organosilicon monomers containing organoboron groups. It was felt that the greatest chance of success lay in the preparation of a silicon compound of the type $R_2BCH_2Si\leftarrow$, where R is an alkyl group, because such a compound would not be likely to lose its boron content during the hydrolytic polymerization of the silane. Boron-carbon linkages are themselves fairly stable to hydrolytic attack provided R is small, i.e., a methyl or ethyl group.

In view of previous results (5), it was decided that the best route for the synthesis of a B-CH₂-Si bond system lay in the reaction of a dialkylboron halide with the Grignard derivative of a chloromethylsilane. However, the preparation of dialkylboron halides, with R = methyl or ethyl, presents certain difficulties in that they are obtained from the very inflammable trialkylborons and had previously been made only in very small amounts.

Despite its hazardous nature, large quantities of trimethylboron were prepared by the usual Grignard reaction (1)



The conversion of trimethylboron to dimethylboron bromide was achieved in large quantities for the first time. The procedure employed was that used by McKennon (2), with certain modifications. The following equations represent the process:

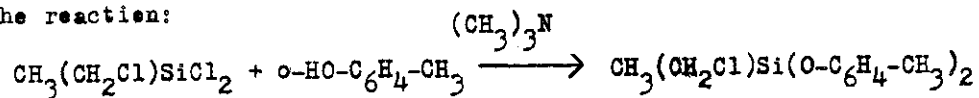


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Aluminum bromide and boron tribromide were prepared by methods given in Inorganic Synthesis (3). The latter compound was found to attack stepcock grease rapidly, and consequently it had to be prepared and used immediately.

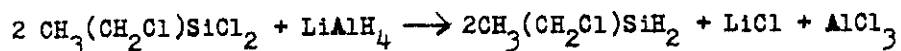
The dimethylboron bromide was handled by means of a simple vacuum system and stored in a steel bomb.

For the chlorination of dimethyldichlorosilane the method suggested by McBride and Beachell (4), using sulfuryl chloride and benzoyl peroxide was first used. The yield of this reaction was very low because of di- and trichlorination of the methyl groups. Consequently this method was replaced by a new direct chlorination technique in which only unchlorinated material was permitted to remain in contact with chlorine resulting in much higher yields (over 80%) of the desired material. The methyl(chloromethyl)dichlorosilane obtained by this method was converted to methyl(chloromethyl)bis(o-cresoxy)silane by means of the reaction:



This hitherto unprepared compound is a viscous liquid boiling at 149-151°C/0.1 mm Hg.

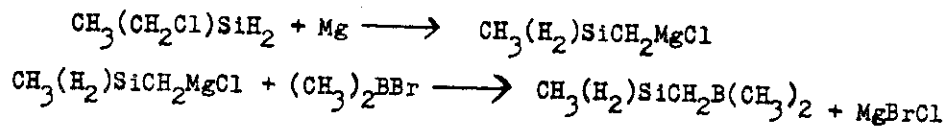
By replacing the chlorine atoms attached to silicon by o-cresoxy groups it was hoped to be able to prepare a Grignard reagent using the chlorine atom in the chloromethyl group. This reaction failed, however, probably because of the steric hindrance caused by two large o-cresoxy groups. This difficulty was overcome by replacing the chlorine atoms attached to silicon with hydrogen. This selective reduction was effected by means of lithium aluminum hydride



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This reaction is exothermic and care should be taken to keep the reaction temperature below 25°C, otherwise complete reduction, i.e., replacement of all the halogen atoms in the molecule will take place.

Methyl(chloromethyl)silane is a new compound with a boiling point of 60-61°C/760 mm Hg. As would be expected, it is extremely hygroscopic. The preparation of a Grignard reagent from methyl(chloromethyl)silane proceeded fairly easily. Addition of dimethylberen bromide to this Grignard reagent also proceeded with ease. The formation of magnesium chloride and bromide readily was observed.



The product was a liquid which could not be separated from ether by distillation. Therefore the dimethylamine adduct was prepared. This complex is a white extremely hygroscopic solid.

Many attempts to resolve this adduct by crystallization using solvents such as acetone, ether, tetrahydrofuran, and benzene failed. The tenacity with which the berenated silicon compound holds on to nitrogen indicates that the proposed inter-chain attraction in silicones containing beren and nitrogen would be quite strong.

It is suggested that synthesis of the pure compound be tried by replacing the ether with benzene after the preparation of the Grignard reagent, and then adding dimethylberen bromide. The halides of magnesium formed in this reaction, being insoluble in benzene, could be easily separated by filtration, and the final separation may then prove much easier than through the route outlined above. Expiration of contract time and funds has prevented further trials of this sort.

Preparation of Trimethylboron.

A 2-l. three-necked round-bottomed flask, equipped with a mechanical stirrer, a dropping funnel, and a dry ice-acetone condenser, was connected to a series of traps. A 72 g. (3.0 g. atom) sample of magnesium turnings was placed in the flask and 250 ml. of dry n-butyl ether were added through the dropping funnel. The entire apparatus was flushed with prepurified nitrogen for about half an hour. Then a solution of 285 g. (3 moles) of methyl bromide in 500 ml. of n-butyl ether was introduced into the reaction flask, the methyl bromide-n-butyl ether solution being prepared by bubbling methyl bromide into the ether very slowly at 0°C. The reaction was triggered by the addition of two small iodine crystals. The addition of methyl bromide to the magnesium turnings took about three hours. The reaction flask was immersed in an ice bath to prevent the temperature of the flask rising above 10°C. Stirring was continued overnight.

A solution of 61 g. (0.9 moles) of BF_3 in 400 ml. of n-butyl ether, prepared by bubbling BF_3 into a flask containing the ether at 0°C, was added very slowly to the Grignard solution with very vigorous stirring. The reaction flask was immersed in an ice bath, and the condenser was filled with a dry ice-acetone mixture. The traps connected to the condenser were immersed in dry ice-acetone baths. The addition of BF_3 to the Grignard solution was carried out over a period of three and one-half hours. At the end of this time, the ice bath was removed and the flask was heated to 60°C by means of an oil bath. The trimethyl boron condensed mainly in the first trap. Occasionally the evolution of $(\text{CH}_3)_3\text{B}$ was greater than the rate of its condensation in the traps and consequently a little product escaped and was observed to burn with green flame. The heating was continued for two hours, then the stopcocks on the cold

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traps containing the product were turned off and the traps were removed and connected to the vacuum system where the product was transferred into a stainless steel cylinder.

The transfer of trimethyl boron from the glass container into the metal cylinder was carried out in the usual manner, that is, by immersing the evacuated (ca. 10^{-4} mm Hg) cylinder in liquid nitrogen and slowly bringing the connected cold glass trap to room temperature. This process required about two hours to transfer 27.2 g. of trimethyl boron. The yield was 49%. The melting point of this compound is -161°C and it boils at -21°C .

To avoid fire or explosion, the reaction flask was flushed with nitrogen before dismantling. Some gaseous trimethylboron was observed to burn on leaving the apparatus. It was apparent that some trimethyl boron had not been recovered from the solution in the reaction flask. Higher yields probably could be obtained by prolonging the time of refluxing, but on the other hand, due to the extreme inflammability of the product it seems wise to be content with somewhat lower yields.

Preparation of Aluminum Bromide.

Aluminum bromide was prepared in a specially designed apparatus (3). The reaction flask was filled with granular aluminum (30 mesh). It was heated to about 100°C with Bunsen burners, and 60 ml. (1.08 moles) of Br_2 were added very slowly. The addition of bromine took about three and one-half hours. The flask was then heated gently for about half an hour to insure complete reaction of bromine with aluminum. AlBr_3 was then distilled from the reaction flask using two Bunsen burners. The distillation took about two hours, 63 g. (82% yield) of AlBr_3 were obtained.

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Preparation of Boron Tribromide

A one-liter round-bottomed flask was sealed to the bottom of a 500 ml. distilling flask by means of a 25 cm. length of 30 mm. glass tubing. The smaller flask served as a condenser to prevent sublimation of large quantities of AlBr_3 with boron tribromide. A side-arm was sealed to the smaller flask and this was connected via a U-tube, cooled with dry ice, to a drying tube. A 3 mm. glass tube extended into the large flask, the other end being connected to a sulfuric acid trap, through which BF_3 could be bubbled into the main reaction flask.

The apparatus was flushed with prepurified nitrogen, and 72 g. (0.28 moles) of aluminum bromide were placed in the reaction flask. The flask was heated with two Meeker burners until the AlBr_3 started to boil. A fast current of BF_3 was then passed through the flask. The heating was continued until all the AlBr_3 reacted with BF_3 . This reaction took approximately three hours. At the end of this period the reaction flask was strongly heated and BBr_3 was distilled into the U-tube. The heating was continued until a white granular residue (AlF_3) remained in the flask. The side arm connecting the reaction flask to the U-tube was then sealed off with an oxygen torch and by this means 47.7 g. BBr_3 were obtained. This product was contaminated with bromine and was redistilled through a small column filled with nichrome helices. 29.2 g. (17.3% yield) of BBr_3 was obtained as a colorless liquid boiling at 90-91°C.

Preparation of Dimethyl boron Bromide.

A high vacuum system was used for the preparation of dimethylboron bromide. The metal cylinder containing $\text{B}(\text{CH}_3)_3$ was connected to the vacuum system and 10 g. of this material was transferred into another metal cylinder which acted as the reaction vessel. A 22 g. (0.09 moles) sample of BBr_3 was then distilled into the reaction vessel together with about 1 cc. (STP) of diborane to act as a catalyst (2). The reaction cylinder

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was removed from the vacuum system and heated over a steam bath for 24 hours. It was then reconnected to the vacuum system and opened to the pumps through a series of vacuum traps cooled to -118° and -196°C . The fraction which condensed at -118°C was stored in a metal cylinder. It weighed 30 g. (92.5% yield) and was identified as dimethylberon bromide.

Analysis: calculated for Br 66.15%
 found for Br 66.15%

Preparation of Methyl(chloromethyl)dichlorosilane

The apparatus used in this preparation consisted of a one-liter three-necked round-bottomed flask, equipped with a 100 ml. Soxhlet extractor, a nitrogen inlet, and a thermometer. The Soxhlet extractor was connected to an Allihn dry ice-acetone condenser by means of a Claisen head, one arm of which was connected to a safety trap and a two-liter flask containing sodium hydroxide solution. The other arm of the Claisen head was connected to a sulfuric acid bubbler, which in turn was joined to a chlorine cylinder. Chlorine was admitted into the Soxhlet extractor by means of a tube reaching to the bottom of the Soxhlet and fitted with a sintered-glass disc of medium porosity. The apparatus was flushed with nitrogen and 314g. (2.43 moles) of dimethyldichlorosilane was placed in the reaction flask and heated by means of a heating mantle. Chlorine was bubbled into the Soxhlet extractor when the level of the dimethyldichlorosilane in the Soxhlet extractor reached the sintered-glass disc. During the passage of chlorine the Soxhlet extractor was irradiated with a Ceesper Hewitt 3660^oA lamp. Care was taken to prevent the ultra-violet light reaching the reaction flask.

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The hydrogen chloride gas generated in this reaction was passed into the sodium hydroxide solution. This solution was prepared by dissolving 116 g. of NaOH pellets in two liters of water to which was added a few drops of bromthymol blue indicator. The passage of chlorine was discontinued as soon as the solution in the Soxhlet extractor siphoned out. It was resumed when the level of the liquid reached the sintered-glass disc. This operation was continued for 10 hours and was stopped when the temperature of the solution in the reaction vessel reached 122°C (the boiling point of the desired product).

The sodium hydroxide solution was titrated with standard acid and by this means the weight of chlorine used in the reaction was calculated on the basis of the hydrogen chloride generated. It was found that 2.43 moles of chlorine had reacted.

Methyl(chloromethyl)dichlorosilane was distilled from the reaction mixture through a 12-inch Vigreux column, 203.4 g. of product was obtained. The yield based on unreacted starting material, $(\text{CH}_3)_2\text{SiCl}_2$, was 81% and based on the weight of chlorine used was 83%. The product boils at 120-121°C.

Analysis: $\text{CH}_3(\text{CH}_2\text{Cl})\text{SiCl}_2$

calculated for hydrolyzable chlorine	43.37%
found for hydrolyzable chlorine	43.37%

Preparation of Methyl(chloromethyl)bis(o-cresoxy)silane.

A 300-ml. three-necked round-bottomed flask was fitted with a condenser, a stirrer, and a dropping funnel. A 50 g. (0.306 moles) sample of methyl(chloromethyl)dichlorosilane was placed in the reaction flask and 18.1 g. (0.306 moles) of trimethylamine was added to it. To this mixture was added 200 ml. of dry ether. The stirrer was started and a solution of 66.3 g. (0.612 moles) of o-cresol, 18.1 g. (0.306 moles) of trimethylamine and 100 ml. of dry ether was added very slowly. The stirring was continued for

3 hours. The copious trimethylamine hydrochloride precipitate was filtered out and washed with 100 ml. of dry ether. The ether was removed by distillation and the product, methyl(chloromethyl)bis(o-cresoxy)silane, was obtained by vacuum distillation. The product distilled at 149-151°C/0.1 mm Hg., and 3.53 g. (11.5% yield) were obtained.

Analysis: $C_{16}H_{19}SiO_2Cl$
calculated: Cl; 11.55%, H; 6.24%, C; 62.63%
found: Cl; 11.75%, H; 6.07%, C; 62.51%

Preparation of Methyl(chloromethyl)silane

A one-liter three-necked flask was equipped with a condenser, stirrer, and a dropping funnel. A strong current of prepurified nitrogen was passed through the apparatus during the entire period of the reaction. A sample of 7.1 g. (0.187 moles) of lithium aluminum hydride was placed in the reaction flask and 150 ml. of dry n-butyl ether was added. The mixture was stirred for 30 minutes and a solution of 42 g. (0.256 moles) of methyl(chloromethyl)dichlorosilane in 100 ml. of dry n-butyl ether was introduced into the reaction flask through the dropping funnel over a period of two hours. The flask was immersed in an ice bath and care was taken to prevent the temperature of the flask rising above 25°C. The stirring was continued for three hours. The flask was then heated very slowly and the product was distilled into an atmosphere of nitrogen. The fraction distilling up to 80°C was collected and redistilled in a 30 plate column in a nitrogen atmosphere. Nine grams (15.3 % yield) of methyl(chloromethyl)silane, boiling at 60-61°/76° mm Hg were obtained.

Analysis $CH_3(CH_2Cl)SiH_2$
calculated: C; 25.39%, H; 7.46%
found: C; 25.81%, H; 7.18%

Attempted Preparation of Methyl(dimethylboromethyl)silane

Magnesium turnings, 2.0 g. (0.083 g. atoms), were placed in a 300 ml. three-necked round-bottomed flask, which was equipped with a nitrogen inlet tube, a thermometer, a dry ice-acetone condenser, a dropping funnel, and a nitrogen outlet tube. A magnetic stirrer was also placed in this flask. 15 ml. dry ether was added to the Mg turnings. To this mixture was added, very slowly, a solution of methyl(chloromethyl)silane, 6.4 g. (0.068 moles), in 10 cc. dry ether. The Grignard reaction was triggered with a small iodine crystal. The stirring was continued for three hours. A sample of 8 g. (0.068 moles) of dimethylboron bromide was condensed in a glass bulb and sealed off by means of an oxygen torch. The capillary extension of the bulb was inserted into vacuum rubber tubing, which was connected to an inlet tube and stopcock leading into the flask. The capillary tube of the bulb was crushed and its contents were transferred into the reaction flask by simply warming the bulb with the palm of the hand. Immediately a copious precipitate of magnesium chloride bromide was obtained. The stirring was continued and a strong current of nitrogen was passed through the flask to remove the unreacted dimethylboron bromide. The liquid in the reaction flask was then transferred into another three-necked flask of the same size under nitrogen. Then 25 ml. of dry ether was added to the solid material in the reaction flask and the precipitate was washed and filtered, under nitrogen, adding the washings to the second flask. 2.88 g. (0.064 moles) of dimethylamine was added to the ether solution through a dropping funnel. A white precipitate was obtained. This was washed several times with dry ether and dried in a current of dry nitrogen.

The product, dimethylamine adduct of methyl(dimethylboromethyl)silane, is an extremely hygroscopic white solid which burns with a greenish flame upon ignition and leaves a white residue.

By the above process 0.9 g. (0.006 moles) of this material were obtained. This compound does not have a well defined melting point, but it decomposes between 58-68°C.

A series of analyses were conducted on this material. The initial analysis indicated the presence of silicon, boron, carbon, hydrogen, and nitrogen, but the percentages of all these elements were low, indicating contamination by inorganic material (probably $MgBr_2$ from the ether).

Many solvents were tried for purification of this compound without any appreciable success. Acetone, benzene, ether, and tetrahydrofuran were used. The major impurity is believed to be magnesium bromide which is soluble in ether, and which could not be separated from the product. A sample of this compound was dissolved in water and a few drops of silver nitrate solution were added to it. There was definite formation of silver halides.

Contrails
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