

WADC TECHNICAL REPORT 54-102

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

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*July 1954*

**Materials Laboratory  
Contract No. AF 33(616)-479  
RDO No. 617-11**

**Wright Air Development Center  
Air Research and Development Command  
United States Air Force  
Wright-Patterson Air Force Base, Ohio**

Carpenter Litho & Prtg. Co., Springfield, O.  
200 - 7 October 1954

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## FOREWORD

This report was prepared by the Harvard University, Cambridge, Massachusetts under USAF Contract No. AF 33(616)-479. The contract was initiated under Research and Development Order No. R617-11, "Synthesis and Evaluation of New Polymers", and was administered under the direction of the Materials Laboratory, Directorate of Research, Wright Air Development Center, with Capt R. T. Clark, Jr. acting as project engineer.

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In accordance with the proposed objectives of this research a study of the possible synthesis of nitrogen and boron containing polymerizable silicon monomers of the  $p-R_2MC_6H_4Si(CH_3)X_2$ , (where M is either nitrogen and boron and X is a hydrolyzable group like chloro or alkoxy) was undertaken. Two nitrogen-containing silicon monomers methyl-*p*-dimethylaminophenyldichlorosilane and methyl-*p*-dimethylaminophenyldimethoxysilane were prepared by reacting *p*-dimethylaminophenyllithium with methyltrichloro- and methyltrimethoxysilane, respectively.

Various methods were attempted to prepare a suitable boron-containing silicon monomer without success. Incidental with these attempts it was found that *p*-bromophenyldichloroboron could be prepared by disproportionation of tri-*p*-bromophenylboron and boron trichloride. Symmetrical organoboron compounds were prepared by reacting the suitable Grignard reagent with boron trichloride or trimethyl borate. Di-*n*-butyl- and di-*n*-propylbromoboron were prepared by reacting the respective symmetrical compounds with bromine.

It was possible to prepare Grignard reagents of methyl-*p*-bromophenyldiphenoxysilane and methyl-*p*-bromophenyldi-*o*-cresoxysilane. Only the latter reagent proved to be of use in subsequent reactions.

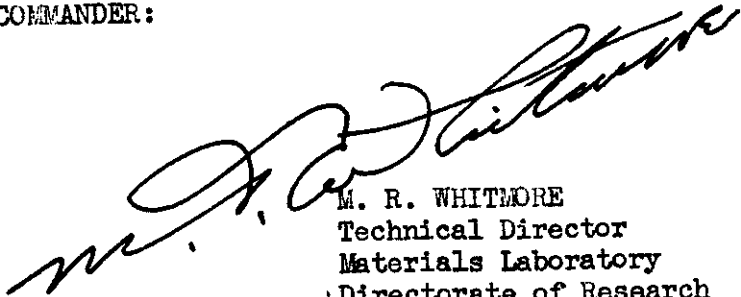
Trimethylallylsilane and trichlorosilane were condensed, under the activation of benzoyl peroxide, to form trimethyl-3-trichlorosilylpropylsilane. Under similar conditions, trimethylallylsilane did not condense with methyldichlorosilane. It is planned to attempt to condense trichlorosilane with triallylboron and di-*p*-propylallylboron.

Reference has been made to the difficulties involved in the analysis of organosilicon and organoboron compounds, and some suggestions have been made. From the infrared spectra of the organoboron compounds that were prepared a tentative assignment of the carbon-boron absorption frequency has been made at 1370-1390  $cm^{-1}$  or 1320-1340  $cm^{-1}$ . Three tables containing the new compounds prepared during the course of this research are included.

#### 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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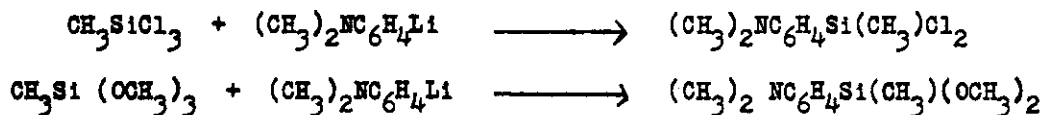
## INTRODUCTION

The results discussed herein were obtained under Contract No. AF 33 (616)-479, administered by the Rubber and Plastics Branch Materials Laboratory, Wright Air Development Center. The proposed objective of this research was the preparation of organosiloxane polymers containing polar groups in the side chains.

A study of the possible synthesis of nitrogen and boron-containing polymerizable silicon monomers of the type  $p\text{-R}_2\text{MC}_6\text{H}_4\text{Si}(\text{CH}_3)\text{X}_2$ , (where M is either nitrogen or boron and X is a hydrolyzable group like chloro or alkoxy) was undertaken. It was hoped that the well known mutual affinity of nitrogen and boron would remain active in the resulting organosiloxane polymers thereby increasing the attraction between siloxane chains.

## DISCUSSION

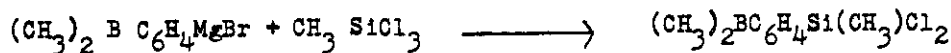
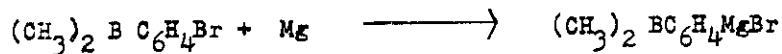
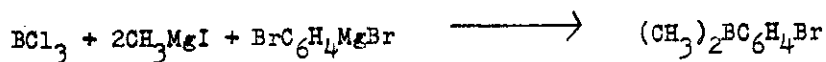
The synthesis of the desired nitrogen-containing silicon monomer was achieved by the reaction of methyltrichlorosilane with  $p$ -dimethylaminophenyllithium to form methyl- $p$ -dimethylaminophenyldichlorosilane (32%). Methyl- $p$ -dimethylaminophenyl-dimethoxysilane (31%) was similarly prepared by substituting methyltrimethoxysilane for methyltrichlorosilane.



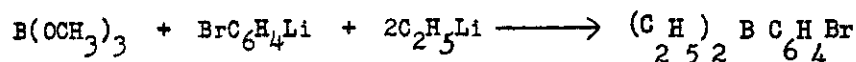
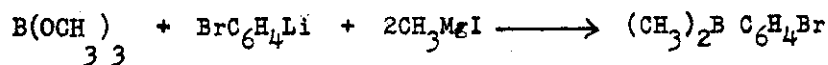
The preparation of the desired boron-containing silicon monomer could not be achieved by similar methods. The first approach to this part of the problem was the attempted preparation of dimethyl- $p$ -bromophenylboron. It was hoped that this compound

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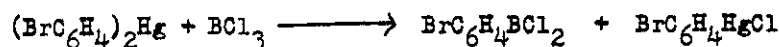
would react with magnesium or lithium to form an active organometallic compound.



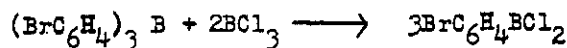
Two methods were tried to prepare dimethyl-*p*-bromophenylboron. The first of these, the direct reaction of boron trichloride with 2 equivalents of methylmagnesium iodide and 1 equivalent of *p*-bromophenylmagnesium bromide, was unsuccessful. The only boron-containing compounds isolated were boron trichloride and trimethylboron. The reaction of *p*-bromophenyllithium, methylmagnesium iodide and methyl borate, and of *p*-bromophenyllithium, ethyllithium and methylborate did not succeed in preparing the desired compound.



As the direct method did not succeed, it was decided to try to prepare the compound in two steps. The preparation of aromatic boron dihalides has been described (1) and the synthesis of *p*-bromophenyldichloroboron (46%) was achieved by the reaction of di-*p*-bromophenylmercury (2) with boron trichloride in a sealed tube.



*p*-Bromophenyldichloroboron (25%) was also prepared by the disproportionation of tri-*p*-bromophenylboron and boron trichloride. This latter method is actually the more desirable, although

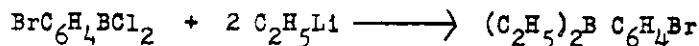


the yield is lower, as a larger amount of product can be synthesized in a single preparation.



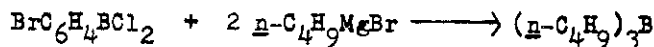
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Several attempts were made to alkylate the *p*-bromophenyldichloroboron with uncertain results. The first of these was the reaction of dichloride with two equivalents of ethyllithium. Although the ethyllithium reacted, as evidenced by Color Test I

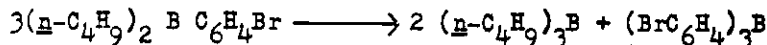


(3), the desired product was not isolated. The reaction which came closest to achieving success was that of ethylmagnesium bromide and the dichloride. A liquid distilling at 55°/26.0 mm. was isolated. Although it was thought that a pure compound had been obtained, the elemental analysis was not close enough for a definite assignment. Further comment will be made on the difficulties involved in analyzing organoboron compounds later.

In a third attempt at alkylation, the dichloride was reacted with *n*-butylmagnesium bromide. The only product isolated was tri-*n*-butylboron (60%). This result suggests



the possibility that the inate character of the boron atom may prevent the existence of completely carbon-substituted organoboron compound where there is gross unsimilarity in the alkyl and/or aryl groups. Such unsymmetrical structures may be formed as intermediates which then rearrange to form symmetrical compounds.



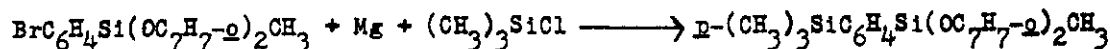
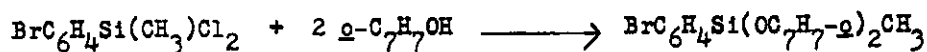
An attempt was made to form the mono-Grignard reagent of tri-*p*-bromophenylboron and the Grignard of diethyl-*p*-bromophenylboron (?) without success.

As these various attempts to prepare an organoboron compound from which a Grignard or other active organometallic could be made did not succeed, other methods for preparing the desired organo-boron-silicon compounds were sought.

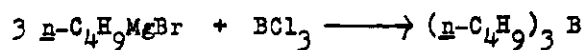
Frisch and Shrogg (4) reported that the Grignard reagent of trimethyl-*p*-bromophenoxysilane was prepared in an 83% yield. This suggested that by reversing our approach and preparing a Grignard reagent of an organosilicon compound which was polymerizable, and then reacting this with an appropriate boron chloride, perhaps the desired end would be attained.

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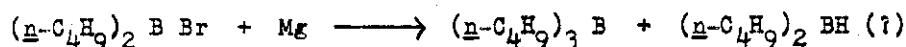
This was investigated by the following series of reactions:



These reactions worked well with the silicon compounds and methyl-p-trimethylsilylphenyl-di-o-cresoxysilane was prepared in fair overall yield. Di-n-butylbromoboron (70%) was prepared as outlined by Johnson and co-workers (5) by the cleavage of tri-n-butylboron with bromine.

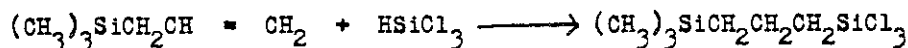


Although trimethylchlorosilane does not react with magnesium turnings, di-n-butylbromoboron does. This result severely limited the usefulness of this approach as it increased the chance of side reactions in a system where ample possibilities already existed. The products formed in the reaction between di-n-butylbromoboron and magnesium were tri-n-butylboron and di-n-butylboron hydride (?).



A reaction of methyl-p-bromophenyldi-o-cresoxysilane, di-n-butylbromoboron and magnesium led only to the recovery of the cresoxysilane and formation of tri-n-butylboron and di-n-butylboron hydride.

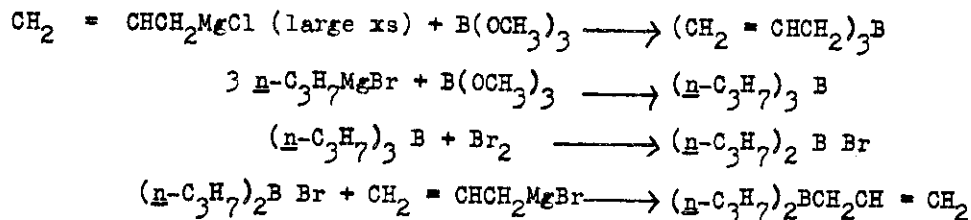
Following the lead of Sommer and Whitmore (6) and research carried out in this laboratory, the possibility of condensing a boron-containing olefin with trichlorosilane was investigated. In a model reaction trimethylallylsilane and trichlorosilane were condensed. No reaction took place using ultraviolet irradiation but the use of benzoyl peroxide led to the formation of trimethyl-3-trichlorosilyl-n-propylsilane (41%). Under similar conditions no reaction took place between trimethylallylsilane and methyldichlorosilane.



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# Conclusions

Tri-n-allylboron (25%) and di-n-propylallylboron (51%) were prepared by the methods outlined earlier.



It was noted that the cleavage of tri-n-propylboron with bromine was accomplished much more slowly than that of tri-n-butylboron. This is a reversal of the ease of cleavage by acidic reagents of organic groups in organometallic compounds (7), and, as such, is worthy of further investigation. The actual attempted condensation of these unsaturated organoboron compounds has not been carried out as of this writing.

Throughout the course of this research the analysis of the organoboron and organo-silicon compounds has proved to be difficult. Carbon and hydrogen have been analyzed by the usual dry oxidation methods and the carbon results have been low. This may be due to the formation of carbides in the oxidation train. A wet oxidation method might eliminate this difficulty. Silicon has been determined by Parr bomb fusion and these determinations have been low almost without exception. Oxidation in a platinum crucible with concentrated sulfuric acid might be the better method in this case. Future investigators are strongly advised to devise adequate methods of analysis for themselves at the outset of their research. The organobromoboron compounds were easily and accurately analyzed by the Volhard method of adding excess silver nitrate and back titrating with thiocyanate, using ferric iron as indicator.

The use of infrared analysis proved to be very useful in the preparations of di-n-butylbromoboron and di-n-propylbromoboron. Tri-n-butylboron has a medium absorption band at  $2015 \text{ cm}^{-1}$  but this band is absent in the spectrum of di-n-butylbromoboron. The same situation exists for tri-n-propylboron and di-n-propylbromoboron. Therefore it was

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a simple matter to ascertain if these monohalides were free of the symmetrical organoboron compound. An analysis of the infrared spectra included herein shows absorption bands at  $1370-1390\text{ cm}^{-1}$  and  $1320-1340\text{ cm}^{-1}$  consistently. A tentative assignment of the carbon-boron absorption frequency can be made for either of these positions.

Tables I, II and III contain a list of the new compounds prepared during the course of this research, together with their boiling points (and/or melting points) and their elemental analyses.

## EXPERIMENTAL

Preparation of Methyl-p-dimethylaminophenyldichlorosilane.- p-Dimethylaminophenyllithium (0.27 mole) in 225 ml. of ether was added to 80.0 g. (0.54 mole) of methyltrichlorosilane in 500 ml. of ether dropwise and with good stirring. Fractional distillation led to the isolation of 20.0 g. (32.0%) of methyl-p-dimethylaminophenyldichlorosilane distilling at  $106-110^{\circ}/0.7\text{ mm.}$ , n.  $41.5^{\circ}$ .

Anal. Calcd. for  $C_9H_{13}Cl_2NSi$ : Cl, 30.22; N, 5.99

Found: Cl, 29.20; N, 6.30.

Preparation of Methyl-p-dimethylaminophenyldimethoxysilane.- p-Dimethylaminophenyllithium (0.25 mole) in 225 ml. of ether was added to 68.0 g. (0.5 mole) of methyltrimethoxysilane in 500 ml. of ether dropwise and with good stirring. Fractional distillation led to the recovery of 20.0 g. (58.8%) of methyltrimethoxysilane, b.  $98-100^{\circ}$  760 mm. and the isolation of 15.4 g. (31.3%) of methyl-p-dimethylaminophenyldimethoxysilane distilling at  $88-90^{\circ}/0.3\text{ mm.}$

Anal. Calcd.  $C_{11}H_{19}O_2NSi$ : C, 58.75; H, 8.51; N, 6.23.

Found: C, 58.78; H, 8.41; N, 7.22.

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Attempted Preparation of Dimethyl-p-bromophenylboron.- p-Bromophenylmagnesium bromide (0.86 mole) was prepared by stirring 201.5 g. (0.86 mole) of p-dibromobenzene with 20.89 (0.86 g. atom) of magnesium turnings in 500 ml. of ether until all the metal was dissolved. Methylmagnesium iodide (2.1 mole) was prepared from 298.0 g. (2.1 mole) of methyl iodide and 60.6g. (2.5 g. atom) of magnesium turnings in 600 ml. of ether.

Into a 2 liter flask equipped with a cold condenser, electric stirrer and dropping funnel, and surrounded by a Dry Ice-acetone bath ( $-30^{\circ}$ ) was let 95.0 g. (0.81 mole) of cold boron trichloride. Then 100 ml. of ether was cautiously added followed by addition of the p-bromophenylmagnesium bromide solution. One hour after addition was completed Color Test I (3) was negative. Then the methylmagnesium iodide solution was added and the reaction mixture was stirred overnight.

Work-up of the reaction by fractional distillation at 760 mm. led to the recovery of trimethylboron, boron trichloride and bromobenzene in trace amounts.

A second reaction was carried out using p-bromophenyllithium, methylmagnesium iodide and methyl borate. Once again only trimethyl boron and bromobenzene were isolated.

Attempted preparation of Diethyl-p-bromophenylboron.- p-Bromophenyllithium (0.25 mole) was prepared by the addition of 0.25 mole of ethyllithium in 173 ml. of ether to 59.0 g. (0.25 mole) of p-dibromobenzene in 250 ml. of ether at  $-40^{\circ}$ .

Into a 2 liter flask equipped with a cold condenser, stirrer and dropping funnel, and surrounded by a Dry Ice-acetone bath ( $-40^{\circ}$ ) was placed 26.0 g. (0.25 mole) of methyl borate in 500 ml. of ether. The p-bromophenyllithium solution was then added with good stirring. Fifteen minutes after addition Color Test I was negative. Then 0.50 mole of ethyllithium in 346 ml. of ether was added. The reaction mixture was slowly brought to reflux, maintained there for 3 hours and then allowed to stand overnight.

Hydrolysis was carried out by the addition of 350 ml. of sat. ammonium chloride solution. The ether layer was dried over sodium sulfate, filtered and fractionally

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distilled. After ether removal the remaining liquid was distilled under reduced pressure. The main fraction (8.7 g.) distilled at  $71^{\circ}/2.6$  mm. This material redistilled at  $26^{\circ}/0.4$  mm to give 5.6 g. of product.

Anal: Calcd.  $C_{10}H_{14}BBr$ : Br, 35.55. Found: Br, 24.46.

Redistillation of the analyzed liquid yielded a single fraction;

b.  $52-54^{\circ}/12.5$  mm.

Anal: Calcd.  $C_{10}H_{14}BBr$ : Br, 35.55. Found: Br, 18.82

Preparation of p-Bromophenyldichloroboron.— In a Carius tube were placed 38.0 g. (0.07 mole) of di-p-bromophenylmercury and 41.0 g. of boron trichloride (1). The tube was sealed, heated at  $200^{\circ}$  for 4 hours, gradually cooled to  $-30^{\circ}$  and opened. Then 10 ml. of dry benzene was added to the tube, and the liquid portion was decanted in a 100 ml. flask and fractionally distilled. The boron trichloride and benzene distilled first, then at 1.0 mm. one fraction distilling at  $61-65^{\circ}$  was obtained. Total yield of p-bromophenyldichloroboron was 8.1 g. (46%).

Anal: Calcd. for  $C_6H_4BBrCl_2$ : Neut. Equiv., 118.9. Found: Neut. Equiv., 113.9.

In a 500 ml. flask equipped with a low temperature condenser were placed 60.2 g. (0.126 mole) of tri-p-bromophenylboron and 26.5 g. (0.252 mole) of boron trichloride. The flask temperature was gradually raised from  $30^{\circ}$  to  $200^{\circ}$  and the condenser maintained at  $-70^{\circ}$  by means of a Dry Ice-Acetone mixture. The solid gradually turned dark brown and eventually melted. The molten mass was heated for a total of 5 hours, during the last hour the temperature was maintained at  $200^{\circ}$ .

Upon cooling the contents of the flask, a syrupy liquid, was transferred to a 100 ml. flask and distilled under reduced pressure. One fraction, distilling at  $34-82^{\circ}/0.7-1.5$  mm. was obtained.

Neut. Equiv. Calcd. for  $C_6H_4BBrCl_2$ , 118.9. Found 110.0

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The fraction was redistilled and after a minor forerun 2 fractions were obtained. Cut 1 distilled at 60-68°/0.7 mm. and weighed 5.6 g.; Cut 2 distilled at 68°/0.7 mm. and weighed 14.5 g; Cut 2 solidified on cooling and melted at 22-24°. Cut 1, although easily solidified, was a liquid at this temperature.

Infrared spectra of the 2 fractions were virtually identical. Total yield of p-bromophenyldichloroboron was 20.1 g. (22.4%).

Attempted Preparation of Diethyl-p-bromophenylboron. - The 8.1 g. (0.034 mole) of p-bromophenyldichloroboron prepared above was added to 100 ml. of ether in a 300 ml. flask. To this 0.070 mole of ethyllithium in 52 ml. of ether was added, dropwise and with good stirring. Color Test I was negative 30 minutes after the addition was completed. The reaction mixture was hydrolyzed and worked up.

In the final distillation 1.6 g. of material distilling at 27°/1.0 mm. was obtained.

Anal. Calcd. for  $C_{10}H_{14}BBr$ : Br, 35.55. Found: Br, 20.69.

In a 500 ml. flask were placed 14.5 g. (0.06 mole) of the p-bromophenyldichloroboron prepared above and 100 ml. of ether. To this was added 0.12 mole of ethylmagnesium bromide in 200 ml. of ether over a 1 hour period. A colorless solid precipitated from the solution after addition of 20 ml. of Grignard solution. The reaction mixture was gently refluxed for 1 hour after addition. The reaction mixture was then hydrolyzed by the cautious addition of 100 ml. of a saturated ammonium chloride solution. After drying the ether layer over Drierite, the ether was removed by distillation and the residual oil was vacuum distilled.

One fraction distilling at 56°/26 mm. was obtained; weight, 4.9 g. This was redistilled; b. 55°/26 mm; weight 3.0 g. This material, after fusion, melted at -30° to -28°.

Anal. Calcd. for  $C_{10}H_{14}Br$ : C, 53.49; H, 6.27. Found: C, 47.59; H, 4.53.

There was some evidence of partial decomposition upon vacuum distillation of this material.

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Reaction of p-Bromophenylboron Dichloride with n-Butylmagnesium Bromide.- In a 500 ml. flask were placed 24.9 g. (0.105 mole) of p-bromophenylboron dichloride and 100 ml. of ether. To this was added, dropwise and with good stirring, 0.21 mole of n-butylmagnesium bromide in 173 ml. of ether. The reaction mixture was stirred for fifteen minutes after addition was completed, filtered under nitrogen and the ether removed under reduced pressure.

The residue was vacuum distilled to yield one fraction, b. 51-53°/0.7 mm., wt. 7.0 g. The infrared spectrum of this material showed none of the characteristic aromatic absorption and, indeed, was identical with that of an authentic specimen of tri-n-butylboron. The yield of tri-n-butylboron was 7.0 g. (60.4%).

Reaction of p-Bromophenyldiethylboron (?) with Magnesium.- No apparent reaction took place between p-bromophenyldiethylboron in ether and magnesium metal.

Preparation of Methyl-p-bromophenyldichlorosilane.- To a rapidly stirred solution of 112 g. (0.75 mole) of methyltrichlorosilane in 750 ml. of ether was added 0.5 mole of p-bromophenylmagnesium bromide in 500 ml. of ether. After addition was completed, the mixture was refluxed for 2 hours and allowed to stand overnight. The ethereal solution was filtered under nitrogen and the ether and excess methyltrichlorosilane distilled from a steam bath. The liquid residue was then fractionally distilled. Two fractions were obtained.

Fraction 1 distilled at 89-91°/0.7 mm. It partially solidified on standing. The liquid portion was decanted and redistilled. A forerun, which solidified upon reaching the water condenser, distilling at 64-68°/0.3 mm. and a liquid fraction distilling at 65-68°/0.3 mm. were obtained. The solid was combined with the solid previously isolated. The liquid fraction was then subjected to a vacuum sublimation. The liquid was maintained at 100° and 0.2 mm., and the solid which sublimed was caught on the walls of a cold condenser. The residual liquid was then analyzed.



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Anal. Calcd. for  $C_7H_7BrCl_2Si$ : C, 31.13; H, 2.58. Found: C, 31.41%; H, 2.73.

Fraction 2 distilled at  $94-174^\circ/0.7$  mm. This was redistilled to yield a solid forerun distilling at  $58-60^\circ/0.3$  mm. and a liquid fraction distilling at  $67-70^\circ/0.3$  mm. Each fraction was treated as above.

The combined solid was crystallized from ethanol to yield 3.0 g. of p-dibromobenzene melting at  $83-85^\circ$ . The two liquid fractions were combined to give a total of 37.1 g. (27.5%) of methyl-p-bromophenyldichlorosilane.

Preparation of Methyl-p-bromophenyldiphenoxysilane.- In a 1 l. flask were placed 57.9 g. (0.213 mole) of methyl-p-bromophenyldichlorosilane, 23 g. of triethylamine and 250 ml. of ether. To this was added 40.0 g. (0.426 mole) of phenol and 22 g. of triethylamine in 250 ml. of ether. The reaction mixture was refluxed for 4 hours, cooled and filtered. The ether was distilled and the oily residue was fractionally vacuum distilled. Two fractions were obtained.

Fraction 1 distilled at  $56-90^\circ/3.0$  mm. A semi-solid with pronounced phenol-like odor.

Fraction 2 distilled at  $190-206^\circ/1.1$  mm. A viscous yellow oil, wt. 58.9 g. This material was redistilled to yield 43.5 g. (54.4%) of methyl-p-bromophenyldiphenoxysilane distilling at  $183-185^\circ/0.9$  mm., m.  $43-44^\circ$ .

Anal. Calcd. for  $C_{19}H_{17}BrO_2Si$ : C, 59.23; H, 4.45. Found: C, 57.63; H, 4.55.

Preparation of Methyl-p-trimethylsilylphenyldiphenoxysilane.-

Run One - A solution of 42.0 g. (0.11 mole) of methyl-p-bromophenyldiphenoxysilane in 100 ml. of ether was refluxed with 3.0 g. of magnesium metal for 18 hours. No apparent reaction took place and Color Test I was negative. A small piece of iodine was added and reflux continued for 3.5 hours. The iodine color was gradually discharged and the metal appeared to be attacked. Color Test I became positive. The Grignard solution

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was decanted into a dropping funnel and added to a solution of 12.0 g. (0.11 mole) of trimethylchlorosilane in 100 ml. of ether. A total of 0.7 g. of magnesium was recovered indicating an 86% yield of Grignard. The reaction mixture was stirred and refluxed overnight, cooled, and filtered. The ether was carefully distilled using a Vigoreaux column (no trimethylchlorosilane was recovered) and the residue was fractionally vacuum distilled. Two fractions were obtained:

Fraction 1 distilled at 48-50°/0.7 mm;  $n_D^{24.4}$  1.4760. It has been reported that trimethylphenoxy-silane distills at 81°/23 mm;  $n_D^{25}$  1.4753. The yield of trimethylphenoxy-silane was 9.6 g. (53%).

Fraction 2 distilled at 178-190°/0.7 mm. This was redistilled to yield a small forerun and a main fraction distilling at 170°/1.1 mm.; weight 1.2 g. (2.9%). It was thought that this material was the desired methyl-p-trimethylsilylphenyldiphenoxysilane.

Anal. Calcd. for  $C_{22}H_{26}O_2Si_2$ : C, 69.80; H, 6.93. Found: C, 48.42; H, 5.35.

Run Two - In this reaction 14.3 g. (0.037 mole) of methyl-p-bromophenyldiphenoxysilane, 0.9 g. (0.037 g. atom) of magnesium turnings, 8.0 g. (0.074 mole) of trimethylchlorosilane and 50 ml. of ether were combined in a 100 ml. flask. The reaction was initiated by the addition of 0.5 ml. of ethylbromide, and was stirred and refluxed for 3.5 hours. The ethereal solution was filtered and worked up as above.

No low boiling fraction was obtained on vacuum distillation. One fraction distilling at 156-180°/1.0 mm. was obtained. This was redistilled to yield 2.0 g. (14.0%) of methyl-p-trimethylsilylphenyldiphenoxysilane distilling at 172°/1.0 mm.

Anal. Calcd. for  $C_{22}H_{26}O_2Si_2$ : C, 69.80; H, 6.93. Found: C, 70.12; H, 6.12.

The infrared spectra of the desired products isolated in Runs One and Two proved to be identical. Evidently the analysis in Run One was in error.

Preparation of Methyl-p-bromophenyldi-o-cresoxysilane.- Crude methyl-p-bromophenyldichlorosilane was prepared by the addition of 0.70 mole of p-bromophenylmagnesium bromide (from 165.2 g. (0.7 mole) of p-dibromobenzene and 17.0 g. (0.7 g. atom) of magnesium) in 750 ml. of ether to 1.4 mole of methyltrichlorosilane in 2 l. of ether; the ethereal solution was filtered, and the ether and excess methyltrichlorosilane removed by distillation.

To the crude material was added 71.0 g. (0.7 mole) of triethylamine in 1 l. of ether. A solution of 151.0 g. (1.4 mole) of o-cresol and 71.0 g. of triethylamine in 250 ml. of ether was added to the reaction solution in a thin stream with good stirring. After addition completion the mixture was stirred overnight. The ethereal solution was filtered from the dense solid and the ether was removed by distillation. The residue was then vacuum distilled.

Two fractions were obtained. Fraction 1 distilled at 60-140°/1.3 mm. and Fraction 2 at 170-285°/1.3 mm. Fraction 1 was redistilled at atmospheric pressure and 44.1 g. (29.2%) of o-cresol was recovered. Cut 2 was redistilled to yield a forerun distilling at 162-180°/1.0 mm. and 66.5 g. (22.3% overall, 32.2% based on recovered o-cresol) of methyl-p-bromophenyldi-o-cresoxysilane distilling at 196-200°/1.0 mm.

Anal. Calcd. for  $C_{21}H_{21}BrO_2Si$ : C, 61.10; H, 5.12. Found: C, 61.05; H, 5.10.

Preparation of Methyl-p-trimethylsilylphenyldi-o-cresoxysilane.- In a 300 ml. flask were placed 31.5 g. (0.076 mole) of methyl-p-bromophenyl-di-o-cresoxysilane, 16.5 g. (0.152 mole) of trimethylchlorosilane, 3.4 g. (0.15 g. atom) of magnesium turnings and 100 ml. of ether. The reaction was initiated by the addition of 4.3 g. (0.04 mole) of ethyl bromide and was then stirred and refluxed for 6 hours. The ethereal solution was filtered, the ether removed by distillation, and the residue vacuum distilled.

After a small forerun, the fraction distilling at 175-200°/1.0 mm. was collected.

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This was carefully redistilled to yield 12.8 g. (41.5%) of methyl-p-trimethylsilyl di-o-cresoxysilane distilling at 182-185°/0.6 mm.

Anal. Calcd. for  $C_{24}H_{30}O_2Si_2$ : C, 70.90; H, 7.44. Found: C, 72.94; H, 7.03.

## Reaction of Methyl-p-bromophenyldi-o-cresoxysilane, Di-n-butylboron Bromide and Magnesium.-

In a 300 ml. flask were placed 33.5 g. (0.08 mole) of methyl-p-bromophenyldi-o-cresoxysilane, 29.6 g. (0.14 mole) of di-n-butylboron bromide and 125 ml. of ether. To this 2.4 g. (0.1 g. atom) of magnesium turnings was added. Almost immediately vigorous refluxing commenced. When the spontaneous refluxing had stopped, the reaction mixture was stirred and refluxed for an additional 2 hours by outside heating. At the end of this time all the magnesium appeared to have been used. Upon cooling the ethereal solution was decanted from the colorless solid.

The ethereal solution was cooled overnight in Dry Ice. Two layers formed. The upper layer (by far the greater portion) was siphoned off and the very viscous lower layer was evacuated at the vacuum pump leaving a grey solid. The volatile material was added to the upper layer. The colorless solid referred to above and the grey solid proved to be magnesium dibromide.

The ether was then removed at the vacuum pump and many attempts were made to crystallize the residual oil, without success. Then 100 ml. of toluene was added to this oil and once again attempts to gain a crystalline substance were made, without success. Finally the material was fractionally vacuum distilled. In the first distillation 3 fractions were obtained.

Fraction 1 distilled below room temperature at 1.0 mm. This proved to be toluene.

Fraction 2 distilled at 48-160°/0.5 mm. The infrared spectra of the material was similar to that of tri-n-butylboron. This was redistilled to yield 2.8 g. (15.8%) of di-n-butylboron hydride distilling at 33-40°/1.0 mm. and 2.3 g. (12.3%) of tri-n-butylboron distilling at 60-63°/1.0 mm.

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Fraction 3 distilled at 170-205°/0.6 mm. The infrared spectrum of the material was similar to that of methyl-p-bromophenyldi-g-cresoxysilane. This liquid was redistilled to yield 8.5 g. (25.4% recovery) of methyl-p-bromophenyldi-g-cresoxysilane distilling at 194-204°/1.2 mm.

Preparation of Tri-n-butylboron.— To 67.5 g. (0.575 mole) of boron trichloride in 1 l. of ether was added 2.0 mole of n-butylmagnesium bromide in 1 l. of ether. Color Test I was weakly positive at the completion of the reaction. The whole mixture was transferred to a 3 l. flask, the ether removed and the salt cake vacuum distilled. The vacuum distillate was redistilled.

A total of 49.4 g. (47.2%) of tri-n-butylboron distilling at 58-60°/0.7 mm. was obtained.

In a second preparation 3.5 mole of n-butylmagnesium bromide was reacted with 104 g. (1.0 mole) of methyl borate. The reaction mixture was hydrolyzed by the cautious addition of water; the ether layer was siphoned and dried over sodium sulfate. The ether was removed and the residue vacuum distilled.

A total of 82.0 g. (45.1%) of tri-n-butylboron distilling at 60-62°/0.5 mm. was obtained.

Preparation of Di-n-butylboron Bromide.— This preparation was carried out as outlined by Johnson and co-workers (5). In a 100 ml. flask was placed 36.9 g. (0.20 mole) of tri-n-butylboron. To this 32.4 g. (0.20 mole) of bromine was added dropwise. The color was allowed to discharge before each new drop was added. The solution was then vacuum distilled. By a series of three vacuum distillations it was possible to obtain 27.4 g. (66.0%) of di-n-butylboron bromide distilling at 46-48°/0.5 mm. and recover 2.3 g. (6.2%) of tri-n-butylboron distilling at 65°/0.6 mm.

Anal. Calcd. for  $C_8H_{18}BBr$ : Neut. Equiv., 205. Found: Neut. Equiv., 201.

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Reaction of Di-n-butylboron Bromide with Magnesium.- In a 100 ml. flask was placed 24.3 g. (0.12 mole) of di-n-butyl-boron Bromide in 50 ml. of ether. To this was added 1.5 g. (0.06 g. atom) of magnesium turnings. Stirring was begun and after a few minutes vigorous refluxing commenced. This continued for about 1 hour. The mixture was then refluxed for an additional 30 minutes by outside heating. On cooling the ethereal solution was decanted from the colorless solid, the ether was removed by distillation, and the liquid residue vacuum distilled. Three fractions were obtained.

Fraction 1 distilled at 26-32°/0.7 mm. This was a minor forerun and was ignored.

Fraction 2 distilled at 33-37°/0.7 mm. and weighed 8.5 g. This liquid contained no ionizable bromine.

Anal. Calcd. for  $C_8H_{19}B$ : C, 76.20; H, 15.20; B, 8.60. Found: C, 56.62; H, 13.78; B, 6.79.

Anal. Calcd. for  $C_{16}H_{36}B_2$ : C, 76.85; H, 14.50; B, 8.65. Found: C, 56.62; H, 13.78; B, 6.79.

Fraction 3 distilled at 53-55°/0.77 mm. and weighed 6.2 g. (42.7%). The infrared spectra of this liquid was identical with that of tri-n-butylboron.

Anal. Calcd. for  $C_{21}H_{21}BrO_2Si$ : C, 61.10; H, 5.12, Found: C, 60.89; H, 5.10.

There was a considerable amount of charred material left in the still pot at the end of the first distillation and this may well have been the desired product decomposed by the high temperature needed in the distillation.

Preparation of Trimethylallylsilane.- In a 2 liter flask was placed 27.8 g. (1.14 g. atom) of magnesium turnings in 200 ml. of ether. Then 84.2 g. (1.10 mole) of allyl chloride in 200 ml. of ether and 109 g. (1.0 mole) of trimethylchlorosilane in 200 ml. of ether were added simultaneously, at a dropwise rate, to the reaction flask. As soon as the reaction was initiated the flask was surrounded by a large ice bath. After

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addition was completed the mixture was stirred overnight, hydrolyzed, and the ether layer dried over sodium sulfate.

After filtration the ether was removed by slow distillation through a 4" vacuum jacketed column packed with glass helicies. The fraction distilling at 80-86°/760 mm. was dried with some calcium hydride, and was redistilled to yield 56.9 g. (50%) of trimethylallylsilane; b. 86°/760 mm.,  $n_D^{24}$  1.4040; b. 84.9°/760 mm.,  $n_D^{15}$  1.4074 has been reported .

## Preparation of Trimethyl- $\delta$ -trichlorosilylpropylsilane.-

Run 1.- A solution of 17.1 g. (0.15 mole) of trimethylallylsilane and 61.0 g. (0.45 mole) of trichlorosilane was submitted to 17 hours of intense ultraviolet irradiation. A cold finger condenser charged with a Dry Ice-acetone bath was used to hold the volatile trichlorosilane in the reaction flask. Distillation of the solution yielded only starting materials.

Run 2.- The reactants were combined in the same amounts and 3.0 g. (0.013 mole) of benzoyl peroxide was added. The solution was refluxed for 66 hours and distilled. Two fractions were taken.

Fraction 1 distilled at 30-100°/760 mm; mostly starting materials.

Fraction 2 distilled at 100-200°/760 mm. This was redistilled and, after a small forerun, 15.3 g. (41.0%) of trimethyl- $\delta$ -trichlorosilylpropylsilane distilling at 158-160°/760 mm. was obtained.

Anal. Calcd. for  $C_6H_{15}Cl_3Si_2$ : C, 28.84; H, 6.06; neut. equiv., 83.23.  
Found: C, 33.03; H, 5.86; neut. equiv., 82.2.

Preparation of Triallylboron.- In a 2 liter flask was placed 53.5 g. (2.2 g. atom) magnesium turnings in 266 ml. of ether. The flask was surrounded by a large ice bath. Then 153.0 g. (2.0 mole) of allyl chloride in 266 ml. of ether was added at an extremely

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slow rate (9 hours). A heavy suspension resulted. Then 58.5 g. (0.5 mole) of boron trichloride was allowed to evaporate spontaneously into the reaction flask. The mixture was hydrolyzed and worked up in the usual manner. A total of 17.0 g. (25.4%) of triallylboron distilling at 55-58°/16 mm. was obtained.

Anal. Calcd.  $C_9H_{15}B$ : C, 80.65; H, 11.28. Found: C, 75.54; H, 10.84.

Preparation of tri-n-propylboron.- This compound was prepared as outlined for tri-n-butylboron using the hydrolysis method. In a 0.52 mole run the yield of product was 34.6 g. (52.5%) and in a 0.78 mole run, 58.0 g. (52.8%). Tri-n-propylboron distilled at 52-54°/14.0 mm; 160-162°/760 mm.

Preparation of Di-n-propylboron Bromide.- This compound was prepared as outlined for di-n-butylboron bromide. In a 0.24 mole run the yield of di-n-propylboron bromide was 13.1 g. (33.5%); b. 44°/17 mm. A recovery of 10.2 g. (30.1%) of tri-n-propylboron was made.

Anal. Calcd. for  $C_6H_{14}BBr$ : Br, 45.00; mole wt., 177.9. Found: Br, 44.00; mole wt., 181.4.

Preparation of Di-n-propylallylboron.- To 35 g. (0.187 mole) of di-n-propyl bromide in 300 ml. of ether was added 0.35 mole of allylmagnesium bromide in 500 ml. of ether. The mixture was stirred and refluxed for 3 hours. Two liquid layers formed. The top layer was siphoned off and fractionally distilled. One high boiling fraction, b. 114-117°/760 mm. was isolated. This material was spontaneously flammable on exposure to air, burning with a green flame. Total yield of di-n-propylallylboron was 13.2 g. (51.2%).



# Contrails

## NEW COMPOUNDS

### Organosilicon Compounds

TABLE I

Compound	b.	Anal.	
		Calcd.	Found
Methyl- <i>p</i> -dimethylaminophenyldichlorosilane	106-110°/0.7 mm. m. 41-42°	Cl, 30.22; N, 5.99	Cl, 29.20; N, 6.30
Methyl- <i>p</i> -dimethylaminophenyldimethoxysilane	88-90°/0.3 mm.	C, 58.75; H, 8.51	C, 58.78; H, 8.41
Methyl- <i>p</i> -bromophenyldichlorosilane	66-69°/0.3 mm.	C, 31.13; H, 2.58	C, 31.41; H, 2.73
Methyl- <i>p</i> -bromophenyldiphenoxysilane	183-185°/0.9 mm.	C, 59.23; H, 4.45	C, 57.63; H, 4.55
Methyl- <i>p</i> -bromophenyl-di- <i>o</i> -cresoxysilane	198-200°/1.0 mm.	C, 61.10; H, 5.12	C, 61.05; H, 5.10
Methyl- <i>p</i> -trimethylsilylphenyldiphenoxysilane	172°/1.0 mm.	C, 69.80; H, 6.93	C, 70.12; H, 6.12
Methyl- <i>p</i> -trimethylsilylphenyl-di- <i>o</i> -cresoxysilane	182-185°/0.6 mm.	C, 70.90; H, 7.44	C, 72.94; H, 7.03
Trimethyl-3-trichlorosilyl- <i>n</i> -propylsilane	158-160°/760 mm.	C, 28.84; H, 6.06; Neut. Equiv., 83.2	C, 33.03; H, 5.86; Neut. Equiv., 82.2
Trimethyl- <i>o</i> -cresoxysilane	37°/1.0 mm.	C, 66.60; H, 8.94	C, 66.94; H, 9.00

### Organoboron Compounds

TABLE II

Compound	b.	Anal.	
		Calcd.	Found
<i>p</i> -Bromophenyldichloroboron	68°/0.7 mm; m. 26-27°	Neut. Equiv., 118.9	Neut. Equiv., 113.9
Tri- <i>p</i> -bromophenylboron	dec. 265°		
Diethyl- <i>p</i> -bromophenylboron	55-56°/26 mm.	C, 53.49; H, 6.27	C, 47.59; H, 4.53

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## Organoboron Compounds

TABLE II  
(continued)

Compound	b.	Anal.	
		Calcd.	Found
Cyclopentamethyleneboron-chloride	109-112°/760 mm.	C, 51.60; H, 8.59; Cl, 31.33	C, 34.51; H, 7.26 Cl, 28.67
Di-n-butylboron Hydride	33-37°/0.7 mm.	C, 76.20; H, 15.20; B, 8.60	C, 56.62; H, 13.78; B, 6.79
Triallylboron	55-58°/16 mm.	C, 80.65; H, 11.28	C, 75.54; H, 10.84
Di-n-propylbromoboron	44°/17 mm.	Br, 45.00	Br, 44.00
Di-n-propylallylboron	114-117°/760 mm.		
Ethylcyclopentamethyleneboron	75-78°/760 mm.	C, 76.39; H, 13.77; B, 9.84	C, 51.47; H, 12.60; B, 5.35

## Miscellaneous Compounds

TABLE III

Compound	b.	Anal.	
		Calcd.	Found
p-Bromo- <i>o</i> -(p-bromomethylphenyl) toluene	m. 112-113°	C, 49.43; H, 3.56	C, 49.83; H, 3.72

INFRARED SPECTRA

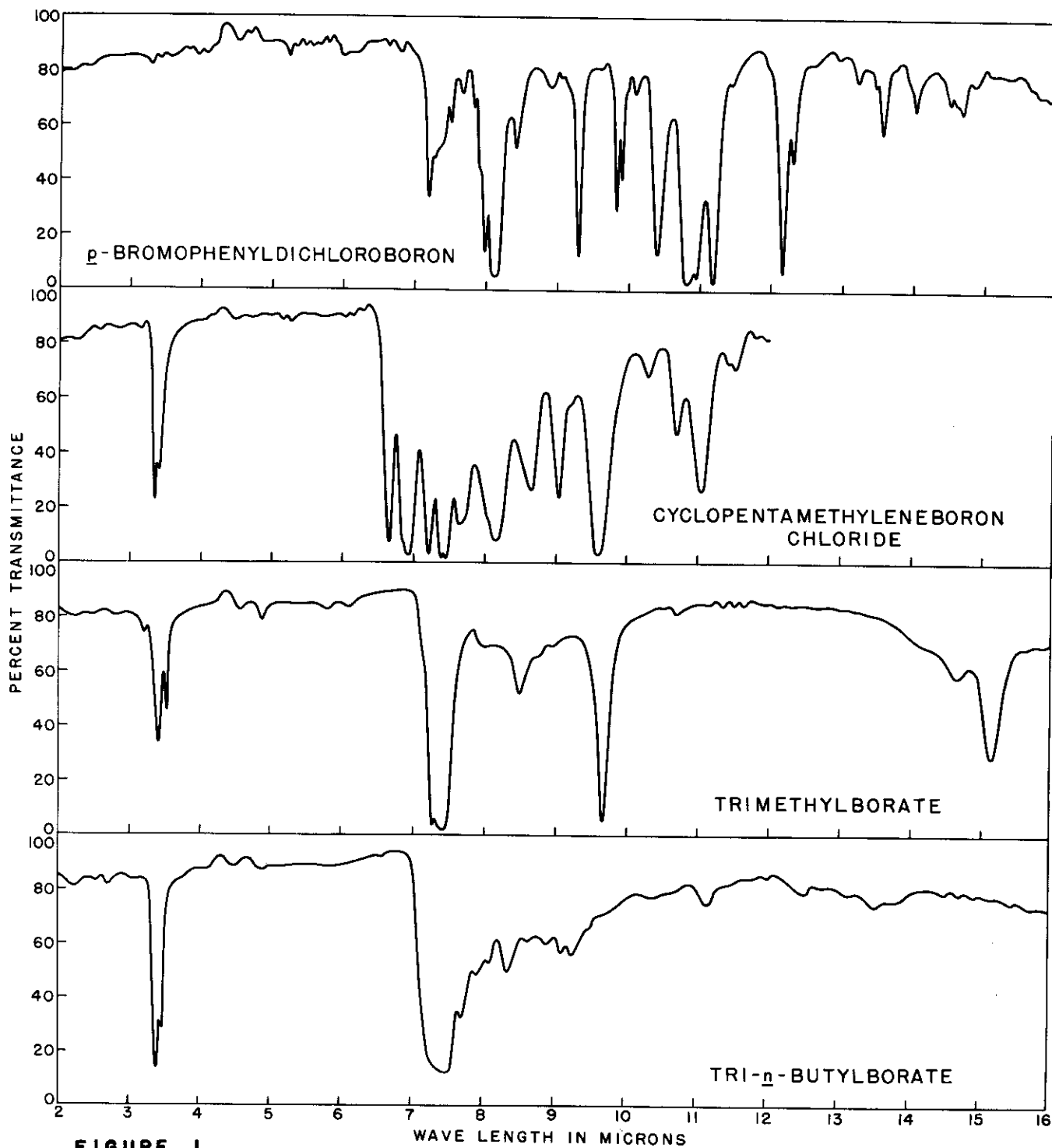


FIGURE 1

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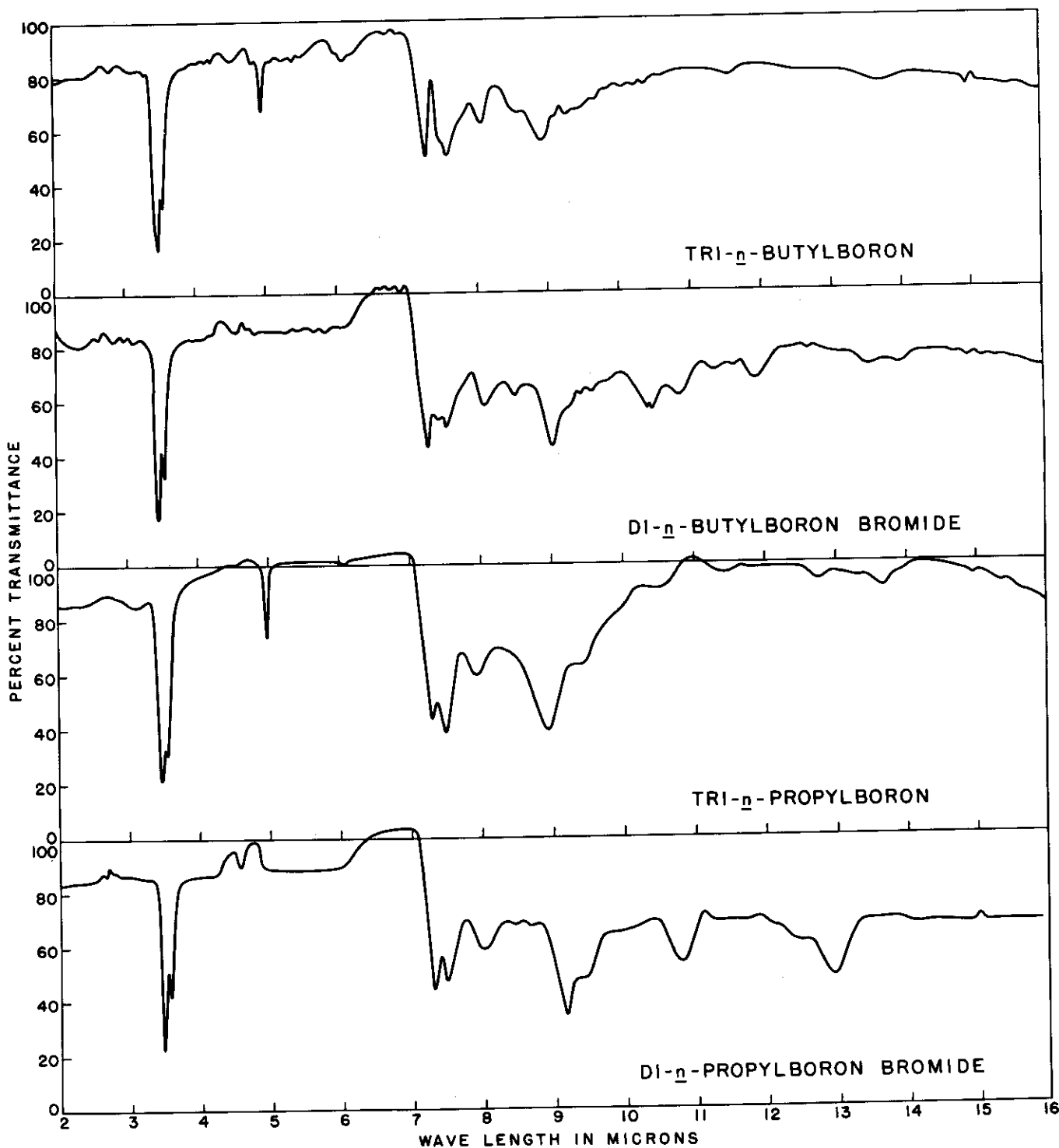


FIGURE 2

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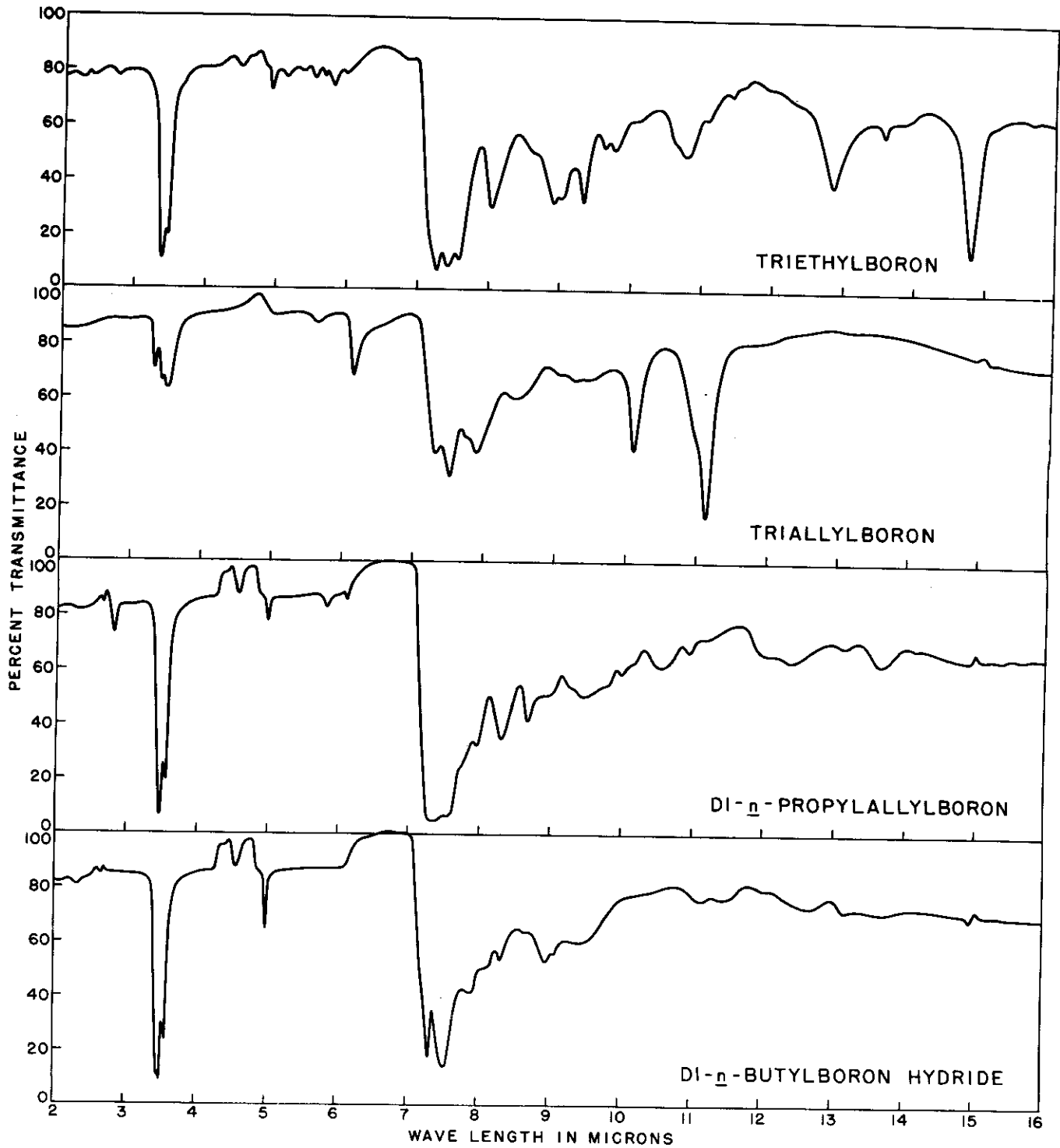


FIGURE 3

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