

ORGANIC AND BIOLOGICAL CHEMISTRY

[CONTRIBUTION FROM THE ETHYL CORPORATION]

New Syntheses of Trialkylboranes¹

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Triethylamine-borane reacts readily with such olefins as isobutylene, 1-hexene, 1-octene and cyclohexene in the absence of a solvent at 200° to produce the expected trialkylborane in yields of 77–95%. The internal olefin 2-hexene produces the isomerized product tri-*n*-hexylborane. Other amine-boranes such as pyridine-borane, trimethylamine-borane and tributylamine-borane are applicable. Trialkylboranes with alkyl groups greater than five carbon atoms undergo olefin elimination during fractional distillation at reduced pressure. The effect is increased as the length of the alkyl group increases. Triethylaluminum and ethylaluminum sesquichloride, when reacting with boric oxide at 160–200°, produced triethylborane in poor yield. When the boric oxide was treated first with triethylborane, the resulting triethylboroxine reacted with triethylaluminum at room temperature to produce triethylborane in nearly quantitative yield. Triethylaluminum and ethylaluminum sesquichloride were treated with trimethoxyboroxine at room temperature to produce triethylborane in 88–91% yield.

Introduction

In recent years there has been an increasing interest in the trialkylboranes. This class of compounds has received attention as polymerization catalysts,^{2,3} high energy fuels for military applications⁴ and chemical intermediates.⁵ Consequently, some time ago we undertook a study of convenient and economical methods for the preparation of the trialkylboranes. Two recent articles by Köster, reporting the reaction of triethylamine-borane with cyclododecatriene to produce the corresponding trialkylborane⁶ and the reaction of triethylaluminum with triethylboroxine to produce triethylborane,⁷ have prompted us to report our more detailed study of these reactions.⁸

Results and Discussion

The addition of diborane to olefins was first reported by Hurd,⁹ who described the reactions of ethylene and isobutylene with diborane in the gas phase to produce the corresponding trialkylboranes. Stone and Emeléus¹⁰ reported similar reactions with styrene, acrylonitrile and other substituted olefins. More recently Brown and SubbaRao have reported improvements in this reaction; according to these authors, diborane adds to olefins rapidly at room temperature in the presence of glycol ether solvents.

We now wish to report the reaction of amine-boranes with olefins, in the absence of solvents, to produce trialkylboranes in yields of 78–95%. This reaction is run by adding the stable liquid or solid amine-borane to the olefin at room tempera-

ture and heating the resulting solution for four hours at 200°. The product mixture is a colorless

liquid or solid. The trialkylborane is easily separated from the by-product amine by distillation.

TABLE I
REACTION OF AMINE-BORANES WITH OLEFINS

Trialkylamine-borane	Olefin	Yield of trialkylborane, %
BH ₃ NEt ₃	Isobutylene	80.0
BH ₃ NEt ₃	1-Hexene	91.3
BH ₃ NEt ₃	2-Hexene	94.7 ^a
BH ₃ NEt ₃	Cyclohexene	77.6
BH ₃ NEt ₃	1-Octene	85.4
BH ₃ NBu ₃	1-Octene	82.5
BH ₃ Py	1-Hexene	87.3
BH ₃ NMe ₃	1-Octene	92.7

^a Tri-*n*-hexylborane produced.

This route to the trialkylboranes is convenient due to the fact that the amine-boranes are readily available and no solvent is required as in the conventional diborane reaction.⁵ Manipulation is simple since the amine-boranes used in this study are neither pyrophoric nor sensitive to air or moisture.

The temperature and time of reaction were arbitrarily chosen at 200° and four hours. In all cases tested this proved to be sufficient for complete reaction. It was found later that the minimum temperature and time required are considerably less. In one experiment triethylamine-borane was treated with 1-octene under the conditions of atmospheric pressure reflux. The progress of the reaction was followed by the disappearance of the infrared absorption bands characteristic of the carbon-carbon double bond vibration and the boron-hydrogen stretching vibration. After a reflux period of 5 minutes (pot temperature 124°, vapor temperature 95°) the reaction mixture was sampled. Infrared analysis showed the reaction to be 93% complete. After an additional 55 minutes of refluxing the reaction was 100% complete. In another experiment triethylamine-borane was treated with 1-hexene at atmospheric pressure reflux. After a 5-minute reflux period (pot temperature 69.5°, vapor temperature 64.5°) a sample

(1) Presented at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

(2) J. Furukawa, T. Tsuruta and S. Inoue, *J. Polymer Sci.*, **113**, 234 (1957).

(3) G. S. Kolensnikov and N. V. Klimentova, *Izvest. Akad. Nauk, S.S.S.R., Otdel. Khim. Nauk*, 652 (1957).

(4) R. A. Carpenter, *Ind. Eng. Chem.*, **49**, No. 4, 42A (1957).

(5) H. C. Brown and B. C. SubbaRao, *J. Org. Chem.*, **22**, 1136 (1957).

(6) R. Köster, *Angew. Chem.*, **69**, 684 (1957).

(7) R. Köster, *ibid.*, **70**, 371 (1958).

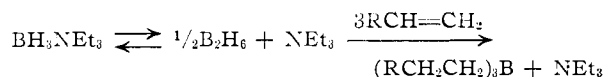
(8) Shortly after this paper was submitted for presentation at the 135th Meeting of the American Chemical Society in Boston, work related to the amine-borane reactions reported here also was reported by M. F. Hawthorne, *J. Org. Chem.*, **23**, 1788 (1958). The amine-boranes and procedures employed are substantially different, however.

(9) D. T. Hurd, *THIS JOURNAL*, **70**, 2053 (1948).

(10) F. G. A. Stone and H. J. Emeléus, *J. Chem. Soc.*, 2755 (1950).

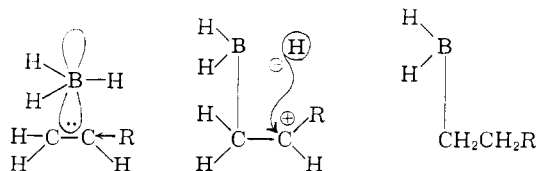
of the reaction mixture was taken. Infrared analysis showed that the reaction had not proceeded to any measurable degree. Over a 22-hour reflux period the pot temperature rose slowly to 102.0° and the vapor temperature to 79.0°. Infrared analysis then showed the reaction to be 85% complete. Hence with 1-octene (pot temperature 124°) the reaction was 93% complete after only 5 minutes whereas with 1-hexene (initial pot temperature 69.5°) the reaction was only 85% complete in 22 hours.

The above data provide some insight as to the probable mechanism of the reaction of amine-boranes with olefins. It seems logical that the p-orbital of the boron atom in the amine-boranes is relatively unavailable for interaction with the π -electrons of the carbon-carbon double bond in the olefin as compared to the p-orbital of the boron atom in diborane. Hence, it is suggested that a sufficiently high temperature must be employed to effect partial dissociation of the boron-nitrogen bond in the amine-boranes. Boron-hydrogen additions *via* boron p-orbital interaction with the π -electrons then can take place. The sequence of proposed reactions is



The large increase in the rate of reaction from a temperature of 69–102° to a temperature of 124° supports this mechanism since an increased boron-nitrogen dissociation would be expected with an increase in temperature. Since diborane reacts rapidly with olefins in solution at room temperature, the dissociation of the amine-borane is probably the rate-determining step.

Since diborane can be dissociated into BH_3 units by means of weak bases such as dialkyl sulfides and tetrahydrofuran, it is postulated that an olefin, which also may be considered a weak base by virtue of its available π -electrons, may also dissociate diborane into BH_3 units. The mechanism may then be more exactly described by the steps



The above mechanism is based on the available qualitative data. A kinetic study of the reaction of amine-boranes with olefins should reveal whether or not this reaction is first order, supporting the amine-borane dissociation mechanism, or second order, supporting the alternative mechanism based on direct addition of the amine-borane to the olefin.

It is interesting to note that the reaction of triethylamine-borane with 2-hexene produced *n*-hexylborane, as did the reaction of triethylamine-borane with 1-hexene. This is in accord with the isomerization of secondary and tertiary

alkylboranes to the corresponding primary alkylboranes, in the absence of a coordinating solvent, as first reported by McCusker and co-workers.¹¹

During the study of the reactions of amine-boranes with 1-octene to produce trioctylborane, it was discovered that this trialkylborane, when subjected to fractional distillation under vacuum in a packed column, eliminated one alkyl group as the olefin and was isolated as the tetraalkyldiborane. The reaction of triethylamine-borane with 1-octene did indeed produce trioctylborane as evidenced by the infrared spectrum and boron analysis of the product before distillation. When this compound was distilled at 169° at 0.2 mm., *trans*-2-octene was collected in the cold trap and tetraoctyldiborane was produced. The infrared spectrum of this compound contained a strong absorption band at 6.38 μ , which has been designated as the boron-hydrogen bridge absorption, characteristic of tetraalkyldiboranes.¹² When trioctylborane was subjected to rapid simple distillation (b.p. 141–146° at 0.03 mm.) infrared and boron analyses showed that the distillate was a 50/50 mixture of trioctylborane and tetraoctyldiborane. In neither the product from fractional distillation nor that from flash distillation was any absorption observed in the infrared region at 4.0 μ characteristic of dialkyldiboranes. An examination of the infrared spectra of other trialkylboranes that had been distilled through a packed column under vacuum revealed that this effect did not become significant until the number of carbon atoms in the alkyl group was greater than five. Triethylborane and tributylborane exhibited no absorption band at 6.38 μ when distilled under vacuum below 100°. Trihexylborane, distilled at 133° at 1.8 mm., showed a weak band at 6.38 μ which indicated some tetrahexyldiborane present. A boron analysis of this compound indicated approximately 40% of tetrahexyldiborane. The first observance of a similar effect was recorded by Rosenblum.¹³ He observed that tributylborane, when subjected to a temperature of 125–130° at 10 mm. for 10 days, produced some *trans*-2-butene and dibutyldiborane.

The oldest method for the preparation of trialkylboranes is by the reaction of an organometallic alkylating agent with a boron salt. Frankland and Duppa¹⁴ originally prepared trialkylboranes by the reaction of dialkylzinc compounds with boron trichloride. However, more recent investigators,^{15,16} have found it more convenient to use Grignard reagents as the alkylating agent. Recently, a more economical and convenient source of alkyl groups has become available commercially. This source is the trialkylaluminum compounds and the alkylaluminum sesquihalides. Several trialkylaluminum compounds are readily available from aluminum, hydrogen and olefins, and several

(11) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *This Journal*, **79**, 5190 (1957).

(12) I. Shapiro, C. O. Wilson and W. J. Lehmann, *J. Chem. Phys.*, **29**, 237 (1958).

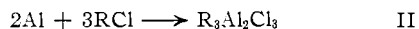
(13) I. Rosenblum, *This Journal*, **77**, 5016 (1955).

(14) E. Frankland and D. F. Duppa, *Ann. chim. phys.*, **60**, 371 (1860).

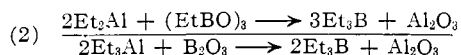
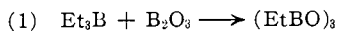
(15) E. Krause and R. Nitsche, *Ber.*, **55**, 1261 (1922).

(16) P. A. McCusker and L. J. Glunz, *This Journal*, **73**, 2674 (1951).

of the alkylaluminum sesquihalides are readily available from aluminum and the alkyl halides.



Gilman¹⁷ has reported the reaction of ethylaluminum sesquichloride with methyl borate to produce triethylborane in good yield. This reaction has been used to prepare triethylborane commercially. Since boric oxide is a more economical and convenient source of boron, the reaction of triethylaluminum and ethylaluminum sesquichloride with boric oxide was explored. Under apparently optimum conditions of 160–200°, high speed stirring in a creased flask, and the use of a special grade of active boric oxide, only a small yield of triethylborane was realized. In two separate experiments triethylborane and aluminum chloride were used as catalysts, and in a third experiment these two were combined. However, only a small increase in yield was realized. The steps envisioned in the triethylborane catalysis are

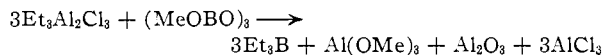
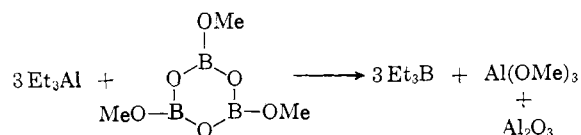


The fact that triethylborane does not catalyze this reaction indicates that step 1 is very slow compared to step 2. This fact has since been definitely established. Also it is believed that the aluminum oxide formed in the reaction coats the surface of the already insoluble boric oxide and hence retards the reaction.

The failure of boric oxide to react appreciably with triethylaluminum was overcome by transforming the boric oxide into a soluble form. The boric oxide was treated first with triethylborane to produce triethylboroxine, a stable liquid. The triethylboroxine then was treated with triethylaluminum to produce triethylborane in the reaction sequence shown in steps 1 and 2. The reaction between triethylborane and boric oxide, first reported by McCusker and co-workers,¹⁸ was slow and necessitated a reflux period of 48 to 96 hours for complete reaction. However, by carrying out the reaction in an autoclave at 200°, a satisfactory reaction rate was achieved and triethylboroxine was produced in over 90% yield in less than 24 hours. It was not necessary to distill the triethylboroxine before it was treated with triethylaluminum in the second step. This reaction took place rapidly at room temperature and was nearly quantitative. No solvent or diluent was required in either step of this process. The triethylborane product was separated from the aluminum oxide by distillation from the reaction flask, leaving behind the aluminum oxide as a colorless, dry, free-flowing powder. In this process one begins with one mole of triethylborane and produces three moles, necessitating the recycle of one-third of the product.

The alkylation of trimethoxyboroxine was studied by allowing this compound to react separately

with triethylaluminum and ethylaluminum sesquichloride.



In these reactions mineral oil was used as a solvent and the reactions were run at room temperature. The reactions are rapid and nearly quantitative. The triethylborane was isolated by distillation from the reaction vessel, leaving behind a slurry of aluminum salts. This approach to the trialkylboranes has the advantage of introducing two-thirds of the boron as boric oxide without product recycle as in the case of the triethylboroxine route. Trimethoxyboroxine is a stable liquid below 100°, and is prepared by heating equimolar quantities of methyl borate and boric oxide.¹⁹ This reaction requires no solvent and is quantitative, eliminating the necessity of purification before further reaction. Trimethoxyboroxine and other alkoxyboroxines are readily available compounds.

For the preparation of large laboratory quantities of trialkylboranes, the reaction of trialkylaluminum compounds with trimethoxyboroxine is suggested for those compounds where the corresponding aluminum compound is readily available. At the present time, this includes trimethyl-, triethyl- and triisobutylaluminum. For all other trialkylboranes, the reactions of amine-boranes with the corresponding olefins are suggested.

Acknowledgment.—The author wishes to thank Dr. W. E. Foster for helpful suggestions concerning this manuscript and Mr. R. L. Seab for assistance in conducting these experiments. Dr. R. P. Curry conducted and interpreted the infrared analyses and Mr. W. J. Easley conducted the elemental analyses.

Experimental

All manipulations of the trialkylboranes, triethylaluminum, ethylaluminum sesquichloride, trimethoxyboroxine, triethylboroxine, boric oxide and the amine-boranes were performed in a nitrogen-filled dry-box. All equipment used in these experiments, when assembled, was flash flamed and allowed to cool under a nitrogen atmosphere.

Olefins.—All olefins were obtained from Eastman Organic Chemicals and were dried over sodium wire and used without any further purification.

Triethylamine-borane was prepared in 100-ml. quantities by the reaction of triethylborane with triethylamine at 200° and 200 atm. of hydrogen according to the procedure reported by Ziegler²⁰ and Köster.²¹ The product was distilled through a 60-cm. glass helix packed column at 97.0° at 12 mm. pressure. The infrared spectrum of this compound was identical to the spectrum of the product formed from diborane and triethylamine.

Tributylamine-borane was prepared from triethylborane, tributylamine and hydrogen by the same procedure described above for the preparation of triethylamine-borane. The compound boiled at 103–105° at 0.1 mm.

Anal. Calcd. for C₁₂H₃₀NB: B, 5.53; N, 7.04. Found: B, 5.49; N, 7.16.

(19) M. F. Lappert, *J. Chem. Soc.*, 2790 (1958).

(20) Belgian Pat. 558,170.

(21) R. Köster, *Angew. Chem.*, **69**, 94 (1957).

(17) H. Gilman, PB Report 5596, OSRD No. 871, 1942.

(18) G. F. Hennion, P. A. McCusker, E. C. Ashby and A. J. Rutkowski, *This Journal*, **79**, 5194 (1957).

Trimethylamine-borane and pyridine-borane were obtained from the Callery Chemical Co.

Triisobutylborane.—Twenty-three grams (0.2 mole) of triethylamine-borane was added to 33.6 g. (0.6 mole) of isobutylene in a 100-ml. Magne-Dash autoclave equipped with a magnetic plunger type stirrer. The resulting solution was heated to 200° for four hours. The contents of the bomb were distilled under vacuum, the main fraction boiling at 68° at 7 mm. The infrared spectrum of this product was found to be identical to the infrared spectrum of triisobutylborane prepared from isobutylmagnesium chloride and boron trichloride. The yield was 29.0 g. or 80% of the theoretical.

Tri-*n*-hexylborane. A. From Triethylamine-borane.—Twenty-five milliliters (0.17 mole) of triethylamine-borane was added to 100 ml. (0.70 mole) of 1-hexene in a 250-ml. Magne-Dash autoclave. The resulting solution was heated to 200° for four hours. The contents of the autoclave were distilled under vacuum, the main fraction boiling at 133° at 1.8 mm. The infrared spectrum of the distilled product was found to be identical to the spectrum of tri-*n*-hexylborane prepared from *n*-hexylmagnesium chloride and boron trichloride. An absorption band was present at 6.38 μ which is characteristic of the B-H bridge absorption in the tetraalkyldiboranes. The boron analysis of this compound indicated about 40% tetrahexyldiborane. Infrared analysis of the product mixture before distillation did not show a band at 6.38 μ . The yield of trihexylborane based on the undistilled product was 41.2 g. or 91.3% of the theoretical. The distilled product was analyzed.

Anal. Calcd. for C₁₈H₃₉B: B, 4.13. Found: B, 4.90. Calcd. for C₁₂H₂₇B: B, 6.04.

This reaction was repeated at atmospheric pressure at the reflux temperature of the mixture. The initial pot temperature of 69.5° and vapor temperature of 64.5° rose slowly over a 22-hour period to 102.0° and 79°, respectively. At the end of this time the reaction had proceeded to 85% completion as determined by the disappearance of the B-H stretch band (4.2 μ) and C=C band (6.07 μ) in the infrared region.

B. From Pyridine-borane.—Pyridine-borane was treated with 1-hexene in the same manner as described in A. The infrared spectrum of the distilled product was identical to that of the distilled product reported in A. The yield of trihexylborane, based on the undistilled product, was 87.3%.

Reaction of Triethylamine-borane with 2-Hexene.—Triethylamine-borane and 2-hexene were combined in the same quantities as reported above for the reaction of 1-hexene with triethylamine-borane. The reaction was run at 200° for four hours. The contents of the autoclave were distilled at 133° at 1.8 mm. The infrared spectrum of the distilled product was identical to the spectrum of the distilled product obtained from the reaction of 1-hexene with triethylamine-borane. The yield based on undistilled product was 42.7 g. or 94.7% of the theoretical.

Trioctylborane. A. At Atmospheric Pressure.—Twenty-five milliliters (0.17 mole) of triethylamine-borane was added to 57 g. (0.51 mole) of 1-octene. The pot temperature and vapor temperature registered 124 and 95°, respectively, after the solution was refluxed for five minutes. A sample of the mixture taken at this point showed that the reaction was 93% complete. This was determined by the disappearance of the B-H stretch band (4.2 μ) and C=C band (6.07 μ) in the infrared region. After one hour of reflux the reaction was shown by infrared analysis to be 100% complete. The by-product triethylamine was removed under vacuum at room temperature. Infrared analysis and boron analysis of the undistilled product showed the compound to be trioctylborane. The product then was fractionated through a 60-cm. glass helix packed column at 169° at 0.2 mm. The infrared spectrum of the distillate showed a strong band at 6.38 μ which is characteristic of the B-H bridge absorption. This band was not present before distillation. The distillation showed no infrared absorption at 4.0 μ characteristic of the B-H stretching frequency in dialkyldiboranes. Boron analysis of the fractionated product showed this compound to be tetraoctyldiborane. During the distillation *trans*-2-octene was collected in the cold trap and identified by infrared analysis. Yield of trioctylborane, prior to distillation and containing no tetraoctyldiborane, was 85.4%.

Anal. Calcd. for C₂₄H₅₁B: B, 3.14. Found: B, 3.27. Calcd. for C₁₆H₃₅B: B, 4.62. Found: B, 4.64.

A flash distillation of trioctylborane having no absorption band at 6.38 μ was performed at 141–146° at 0.03 mm. The resulting product contained approximately a 50/50 mixture of trioctylborane and tetraoctyldiborane as evidenced by infrared and boron analysis.

Anal. Calcd. for C₂₄H₅₁B: B, 3.14. Found: B, 3.90. Calcd. for C₁₆H₃₅B: B, 4.62.

B. Under Pressure.—Triethylamine-borane and 1-octene were allowed to react in a Magne-Dash autoclave in the same quantities reported in A for the reaction at atmospheric pressure. The infrared spectrum and boron analysis before and after distillation were identical with the data reported in A for the reaction at atmospheric pressure.

C. From Trimethylamine-borane.—Trimethylamine-borane was treated with 1-octene in the same stoichiometric ratio and under the same conditions as reported in B. The yield was 92.7%.

D. From Tributylamine-borane.—Tributylamine-borane and 1-octene were treated in the same stoichiometric ratio and under the same conditions as reported in B. The yield of trioctylborane was 82.5%.

Tricyclohexylborane.—Twenty-five milliliters (0.17 mole) of triethylamine-borane was added to 51.5 ml. (0.51 mole) of cyclohexene in a 100-ml. Magne-Dash autoclave. The resulting solution was heated at 200° for four hours. The product mixture was distilled under vacuum through a packed column. The main fraction boiled at 135–147° at 1.5 to 2.5 mm. The infrared spectrum of this product was identical to the spectrum of the product produced from the reaction of cyclohexylmagnesium bromide with boron trichloride. No B-H bridge band at 6.38 μ was observed in the spectrum of this product. The yield of white solid was 35.0 g. or 77.6% of the theoretical.

Triethylaluminum.—The triethylaluminum used in this study was a pilot plant product prepared by the Ethyl Corporation and was shown to have a purity of 97% based on aluminum analysis and gas evolution.

Ethylaluminum sesquichloride was a pilot plant product prepared by the Ethyl Corporation and was a colorless liquid. Analysis showed the empirical formula to be Et_{1.75}AlCl_{1.25}.

Trimethoxyboroxine.—The trimethoxyboroxine used in this study was obtained from the American Potash and Chemical Corporation. This compound is a clear viscous liquid and was used without any further purification.

Boric oxide was prepared by the slow thermal dehydration of boric acid as described by Lang.²²

Reaction of Triethylaluminum with Boric Oxide.—One hundred and fourteen grams (1.0 mole) of triethylaluminum was added to 17.5 g. (0.25 mole) of boric oxide. With high speed stirring in a creased flask, the contents were heated by means of an oil-bath to 160° for 6 hours. During this time approximately 2 g. (0.02 mole) of triethylborane was distilled from the reaction flask. The yield was 2% based on triethylaluminum.

Reaction of Triethylaluminum with Boric Oxide in the Presence of Catalysts.—Triethylaluminum and boric oxide were allowed to react in the same quantities and under the identical conditions described above with the exception that 5 g. (0.05 mole) of triethylborane was used as a catalyst in one case and 1 g. (0.008 mole) of aluminum chloride was used as a catalyst in a second case. When triethylborane was used as a catalyst, the reaction was run for four hours at 110° before the temperature was raised to 160°. In both cases the use of a catalyst failed to increase the yield of triethylborane by more than 2%.

Reaction of Ethylaluminum Sesquichloride with Boric Oxide.—Ethylaluminum sesquichloride and boric oxide were treated in exactly the same manner and mole ratio as reported above for the reaction of triethylaluminum with boric oxide. After a 6-hour reaction period at 160° with high speed stirring, a 3.5% yield of triethylborane was realized.

Triethylboroxine. A. At Atmospheric Pressure.—Ninety-eight grams (1.0 mole) of triethylborane was added to 70 g. (1.0 mole) of boric oxide. The contents of the flask were refluxed for four days until the boric oxide went into solution, indicating that the reaction had taken place. The contents of the flask were then distilled through a packed column at 148–152°, producing 146 g. of triethylboroxine,

(22) W. Lang in "Inorganic Syntheses," Vol. II, edited by W. C. Fernelius, McGraw-Hill Book Co., Inc., New York, N. Y., 1946, p. 22.

or 87% yield. A forerun of 10–15 ml., collected between 110 and 148°, was not identified.

B. Under Pressure.—Forty-nine grams (0.5 mole) of triethylborane was added to 35 g. (0.5 mole) of boric oxide in a 100-ml. Magne-Dash autoclave. The mixture was heated for 20 hours at 220° with agitation. The reaction product was distilled through a packed column at 149–151°, producing 78 g. of triethylboroxine or a 95.0% yield. The infrared spectra of the products from A and B were identical to the infrared spectrum of triethylboroxine prepared by the dehydration of ethylboronic acid.

Triethylborane from Triethylaluminum and Triethylboroxine.—To 33.6 g. (0.2 mole) of triethylboroxine was added 45.6 g. (0.4 mole) of triethylaluminum. The addition was performed dropwise with high speed stirring. The addition took one hour due to the exothermic nature of the reaction. When allowed to cool, the reaction mixture set up as a gel. The triethylborane was distilled from the reaction flask after replacing the condenser with a distilling head and receiver. The product boiled at 94–95° and weighed 56.2 g., representing a 95.6% yield. The product was determined by gas chromatography to be at least 99.3% pure. The residual aluminum oxide remaining after distillation did not fume in air and was removed easily from the flask as a free-flowing white powder.

Triethylborane from Triethylaluminum and Trimethoxyboroxine.—To 84 ml. (0.6 mole) of triethylaluminum dissolved in 100 ml. of mineral oil was added, slowly with efficient stirring, 29 ml. (0.2 mole) of trimethoxyboroxine. One hour was again required for the addition due to the large heat of reaction. The product was distilled from the reaction mass at 94–95° and weighed 49.0 g., representing an 88% yield. The infrared spectrum of the product was identical to that in the Sadtler index for triethylborane. The resulting aluminum oxide–aluminum methoxide by-product formed a white, viscous slurry in the mineral oil diluent.

Triethylborane from Ethylaluminum Sesquichloride and Trimethoxyboroxine.—To 160 g. (0.65 mole) of ethylaluminum sesquichloride dissolved in 150 ml. of mineral oil was added slowly 29 ml. (0.2 mole) of trimethoxyboroxine in exactly the same manner as described for the reaction of triethylaluminum with trimethoxyboroxine. The product was distilled from the reaction flask at 94–95° and weighed 52.0 g., representing a 91.2% yield. The infrared spectrum of the product was identical to that in the Sadtler index for triethylborane.

BATON ROUGE, LA.

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Copper Phthalocyanine Polymers¹

BY WILLIAM C. DRINKARD AND JOHN C. BAILAR, JR.

RECEIVED MARCH 9, 1959

Polymeric copper phthalocyanines have been produced by the reaction of pyromellitic dianhydride, copper(II) chloride, urea and catalyst at 180°. Molecular weights and equivalent weights have been determined by elemental analysis and by potentiometric titration and the shapes of the molecules have been determined. Average molecular weights as high as 4000 have been identified.

Introduction

The high thermal stability of copper phthalocyanine makes it an interesting unit for the formation of polymers. Since it is proposed that a large measure of stability is gained through the resonance energy, it would be desirable to preserve and if possible enhance the resonance feature. Several studies of polymeric phthalocyanines have been made^{2–6} but only that of Marvel and Martin has led to high molecular weight substances.

The investigation reported here involves the formation of polymers by substitution of pyromellitic dianhydride for phthalic anhydride in the conventional phthalocyanine synthesis. The size of the polymer thus obtained has been investigated and the effect of reaction conditions on polymer growth has been studied. Since growth of the

polymer may produce sheet-like or linear arrangements, the shape of the polymer molecules has been determined.

Experimental Results

Polymeric copper phthalocyanine has been prepared by heating a mixture of pyromellitic dianhydride, copper(II) chloride, urea and catalyst. The reaction proceeds smoothly at 180° in a manner analogous to the monomeric copper phthalocyanine synthesis.⁷ The molecular weight may be varied within limits by suitable control of the reaction conditions.

It is important to note that pyromellitic dianhydride may produce sheet-like polymers, chains, or a mixture of both. The fact that elemental analysis and equivalent weights change rapidly at low molecular weights with a change in number and arrangement of the copper phthalocyanine units makes it possible to determine whether the polymers are linear, as illustrated by the trimer shown in Fig. 1, or sheet-like as illustrated in Fig. 2. No evidence for the sheet-like arrangement has been found.

Molecular Weight by Elemental Analysis.—Because the growth of a polymeric copper phthalocyanine changes the carbon to nitrogen ratio, it is possible to estimate the size of low molecular weight molecules by carbon, hydrogen and nitrogen analyses. Table I gives the relationship of structure to analysis. It may be seen that such a system works best for polymers of low molecular weight and that

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(2) (a) Swiss Patent 263,655 (1949); (b) U. S. Patent 2,492,732 (1949).

(3) Sprague Electric Co., Final Report under Contract No. DA-36-039-SC-87 to the U. S. Army Signal Corps, May 14–Oct. 15, 1952.

(4) E. A. Lawton and D. D. McRitchie, WADC Technical Report 57-642, November, 1957.

(5) C. S. Marvel and J. H. Rassweiler, *THIS JOURNAL*, **80**, 1196 (1958).

(6) C. S. Marvel and M. M. Martin, *ibid.*, in press.

(7) F. H. Moser, U. S. Patent 2,549,842, April 24, 1951.