boron in the chains. Characterization[23] of the phase as a solid solution of carbon in boron is consistent with the experimental absence[24] of extrema in physical properties at any stoichiometric composition throughout the entire range. (Although it is not a system in which one imagines that complete thermodynamic equilibrium, involving the reconstitution and sorting of chains, will be readily attained.)

Acknowledgments.—We wish to thank Dr. H. A. Weakliem, Jr., for expert aid in carrying out some of the computations and the Cornell Computing Center for allowing us the necessary time on IBM equipment.

ITHACA, NEW YORK

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF FLORIDA]

The Chemistry of Borazene. I. The Reaction of B-Trichloro-N-trimethylborazene with Grignard Reagents[1]

BY G. E. RYSCHKEWITSCH, J. J. HARRIS AND HARRY H. SISLER

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B-Trichloro-N-trimethylborazene reacts smoothly with Grignard reagents to give B-alkyl derivatives. B-Triethyl-N-trimethyl-, B-triallyl-N-trimethyl- and B-tri-(*n*-butyl)-N-trimethylborazene were prepared. B-Di-(*n*-butyl)-B-chloro- and B-*n*-butyl-B-dichloro-N-trimethylborazene were prepared using a deficiency of Grignard reagents.

Introduction

General methods for the preparation of B-alkyl substituted borazenes previously published involve vacuum techniques[2-4] or the use of relatively inaccessible intermediates.[5]

None of these methods is especially attractive for the synthesis of borazene derivatives containing different substituents on boron atoms in the same molecule. Redistribution reactions between substituted boranes and a borazene seem to be unsatisfactory in general, since unsymmetrical borazenes prepared from substituents that are readily redistributed in boranes may be expected to be susceptible to redistribution here, too. Another conceivable method for the preparation of unsymmetrically B-substituted borazenes could start with the desired boron substitution before the ring is formed. If, *e.g.*, a B-alkyl-B-chloroborazene is desired, this would necessitate treating a mixture of $RBCl_2$ and BCl_3 with an amine and pyrolyzing the resulting mixture of addition compounds. Since several reaction steps are involved before the borazene ring is formed in which the difference in boron substitution may exert a strong electronic or steric influence, it is highly questionable whether or not reasonable yields of the desired product can be obtained by this method.

The work reported here gives a simple synthetic method for the synthesis of B-trialkyl, B-dialkyl-B-monochloro and B-alkyl-B-dichloroborazenes from readily available starting materials through the reaction of B-trichloro-N-trimethylborazene with Grignard reagents.[6] The reaction should prove to be of general applicability in view of the similar reactivity of the boron–halogen bond in different N-substituted borazenes and the reactivity of boron halides toward a variety of Grignard reagents.

Experimental

B-Trichloro-N-trimethylborazene, $B_3Cl_3N_3(CH_3)_3$.—B-Trichloro-N-trimethylborazene was prepared from boron trichloride and methylamine hydrochloride in refluxing chlorobenzene by a slight modification of the method of Brown and Laubengayer.[7] Using a few per cent. excess boron trichloride and extending the reaction time till no more HCl was produced gave practically quantitative yields of pure product.

B-Triethyl-N-trimethylborazene, $B_3(C_2H_5)_3N_3(CH_3)_3$.—Into a 250-ml. two-neck round-bottom flask were placed 75 ml. of anhydrous ethyl ether, 9.0 g. (0.37 mole) of magnesium turnings and 25 g. (0.11 mole) of B-trichloro-N-trimethylborazene. The flask was fitted on one neck with a reflux condenser and Dry Ice cold-finger condenser in series and a dropping funnel in the other neck. The whole system was vented to the atmosphere through a Drierite tube. Forty grams (0.36 mole) of ethyl bromide slowly was added (1 to 2 hr.) through the dropping funnel to the magnetically stirred reaction mixture after adding a crystal of iodine to start the Grignard reaction. An exothermic reaction with precipitation of magnesium halide resulted. After all the alkyl bromide had been added, the reaction mixture was refluxed for another 3 to 4 hr.

The solid precipitate and any unreacted magnesium was removed by filtration through a fritted glass filter in the drybox and washed several times with dry ethyl ether. Filtrate and washings were combined and distilled, first at atmospheric pressure and then under vacuum to remove all traces of solvent. There remained a light yellow liquid. On fractionation of the crude product under reduced pressure, there was obtained 15 g. of a colorless liquid with the following physical constants: b.p. 82° (0.65 mm.), 98° (1.8 mm.), $n^{22.5}_{\mathrm{D}}$ 1.4791, f.p. 1–2°. The yield was 66% of theoretical. *Anal.* Calcd. for $B_3(C_2H_5)_3N_3(CH_3)_3$: B, 15.70; N, 20.33; Cl, 0.00. Found: B, 15.86; N, 19.45; Cl, 0.6.

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(1) Presented at the 132nd Meeting of the American Chemical Society, New York, N. Y., September 9, 1957. The names borazole and borazine have been used also for the compound $B_3N_3H_6$.

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(6) S. J. Groszos and S. F. Stafiej, Abstracts of Papers, 131st Meeting, American Chemical Society, Miami, Florida, April 1957, 53-O, report the preparation of B-trialkyl derivatives of N-triphenyl borazene through the use of Grignard reagents.

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The infrared spectrum of the compound in CCl_4 showed strong absorption bands at the following wave lengths: 3.41, 6.82, 7.12, 7.28, 7.57, 8.17, 9.09, 9.66, 9.91, 10.26 and 10.76 μ. When a solution of B-trichloro-N-trimethylborazene was added rapidly to a solution of ethylmagnesium bromide, the triethyl derivative was not obtained.

B-Tri-*n*-butyl-N-trimethylborazene, $B_3(n\text{-}C_4H_9)_3N_3(CH_3)_3$.—22.3 g. (0.0987 mole) of B-trichloro-N-trimethylborazene, 7.2 g. (0.30 mole) of Mg and 40.6 g. (0.296 mole) of *n*-butyl bromide reacted and worked up as above; 21.2 g. of a colorless liquid was obtained after fractionation at reduced pressure, b.p. 140° (1.1 mm.), $n^{22.5}D$ 1.4759, f.p. −18° to −17°. The yield was 74% of theoretical. *Anal.* Calcd. for $B_3(n\text{-}C_4H_9)_3N_3(CH_3)_3$: B, 11.16; N, 14.45; Cl, 0.00. Found: B, 10.92; N, 13.73; Cl, 0.0.

The infrared spectrum of the compound in CCl_4 showed strong absorption bands at the following wave lengths: 3.42, 6.85, 7.14, 7.26, 7.37, 7.47, 9.10, 9.23 and 9.54 μ.

B-Triallyl-N-trimethylborazene, $B_3(CH_2CHCH_2)_3N_3(CH_3)_3$.—Allylmagnesium bromide was prepared from 60 g. (0.50 mole) of allyl bromide and 14.6 g. (0.58 mole) of magnesium in 125 ml. of anhydrous ethyl ether by direct reaction of the halide with magnesium. Thirty g. (0.133 mole) of B-trichloro-N-trimethylborazene and 100 ml. of anhydrous ether were placed into a 500-ml. two-neck round bottom flask equipped with reflux condensers and dropping funnel as before. The Grignard reagent was added in small portions to the chloroborazene with magnetic stirring over a period of about 30 minutes. After complete addition, reflux of the ether was maintained for 10 hr. The precipitated magnesium salts were filtered off as before and the solvent ether removed from the filtrate by vacuum distillation. On fractionation, somewhat more than 16 g. of a clear colorless liquid was obtained; b.p. 110–112° (1.3 mm.), $n^{22.5}D$ 1.5047, f.p. −37° to −39°. *Anal.* Calcd. for $B_3(C_3H_5)_3N_3(CH_3)_3$: B, 13.37; N, 17.31; Cl, 0.00. Found: B, 13.32; N, 16.66; Cl, 0.00. The infrared spectrum of the compound showed strong absorption bands at the following wave lengths: 3.28, 3.44, 3.54, 6.11, 6.89, 7.14, 7.56, 8.49, 9.10, 9.49, 9.98 and 11.13 μ.

B-Di-(*n*-butyl)-B-chloro-N-trimethylborazene, $B_3(n\text{-}C_4H_9)_2ClN_3(CH_3)_3$. B-*n*-Butyl-B-dichloro-N-trimethylborazene, $B_3(n\text{-}C_4H_9)Cl_2N_3(CH_3)_3$.—A solution of 33.1 g. (0.147 mole) of B-trichloro-N-trimethylborazene in 125 ml. of dry benzene was placed into a 500-ml. round bottom flask equipped with dropping funnel and condensers as previously. A solution of *n*-butylmagnesium bromide prepared from 40 g. (0.29 mole) of *n*-butyl bromide was added in small portions over a 0.75-hour period. After refluxing for 3 to 4 hours, the reaction mixture was filtered in the dry box. Removal of solvent from the filtrate and washings was followed by careful heating under vacuum to sublime any unreacted starting material.

The remaining liquid was fractionated to give 45% B-tri-(*n*-butyl)-N-trimethylborazene, b.p. 140° (1.1 mm.); 35% B-di-(*n*-butyl)-B-chloro-N-trimethylborazene, b.p. 122° (1.13 mm.), $n^{22.5}D$ 1.4807; and 20% B-(*n*-butyl)-B-dichloro-N-trimethylborazene, b.p. 101° (1.1 mm.); $n^{22.5}D$ 1.4876; f.p. −4 to −6°. The over-all yield of borazene derivatives was approximately 75%. *Anal.* Calcd. for $B_3(n\text{-}C_4H_9)_2ClN_3(CH_3)_3$: B, 12.05; N, 15.61; Cl, 13.17. Found: B, 12.19; N, 15.22; Cl, 12.73. *Anal.* Calcd. for $B_3(n\text{-}C_4H_9)Cl_2N_3(CH_3)_3$: B, 13.11; N, 16.91; Cl, 28.05. Found: B, 13.04; N, 16.53; Cl, 27.61.

The infrared spectrum of $B_3(n\text{-}C_4H_9)_2ClN_3(CH_3)_3$ in CCl_4 showed strong absorption bands at these wave lengths: 3.41, 6.83, 7.08, 7.23, 7.37, 7.47, 9.09, 9.26, 9.60, 10.28 μ. The infrared spectrum of $B_3(n\text{-}C_4H_9)Cl_2N_3(CH_3)_3$ in CCl_4 showed strong absorption bands at the wave lengths: 3.41, 6.81, 7.10, 7.23, 7.47, 7.75, 9.25, 9.64, 10.07, 10.27 and 14.73 μ.

Attempts to Prepare B-Diethyl-B-chloro-N-trimethylborazene and B-Ethyl-B-dichloro-N-trimethylborazene.—Several experiments were made using the methods described above in which ethylmagnesium bromide was employed in amounts not sufficient to replace all the boron-attached chlorine. After subliming off any unreacted B-trichloro-N-trimethylborazene, the remaining liquid was fractionated in an efficient column. In no case was it possible to isolate a fraction that corresponded to a definite composition. On prolonged refluxing or repeated fractionation, B-trichloro-N-trimethylborazene was obtained. Elemental analysis of the distillate was consistent with mixtures of partially alkylated derivatives.

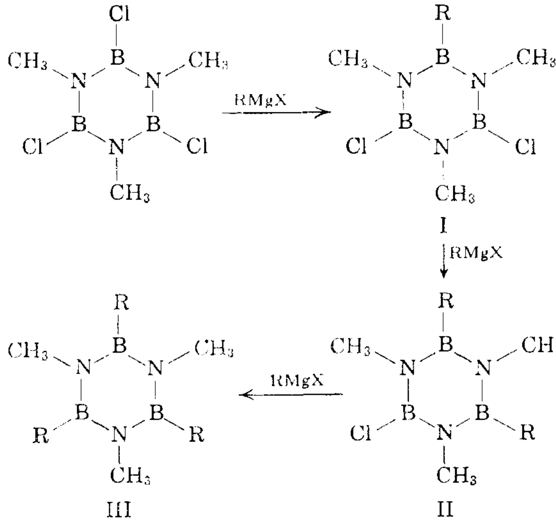
Attempt to Prepare B-Diallyl-B-chloro-N-trimethylborazene and B-Allyl-B-dichloro-N-trimethylborazene.—Experiments analogous to the preparation of B-triallyl-N-trimethylborazene, but using smaller amounts of allylmagnesium bromide, gave mixtures of borazene derivatives which were difficult to separate by fractionation. The presence of a volatile solid product in addition to liquid B-triallyl-N-trimethylborazene and the apparent proximity of boiling points did not seem to permit the isolation of the expected pure B-diallyl and B-allyl derivatives.

Analytical.—All samples were treated with 50% H_2SO_4 and hydrogen peroxide under reflux to ensure complete degradation to methylammonium ion, boric acid and chloride. Boron was titrated directly as boric acid in mannitol solution; nitrogen was titrated as methylamine after distillation from alkaline solution; chloride was determined by the Volhard method.

Results and Discussion

The assignment of the borazene structure to the compounds prepared is supported by the analysis and method of their preparation, their volatilities and comparison of their infrared spectra with the spectrum of N-trimethylborazene. The most intense band of N-trimethylborazene appears at 7.02 μ. This band has been assigned to in-plane vibrations of the borazene ring.[8] The compounds reported here all show extremely intense absorption in the neighborhood of 7.10 μ.

The reaction of Grignard reagents with B-trichloro-N-trimethylborazene proceeds rapidly at room temperature in the stepwise fashion indicated below.



When the mole ratio of Grignard reagent to B-trichloro-N-trimethylborazene is less than 3:1, the intermediate, incompletely alkylated, products I and II may be obtained.

The fact that both mono- and di-butyl derivatives can be obtained in reasonable yields from the same reaction mixture seems to indicate that alkyl substitution on one boron atom does not profoundly affect the rate for the next reaction step. A comparison of calculated product ratios expected from a series of consecutive reactions with the same reagent with the yields obtained for the *n*-butyl derivatives further suggests that the relative specific

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[8] W. C. Price, *et al.*, *Disc. Faraday Soc.*, 131 (1950).

rates of the individual steps are mainly determined by the statistical distribution of the halogen on the rings and possible changes in activation energies would be slight. However, a definite answer to this problem could be had only from more detailed data than are reported here.

We interpret our inability to isolate pure derivatives containing both B-ethyl and B-chloro substitution as due to a fairly rapid redistribution equilibrium that is disturbed during the separation. Comparing this to the apparent resistance to redistribution of the corresponding butyl derivatives, one can rationalize the difficulties that previous workers have encountered in attempts to prepare the analogous methyl derivatives.[9] If one proposes a bridged dimer transition state[10] for the redistribution reaction and recalls the decrease of stability of aluminum trialkyl dimers with increase in the length of alkyl groups, it is reasonable to suppose that a *n*-butyl group functions less efficiently in the formation of alkyl bridges than ethyl. More detailed and exact data on redistribution reactions in this system and of boranes in general would be required to give a definite answer.

Acknowledgment.—The support of this work by the Koppers Company through a research contract with the University of Florida is gratefully acknowledged.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Decomposition of Diborane in a Silent Discharge. Isolation of B_6H_{10} and B_9H_{15}

BY WILLIAM V. KOTLENSKY AND RILEY SCHAEFFER

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The decomposition of diborane in a silent discharge in the presence of an inert gas produces B_4H_{10} in 40% yield, B_5H_9 in 20% yield, B_5H_{11} in 30% yield and small amounts of B_6H_{10} and a previously unidentified hydride, B_9H_{15}. This is the first new borane isolated since the work of Stock more than thirty years ago. A partial mass spectrum of B_6H_{10} is presented.

The early efforts of Jones and Taylor[1,2] and others[3-5] to prepare a boron hydride by the acid hydrolysis of magnesium boride were unsuccessful. Development by Stock[6] of adequate methods for handling volatile materials in the absence of air or moisture enabled him to isolate and identify a series of highly reactive boron hydrides as the products of this hydrolysis. Despite the difficult and thorough examination by Stock of the effect of experimental conditions, the yield of boron hydride by hydrolysis methods never exceeded one per cent. of the theoretically obtainable amount. In one experiment, decomposition of 4200 g. of magnesium boride produced only 6 g. of B_4H_{10}, and lesser amounts of other boron and silicon hydrides. In another experiment, decomposition of 2000 g. of the boride produced a mixture from which he isolated 60 mg. of B_5H_9 and one gram of B_6H_{10}. Investigation of the reactions of higher boron hydrides has been limited by the difficulties met in their preparation.

Tetraborane is always the major product of the boride hydrolysis and was used by Stock to prepare the other boranes. Decomposition of B_4H_{10} at elevated temperatures produced B_5H_9, $B_{10}H_{14}$ and B_2H_6; B_5H_{11} was prepared by thermal decomposition of B_2H_6. No measurable amount of B_6H_{10} was observed as a product of the thermal decomposition of either B_2H_6 or B_4H_{10}.

In 1930, Schlesinger and Burg[7] reported that diborane could be prepared by passing boron trichloride and hydrogen through a high voltage discharge. Schlesinger and co-workers[8,9] later developed several methods for preparing diborane in nearly quantitative yield from readily available materials; consequently efforts to prepare the higher hydrides of boron have been largely concentrated on the elucidation of the mechanism of thermal decomposition of diborane and the effects of catalysts and other experimental conditions on the yields of various boranes.[10-12]

The most difficult boron hydride to prepare is B_6H_{10} although several methods for preparing it have been described in the literature. Stock[6] obtained comparatively small yields of B_6H_{10} in his tedious boride hydrolysis method. Wiberg and Stecher[13] claimed to have isolated very small quantities of B_6H_{10} from the products of the reaction between trimethylamine and B_5H_{11}. Mass spectral evidence of the formation of hexaborane by decomposition of B_5H_{11} at −80° over a period of several months has been reported by Norton.[14] Stock and Mathing[15] have reported that B_6H_{10} could be obtained by decomposing the brown solid formed when diborane was decomposed in a silent discharge. On slowly heating 30 mg. of this solid to 1000°, 0.4 cc. of B_6H_{10} was formed.

This investigation was undertaken to develop

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