tion of triphenylboroxin with boron trichloride at 80–85°. The crude material was purified by fractional distillation and the portion boiling 86–88° at 40 mm. used. The reported boiling point is 85–88° at 40 mm. The freshly distilled phenyldichloroborane (0.202 mole) was dissolved in 150 ml. of freshly distilled anhydrous benzene and added to a slurry of *p*-phenylenediamine (0.202 mole) in anhydrous benzene. After stirring for 11 hr. the benzene was decanted from the pink 1:1 adduct, the adduct was extracted with benzene and the product dried *in vacuo.*

Anal. Calcd. for $C_6H_8N_2 \cdot C_6H_5BCl_2$: Cl, 26.56. Found: Cl, 26.59.

All operations were done in an atmosphere of dried, oxygen free nitrogen. Yield approximately 95%.

Pyrolysis in vacuo. A sample of the pink 1:1 adduct (0.0237 mole) was heated for 6 hr. at 225° *in vacuo* in a vacuum sublimation apparatus. Evolved gases were trapped out at $-195°$ and fractionated by bulb distillation on a vacuum chain. Traces of benzene and 0.0310 mole of hydrochloride (65.2% of all the original chloride) were obtained.

A solid white sublimate, corresponding to 17.3% of the original adduct, collected on the water-cooled finger of the sublimation apparatus and a dark brown material, corresponding to 54.2% of the original adduct, remained as residue.

The white sublimate was identified as a mixture of the mono- and dihydrochlorides of *p*-phenylenediamine by its infrared spectrum and chloride analysis. (Calculated for *p*-phenylenediamine·2HCl:Cl, 39.2. Found: 31.9.) Only *p*-phenylenediamine could be extracted after neutralization of the sublimate with sodium hydroxide.

The dark residue was extracted with benzene and the benzene soluble portion, roughly 95% of the residue, was recrystallized twice from benzene to give a white crystalline material, m.p. 166–168°.

Anal. Calcd. for $C_{54}H_{54}B_6N_6O_6$: C, 68.42; H, 5.74; N, 8.87; Cl, 0.00; B, 6.85. Found: C, 68.64; H, 5.70; N, 8.66; Cl, 0.00; B, 6.91. The material did not change color, fume, gain, or lose weight on exposure to moist air for 5 days.

Pyrolysis in refluxing xylene. A large sample (0.121 mole) of the 1:1 adduct was refluxed in anhydrous xylene (140–141°) in a nitrogen atmosphere until hydrogen chloride evolution ceased (12 hr.). At the end of this time 60.3% of all available chloride had been evolved as hydrogen chloride.

The slurry which formed on refluxing was filtered under nitrogen and the solid material extracted in a Soxhlet extractor with 1000 ml. of benzene. No hydrogen chloride was evolved during the extraction and about 10 g. of a white solid remained in the thimble. This white solid was identified by chloride analysis, infrared spectrum and extraction of pure *p*-phenylenediamine after neutralization with sodium hydroxide, as a mixture solely of the mono- and dihydrochlorides of *p*-phenylenediamine.

The benzene solution from the extraction was evaporated almost to dryness, filtered and the product recrystallized twice from benzene. The material melted at 167–168°.

Anal. Calcd. for $C_{54}H_{54}B_6N_6O_6$: C, 68.42; H, 5.74; N, 8.87; Cl, 0.00; B, 6.85. Found: C, 68.79; H, 5.86; N, 8.58, 8.87; Cl, 0.00; B, 7.21.

The infrared spectrum was quite similar to that of a composite spectrum of pure triphenylboroxin and *p*-phenylenediamine. The ebullioscopic molecular weight in benzene was 200 g. per mole and 203 g. per mole on two separate determinations. If the product $C_{54}H_{54}B_6N_6O_6$ is actually the weakly bonded adduct 2(triphenylboroxin)·3(*p*-phenylenediamine), then it is reasonable to assume that one mole of this adduct will dissociate to form five moles of particles in boiling benzene. Thus, the molecular weight for the undissociated product should be five times the observed molecular weight,—*i.e.* 1000 and 1015 g. per mole. The calculated molecular weight for $C_{54}H_{54}B_6N_6O_6$ is 947 g. per mole.

A sample of the product was hydrolyzed with 1*N* hydrochloric acid, the solution made basic with sodium hydroxide, evaporated to dryness, and the residue extracted with benzene. Only pure *p*-phenylenediamine, m.p. 138–140° was obtained. A second sample was hydrolyzed with 1*N* hydrochloric acid, evaporated to dryness and the residue extracted with petroleum ether. The ether extract was evaporated to dryness, the residue dried at 110° for 12 hr. and identified as pure triphenylboroxin, m.p. 211–216°.

A sample of the product was sublimed *in vacuo;* pure *p*-phenylenediamine appeared as sublimate and pure triphenylboroxin as residue.

The adduct 2(triphenylboroxin)·3-(*p*-phenylenediamine) has been synthesized by method independent of the pyrolysis reactions by triturating mixtures of pure triphenylboroxin and pure *p*-phenylenediamine in 2:3 mole ratio under anhydrous benzene. The benzene was removed by evaporation on the vacuum chain and the crude product recrystallized from a small quantity of benzene. The melting point of this product was 165–167° and the infrared spectrum was identical to that of the product from the pyrolysis reaction. Similar results are obtained if pure samples of the boroxin and the base are dissolved in benzene, the benzene solutions mixed so as to give a 2:3 mole ratio of boroxin to base, and the benzene removed by evaporation.

The phase diagram (Figure I) for the system triphenylboroxin-*p*-phenylenediamine was determined by the method of Rheinboldt.[12] Accurately weighed samples of triphenylboroxin and *p*-phenylenediamine were ground together under a few drops of benzene, the benzene removed by evaporation on the vacuum chain, and the melting range of the sample determined in a conventional capillary melting point type of apparatus. The lower limit of the melting range was taken as that temperature at which the first droplet of liquid could be seen; the upper limit, as the temperature at which the last bit of solid melted.

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(11) L. J. Schupp, Ph.D. thesis, Western Reserve University, 1955.

(12) H. Rheinboldt, K. Hennig, and M. Kircheisen, *J. prakt. Chem.*, 111, 242 (1925).

Biborazinyl

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Although considerable research on borazine chemistry has been reported in the last decade, little is known of biborazinyls and similar higher homo-condensates. The preparations of borazine analogs of naphthalene and biphenyl have recently been described.[1] Borazinylamine polymers are also known.[2] Condensation of the di-Grignard from 1,4-dichlorobutane with 1,3,5-trimethyl-2,4-di-*n*-butyl-6-chloroborazine has led to 1,4-bis(1,3,5-trimethyl - 4,6 - di - *n* - butyl - 2 - borazinyl)-butane.[3]

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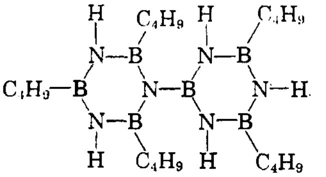
(1) Paul C. Moews and A. W. Laubengayer, 136th A.C.S. Meeting Abstracts 53N.

(2) D. W. Aubrey and M. F. Lappert, *J. Chem. Soc.*, 2927–2931, 1959.

(3) J. J. Harris, Ph.D. dissertation, University of Florida, 1958.

$$2(CH_3)_3N_3Bu_2B_3Cl + (ClMgC_2H_4)_2 \longrightarrow 2MgCl_2 + [((CH_3)_3N_3Bu_2B_3)C_2H_4]_2$$

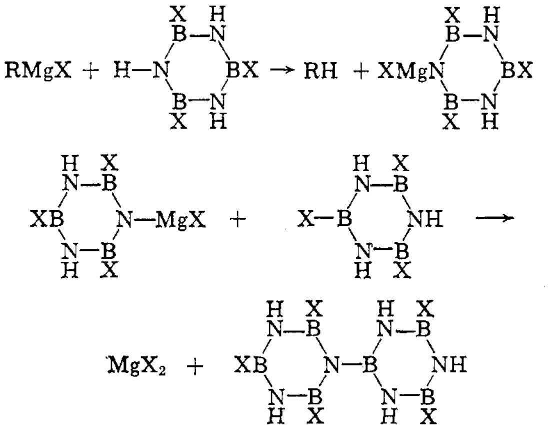
We have discovered that the reaction of butylmagnesium halides with 2,4,6-tribromoborazine or 2,4,6-trichloroborazine gives in addition to 2,4,6-tri-*n*-butylborazine small yields of 2,4,4′,6,6′-pentabutyl-1,2′-biborazinyl (I) and higher condensates in which the rings are linked through B—N bonds.



I

The biborazinyl and higher analogs may have been formed by pyrolysis of 2,4,6-tri-*n*-butylborazine during distillation, which involved relatively high bath temperatures (150–200°). However, as 2,4,6-tri-*n*-butylborazine can be repeatedly redistilled at these temperatures with very little decomposition, this mechanism seems unlikely.

A more probable mechanism comprises the initial reaction of Grignard reagent with an active hydrogen on one of the borazine nitrogens followed by metathesis of the resulting nitrogen Grignard reagent with a halogen atom of a borazine molecule.

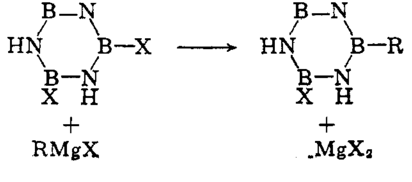


(1)

(2)

Formation of higher condensates may then proceed by the same general mechanism. A mechanism of this type is supported by the mass spectrographic identification of butane evolved during the reaction.

In connection with the above mechanism it is of interest to compare the rate of reaction (1) with the coupling reaction (3).



(3)

It was found that when ethylmagnesium bromide and 2,4,6-tribromoborazine were used in a 3-1 ratio, 20% of the Grignard reagent was consumed in ethane formation indicating reaction 3 to be more rapid than reaction 1. When it is considered that the sites available for coupling decrease at a much faster rate than those available for exchange, it is apparent that the coupling reaction is much faster than the exchange reaction. The same inference may be drawn from the isolation of 2,4,6-tri-*n*-butylborazine in appreciable yields from the reaction of 2,4,6-tribromoborazine and *n*-butylmagnesium bromide as this is possible only if reaction 3 is much more rapid than reaction 1.

EXPERIMENTAL

2,4,6-Tribromoborazine was prepared from ammonium bromide and boron tribromide[3] while 2,4,6-trichloroborazine was supplied by U. S. Borax Research Corporation. Benzene was dried over calcium hydride before use, while Mallinckrodt anhydrous ether was used without further treatment. The Grignard reagents were prepared by standard procedures.

Addition of 0.31 mole of *n*-butyl magnesium bromide slowly to a stirred solution of 30 g. (0.946 mole) of 2,4,6-tribromoborazine in 100 ml. of ether, or benzene (dry nitrogen atmosphere) gave, after removal of magnesium bromide (as its insoluble etherate at 0°), a thick slurry which was fractionally distilled at reduced pressure. The fraction boiling at 97–102° at 0.95 mm., was 2,4,6-tri-*n*-butylborazine, 5.2 g. (0.02 mole) (ebulliscopic mol. wt., benzene 248, theory 249). The second fraction was compound I, boiling at 182–187° at 0.6 mm., 2.65 g. (0.006 mole). The third fraction, 1.15 g., boiling at 190–250°, 0.6 mm., is believed to be largely a mixture of triborazinyls. Use of *n*-butyl magnesium chloride gave a higher percentage of triborazinyls. Reaction of 2,4,6-trichloroborazine with *n*-butylmagnesium bromide gave better yields of 2,4,6-tri-*n*-butylborazine and less bi- and triborazinyl.

By VPC on a silicon greased column operated at 250° and 50 mm., the pentabutylbiborazinyl (I) was shown to be free of more volatile impurities (the higher molecular weight condensates could not be eluted). Its molecular weight, determined ebullioscopically in benzene, was 438 (calculated 440).

Anal. Calcd. for $C_{20}H_{30}N_6B_6$: C, 54.65; H, 11.46; B, 14.77; N, 19.12. Found: C, 54.65; H, 11.21; B, 14.72; N, 19.17.

Major infrared bands as determined in the liquid phase on a Perkin-Elmer Infracord were at 2.9(m), 3.4(s), 3.45(s), 3.52(s), 6.9(vs), 7.1(s), 7.25(s), 7.32(s), 7.42(s), 7.52(s), 8.50(w), 8.75(w), 9.1(w), 11.2(w), 12.5(w), 12.85(w), and 13.9 (s diff.) μ. The specific gravity 20/4 was .913 and n_D^{20} 1.4745. The sample liberated no hydrogen in refluxing 30% sulfuric acid, precluding boron-boron bonding in I.

To compare the ratio of reactions 1 and 3 a solution of ethylmagnesium bromide prepared from 27 g. (0.246 mole) of ethyl bromide and excess magnesium was added to a solution of 24.25 g. (0.0765 mole) of 2,4,6,-tribromoborazine. During addition 1130 ml., corrected to STP (0.05 mole) gas were evolved, indicating approximately 20% of the Grignard reagent reacted according to reaction 1.

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