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Formation of an Adduct of Triphenylboroxin and *p*-Phenylenediamine[1]

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Pyrolysis of the 1:1 adduct of boron trichloride and aniline is reported[5] to give good yields of 2,4,6-trichloro-1,3,5-triphenylborazine; hexaphenylborazine has been prepared[6] by pyrolysis of the adduct formed between phenyldichloroborane and aniline. Previous work in this laboratory[7] has shown that the 1:1 adduct of boron trichloride and *p*-phenylenediamine can be pyrolyzed to the cyclic trimer $(C_6H_5N_2B)_3$ and that pyrolysis of the 1:1 adduct of phenyldichloroborane and *p*-phenylenediamine leads to the monomeric $C_6H_4(NH)_2BC_6H_5$. We have extended this study to the pyrolysis of the 1:1 adduct of phenyldichloroborane and *p*-phenylenediamine.

The major products isolated from the pyrolysis of this adduct, whether the pyrolysis was done *in vacuo* or in refluxing xylene, were the mono- and dihydrochlorides of *p*-phenylenediamine and a new compound of formula $C_{54}H_{54}B_6N_6O_6$, which is best formulated as 2(triphenylboroxin)·3(*p*-phenylenediamine).

This compound melts at 167–168°, dissociates in benzene to form five moles of particles per mole of compound dissolved, dissociates to pure triphenylboroxin and *p*-phenylenediamine on heating *in vacuo* with the base appearing as a sublimate, and has an infrared spectrum very similar to a composite spectrum formed by combining the spectra of triphenylboroxin and *p*-phenylenediamine. Significant changes in the infrared spectrum of the compound, as compared with the composite spectrum, appear (1) in the N—H stretching vibrations of *p*-phenylenediamine where a shift from 2.98 μ to 2.90 μ and from 3.10 μ to 2.99 μ is observed (2), in the absorption at 7.54 μ which diminishes in intensity, and (3) in the boroxin ring absorption which is shifted from 14.5 μ to 14.85 μ.

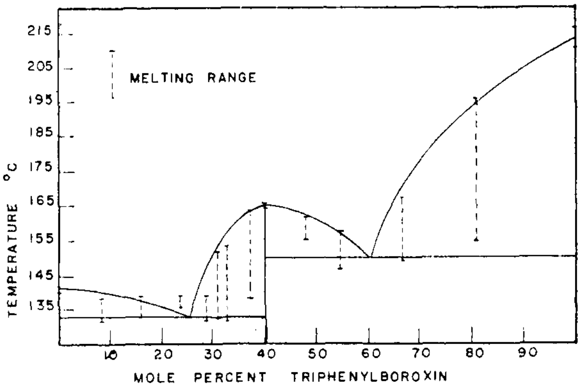

Fig. 1. Phase diagram of triphenylboroxin-*p*-phenylenediamine

The compound may be synthesized independently of the pyrolysis reaction by triturating triphenylboroxin and *p*-phenylenediamine in benzene in a 2:3 mole ratio and removing the benzene by vacuum distillation at room temperature. The phase diagram of the system triphenylboroxin–*p*-phenylenediamine indicates a congruently melting compound, m.p. 168°, at 40 mole% triphenylboroxin.

The presence of oxygen in the compound was not expected; care had been taken to avoid exposure of the system to moisture or the atmosphere. Residual moisture in the solvents used in working up the reaction mixture is the most likely source of the oxygen.

Similar compounds of the boroxin ring system and organic bases have been reported. Yabroff and Branch[8] have reported that simple amines will react to form adducts with phenylboric acid. Burg[9] reports a 1:1 compound of trimethylboroxin and trimethylamine. Snyder[10] reports a 1:1 compound of triphenylboroxin and pyridine and a 2:1 compound of triphenylboroxin and 3,6-diaminoacridine. The 2:3 compound of triphenylboroxin and *p*-phenylenediamine reported here is apparently of the same type as those reported by Burg, by Yabroff and Branch and by Snyder.

EXPERIMENTAL

Preparation of the 1:1 adduct. Phenyldichloroborane was prepared, following the method of Schupp,[11] by the chlorina-

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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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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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