PERFLUOROPHENYL DERIVATIVES OF THE ELEMENTS

PART III*. *B*-TRIS(PENTAFLUOROPHENYL)BORAZINE

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INTRODUCTION AND DISCUSSION

Although perfluoroalkyl and perfluorophenyl derivatives of boron are now well known[1], the corresponding *B*-substituted borazines have not been described. We have obtained low yields of *B*-tris(pentafluorophenyl)borazine, $(C_6F_5)_3B_3N_3H_3$, by treating trichloroborazine with either pentafluorophenyllithium or pentafluorophenylmagnesium bromide in ether. Early experiments failed to produce any *B*-tris(pentafluorophenyl)borazine at all, and it was only after the *B*-trichloroborazine had been purified by vacuum sublimation immediately prior to use that success was achieved. The commercial sample of *B*-trichloroborazine used in these experiments contained a high percentage of involatile impurities, possibly hydrolysis products, which contaminated the *B*-tris(pentafluorophenyl)borazine if the preparation was carried out without purification of the trichloroborazine starting material.

B-Tris(pentafluorophenyl)borazine is a white solid, stable in dry air and soluble in benzene and ether. It sublimes readily at 200° in a good vacuum with little apparent decomposition and this appears to be the most efficient method of purification. We studied its thermal decomposition under vacuum conditions in the hope that isolable polymers of low molecular weight might be obtained by loss of pentafluorobenzene, C_6F_5H, in an intermolecular condensation; although pentafluorobenzene was evolved at high temperature, the resulting product (which showed broad infrared bands at 1140, 970 and 750 cm^{-1} characteristic of B–N rings) was insoluble in the solvents tried and was apparently highly polymeric. After heating for several days at 280° it was possible to isolate over 50 % of the pentafluorophenyl groups as pentafluorobenzene, but no hydrogen or perfluorobiphenyl could be detected, probably indicating that no nitrogen–nitrogen or boron–boron bonds had been formed during the decomposition.

Interestingly, it was observed that although the material not in the vapour state decomposed rapidly at 280°, the vaporised *B*-tris(pentafluorophenyl)borazine was apparently unaffected by the high temperature and condensed out as large colourless crystals when the vessel was cooled to room temperature. The cycle of heating to 280° and then recooling to room temperature was repeated many times with no visible decrease in the amount of crystals which condensed out. This behaviour is similar to that noted previously for borazine[2].

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* For Part I, see ref. 1; for Part II, see page 437.

Although it is possible to prepare *B*-substituted borazines by heating certain boron–amine adducts, no *B*-tris(pentafluorophenyl)borazine was produced during the pyrolysis of ammonia–tris(pentafluorophenyl)boron; indeed this adduct was found to be remarkably stable to heat and it only evolved small quantities of pentafluorobenzene even after many hours at 220°.

B-Tris(pentafluorophenyl)borazine did not react with dry hydrogen chloride either by addition of the hydrogen chloride or by cleavage of pentafluorophenyl groups as pentafluorobenzene. No reduction by hydrogen took place at 160° although some thermal decomposition of the borazine occurred at this temperature. As was the case with tris(pentafluorophenyl)boron, the pentafluorophenyl groups in *B*-tris(pentafluorophenyl)borazine were sensitive to water at room temperature and up to 40% cleavage to give pentafluorobenzene was found after five days.

Such a ready water-cleavage of pentafluorophenyl groups bound to boron is not encountered in normal alkyl or aryl boron derivatives, although perfluorovinyl boron compounds hydrolyse readily at 100°. [Unexpectedly, water also cleaves pentafluorophenyl groups from triphenyl(pentafluorophenyl)lead[4] at temperatures as low as 100°.] It is possible that electron-withdrawal by the pentafluorophenyl groups allows partial removal of the formal negative charge from the boron atoms in the borazine ring; if this occurred it would allow the boron atoms to be more easily attacked by a highly polar molecule like water.

The infrared spectrum of *B*-tris(pentafluorophenyl)borazine has a sharp peak at 3508 cm^{-1} which can be assigned to the N–H stretching mode; the peaks at 1497 and 1481 cm^{-1} may be due to ^{10}B–N and ^{11}B–N vibrations[3] since their frequency ratio, 1.01, is in close agreement with the theoretical value. The strong absorptions at 1644, 1142 and 974 cm^{-1} are typical of pentafluorophenyl groups bound to boron[1].

EXPERIMENTAL

All manipulations were carried out either under an atmosphere of dry, oxygen-free nitrogen or in a vacuum. Analyses were performed by Alfred Bernhardt, Mülheim, Ruhr. The sample of *B*-trichloroborazine was kindly donated by Borax Consolidated Ltd., and was purified by vacuum sublimation prior to use.

Thermal stability of B-trichloroborazine

It has been stated[5] that *B*-trichloroborazine is thermally unstable and slowly evolves hydrogen chloride at room temperature when stored in an atmosphere of dry nitrogen. To investigate this decomposition we sublimed a sample (610 mg) of *B*-trichloroborazine into a baked-out, pyrex vessel which was then sealed under vacuum. After 8 days at room temperature (18°) no hydrogen chloride could be detected; *i.e.* less than 0.2 ml, or 0.01 mmole, had been formed. The bulb was resealed and held at 45° for six days; again no hydrogen chloride could be detected. Clearly, *B*-trichloroborazine is thermally more stable than previously supposed and it was only when the temperature was taken up to 90° that signs of slight decomposition (*ca.* 3%) could be detected by the evolution of 0.11 mmoles of hydrogen chloride over a period of six days.

Preparation of B-tris(pentafluorophenyl)borazine

a) From pentafluorophenyllithium. A solution of butyllithium (0.05 mole) in *n*-hexane (10 ml) was added to a cold (—78°), stirred etherial solution of bromopentafluorobenzene (12.4 g; 0.05 mole) contained in a 500 ml flask, fitted with a stirrer, a nitrogen inlet and a short piece of nylon tubing which acted both as a nitrogen outlet and a syphon. A solution of *B*-trichloroborazine (3.07 g; 0.016 mole) in dry ether was dripped into the pentafluorophenyllithium solution during 15 min; the total volume of solution was now 400 ml. As the stirred mixture was allowed to warm up slowly towards room temperature, a white precipitate began to settle out of solution at about —20°. The precipitate was allowed to settle (1 h at room temperature) and the clear, supernatant liquid syphoned into a flask flushed with dry nitrogen. The solvent was removed in a vacuum to leave a sticky solid; sublimation between 140 and 200° yielded a white solid which on a further sublimation at 200° gave analytically pure *B*-tris(pentafluorophenyl)borazine of m.p. 211–213° (500 mg; 5% yield based on *B*-trichloroborazine). (Found: C, 37.3; H, 0.7; F, 49.1; N, 7.4; mol. wt. osmometrically in benzene at 30°, 606. $C_{18}H_3B_3F_{15}N_3$ calcd.: C, 37.5; H, 0.5; F, 49.3; N, 7.3%; mol. wt., 579.)

b) From pentafluorophenylmagnesium bromide. Bromopentafluorobenzene (6.2 g; 0.025 mole) was added to 0.61 g of magnesium turnings in 50 ml of refluxing ether contained in a 500-ml flask. The Grignard reaction started at once; when it was complete a further 200 ml of ether were added to the flask. An ether solution of *B*-trichloroborazine (1.5 g; 0.008 mole) was added dropwise and the stirred solution refluxed for three hours. On removal of the ether under vacuum, a pale brown solid remained which gave 500 mg of *B*-tris(pentafluorophenyl)borazine on sublimation at 200° (10% yield).

Pyrolysis of B-tris(pentafluorophenyl)borazine

A sample of *B*-tris(pentafluorophenyl)borazine (172 mg; 0.31 mmole) was sealed in an evacuated glass bulb and heated at 210° for 24 h. Slight discolouration of the white solid was observed after about 2 h; on cooling the bulb to room temperature large colourless crystals condensed out of the gas phase. Their infrared spectrum and melting point showed them to be pure *B*-tris(pentafluorophenyl)borazine. The only product volatile at room temperature was pentafluorobenzene, C_6F_5H. See Table below:

Mmole of C_6F_5H removed	*Temperature, °C*	*Reaction time (h) at each temperature*
0.29	210	24
0.08	260	46
0.11	280	120
0.01	280	48
Total 0.49 (53%)		238

Reaction of B-tris(pentafluorophenyl)borazine with chlorine

B-Tris(pentafluorophenyl)borazine (157 mg; 0.27 mmole) was sealed in an evacuated glass vessel with an excess of dry chlorine. No reaction was apparent after 72 h at room temperature; after a further 72 h at 110° the tube was opened and the contents removed to a vacuum apparatus; no volatile material other than chlorine could be detected and the solid remaining in the reaction vessel had an infrared spectrum identical to that of pure *B*-tris(pentafluorophenyl)borazine; the latter compound must therefore be stable to attack by chlorine at 110°.

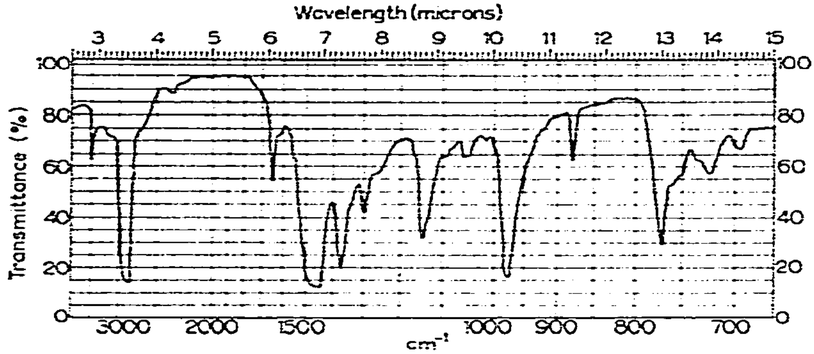

Fig. 1. The infrared spectrum of *B*-tris(pentafluorophenyl)borazine in a nujol mull.

Reaction of B-tris(pentafluorophenyl)borazine with hydrogen chloride

B-Tris(pentafluorophenyl)borazine (62.9 mg; 0.11 mmole) and dry hydrogen chloride (0.95 mmole) were sealed into an evacuated glass bulb; after 15 days at room temperature the vessel was opened and the hydrogen chloride (0.94 mmole) measured; no pentafluorobenzene was present. The hydrogen chlorine was resealed into the vessel which was then held at 90° for five days; the only volatile material consisted of hydrogen chloride (0.88 mmole; 93 % recovery) and pentafluorobenzene (0.01 mmole).

Reaction of B-tris(pentafluorophenyl)borazine with hydrogen

When hydrogen and *B*-tris(pentafluorophenyl)borazine (80.3 mg; 0.14 mmole) were heated together *in vacuo* at 160° for 72 h, no hydrogen was consumed. The only volatile product was pentafluorobenzene (0.16 mmole) which probably arose from thermal decomposition of the borazine.

Reaction of B-tris(pentafluorophenyl)borazine with water

B-Tris(pentafluorophenyl)borazine (149 mg; 0.26 mmole) was sealed in an evacuated glass bulb with a large excess of water (5.62 mg) in which it was insoluble, and held at room temperature for five days without stirring or shaking. After this time, the water vapour was removed from the volatile material by condensing the whole onto phosphorus pentoxide to leave pentafluorobenzene (0.31 mmole; 40 % cleavage of the C_6F_5 groups).

Pyrolysis of ammonia–tris(pentafluorophenyl)boron

Ammonia–tris(pentafluorophenyl)boron (220 mg; 0.42 mmole) showed slight charing on being held at 160° for 3 days in vacuum; the only volatile material released was pentafluorobenzene (0.09 mmole). After a further 2 days at 220° only a small amount of pentafluorobenzene (0.09 mmole) was formed. Had the decomposition given rise to a quantitative yield of *B*-tris(pentafluorophenyl)borazine, the amount of pentafluorobenzene formed would have been 0.84 mmole. The crystals remaining in the vessel proved to be virtually pure starting material.

Infrared spectrum of B-tris(pentafluorophenyl)borazine

The infrared spectrum was recorded on a Grubb-Parsons double beam grating spectrophotometer; the peaks reported are in cm^{-1}, for nujol and hexachlorobutadiene mulls: 3508 m, 1748 w, 1644 m, 1631 w, 1607 w, 1562 s, 1497 msh, 1481 s, 1466 msh, 1440 vw, 1388 m, 1303 m, 1142 s, 1133 m, 1096 w, 1070 w, 1059 w, 1049 w, 1016 w, 1001 w, 974 s, 877 m, 769 s, 759 wsh, 734 m, 698 w, 694 w, 668 vw.

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SUMMARY

The preparation and some properties of *B*-tris(pentafluorophenyl)borazine, the first perfluoroalkyl- or aryl-substituted borazine to be isolated, are described. Pyrolysis produces up to 50% of the theoretical quantity of pentafluorobenzene. No reaction was detected with hydrogen, chlorine and dry hydrogen chloride but hydrolysis occurs at room temperature to give pentafluorobenzene.

REFERENCES

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