

580. Phosphorus-Boron Compounds. Part II.¹ The Halogenation of 1,1,3,3,5,5-Hexaphenylcyclotriposphinoborine

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1,1,3,3,5,5-Hexaphenylcyclotriposphinoborine has been prepared in >80% yield. Reaction with an excess of chlorine, *N*-chlorosuccinimide, or iodine monochloride gives the hexachloride, $P_3Ph_6B_3Cl_6$. With an excess of bromine or *N*-bromosuccinimide it gives the hexabromide, $P_3Ph_6B_3Br_6$, and with an excess of iodine the tri-iodide, $P_3Ph_6B_3H_3I_3$, to which a nongeminal structure is assigned. The hexachloride and hexabromide are inert to various reagents which normally react readily with compounds containing boron-halogen bonds.

THE preparation and properties of 2,2,4,4-tetrahalogeno-1,1,3,3-tetraphenylcyclophosphinoborines, $P_2Ph_4B_2X_4$ ($X = Br$ or I), were described in Part I. Tetraphenylcyclophosphinoborine, $P_2Ph_4B_2H_4$, is so far unknown whereas hexaphenylcyclotriposphinoborine, $P_3Ph_6B_3H_6$ (I), is readily prepared by methods that are described

in technical reports by Wagner and his co-workers.² Pyrolysis of the addition compound, $Ph_2PH.BH_3$, prepared from diphenylphosphine and diborane, is reported² to give up to 55% yield of (I), and we now show that improved yields of over 80% can be achieved provided careful control of the temperature is maintained. It is of interest that this reaction gives a cyclotriposphinoborine whereas cyclophosphinoborines are obtained by reaction of the addition compounds $Ph_2PH.BBr_3$ and $Ph_2PH.BI_3$ with triethylamine.¹

The phosphinoborine (I) is comparatively inert to oxidation, hydrolysis, and thermal decomposition.² Its reaction with chlorine has been reported,² but the product was not well characterised. Reactions with an excess of chlorine, bromine, iodine, iodine monochloride, *N*-chlorosuccinimide, and *N*-bromosuccinimide are described here. Hexaphenylcyclotriposphinoborine has negligible reducing properties compared with those of the boron hydrides, and it does not react with acetaldehyde in boiling diglyme (2,2'-dimethoxydiethyl ether).

In solution in carbon tetrachloride it reacts vigorously with an excess of chlorine or bromine to give high yields of the hexahalides, $P_3Ph_6B_3X_6$ ($X = Cl$ or Br). Reaction with an excess of iodine monochloride gives iodine-containing intermediates, and eventually the hexachloride. The hexachloride is formed also by treating the hexabromide with chlorine. Slow reaction of (I) with iodine in boiling carbon tetrachloride or *n*-butyl iodide gives the tri-iodide, $P_3Ph_6B_3H_3I_3$, and further substitution by iodine does not occur, even on prolonged heating. The importance of *N*-halogenosuccinimides in the halogenation of inorganic hydrides is discussed elsewhere,³ and this method can be applied to the preparation of substituted phosphinoborines. A solution of (I) reacts with an excess of *N*-chloro- or *N*-bromo-succinimide in boiling carbon tetrachloride to give the fully substituted products, $P_3Ph_6B_3Cl_6$ and $P_3Ph_6B_3Br_6$, respectively. The reaction with *N*-chlorosuccinimide is catalysed by benzoyl peroxide.

The halogenohexaphenylphosphinoborines are stable in moist air, and the boron-halogen bonds are less reactive than those in halogenoboranes or *B*-halogenoborazoles. The hexachloride, $P_3Ph_6B_3Cl_6$, does not react with ammonia in carbon tetrachloride at room temperature or with diethylamine in boiling toluene (8 hr.). It did not react with potassium thiocyanate in boiling acetone (5 hr.), or with sodium ethoxide in boiling dioxan (4 hr.). Similar observations on the unreactive nature of 2,2,4,4,6,6-hexachloro-1,1,3,3,5,5-hexamethylcyclotriposphinoborine were made by Wagner and his co-workers,²

¹ Part I, W. Gee, R. A. Shaw, and B. C. Smith, *J.*, 1964, 4180.

² R. I. Wagner *et al.*, *WADC Technical Report 57-126*, Part I. (1957); Part II (1958); Part III (1959); Part IV (1960); Part V (1961); Part VI (1962).

³ W. Gee, R. A. Shaw, and B. C. Smith, *J.*, 1964, 2845.

and by Biddulph *et al.*⁴ The boron-halogen bonds are not broken by reaction with sodium in di-n-butyl ether at 140° and are not reduced by lithium aluminium hydride in di-n-butyl ether at 80°.²

The hexabromide, $P_3Ph_6B_3Br_6$, and the previously described¹ tetrabromide, $P_2Ph_4B_2Br_4$, have different chemical and physical properties. The former is stable in moist air, in which the latter is decomposed. There is no reaction between the hexachloride and secondary amines, whereas the tetrabromide reacts with diethylamine to give tris(diethylamino)borane.¹ The hexabromide, like the tetrabromide, does not react with Grignard reagents, or with silver cyanate or thiocyanate in benzene. It does not react with dimethyl sulphoxide in boiling carbon tetrachloride (2 hr.) although many inorganic acid halides undergo hydroxylation under these conditions.⁵

Some hexaphenylcyclotriphosphinoborines form crystalline solvates, suggesting the presence of specific interactions or crystal structures which are particularly suitable for clathrate formation. The compounds $P_3Ph_6B_3Br_6$ and $P_3Ph_6B_3H_3I_3$ crystallise with one molecule of chloroform, which is removed by heating *in vacuo* or by recrystallisation from a different solvent.

The infrared spectra of some phosphinoborines have been reported previously.^{4,6} The BH_2 stretching modes in the hydride, $P_3Ph_6B_3H_6$, appear as the expected doublet^{7,8} at 2418 and 2376 cm^{-1} (cf.⁶ 2395 and 2355 cm^{-1}) near the low end of the range, 2630—2350 cm^{-1} , assigned by Bellamy, Gerrard, Lappert, and Williams.⁸ The splitting in phosphinoborines (30—50 cm^{-1}) is less than that observed in boron hydrides containing BH_2 groups (*ca.* 100 cm^{-1}).⁹ The BH_2 scissor deformation occurs at 1120 cm^{-1} (cf.⁶ 1115 cm^{-1}), below the low-frequency end of the range assigned⁸ for boron hydrides, 1205—1140 cm^{-1} . The peak at 985 cm^{-1} (cf.⁶ 984 cm^{-1}), assigned to the BH_2 wagging deformation, is above the high-frequency end of the range assigned⁸ for boron hydrides, 975—945 cm^{-1} . The peak at 1106 cm^{-1} (cf.⁶ 1092 cm^{-1}) appears at 1098 and 1093 cm^{-1} in the spectra of the hexachloride and hexabromide, respectively, and cannot therefore be assigned to the BH_2 scissor deformation. The other bands are absent from the spectra of the hexachloride and of the hexabromide.

It is not surprising that the frequencies observed for phosphinoborines differ from those of boron hydrides, which have very different chemical properties.

The tri-iodide shows a singlet at 2425 cm^{-1} characteristic of B-H stretching.⁷⁻⁹ The absence of a doublet in this region indicates a nongeminal configuration. There is no peak at 1120 or 985 cm^{-1} , although there is a weak broad band near 970 cm^{-1} which can be associated with B-H deformations, cf. borazole.⁷

All the compounds show intense absorption at 1440 and 1000 cm^{-1} , which in this case can be associated with the presence of *P*-phenyl bands,¹ although the exact assignment is uncertain.¹⁰ Bands near 740 and 690 cm^{-1} are associated with the presence of mono-substituted benzenes.¹¹

EXPERIMENTAL

Diphenylphosphine was prepared from triphenylphosphine by reaction with sodium in liquid ammonia.¹² Diborane was prepared from methanesulphonic acid and sodium borohydride.¹³

⁴ R. H. Biddulph, M. P. Brown, R. C. Cross, R. Long, and H. B. Silver, *J.*, 1961, 1822.

⁵ S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature*, 1962, **196**, 372; M. F. Lappert and J. K. Smith, *J.*, 1961, 3224.

⁶ A. C. Chapman, *Trans. Faraday Soc.*, 1963, **59**, 806.

⁷ W. C. Price, R. D. B. Frazer, T. S. Robinson, and H. C. Longuet-Higgins, *Discuss. Faraday Soc.*, 1950, **9**, 131.

⁸ L. J. Bellamy, W. Gerrard, M. F. Lappert, and R. L. Williams, *J.*, 1958, 2412.

⁹ N. J. Blay, R. J. Pace, and R. L. Williams, *J.*, 1962, 3416.

¹⁰ G. Witschard and C. E. Griffin, *Spectrochim. Acta*, 1963, **19**, 1905.

¹¹ L. J. Bellamy, "Infra-red Spectra of Complex Molecules," Methuen, London, 2nd edn., 1958, p. 76.

¹² W. Hewertson and H. R. Watson, *J.*, 1962, 1490.

¹³ H. G. Heal, personal communication.

1,1,3,3,5,5-Hexaphenylcyclotriphosphinoborine (I).—An excess of diborane was passed through a stirred solution of diphenylphosphine (32.6 g., 0.175 mole) in dry pentane (100 ml.) at 0° in an atmosphere of nitrogen. The solvent was removed under reduced pressure, and the colourless crystalline diphenylphosphine-borane, m. p. 48–50° (lit.,² 49–52°), was heated in an oil-bath (2 hr.) at 190–200°. Recrystallisation from benzene-ethanol gave (I) as colourless crystals (28.0 g., 82%), m. p. 161° (lit.,² 160°) [Found: C, 72.6; H, 6.0; B, 5.6; P, 15.8%; *M*, 620 (by ebullimetry in benzene), 583 (by cryoscopy in benzene). Calc. for C₃₆H₃₆B₃P₃: C, 72.8; H, 6.1; B, 5.5; P, 15.6%; *M*, 592].

2,2,4,4,6,6-Hexachloro-1,1,3,3,5,5-hexaphenylcyclotriphosphinoborine.—(a) An excess of dry chlorine was passed through a solution of the phosphinoborine (I) (2.2 g., 3.7 mmoles) in carbon tetrachloride (100 ml.) at room temperature. An immediate exothermic reaction took place, and hydrogen chloride was evolved. Recrystallisation of the pale yellow precipitate from benzene-ethanol and chloroform-light petroleum (b. p. 60–80°) gave the colourless crystalline hexachloro-derivative (2.5 g., 84%), m. p. 258–259° (Found: C, 54.0; H, 3.8; B, 3.7; Cl, 26.7; P, 11.5%; *M*, 782. C₃₆H₃₀B₃Cl₆P₃ requires C, 54.0; H, 3.8; B, 4.0; Cl, 26.6; P, 11.6%; *M*, 801).

(b) *N*-Chlorosuccinimide (2.8 g., 20 mmole) and the phosphinoborine (I) (2.0 g., 3 mmoles) in carbon tetrachloride (150 ml.) were heated under reflux (3 hr.). After this time, only a small quantity of succinimide floated on the surface of the solution. Benzoyl peroxide (*ca.* 0.3 g.) was added as catalyst, the mixture was again boiled under reflux (3 hr.), and the succinimide was removed by filtration. Evaporation of the filtrate gave a colourless residue which dissolved in benzene (200 ml.), and the solution was eluted down a short alumina column. Evaporation and recrystallisation from benzene-ethanol and chloroform-light petroleum (b. p. 60–80°) gave the hexachloro-derivative (2.1 g., 81%), m. p. and mixed m. p. 258–259°.

(c) The phosphinoborine (I) (2.5 g., 4.2 mmoles) was boiled under reflux with an excess of iodine monochloride (14.5 g., 89 mmoles) for 8 days until thin-layer chromatography indicated the presence of only one product. The carbon tetrachloride was removed under reduced pressure, the solid product was then dissolved in hot benzene, and purified by passing down an alumina column (10 × 1.5 cm.). The product was recrystallised from benzene-alcohol- and chloroform-alcohol to give the hexachloro-derivative (1.8 g., 54%) m. p. and mixed m. p. 258–259°.

2,2,4,4,6,6-Hexabromo-1,1,3,3,5,5-hexaphenylcyclotriphosphinoborine.—(a) An excess of bromine was added to a solution of (I) in carbon tetrachloride (100 ml.). The mixture was boiled under reflux (1 hr.), the solvent evaporated, and the excess of bromine removed at 60°/0.01 mm. A solution of the residue in benzene was eluted down an alumina column, and evaporated. Recrystallisation of the product from chloroform-light petroleum (b. p. 60–80°) gave colourless crystalline 2,2,4,4,6,6-hexabromo-1,1,3,3,5,5-hexaphenylcyclotriphosphinoborine-chloroform, decomp. 160° (Found: C, 37.4; H, 2.4; B, 2.9; Br, 38.4; Cl, 7.3; P, 7.3. C₃₂H₃₁B₃Br₆Cl₃P₃ requires C, 37.3; H, 2.6; B, 2.8; Br, 40.4; Cl, 8.9; P, 7.8%). Chloroform was removed by heating at 160° *in vacuo* (Weight loss: Found, 10.1%; Calc., 10.1%). Recrystallisation of the product or the chloroform addition compound from benzene gave colourless needles of the hexabromo-derivative, m. p. 274° (Found: C, 40.8; H, 2.8; B, 3.1; Br, 44.3; P, 8.7%; *M*, 1097. C₃₆H₃₀B₃Br₆P₃ requires C, 40.5; H, 2.8; B, 2.8; Br, 44.9; P, 8.7%; *M*, 1068).

(b) Recrystallised *N*-bromosuccinimide (5.6 g., 30 mmoles) and (I) (3.0 g., 5 mmoles) in carbon tetrachloride (150 ml.) were heated under reflux (1 hr.). The solvent was evaporated under reduced pressure, and the product was then extracted with hot benzene (200 ml.). Succinimide remained at the top when the mixture was eluted down a short alumina column. Evaporation of the benzene solution under reduced pressure gave the hexabromo-derivative (5.0 g., 92%), m. p. and mixed m. p. 274°.

2,4,6-Tri-iodo-1,1,3,3,5,5-hexaphenylcyclotriphosphinoborine.—A solution of (I) (0.71 g., 1.2 mmoles) and iodine (6.2 g., 24 mmoles) in carbon tetrachloride (50 ml.) was boiled under reflux (6 weeks) until thin-layer chromatography indicated the presence of only one product in the mixture. The solvent was evaporated under reduced pressure and the solid residue was dissolved in hot benzene (50 ml.). The excess of iodine was removed by shaking with concentrated aqueous sodium thiosulphate. The benzene layer was dried by elution down a short column (Na₂SO₄). Concentration followed by the addition of hot ethanol gave a colourless crystalline precipitate (0.75 g., 65%), which, on heating at 139°/0.05 mm. (10 hr.), gave the

tri-iodo-derivative, decomp. 285° (Found: C, 44.45; H, 3.6; I, 38.9; P, 9.5. $C_{36}H_{33}B_3I_3P_3$ requires C, 44.5; H, 3.4; I, 39.2; P, 9.6%). The same product was obtained (70%) from a similar reaction in n-butyl iodide (7 days). Recrystallisation of the tri-iodide from chloroform–light petroleum (b. p. 60–80°) gave the *monochloroform adduct* (Found: Cl, 9.7. $C_{37}H_{34}B_3Cl_3I_3P_3$ requires Cl, 9.8%).

Infrared Spectra.—Spectra were recorded on a Unicam SP 100 Mk. II using sodium chloride optics. The recorded frequencies, which refer to samples in KBr discs, were almost the same as those observed for solutions in carbon disulphide.

The authors thank Dr. H. G. Heal for providing experimental details of the preparation of diborane, before publication.

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[Received, September 2nd, 1964.]
