609. Phosphorus–Boron Compounds. Part III.[1] Reactions of White Phosphorus with Boron Tribromide and Boron Tri-iodide

By W. GEE, R. A. SHAW, and B. C. SMITH

Reactions of white phosphorus with boron halides have been investigated. Reactions in chloroform give solvent-free products, P_2BBr_3 and P_2BI_3. Solvent-containing products are obtained from reactions in methyl iodide and carbon disulphide. Pyrolysis of P_2BI_3,CS_2 gives the compound PBI_2. The use of methyl iodide as a solvent for white phosphorus is suggested.

MOISSAN [2] reported that reaction of boron tri-iodide with a solution of white phosphorus in carbon disulphide gave a hygroscopic red solid of empirical formula PBI_2, which sublimed at 190° in a vacuum or in a stream of carbon dioxide. When this compound was heated in hydrogen, a less hygroscopic orange solid of empirical formula PBI was obtained. The compound PBI_2 has been prepared also by Evers and Salmon [3] and some of its reactions were investigated. Our observations on the reactions of white phosphorus with boron tribromide and boron tri-iodide are reported here. No reaction occurs with boron trichloride under similar conditions.

White phosphorus appears to be insoluble in boron tribromide, and two immiscible liquid layers are formed above 44°, the melting point of white phosphorus. The addition of boron tribromide to a dispersion of white phosphorus in chloroform causes the slow precipitation of a yellow amorphous solid of empirical formula P_2BBr_3. Reaction of boron tribromide with a solution of white phosphorus in carbon disulphide gives a yellow amorphous precipitate, which contains sulphur even after drying at 60°/0·5 mm. (6 hr.), but consistent analyses were not obtained. Reaction of boron tri-iodide with a dispersion of white phosphorus in chloroform gives a red precipitate of empirical formula P_2BI_3, reaction with a solution of white phosphorus in methyl iodide gives a dark rust precipitate

---

[1] Part II, W. Gee, J. B. Holden, R. A. Shaw, and B. C. Smith, *J.*, 1965, 3171.

[2] H. Moissan, *Compt. rend.*, 1891, **113**, 787.

[3] J. F. Salmon, *Diss. Abs.*, 1962, **23**, 431.

of empirical formula P_2BI_3,MeI, and reaction with a solution of white phosphorus in carbon disulphide gives a light rust precipitate of empirical formula P_2BI_3,CS_2.

All the products are amorphous involatile, probably polymeric, solids which show no *X*-ray powder diffraction patterns. They are insoluble in common organic solvents, with the possible exception of carbon disulphide. They are unstable in air, and are decomposed by water, acids, and alkalis. The compounds containing iodine inflame and liberate iodine on treatment with concentrated nitric acid in air. Pyrolysis at 700—1000° in an atmosphere of nitrogen gives black boron phosphide, BP, and pyrolysis in air gives white boron phosphate, BPO_4.

The compound P_2BI_3,CS_2 is thermally stable up to 150°/0·001 mm., but above this temperature traces of a yellow solid, m. p. 120—130°, presumably diphosphorus tetraiodide (lit.,[4] m. p. 124·5°), sublime on to a cold finger. Further decomposition occurs on heating in a long tube at 210°/0·001 mm. Carbon disulphide is evolved and a yellow-brown sublimate containing phosphorus and iodine forms near the neck of the tube. An orange-red crystalline sublimate of composition PBI_2 forms immediately above the hot zone. This compound is slightly soluble in carbon disulphide. The solution is unstable in air, and iodine is liberated on exposure to light in an inert atmosphere.

For a given tervalent phosphorus atom the donor properties decrease [5] and the acceptor properties increase with an increasing number of bonds to other phosphorus atoms, although the situation may be complicated by the unusual bond angle in the P_4 molecule. The tendency to form complexes with carbon disulphide or to quaternise with methyl iodide decreases along the series $R_3P > R_2P{\cdot}PR_2 > (RP)_n > P_4$. It is significant that stoicheiometric quantities of carbon disulphide and methyl iodide are retained in the initial products of reaction between white phosphorus and boron halides. Some type of specific interaction [6] would account for the exceptionally high solubility of white phosphorus in carbon disulphide, and also for the considerable solubility of white phosphorus in alkyl iodides.

We find that methyl iodide is a convenient solvent for white phosphorus. There is no reaction with methyl iodide on boiling in the absence of light, or on heating in a sealed tube at 120°. Reaction does occur on heating white phosphorus with alkyl halides in sealed tubes above 140°, and the reactivity decreases in the order MeI > EtI > EtBr. The products are tetra-alkylphosphonium halides and polymeric red solids containing carbon, hydrogen, phosphorus, and halogen, which are hydrolytically unstable and which inflame on treatment with concentrated nitric acid. The composition of the product obtained from the reaction of methyl iodide with white phosphorus appears to be independent of the relative concentrations of the reactants. The carbon and phosphorus analyses are similar to those obtained by Kraft and Parini,[7] but their iodine analyses are lower, possibly because of hydrolysis. The elemental analyses suggest that the product is a type of red phosphorus with approximate composition P_{14},MeI.

The reactions of white phosphorus with boron halides are slow and irreversible, and reactivity decreases in the order $BI_3 > BBr_3 > BCl_3$. This would be in accord with a free-radical, nucleophilic, or electrophilic mechanism, and does not help to distinguish between them. All three types of mechanism are known to occur with tervalent phosphorus compounds.[8-10] Electrophilic attack by tetraphosphorus on boron halides would involve the type of reaction scheme, shown on p. 3356:

---

[4] J. R. Van Wazer, " Phosphorus and its Compounds," Interscience, New York, vol. I, 1958, p. 185.

[5] See, *e.g.*, W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2296, 2871; W. Mahler and A. B. Burg, *J. Amer. Chem. Soc.*, 1957, **79**, 251; 1958, **80**, 6161.

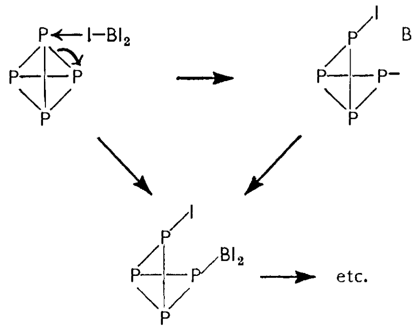
[6] S. Peter, *Phys. Rev.*, 1954, **93**, 940.

[7] M. Y. Kraft and V. P. Parini, *Doklady Akad. Nauk S.S.S.R.*, 1951, **77**, 57.

[8] M. Grayson, I.U.P.A.C. Symposium on Organophosphorus Compounds, Heidelberg, May 1964; M. M. Rauhut, " Topics in Phosphorus Chemistry," ed. M. Grayson and E. J. Griffith, Wiley, New York, vol. I, 1964.

[9] R. R. Holmes, *J. Phys. Chem.*, 1960, **64**, 1295; *J. Amer. Chem. Soc.*, 1960, **82**, 5285.

[10] S. K. Ray, R. A. Shaw, and B. C. Smith, *Nature*, 1962, **196**, 372; E. H. Amonoo-Neizer, S. K. Ray, R. A. Shaw, and B. C. Smith, I.U.P.A.C. Symposium on Organophosphorus Compounds, Heidelberg, May 1964; *J.*, 1965, in the press.



Solvated BH_2^+ and BPh_2^+ species are well established.[11] Whatever the mechanism, the initial product probably contains segments of $-P(I)-P(BI_2)-$ groups, and the amorphous nature suggests a random arrangement. Heating gives a crystalline product probably containing $-P(BI_2)-P(BI_2)-$ or $-P(I)-B(I)-$ groups.

EXPERIMENTAL

Chloroform, carbon disulphide, and methyl iodide were distilled freshly from phosphorus pentoxide. All manipulations were carried out in an atmosphere of nitrogen which had been deoxygenated with manganous oxide and dried with phosphorus pentoxide.

Reactions with Boron Halides.—The reaction vessel consisted of a three-necked cylindrical flask (250 ml.) with a No. 4 sintered glass base (2·5 cm.), from which a glass tube led up to a tap. The flask was fitted with a centrifugal stirrer, a water condenser and nitrogen inlet, and a molecular-sieve column. The apparatus was assembled when hot, and evacuated and filled with nitrogen three times. Weighed quantities of white phosphorus were dried by elution with carbon disulphide down the molecular-sieve column into the reaction flask. The phosphorus was quantitatively eluted. Carbon disulphide was evaporated under reduced pressure before the reactions in chloroform and methyl iodide. The molecular-sieve column was replaced by a tap-funnel with a sintered glass filter which was used for addition of the boron halide and solvent. Complete reaction occurred (4—7 days) in carbon disulphide and methyl iodide at room temperature and in boiling chloroform. Solvents were removed by filtration, and the products were washed with fresh solvent. Typical analytical data are recorded in Table 1.

Reactions with Alkyl Halides.—Reaction of white phosphorus (1·5 g.) with methyl iodide (5 ml.) in a sealed tube at 140° (21 hr.) gave tetramethylphosphonium iodide and a red polymeric solid which was separated by filtration and washed with carbon disulphide to remove any residual white phosphorus. Similar polymeric products were obtained from sealed-tube reactions of white phosphorus with ethyl iodide at 160° and ethyl bromide at 210°. Typical analytical data are recorded in Table 2.

TABLE 1

	Found (%)			Required (%)		
Compound	B	P	Hal	B	P	Hal
P_2BBr_3	2·3	20·0	76·3	3·5	19·8	76·7
P_2BI_3.........	2·2	—	83·5	2·4	13·7	83·8
P_2BI_3,CS_2 *	2·0	11·9	71·3	2·0	11·9	71·4
P_2BI_3,MeI...	—	10·6	85·1	1·8	10·4	85·2
PBI_2	3·4	10·65	85·95	3·7	10·5	85·9

* Found: C, 2·2. Calc.: C, 2·3%.

TABLE 2

Alkyl halide	Found (%)			
	C	H	P	Hal
MeI	1·9	0·5	73·1	24·2
EtI	2·0	0·9	82·8	14·0
EtBr	1·5	0·6	94·1	3·9

Analysis.—Samples for phosphorus analysis were dissolved in concentrated nitric–perchloric acid mixtures,[12] and phosphorus was determined colorimetrically at 390 mμ as the vanadate–molybdate.[13] Other samples were dissolved in 2N-potassium hydroxide in the presence of hydrogen peroxide, and the excess of hydrogen peroxide was decomposed by boiling. Bromine was determined gravimetrically as silver bromide. Iodine was liberated on treatment

---

[11] See, *e.g.*, D. R. Schultz and R. W. Parry, *J. Amer. Chem. Soc.*, 1958, **80**, 1, and later Papers; J. M. Davidson and C. M. French, *J.*, 1958, 114; 1962, 3364.

[12] I. Ubaldini, *Analyt. Abs.*, 1956, 1750.

[13] O. B. Michelsen, *Analyt. Chem.*, 1957, **29**, 60.

with potassium iodate in acid solution, and determined colorimetrically at 450 mμ. Boron was determined colorimetrically at 620 mμ as the boric acid–dianthrimide complex in concentrated sulphuric acid.[14]

The authors thank L. Light and Co. Ltd. and Borax Consolidated for gifts of boron tribromide.

DEPARTMENT OF CHEMISTRY, BIRKBECK COLLEGE, UNIVERSITY OF LONDON,
MALET STREET, LONDON W.C.1.
[*Received, November 6th,* 1964.]

[14] Danielsson, *Talanta*, 1959, **3**, 138.