Boron Halides as Reagents in Inorganic Syntheses. Part I. A General Method for the Preparation of Anhydrous Bromides and Oxybromides, and a Comment on Reactions with Elemental Sulphur

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The reaction between boron tribomide and metal, metalloid, and non-metal oxides (and sulphides) appears to offer a general method for preparing anhydrous bromides and oxybromides. It has been demonstrated for (i) As_2O_3, As_2S_3, Sb_2O_3, Sb_2S_3, and TiO_2 (which give corresponding bromides), (ii) As_2O_5, As_2S_5, and Sb_2O_5 (which give bromides in a lower oxidation state), (iii) P_2O_5 and WO_3 (which give corresponding oxybromides), and (iv) V_2O_5 (which gives the reduced oxybromide, $VOBr_2$). The reactions are carried out under reflux, the conversions are essentially quantitative, and separation of pure products is readily achieved.

Interaction of sulphur and dibromophenylborane, $C_6H_5BBr_2$, gave a member of a new cyclic system.

BORON halides are among the most reactive reagents in organic chemistry.[1] Their reactions with inorganic substrates have received little systematic study. We believe that their utility for inorganic syntheses may be considerable. The boron halides are likely to be reactive both for kinetic (they are among the strongest of electrophiles) and also for thermodynamic reasons. The latter features become particularly significant in systems leading to ionic products (*e.g.*, the tetrahalogenoborates), or to compounds having high intrinsic thermochemical bond strengths. Thus, the driving force in the reactions reported here is probably the large value of the heat of formation of B_2O_3 or B_2S_3.

Products of interaction of M_2X_n (X = O or S) and BBr_3

M_2X_n	Product	Yield (%) †	Reaction type (1—4)	Reaction conditions
P_2O_5	$POBr_3$	73·9	3	20°/2 hr.
As_2O_3	$AsBr_3$	81·4	1	90—120/3 hr.
As_2O_5	$AsBr_3$ (+Br_2, 94%)	77·1	2	90—120/3 hr.
As_2S_3	$AsBr_3$	77·6	1	130—140/5 hr.
As_2S_5	$AsBr_3$ (+Br_2, 67%)	71·3	2	120—140/5 hr.
Sb_2O_3	$SbBr_3$	72·6	1	110—140/3 hr.
Sb_2O_5	$SbBr_3$ (+Br_2, 86·4%)	83·0	2	110—140/3 hr.
Sb_2S_3	$SbBr_3$	72·8	1	120—140/5 hr.
TiO_2	$TiBr_4$	61·7	1	200—220/2 hr.
V_2O_5	$VOBr_2$ (+Br_2, 100%)	80·4	4	120—160/4 hr.
WO_3	$WOBr_4$	57·3	3	130—160/3 hr.

† Yields refer to *purified* (distilled or sublimed) products; manipulative losses during separation were substantial.

We now present our initial results (see Table) on reactions of boron tribromide with some oxides and sulphides. Four types of situation have been encountered. The first (1) is that in which the oxide or sulphide is converted into the bromide without change in oxidation state, and is characteristic for As_2O_3, As_2S_3, Sb_2O_3, Sb_2S_3, and TiO_2. The second (2) is that in which the formation of bromide is accompanied by reduction, and was found with As_2O_5, As_2S_5, and Sb_2O_5. The third (3) (as with P_2O_5 and WO_3) and fourth (4) (as with V_2O_5) paths are corresponding processes leading to oxybromides.

$$3M_2X_n + 2nBBr_3 \longrightarrow 6MBr_n + nB_2X_3 \qquad (1)$$

$$3M_2X_n + 2nBBr_3 \longrightarrow 6MBr_{(n-x)} + 3xBr_2 + nB_2X_3 \qquad (2)$$

$$3M_2O_n + 2(n-2)BBr_3 \longrightarrow 6MOBr_{(n-2)} + (n-2)B_2O_3 \qquad (3)$$

$$3M_2O_n + 2(n-2)BBr_3 \longrightarrow 6MOBr_{(n-2-x)} + 3xBr_2 + nB_2O_3 \qquad (4)$$

The experimental procedure is simple. Thus, boron tribromide was slowly added to the oxide or sulphide at room temperature, and in many cases (especially

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[1] W. Gerrard and M. F. Lappert, *Chem. Rev.*, 1958, **58**, 1081.

P_2O_5, As_2O_3, and As_2O_5) mixing was accompanied by evolution of heat. The mixture was heated under reflux, and volatile products were then distilled or sublimed out of the reaction flask, leaving boric oxide or sulphide as residue. Where a bromide is involatile and *unattacked by methanol*, it could conveniently be freed from boric oxide or sulphide by distilling out the latter as the trimethoxyborane–methanol azeotrope.

It appears that the interaction of boron tribromide and a metal, metalloid, or non-metal oxide or sulphide constitutes a new general method for preparing anhydrous bromides or oxybromides of those elements. Its advantages over earlier procedures are (i) the starting materials are generally available or easily made in pure form, (ii) the oxide or sulphide need not be excessively dry, since water is converted into boric oxide and hydrogen bromide, (iii) manipulations of starting materials are easy and subsequent operations not difficult, (iv) conversion is complete and the only losses are manipulative ones, (v) the conditions are mild and complicated apparatus is not required, and (vi) separation of products is simple, with the bromides or oxybromides obtained very pure. Features (i)—(iv) are similar to those described by Knox, Tyree, and their co-workers[2] as characteristic for the synthesis of anhydrous chlorides using carbon tetrachloride (a procedure which does, however, require much more forcing conditions: *ca.* 400°, under pressure). The related reactions for bromides, using carbon tetrabromide or other brominated hydrocarbons, are, however, not generally applicable,[3] although uranium(IV) bromide has been obtained by this route.[4]

Anhydrous metal chlorides have sometimes been prepared from oxides by use of non-metal chlorides. For example, uranium (IV) oxide can be converted into its chloride by means of carbon tetrachloride, hexachlorobutadiene, carbonyl chloride, phosphorus(V) chloride, thionyl chloride, or sulphur monochloride,[5] whilst uranium(VI) oxide affords $UCl_5,SOCl_2$ when treated with thionyl chloride.[6] Octachlorocyclopentene converted niobium(V), iron(III), titanium(IV), and vanadium(V) oxides into anhydrous Nb^{V}, Fe^{III}, Ti^{IV}, and V^{III} chlorides, respectively, at the normal b. p. of the solvent (285°), whilst WO_3 gave $WOCl_4$.[7] Aluminium trichloride has been widely used, but invariably under severe conditions. Thallium(III) oxide has been so converted into the univalent chloride by treatment at 300°, and a similar method was effective with aluminium bromide or iodide.[8] Actinium(III) bromide and iodide have been obtained similarly.[9] Sealed-tube reactions have provided paths to $AsCl_3$, $TiCl_4$, $NbCl_5$, $TaCl_5$, $CrCl_2$, $WOCl_4$, and $FeCl_3$.[10] Recently the aluminium trichloride method has been extended by using as a reaction medium a molten equimolar mixture of lithium, sodium, and potassium chlorides.[11]

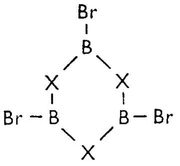
A number of features of the boron tribromide reactions are being examined further, *e.g.*, (i) a more comprehensive list of oxides and sulphides, to determine the range of application of the procedure, (ii) the stoicheiometry, (iii) intermediates, (iv) extensions of the reaction (*e.g.*, the oxyanion–boron tribromide system, as a route to bromometallate anions).

As to (ii), it is necessary to determine whether the variable reaction paths (see equations 1—4) are a function of reaction conditions and stoicheiometry, or are an intrinsic property associated with the specific oxide or sulphide. Thus, it is probable that oxybromides may at least in some cases by converted into bromides, either without or with reduction. Precedents are established in related reactions, by Frazer (see equation 5)[12] and Johannsen and Krauss (see equation 6).[13]

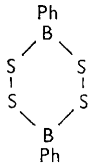
$$3SeOCl_2 + 2MCl_3 \xrightarrow{M = B \text{ or } Al} 3SeCl_4 + M_2O_3 \qquad (5)$$

$$6CrO_2Cl_2 + 4BCl_3 \longrightarrow 6CrOCl_3 + 3Cl_2 + 2B_2O_3 \qquad (6)$$

As to (iii), it is likely that oxybromides and thiabromides of boron are intermediates. The only species at present known are the boroxoles (I; X = O) and borthi-ins (I; X = S). In an attempt to prepare further intermediates, boron tribromide was refluxed with elemental sulphur, but no reaction at autogenous pressure was observed. However, with dibromophenylborane, a stable compound (II) having a novel[14] ring system was isolated and characterised. Upon hydrolysis, it afforded benzeneboronic acid, $C_6H_5B(OH)_2$.



(I)



(II)

It is important to have available a convenient method for the preparation of pure, anhydrous bromides and bromometallates, as many physical data (especially electronic and vibrational spectra, magnetic properties,

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[2] K. Knox, S. Y. Tyree, R. D. Srivastava, V. Norman, J. Y. Bassett, and J. H. Holloway, *J. Amer. Chem. Soc.*, 1957, **79**, 3358; A. Michael and A. Murphy, *Amer. Chem. J.*, 1910, **44**, 365.

[3] S. Y. Tyree, personal communication.

[4] J. Prigent, *Compt. rend.*, 1954, **238**, 102.

[5] J. J. Katz and G. T. Seaborg, " The Chemistry of the Actinide Elements," Methuen, London, 1957.

[6] H. Hecht, G. Jander, and H. Schlapmann, *Z. anorg. Chem.*, 1947, **254**, 255; D. C. Bradley, B. N. Chakravarti, and A. K. Chatterjee, *J. Inorg. Nuclear Chem.*, 1957, **3**, 367.

[7] A. B. Bardawill, F. N. Collier, and S. Y. Tyree, *J. Less-Common Metals*, 1965, **9**, 24.

[8] M. Chaigneau, M. Chastagnier, and M. Guittard, *Bull. Soc. chim. France*, 1961, 58.

[9] S. Fried, F. Hagemann, and W. H. Zachariasen, *J. Amer. Chem. Soc.*, 1950, **72**, 771.

[10] H. Schäfer, C. Göser, and L. Bayer, *Z. anorg. Chem.*, 1950, **263**, 87.

[11] R. S. Drago and K. H. Whitten, *Inorg. Chem.*, 1966, **5**, 677.

[12] M. J. Frazer, *J. Chem. Soc.*, 1961, 3165.

[13] R. B. Johannsen and H. L. Krauss, *Chem. Ber.*, 1964, **97**, 2094.

[14] R. H. Cragg and M. F. Lappert, *Organometallic Chem. Rev.*, 1966, **1**, 43.

and electric dipole moment measurements) remain to be measured and interpreted.

EXPERIMENTAL

Mole fractions are calculated on the basis of *empirical* formulæ.

Reactions of Tribromoborane.—With phosphorus(V) *oxide.* Tribromoborane (12·2 g., 0·0487 mole) was added cautiously with stirring to phosphorus(V) oxide (6·92 g., 0·0487 mole). There was a very vigorous reaction. The mixture was held at 20° for 2 hr., whereafter distillation afforded phosphoryl(V) bromide (10·32 g., 73·9%), b. p. 125°/20 mm., m. p. 54—56° (Found: Br, 83·0. Calc. for $POBr_3$: Br, 83·7%).

With arsenic(III) *oxide.* Tribromoborane (16·2 g., 0·0644 mole) was added slowly to arsenic(III) oxide (6·35 g., 0·0322 mole) at 20°. There was a very vigorous reaction. The mixture was kept at 90—120° for 3 hr. Upon distillation, tribromoborane (3·7 g., 22·81%), b. p. 90—92°, was recovered. On further distillation, arsenic(III) bromide [12·7 g., 81·4% (actual conversion)], b. p. 90°/5 mm., m. p. 32—33° (Found: Br, 67·0. Calc. for $AsBr_3$: Br, 67·19%) was obtained.

With arsenic(V) *oxide.* Tribromoborane (24·2 g., 0·0965 mole) was added slowly to arsenic(V) oxide (6·65 g., 0·029 mole) at 20°. Mixing was noticeably exothermic. The mixture was heated at 90—120° for 3 hr. Distillation afforded bromine (8·7 g., 94·1%) and arsenic(III) bromide (14·08 g., 77·1%), b. p. 90°/5 mm., m. p. 32—33° (Found: Br, 67·4%).

With arsenic(III) *sulphide.* Tribromoborane (10·73 g., 0·0428 mole) and arsenic(III) sulphide (5·3 g., 0·0214 mole) were treated substantially as described above at 130—140° for 5 hr. There was recovered tribromoborane (1·1 g., 10·3%), b. p. 90—93° (Found: B, 4·0; Br, 94·8. Calc. for BBr_3: B, 4·3; Br, 95·5%). A higher-boiling fraction was identified as arsenic(III) bromide [9·4 g., 77·6% (actual conversion)], b. p. 100—103°/14 mm., m. p. 31—33° (Found: Br, 66·9%).

With arsenic(V) *sulphide.* Tribromoborane (14·7 g., 0·0586 mole) and arsenic(V) sulphide (5·46 g., 0·0176 mole) were heated at 120—140° for 5 hr. Distillation afforded bromine (3·78 g., 66·2%) and arsenic(III) bromide (7·89 g., 71·3%), b. p. 90°/5 mm., m. p. 32—33° (Found: Br, 67·24%).

With antimony(III) *oxide.* Tribromoborane (17·2 g., 0·0683 mole) was added to antimony(III) oxide (9·93 g., 0·0341 mole) at 20°. The mixture was heated at 110—140° for 3 hr. Distillation afforded antimony(III) bromide (17·81 g., 72·6%), b. p. 135°/2 mm., m. p. 95—97° (Found: Br, 66·1. Calc. for $SbBr_3$: Br, 66·5%).

With antimony(V) *oxide.* Tribromoborane (15·7 g., 0·0626 mole) and antimony(V) oxide (6·08 g., 0·0188 mole) were heated at 110—140° for 3 hr. Distillation furnished bromine (5·2 g., 86·4%), b. p. 58—59°, and antimony(III) bromide (11·2 g., 83·0%), b. p. 135°/2 mm., m. p. 95—96° (Found: Br, 66·7%).

With antimony(III) *sulphide.* Tribromoborane (18·7 g., 0·0746 mole) was added to antimony(III) sulphide (12·67 g., 0·0373 mole) and the mixture was heated at 120—140° for 5 hr. Distillation gave antimony(III) bromide (19·6 g., 72·8%), b. p. 127—29°/1 mm., m. p. 96—97° (Found: Br, 66·4%).

With titanium(IV) *oxide.* Tribromoborane (13·4 g., 0·0535 mole) and titanium(IV) oxide (3·2 g., 0·040 mole) were heated at 200—220° for 2 hr. Distillation afforded titanium(IV) bromide (9·1 g., 61·7%), b. p. 110—114°/3 mm., m. p. 29—30° (Found: Br, 86·8. Calc. for $TiBr_4$: Br, 87·2%).

With vanadium(V) *oxide.* Tribromoborane (22·6 g., 0·0901 mole) and vanadium(V) oxide (8·2 g., 0·0450 mole) were heated at 120—160° for 4 hr. Distillation afforded bromine (7·2 g., 100%), b. p. 58—59°, vanadyl(IV) bromide (16·4 g., 80·4%), sublimed at 100—105°/15 mm., m. p. 178—180° (decomp.) (Found: Br, 70·0. Calc. for $VOBr_2$: Br, 70·6%), and an involatile residue (7·0 g.). There was some decomposition during sublimation, and some bromine was trapped at −78°.

With tungsten(VI) *oxide.* Tribromoborane (16·4 g., 0·0655 mole) and tungsten(VI) oxide (11·4 g., 0·0492 mole) reacted at 130—160° for 3 hr. Upon distillation, tungstyl(VI) bromide (14·6 g., 57·3%) sublimed at 168—172°/0·5 mm., m. p. 273—276° (Found: Br, 60·8. Calc. for $WOBr_4$: Br, 61·6%) was obtained.

With sulphur. Tribromoborane (13·7 g.) and sulphur (5·8 g.) were refluxed for 4 hr. Distillation gave the reactants essentially quantitatively.

Interaction of Dibromophenylborane and Sulphur.—Sulphur (12·04 g., 0·376 mole) was heated with dibromophenylborane (15·5 g., 0·0627 mole) at 130—160° for 7 hr. Distillation gave fractions: (*a*) b. p. 40°/20 mm. (0·9 g.), (*b*) b. p. 100—110°/20 mm. (1·9 g.), (*c*) b. p. 74—78°/0·15 mm. (2·4 g.), and (*d*) b. p. 80—100°/0·15 mm. (1·3 g.), which appeared to be mixtures and were not identified. The final fraction, b. p. 134—36°/0·1 mm. (5·7 g., 60·0%), which solidified on standing, was identified as the *cyclic boron–sulphur compound* (II) [Found: C, 47·8; H, 3·9; B, 7·1%. *M* (cryoscopic in benzene), 324. $C_{12}H_{10}B_2S_4$ requires C, 47·5; H, 3·3; B, 7·1%; *M*, 304].

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