

525. Diboron Tetrafluoride. Part II.¹ Reactions with Some Oxides and Organometallic Compounds.

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Diboron tetrafluoride reacts with oxygen difluoride to give boron trifluoride and boric oxide; there is no reaction with sulphur dioxide. Metal oxides react vigorously with diboron tetrafluoride to give boric oxide and boron trifluoride, and with $(BF)_n$ to give oxygen. Diphenylmercury is reduced by the tetrafluoride to the metal, giving phenylboron difluoride; diethylmercury and tetravinyltin yield hydrocarbons RH ($R = Et$ and $CH_2=CH$, respectively) in addition to the difluorides RBF_2 .

IN our previous report¹ of the reactions of diboron tetrafluoride with oxygen and nitric oxide, the presence of a reaction product with similarities to oxygen difluoride, but containing boron, was noted; this was referred to as "BOF." Our present study of the reaction of diboron tetrafluoride with oxygen difluoride suggests that the latter is unlikely to be present with unchanged tetrafluoride, and no further light is thrown on the constitution of "BOF;" the same small amounts of this fraction (together with silicon tetrafluoride), which were noted in our previous work, appeared in almost all the reactions reported here.

The recent report² of the reaction of boron monoxide with sulphur tetrafluoride to yield diboron tetrafluoride and thionyl fluoride prompted us to investigate the reaction of diboron tetrafluoride with sulphur dioxide, with the possibility of producing thionyl fluoride and boron monoxide, or, simply, of reduction of the sulphur dioxide. No reaction of any kind could be detected. In contrast, reaction of some solid metal oxides was vigorous and exothermic.

Attempts to prepare organodiboron compounds, B_2R_4 , from other diboron compounds have been unsuccessful,³ and instability in such compounds has been attributed to lack of electrons available for π -bond stabilisation of the molecules (when $R = alkyl$). However, tetra-allyldiboron⁴ and compounds of the type $R(Me_2N)B-B(NMe_2)R$ ($R = Me, Et, etc.$)⁵ are known, and since diboron tetrafluoride has greater thermal stability than the tetrachloride, it seemed possible that compounds $R(F)B-B(F)R$ might exist, particularly where R is a group containing π -bonds. We have therefore studied the reactions of diboron tetrafluoride with diphenyl- and diethyl-mercury, and with tetravinyltin, in an attempt to prepare such compounds.

EXPERIMENTAL AND RESULTS

Diboron tetrafluoride was prepared as previously described.¹ Oxygen difluoride was purified by pumping at -196° and then by fractionation through a trap at -183° ; it had v. p. at -196° , 1 mm. Sulphur dioxide was fractionated through a trap at -80° ; it had v. p. at -23° , 400 mm. Metal oxides were freed from occluded air and water by prolonged pumping at room temperature. Diphenylmercury was recrystallised from 1 : 1 alcohol : chloroform, and kept in the dark; it had m. p. 124° . Diethylmercury was fractionated from a trap at 20° through a 0° trap; the 0° -involatile fraction gave v. p. at 22° , 4 mm., and the correct infrared spectrum. Tetravinyltin was similarly purified, and the purity checked spectroscopically; it had v. p. at 22° , 4-5 mm.

Experiments were carried out with quantities of the order of 1 mmole, and units are in mmoles unless otherwise stated. Analyses were carried out by methods previously described.¹

¹ Part I, Holliday and Taylor, *J.*, 1962, 2767.

² Brotherton, McCloskey, and Manasevit, *Inorg. Chem.*, 1963, **2**, 41.

³ Urry, Wartik, Moore, and Schlesinger, *J. Amer. Chem. Soc.*, 1954, **76**, 5293.

⁴ Winternitz and Carotti, *J. Amer. Chem. Soc.*, 1960, **82**, 2430.

⁵ Nöth and Fritz, *Angew. Chem.*, 1961, **73**, 408; *Z. anorg. Chem.*, 1963, **324**, 129.

Oxygen Difluoride.—The results are summarised in the Table; the reaction temperature was -80° . The amounts of oxygen difluoride are approximate, because of the difficulty of condensing it quantitatively. Inflammation occurred after mixing at -80° ; mixing at lower temperatures did not prevent inflammation on warming to -80° . Boron trifluoride was a volatile product in all reactions, as was fluorine in reactions with no large excess of diboron tetrafluoride. Boron trifluoride was separated from unchanged oxygen difluoride by addition of trimethylamine, which did not react with the difluoride. Heating of the residues produced only traces of boron trifluoride; evolution of oxygen on alkaline hydrolysis indicated the presence of small amounts of oxygen difluoride. Boron recovery was satisfactory, but fluorine recovery was low.

Experiment.....	1	2	3	4	5	6
B_2F_4 added } (moles)	1.37	1.63	1.11	0.98	1.36	1.00
B_2F_4 reacted }	1.37	1.34	1.11	0.98	1.36	0.95
F_2O added } (moles)	0.57	0.59	1.56	1.31	0.79	1.09
F_2O reacted }	0.51	0.59	0.66	1.31	0.60	0.51
Reaction time (days).....	0.6	3	4	4	5	14
Reaction products (mmoles):						
F_2	—	—	—	0.44	0.04	—
BF_3	1.98	2.04	1.58	1.53	2.00	1.45
Residue, on hydrolysis * $\left\{ \begin{array}{l} O_2 \\ B(OH)_3 \\ F^- \end{array} \right.$	0.17	0.22	—	0.03	—	—
	0.85	1.04	0.46	0.88	0.84	0.55
	0.31	0.23	0.16	0.09	0.10	0.28

* Acid hydrolysis was carried out on the residues of experiments 3, 5, and 6; the remainder were hydrolysed in alkaline solution.

Sulphur Dioxide.—When sulphur dioxide (0.33) was added to diboron tetrafluoride (1.05), liquid was present at -80° and no reaction was noted, even after warming to 20° . After 7 days at -80° , the only product recovered was boron trifluoride (0.10) (expected from normal decomposition), and the sulphur dioxide remained unchanged. A tensiometric experiment at -63° gave no evidence for compound-formation.

Metal Oxides.—(a) When mercuric oxide and diboron tetrafluoride were brought together at -196° and then warmed slowly, inflammation occurred between -80° and room temperature, and much heat was liberated; mercury, boric oxide, and boron trifluoride were produced. In a typical experiment, diboron tetrafluoride (1.72) and yellow mercuric oxide (1.47) were warmed from -196° , but inflammation did not occur until 20° , when a violent reaction threw solid up the reaction vessel. Boron trifluoride (1.25) and unchanged tetrafluoride (0.36) were immediately recovered. White boric oxide was found on the walls of the reaction vessel, and heating of the residues gave only a trace (0.05) of boron trifluoride; alkaline hydrolysis permitted separation of mercury metal (0.70).

(b) When diboron tetrafluoride (1.61) and manganese dioxide (1.19) were warmed slowly from -80° , a red flash occurred at 15° , and white solid was deposited on the sides of the reaction vessel; boron trifluoride (0.67) and unchanged tetrafluoride (0.68) were recovered. A similar experiment with cupric oxide (0.77) and excess of tetrafluoride (2.25) produced a vigorous exothermic reaction at 25° , but no inflammation.

(c) Small samples of "boron monofluoride," $(BF)_n$, were produced by thermal disproportionation of the tetrafluoride, and then mixed with the metal oxide. Reaction at room temperature was immediate with manganese dioxide and with cupric oxide, but less rapid with mercuric oxide; oxygen was the only volatile product.

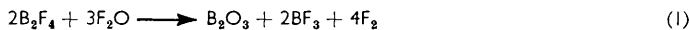
Diphenylmercury.—Reaction with diboron tetrafluoride was very slow at -80° , and even at -33° required several days for completion. The volatile reaction products were boron trifluoride and a colourless liquid, which after repeated refractionation gave m. p. -36.5° and M 122 (phenylboron difluoride has m. p. -36.2° and M 126); 0.43 mmole, on hydrolysis and addition of calcium chloride, gave calcium fluoride (0.57) and boric acid (0.55). The slightly high boron and fluorine values are attributed to traces of boron trifluoride. Hydrolysis and benzene-extraction of the grey residue left mercury metal, an aqueous layer containing no mercury, and the benzene layer containing only diphenylmercury. In a typical experiment, diboron tetrafluoride (1.15) reacted with diphenylmercury (0.98) for 6 days at -33° to give phenylboron difluoride (1.10), boron trifluoride (0.45), and mercury (0.65); the hydrolysate gave boron (0.62) and fluoride (1.01), and there was no diphenylboron fluoride.

Diethylmercury.—Reactions were carried out over the range -80° to -33° . The major volatile products were ethylboron difluoride, boron trifluoride, and ethane; minor products included methane, triethylboron, and (in some experiments) traces of ethylene. Ethylboron difluoride was identified by means of its infrared spectrum, v. p. (1.3 mm. at -84°), m. p. ($-100 \pm 5^{\circ}$), and its reaction with propionic acid, where 1.41 mmole gave ethane (1.40); separation from diboron tetrafluoride was effected by reaction of the latter with ethylene (no diboron tetrafluoride-ethylene was found in the original products). Triethylboron was identified by means of its infrared spectrum and its molecular weight (Found: M 98.4. Calc. for Et_3B : M 98.0), and was separated from ethane by treatment with trimethylamine. The residues contained mercury, but evolved no volatile material when thermally or hydrolytically decomposed. In a typical experiment, diboron tetrafluoride (1.71) reacted with diethylmercury (3.21) to give ethylboron difluoride (1.56), boron trifluoride (1.40), ethane (0.43), methane (0.09), and triethylboron (trace); the residue contained metallic mercury (1.04), and hydrolysis gave B (0.69), F (0.12), and Hg (0.30).

Tetravinyltin.—Reaction occurred slowly at -80° to give finally a red viscous oil and a grey solid. Ethylene was a major volatile product but diboron tetrafluoride-ethylene was not identified. Only a trace of boron trifluoride was formed. Vinylboron difluoride was always obtained, in variable amounts, and more of it was sometimes evolved, together with ethylene, when the non-volatile products were heated. Hydrolysis of the residues gave small amounts of hydrogen, together with ethylene in some experiments; the analysis for tin, boron, and fluoride was unsatisfactory. Separation of excess of diboron tetrafluoride from vinylboron difluoride (identified by its infrared spectrum) was effected by addition of ethylene. In a typical experiment, diboron tetrafluoride (1.99) reacted with tetravinyltin (2.72) at -80° to give ethylene (0.21) and vinylboron difluoride (0.20); heating of the residue gave more (0.82) of the latter, and boron trifluoride (0.08), and subsequent hydrolysis gave hydrogen (0.06) and ethylene (0.64).

DISCUSSION

Oxygen Difluoride.—The absence of fluorine in reactions where an appreciable excess of diboron tetrafluoride was used suggests that reaction of these compounds occurred (cf. the corresponding reaction of diboron tetrachloride with chlorine⁶). A reasonable reaction is then



giving



as the overall reaction with excess of tetrafluoride. The ratios $\text{BF}_3 : \text{B}_2\text{F}_4$ and $\text{F}_2 : \text{B}_2\text{F}_4$ for the reactions listed in the Table lie within the limits required by equations (1) and (2), but in some of these reactions the reactant ratio, $\text{B}_2\text{F}_4 : \text{F}_2\text{O}$, is greater than that required by equation (2). This implies production of boron trifluoride without participation of oxygen difluoride, probably by the disproportionation reaction

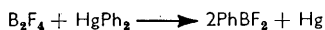


Metal Oxides.—The exothermic character of the reactions here must have produced considerable disproportionation of the kind just described; a detailed study was therefore not made, but it seems clear that, with mercuric oxide, reduction to the metal and formation of boric oxide must have occurred (as with the non-metallic oxides nitric oxide and oxygen difluoride) and yielded boron trifluoride as the major volatile product. Reactions with the other oxides followed a similar course, the order of the vigour of the reactions being that expected from the ease of oxygen liberation (by heating) from these oxides, *i.e.*, $\text{HgO} > \text{MnO}_2 > \text{CuO}$. The chief point of interest is, however, the vigorous reactions of these oxides with $(\text{BF})_n$ to give oxygen. Since diboron tetrafluoride is likely to deposit small amounts of $(\text{BF})_n$ as soon as it is allowed to warm up in a reaction vessel, reaction of the metal oxide may be initiated, to give metal (or lower oxide) and oxygen;

⁶ Apple and Wartik, *J. Amer. Chem. Soc.*, 1958, **80**, 6153.

the subsequent reaction of oxygen with the tetrafluoride would then explain any inflammation, and would produce boric oxide.¹

Organometallic Compounds.—Although these reactions were studied at low temperatures, to preserve any organoboron compounds containing B-B bonds, no evidence for such compounds was obtained. The reaction with diphenylmercury was notably simple:



with no formation of phenylmercury fluoride or of diphenylboron fluoride; some disproportionation of diboron tetrafluoride to give boron trifluoride occurred. A possible mechanism for the former reaction would be addition of the diphenylmercury molecule to the tetrafluoride molecule to give (I), followed by fission of Hg-C and B-B bonds. The



almost quantitative formation of phenylboron difluoride is in contrast to the poorer yield of ethylboron difluoride from diethylmercury; this suggests that in the adduct (I), there is some donation from the π -orbitals of the phenyl groups to the boron atoms before the Hg-C bonds break, and a transition state (II) is plausible. With diethylmercury, there is less effective boron-carbon association when the Hg-C bonds break, and the appearance of hydrocarbons suggests that ethyl radicals may have been formed; however, ethylene, expected (with ethane) as one of the disproportionation products, was found free only in traces, and no diboron tetrafluoride-ethylene, $\text{F}_2\text{B}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{BF}_2$, was recovered. The poor recovery of carbon and hydrogen in the volatile products therefore indicates that involatile, possibly polymeric, residues containing B-C and C-C bonds must have been formed. The production of small amounts of triethylboron, but no ethyl fluoride, was also unexpected, particularly since the reaction of triethylboron with a mercuric salt has been used⁷ to prepare diethylmercury.

The reaction with tetravinyltin was similar in some respects to that with diethylmercury—indeed, the two could be summarised by the statement that reduction to the metal *and* to the hydrocarbon RH (R = $\text{CH}_2=\text{CH}$ and Et, respectively) occurred. Again, other volatile products which might have arisen from the disproportionation of vinyl radicals were absent, and, even when excess of diboron tetrafluoride was used (and the excess recovered), no formation of diboron tetrafluoride-ethylene occurred, although ethylene was present in appreciable amount. The reaction of diboron tetrafluoride with ethylene is certainly slow at -80° , but since long reaction-times were used, some reaction might have been expected. A possible explanation may be found in the virtual absence of boron trifluoride; these are the only reactions in which it was *not* found in appreciable quantities. It is known⁸ that diboron tetrafluoride is stabilised against disproportionation by olefins, which need not form stable adducts with it; in the present experiments, this stabilisation, preventing formation of boron trifluoride or addition of ethylene, may have been attained by loose addition to olefinic groups in the reactants, and also in the reaction residues.

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⁷ Honeycutt and Riddle, *J. Amer. Chem. Soc.*, 1959, **81**, 2593.

⁸ Ceron, Finch, Frey, Kerrigan, Parsons, Urry, and Schlesinger, *J. Amer. Chem. Soc.*, 1959, **81**, 6368; Feeney, Holliday, and Marsden, *J.*, 1961, 356.