If the reactions of alcohols with tetraalkoxydiborons are similar to those of tetra-(amino)-diborons with hydroxylic reagents, transesterification should occur according to eq. 3.

$$(RO)_2B\text{–}B(OR)_2 + 4R'OH \longrightarrow (R'O)_2B\text{–}B(OR')_2 + 4ROH \quad (3)$$

However, the stability of boron–boron bonds under alcoholysis conditions has not been investigated thoroughly, and B–B cleavage to give trialkoxyboranes might be expected also. Hydrolysis data[4] on tetraalkoxydiborons do not give a clear basis for prediction of B–B bond stability in transesterification reactions: tetraethoxydiboron and tetraisopropoxydiboron reacted with water to give quantitative yields of tetrahydroxydiboron; tetramethoxydiboron underwent extensive B–B cleavage under similar conditions. In boron hydrides containing B–B bonds, reaction of tetraborane or pentaborane-9 with alcohol was reported[5] to give rapid cleavage of the B–B bonds in these molecules. Tetraalkoxydiboron intermediates were postulated in these reactions. Thus, some evidence exists which suggested that B–B cleavage and trialkoxyborane formation might occur in the reaction of tetraalkoxydiborons with alcohols (eq. 4 and 5).

It now has been shown that transesterifications of the type shown in eq. 3 can be carried out without apparent B–B cleavage.

Experimental

Conversion of Tetramethoxydiboron to Tetraisopropoxydiboron.—Tetramethoxydiboron (4.0 g., 0.0275 mole) was dissolved in 25 ml. of petroleum ether (b.p. 60–65°). Isopropyl alcohol (7.20 g., 0.120 mole) was added and the solution refluxed for 65 hr. Solvent and volatile materials then were removed by distillation at 30° (0.3 mm.), leaving 3.02 g. (42.7% yield) of residual tetraisopropoxydiboron, $n^{26}\text{D}$ 1.3971 [lit.[6] for $B_2(O\text{-}i\text{-}C_3H_7)_4$, $n^{25}\text{D}$ 1.3970]. The infrared spectrum was identical with an authentic sample prepared by published[6] procedures.

Anal. Calcd. for $B_2(O\text{-}i\text{-}C_3H_7)_4$, $C_{12}H_{28}B_2O_4$: B, 8.39. Found: B, 8.41.

Conversion of Tetramethoxydiboron to Tetraethoxydiboron (a).—Tetramethoxydiboron (4.0 g., 0.0275 mole) was dissolved in ethanol (10.12 g., 0.22 mole). The solution was distilled through a 3-in. Vigreux column, gradually reducing the pressure so that the last distillate was removed at 30° (2 mm.). The total distillation time was 1 hr.; the pot temperature varied from 35 to 45°. Tetraethoxydiboron, 3.50 g. (63% yield), remained as residue in the distillation flask, $n^{26}\text{D}$ 1.3953 [lit.[6] for $B_2(OC_2H_5)_4$, $n^{25}\text{D}$ 1.3960]. The infrared spectrum was identical with an authentic sample prepared by published[6] procedures.

Anal. Calcd. for $B_2(OC_2H_5)_4$, $C_8H_{20}B_2O_4$: B, 10.74. Found: B, 10.83.

(b).—Tetramethoxydiboron (0.7987 g., 5.49 mmoles) was condensed into a trap in a high vacuum system, and ethanol (9.97 g., 219.6 mmoles) condensed into the same trap at −196°. The trap was isolated from the system, warmed to 55–60° for 1 hr., then again cooled to −196°. No observable pressure of non-condensable gas was registered on the manometer. The temperature of the liquid then was raised to 0° and volatiles were removed. The residual liquid, 0.5695 g., showed no observable vapor pressure at 25° (pressure of tetramethoxydiboron at 25° = 7.2 mm.). Its infrared spectrum matched tetraethoxydiboron (51% yield), $n^{25}\text{D}$ 1.3950 [lit.[6] for $B_2(OC_2H_5)_4$, $n^{24}\text{D}$ 1.3960; for $B_2(OCH_3)_4$, $n^{26}\text{D}$ 1.3888].

Reaction of Tetramethoxydiboron with *t*-Butyl Alcohol.—Tetramethoxydiboron (3.802 g., 0.0261 mole) was added to *t*-butyl alcohol (16.14 g., 0.218 mole) which had been freshly distilled from calcium oxide. Low boiling constituents were removed by distillation through a short Vigreux column at 140 mm. The residue, 3.64 g., was distilled through a 20-cm. spiral wire column to give the following fractions: (A) 1.08 g. of clear liquid, b.p. 47–49° (4 mm.); (B) 0.90 g. of clear liquid, b.p. 47° (2 mm.); (C) white solid residue. Infrared spectra of the products showed no absorption in the 4–5 μ region. All fractions reduced silver nitrate solution.

Anal. Calcd. for $B_2(OCH_3)_4$, $C_4H_{12}B_2O_4$: B, 14.84; for $B_2(O\text{-}t\text{-}C_4H_9)_4$, $C_{16}H_{36}B_2O_4$: B, 6.89. Found: (A) B, 9.88; (B) B, 8.43; (C) B, 22.4.

Results and Discussion

Tetramethoxydiboron was converted to tetraethoxydiboron and to tetraisopropoxydiboron by transesterification with the appropriate alcohol, as shown in eq. 3. If some concomitant B–B cleavage occurred, an intermediate B–H compound would be formed, which might be expected to yield hydrogen under the reaction conditions[7] (1 hr. at 60°), according to eq. 4 and 5. The reaction of tetramethoxydiboron with ethanol therefore

$$(CH_3O)_2B\text{–}B(OCH_3)_2 + C_2H_5OH \longrightarrow (CH_3O)_2BOC_2H_5 + H\text{–}B(OCH_3)_2 \quad (4)$$

$$H\text{–}B(OC_2H_5)_2 + C_2H_5OH \longrightarrow (C_2H_5O)_3B + H_2 \quad (5)$$

was carried out under conditions which would allow detection of small quantities of hydrogen, but no trace could be found.

The absence of hydrogen formation during ethanolysis indicates complete retention of the B–B structure, even for the by-products, which presumably are mixed alkoxydiboron compounds. This is in contrast to the interpretations presented for tetraborane and pentaborane ethanolysis, and suggests that the B–B cleavage observed in those cases occurred somewhere along the reaction coördinate prior to complete substitution of the B–B units, and that tetraalkoxydiborons were not intermediates in the reaction.

Steric limitations in the transesterification reaction were demonstrated in the reaction of *t*-butyl alcohol with tetramethoxydiboron: no $B_2(O\text{-}t\text{-}C_4H_9)_4$ was obtained, although the products did retain B–B bonds. Presumably, mixed methoxy-*t*-butoxydiborons were produced.

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(4) A. L. McCloskey, R. J. Brotherton, and J. L. Boone, *J. Am. Chem. Soc.*, **83**, 4750 (1961).

(5) I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **63**, 1319 (1959).

(6) R. J. Brotherton, A. L. McCloskey, J. L. Boone, and H. M. Manasevit, *J. Am. Chem. Soc.*, **82**, 6245 (1960).

(7) Shapiro and Weiss (ref. 5) report the rate of formation of $B(OC_2H_5)_3$ from $HB(OC_2H_5)_2$ to be slow at room temperature.

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The Preparation of Some Unsymmetrical Tri-(amino)-boranes

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A variety of tri-(amino)-boranes derived from both

TABLE I

PREPARATION AND PROPERTIES OF UNSYMMETRICAL TRI-(AMINO)-BORANES

Amine	Amine/ $B[N(CH_3)_2]_3$ molar ratio	Product	B.p., °C. (mm.)	Yield, %	Refractve index		Analyses C	H	N	B
$(n\text{-}C_3H_7)_2NH$	1/1	$(n\text{-}C_3H_7)_2NB[N(CH_3)_2]_2$	32 (0.05)	48	24.5° 1.4485	Calcd.	60.3	13.3	21.1	5.45
						Found	60.65	13.42	21.34	5.67
$C_6H_5NH_2$	1/1	$C_6H_5NHB[N(CH_3)_2]_2$	72–75 (0.1)	40	24.5° 1.5353	Calcd.	62.9	9.51	22.0	5.68
						Found	61.63	9.96	22.8	5.92
$C_6H_5NHCH_3$	1/1	$C_6H_5\overset{CH_3}{\overset{\vert}{N}}B[N(CH_3)_2]_2$	68–69 (0.1)	78	24.5° 1.5338	Calcd.	63.9	9.83	20.5	5.28
						Found	63.02	9.97	19.86	5.36
$(n\text{-}C_3H_7)_2NH$	2/1	$[(n\text{-}C_3H_7)_2N]_2BN(CH_3)_2$	75 (0.2)	38	22° 1.4530	Calcd.	65.9	13.4	16.45	4.25
						Found	66.08	13.76	15.77	4.34

primary and secondary amines have been reported. In all earlier work these derivatives have been symmetrical; *i.e.*, the boron atoms have been bonded to three identical amine substituents. However, Aubrey, *et al.*,[1] recently have reported the first examples of unsymmetrical tri-(amino)-boranes. These materials were prepared by the reaction of chloro-bis-(diisopropylamino)-borane with either primary or secondary amines as shown in eq. 1. In some cases triethylamine was

$$ClB[N(i\text{-}C_3H_7)_2]_2 + 2RR'NH \longrightarrow RR'NB[N(i\text{-}C_3H_7)_2]_2 + RR'NH\cdot HCl \quad (1)$$

$$R = \text{alkyl};\ R' = \text{alkyl or hydrogen}$$

used to complex the hydrogen chloride formed rather than a second molar equivalent of the amine reactant.

We now wish to report an alternative method which can be used for the preparation of related unsymmetrical tri-(amino)-boranes derived from aliphatic and aromatic amines. This general method is based on the transamination reaction reported earlier[2] for the preparation of symmetrical tri-(amino)-boranes (eq. 2).

$$B(NR_2)_3 + 3R_2'NH \longrightarrow B(NR_2')_3 + 3R_2NH \quad (2)$$

The partial transamination of tris-(dimethylamino)-borane with equimolar amounts of di-*n*-propylamine, aniline, and N-methylaniline proceeded readily to give the unsymmetrical products shown in eq. 3.

$$B[N(CH_3)_2]_3 + RR'NH \longrightarrow RR'NB[N(CH_3)_2]_2 + (CH_3)_2NH \quad (3)$$

$$\text{I, } R = R' = n\text{-}C_3H_7;\ \text{II, } R = C_6H_5,\ R' = H;\ \text{III, } R = C_6H_5,\ R' = CH_3$$

The comparable replacement of a dimethylamino group by diisopropylamine proved to be impossible under similar reaction conditions even in the presence of an amine hydrochloride catalyst.[2] Earlier attempts to transaminate tris-(diethylamino)-borane and tris-(isopropylamino)-borane also were unsuccessful.[2] Aubrey, *et al.*,[1] have discussed the relative importance of steric and electronic effects in related reactions (eq. 1) and conclude from their data that electronic effects may be significant in these exchange and hydrolysis reactions involving tri-(amino)-boranes. Their results, as well as those presented here, also can be explained on the basis of steric effects.

The displacement of two molar equivalents of dimethylamine by *n*-propylamino groups also has been carried out as shown in eq. 4.

$$B[N(CH_3)_2]_3 + 2(n\text{-}C_3H_7)_2NH \longrightarrow (CH_3)_2NB[N(n\text{-}C_3H_7)_2]_2 + 2(CH_3)_2NH \quad (4)$$

All of these unsymmetrical tri-(amino)-boranes, as well as those prepared earlier,[1] could be distilled without apparent decomposition or disproportionation.

Experimental

All experiments were carried out in an atmosphere of dry nitrogen. Elemental analyses for carbon, hydrogen, and nitrogen were done by Dr. Adelbert Elek, Los Angeles, California. Boron was determined by the Parr-bomb fusion method described by Hunter, *et al.*[3]

Preparation of Unsymmetrical Tri-(amino)-boranes.—The same general experimental procedure was used in preparing each of the tri-(amino)-boranes described in Table I. A mixture of the stoichiometric amounts of amine and tris-(dimethylamino)-borane was heated in refluxing toluene for 20–30 hr. Each reaction was terminated when the theoretical amount of dimethylamine was evolved. This amine was analyzed by sweeping the volatile reaction products in a stream of dry nitrogen through a water-cooled reflux condenser into standard acid. The unsymmetrical tri-(amino)-boranes were recovered by distillation of the reaction mixture. Subsequently they were fractionated and shown to be single compounds by vapor phase chromatography.

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Effect of Concentration on the Partition of Osmium Tetroxide between Aqueous Solutions and Carbon Tetrachloride

BY GERALD GOLDSTEIN

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The partition ratio of OsO_4 between aqueous solutions

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(1) Operated for the United States Atomic Energy Commission by Union Carbide Corporation.