evaporating an aqueous solution of the *trans* complex was followed but in every instance a green glass-like residue was obtained. It may be argued that the *cis* isomer is not obtained due to the use of *trans* salts which have not been completely freed of hydrogen chloride. However, even when the residue was redissolved and the evaporation procedure repeated several times in an attempt to liberate the slight excess of hydrogen chloride, there still was no sign of any purple *cis* compound.

Experimental

Substituted Ethylenediamines.—The anhydrous N-alkylethylenediamines were obtained from Mr. R. Kent Murmann.[9] The dihydrochlorides of isobutylenediamine and tetramethylethylenediamine were furnished by Dr. Yun-Ti Chen and R. Kent Murmann, respectively. These hydrochlorides were converted to the free amine by the treatment of concentrated aqueous solutions of the salt with an excess of solid sodium hydroxide. The mixture was in turn extracted with ether and finally the ether removed with the aid of a water aspirator. The residual-free amine was used without further purification.

trans-Dichlorobis-(N-alkylethylenediamine)-cobalt(III) Chlorides.—The procedure described here for the preparation of *trans*-dichlorobis-(N-methylethylenediamine)-cobalt(III) chloride was likewise employed in the synthesis of corresponding ethyl and *n*-propyl derivatives. A solution of 7.5 g. of N-methylethylenediamine in 70 cc. of water was added to 50 cc. of a solution containing 16 g. of cobalt(II) chloride hexahydrate. A stream of air previously washed with water was slowly bubbled through the dark brown opaque reaction mixture for eight hours. At the end of this time 35 cc. of concentrated hydrochloric acid was added to the mixture and the acid solution was concentrated on a steam-bath. The green viscous concentrate was dissolved in 20 cc. of methanol and absolute ethanol was added just short of causing the separation of a green oil (approximately 75 cc.). The solution was allowed to stand overnight during which time a green crystalline product separated. This salt was collected on a filter washed with absolute ethanol followed by ether and dried overnight at 110°. A yield of 7 g. or 40% based on the diamine was obtained. *Anal.* Calcd. for [Co(N-Meen)₂Cl₂]Cl·0.1HCl: Cl, 37.1. Found: Cl, 37.3.

In the same manner a yield of 28% of *trans*-dichlorobis-(N-ethylethylenediamine)-cobalt(III) chloride was isolated. *Anal.* Calcd. for [Co(N-Eten)₂Cl₂]Cl·0.6HCl: Cl, 35.2. Found: Cl, 35.4.

The yield of *trans*-dichlorobis-(N-*n*-propylethylenediamine)-cobalt(III) chloride was 36%.

Anal. Calcd. for [Co(N-*n*-Pren)₂Cl₂]Cl·0.5HCl: Cl, 32.2. Found: Cl, 32.2.

trans-Dichlorobis-(isobutylenediamine)-cobalt(III) Chloride.—A solution of 5 g. of isobutylenediamine in 15 cc. of water was added to that of 5 g. of cobalt(II) chloride in 20 cc. This mixture was then treated with 5 cc. of 30% hydrogen peroxide. A vigorous exothermic reaction occurred accompanied by the voluminous evolution of oxygen. After standing for 1 hr. at 60° the reaction mixture was made acid by the addition of 15 cc. of concentrated hydrochloric acid. This solution was concentrated on a steam-bath until crystals began to separate at which time the concentrate was removed from the bath and allowed to stand at room temperature overnight. The crystalline product was finally collected on a filter, washed with absolute ethanol and ether, then dried overnight at 110°. The product weighed 2 g. or was obtained in only a 19% yield. *Anal.* Calcd. for [Co-(iso-bn)₂Cl₂]Cl·0.5HCl: Cl, 33.7. Found: Cl, 33.9.

trans-Dichlorobis-(tetramethylethylenediamine)-cobalt-(III) Chloride.—A small amount of crystalline material separated upon the addition of 5 g. of tetramethylethylenediamine in 10 cc. of water to a 20-cc. solution containing 5 g. of cobalt(II) chloride. However, this substance is completely dissolved during the gradual addition of 5 cc. of 30% hydrogen peroxide to the mixture. Unlike the procedure followed above this reaction mixture did not yield the desired *trans* complex when treated directly with concentrated hydrochloric acid. Instead it was found necessary to first

allow the solution to concentrate to dryness at 60°. This residue was then extracted with 10 cc. of concentrated hydrochloric acid and the less soluble green salt collected on a filter. This crystalline material was dissolved in a minimum amount of methanol and then an excess of ether was added to the solution. After standing in an ice–salt-bath for several hours, the green product was collected, washed with ether and dried overnight, at 110°. The dry salt weighed 3.5 g. or was obtained in a 39% yield. *Anal.* Calcd. for [Co(tetra-Meen)₂]Cl₂·0.6HCl: Cl, 30.5. Found: Cl, 30.6.

Spectral Measurements.—All measurements were made with a Beckman model DU spectrophotometer in silica cells having a 1-cm. light path. Extinction coefficients were calculated from the familiar equation

$$\epsilon = 1/cd \, \log_{10} (I_0/I)$$

Methanol was used as a solvent and measurements were made at room temperature.

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The Behavior of Tetraborane toward Trimethylamine and Ethanol

BY ANTON B. BURG AND F. G. A. STONE

In the search for more knowledge of the chemistry of tetraborane (B₄H₁₀)—especially with reference to structural implications—we have found that it reacts according to the equation B₄H₁₀ + (3 + x) (CH₃)₃N → 3(CH₃)₃NBH₃ + BH·x(CH₃)₃N when it is added to trimethylamine (excess) dissolved in tetrahydrofuran at −78°. A similar, but less stoichiometric, result was obtained when the solvent was omitted, or when a deficiency of trimethylamine was used. The value of x ranged from 0.54 to 0.37; this trimethylamine was retained *in vacuo* at room temperature, in the white or yellowish polymeric solid. Non-volatile B–H material was obtained also when tetraborane was allowed to react with an amount of ethanol too small for complete solvolysis, forming also hydrogen, diethoxyborine and triethyl borate.

From these results, it appears that tetraborane behaves like diborane, except that it furnishes three BH₃ groups for reaction, instead of two, and leaves polymeric material as a by-product. It is difficult to conceive of a B₄H₁₀ structure in which three essentially intact BH₃ groups are attached to a BH unit by conventional bonds; hence the easy delivery of three BH₃ groups may well be due to a very labile structure which shifts easily to make them available for reaction. In fact, it is possible to write a structure based upon the principles recognized in B₅H₉,[1,2] such that three BH₃ groups would result solely from the breaking of B–H–B bridge bonds; and such a structure is consistent with preliminary results of the electron-diffraction study of tetraborane.[3]

In none of our experiments was it possible to find any evidence of compounds involving a covalent B–B bond of unit order. It appears that any unique B–B bond in tetraborane must be extremely

(9) F. Basolo and R. K. Murmann, THIS JOURNAL, 74, 2373 (1952).

(1) K. Hedberg, M. E. Jones and V. Schomaker, THIS JOURNAL, 73, 3538 (1951).

(2) W. J. Dulmage and W. N. Lipscomb, *ibid.*, 73, 3539 (1951).

(3) Private communication from K. Hedberg and V. Schomaker at the California Institute of Technology.

labile, or of order less than unity, or both. Also, since tetraborane furnishes three BH₃ groups per molecule, for reaction with trimethylamine, it would appear that the experimental facts concerning its ammonia chemistry[4] require an even more thorough reinterpretation than would be obvious from the intervening work on ammoniated diborane.[5]

Experimental Part

Preparation of Tetraborane.—Pure tetraborane was prepared by the action of hydrogen upon the unstable pentaborane B_5H_{11}, during ten minutes at 100°,[6] followed by careful fractionation and a check of the vapor tension of the product at 0°.[7] The B_5H_{11} was easily obtained by flow-heating of diborane at 120°,[6] using the apparatus indicated by Fig. 1. This demountable attachment to the vacuum system operated much in the manner of the original fixed apparatus, but was far more convenient.

Reaction of Tetraborane with Trimethylamine.—A 41.1-cc. (gas at S.C.) sample of B_4H_{10} was added in five equal portions over a period of 5 hours, to 185 cc. (gas at S.C.) of $(CH_3)_3N$ dissolved in 1.7572 g. of tetrahydrofuran. The mixture was magnetically stirred between additions of B_4H_{10}, and subsequently for a period of 72 hours. During the first 48 hours, the temperature was −78°; thereafter it was raised gradually to −30°, with evolution of 1.26 cc. of hydrogen. The solvent was then removed and separated by fractional condensation (through −45° and trapped at −78°; weight 1.7616 g.), and the other components were brought together again in the reaction tube; during 15 hours at 0°, the recoverable $(CH_3)_3N$ fell from 48.7 to 46.8 cc.

The volatile solid was identified as $(CH_3)_3NBH_3$ by its melting point (94.5–95°) and vapor tensions (77.2 mm. at 96.9° or 48.3 mm. at 86.8°—1% above literature values)[8] as well as by a hydrolytic analysis (31.6 cc. gas at S.C. yielded 90.8 cc. of H_2 and 32.9 cc. of B calcd. as gas atoms). Its weight was equivalent to 122.0 cc. of standard gas, so that the ratio $B_4H_{10}:(CH_3)_3N$ (used):$(CH_3)_3NBH_3$ was 1:3.37:2.98. Hence the residual solid had the composition $BH·0.37(CH_3)_3N$.

Preliminary experiments had shown that this solid was not entirely hydrolyzed by aqueous HCl alone; hence in this case it was first heated with ethanol in a sealed tube (110°), yielding 51.4 cc. of hydrogen, and then during 15 hours with dilute HCl at 110° it gave a further 3.16 cc. of hydrogen. Since the hydrogen was expected to amount to 82.2 cc., and since the boric acid titration gave only 32.3 cc. of B-gas instead of 41.1, it was evident that the hydrolysis is very difficult to complete. After the indicated treatment, the odor of B–H solids persisted.

In a second experiment very like the one just described, the ratio $B_4H_{10}:(CH_3)_3N$ (used):$(CH_3)_3NBH_3$ was found to be 1:3.54:2.98.

In two experiments in which no solvent was used, such ratios were 1:2.98:2.49 and 1:2.86:2.54, respectively. The non-volatile white or yellowish solids failed to react with either trimethylamine or diborane, the latter having been used in an attempt to regain tetraborane from any possible amine-complex of a B–B bonded material.

Reaction of Tetraborane with Ethanol.—The action of a deficient proportion of ethanol upon tetraborane at −78° was undertaken in the hope of obtaining a volatile B–B linked compound. No such substance could be obtained in any of a considerable number of experiments; instead, about 13% of the boron from the unrecovered B_4H_{10} appeared in a colorless polymer, evidently containing ethoxy groups, while the rest was recovered as di- and triethoxyborines and a trace of diborane. In a typical experiment, 97.0 cc. of ethanol and 22.4 cc. of B_4H_{10} (gases at S.C.) were mixed at −78°, yielding 92.1 cc. of H_2 during 60 hours at that temperature. Fractional condensation then gave 0.55 cc. of B_2H_6 and 11.8 cc. of B_4H_{10} (confirmed by hy-

(4) A. Stock, E. Wiberg and H. Martini, *Ber.*, **63B**, 2931 (1930).

(5) H. I. Schlesinger and A. B. Burg, THIS JOURNAL, **60**, 290 (1938).

(6) A. B. Burg and H. I. Schlesinger, *ibid.*, **55**, 4009 (1933).

(7) A. Stock and E. Kusz, *Ber.*, **56B**, 795 (1923).

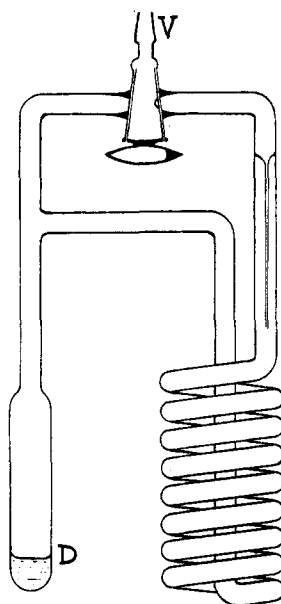(8) A. B. Burg and H. I. Schlesinger, THIS JOURNAL, **59**, 785 (1937).

Fig. 1.—Diborane from D at −78° goes through the coil at 120° and is trapped at −196° in the vacuum system beyond the joint V. For further runs, the stopcock (Apiezon L grease) is turned the other way and the diborane is distilled back to D, leaving the higher boranes in the main system.

drolysis to yield boric acid and hydrogen in amounts corresponding to the stated gas volumes); a further 0.4 cc. of B_4H_{10} was demonstrated as excess $B(OH)_3$ and H_2 from the hydrolysis of the $(C_2H_5O)_2BH$ fraction; it had been shown by work with a known mixture, that a trace of B_4H_{10} is very difficult to remove from $(C_2H_5O)_2BH$ by distillation methods alone. The $(C_2H_5O)_2BH$ amounted to 13.6 cc., and the $(C_2H_5O)_3B$ to 19.8 cc. (gases at S.C.). A fraction of $(C_2H_5O)_2BH$, which was purified after recovering from the $(C_2H_5O)_3B$ fraction, showed a vapor tension of 36.5 mm. at 0° (literature 37.5).[9] The glassy solid, remaining in the original reaction tube, was hydrolyzed to form 5.5 cc. of H_2 and $B(OH)_3$ equivalent to 5.4 cc. of B-gas. Thus it appeared that 10.2 cc. of B_4H_{10} had reacted to form 92.1 cc. of H_2, 0.55 cc. of B_2H_6, 13.6 cc. of $(RO)_2BH$, 19.8 cc. of $(RO)_3B$ and 5.4 cc. of BH material. This result would account for 98% of the B and 102% of the H_2 which would correspond to the hydrolysis of 10.2 cc. of B_4H_{10}.

(9) H. C. Brown, H. I. Schlesinger and A. B. Burg, *ibid.*, **61**, 676 (1939).

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Interactions of the Aminobenzoate Ions and Serum Albumin[1]

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It has been shown that the anions derived from methyl red and two of its isomers exhibit differences in the extents of their interactions with bovine and human serum albumins. The anion derived from "*meta*-methyl red" (4′-dimethylaminoazobenzene-3-carboxylic acid) was found to react with these two proteins to a greater extent than the anions derived from either of its isomers, methyl red or "*para*-methyl red" (4′-dimethylaminoazobenzene-2-carboxylic acid and 4′-dimethylaminoazobenzene-4-carboxylic acid, respectively).[2] Preliminary

(1) Supported by a grant-in-aid from the American Cancer Society upon recommendation of the Committee on Growth of the National Research Council.

(2) I. M. Klotz, R. K. Burkhard and J. M. Urquhart, *J. Phys. Chem.*, **56**, 77 (1952).