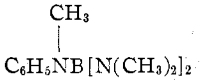
TABLE I

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	 $\overset{\displaystyle CH_3}{\overset{\vert}{C_6H_5N}}B[N(CH_3)_2]_2$	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

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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.

and CCl_4 has been determined for initial OsO_4 concentrations of 10^{-3} to 10^{-4} M.[2,3] Polymerization of OsO_4 into tetramers in CCl_4 also has been reported,[4] but this conclusion has been criticized.[5] Because polymerization of OsO_4 would cause the partition ratio to be concentration dependent, a study of the distribution of OsO_4 as a function of concentration was made using osmium-191 tracer. The results show no concentration dependence over a wide range and are in agreement with the previously reported values for the partition ratio of OsO_4.

Experimental

Reagents.—A standard OsO_4 solution, 4.43×10^{-3} M, in 0.1 N H_2SO_4 was prepared by dissolving 0.5 g. of analytical reagent grade perosmic acid (Mallinckrodt No. 2768) in 500 ml. of 0.1 N H_2SO_4 and standardizing this solution by ultraviolet spectrophotometry.[6]

Osmium-191 tagged solutions were prepared by adding osmium-191 (available from Oak Ridge National Laboratory) to 10 ml. of standard osmium solutions. Initial experiments indicated that not all the active osmium was present as OsO_4, and, therefore, this solution was extracted five times with 10 ml. of analytical reagent grade CCl_4, a sufficient number of times to remove all the inactive OsO_4. The extracts then were diluted to a specific volume with CCl_4 to provide solutions of known OsO_4 concentration and containing tracer osmium as OsO_4. In one experiment no inactive osmium was added to the tracer. The radiochemical purity of these solutions was checked.

Extraction Procedure.—Portions of the tagged OsO_4 solutions in CCl_4 (10 ml.) were equilibrated with an equal volume of either distilled, de-ionized water or 1.0 N $NaClO_4$ by mechanical stirring for 10 min. Aliquots of both phases were withdrawn, placed in a 10 × 75 mm. Pyrex tube with a cork stopper, and immediately counted in a well-type γ-scintillation detector for a sufficient length of time so that the standard deviation was less than 1%. It was found that after several hours the osmium activity tended to accumulate in the cork. Material balances indicated no loss of osmium activity during the extraction.

Results and Discussion

Data for the distribution of OsO_4 at the tracer level and at other concentration levels are presented in Table I. The results show no dependence on the osmium concentration and are in agreement with previously reported values of 12.3[2] and 13.0[3] at zero ionic strength and 14.8[3] at 1.0 M ionic strength. Assuming that polymerization is negligible in 10^{-9} M OsO_4 solutions in CCl_4, it is apparent that any polymerization in more concentrated solutions also must be very small.

TABLE I

PARTITION RATIO OF OsO_4 AT VARIOUS CONCENTRATION LEVELS

Initial concn. of OsO_4 in CCl_4, M	D = (c.p.m./ml.) org./(c.p.m./ml.) aq. Ionic strength 0.0	1.0
$\sim 10^{-9}$	12.4	14.7
8.86×10^{-6}	11.9	14.4
8.86×10^{-5}	12.2	14.2
8.86×10^{-4}	12.1	15.0
Average	12.2	14.6

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Correspondence

π-Bonding in Transition Metal Complexes

Sir:

The two types of π-bonding in transition metal complexes commonly are referred to as ligand-to-metal and metal-to-ligand. In the first instance the more stable π-molecular orbital for an interacting metal–ligand π-orbital pair mainly is located on the ligand, and in the second instance the more stable π-molecular orbital mainly is located on the metal. For octahedral complexes, there are three metal d-orbitals of the π-type; thus it is possible to make a total of three pure π-bonds ($^1/_2$ for each ligand).

For distorted octahedral complexes, the principal problem is in describing how the three d_π-orbitals are distributed among the ligands. In recent papers, we have considered the electronic structures of metal complexes exhibiting extremes of ligand-to-metal (MO oxycations)[1–3] and metal-to-ligand (M–NO nitrosyls)[4,5] π-bonding In sorting out the π-bonding in these distorted octahedral complexes, we formulated the rule given below.

For distorted octahedral complexes with tetragonal symmetry (ML_5X), nearly all the π-bonding is axially directed and involves the metal d_{xz} and d_{yz} orbitals. The stronger axial π-bonding may be either M–X or M–L, depending on whether the π-orbital energies of X or L more closely approximate the metal d_π orbital energies. It is a good approximation to neglect planar π-bonding and approximate the metal d_{xy} orbital as non-bonding.

In the case of vanadyl complexes, the optical spectral,[1,6] e.s.r.,[1,6] and the infrared[7] evidence, as well as

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