The excess sodium hydride was filtered off and 50 ml. of hexane was added. Sodium diethylaluminum hydride was found to be less soluble than the sodium triethylaluminum hydride in the toluene–hexane mixture. Recrystallization from the toluene solution by the addition of hexane gave a product melting at 83–85°, with specific conductivity, K_{100}, of 0.0358 ohm^{-1} cm.$^{-1}$.

Anal. Calcd. for $NaAl(C_2H_5)_2H_2$: Na, 20.89. Found: Na, 20.55.

Sodium triisobutylaluminum hydride was prepared by heating 2.3 g. (0.10 mole) of sodium hydride and 16.0 g. (0.08 mole) of triisobutylaluminum at 125–150° for 5 min. The mixture was cooled to room temperature, 200 g. of hexane was added, and the excess sodium hydride was removed by filtration. The hexane was removed by vacuum distillation to produce a white solid product.

Anal. Calcd. for $NaAl(i\text{-}C_4H_9)_3H$: Al, 12.14; Na, 10.34. Found: Al, 12.44; Na, 10.94.

Sodium tetraethylaluminum was prepared from triethylaluminum and a sodium dispersion.[10] Sodium pellets (18.0 g., 0.78 mole) were dispersed in 500 ml. of toluene with vigorous stirring. Triethylaluminum (86 g., 0.75 mole) was slowly added to the dispersion at 105–110° and refluxed for 90 min. The by-product aluminum and excess sodium were allowed to settle and the clear solution was drawn up into an evacuated flask. On cooling, a white solid precipitated from this solution. The solid material was filtered, washed with dry hexane, and dried at room temperature under vacuum; m.p. 122–124° (uncorrected).[11]

Anal. Calcd. for $NaAl(C_2H_5)_4$: Al, 16.23; Na, 13.84. Found: Al, 16.23; Na, 14.49.

Reactions of Trialkylaluminum Hydrides with Acetylene.—Acetylene was bubbled for 1–3 hr. through 20–25 g. of sodium triisobutylaluminum hydride dissolved in hexane at 0°. The reaction also occurs in toluene and *n*-octane. Hydrogen was evolved. The solvent was removed and a white crystalline solid was obtained which decomposed above 200° without melting.

Anal. Calcd. for $Na(i\text{-}C_4H_9)_3AlC\equiv CAl(i\text{-}C_4H_9)_3Na$: Al, 11.6; Na, 9.86. Hydrolysis gas composition: H_2, 0.0; $i\text{-}C_4H_{10}$, 85.7; C_2H_2, 14.3. Found: Al, 11.3; Na, 10.5. Gas: H_2, 0.0; $i\text{-}C_4H_{10}$, 87.2; C_2H_2, 12.8.

A similar treatment was given to sodium triethylaluminum hydride in toluene at 0°.

Anal. Calcd. for $Na(C_2H_5)_3AlC\equiv CAl(C_2H_5)_3Na$: Al, 18.1; Na, 15.4. Hydrolysis gas composition: H_2, 0.0; C_2H_6, 85.7; C_2H_2, 14.3. Found: Al, 17.4; Na, 14.6. Gas: H_2, 0.5; C_2H_6, 85.8; C_2H_2, 13.7.

Preparation of Sodium Triethylaluminum Hydride.—Sodium tetraethylaluminum (20 g., 0.12 mole) and 2.3 g. of 95% pure sodium aluminum hydride (0.04 mole) were heated at 80–100° for 10 min. The resulting product was completely soluble (except for impurities present in $NaAlH_4$) in both toluene and benzene, from which it was recrystallized. The compound had the same melting point, solubility in various solvents, and conductivity as the one prepared by the Ziegler methods[6,7]: m.p., 57–59° (uncorrected); $K_{100} = 0.0281$ ohm^{-1} cm.$^{-1}$.

Preparation of Sodium Diethylaluminum Hydride.—An equimolar mixture of sodium tetraethylaluminum (15 g., 0.09 mole) and sodium aluminum hydride (5.1 g., 95% pure) was heated at 90–100° for 10 min. The product was completely soluble (except for impurities in $NaAlH_4$) in both toluene and benzene and could be recrystallized by adding hexane to the toluene or benzene solution; m.p. 83–85° (uncorrected); $K_{100} = 0.0364$ ohm^{-1} cm.$^{-1}$.

Preparation of Triethylaluminum Adducts of Lithium Aluminum Hydride and their Redistribution Products.[12]—Lithium aluminum hydride and triethylaluminum in mole ratios of 1 mole of lithium aluminum hydride to 2, 3, and 4 moles of triethylaluminum were heated at 80° for 1 hr. At the end of this time the lithium aluminum hydride had gone into the liquid phase. Since no solvents were used, the materials were filtered while hot to remove impurities (arising from the $LiAlH_4$). When more than 4 moles of triethylaluminum was used, a second liquid phase formed.

The $LiAlH_4 \cdot 2Al(C_2H_5)_3$ product melted sharply at 29° (uncorrected) and gave a specific conductivity value, K_{100}, of 0.00146 ohm^{-1} cm.$^{-1}$. The products obtained at mole ratios of 1:3 and 1:4 were liquids at room temperature with K_{100} values of 0.00255 and 0.00372 ohm^{-1} cm.$^{-1}$, respectively.

The products containing 2, 3, and 4 moles triethylaluminum could be filtered to remove impurities; however, the 1:1 adduct, $LiAlH_4 \cdot Al(C_2H_5)_3$, could not be filtered. The $LiAlH_4 \cdot Al(C_2H_5)_3$ compound was prepared by reaction of 6.8 g. (0.17 mole) of 95% pure $LiAlH_4$ and 20.5 g. (0.18 mole) of $Al(C_2H_5)_3$ at 100° for 2 hr. After cooling, the solids were stirred in petroleum ether, filtered, and dried. The presence of alkylaluminum was observed in the filtrate. A white solid residue weighing 15 g. was obtained after drying under vacuum.

Anal. Calcd. for $LiAlH_4 \cdot Al(C_2H_5)_3$: Li, 4.56; Al, 35.5. Hydrolysis gas composition: H_2, 57.1; C_2H_6, 42.9. Calcd. for $LiAl(C_2H_5)H_3$: Li, 10.5; Al, 40.9. Gas: H_2, 75; C_2H_6, 25. Found: Li, 9.79; Al, 47.28. Gas: H_2, 75; C_2H_6, 25.

The analyses fit the formula $LiAl(C_2H_5)H_3$ fairly well. Apparently alkyl groups from the $Al(C_2H_5)_3$ exchange with $LiAlH_4$.

The infrared spectra of all these adducts contained a band at 5.7 μ believed to be characteristic of aluminum–hydrogen bridge vibrations.[8]

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CONTRIBUTION FROM U. S. BORAX RESEARCH CORPORATION,
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Triethylborane from Triethylaluminum and Borazines

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Exchange reactions between alkyl substituents on aluminum and a variety of substituted boron compounds are known. For example, the reactions of trialkylaluminum or alkylaluminum halides with boron trifluoride,[1–3] boric acid esters,[3–5] trialkylboroxine,[6] and alkyl metaborates[7,8] to give trialkylboranes have been reported. Similarly, diisobutylaluminum hydride and isopropyl borate produce triisobutylborane in the presence of triethylamine.[9] The exchange of alkyl and aryl groups between trialkylaluminums and trialkyl- or triarylboranes has been studied exten-

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sively.[10–12] No reports appear to be available of the reaction of alkylaluminum compounds with borazines or aminoboranes.

In an attempt to prepare partially alkylated chloroborazines from B-trichloroborazines in the absence of ether, metal alkyls other than Grignard reagents were investigated. The reaction of B-trichloro-N-trimethylborazine and dimethylcadmium was found to be slow (only 17% reaction in 3 hr. in boiling benzene). When B-trichloroborazine in *n*-dodecane was treated with one molar equivalent of triethylaluminum in the presence of sodium chloride, an exothermic reaction occurred and triethylborane was evolved on heating. This reaction was repeated using three molar equivalents of triethylaluminum and an 81% yield of triethylborane was obtained (eq. 1). The presence of sodium chloride had

$$(\mathrm{ClBNH})_3 + 3\mathrm{Al(C_2H_5)_3} \longrightarrow 3\mathrm{B(C_2H_5)_3} + (\mathrm{ClAlNH})_x \quad (1)$$

little effect on the yield although it is reported[13] to improve the yield of trialkylborane from the reaction of trialkylaluminum and boron trichloride.

The solid residue was not investigated in this case; similar condensed aluminum–nitrogen polymers have been obtained *via* a pyrolytic route from dialkylaluminum chloride–amine complexes.[14] B-Triphenylborazine and triethylaluminum afforded 80% of triethylborane and a dodecane-insoluble, solid residue which had an aluminum content equal to that calculated for $(\mathrm{C_6H_5AlNH})_x$. A similar reaction with hexamethylborazine produced only 61.5% of the expected triethylborane. The residual yellow resin in this case was thermoplastic and soluble in *n*-dodecane and benzene. Analysis and molecular weight measurements suggest that the resin is an aluminum–nitrogen polymer containing methyl and ethyl groups and a small amount of boron, although this is speculative.

The reaction of triethylaluminum with tris-(diethylamino)-borane was attempted in order to determine the generality of the reaction of trialkylaluminum with boron–nitrogen derivatives. No heat was evolved on mixing the reactants and distillation gave *n*-dodecane containing a small amount of unreacted aminoborane along with an unidentified component. Similarly, when tris-(dimethylamino)-borane was treated neat with triethylaluminum, only unreacted aminoborane was obtained on distillation.

The failure of the reaction in the case of tris-(dialkylamino)-boranes may be due to steric hindrance. Spectroscopic evidence[15] indicates that the dialkylamino groups are twisted out of the $\mathrm{BN_3}$ plane in tris-(dialkylamino)-boranes. This could account for the failure to observe reaction in the case of tris-(dialkylamino)-boranes, since the geometry is unfavorable for the attainment of a four-center transition state with the aluminum alkyl. Such steric inhibition is absent in the case of the planar borazoles.

Experimental

Materials.—Triethylaluminum (Koppers Co.) of 90% minimum purity was used without further purification. B-Trichloroborazine (U.S. Borax Research Corp., Anaheim, Calf.) was purified by distillation from mineral oil. Hexamethylborazine and B-triphenylborazine were prepared by the well known Grignard method from B-trichloro-N-trimethylborazine and B-trichloroborazine followed by sublimation and recrystallization, respectively. All melting points agreed with reported values in the literature.[16] Tris-(dimethylamino)-borane and tris-(diethylamino)-borane were synthesized from boron trichloride and the dialkylamines and were distilled before use, a center cut being used. All reactions and manipulations were performed under a blanket of dry nitrogen. The *n*-dodecane was distilled and stored over sodium wire. All temperatures are uncorrected.

Reactions of B-Trichloroborazine and Triethylaluminum. (a).—To a stirred slurry of 14.9 g. (0.081 mole) of B-trichloroborazine and 6 g. (0.0125 mole) of sodium chloride in 75 ml. of *n*-dodecane was added slowly 11 ml. (9.24 g., 0.081 mole) of triethylaluminum at room temperature. The reaction mixture became hot and ice cooling was necessary. When the mixture had been stirred for 2 hr., a 10-ml. aliquot of the white slurry was removed and distilled to give 1–2 ml. of pyrophoric liquid, b.p. up to 200°, shown by its infrared spectrum to be mainly triethylborane. A 1.00-ml. portion of the original, unheated reaction mixture was transferred to a vacuum system and found to contain only a small quantity of triethylborane.

(b).—To a stirred slurry of 1.84 g. (0.01 mole) of B-trichloroborazine and 5 g. of sodium chloride in 50 ml. of dodecane at 0° was added 4.2 ml. (3.53 g., 0.031 mole) of triethylaluminum. When the addition was complete, distillation gave 0.87 g. of a pyrophoric liquid, b.p. 46–52° (non-equilibrium conditions), shown by its infrared spectrum and vapor pressure at 0 and 25° to be pure triethylborane. The distillation was continued until the vapor temperature reached 121°. An additional 1.50 g. of pyrophoric liquid distillate was collected for a total of 2.37 g. (81%). The insoluble residue was removed by filtration from the residual mixture, 7.75 g. [100% for $(\mathrm{ClAlNH})_x$].

(c).—To a slurry of 1.84 g. (0.01 mole) of B-trichloroborazole in 35 ml. of dodecane was added 4.3 ml. (0.032 mole) of triethylaluminum at room temperature. The reaction was exothermic and cooling with an ice bath was necessary. Distillation over a period of 1 hr. gave 2.15 g. (73%) of triethylborane, b.p. 95°.

Reaction of Triethylaluminum and B-Triphenylborazine.—To a stirred slurry of 3.08 g. (0.010 mole) of B-triphenylborazine in 35 ml. of dodecane was added 4.1 ml. (0.030 mole) of triethylaluminum at room temperature. On warming, the slurry became a clear, colorless solution. The solution was heated over a 1.5-hr. period to give 2.35 g. (80%) of triethylborane as distillate, b.p. 89–95.5°. An amorphous white solid separated as the residual solution was cooled. Filtration gave 1.50 g. of off-white powder which was infusible below 500° and insoluble in benzene.

Anal. Calcd. for $(\mathrm{C_6H_5AlNH})_x$: Al, 22.65. Found: Al, 22.71.

Reaction of Triethylaluminum and Hexamethylborazine.—To a solution of 1.65 g. (0.01 mole) of hexamethylborazine in 35 ml. of dodecane was added 4.3 ml. (0.032 mole) of triethylaluminum. Distillation through a short Vigreux column gave 1.82 g. (61.5%) of triethylborane, b.p. 95°, in addition to a small amount of lower boiling borane collected in a −80° trap. The residual yellow solution was evaporated *in vacuo* to give a yellow-green resin which was dissolved in benzene and allowed to stand. A small amount of insoluble foreign matter and 0.05 g. of colorless crystals (infusible, dec. 150–334°) were removed by filtration.

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Evaporation *in vacuo* gave a yellow resin, m.p. 104–115°, dec. 450–490°, which gave a positive flame test for boron and which was readily attacked by atmospheric moisture and/or oxygen.

Anal. Found: Al, 27.91; mol. wt. (cryoscopic in benzene), 1440.

Attempted Reactions of Triethylaluminum and Tris-(dialkylamino)b-oranes. (a).—Freshly distilled tris-(diethylamino)-borane (6.81 g., 0.030 mole) in 35 ml. of dodecane appeared to be unaffected by the addition of triethylaluminum (4.3 ml., 0.032 mole). No heat was evolved and the solution remained clear. Heating the solution under a short Vigreux column gave 3.53 g. of a liquid, b.p. up to 206°. An infrared spectrum showed no triethylborane was present and only a trace of tris-(diethylamino)-borane. In addition to dodecane, the distillate exhibited unknown absorption at 7.7, 8.35, 8.7, 9.4, 9.8, and 11.85 μ. An attempt to redistil the liquid was unsuccessful due to decomposition.

b.—To 4.10 g. (0.0286 mole) of tris-(dimethylamino)-borane at −80° was added 4.0 ml. (3.36 g., 0.0295 mole) of triethyl aluminum. The cold solids were brought to room temperature to give a clear colorless solution. Heating the liquid to a pot temperature of 140° produced no distillate. A clear liquid, 2.13 g., was obtained at a pot temperature of 164–189°. The infrared spectrum of this material was identical with that of tris-(dimethylamino)-borane.

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Mixed Ligand Complex Formation in Lead-Chloride-Bromide Solutions

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The clear separation of the well defined absorption peaks of lead(II) in 1 *M* or greater alkali chloride and alkali bromide solutions suggested the applicability of the spectrophotometric technique of Newman and Hume[1] to solutions of lead(II) in chloride–bromide mixtures for the investigation of possible mixed halide complex formation in these media. The binary complexes of lead with chloride and bromide are known, however, to be weak and even in 1 *M* halide medium there is no convincing evidence for the formation of species containing more than three chloride or bromide ions in aqueous solution.[2] In the present investigation, efforts to force the complexes to saturation were unsuccessful, even in 10 *M* aqueous hydrogen halide solutions, in alcoholic hydrogen halide solutions up to 6.4 *M*, in 3 *M* calcium chloride–95% ethanol medium, and in 3.4 *M* lithium chloride or bromide in 95% ethanol, as shown by persisting dependence of extinction coefficients and wave length of peak absorption on halide concentration. Nevertheless, the spectra of lead in chloride–bromide mixtures give clear-cut evidence of the presence of a mixed chloride–bromide complex or complexes. Figure 1 shows spectra of such mixtures in a 3.4 *M* mixture of lithium chloride and bromide in 95% ethanol. The curves 2, 3, and 4 cannot be generated by any combination of curves 1 and 5, and the conclusion that mixed species are formed is unavoidable. From the formation constants given for aqueous media[2] one would expect that the principal species present in the chloride and in the bromide media should be $PbCl_3^-$ and $PbBr_3^-$, respectively. In this event, the mixed ligand species would be $PbCl_2Br^-$ and $PbClBr_2^-$. The similarity of the curves to those in the corresponding bismuth system indicates that here, too, bromide replaces chloride more readily than chloride replaces bromide, and that both mixed species probably are formed.[1] This is in harmony also with previous results on the mercury mixed halide complexes[3,4] and supports the view that, in general, all the structurally feasible mixed ligand species are formed when metal ions are present in mixtures of ligands of comparable binding power with which they form labile complexes.

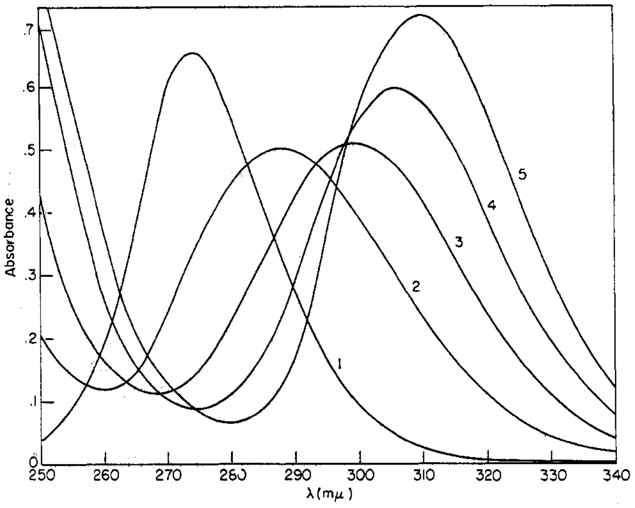

Fig. 1.—Spectra of 0.04 m*M* lead(II) perchlorate in 95% ethanol containing 3.4 *M* lithium halide with the following ratios of bromide to chloride: 1, 0.00; 2, 0.33; 3, 0.50; 4, 0.67; 5, ∞. Measurements were made on a Cary Model 11 spectrophotometer, at 25°.

Incidental to the mixed ligand investigation, a short study was made of the feasibility of determining spectrophotometrically the formation constants of the complexes of lead(II) with chloride ion. Absorption measurements with a Beckman DU spectrophotometer were made on 0.126 and 0.252 m*M* solutions of lead perchlorate over a range of 0.0 to 0.05 *M* chloride ion at a constant ionic strength of 4.00 *M*. Analysis of the data indicated three species (presumed to be Pb^{+2}, $PbCl^+$, and $PbCl_2$) to be present and contributing significantly to the absorption at the wave lengths

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