plexes are all prisms or plates belonging to the monoclinic system. The nitrate and bromide are very soluble in water, the perchlorate considerably less so. Although in dilute solution the complex hydrolyzes readily to a binuclear complex, it is very stable in concentrated solution, at least at room temperature.

Complex II.—To an ice-cooled solution of complex I nitrate (4 g.) in 15 ml. of water was added dropwise 5 ml. of an ice-cooled 6 N sodium hydroxide solution with stirring. The violet crystalline powder which separated was washed with a small amount of cold water and then with alcohol and dried in air; yield 2 g. As complex II is not as soluble in water or as stable in solution as complex I, recrystallization from water was not attempted. The yield depends upon the concentration of the solution of the original complex. The crystals obtained from dilute solution were small cubes.

Measurement of Absorption Spectra.—A Shimadzu Quartz Spectrograph and a Beckman DU Spectrophotometer were used for the absorption measurements. As both complexes are rather unstable, the measurements were made as quickly as possible on freshly prepared solutions which were replaced frequently.

The Amine Complexes of Aluminum Hydride. I.

BY JOHN K. RUFF AND M. FREDERICK HAWTHORNE

A new synthesis has been developed for the tertiary alkyl amine complexes of aluminum hydride utilizing lithium aluminum hydride and an amine hydrochloride. Substituted amino aluminum hydrides also have been prepared. Molecular weight determinations on the products have shown them to be associated and their probable structure is discussed.

Aluminum hydride has been found to form a 1:1 and a 2:1 complex with trimethylamine.[1] Several other 1:1 complexes with tertiary alkyl amines were reported[2] later in a brief communication. These complexes were prepared by direct combination of aluminum hydride with the appropriate anhydrous amine.

The formal similarity between diborane and aluminum hydride suggested an alternate route to these compounds which was analogous to the preparation of trimethylamine borane from lithium borohydride and trimethylammonium chloride,[3] the reaction between lithium aluminum hydride and trialkyl ammonium chlorides.

Experimental

All the alkylamine alanes prepared were extremely sensitive to oxygen and moisture. Therefore all handling and storage of the products, melting points and preparation of solutions were performed in a nitrogen filled dry box.

Materials.—The lithium aluminum hydride used was the commercial grade obtained from Metal Hydrides, Inc. The alkylammonium chlorides were prepared from the anhydrous amine and hydrogen chloride gas in diethyl ether solution and were handled under a blanket of nitrogen and dried under high vacuum before use.

Trimethylamine Alane. Method A.—A sample of finely ground lithium aluminum hydride weighing 2.2 g. was placed together with 4.5 g. of trimethylammonium chloride in a 200 ml. flask. The flask was attached to the vacuum line and 100 ml. of dried ether was condensed into it with liquid nitrogen. The flask was allowed to warm slowly to room temperature with stirring. After gas evolution had ceased the flask was attached to a vacuum sublimation apparatus. The solvent was removed under vacuum until a paste remained in the flask. Then a −50° bath (Dry Ice and acetone) was placed around the trap of the sublimer. A warm water bath (35–40°) was placed around the flask and the product collected in the trap. Sublimation was complete in approximately 2 hr. The sublimation apparatus was removed to the dry box where it was opened. The yield was 3.7 g. or 89%.

Method B.—A sample of finely ground lithium aluminum hydride weighing 4.0 g. was stirred in 150 ml. of dry ether in the dry box for twenty minutes. Then 8.0 g. of trimethylammonium chloride was added slowly to the ethereal solu-

tion. About half way through the addition more ether had to be added to the mixture to replace that lost by evaporation. After gas evolution had ceased the mixture was filtered and the clear filtrate was poured into a 200 ml. flask. The flask was removed from the dry box and attached to the vacuum sublimation apparatus. It was treated as described in Method A. The yield was 7.3 g. or 88%.

The other trialkylamine alanes and the N-dialkylaminoalanes were prepared similarly. All sublimed readily at temperatures up to 40° except the tri-n-propylamine alane which sublimed very slowly. It also could be recrystallized from hexane at −80°.

Analysis.—The products were analyzed for active hydrogen in the following manner. A sample of the compound was weighed directly in a small flask. The flask was attached to the vacuum line and evacuated briefly. Then about 20 ml. of dry ether was condensed into the flask, followed by 10 ml. of methanol. The mixture was allowed to warm. After the reaction was complete the mixture was cooled to −196° and the gas that was evolved was transferred to a system of calibrated storage bulbs via a Toepler pump.

Aluminum analysis was accomplished by preparing a standard ethereal solution of the compound in the dry box. The ethereal solution was carefully hydrolyzed with methanol and a mixture consisting of 40 ml. of isopropyl alcohol and 5 ml. of concd. nitric acid was added to it. The solution was evaporated on a water-bath to near dryness before taking up with dilute hydrochloric acid. The aluminum content of the aqueous solution was determined by the 8-hydroxyquinoline method.

A weighed sample of the polymer prepared by heating dimethylallylamine alane was hydrolyzed with methanol and the amount of active hydrogen present determined. The aluminum content of the resulting methanol solution also was determined. The molar ratio of active hydrogen to aluminum was found to be 2.10. For a sample of 0.261 g., 4.76 × 10^{-3} mole of hydrogen gas was produced and 2.27 × 10^{-3} mole of aluminum was found. The percentage of aluminum content, 23.5, agrees closely with that calculated for the monomer (see Table I).

Molecular Weights.—The molecular weight apparatus consisted of a cell within a vacuum jacket. Two thermocouple wells and a magnetically driven stirrer were fitted into the top of the cell so that a closed system resulted when the apparatus was assembled. Temperature measurements were made with eight multiple copper–constantan thermocouples. A Leeds and Northrup potentiometer (Mod. 8662) and galvanometer (Mod. 2430-C) were used to measure e.m.f.

The benzene used as solvent was dried over lithium aluminum hydride at the reflux temperature for several hours prior to distillation. The molal freezing point depression constant was determined in mv. by utilizing standard solutions of toluene in benzene. An average value of 1.499 ± 0.005 mv. g./mole was obtained for five runs.

(1) E. Wiberg, H. Grat and R. Usom. Z. anorg. u. allgem. Chem., **272**, 221 (1953).

(2) E. Wiberg and H. Noth, Z. Naturforsch., **106**, 237, 1955.

(3) G. W. Schaeffer and E. T. Anderson, THIS JOURNAL, **71**, 2143 (1949).

TABLE I

AMINE COMPLEXES OF ALUMINUM HYDRIDE

	Method	M.p., °C.	Al, calcd.	Active H, calcd.	Al, found	Active H, found	Yield, %
(CH₃)₃NAlH₃	A, B	76	30.30	3.37	29.68	3.36	88
(CH₃)₂N⟨CH₂CH=CH₂ / AlH₃	A	12	23.48	2.61	23.29	2.62	89
(CH₃)N(C₂H₅)₂AlH₃	A	Liq.	23.04	2.56	22.80	2.56	78
(C₂H₅)₃NAlH₃	A, B	18–19	20.61	2.27	20.86	2.28	82
(C₃H₇)₃NAlH₃	A	80–81	15.59	1.73	15.90	1.72	56
(CH₃)₃NAlD₃	A	77–78	...	6.52	...	6.54ᵃ	93
(CH₃)₂NAlH₂	A, B	89–90	36.99	2.74	37.18	2.76	63
(C₂H₅)₂NAlH₂	A	42	26.75	1.98	27.59	1.98	91

ᵃ Mass spectrum analysis showed an H/D ratio of 1.02 upon hydrolysis with methanol.

TABLE II

MOLECULAR WEIGHT OF THE AMINE COMPLEXES OF ALUMINUM HYDRIDE

Compound	Form. wt.								Average degree of association $\bar{n}$	$\bar{n}$ Wiberg
Me₃NAlH₃	89.1	Molal concn.	0.61	0.43	0.33	0.26				
		Mol. wt.	127	124	122	124			1.40	1.44
Me₃NAlD₃	92.1	Molal concn.	0.89	0.70	0.56	0.47				
		Mol. wt.	133	130	130	135			1.43	..
Me₂N⟨CH₂CH=CH₂ / AlH₃	114.2	Molal concn.	0.47	0.32	0.24	0.19				
		Mol. wt.	158	159	156	159			1.37	..
MeNEt₂·AlH₃	117.2	Molal concn.	0.74	0.57	0.48					
		Mol. wt.	155	157	159				1.33	..
Et₃NAlH₃	131.2	Molal concn.	0.36	0.27	0.19	0.40ᵃ	0.26ᵃ	0.39ᵃ		
		Mol. wt.	143	137	138	151	151	147	1.10	1.57
Pr₃NAlH₃	173.2	Molal concn.	0.57	0.45	0.35	0.30				
		Mol. wt.	183	180	184	179			1.05	1.12
Me₂NAlH₂	73.1	Molal concn.	0.91	0.63	0.48	0.39	1.37ᵃ	0.90ᵃ		
		Mol. wt.	217	218	221	219	220	215	2.99	2.16ᵇ
Et₂NAlH₂	101.1	Molal concn.	1.51		1.19	0.96				
		Mol. wt.	215		216	210			2.12	..

ᵃ The products from separate preparations were used. ᵇ Obtained by boiling point elevation in ether.

The alkyl amine alane solutions were prepared by weight, and the molecular weight cell was loaded with a weighed amount of solution in the dry box. Dilutions were made with a weight buret under a blanket of dry nitrogen.

The general procedure employed the determination of the freezing point of pure solvent, then that of the solution or solutions and finally the freezing point of the pure solvent again. The freezing point was always reproduced to better than ± 0.01 mv.

Infrared and N.m.r. Spectra.—The infrared spectra of AlH₃·N(CH₃)₃ and AlD₃·N(CH₃)₃ were determined with a 1% solution in a 0.1 mm. fixed cell. The nuclear magnetic resonance spectra were obtained with a Varian Model V4300B spectrometer at forty megacycles. All samples and solutions were handled in the dry box.

Discussion

Lithium aluminum hydride and trialkylammonium chlorides react rapidly and smoothly in ether at temperatures from −30 to 25° to produce trialkylamine alanes[4] in good yield.

$$\text{LiAlH}_4 + \text{R}_3\text{NHCl} \longrightarrow \text{H}_2 + \text{LiCl} + \text{R}_3\text{N·AlH}_3 \quad (1)$$
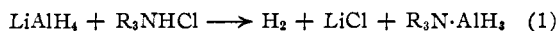
Under similar conditions dialkylammonium chlorides and lithium aluminum hydride give N-dialkylamino alanes.

$$\text{LiAlH}_4 + \text{R}_2\text{NH}_2\text{Cl} \longrightarrow 2\,\text{H}_2 + \text{LiCl} + \text{R}_2\text{NAlH}_2 \quad (2)$$
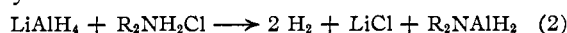
(4) The AlH₃ unit will be referred to in this paper and other papers of this series as "alane" and derivatives of this unit will be named accordingly (e.g., H₂AlCl·N(CH₃)₃ will be called trimethylamine chloro alane).

At temperatures around −40° only one mole of hydrogen per mole of dialkylammonium chloride was evolved, indicating the formation of a dialkylamine alane (AlH₃·NHR₂). On warming to −10° the second mole of hydrogen was evolved.

Either reaction could be carried out by the addition of the solid alkylammonium chloride to an ethereal solution containing a slight excess of lithium aluminum hydride. Alternately, the alkylammonium chloride was mixed with a slight excess of solid lithium aluminum hydride and ether condensed into the reaction vessel with liquid nitrogen. In both cases, the products were isolated from the reaction mixture by distillation of the solvent under reduced pressure and by subsequent sublimation of the product in high vacuum. The aluminum compound was condensed in the sublimation apparatus by means of a −50° bath. Yields ranged between 93 and 56% based on reactions 1 and 2 and the amount of alkylammonium chloride used. Table I presents the compounds prepared.

Evidence has been presented by Wiberg[1,2] for the association in the trialkylamine alanes in an inert solvent. We have corroborated, in part, these findings. Molecular weights of all the compounds prepared were determined cryoscopically in benzene at several concentrations. The molecular weights found are presented in Table II. Two notable dis-
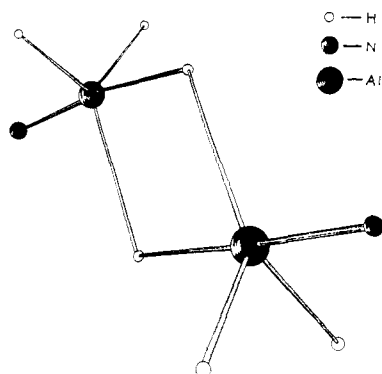
○ — H
◑ — N
● — Al

Fig. 1.—The proposed structure for the trimethylamine alane dimer.

crepancies appear between our data and those published by Wiberg. The difference in the degree of association found for N-dimethylaminoalane could in part be due to different conditions since Wiberg used the ebullioscopic method in diethyl ether. No explanation can be made for the difference found in the molecular weight of triethylamine alane. In order to check this discrepancy we determined the molecular weight of the compound three times at different concentrations on the product of one preparation and once each on the product from three different preparations. All the products exhibited the same melting point.

The association of the trialkylamine alanes indicates a tendency for aluminum to assume a coördination number of five in these compounds. Association is believed to occur through hydrogen bridges, although no evidence is found for hydrogen bridge adsorption in their infrared spectra.

The bond hybridization of the aluminum, when it exhibits a coördination of five must necessarily involve the 3s and 3p orbitals and one of the lower lying 3d orbitals. Two types of hybridization of these orbitals can be considered here; sp³d hybridization which results in a symmetrical trigonal bipyramid structure and sp³spd hybridization as discussed by Gillespie.[5] The geometry of the latter type hybridization consists of three normal sp³ orbitals and two spd orbitals which replace the missing sp³ in the usual tetrahedral configuration. The angle between the two spd orbitals is 71°.

An estimate of 1.7 to 1.8 Å. for the Al–H bridge distance[6] precludes the possibility of sp³d hybridization because the calculated Al–Al distance for two regular bipyramids sharing a common edge is less than twice the covalent radius of aluminum. A similar calculation based on sp³spd hybridization results in an Al–Al distance that is reasonable.

The structure proposed for the trimethylamine alane dimer is thus pictured in Fig. 1.

(5) R. J. Gillespie, J. Chem. Soc., 1002 (1952).

(6) The estimate of the Al–H bridge distance was made in two ways. From the B–H bridge distance in diborane, the covalent radius of the "bridge hydrogen" was calculated on the assumption that boron exhibited a normal covalent radius. The sum of the normal covalent radius of aluminum and the radius of the "bridge hydrogen" gave a value of 1.75 Å. for the Al–H bridge distance. The second approach used was to assume that the bridging carbon in trimethyl aluminum had a normal covalent radius and from the Al–C bridge distance an "aluminum bridge" covalent radius was calculated. The sum of this value and the normal covalent radius of the hydrogen gave 1.77 Å. as a Al–H bridge distance.
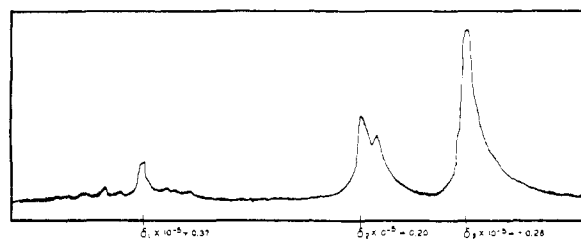

Fig. 2.—N.m.r. spectrum of dimethylallylamine alane.

The apparent discontinuity in the degree of association of the trialkylamine alanes with the successive replacement of methyl groups by larger groups (e.g. ethyl or allyl) is felt to be due to steric interactions. The size of the alkyl groups on the nitrogen can influence both the formation constant of the complex, as is found in the case of the amine complexes of trimethylborane, and the subsequent dimerization constant of the complex. The former effect is probably not important for the amine complexes considered here. As the coördination number of aluminum changes from four to five, the two non-bridging hydrogens are forced closer to the nitrogen and steric interaction will occur between the alkyl groups and these hydrogens. Since the hybridization of the nitrogen is undoubtedly tetrahedral, two of the alkyl groups are situated such that direct steric interaction with the hydrogens is virtually impossible. Thus the differences found in the degree of association for the complexes with trimethylamine, dimethylallylamine and diethylmethylamine are much smaller than the difference found between the complexes formed from triethylamine and diethylmethylamine. A secondary effect should exist in which the larger alkyl groups force the third group closer to the Al–N bond and thus enhance steric interference with the hydridic hydrogens. This effect should be much smaller than that caused by an increase in the size of the third alkyl group of the amine.

The association of the N-dialkyl-amino alanes probably occurs through nitrogen bridges as has been found by X-ray analysis of the analogous boron compound [BH₂·N(CH₃)₂]₃.[7]

$$CH_3 \diagdown \diagup CH_3$$

CH₃ ╲ ╱ CH₃
H ╲ N ╱ H
H–Al ╲ ╱ Al–H
CH₃–N ┊ ┊ N–CH₃
CH₃ ╲ Al ╱ CH₃
H ╱ ╲ H
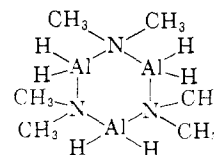
The proton nuclear magnetic resonance spectra of several of the amine complexes of aluminum hydride and trimethylaluminum and dimethylaluminum hydride were obtained and the results are presented in Table III. The n.m.r. spectrum of dimethylallylamine alane is shown in Fig. 2. Fig. 3 presents the n.m.r. spectrum of the same complex after heating the pure liquid sample at 85° for 48 hr. It is evident that some reaction has occurred in which the vinyl group has disappeared. In the light of Ziegler's recent work it was felt that the reaction

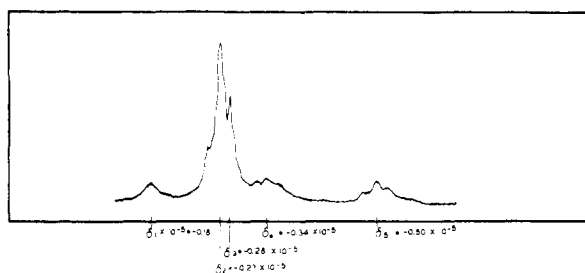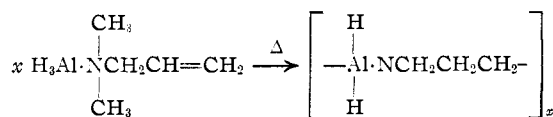(7) L. M. Trefonas and W. N. Lipscomb, THIS JOURNAL, 81, 4435 (1959).

Fig. 3.—N.m.r. spectrum of dimethylallylamine alane after heating at 85° for forty-eight hours.

$$x\ H_3Al\cdot N\substack{CH_3 \\ | \\ CH_2CH=CH_2 \\ | \\ CH_3} \xrightarrow{\Delta} \left[\ -Al\cdot N\substack{H \\ | \\ CH_2CH_2CH_2- \\ | \\ H}\ \right]_x$$

had occurred. However, an alternative mode of polymerization is possible[8]

$$x\ H_3Al\cdot N\substack{CH_3 \\ | \\ CH_2CH=CH_2 \\ | \\ CH_3} \xrightarrow{\Delta} \left[\substack{-CH_2CH- \\ | \\ CH_2 \\ | \\ (CH_3)_2N\cdot AlH_3}\right]_x$$
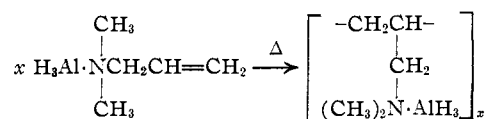
TABLE III

NUCLEAR MAGNETIC RESONANCE SPECTRA OF THE AMINE
COMPLEXES OF ALUMINUM HYDRIDE

$$\delta = \frac{Hr-H}{Hr} \times 10^{-5}$$

	δCH_3	δH
HAl(CH₃)₂ (pure liquid)	−0.56	−0.21
Al₂(CH₃)₆, pure liquid,	− .52	
11% in benzene	− .58	
AlH₃·N(CH₃)₃, 10% in benzene	− .35	− .17
AlD₃·N(CH₃)₃, 20% in benzene	− .35	a
(CH₃)₂		
AlH₃·NCH₂CH₂=CH₂, 12% in benzene	− .35	− .16
[(CH₃)₂NAlH₂]₃, 37% in benzene	− .32	− .15

ᵃ Not observable.

A determination of the ratio of active hydrogen to aluminum in the polymer serves to distinguish between the two modes of polymerization. The value of 2.1 found indicates that hydride addition to the double bond predominates. The n.m.r.

(8) We are indebted to one of the reviewers for suggesting this less novel mode of polymerization.

spectrum is in agreement with this mode of polymerization.

Band assignments were made for the unheated compound as follows: δ_1 is due to the vinyl group, δ_2 is due to the N–CH₂ group and δ_3 is due to the methyl groups on nitrogen. (The n.m.r. spectrum of pure dimethylallylamine was identical to that shown in Fig. 2.) The hydride bond resonance is not found in pure dimethylallylamine alane but it is found in the spectrum of a 12% benzene solution. The existence of two distinct triplets in the spectrum of the polymer indicates that there are two hydrogen bearing carbons, with different electronic environments, bonded to a CH₂ group. If a vinyl type of polymerization had occurred, one or more doublets arising from spin–spin coupling with the CH group should be found in the spectrum. The band assignments for the heated complex were made on the basis of the chemical shifts for some of the compounds listed in Table III. Bulk susceptibilities were neglected. δ_1 was assigned to the hydridic hydrogen by analogy with the chemical shift found in trimethylamine alane; δ_5 was assigned to a methylene group bonded to aluminum and coupled with another CH₂ group, since it was a triplet. δ_5 was similar in value to that found for the methyl groups bonded to aluminum in trimethyl aluminum and dimethylaluminum hydride. The other triplet δ_4 was assigned to a methylene group bonded to nitrogen, which was also coupled with another CH₂ group. δ_2 and δ_3 were assigned to the methyl groups. Since δ_3 has the same value as the methyl groups in the unheated material, it is possible that some unreacted dimethylallylamine alane is present. The bands expected for the remaining methylene group are not observed and probably are spread out under the methyl peaks.

The characteristic position of the Al–H infrared absorption band was determined in benzene solution by comparison of the infrared spectra of trimethylamine alane and trimethylamine alane-D.[3] The observed wave lengths were almost isotopically normal, being 5.65 μ for the Al–H absorption and 7.72 for the Al–D. The calculated absorption for Al–D is 7.98.