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The Amine Complexes of Aluminum Hydride. III. Substitution Reactions

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Organomercury and organolithium compounds were shown to be excellent alkylating agents for lithium aluminum hydride, trimethylamine alane and dimethylamino alane. Several new compounds were prepared and their molecular weights were determined.

It has been reported that lithium aluminum hydride¹ reacts with alkyl compounds of the Group I and II metals. An exchange reaction occurred in which the alkyl group was displaced by hydride. This reaction was reported primarily as a preparation of the Group I and II metal hydrides, so that a complete characterization of the alkylated lithium aluminum hydride produced in the reaction was not made. A reinvestigation of this reaction as a possible route to organo aluminum compounds was begun. The reaction of several aluminum hydride derivatives with some typical organo lithium and mercury compounds was chosen for study. Very recently Bartocha² reported the preparation of lithium tetravinyl aluminate and trimethylamine trivinyl aluminum from lithium aluminum hydride and divinylmercury and trimethylamine alane and divinylmercury, respectively.

Experimental

All handling of the reactants and products was performed in a nitrogen filled drybox, since the materials were sensitive to oxygen and moisture.

Materials.—Trimethylamine alane and dimethylamino alane were prepared as described previously.³

Commercial grade lithium aluminum hydride was extracted with diethyl ether, filtered and the solvent removed *in vacuo*. The residue was dried at 60° for 3 hr. under high vacuum. The purity of the resulting lithium aluminum hydride was determined by active hydrogen analysis.

Di-*n*-butylmercury and diphenyl mercury obtained from Eastman Company were used without further purification. Divinyl mercury⁴ and dipentynylmercury⁵ were prepared as described in the literature.

The *n*-butyl lithium and phenyl lithium were used as obtained from Orgmet Company.

Reaction of Aluminum Hydride Derivatives with Mercury Compounds.—A similar procedure was used for all the aluminum compounds prepared from the aluminum hydride derivatives and mercury compounds. The reaction conditions, solvent, yields and method of purification employed in the preparation of these materials are given in Table I.

The aluminum hydride derivative (10 to 50 mmoles) contained in a flask attached to the vacuum line was allowed to react with a slightly greater than stoichiometric amount of the mercurial. After the solvent had been condensed into the flask, it was warmed to the reaction temperature and the mercury compound was added by means of side-arm dumper. When the reaction was performed at a temperature greater than 25°, the vacuum line was pressurized with an atmosphere of dry nitrogen and a water condenser was used between the flask and the manifold to contain the solvent. Hydrogen evolved during the reaction was allowed to escape through a mercury blowout manometer. After gas evolution had ceased, the reaction mixture was filtered by means of a

vacuum filtration apparatus. The solvent was removed *in vacuo* and the residue was purified in the drybox.

The halo-substituted trimethylamine alanes and the halo-substituted dimethylamino alanes were prepared by the procedure described above. The reaction was performed at 25° in diethyl ether, although benzene could have been used. Some care had to be taken in the addition of the mercuric halide to the alane solution, as the resulting reaction was quite vigorous. All the derivatives prepared were purified by vacuum sublimation at temperatures below 90°. Table II illustrates the halo-substituted aluminum hydride derivatives prepared.

Reaction of Aluminum Hydride Derivatives with Organo Lithium Compounds. A. Preparation of (C₄H₉)₂AlN(CH₃)₂.—A 2.2 g. sample of dimethylamino alane was weighed into a three-necked flask. Approximately 100 ml. of dried benzene was added. Then 60 ml. of a 1.11 *N* butyllithium solution in pentane was added slowly. Precipitation occurred during addition. A distillation head was fitted to the flask and the pentane was distilled. The benzene solution was refluxed an additional hour. The reaction mixture was filtered and the solvent removed from the filtrate *in vacuo*. A clear, colorless liquid remained. It was purified by distillation in a molecular still. A yield of 4.0 g. of product was obtained.

B. Preparation of (C₆H₅)₂AlN(CH₃)₂.—A 4.4 g. sample of dimethylamino alane was placed in a three-necked flask containing 200 ml. of dried benzene. Then 330 ml. of a 0.36 *N* phenyllithium solution in ether was added slowly. The solution was concentrated to 100 ml. and an additional 100 ml. of benzene was added. The mixture was refluxed 1 hr. and then centrifuged. The supernatant liquid was decanted into a flask and concentrated to 50 ml. The product crystallized out upon standing overnight in the refrigerator. A yield of 5.9 g. was obtained.

Dimethylamino diphenyl alane also can be prepared by the reaction of diphenyl mercury with dimethylamino alane in benzene at reflux for 36 hr., but low yields are obtained.

C. Reaction of LiC₄H₉ with AlH₃·N(CH₃)₃.—(1) A 2.0 g. sample of trimethylamine alane was dissolved in 50 ml. of benzene. Then 7 ml. of a 1.11 *N* butyllithium solution in pentane was added slowly. The mixture was refluxed for 1 hr. after addition was complete. The precipitate which formed was filtered off and dried under high vacuum for 1 hr. at 50°.

Anal. Calcd. for LiAlH₄: Al, 71.1; active hydrogen, 10.5. Found: Al, 70.4; active hydrogen, 10.5.

(2) A solution of 1.0 g. of trimethylamine alane in 50 ml. of benzene was added to a mixture of 20 ml. of the 1.11 *N* butyllithium solution and 40 ml. of benzene. Precipitation occurred immediately. The mixture was refluxed briefly and then filtered. The precipitate was washed with pentane and dried as described above.

Anal. Calcd. for LiH: active hydrogen, 12.7. Found: active hydrogen, 12.9.

Analysis.—The preparation of the samples for analysis for aluminum, chlorine and active hydrogen was the same as described previously.⁶

Tensiometric Titration.—The procedure and apparatus used are described elsewhere.⁶ Three titrations were performed with trimethylamine as the volatile constituent. The compounds titrated with trimethylamine were dimethylamino diphenyl alane, dimethylamino di-*n*-butyl alane and dimethylamino dichloro alane. A linear increase in pressure was observed in each titration after the addition of trimethylamine. Therefore, it is believed that no strong inter-

(1) B. D. Barbaras, *et al.*, *J. Am. Chem. Soc.*, **73**, 4585 (1951).

(2) B. Bartocha, A. J. Bilbo and M. Y. Gray, *Angew. Chem.*, **72**, 36 (1960).

(3) J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

(4) B. Bartocha and F. G. A. Stone, *Z. Naturforsch.*, **13b**, 347 (1958).

(5) J. R. Johnson and W. L. McEwen, *J. Am. Chem. Soc.*, **48**, 469 (1926).

(6) J. K. Ruff and M. F. Hawthorne, *ibid.*, **83**, 535 (1961).

TABLE I

PREPARATION AND PROPERTIES OF ORGANO ALUMINUM DERIVATIVES									
	—Analyses—		M.p. (b.p.)	Yield, %	Solvent	Reaction conditions	Method of purification	Al	
	calcd.	found						calcd.	found
(C ₆ H ₅) ₂ Al·N(CH ₃) ₃	8.50	8.51	227–229	43	Benzene	Reflux—3 hr.	Rx from benzene		
(C ₆ H ₅) ₂ Al·N(CH ₃) ₂ ^a	12.00	11.95	202–204	37	Benzene	Reflux—1 hr.	Rx from benzene		
(C ₄ H ₉) ₃ Al·N(CH ₃) ₃	10.94	11.04	B.p. 73–75/10 ⁻⁴ mm.	43	Benzene	Reflux—3 hr.	Distillation		
(CH ₂ =CH) ₃ Al·N(CH ₃) ₃	16.16	16.41	C. b.p. 40/10 ⁻² mm.	50	Ether	25°—12 hr.	Distillation		
(C ₆ H ₇ C≡C) ₃ Al·N(CH ₃) ₃	9.42	9.71	38–39	58	Ether	0°—2 hr.	Rx from hexane		
(C ₄ H ₉) ₂ Al·N(CH ₃) ₂ ^a	14.59	14.33	Butane/Al = 2.01	72	Benzene	Reflux—1 hr.	Distillation		
LiAl(CH=CH ₂) ₄	20.21	19.2	Li calcd. 4.93 Li found 4.91	32	Ether	25°—12 hr.	Rx from benzene		
LiAl(C≡CC ₂ H ₇) ₄ ·THF	7.22	7.38	Li calcd. 1.84 Li found 1.90	..	Tetrahydrofuran	25°—1 hr.	No purification Pot residue taken		

^a Prepared from phenyl or butyl lithium and the alane. All the rest were prepared from the corresponding organo mercury compounds.

TABLE II

PREPARATION AND PROPERTIES OF THE CHLORO ALUMINUM HYDRIDES									
	—Analyses—						Yield, %	M.p., °C.	M.p. (lit. 7)
	Al, calcd.	Cl, calcd.	Active hydrogen calcd.	Al, found	Cl, found	Active hydrogen, found			
H ₂ AlCl·N(CH ₃) ₃	1.62	1.63	92	51–53	51–53
HAlCl ₂ ·N(CH ₃) ₃	0.632	0.638	30	100–103	99–103
H ₂ AlBr·N(CH ₃) ₃	1.18	1.20	74	33–34	33–35
HAlBr ₂ ·N(CH ₃) ₃	0.405	0.400	40	104–106	105–108
HAlCl·N(CH ₃) ₂	25.13	32.98	0.929	25.48	32.63	0.939	59	83
AlCl ₂ ·N(CH ₃) ₂	19.03	50.01	...	19.17	49.80	...	42	151
AlCl ₃ ·N(CH ₃) ₃	14.02	55.28	...	14.06	56.50	...	79	156–157	155–156

action occurs between any of the three compounds and trimethylamine.

Molecular Weight Determination.—The apparent molecular weights of the compounds prepared were determined cryoscopically in benzene in an apparatus described previously.⁶ They are listed in Table III. A solution of 1 to 2 g. of the compound per 35 g. of benzene was prepared in the drybox. The cell was loaded and the freezing point of the solution was determined. The freezing point of the solvent was determined both before and after that of the solution. The values for benzene were reproducible to ±0.01°.

TABLE III

MOLECULAR WEIGHTS OF SOME ORGANO ALUMINUM DERIVATIVES

	Mol. wt. (obsd.)	Degree of association
AlH ₃ ·N(CH ₃) ₃	127	1.43
AlH ₂ Cl·N(CH ₃) ₃	163	1.32
AlHCl ₂ ·N(CH ₃) ₃	231	1.46
AlCl ₃ ·N(CH ₃) ₃	262	1.36
H ₂ AlNMe ₂	219	3.00
(C ₄ H ₉) ₂ Al·N(CH ₃) ₂	367	1.98
(C ₆ H ₅) ₂ Al·N(CH ₃) ₂	470 ^a	2.09
Cl ₂ AlN(CH ₃) ₂	301 ^a	2.12
(C ₆ H ₇ C≡C) ₃ Al·N(CH ₃) ₂	293	1.03

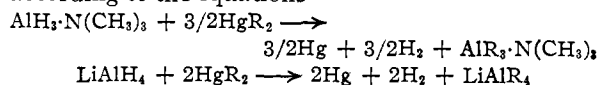
^a Obtained by boiling point elevation in benzene.

Infrared Spectra.—The infrared spectra of several of the unsaturated organo aluminum derivatives were taken in Nujol mulls or as capillary layers. The infrared spectra of the two pentynyl derivatives, LiAl(C≡CC₂H₇)₄·THF and Al(C≡CC₂H₇)₃·N(CH₃)₃, showed strong triple bond absorption at 4.72μ and 4.68μ, respectively. The infrared spectra of (CH₂=CH)₃Al·N(CH₃)₃ and LiAl(CH=CH₂)₄ showed double bond absorption at 6.35 and 6.42μ.

Results

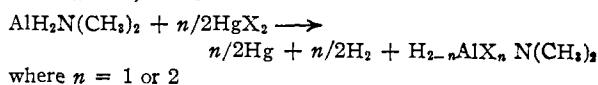
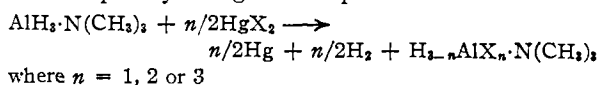
The preparation of organo aluminum compounds by the reaction of organo lithium or organo mercury compounds with aluminum hydride derivatives was accomplished readily in most of the cases studied. Organo mercury compounds were found

to react with the aluminum hydride derivatives according to the equations



The evolution of hydrogen ensures that the equilibrium is continually shifted in the direction of exchange; thus high yields are obtained in most instances. Another consequence of the hydrogen production is that the crude products are obtained in a relatively high state of purity. The specific compounds prepared are listed in Table I.

Mercuric halides were found to react with trimethylamine alane and dimethylamino in an analogous manner. It was possible to isolate the partially substituted derivatives as well as the completely halogenated species.

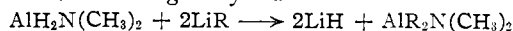


Wiberg has also obtained several of these materials by the reaction of the anhydrous hydrogen halide with aluminum hydride.⁷ Analytical data for the compounds prepared are presented in Table II.

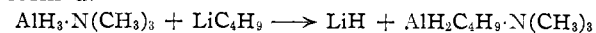
Due to a difference in reactivity of the aluminum hydride derivatives used in the reaction, it was not possible to prepare a dimethylamino dialkyl alane from dimethylamino alane and a dialkyl mercury. Therefore, a more active alkylating agent was sought. The reaction of methyl lithium with lithium aluminum hydride was reported to proceed readily.¹ The precipitation of lithium

(7) E. Wiberg, K. Modritzner and R. Uson, *Rev. acad. cienc. exact fis. quim. y nat. Zaragoza*, **9**, No. 1, 91 (1954).

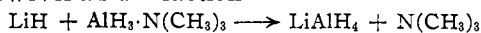
hydride during reaction also ensures that the equilibrium will be continually shifted in the desired direction. When dimethylamino alane was treated with *n*-butyllithium or phenyllithium, the corresponding organo aluminum compounds were obtained in good yield.



When *n*-butyllithium was allowed to react with trimethylamine alane lithium hydride was formed.

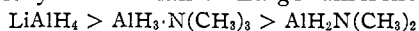


However a side reaction

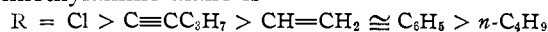


made it difficult to control the stoichiometry of the desired reaction. The facile displacement of trimethylamine by the hydride ion already has been discussed.⁶ Either lithium hydride or lithium aluminum hydride can be isolated depending upon the order of addition and the relative quantities of the reactants used.

A considerable difference was noted in the reactivity of the aluminum hydride derivatives toward a common mercury compound. The reactivity decreased from lithium aluminum hydride to dimethylamino alane. Large differences were



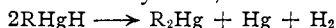
also found in the rate of reaction of different mercury compounds with a common aluminum hydride derivative. The qualitative order of reactivity of the mercury compounds (HgR_2) with trimethylamine alane is



Discussion

Mechanism of the Mercurial Reaction.—The order of reactivity of the different mercury compounds with trimethylamine alane suggest an electrophilic attack by the aluminum on the aryl or alkyl group of the mercurial. This also was pointed out by Traylor⁸ who observed a similar order. Winstein and Traylor⁹ obtained camphane from the reduction of 4-camphyl mercuric chloride with lithium aluminum hydride. Although they apparently did not attempt to isolate a camphyl aluminum derivative, it is reasonable to postulate its formation. The mechanism of this reaction would be an electrophilic substitution with retention of configuration, since no inversion is possible at the bridgehead carbon. It is believed that the mechanism of the reaction of other mercury compounds with the aluminum-hydrogen bond is similar.¹⁰

The production of hydrogen and mercury metal is believed to arise from the decomposition of mercuric hydride, which is known to be very unstable,¹¹ or from the disproportionation of an alkyl or aryl mercuric hydride,



Association of Organo Aluminum Compounds.—

There are numerous examples in the literature of

(8) T. G. Traylor, *Chem. and Ind.*, No. 39, 1223 (1959).

(9) S. Winstein and T. G. Traylor, *J. Am. Chem. Soc.*, **78**, 2597 (1956).

(10) Preliminary studies of the deuterium isotope effect on the reaction between trimethylamine alane and mercuric chloride give a ratio of the rate constants k_H/k_D of 1.4. This is indicative of a non-linear transition state (see K. Wiberg, *Chem. Revs.*, **55**, 713 (1955)).

(11) F. Wiberg and W. Henle, *Z. Naturforsch.*, **6b**, 461 (1951).

association of organo aluminum compounds.^{12,13} The most unexpected class of associated compounds is that composed of the simple aluminum trialkyls,¹⁴ in which a carbon atom forms a bridge between two aluminum atoms. Bridge formation also occurs when dimethylamino groups are substituted for alkyl, aryl, halide or hydride³ on aluminum (see Table III). Similar results are obtained when OR, SR and PR₂ groups are substituted for a methyl group in trimethylaluminum.¹² Many of the analogous boron compounds, however, are monomeric or show both dimeric and monomeric forms. For example, $(\text{CH}_3)_2\text{BN}(\text{CH}_3)_2$,¹⁵ $[(\text{CH}_3)_2\text{N}]_2\text{B}$ ¹⁶ and $(\text{CH}_3)_2\text{BOCH}_3$ ¹⁷ are monomeric and $(\text{CH}_3)_2\text{BNH}_2$ ¹⁸ and $(\text{CH}_3)_2\text{NBCl}_2$ ¹⁶ exist in both monomeric and dimeric forms. Stabilization of the boron monomers can occur through overlap of the unshared pair of electrons on the nitrogen or oxygen with the vacant *p* orbital on the boron. Evidently, if back coordination occurs in the aluminum nitrogen bond, it does not stabilize a monomeric form. The stability of the nitrogen bridge in dimethylamino alane⁶ and dimethylamino dimethyl aluminum¹² is such that no reaction occurs with trimethylamine. Analogous behavior was found when either dimethylamino-dichloro alane, dimethylaminodiphenyl alane or dimethylamino-di-*n*-butyl alane was allowed to react with trimethylamine.

Another type of association of organo aluminum compounds has been observed. In inert solvents the trialkylamine alanes exhibit partial polymerization.^{3,19} The structure of the dimers is not known but two alternatives have been considered. Dimerization is believed to occur through hydrogen bridges^{3,19} or as a result of dipole-dipole interaction in solution.²⁰ The effect of substitution of hydride by chloride in trimethylamine alane produced little change in the degree of association of the alane in benzene (see Table III). The association of aluminum chloride trimethylamine, which is similar in degree to that exhibited by trimethylamine alane, has been attributed to dipole-dipole interaction²¹ rather than dimerization through chlorine bridges. This suggests that the association of the trialkylamine alanes and the chloro derivatives of trimethylamine alane is due to dipole-dipole interaction, rather than hydride bridge formation.

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(12) N. Davidson and H. C. Brown, *J. Am. Chem. Soc.*, **64**, 316 (1942).

(13) E. G. Hoffman, *Ann.*, **629**, 104 (1960).

(14) K. S. Pitzer and H. S. Gutowsky, *J. Am. Chem. Soc.*, **68**, 2204 (1946).

(15) G. E. Coates, *J. Chem. Soc.*, 3481 (1950).

(16) E. Wiberg and K. Schuster, *Z. anorg. Chem.*, **213**, 77 (1933).

(17) A. Burg and R. Wagner, *J. Am. Chem. Soc.*, **75**, 3872 (1953).

(18) J. Goubeau and R. Link, *Z. anorg. Chem.*, **267**, 27 (1951).

(19) E. Wiberg, J. Graf and R. Uson, *Z. anorg. u. allgem. Chem.*, **272**, 221 (1958).

(20) G. Schomburg and E. G. Hoffman, *Z. Elektrochem.*, **61**, 1110 (1957).

(21) H. Ulich and W. Nespital, *Z. angew. Chem.*, **44**, 750 (1931).