

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA 30332

Aminoalanes. Direct Synthesis from Aluminum, Hydrogen, and Secondary Amines. Structure and Stability Elucidation by Nuclear Magnetic Resonance, Infrared Spectra, and Differential Thermal and Thermal Gravimetric Analysis

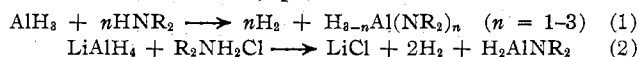
BY R. A. KOVAR AND E. C. ASHBY*

Received August 11, 1970

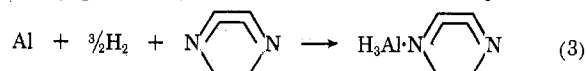
Detailed studies of the synthesis of aminoalanes by the direct reaction of aluminum, hydrogen, and secondary amines are reported. Tris- and bis(diethylamino)alanes are prepared in high yield depending on the reaction conditions and on the initial amine to aluminum molar ratio. Reaction of aluminum and diethylamine in molar ratios ranging from 1:1 to 2:1 at 150° afforded high yields of bis(diethylamino)alane ($\text{HAl}[\text{N}(\text{C}_2\text{H}_5)_2]_2$). Only low yields of diethylaminoalane ($\text{H}_2\text{AlN}(\text{C}_2\text{H}_5)_2$) were formed in admixture with bis(diethylamino)alane under conditions most suitable for forming only diethylaminoalane. The reactions of aluminum and hydrogen with dimethyl-, diisopropyl-, and diphenylamine, pyrrolidine, and piperidine were also carried out. As in the case with diethylamine, predominant formation of the bis(dialkylamino)alane was observed with dimethylamine, piperidine, and pyrrolidine. No reactions were observed with diisopropyl- and diphenylamine. Predominant formation of bis(dialkylamino)alanes in preference to dialkylaminoalanes is attributed to the greater thermodynamic stability of the former compounds. Verification of this point was accomplished by dta-tga and solution pyrolysis studies. Proton magnetic resonance and infrared spectral measurements of the aminoalanes are reported and interpreted to yield valuable analytical and structural information.

Introduction

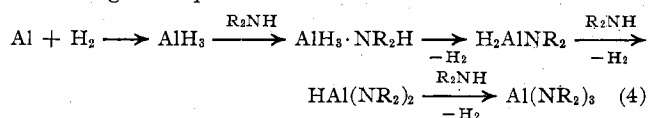
Aminoalanes ($\text{H}_{3-n}\text{Al}(\text{NR}_2)_n$, $n = 1-3$) have been used as polymerization catalysts,¹ reducing agents,² and synthetic intermediates;³ however more widespread use of these compounds is limited by the inconvenience of preparation and high cost of these reagents. Until now aminoalanes have been prepared by the reactions of (1) alane⁴ or trimethylamine-alane⁵ with secondary amines (eq 1) and (2) lithium aluminum hydride and dialkylammonium chlorides⁶ (eq 2).



In 1964 we reported the direct synthesis of an amine-alane by the reaction of triethylenediamine with aluminum and hydrogen in tetrahydrofuran under mild conditions⁷ (eq 3). The reaction of a secondary amine,



aluminum, and hydrogen was predicted to follow an analogous path involving intermediate formation of AlH_3 followed by complexation of the secondary amine to form $\text{AlH}_3\text{NR}_2\text{H}$. Since dialkylamine-alanes are unstable and lose hydrogen well below room temperature,³ the dialkylaminoalane (H_2AlNR_2) should be the first product capable of being isolated. In the presence of additional secondary amine, the dialkylaminoalane should react further to form the bis(dialkylamino)alane [$\text{HAl}(\text{NR}_2)_2$] and in the presence of additional dialkylamine, the tris(dialkylamino)alane, [$\text{HAl}(\text{NR}_2)_3$], according to eq 4. We have now made a detailed



study⁸ of the reaction of aluminum, hydrogen, and secondary amines as a route to aminoalanes and wish to report the results herein. This reaction represents such a convenient and economic route to aminoalanes that further investigation of new uses of aminoalanes should be encouraged. We are at present carrying out a detailed evaluation of this class of compounds as selective reducing agents in organic chemistry.

Experimental Section

Equipment and Materials.—Manipulation of air-sensitive materials was accomplished by use of standard bench-top techniques⁹ or employment of a drybox equipped with a recirculating atmosphere purification system for removal of oxygen and moisture.¹⁰ Infrared spectral measurements were obtained using a Perkin-Elmer 621 automatic grating spectrophotometer. Samples were prepared for analysis in the drybox. Spectra of liquid samples were obtained using neat material between KBr salt plates while spectra of solid samples were obtained as the Nujol mull. Proton magnetic resonance spectra were obtained using a Varian A-60 magnetic resonance spectrometer using the solvent signal (benzene) as internal standard.

Benzene, used as the solvent in the hydrogenation reactions, was purchased from Fisher Chemical Co. (Certified ACS grade) and distilled from NaAlH_4 prior to use. Dimethylamine (anhydrous) was purchased from the Matheson Corp. and passed through a KOH drying tube prior to use. Diethyl-, diisopropyl-, and diphenylamine, piperidine, and pyrrolidine were purchased from Eastman Chemical Co. The liquid dialkylamines were either distilled from anhydrous KOH or distilled onto active molecular sieve, Type 4-A, prior to use. Diphenylamine was used without further purification. Aluminum powder (600 mesh) was obtained from the Alcan Aluminum Corp. Aluminum was "activated" prior to use by the method described by Ziegler.¹¹ Ultra pure hydrogen (99.9995%) was obtained from the Matheson Corp. and used without further purification.

Analyses.—Aminoalanes are readily hydrolyzed by water and dilute acids. Analyses were performed by hydrolyzing a tared sample with a water-acid mixture and determination of the hydrogen content by gas evolution analysis. Aluminum in the same sample was determined by EDTA titration. Amines were

(1) S. A. Snam, Belgian Patent 654,406 (April 15, 1965).
 (2) S. Cesca, M. Santoslas, W. Marconi, and N. Palladino, *Ann. Chim. (Rome)*, **55**, 704 (1965).
 (3) H. Nöth and E. Wiberg, *Fortschr. Chem. Forsch.*, **8**, 323 (1967).
 (4) E. Wiberg and A. May, *Z. Naturforsch. B*, **10**, 234 (1955).
 (5) W. Marconi, A. Mazzei, F. Bonati, and M. de Malde, *Gazz. Chim. Ital.*, **92**, 1062 (1962).
 (6) J. K. Ruff, *J. Amer. Chem. Soc.*, **83**, 2835 (1961).
 (7) E. C. Ashby, *ibid.*, **86**, 1882 (1964).

(8) A preliminary report concerning this study has appeared: E. C. Ashby and R. A. Kovar, *J. Organometal. Chem.*, **22**, C34 (1970).
 (9) D. F. Shriver, "The Manipulation of Air Sensitive Compounds," McGraw-Hill, New York, N. Y., 1969.
 (10) T. L. Brown, D. W. Dickerhoof, D. A. Bafus, and G. L. Morgan, *Rev. Sci. Instrum.*, **33**, 491 (1962).
 (11) E. C. Ashby, G. J. Brendel, and H. E. Redman, *Inorg. Chem.*, **2**, 499 (1963).

determined by potentiometric titration of the solution obtained on hydrolysis of a tared sample after removal of the $\text{Al}(\text{OH})_3$.

Synthesis.—Hydrogenation reactions were performed using a 300-ml Magnedrive autoclave (Autoclave Engineers, Inc.). The chamber was usually charged in the drybox. The contents were then heated under hydrogen for a predetermined period. After sufficient cooling the chamber was vented and soluble products were filtered from excess unreacted aluminum in the drybox. The solvent was then removed from the clear filtrate under vacuum and the product was analyzed as the neat material. Reaction conditions and results for the reactions studied are reported in Table II and elemental analyses of the reaction products are reported in Table I. The analyses were performed

TABLE I
ELEMENTAL ANALYSIS OF AMINOALANES

Compd	Mol wt	Al		Amine		Hydric hydrogen	
		Calcd	Found	Calcd	Found	Calcd	Found
$\text{Al}[\text{N}(\text{CH}_3)_2]_3$	159	17.0	16.8
$\text{HAl}[\text{N}(\text{CH}_3)_2]_2$	116	23.3	24.6	0.863	0.93
$\text{Al}[\text{N}(\text{C}_2\text{H}_5)_2]_3$	243	11.1	12.8	88.9	87.6
$\text{HAl}[\text{N}(\text{C}_2\text{H}_5)_2]_2$	172	15.7	16.0	83.7	84.4	0.582	0.612
$\text{H}_2\text{AlN}(\text{C}_2\text{H}_5)_2$	101	26.7	26.1	71.3	71.9	1.98	1.96
$\text{HAl}(\text{N} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_{10} \\ \diagdown \end{array})_2$	196	13.8	13.8	85.7	85.6	0.510	0.53
$\text{H}_2\text{AlN} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_{10} \\ \diagdown \end{array}$	113	23.9	24.1	74.3	74.1	1.77	1.83
$\text{HAl}(\text{N} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_8 \\ \diagdown \end{array})_2$	168	16.1	15.8	83.3	82.8	0.595	0.599
$\text{H}_2\text{AlN} \begin{array}{c} \diagup \\ \text{C}_6\text{H}_8 \\ \diagdown \end{array}$	99	27.3	27.2	70.7	68.9	2.01	1.87
$\text{HAl}[\text{N}(\text{i-C}_3\text{H}_7)_2]_2$	228	11.8	12.2	87.7	86.7	0.439	0.441
$\text{H}_2\text{AlN}(\text{i-C}_3\text{H}_7)_2$	129	20.9	19.8	77.5	77.3	1.55	1.49

on the unpurified reaction product. Further establishment of the nature of the reaction products was made by infrared and nmr comparisons with an authentic sample of the product synthesized by unequivocal means. In every case the spectra were identical.

Reaction of Aluminum, Hydrogen, and $\text{Al}[\text{N}(\text{CH}_3)_2]_3$.—Tris(dimethylamino)alane (0.10 mol from the reaction of 0.1 mol of trimethylamine-alane and excess dimethylamine), aluminum, (5 g or 0.15 mol), and benzene (100 ml) were heated at 120° under 4000 psig of hydrogen for 12 hr. The resulting mixture was filtered in the drybox yielding a clear filtrate. The filtrate was diluted to a known volume (120 ml) with benzene and analyzed for hydric hydrogen and aluminum. *Anal.* Found: H, 1.11 M; Al, 1.19 M. The hydrogen:aluminum ratio was 0.93:1.00, indicating formation of bis(dimethylamino)alane. The proton nmr spectrum of the benzene solution matched exactly that of authentic bis(dimethylamino)alane. These analytical data indicate that the yield of bis(dimethylamino)alane is 0.145 mol.

Unequivocal Synthesis of Aminoalanes.—Dialkylamino- and bis(dialkylamino)alanes were prepared by the reaction of trimethylamine-alane and 1 or 2 equiv of the appropriate secondary amine, in benzene solution.⁹ The solutions were usually stirred for 2 hr after initial mixing of the reagents. Products were isolated by removing the solvent under vacuum. These compounds were analyzed for hydrogen and aluminum and the experimental values were found to agree with the calculated values to within 5% in all cases. The following compounds were synthesized: $\text{H}_2\text{AlN}(\text{C}_2\text{H}_5)_2$, $\text{HAl}[\text{N}(\text{C}_2\text{H}_5)_2]_2$, $\text{H}_2\text{AlNC}_5\text{H}_{10}$, $\text{HAl}(\text{NC}_5\text{H}_{10})_2$, $\text{H}_2\text{AlNC}_6\text{H}_8$, $\text{HAl}(\text{NC}_6\text{H}_8)_2$, $\text{H}_2\text{AlN}(\text{i-C}_3\text{H}_7)_2$.

Forcing conditions and additional time were required for the preparation of bis(diisopropylamino)alane. The hydrogen and aluminum ratio of a 2:1 M mixture of diisopropylamine and trimethylamine-alane in benzene was found to be 1.8:1.0 after simple stirring at room temperature for 2 hr. This ratio was reduced to 1.5:1.0 and 1.05:1.00 after heating at reflux for 24 and 48 hr, respectively.

Tris(dimethylamino)alane was prepared by the reaction of trimethylamine-alane in benzene solution with excess dimethylamine. (Dimethylamine was allowed to bubble through the stirred alane solution at room temperature until liberation of hydrogen at the gas dispersion frit was observed to cease.) Attempts to prepare tris(diethylamino)alane by the reaction of

equimolar mixtures of bis(diethylamino)alane and diethylamine by refluxing these reagents in benzene solution for as long as 12 hr failed as evidenced by the fact that hydric hydrogen was found in solution. The reaction could be forced to completion by the reaction of bis(diethylamino)alane in diethylamine for 12 hr at reflux temperature. Tris(piperidino)alane was prepared in an analogous way by the reaction of trimethylamine-alane and ~10-fold excess piperidine in benzene.

Pyrolysis Studies of Aminoalane Compounds. A. Pyrolysis of $\text{H}_2\text{AlNC}_5\text{H}_{10}$ in Refluxing Toluene.—Piperidinoalane (1.08 g or 9.6 mmol) was dissolved in 30 ml of toluene and heated at reflux with stirring. Aliquot samples (2.0 ml) were withdrawn at appropriate intervals with a syringe. Toluene was removed under vacuum and the solid thus obtained was dissolved in 0.5 ml of benzene (toluene was removed since the methyl resonance of toluene was found to interfere in the proton magnetic resonance study) and proton magnetic resonance spectra of the samples were recorded. These spectral data are shown in Figure 1.

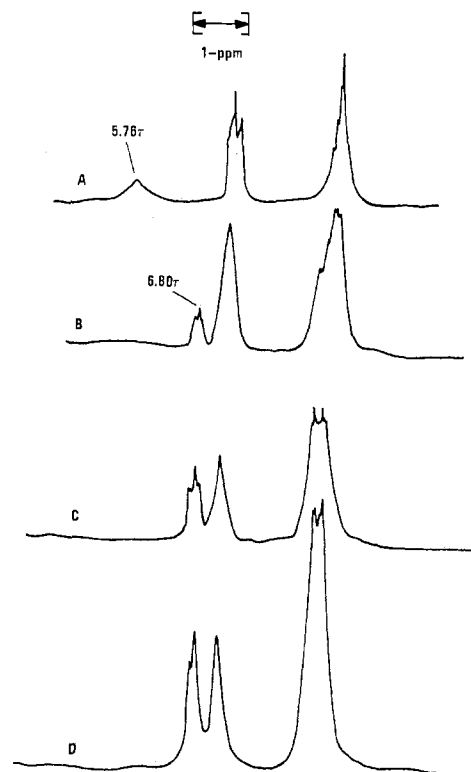


Figure 1.—Proton magnetic resonance spectral study of the pyrolysis of $\text{H}_2\text{AlNC}_5\text{H}_{10}$ in boiling toluene. Spectra were recorded in benzene solution: A, $t = 0$ spectrum of piperidinoalane; B, spectrum obtained after heating for 2.5 days; C, after heating for 6.5 days; D, after heating for 8.5 days.

The spectral changes were complete after heating for 8.5 days. After this period of heating the aluminum to hydrogen ratio was found to be 1.0:1.1. A dark gray, metallic precipitate (presumed to be aluminum) formed during this period.

B. Dta-Tga Analysis of Aminoalanes.—The thermal behavior of H_2AlNR_2 and $\text{HAl}(\text{NR}_2)_2$ compounds ($\text{NR}_2 = \text{N}(\text{C}_2\text{H}_5)_2$, NC_5H_{10} , NC_6H_8) was studied by simultaneous differential thermal and thermal gravimetric analyses of these compounds using Mettler Thermoanalyzer II instrumentation. Samples were loaded into tared platinum crucibles in the drybox and subjected to dta-tga analysis under a steady flow of argon. Representative thermal data obtained for analysis of $\text{H}_2\text{AlNC}_5\text{H}_{10}$ and $\text{HAl}(\text{NC}_5\text{H}_{10})_2$ are shown in Figure 2. The bulk of the thermal properties are summarized in Table IV.

C. Pyrolysis of H_2AlNR_2 Compounds in Evacuated, Sealed Tubes.—Piperidinoalane (0.1247 g or 1.107 mmol) was sealed in an evacuated break-seal bulb of approximately 20-ml volume. The entire assembly was submerged into a 200° oil bath for 15 min. After cooling, the tube was attached to a vacuum manifold by means of an "O" ring gasket seal and hydrogen (0.755

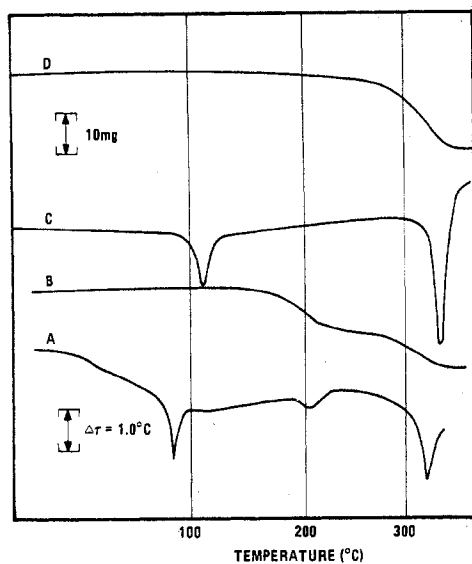


Figure 2.—Dta-tga traces of $\text{H}_2\text{AlNC}_5\text{H}_{10}$ and $\text{HAl}(\text{NC}_5\text{H}_{10})_2$. A and B are dta and tga traces for $\text{H}_2\text{AlNC}_5\text{H}_{10}$, respectively (sample size 53.0 mg); C and D are dta and tga traces for $\text{HAl}(\text{NC}_5\text{H}_{10})_2$, respectively (53.7 mg).

mmol) was determined by gas evolution analysis after opening the break-seal with a magnet. Residual solid was dissolved in benzene and the proton magnetic resonance spectrum of the resulting solution was recorded. This spectrum was found to be identical with that of authentic bis(piperidino)alane (Figure 3).

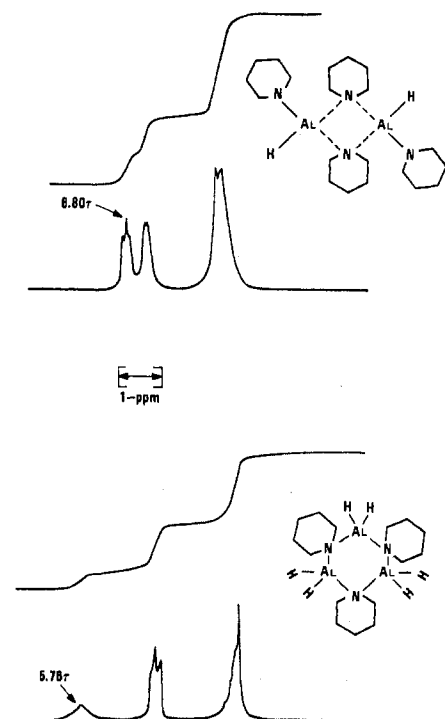


Figure 3.—Representative proton magnetic resonance spectra of mono- and bis(piperidino)alane in benzene solution.

Hydrogen (1.1 mmol) was isolated in an analogous experiment by heating diethylaminoalane (0.1531 g or 1.516 mmol) at 180° for 15 min. A dark gray, metallic precipitate (assumed to be aluminum) formed during each of these pyrolyses.

Results and Discussion

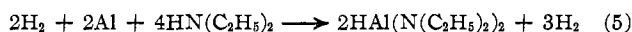
Direct Preparation of Aminoalanes.—The reaction of aluminum and hydrogen with secondary amines was studied in most detail with diethylamine and the

TABLE II
REACTIONS OF ALUMINUM, HYDROGEN,
AND DIETHYLAMINE IN BENZENE SOLVENT^a

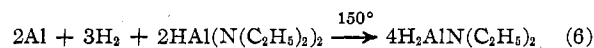
Reaction no.	Al:amine molar ratio	Time, hr	Products	Yield, %
1	1:1	3	$\text{HAl}(\text{NR}_2)_2$	92
2	Excess Al	3	$\text{HAl}(\text{NR}_2)_2$	98
3	Excess Al	7	$\text{HAl}(\text{NR}_2)_2$	86
4	Excess Al	16	$\text{HAl}(\text{NR}_2)_2$ H_2AlNR_2	91 4
5	Excess Al	28	$\text{HAl}(\text{NR}_2)_2$ $\text{H}_2\text{Al}(\text{NR}_2)$	90 3
6	Excess Al ^b	24	$\text{HAl}(\text{NR}_2)_2$ H_2AlNR_2	78 15
7	1:4	3	$\text{HAl}(\text{NR}_2)_2$ $\text{Al}(\text{NR}_2)_3$	5 88
8	Excess amine (amine solvent)	4	$\text{Al}(\text{NR}_2)_3$	91

^a $\text{R} = \text{C}_2\text{H}_5$; $n = 1-3$; temperature 150° ; pressure 3000–4000 psi. ^b Reaction temperature 65° .

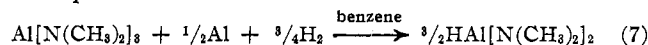
results are summarized in Table II. Bis(diethylamino)alane was the only compound formed when equivalent quantities of aluminum and diethylamine were heated under hydrogen pressure for 3 hr (reaction 1, Table II). The product from this reaction was isolated and analyzed successfully for $\text{HAl}(\text{N}(\text{C}_2\text{H}_5)_2)_2$. The proton magnetic resonance spectrum (in benzene) and infrared spectrum were identical with spectra of the analogous product prepared by unequivocal synthesis. Although bis(diethylamino)alane was formed



in high yield, efforts to prepare diethylaminoalane by increasing the aluminum to diethylamine molar ratio (reaction 2) and extending reaction times (reactions 3–5) were largely unsuccessful. The hydrogen:aluminum ratio in the products obtained in these reactions was always slightly higher than unity, indicating a low yield of the diethylaminoalane (yields ranged from 3 to 9%). These results indicate that the reaction of aluminum, hydrogen, and bis(diethylamino)alane to form diethylaminoalane does not occur to any appreciable extent at 150° . Reaction at 65° produced a material



which revealed a hydrogen to aluminum ratio of 1.19:1.0 indicating a ratio of bis(diethylamino)alane to diethylaminoalane of 78:15. Infrared analysis also revealed the product to be a mixture of the mono- and bis(amino)alane. On the other hand tris(dimethylamino)alane reacted readily and cleanly according to the equation



These data suggest that bis(diethylamino)alane is the preferred product in this reaction and is thermodynamically more stable than diethylaminoalane and thus the former compound is produced in high yield under conditions predicted to form either. This was verified by pyrolysis studies of diethylaminoalane (*vide infra*).

It is interesting to note that even at an aluminum:amine ratio of 1:4 some (5%) bis(diethylamino)alane remained in admixture with tris(diethylamino)alane; however, the latter compound was produced in high yield (91%) when diethylamine was used as the sol-

vent. These results suggest that forcing conditions are required to prepare tris(dialkylamino)alanes, due presumably to steric crowding in the product. This conclusion was substantiated by our attempts to prepare tris(diethylamino)alane by the reaction of equivalent molar quantities of bis(diethylamino)alane and diethylamine in benzene solution. The replacement of all hydridic hydrogen was incomplete even after refluxing for 12 hr. The reaction could only be forced to completion by using diethylamine as the solvent and refluxing for 12 hr.

The scope of the reaction of aluminum, hydrogen, and diethylamine was investigated using other secondary amines. The amines were chosen based on their relative base strengths as determined by both electronic and steric factors. These included dimethyl-, diisopropyl-, and diphenylamine, piperidine, and pyrrolidine. The results of these experiments are summarized in Table III.

TABLE III
REACTIONS OF ALUMINUM, HYDROGEN,
AND SELECTED DIALKYLAMINES IN BENZENE SOLVENT^a

$$\text{Al} + \frac{3}{2}\text{H}_2 + n\text{R}_2\text{NH} \xrightarrow{\Delta, P} \text{H}_{3-n}\text{Al}(\text{NR}_2)_n + n\text{H}_2$$

Reaction no.	Amine	Time, hr	Temp, °C	Products	Yield, %
1	HN(CH ₃) ₂	4	150	HAl(N(CH ₃) ₂) ₂	91
2	HN(CH ₃) ₂	20	110	HAl(N(CH ₃) ₂) ₂ H ₂ AlN(CH ₃) ₂	72 18
3	HN(CH ₃) ₂	20	60	No reaction	
4	Piperidine	5	180	H ₂ AlNC ₅ H ₁₀ HAl(NC ₅ H ₁₀) ₂	0.9 83
5	Piperidine	20	110	H ₂ AlNC ₅ H ₁₀ HAl(NC ₅ H ₁₀) ₂	3.5 89
6	Pyrrolidine	12	150	HAl(NC ₄ H ₈) ₂	88
7	HN(<i>i</i> -C ₂ H ₅) ₂	4	110	No reaction	
8	HN(C ₆ H ₅) ₂	4	140	No reaction	

^a Pressure 3000–4000 psi; aluminum:amine ratio 1.5:1.

As was the case with diethylamine, predominant formation of the bis(dialkylamino)alane was observed by reaction of aluminum (in excess) with dimethylamine (reaction 1), piperidine (reaction 4), and pyrrolidine (reaction 6). Low yields of the corresponding dialkylaminoalane were observed when these reactions were run at lower temperature (reactions 2, 5).

No reaction was observed when the secondary amine was diisopropylamine or diphenylamine, indicating that the base strength of the secondary amine is an important factor in the direct preparation reaction. It is believed that AlH₃ is generated in this reaction but that further reaction with these secondary amines is not sufficiently fast nor is the ΔH_f of the amine-alane sufficiently large to compete with thermal autodecomposition of the AlH₃.¹² This explanation is supported by our observations concerning the relative reactivities of a series of secondary amines with trimethylamine-alane in benzene. This route to the bis(dialkylamino)alanes proceeded rapidly and cleanly in ~2 hr by simple stirring of the amine-alane with diethylamine, piperidine, and pyrrolidine, while forcing conditions and a reaction time of ~48 hr (see Experimental Section) were required for the preparation of bis(diisopropylamino)alane.

Thermal Properties of Aminoalanes.—The direct-

synthesis study suggests that bis(dialkylamino)alanes are thermodynamically more stable than the corresponding dialkylaminoalanes and thus the former compounds are formed preferentially at the reaction temperatures employed. Unfortunately little information is available concerning the thermal stabilities of aminoalanes. Wiberg⁴ reported that dialkylaminoalanes decompose upon heating above their melting points with precipitation of dark flakes. No details concerning the pyrolysis were reported and the exact products of decomposition are unknown. Nöth³ suggested that the expected decomposition products might include aluminum, hydrogen, HAl(NR₂)₂, or Al(NR₂)₃, etc. On the other hand, it is known that the corresponding bis(dialkylamino)alanes are quite stable thermally. Thus, it has been reported that bis(dimethylamino)- and bis(diisopropylamino)alane can be heated under normal pressure with refluxing, without decomposition.³

The thermal decomposition of dialkylaminoalanes has been studied by quantitative determination of pyrolysis products under exact pyrolysis conditions. The pyrolysis of piperidinoalane was studied most thoroughly since this compound can be separated easily from possible decomposition products by sublimation. In addition, spectroscopic properties of this compound and predicted decomposition products are unique and can in fact be used to follow the pyrolysis reaction. It was intended that results obtained from a study of this system could be extended to describe pyrolysis of other dialkylaminoalanes.

In one pyrolysis experiment, piperidinoalane was heated at reflux in toluene. Aliquot samples were withdrawn at appropriate intervals, the solvent was removed under vacuum and replaced by benzene, and the proton magnetic resonance spectrum of the benzene solution was recorded. These data are summarized in Figure 1. The initial ($t = 0$) spectrum of piperidinoalane changed considerably by heating at 110° for 2.5 days. The hydride signal of this compound at τ 5.76 is broadened and a new signal (triplet at τ 6.80) is present. The pyrolysis was continued by refluxing for longer periods. After 6.5 days the signal due the hydridic proton was no longer present and the triplet at τ 6.80 was found to be equal to the area of the signal at τ 7.10. The spectrum at this point is identical with that of bis(piperidino)alane (see Figure 3). These spectral data were found to be insensitive to further heating. The aluminum:hydrogen ratio was determined for an aliquot and found to be 1:1. A gray precipitate (assumed to be aluminum) formed during this pyrolysis. This spectral study of the aminoalane decomposition does show that the soluble species formed is bis(piperidino)alane and that the pyrolysis reaction stops with formation of this species. We propose the following pyrolysis reaction to account for these data



Attempts were made to obtain quantitative characterization of this conversion by employing simultaneous gravimetric and differential thermal analysis. Dta-tga data obtained for mono- and bis(piperidino)alanes are shown in Figure 2. The dta of piperidinoalane exhibited three *endothermic* effects at 60, 195, and 310°. The first is assigned to melting and corresponds to the reported melting point of 58°. The effect at

(12) E. Wiberg, M. Schmidt, and U. R. Uson, *Z. Naturforsch. B*, **6**, 393 (1951).

195° is tentatively assigned to the decomposition of piperidinoalane to bis(piperidino)alane, aluminum, and hydrogen; however, the weight loss at this point (curve B) was always found to be greater (by ~50%) than that predicted on the basis of the proposed pyrolysis reaction. Some material, however, was always found to "blow" out of the crucible and observed to collect on the inner surface of the furnace assembly. It was found that this extraneous weight loss could be diminished by using a crucible cover and heating at a slower rate, but it could never be eliminated completely. The last endotherm (310°) is assigned to decomposition of bis(piperidino)alane. This assignment is verified by the thermogram obtained for bis(piperidino)alane (C) which exhibited, in addition to endothermic melting at 100°, a similar decomposition endotherm at 310°. (The tga trace (D) indicates only *one* weight loss for bis(piperidino)alane which most logically corresponds to the endotherm at 310°.)

A sealed-tube pyrolysis experiment was performed in order to gain more information about the endothermic transition at ~200°. Hydrogen (0.755 mmol) was obtained when piperidinoalane (1.10 mmol) was heated at 200° for 15 min in a sealed tube. This is 90% of the calculated amount based on eq 8. The proton magnetic resonance spectrum of the benzene-soluble pyrolysate was found to be identical with that of authentic bis(piperidino)alane. These data are taken as verification of the proposed pyrolysis.

The conversion of dialkylaminoalanes to the corresponding bis(dialkylamino)alane appears to be a perfectly general reaction as evidenced by dta-tga studies of diethylamino- and pyrrolidinoalane (Table IV).

TABLE IV
THERMAL PROPERTIES OF AMINOALANES AS
DETERMINED BY DTA-TGA ANALYSIS

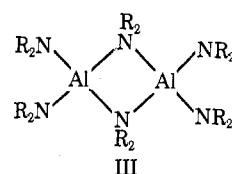
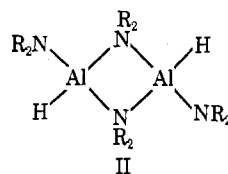
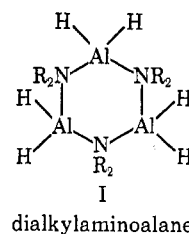
Compd	Temp of dta effect (endotherm), °C	Assignment
$H_2AlN(C_2H_5)_2$	30	Melting
	180	Formn of $HAl(N(C_2H_5)_2)_2$, Al, and H_2
	240	Decompn of $HAl(N(C_2H_5)_2)_2$
$HAl(N(C_2H_5)_2)_2$	240	Decompn of $HAl(N(C_2H_5)_2)_2$
	90	Melting
$H_2AlNC_4H_8$	150	Formn of $HAl(NC_4H_8)_2 + Al + H_2$
	305	Decompn of $HAl(NC_4H_8)_2$
	300	Decompn of $HAl(NC_4H_8)_2$
$H_2AlNC_5H_{10}$	60	Melting
	195	Formn of $HAl(NC_5H_{10})_2$, Al, and H_2
	310	Decompn of $HAl(NC_5H_{10})_2$
$HAl(NC_5H_{10})_2$	100	Melting
	310	Decompn of $HAl(NC_5H_{10})_2$

The dta trace of diethylaminoalane showed endothermic effects at 30, 180, and 240° (Table IV). These effects are assigned to melting of the starting material, thermal decomposition according to eq 8, and decomposition of bis(diethylamino)alane, respectively. Verification of the assignment of the effect occurring at 240° was obtained from dta-tga analysis of bis(diethylamino)alane which showed a similar decomposition endotherm at 240°. The weight loss accompanying the effect occurring at 180° was always greater than that predicted on the basis of eq 8. This we believe is due to extraneous weight loss due to excessive "bumping" of the material which was mentioned earlier. Quantitative characterization of this reaction was obtained

by heating diethylaminoalane in an evacuated, sealed tube at 180° followed by analysis for hydrogen. Hydrogen (0.965 mmol) was obtained from 1.52 mmol of diethylaminoalane under these conditions. This is 90% of the calculated amount based on eq 8. Pyrrolidinoalane decomposes in an analogous fashion. Three endothermic effects (Table IV) at 90, 150, and 305° were observed. These are assigned to melting of the reagent, decomposition according to eq 8, and decomposition of bis(pyrrolidino)alane, respectively. Bis(pyrrolidino)alane exhibited a similar decomposition endotherm at 300°.

These pyrolyses confirm conclusions based on our studies of the direct synthesis of aminoalanes and in particular on our inability to prepare the dialkylaminoalanes in high yield. Dialkylaminoalanes have been shown to decompose according to reaction 8 slowly by refluxing in hydrocarbon solvent and rapidly by heating the neat material at the decomposition temperature.

Spectroscopic Studies of Aminoalanes.—Aminoalanes are associated in hydrocarbon solution. Dialkylaminoalanes are trimeric in benzene while the corresponding bis(dialkylamino)alanes are mainly dimeric.³ The smaller degree of association of the bis(dialkylamino)alanes is undoubtedly a result of greater steric crowding in the more highly substituted alane derivatives. Tris(dimethylamino)alane is the only known tris(amino)alane which is associated in benzene, that being as a dimer. Aminoalanes could conceivably associate with formation of NR_2 or H bridges; the latter is improbable since dimerization through coordinatively bonded amino groups is considerably more favored thermodynamically over an Al-H-Al three-centered bridge bond. The most logical structures for the aminoalanes based on these general considerations are I-III. In addition, these structures are consistent with those which have been demonstrated for homologous aminoboranes¹³ and proposed for alkoxyalanes¹⁴ on the basis of X-ray, nmr, infrared, and dipole moment studies.



The expected range for the Al-H stretching vibration¹⁵ is 1600–1900 cm^{-1} , with a bridging hydride showing a relatively broad band around 1600 cm^{-1} . An increase in coordination on the aluminum atom normally shifts the Al-H bands to lower frequency. Sub-

(13) L. M. Trefonas and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **81**, 4435 (1959).

(14) H. Nöth and H. Suchy, *Z. Anorg. Allg. Chem.*, **355**, 44 (1968).

(15) H. M. Alpatova, T. N. Dymova, Yu. M. Kessler, and Om. R. Osipov, *Russ. Chem. Rev.*, **37**, 99 (1968).

stitution of hydride hydrogen atoms by electronegative substituents strengthens the Al-H bond as a consequence of inductive effects.

The Al-H stretching vibration for the dialkylaminoalanes (neat or in solution) occurs at $\sim 1830\text{ cm}^{-1}$ (Table V). The Al-H deformation frequencies ranged

TABLE V
INFRARED SPECTRAL DATA OF AMINOALANES

Compd	Al-H	Al-H	Compd	Al-H	Al-N
	str	def		str	def
	freq,	freq,		freq,	freq,
	cm^{-1}	cm^{-1}		cm^{-1}	cm^{-1}
$\text{HAl}(\text{N}(\text{CH}_3)_2)_2$	1824	...	$\text{HAl}(\text{NC}_4\text{H}_9)_2$	1824	695
$\text{H}_2\text{AlN}(\text{C}_2\text{H}_5)_2$	1829	734	$\text{H}_2\text{AlNC}_3\text{H}_7$	1828	725
$\text{HAl}(\text{N}(\text{C}_2\text{H}_5)_2)_2$	1822	692	$\text{HAl}(\text{NC}_3\text{H}_7)_2$	1825	688
$\text{H}_2\text{AlNC}_4\text{H}_9$	1832	729			

from 725 to 735 cm^{-1} . The position of these bands suggests a tetravalent aluminum with hydrogen atoms bonded in *terminal* positions, in support of the amino-bridged structure (I). The proton magnetic resonance spectral data are also in support of this structure. The dialkylaminoalanes exhibited only one kind of hydridic hydrogen and dialkylamino environment (Table VI).

TABLE VI
PROTON MAGNETIC RESONANCE SPECTRAL PARAMETERS OF AMINOALANES IN BENZENE

Compd	δ	τ	Multiplicity	Rel area	Assignment
$\text{H}_2\text{AlN}(\text{CH}_3)_2$	2.9	4.2	Singlet	...	Al-H
		5.9	Singlet	...	Nitrogen methyl
$\text{HAlN}(\text{CH}_3)_2$	2.4	6.17	Singlet	1.0	Al-H
		7.19	Singlet	6.0	Terminal dimethylamino
		7.67	Singlet	6.0	Bridging dimethylamino
$\text{Al}(\text{N}(\text{CH}_3)_2)_3$	2.2	7.23	Singlet	2.0	Terminal dimethylamino
		7.51	Singlet	1.0	Bridging dimethylamino
$\text{H}_2\text{AlNC}_3\text{H}_7$	2.4	5.76	Singlet	1.0	Al-H
		7.13	Triplet	1.1	Bridging nitrogen α -methylene proton
$\text{HAl}(\text{NC}_3\text{H}_7)_2$	2.2	8.63	Multiplet	3.2	Bridging nitrogen β - and γ -methylene protons
		6.80	Triplet	1.0	Terminal nitrogen α -methylene proton
		7.10	Triplet	2.0	Bridging nitrogen α -methylene proton
$\text{H}_2\text{AlNC}_4\text{H}_9$	3.0	8.43	Multiplet	3.0	Superimposition of terminal and bridging nitrogen β - and γ -methylene protons
		6.79	Triplet	1.0	Bridging nitrogen α -methylene proton
		8.32	Triplet	1.0	Bridging nitrogen β -methylene proton
$\text{HAl}(\text{NC}_4\text{H}_9)_2$	2	6.69	Triplet	1.0	Terminal nitrogen α -methylene proton
		6.99	Triplet	1.0	Bridging nitrogen α -methylene proton
		8.29	Multiplet	2.0	Terminal and bridging nitrogen β -methylene proton
$\text{HAl}(\text{N}(\text{C}_2\text{H}_5)_2)_2$...	~ 6.9	Multiplet	2.0	Ethyl-methylene
		~ 8.8	Multiplet	3.0	Ethyl-methyl
$\text{H}_2\text{AlN}(\text{C}_2\text{H}_5)_2$	2.1	6.83	Quartet	2.0	Ethyl-methylene
		8.84	Triplet	3.0	Ethyl-methyl
$\text{H}_3\text{AlN}(\text{CH}_3)_3$	1.4	5.80	Singlet	1.0	Al-H
		7.96	Singlet	3.0	Nitrogen methyl

The proton magnetic resonance spectrum of piperidinoalane is shown in Figure 3. The signals at τ 5.76 (singlet), 7.13 (triplet), and 8.63 (multiplet) of relative intensities 1.0:2.1:3.2 are assigned to hydridic hydrogen, bridging nitrogen α -methylene, and superimposition of bridging nitrogen β - and γ -methylene protons, respectively. It occurred to us that the hydride resonance appears at an abnormally low chemical shift for a main group metal hydride; however, the compounds $\text{R}_2\text{AlH}^{16}$ and $\text{H}_3\text{AlN}(\text{CH}_3)_3$ were found to exhibit hydride signals at τ 6.3 and 5.8, respectively. Proton magnetic resonance spectra of the remaining dialkylaminoalanes (Table VI) are also consistent with structure I, although a hydride resonance was not observed for all of these. The absence of a visible hydride resonance is probably due to the extensive broad-

ening by the relatively large electric quadrupole moment associated with the ^{27}Al nucleus.

The Al-H stretching frequencies of the bis(dialkylamino)alanes (neat or in solution) occur in the range $1822\text{--}1830\text{ cm}^{-1}$ (Table V). Absorption in this region is indicative of four-coordinate aluminum with Al-H bonds in terminal positions, in accord with structure II. The proton magnetic resonance spectra of the bis(dialkylamino)alanes showed only one hydridic environment (when this could be observed) and two non-equivalent dialkylamino environments of equal intensity. These data are also consistent with structure II. Specifically, bis(dimethylamino)alane exhibited proton signals at τ 6.17, 7.19, and 7.67 of relative areas 1.6:6.0:6.0 (Figure 4). These are assigned to hydridic hydrogen, terminal, and bridging dimethylamino environments, respectively. The dimethylamino resonances were assigned by reference to the spectrum of dimeric tris(dimethylamino)alane (Figure 4) in benzene which shows terminal and bridging dimethylamino signals at τ 7.23 and 7.51, respectively (relative area ratios 2.0:1.0, respectively). The spectral assignment for bis(piperidino)alane is a bit more complex owing to

the presence of nitrogen α -, β -, and γ -methylene environments. The spectrum of this compound in benzene solution consisted of signals at τ 6.80 (triplet), 7.10 (triplet), and 8.43 (complex multiplet) of relative areas 1.0:1.0:3.0, respectively (Figure 3). These are assigned to terminal nitrogen α -methylene, bridging nitrogen α -methylene, and superimposition of both terminal and bridging nitrogen β - and γ -methylene protons, respectively. Resonance of the hydridic proton was not observed.

The proton magnetic resonance spectrum of bis(diethylamino)alane was the most complex and requires detailed explanation (Figure 5). The spectrum is consistent with a dimer of structure II but is complicated by fortuitous overlap of bridging and terminal nitrogen methylene quartets and methyl triplets. Two fairly distinct methylene quartets of approximately equal area are resolved; however, the signals for the

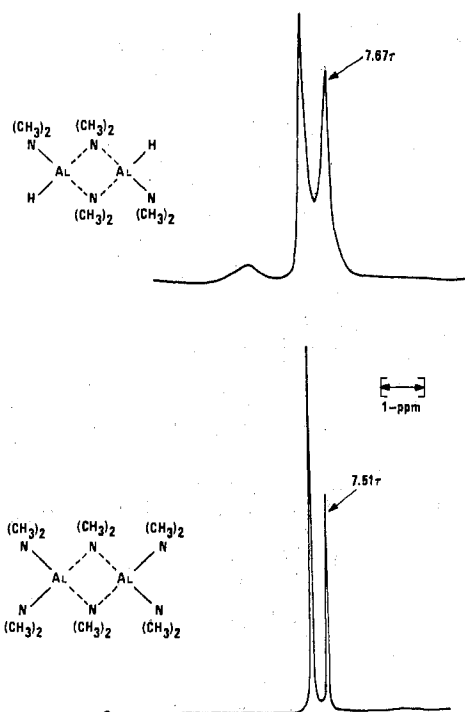


Figure 4.—Proton magnetic resonance spectra of bis- and tris(dimethylamino)alane in benzene solution.

methyl groups appear as a 1:4:4:1 quartet. This is presumably due to overlapping of both the central- and high-field components of one methyl triplet with the central- and low-field components of the other. A 1:4:4:1 quartet is predicted if the two triplet signals which overlap are each present in equal intensity.

In summary, this work provides a reasonably de-

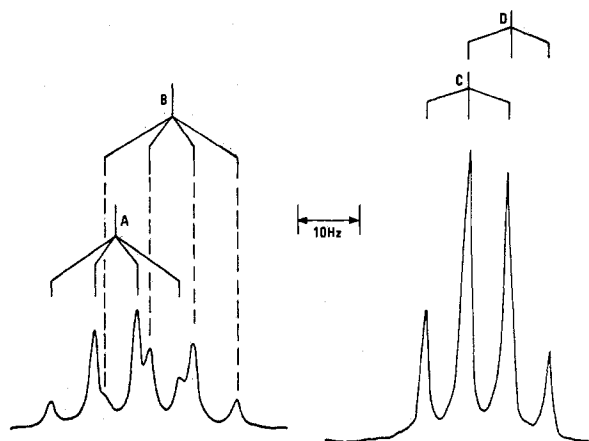


Figure 5.—Expanded-scale proton magnetic resonance spectrum of bis(diethylamino)alane in benzene solution: A, methylene quartet at τ 6.80; B, methylene quartet at τ 6.93; C, methyl triplet at τ 8.77; D, methyl triplet at τ 8.91.

tailed study of the direct synthesis of aminoalanes by the reaction of aluminum, hydrogen, and secondary amines. Although bis- and tris(dialkylamino)alanes were synthesized in high yields, dialkylaminoalanes could be prepared only in modest yield due to the thermal instability of these compounds. Spectroscopic data (infrared and proton nmr) were compiled for these compounds and used to (1) characterize reaction products, (2) monitor pyrolysis reactions, and (3) provide structural information.

Acknowledgment.—We are indebted to the Office of Naval Research under Contract No. N000 14-67-A-0159-0005 and ONR Contract Authority No. NR-93-050/12-5-67-429 for support of this work.