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Aluminum–Nitrogen Polymers. The Formation and Condensation of Adducts of Triphenylalane with Methylamine and Dimethylamine

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Triphenylalane[2] and methylamine have been shown to react in toluene solution, forming methylamine triphenylalane, $CH_3H_2N:Al(C_6H_5)_3$. This adduct loses benzene when heated to 100–120° *in vacuo*, forming methylaminodiphenylalane, $[CH_3HNAl(C_6H_5)_2]_n$, which in turn evolves benzene at 180–230° to form methyliminophenylalane, $(CH_3NAlC_6H_5)_{ny}$. Triphenylalane and dimethylamine react in toluene solution to form dimethylamine triphenylalane, $(CH_3)_2HN:Al(C_6H_5)_3$, which when heated to 150–180° evolves benzene, forming $[(CH_3)_2NAl(C_6H_5)_2]_n$. These new crystalline compounds have been characterized by chemical analyses, X-ray powder diffraction patterns, infrared spectra, and by molecular weight studies. The nature of the condensation polymerization processes and the probable structural pattern followed in the proliferation of the aluminum–nitrogen frameworks are discussed.

Introduction

An earlier paper[3] has discussed the reactions of ammonia and the methylamines with alkylalanes and alkylchloroalanes to form one:one molecular addition compounds. When these monomeric adducts have active groups on both nitrogen and aluminum they readily undergo pyrolytic condensation. By varying the terminal groups on the nitrogen and aluminum atoms and by carefully controlling the conditions it is possible to set up successive reactions which give more and more aluminum–nitrogen bonding, and more and more extended polymeric frameworks result. A general scheme for such reactions has been suggested and the structural pattern characteristic of aluminum–nitrogen polymers appears to be reasonably clear.[3,4] We now report an extension of these general reactions to a study of the formation and condensation of amine adducts of triphenylalane to determine the effect of substituting aromatic groups for alkyl groups on aluminum.

Experimental

Manipulative Methods.—All organo-aluminum compounds were handled either under an atmosphere of dry nitrogen or in a glass vacuum line of conventional design. Oxygen and moisture were rigorously excluded from all reactions.

Analysis for Phenyl Groups Attached to Aluminum.—Hydrolysis of phenylalane compounds by excess water or dilute acid presumably yields one mole of benzene for every C_6H_5–Al bond in the starting material. The benzene formed, however, cannot readily be separated quantitatively from residual water, and so this reaction is not as convenient for phenyl group assay as the analogous hydrolysis of ethylalane compounds is for ethyl group assay. Reaction of the phenylalane compounds with *n*-butanol was investigated in an attempt to replace all C_6H_5–Al bonds by C_4H_9–O–Al with liberation of benzene, which then could have been easily separated from residual butanol in the vacuum line. However, replacement of C_6H_5– by C_4H_9O– apparently was not quantitative within a reasonable period of time. Reaction with excess anhydrous liquid HCl therefore was used for the determination of phenyl groups attached to aluminum, the phenyl groups being replaced by chlorine with liberation of benzene.

$$>Al\text{–}C_6H_5 + HCl \xrightarrow{-96^\circ} >Al\text{–}Cl + C_6H_6$$

$$\textit{e.g.} \qquad Al(C_6H_5)_3 + 3HCl \longrightarrow AlCl_3 + 3C_6H_6$$

The analysis was carried out in a double bulb glass reaction apparatus (bulbs A and B connected by a Y-tube fitted with a standard-taper joint lubricated with Kel-F fluorocarbon grease). A weighed sample (0.1 to 0.2 g.) of the material to be analyzed was put into bulb A in an atmosphere of dry nitrogen, and the apparatus was assembled, attached to the vacuum line, and evacuated. Enough HCl to form 2–5 ml. of liquid then was condensed as a solid at −196° in bulb B. The HCl was warmed to −96°, subjecting the sample to the action of HCl gas at about 400 mm. pressure. Finally bulb A containing the sample was cooled to −96° while bulb B was warmed to room temperature, causing liquid HCl to condense on the sample. (Reaction at higher temperatures was vigorous with formation of some tarry product and less benzene.) The mixture was kept at −96° for 1 hr. with occasional shaking before removal of the volatile components. The benzene was collected in a trap at −96° and weighed.

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[2] Wiberg has proposed the name alane for AlH_3 and its derivatives, in analogy to such terms as borane, silane, germane, etc. This usage is sound and convenient and is adopted in this paper.

[3] A. W. Laubengayer, J. D. Smith, and G. G. Ehrlich, *J. Am. Chem. Soc.*, **83**, 542 (1961).

[4] A. W. Laubengayer, "Inorganic Polymers," Special Publication No. 15, The Chemical Society, London, 1961.

The non-volatile solid residue was normally analyzed for aluminum or amine, for which purpose it was dissolved cautiously in dilute aqueous HCl.

Aluminum Analysis.—The aluminum content of a dilute aqueous acid solution of a weighed sample was obtained by precipitation of the oxinate by the standard method.

Amine Analysis.—The semimicro Kjeldahl method was used for the determination of methylamine and dimethylamine.[5]

Infrared Spectra.—The infrared absorption spectra in the region 5000 to 667 cm.$^{-1}$ of solid compounds were recorded on a Perkin-Elmer Model 21 spectrometer using Nujol mulls between rock salt plates. Mulls in hexachlorobutadiene were used for those regions in which Nujol itself absorbs, 3226 to 2000 cm.$^{-1}$ and 1515 to 1300 cm.$^{-1}$. The absorption spectra of triphenylalane and of all the new compounds are listed in Table II for easy comparison.

X-Ray Powder Diffraction Patterns.—Samples were finely ground in the drybox and sealed in thin-walled capillary tubes. X-Ray powder photographs were taken with a North American Phillips Company Norelco X-ray diffraction unit and 5.73- or 11.46-cm. inside diameter cameras. A copper target with nickel filter was used at 35 kv., 15 mamp., CuKα λ average = 1.5418 Å. The patterns characteristic of all of the new compounds are listed along with that of triphenylalane in Table I.

Materials.—Triphenylalane was prepared by reacting aluminum metal with mercurydiphenyl in refluxing toluene.[6] Because the exact procedure used is very important for obtaining pure triphenylalane the details of our method will be given. In a typical experiment, 20 g. (56 mmoles) of mercurydiphenyl was heated with 9 g. (330 mmoles) of aluminum chips in 120 ml. of refluxing toluene for 36 hr. under an atmosphere of dry nitrogen. The hot solution then was forced by nitrogen pressure from the reaction flask through a tube plugged with glass wool into another flask in which it was allowed to crystallize, after which the mother liquor was removed from the crystals, again by nitrogen pressure. Further crystals were obtained by concentration of the mother liquor, yielding a total of 8.5 g. (33 mmoles) of triphenylalane, m.p. 223–227° with decomposition in a sealed tube. Discolored material was purified either by recrystallization from toluene or by vacuum sublimation at 200–210° onto a water-cooled cold finger. This latter process was not convenient for purification of large samples, as about a quarter of the sample decomposed each time.

Anal. Calcd. for $Al(C_6H_5)_3$: Al, 10.5; C_6H_5, 89.5. Found: Al, 10.6; C_6H_5 (as C_6H_6), 88.6.

Powder X-ray diffraction data for $Al(C_6H_5)_3$ are listed in Table I. The infrared spectrum of mulls of triphenylalane in Nujol and hexachlorobutadiene showed absorption bands at the frequencies shown in Table II. These infrared data are in good agreement with those listed by Costa and Calcinari[7] in the frequency range 1500–670 cm.$^{-1}$ for a Nujol mull of $Al(C_6H_5)_3$.

Methylamine and dimethylamine were purified as described in reference 3.

The Preparation of Methylamine Triphenylalane, $CH_3H_2N:Al(C_6H_5)_3$.—The amine adducts of triphenylalane and their pyrolysis products were prepared in the aforementioned double bulb reaction vessel. $Al(C_6H_5)_3$ (0.841 g., 3.26 mmoles) was treated in bulb A with excess CH_3H_2N (0.265 g., 8.41 mmoles) in 30 ml. of toluene at −78°. The mixture was warmed to 25°, shaken thoroughly so that virtually all the solid was dissolved, and allowed to stand for 6 hr. The solution then was decanted into bulb B from the trace of solid which had settled out. Toluene and unchanged CH_3H_2N (0.161 g., 5.11 mmoles) were pumped from the reaction vessel, leaving a white crystalline solid in the reaction bulb. Thus 3.26 mmoles of $Al(C_6H_5)_3$ had reacted with 3.30 mmoles of CH_3H_2N, suggesting the equation

$$CH_3H_2N + Al(C_6H_5)_3 \longrightarrow CH_3H_2N:Al(C_6H_5)_3$$

The product was removed from the reaction vessel in an atmosphere of dry nitrogen.

Anal. Calcd. for $CH_3H_2N:Al(C_6H_5)_3$: Al, 9.3; CH_3H_2N, 10.7; C_6H_5, 80.0; mol. wt., 289. Found: Al, 9.3; CH_3H_2N, 10.8; C_6H_5 (as C_6H_6) 79.5; mol. wt. (cryoscopy in benzene), 299.

Properties of $CH_3H_2N:Al(C_6H_5)_3$.—Methylamine triphenylalane was a white crystalline solid. On standing in moist air, $CH_3H_2N:Al(C_6H_5)_3$ evolved benzene and methylamine. Samples which had been sealed in ampoules under dry nitrogen decomposed to give a viscous liquid during four months at about 25°. The freshly prepared adduct was soluble in benzene, toluene, and ether, but insoluble in paraffinic hydrocarbons. $CH_3H_2N:Al(C_6H_5)_3$ softened and evolved benzene when heated *in vacuo* to about 110° (see below), but did not actually melt when heated slowly to 300° in a capillary tube under nitrogen, though the decreasing volume of the solid showed that some decomposition took place.

Condensation of $CH_3H_2N:Al(C_6H_5)_3$ to $[CH_3HNAl(C_6H_5)_2]_n$.—$[CH_3HNAl(C_6H_5)_2]_n$ was prepared by heating $CH_3H_2N:Al(C_6H_5)_3$ *in vacuo* to 120°. The adduct $CH_3H_2N:Al(C_6H_5)_3$ was most conveniently pyrolyzed in the apparatus in which it had been prepared, so a two-stage synthesis was normally used without isolation of the intermediate $CH_3H_2N:Al(C_6H_5)_3$. $Al(C_6H_5)_3$ (2.187 g., 8.48 mmoles) and CH_3H_2N (0.314 g., 10.0 mmoles) were allowed to react in 30 ml. of toluene. The solvent and unchanged CH_3H_2N (0.044 g., 1.35 mmoles) were pumped off, leaving 8.48 mmoles of $Al(C_6H_5)_3$ and 8.65 mmoles of CH_3H_2N in the reaction bulb in the form of the white crystalline adduct $CH_3H_2N:Al(C_6H_5)_3$. This bulb then was heated to 100–110° for 10 hr., during which time further CH_3H_2N (0.005 g., 0.16 mmole) was recovered together with 0.640 g. (8.20 mmoles) of benzene, identified by its melting point (5°) and infrared spectrum. In the first hour of heating the bulb contents softened to a paste, which later set to a colorless solid. No more benzene was obtained on 3 hr. further heating to 110–120°. The total amount of unreacted CH_3H_2N recovered and the amount of benzene collected were consistent with the equation

$$nCH_3H_2N:Al(C_6H_5)_3 \longrightarrow [CH_3HNAl(C_6H_5)_2]_n + nC_6H_6$$

The residual solid was readily soluble at 25° in 20 ml. of toluene, from which it could be recovered only by complete evaporation of the solvent at 80–100° *in vacuo*.

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(5) A. Steyermark, "Quantitative Organic Microanalysis," Blakiston, Philadelphia, Pa., 1951.

(6) E. Krause and P. Dittmar, *Ber.*, **63**, 2401 (1930).

(7) G. Costa and R. Calcinari, *Gazz. Chim. Ital.*, **89**, 1415 (1959).

TABLE I

POWDER X-RAY DIFFRACTION DATA (CuKα RADIATION)

$Al(C_6H_5)_3$		$CH_3H_2N:Al(C_6H_5)_3$		$[(CH_3)HNAl(C_6H_5)_2]_n$		$(CH_3NAlC_6H_5)_{ny}$		$(CH_3)_2HN:Al(C_6H_5)_3$		$[(CH_3)_2NAl(C_6H_5)_2]_n$	
d Spacing	Intensity	*d* Spacing	Intensity	*d* Spacing	Intensity	*d* Spacing	Intensity	*d* Spacing	Intensity	*d* Spacing	Intensity
9.70	m	9.33	w	11.30	s	6.71	s	10.34	vw	9.26	s
8.27	m	7.44	w	9.13	m	5.72	m	6.90	w	8.21	w-m
7.26	m	6.32	vw	8.53	w	4.93	m	6.31	w	6.80	s
6.05	w	5.88	vw	8.00	s	4.06	m	5.57	m	5.49	s
4.91	s	5.44	vw	7.15	s	3.51	s	5.04	w	5.21	s
4.40	s	4.90	s	6.56	m	3.22	w	4.65	s	4.78	s
4.17	m	4.62	ms	6.06	vw	2.98	w	4.25	w-m	4.11	s
3.91	s	4.37	m	5.75	s	2.78	w	4.05	w-m	3.89	m
3.61	m	4.08	m	5.45	s	2.63	w	3.85	w-m	3.78	m
3.46	m	3.88	m	4.85	s	2.49	vw	3.46	w	3.59	s
3.25	vw	3.68	m	4.55	s	2.31	m	3.15	w	3.34	w-m
3.05	w	2.95	w	4.24	vw	2.13	vw	3.07	w	3.17	w
2.84	w	2.61	vw	4.08	vs	1.98	vw	2.74	w	3.06	vw
2.72	vw	2.43	vw	3.93	vw	1.84	vw			2.96	vw
2.62	vw	1.64	w	3.83	w	1.67	vw			2.85	w
2.44	vw			3.71	vw					2.48	vw
2.18	vw										

TABLE II

INFRARED ABSORPTION SPECTRA

$Al(C_6H_5)_3$		$CH_3H_2N:Al(C_6H_5)_3$		$[CH_3HNAl(C_6H_5)_2]_n$		$(CH_3NAlC_6H_5)_{ny}$		$(CH_3)_2HN:Al(C_6H_5)_3$		$[(CH_3)_2NAl(C_6H_5)_2]_n$	
Cm.$^{-1}$	Intensity	Cm.$^{-1}$	Intensity	Cm.$^{-1}$	Intensity	Cm.$^{-1}$	Intensity	Cm.$^{-1}$	Intensity	Cm.$^{-1}$	Intensity
3070	w-m	3260	m	3260	w	3080–2920	m	3220	w-m	3030–2940	s
3010	w(sh)	3040	m(sh)	3070	w-m	2830	w	3020	m(sh)		
1582	w-m	2990	m	3010	m	1961	vw	2990	s	2900	s
1484	w-m	1961	vw	1965	vw			1953	w	1961	w
1422	s	1880	vw	1894	vw	1887	vw	1887	w	1890	w
1342	vw	1842	vw	1838	vw	1832	vw	1838	w	1838	w
1316	vw	1580	m	1603	w-m(sh)	1590	s	1783	vw	1645	w
1248	w	1481	w-m	1590	m	1546	ms(sh)	1639	w(sh)	1585	m
1189	w	1460	w-m	1488	w	1471	m	1590	w-m	1477	s
1089	m	1418	m	1466	w	1420	s	1575	w-m	1420	s
1082	m(sh)	1299	w	1422	s	1245	w	1479	m(sh)	1307–1274	w(sh)
1049	ms	1250	m	1328	w-m	1193	w	1466	s		
1018	w-m	1088	s	1247	w-m	1139	w-m	1416	s	1245	m
994	m	1063	w-m	1195	vw	1089	s	1393	w	1230	s
857	vw	1052	w-m	1147	w	1022	s	1259	m	1195	m
769	vw	989	m	1091	s	1004	s	1242	s	1160	m
742	w(sh)	735	s	1059	vw	969	vw	1215	w	1111	s
729	s	730	ms(sh)	1048	vw	892	vw	1112	m	1087	vs
705	s	726	m(sh)	998	w	732	s(sh)	1087	s	1082	vs
698	vs	706	vs	969	s	722	vs	1059	w	1062	w
683	ms	683	s	948	m(sh)	710	s	1025	s	1032	vs
673	ms	673	s	936	s	702	s	737–725	s	997	s
				906	m	679	w			892	vs
				898	m			708–703	s	727	vs
				728	s					710	s(sh)
				702	vs			673	s	702	vs
				685	s					680	s
				671	ms						

Anal. Calcd. for $[CH_3HNAl(C_6H_5)_2]_n$: Al, 12.8; CH_3HN, 14.2; C_6H_5, 73.0. Found: Al, 13.0; CH_3HN (as CH_3H_2N), 14.0; C_6H_5 (as C_6H_6), 72.0; *n* (cryoscopy in benzene) ~ 2.3.

Properties of $[CH_3HNAl(C_6H_5)_2]_n$.—When exposed to moist air, $[CH_3HNAl(C_6H_5)_2]_n$ evolved benzene and CH_3H_2N, although less rapidly than did $CH_3H_2N{:}Al(C_6H_5)_3$. The same products were liberated rapidly on treating the compound with water or dilute acid. When heated *in vacuo* to 125–130°, $[CH_3HNAl(C_6H_5)_2]_n$ slowly sublimed unchanged. Sublimation was more rapid at 150°, but was accompanied by loss of benzene, while at

170° the aminoalane melted and evolved benzene, leaving a solid iminoalane of composition $(CH_3NAlC_6H_5)_{ny}$ (see below).

Condensation of $[CH_3HNAl(C_6H_5)_2]_n$ to Methyliminophenylalane, $(CH_3NAlC_6H_5)_{ny}$.—$(CH_3NAlC_6H_5)_{ny}$ which was prepared by heating $[CH_3HNAl(C_6H_5)_2]_n$ to 180–230° *in vacuo*. A sample of $[CH_3HNAl(C_6H_5)_2]_n$ (1.185 g., $8.53/n$ mmoles), prepared as described above, was heated *in vacuo* to 180°. At about 170° the white solid melted to a clear liquid which evolved a condensable gas, which was identified as benzene (m.p. 5°; infrared spectrum). The liquid became milky as benzene was lost, and finally set to a white solid after 1 hr. at 180°. Three hr. further heating at 180°, followed by 15 hr. at 230°, caused a total of 0.632 g. (8.10 mmoles) of benzene to be lost, but no more benzene was collected during a final heating at 230° for 2 hr., suggesting that the reaction which had occurred was

$$y[CH_3HNAl(C_5H_5)_2]_n \xrightarrow{180\text{–}230°} (CH_3NAlC_6H_5)_{ny} + nyC_6H_6$$

The white solid product was recovered from the reaction vessel by opening this in an atmosphere of dry nitrogen.

Anal. Calcd. for $(CH_3NAlC_6H_5)_{ny}$: Al, 20.3; CH_3N, 21.8; C_6H_5, 57.9. Found: Al, 19.9; CH_3N (as CH_3H_2N), 21.5; C_6H_5 (as C_6H_6), 57.7.

Properties of $(CH_3NAlC_6H_5)_{ny}$.—The white solid evolved benzene and methylamine on exposure to moist air, and reacted readily with water or dilute acid, liberating benzene. There was no change in appearance on heating a sample to 350° under nitrogen. This compound was not sufficiently soluble in benzene to allow satisfactory molecular weight determinations.

Preparation of Dimethylamine Triphenylalane, $(CH_3)_2HN:Al(C_6H_5)_3$.—$Al(C_6H_5)_3$ (1.783 g., 6.91 mmoles) was treated with excess $(CH_3)_2HN$ (0.395 g., 8.78 mmoles) in 20 ml. of toluene at −78°. The bulk of the $Al(C_6H_5)_3$ remained undissolved at this temperature, but dissolved on warming to 25° and shaking the mixture. The solution was decanted from the trace of insoluble material left, allowed to stand for 2 hr., and then cooled to −78°, whereupon colorless crystals formed. Toluene and unchanged $(CH_3)_2HN$ (0.104 g., 2.33 mmoles) were pumped from the reaction vessel. Thus the 6.91-mmole sample of $Al(C_6H_5)_3$ had reacted with 6.45 mmoles of $(CH_3)_2HN$. The apparent mole ratio of slightly greater than one for $Al(C_6H_5)_3$ to $(CH_3)_2HN$ reacting presumably was due to some impurity in the sample of $Al(C_6H_5)_3$, as evidenced by the insoluble residue. The observations are consistent with the reaction equation

$$(CH_3)_2HN + Al(C_6H_5)_3 \xrightarrow{\text{toluene}} (CH_3)_2HN:Al(C_6H_5)_3$$

The crystalline product was removed from the reaction bulb in an atmosphere of dry nitrogen, and its analysis established the correctness of the above equation.

Anal. Calcd. for $(CH_3)_2HN:Al(C_6H_5)_3$: Al, 8.9; $(CH_3)_2HN$, 14.9; C_6H_5, 76.2. Found: Al, 8.9; $(CH_3)_2HN$, 15.1; C_6H_5 (as C_6H_6), 75.3.

Properties of $(CH_3)_2HN:Al(C_6H_5)_3$.—Dimethylamine triphenylalane was a white crystalline solid which on standing in air slowly evolved benzene and dimethylamine. It reacted vigorously with water, leaving a white suspension, and was taken into solution rapidly and completely by dilute aqueous HCl with evolution of heat. The freshly prepared adduct was soluble in benzene, toluene, and ether, but insoluble in paraffinic hydrocarbons. A sample of $(CH_3)_2HN:Al(C_6H_5)_3$ softened when heated to 90° under nitrogen in a sealed capillary tube and melted in the range 125–130°. When heated *in vacuo* for 2 hr. at 90° the compound lost a trace of benzene; at 130° loss of benzene was rapid, a liquid phase was formed, and a white sublimate collected in the cooler parts of the apparatus.

Condensation of Dimethylamine Triphenylalane to Dimethylaminodiphenylalane, $[(CH_3)_2NAl(C_6H_5)_2]_n$.—$Al(C_6H_5)_3$ (2.664 g., 10.33 mmoles) was treated with excess $(CH_3)_2HN$ (0.536 g., 11.91 mmoles) in 20 ml. of dry toluene, and after reaction had occurred the toluene and unchanged $(CH_3)_2HN$ (0.072 g., 1.59 mmoles) were pumped off, leaving the crystalline $(CH_3)_2HN:Al(C_6H_5)_3$ formed from 10.33 mmoles of $Al(C_6H_5)_3$ and 10.32 mmoles of $(CH_3)_2HN$. The temperature of the reaction vessel was raised to 85–95° for 4 hr., in order to ensure complete removal of the toluene solvent. Slight decomposition of the $(CH_3)_2HN:Al(C_6H_5)_3$ took place at this temperature with loss of benzene (0.020 g., 0.26 mmole). The temperature then was raised to 150–160°. At 145° the adduct melted and evolved benzene, but after 3 hr. at 150–160° the mixture slowly solidified. Decomposition of the $(CH_3)_2HN:Al(C_6H_5)_3$ was completed by a further 4 hr. heating at 165–170°, and 1 hr. at 175–180°. At these higher temperatures more than half of the solid sublimed to the cooler parts of the apparatus. The total amount of benzene recovered from the reaction vessel during the pyrolysis was 0.711 g. (9.12 mmoles). This was 1.2 mmoles short of the quantity required by the equation

$$n(CH_3)_2HN:Al(C_6H_5)_3 \longrightarrow [(CH_3)_2NAl(C_6H_5)_2]_n + nC_6H_6$$

The product was removed from the apparatus under dry nitrogen and purified by vacuum sublimation at 190–200° onto a water-cooled cold finger. The sublimate was a white, apparently microcrystalline powder.

Anal. Calcd. for $[(CH_3)_2NAl(C_6H_5)_2]_n$: Al, 12.0; $(CH_3)_2N$, 19.6; C_6H_5, 68.4. Found: Al, 11.9; $(CH_3)_2N$ (as $(CH_3)_2HN$), 19.6; C_6H_5 (as C_6H_6), 67.1.

Properties of $[(CH_3)_2NAl(C_6H_5)_2]_n$.—$[(CH_3)_2NAl(C_6H_5)_2]_n$ evolved benzene and dimethylamine when exposed to moist air, reacted with water forming a suspension of $Al(OH)_3$, and dissolved readily in dilute aqueous HCl. It was soluble in benzene and toluene. In an experiment to determine its phenyl content, a sample of $[(CH_3)_2NAl(C_6H_5)_2]_n$ (0.1306 g., $0.58/n$ mmole) was treated with anhydrous HCl (0.3785 g., 10.37 mmoles). After the reaction, the volatile materials recovered from the reaction vessel were benzene (0.0888 g., 1.14 mmoles) and HCl (0.2927 g., 8.02 mmoles). Thus 0.0858 g. (2.35 mmoles) of HCl had reacted with $0.58/n$ mmole of $[(CH_3)_2NAl(C_6H_5)_2]_n$, forming 1.14 mmoles of benzene. This suggests the equation

$$[(CH_3)_2NAl(C_6H_5)_2]_n + 4nHCl \longrightarrow n(CH_3)_2NH_2^+ + nAlCl_4^- + 2nC_6H_6$$

This is analogous to the reaction reported by Davidson and Brown[8] between HCl and $[(CH_3)_2NAl(CH_3)_2]_2$

$$[(CH_3)_2NAl(CH_3)_2]_2 + 8HCl \longrightarrow 2(CH_3)_2NH_2^+ + 2AlCl_4^- + 4CH_4$$

Ruff[9] has reported that $[(CH_3)_2NAl(C_6H_5)_2]_n$, obtained by reaction of LiC_6H_5 with $(CH_3)_2NAlH_2$, melted at 202–204° and $n = 2.09$ (b.p. elevation in benzene).

The System Trimethylamine–Triphenylalane.—We have investigated the possibility of forming the adduct $(CH_3)_3N:Al(C_6H_5)_3$ by donor–acceptor bonding. When an excess of $(CH_3)_3N$ was brought together with $Al(C_6H_5)_3$ at $-78°$ and then pumped at that temperature some $(CH_3)_3N$ was retained with the alane, but when this material was warmed to 0° and pumped only $Al(C_6H_5)_3$ remained (identified by melting point and X-ray pattern). There may have been some adduct formed at $-78°$, but if so, it did not persist at 0° or above. Several repetitions of this experiment confirmed the above results.

Ruff[9] reports treating $(CH_3)_3NAlH_3$ with $Hg(C_6H_5)_2$ to produce a solid, m.p. 227–229°, which gave the correct aluminum analysis for $(CH_3)_3NAl(C_6H_5)_3$. He lists no other data.

Discussion

General Reaction Pattern.—The experimental data obtained in this investigation establish that reactions of methylamine and dimethylamine with triphenylalane follow the general pattern outlined previously in detail.[3,4] Thus the following reaction scheme for the system methylamine–triphenylalane summarizes the formation of the one:one adduct and the two subsequent stepwise condensations which occur on controlled pyrolysis.

$$CH_3H_2N + Al(C_6H_5)_3 \xrightarrow[\text{cooled}]{\text{toluene}}$$

$$CH_3H_2N:Al(C_6H_5)_3 \xrightarrow[100\text{–}120°]{-C_6H_6}$$

$$\frac{1}{n}[CH_3HNAl(C_6H_5)_2]_n \xrightarrow[180\text{–}230°]{-C_6H_6} \frac{1}{ny}(CH_3NAlC_6H_5)_{ny}$$

And the system dimethylamine–triphenylalane forms a one:one adduct which undergoes one pyrolytic condensation step.

$$(CH_3)_2HN + Al(C_6H_5)_3 \xrightarrow[\text{cooled}]{\text{toluene}}$$

$$CH_3HN:Al(C_6H_5)_3 \xrightarrow[150\text{–}180°]{-C_6H_6} \frac{1}{n}[(CH_3)_2NAl(C_6H_5)_2]_n$$

The stoichiometric data on the reactions and analysis of the crystalline products are consistent with the equations. Comparison of the X-ray diffraction data given in Table I shows that the pattern of triphenylalane disappears and new crystalline phases appear when the amine alane adducts are formed, and the patterns characteristic of the adducts are replaced by new crystalline patterns when condensation to the aminoalane phases and the iminoalane phase takes place.

The formation of benzene when condensation occurs must involve the detachment of phenyl groups from aluminum and hydrogen atoms from nitrogen, with the setting up of more aluminum–nitrogen bonding to give polymeric materials. The degree to which condensation can occur must be a function of the number of hydrogen atoms of the amine and the number of phenyl groups of the alane. Thus $CH_3H_2N:Al(C_6H_5)_3$ readily splits out benzene to give $[CH_3HNAl(C_6H_5)_2]_n$ which, when heated moderately, loses more benzene to form $(CH_3NAlC_6H_5)_{ny}$. This polymer, having no more hydrogen on the nitrogen, cannot undergo a third condensation step and therefore has rather high thermal stability. $(CH_3)_2HN:Al(C_6H_5)_3$ can readily undergo only one condensation.

Infrared Spectra.—Analysis of the infrared absorption data in Table II further confirms the proposed reaction schemes. The spectrum for $Al(C_6H_5)_3$ has been extended beyond that reported previously[7] to include C–H stretching vibrations at 3070 and 3010 cm.$^{-1}$. A peak at 1582 cm.$^{-1}$ may be assigned to in-plane vibrations of the carbon atoms in the phenyl groups.

Generally the essential features of the $Al(C_6H_5)_3$ spectrum are retained upon reaction with the amines. Peaks due to N–H modes were observed to be at lower frequencies when compared with the free amines. This indicates weakening of these bonds by the increased positive condition of the nitrogen atom due to its donor action in the adducts.

$[CH_3HNAl(C_6H_5)_2]_n$, the first compound formed by heating $CH_3H_2N:Al(C_6H_5)_3$, shows greatly reduced N–H stretching vibrations and the absence of NH_2 rocking frequencies. Bands due to phenyl groups can be identified, but new peaks between 969 and 898 cm.$^{-1}$ have not been assigned.

The final pyrolysis product, $(CH_3NAlC_6H_5)_{ny}$, retains the C–H stretching and in-plane $-C{=}C-$ vibrations characteristic of phenyl groups, but the N–H bands have disappeared throughout the spectrum, giving further evidence for the reactions proposed. The hydrogen which reacts with phenyl groups to liberate benzene must be the

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

(9) J. K. Ruff, *ibid.*, **83**, 1798 (1961).

hydrogen which was attached to the nitrogen of the amine.

The condensation product of $(CH_3)_2HN{:}Al(C_6H_5)_3$, *i.e.*, $[(CH_3)_2NAl(C_6H_5)_2]_n$, showed the absence of N–H modes, again lending support to the proposed reactions.

No efforts have been made to assign peaks to Al–N stretching vibrations. A number of the spectra did not show any deviation from $Al(C_6H_5)_3$ in the region where Al–N peaks might be expected (about 714 $cm.^{-1}$). A strong peak regularly appeared at 729 to 739 $cm.^{-1}$, which has been assigned to Al–C vibrations by Costa and Calcinari.[10]

Structure Patterns.—The structural pattern for the aluminum–nitrogen frameworks of the new compounds is believed to follow that suggested previously.[3,4] The tetrahedral coördination for nitrogen and aluminum which is established when the one:one adducts $CH_3H_2N{:}Al(C_6H_5)_3$ and $(CH_3)_2HN{:}Al(C_6H_5)_3$ are formed also should be maintained when condensation takes place, N–H and $Al–C_6H_5$ bonds being broken and Al–N bonding set up. The aminodiphenylalanes, $[CH_3HNAl(C_6H_5)_2]_n$ and $[(CH_3)_2NAl(C_6H_5)]_n$, are volatile solids, soluble in aromatic solvents. These properties, together with the association constants $n = 2.3$ and $n = 2.09$, respectively, for the two aminoalanes, are consistent with the postulate of there being a mixture of dimeric and trimeric cyclic molecules of $[CH_3HNAl(C_6H_5)_2]_n$ and dimeric cyclic molecules of $[(CH_3)_2NAl(C_6H_5)_2]_n$ in benzene solution. The iminodiphenylalane $(CH_3NAlC_6H_5)_{ny}$ behaves as if it is a cross-linked high polymer.

The failure of trimethylamine and triphenylalane to form the adduct $(CH_3)N{:}Al(C_6H_5)_3$, thermally stable at 0°, is puzzling, especially since Ruff[9] reported a melting point of 227–229° for his product. $(CH_3)_3N$ is a strong donor molecule and there appears to be no steric hindrance to the formation of the adduct by sp^3 bonding for aluminum. The adduct also should be stable against condensation with the splitting out of benzene because there would be no active hydrogen atoms bonded to nitrogen.

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[10] G. Costa and R. Calcinari, *Univ. Studi Trieste, Fac. Sci., Ist. Chim.*, **No. 20**, 15 (1957).