Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

Preliminary communication

The direct synthesis of aminoalanes

E. C. ASHBY and ROGER KOVAR
School of Chemistry, Georgia Institute of Technology, Atlanta, Georgia 30332 (U.S.A.)
(Received February 3rd, 1970)

The use of aminoalanes as polymerization catalysts[1], reducing agents[2] and as synthetic intermediates[3] has been reported; however more widespread use of these compounds is limited by the inconvenience of preparation and high cost of the reagents. Until now aminoalanes have been prepared by the reaction of (1) alane[4] or amine-alanes with secondary amines[5] and (2) lithium aluminum hydride and dialkylammonium chlorides[6].

We wish now to report the convenient and economical synthesis of aminoalanes in high yield by the reaction of aluminum, hydrogen, and a secondary amine at moderate temperature and pressure. We believe that this method of preparation should make this class of compounds readily available and inexpensive, thus encouraging exploration as hydroaluminating agents, selective reducing agents, etc.

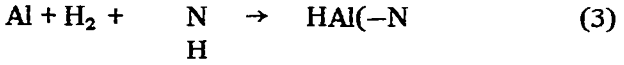
$$\mathrm{Al} + \tfrac{3}{2}\mathrm{H_2} + n\mathrm{R_2NH} \xrightarrow[\text{Benzene}]{\Delta P} \mathrm{H_{3\text{-}n}Al(NEt_2)_{\mathit{n}}} + n\mathrm{H_2} \tag{1}$$

where $n = 1, 2$ and 3

The reaction is believed to proceed through the intermediate formation of AlH_3 followed by complexation of the secondary amine to form $AlH_3 \cdot NR_2H$. Since secondary amine-alanes are unstable and lose hydrogen below room temperature, the dialkylaminoalane is the first product that can be isolated. In the presence of additional secondary amine the dialkylaminoalane reacts to form the bis(dialkylamino)alane and finally in the presence of additional dialkylamine, the tris(dialkylamino)alane is formed.

$$\begin{gathered}\mathrm{Al} + \mathrm{H_2} \rightarrow \mathrm{AlH_3} \xrightarrow{\mathrm{R_2NH}} \mathrm{AlH_3NR_2H} \xrightarrow[-\mathrm{H_2}]{} \mathrm{H_2AlNR_2} \xrightarrow[-\mathrm{H_2}]{\mathrm{R_2NH}} \\ \mathrm{HAl(NR_2)_2} \xrightarrow[-\mathrm{H_2}]{\mathrm{R_2NH}} \mathrm{Al(NR_2)_3}\end{gathered} \tag{2}$$

When the secondary amine was piperidine, the predominant product was the bis(amino)alane when equivalent quantities of aluminum and amine were present as well as when the aluminum to amine ratio was greater than unity.



$$Al + H_2 + \underset{H}{N} \rightarrow HAl(-N \qquad (3)$$

In a typical experiment, 5 g (0.18 mol) of activated[7] aluminum powder, 100 ml benzene and 9.9 ml piperidine (0.10 mol) were heated for 4 h at 110° under 4000 psig hydrogen pressure. The chamber was cooled, vented, and the benzene soluble product separated from unreacted aluminum by filtration. Solvent was stripped under vacuum yielding 9.1 g of a white pyrophoric solid. Analysis revealed a hydrogen and aluminum ratio of 1.1/1.0, indicating predominant formation of the bis(amino)alane. A small amount (0.4 g yield, 3.5%)★ of $H_2AlNC_5H_{10}$ was sublimed when the hydrogenation product was heated at 65°/1 mm. The remainder of the product (8.7 g) was found to be $HAl(NC_5H_{10})_2$ (89% yield). Analysis for hydrogen was by gas evolution and aluminum by EDTA titration. Nitrogen was determined by potentiometric titration of the solution obtained on hydrolysis of a tared sample after removal of the $Al(OH)_3$. (*Anal.*: Found: H, 1.6; Al, 21.9; N, 77.5. $H_2AlNC_5H_{10}$ Calcd.: H, 1.8; Al, 23.9; N, 74.3. Found: H, 0.53; Al, 13.8; N, 85.8. $HAl(NC_5H_{10})_2$ Calcd.: H, 0.51; Al, 13.8; N, 85.7.)

Proton magnetic resonance spectra of these products in benzene solution and infrared spectra of the solids were found to be identical to spectra of the corresponding aminoalane prepared by the reaction of trimethylamine alane and either one or two equivalents of piperidine[5].

The reaction of aluminum and hydrogen with a secondary amine has been studied in more detail with diethylamine. By adjustment of the aluminum/amine ratio, attempts were made to prepare H_2AlNEt_2, $HAl(NEt_2)_2$ and $Al(NEt_2)_3$.

$$Al + H_2 + Et_2NH \rightarrow H_2AlNEt_2 \xrightarrow{Et_2NH} HAl(NEt_2)_2 \xrightarrow{Et_2NH} Al(NEt_2)_3 \qquad (4)$$

Reference to Table 1 shows that $HAl(NEt_2)_2$ appears to be more thermodynamically stable than H_2AlNEt_2 and thus the former compound is produced in high yield (98%) under conditions predicted to form either H_2AlNEt_2 or $HAlNEt_2$. However when aluminum was used in excess and reaction times extended, mixtures of $HAl(NEt_2)_2$ and H_2AlNEt_2 (78/15) were produced. It is interesting that even at a ratio of aluminum to amine of 1/4 some (5%) of $HAl(NEt_2)_2$ remained in admixture with $Al(NEt_2)_3$; however, $Al(NEt_2)_3$ was produced in high yield (91%) when the secondary amine was used as solvent.

We are currently evaluating the general applicability of reaction (1) by characterizing the reaction of aluminum, hydrogen, and a variety of secondary amines and by determining conditions which favor the exclusive formation of mono-, bis- and tris-(amino)alanes. Elucidation of the solution composition (as determined by physical and spectral measurements) and investigation of these compounds as stereospecific reducing agents are in progress.

★ Yields are based on initial quantity of secondary amine.

TABLE 1

REACTIONS OF ALUMINUM, HYDROGEN AND DIETHYLAMINE IN BENZENE SOLVENT

$$Al + \frac{3}{2}H_2 + nEt_2NH \xrightarrow[\text{Benzene solvent}]{\Delta P} H_{3-n}Al(NEt_2)_n + nH_2$$

where $n = 1, 2$ and 3

Molar ratio Al/amine	(H_2) (psig)	Reaction time (h)	Temp. (°C)	Products	Yield (%)[a]
Excess Al	4000	3	150	$HAl(NEt_2)_2$	98
Excess Al	3000	7	150	$HAl(NEt_2)_2$	86
				$H_2Al(NEt_2)$	9
Excess Al	4000	24	65	$HAl(NEt_2)_2$	78
				$H_2Al(NEt_2)$	15
1/1	4000	3	150	$HAl(NEt_2)_2$	92
1/4	3000	3	150	$Al(NEt_2)_3$	88
				$HAl(NEt_2)_2$	5
Excess amine (Amine solvent)	3000	4	150	$Al(NEt_2)_3$	91

[a] Yield based on limiting reactant.

REFERENCES

1 S.A. Snam, Belgian Patent 654, 406, April 15, 1965.
2 S. Cesca, M. Santostasi, W. Marconi and N. Palladino, *Ann. Chim. (Rome)*, 55 (1965) 704.
3 H. Nöth and E. Wiberg, *Fortschr. Chem. Forsch.*, 8 (1967) 323.
4 E. Wiberg and A. May, *Z. Naturforschung* 10b (1955) 234.
5 W. Marconi, A. Mazzei, F. Bonati and M. de Malde, *Gazz. Chim. Ital.*, 92 (1962) 1062.
6 John K. Ruff, *J. Amer. Chem. Soc.*, 83 (1961) 2835.
7 E.C. Ashby, G.J. Brendel and H.E. Redmon, *Inorg. Chem.*, 2 (1963) 499.