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## REACTIONS OF $\text{Me}_2\text{Al-i-Bu}$ AND $\text{Me}_2\text{AlC}\equiv\text{CMe}$ WITH PRIMARY AND SECONDARY AMINES

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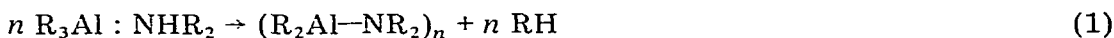
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### Summary

The elimination reaction which takes place in complexes of dimethylisobutylaluminium or dimethylpropynylaluminium and *N*-methylaniline, di-*n*-butylamine or octylamine was investigated. The abilities of methyl, isobutyl and propynyl groups to take part in elimination reactions were different. A radical exchange reaction was observed.

### Introduction

The elimination of hydrocarbon molecules from complexes of organoaluminium compounds with organic bases containing an acidic proton has so far been investigated mainly for alcohols [1,2]; these react rapidly at room temperature. Amine complexes are more stable, however, and usually heating is necessary for the reaction to occur. Complexes of organoaluminium compounds with primary or secondary amines decompose to yield saturated hydrocarbons and the corresponding aluminium amide according to eq. 1. The lower thermal



( $n = 2, 3$ )

stabilities of aromatic amine complexes compared with those of aliphatic amine complexes reflects the higher acidity of the nitrogen bonded protons in aromatic amines [3]. The stability of organoaluminium-amine complexes increases

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TABLE I

TEMPERATURE OF THE ELIMINATION OF HYDROCARBON MOLECULES FROM THE COMPLEXES OF AMINES AND SOME ORGANOALUMINIUM COMPOUNDS

Complex	Reaction temp. (°C)	Ref.
Me <sub>3</sub> Al : NH <sub>2</sub> Me	55—57	5
Et <sub>3</sub> Al : NH <sub>2</sub> Me	0	6
Et <sub>2</sub> (Cl)Al : NH <sub>2</sub> Me	50	4
Et(Cl) <sub>2</sub> Al : NH <sub>2</sub> Me	127	4
Ph <sub>3</sub> Al : NH <sub>2</sub> Me	100—120	7
Me <sub>3</sub> Al : NHMe <sub>2</sub>	90—120	8
Et <sub>3</sub> Al : NH <sub>2</sub> Ph	-78	3
Ph <sub>3</sub> Al : NHMe <sub>2</sub>	150—180	7

with both the number and the electronegativity of substituents bonded to the aluminium atom [4].

Exchange reactions of the substituents have been observed for most uncomplexed organoaluminium compounds. In most cases these are very fast at room temperature [9] but the exchange rate slow down dramatically [10] when a strong organic donor is present in the reaction mixture.

The aim of this work was to compare the elimination reactions between complexes of mixed trialkylaluminium and dialkylalkynylaluminium compounds with amines, and to find out how the exchange of aluminium substituents influences these results.

## Results

Complexes of isobutyldimethylaluminium with *N*-methylaniline (I), di-*n*-butylamine (II) and octylamine (III) react with evolution of two component gases: methane and isobutane. The rate of reaction and the composition and quantity of gases eliminated were observed when the temperature was increased at different rates. Fast elimination was only observed over some temperature ranges. Graphs were plotted to show the dependence of the volume of eliminated gases upon the temperature under different reaction conditions.

In method (a) samples were heated at 3—4 deg/min and the resulting composition and amount of gas were measured. In method (b) samples were heated at 1—2 deg/min and the resulting gas composition and their amounts were measured. In method (c) samples were heated up to a little higher than the first elimination point. When the gases ceased to evolve the reaction mixture was cooled down to room temperature. The samples were kept at 20°C for 2 h and finally heated up according to method (a) resulting in similar reaction runs with four distinct points of elimination). In method (d) the sample was heated to several degrees above the first point of elimination and kept under thermostatically controlled conditions for 48 h. Over 90% of the theoretical volume of gases was evolved. An increase of temperature to the final point of gas evolution (previously detected) caused only a scarcely visible increase in the total volume of gas obtained which was equal to that obtained in each of the experiments (a), (b) and (c).

In Fig. 1, where the reaction of complex  $\text{PhMeNH} : \text{Al-i-BuMe}_2$  (I) is shown, we can see four distinct points of elimination (at 20–25, 79–84, 135–142 and 182–190°C; curves a, b and c). The first and fourth temperature ranges closely correspond to the temperatures of elimination from complexes of this amine with  $\text{Me}_3\text{Al}$  and  $\text{i-Bu}_3\text{Al}$ , respectively.

Very intense gas evolution at 79–84°C must be attributed to the elimination reaction of the  $\text{Me}_2\text{Al-i-Bu}$  complex and the small amount of gas obtained at 135–142°C can only be expected to be obtained from the complex of  $\text{Me-i-Bu}_2\text{Al}$ . The results are in agreement with the increase in stability of more hindered organoaluminium compounds.

The amounts and the composition of gases obtained varied with the rate of heating. The slower the rise in temperature the greater the volume of gases evolved at the first two reaction points, and the greater the proportion of methane in the gases obtained (74.5% for slow heating compared with 71.5% for fast heating). The total amount of gases obtained under the conditions of experiment (c) is equal to that obtained in experiments (a) and (b), but the ratio of methane to isobutane is increased. If the increase in temperature is stopped at 30°C (curve d), only methane is slowly evolved and after 48 h 97% of the theoretical yield of gases are collected (calculated according to eq. 1).

Reaction 1 in the presence of 1 mol uncomplexed amine changes the shape of the curve of the elimination reaction but does not change the temperature regions at which fast elimination of gases occurs. The first point of elimination yields a greater quantity of gases than in 1/1 complexes whereas at the third point evolution is completed (97% of gas evolved), and at the highest point (182–190°C) no reaction occurs.

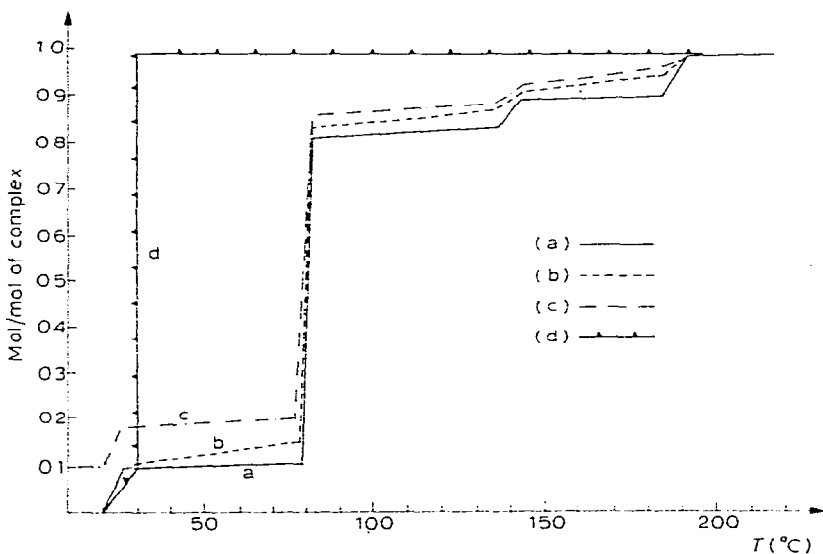


Fig. 1. Gas evolution in the reaction of  $\text{Me}_2\text{-i-BuAl}$  with  $\text{NHMePh}$ , (a) on heating at 3–4 deg/min (70 min); (b) on heating at 1–2 deg/min (180 min); (c) heating after cooling (see text); (d) after 48 h heating at 30°C followed by heating to 200°C.

TABLE 2

TEMPERATURE OF THE ELIMINATION OF HYDROCARBON MOLECULES FROM THE COMPLEXES OF AMINES WITH  $\text{Me}_3\text{Al}$  AND  $i\text{-Bu}_3\text{Al}$

Complex	Reaction temp. ( $^{\circ}\text{C}$ )
$\text{Me}_3\text{Al} : \text{NHMePh}$	20–25
$i\text{-Bu}_3\text{Al} : \text{NHMePh}$	186–198
$\text{Me}_3\text{Al} : \text{NHBu}_2$	120–128
$i\text{-Bu}_3\text{Al} : \text{NHBu}_2$	148–156
$\text{Me}_3\text{Al} : \text{NH}_2\text{Oct}$	65–73
$i\text{-Bu}_3\text{Al} : \text{NH}_2\text{Oct}$	107–115

The complex  $\text{Me}_2\text{-}i\text{-BuAl} : \text{NHBu}_2$  (II) is stable up to  $115^{\circ}\text{C}$ : no reaction was observed when the complex was heated for 2 h at about  $100^{\circ}\text{C}$ . The elimination starts with fast methane evolution at  $120\text{--}128^{\circ}\text{C}$  which reaction temperature corresponds closely to that of  $\text{Me}_3\text{Al} : \text{NHBu}_2$ . In a manner similar to complex I, when the rate of heating is slower complex II releases more gas (methane) at the first point of the reaction (Fig. 2, curves a and b). From  $137$  to  $162^{\circ}\text{C}$  fast evolution of gas was observed with a maximum rate of reaction at  $139\text{--}140^{\circ}\text{C}$  and a less distinct elimination point at  $148\text{--}150^{\circ}\text{C}$ . The end of the reaction appears at about  $165^{\circ}\text{C}$  which temperature is a little higher than that of elimination from the complex  $i\text{-Bu}_3\text{Al} : \text{NHBu}_2$ . The experiment with heating to the

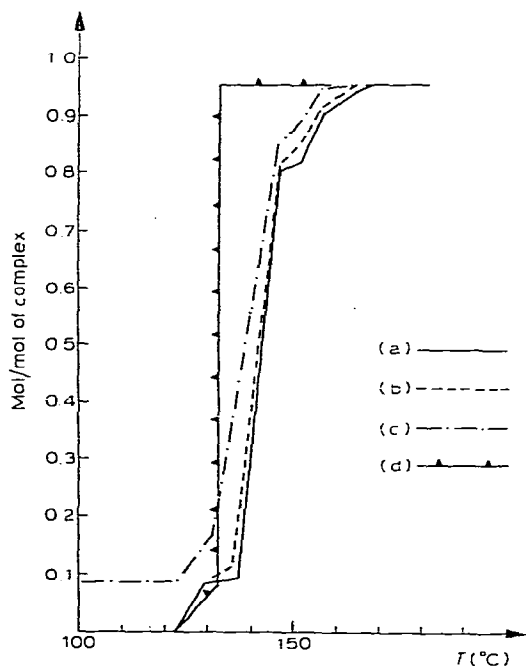


Fig. 2. Gas evolution in the reaction of  $\text{Me}_2\text{-}i\text{-BuAl}$  with  $\text{NHBu}_2$ , (a) on heating at  $3\text{--}4$  deg/min ( $20\text{--}25$  min); (b) on heating at  $1\text{--}3$  deg/min (70 min); (c) heating after cooling (see text); (d) after 48 h heating at  $130^{\circ}\text{C}$  followed by heating to  $190^{\circ}\text{C}$ .

first reaction point followed by cooling and repeated heating up to 170°C gave similar results to complex I (curve c).

Prolonged heating (48 h) at about 130°C caused evolution of methane contaminated with 1.5% of isobutane in a yield of about 97% calculated according to eq. 1 (curve d).

The elimination reaction of the first proton from the complexes of dimethylisobutylaluminium with octylamine (III) is completed at 130°C. The second proton starts to react at about 170°C. The first reaction point, observed at 65–73°C, corresponds to the reaction of trimethylaluminium with octylamine (Table 2). The next three elimination maxima between 78 and 122°C correspond to the reaction of  $\text{Me}_2\text{Al-i-Bu} : \text{NH}_2\text{Oct}$ ,  $\text{MeAl-i-Bu} : \text{NH}_2\text{Oct}$  and  $\text{i-Bu}_3\text{Al} : \text{NH}_2\text{Oct}$  respectively. The experiments were carried out as described previously (method a, b, c and d respectively). The results are presented in Fig. 3. The same types of experiments gave results for complex III very similar to those of the previously investigated complexes I and II.

The elimination of hydrocarbon molecules from the 1/1 monomeric complex of  $\text{Me}_2\text{AlC}\equiv\text{CMe}$  with the three amines mentioned proceeded only at very narrow temperature ranges. The reactivity (temperature of elimination) of amines with  $\text{Me}_2\text{AlC}\equiv\text{CMe}$  corresponds to that of  $\text{Me}_3\text{Al}$ . The yields of gases in the reactions were about 0.9 mol per mol of complex. The molar ratio of methane to propyne in the gases obtained was always higher (Table 3) than the ratio of the radicals bonded to the aluminium atom, but this composition changed with

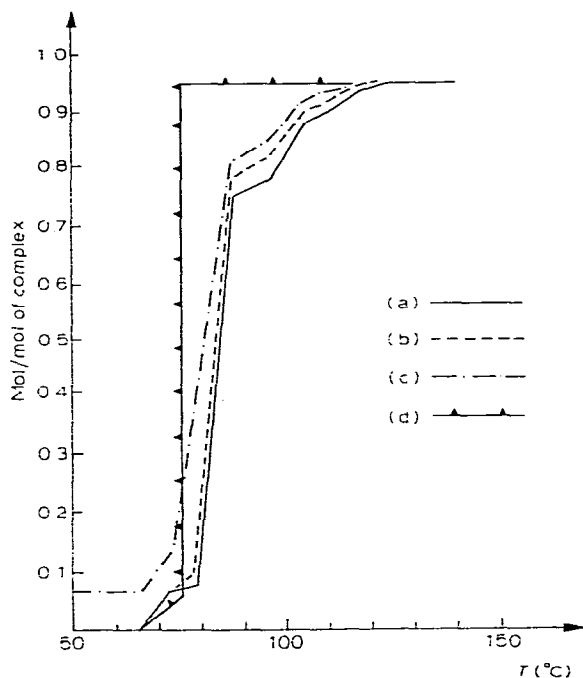


Fig. 3. Gas evolution in the reaction of  $\text{Me}_2\text{-i-BuAl}$  with  $\text{NH}_2\text{Oct}$ : (a) on heating at 3–4 deg/min (25–40 min); (b) on heating at 1–2 deg/min (80–90 min); (c) heating after cooling (see text); (d) after 48 h heating at 69°C followed by heating to 140°C.

TABLE 3

GAS COMPOSITION EVOLVED IN THE REACTION OF COMPLEXES OF  $\text{Me}_2\text{AlC}\equiv\text{CMe}$  AND AMINES

Complex	Reaction temp. (°C)	Composition at the beginning of the reaction (%)		Composition at the end of the reaction (%)		Total (%)		Total yield (%)
		CH <sub>4</sub>	C <sub>3</sub> H <sub>4</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>4</sub>	CH <sub>4</sub>	C <sub>3</sub> H <sub>4</sub>	
$\text{Me}_2(\text{MeC}\equiv\text{C})\text{Al} : \text{NHMePh}$	34-36	81	19	59	41	71	29	95
$\text{Me}_2(\text{MeC}\equiv\text{C})\text{Al} : \text{NHBu}_2$	118-126	80.5	19.5	58.5	41.5	70.5	29.5	93
$\text{Me}_2(\text{MeC}\equiv\text{C})\text{Al} : \text{NH}_2\text{Oct}$	82-96	80.5	19.5	57.5	42.5	70.0	30	90

time of reaction. The same composition of gases was observed when investigating elimination from the  $\text{Me}_2\text{AlC}\equiv\text{CMe} + \text{PhOH}$  system [11]: the initial amount of methane was about 80% whereas the last 20% of eliminated gases contained less than 60% methane.

The reaction, once started, was fast and it was hardly possible to conduct it according to the conditions of methods (c) and (d) in experiments with complexes of  $\text{Me}_2\text{Al-i-Bu}$ .

The NMR spectra of the reaction products of all complexes were recorded. In the spectrum of complex I, peaks of dimeric  $\text{Me}_2\text{AlNMePh}$  and  $\text{i-Bu}_2\text{AlNMePh}$  were found together with peaks of other unidentified compounds. The other spectra were too complicated even to recognise one reaction product.

## Discussion

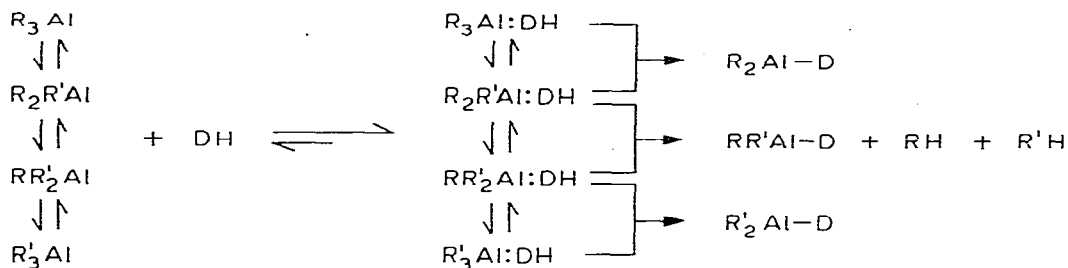
Primary and secondary amines usually form well-defined 1/1 complexes which are stable towards elimination reactions at room temperature. The temperature of elimination of hydrocarbon molecules depends on electronic and steric factors of the complex: compounds with bulky substituents, or at least with a greater number of larger substituents are less reactive (Tables 1 and 2). This is also obvious from the diagrams presented.

An electron withdrawing group (e.g. phenyl) bonded to the nitrogen atom increases the reactivity of the complex: conversely electron withdrawing substituents bonded to the aluminium atom increase the stability of the complex (e.g. phenyl, Cl). The propynyl group in  $\text{Me}_2\text{AlC}\equiv\text{CMe}$  slightly stabilises the amine complex when compared with the  $\text{Me}_3\text{Al}$  adduct. As the steric hindrance should be greater for a methyl than a propynyl group it seems that the alkynyl group is acting here as a weak electron withdrawing substituent.

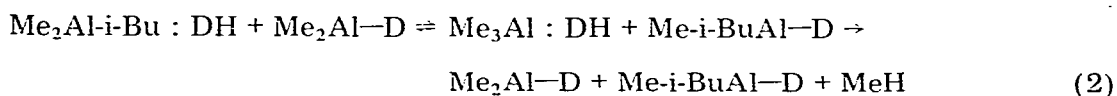
While the complexes under discussion are stable towards elimination reactions at room temperature they do undergo exchange reactions of the aluminium substituents. An equilibrium is not observed in NMR for  $\text{Me}_2\text{Al-i-Bu}$  complexes probably because of lack of chemical shift differences, but the points of fast elimination are strong evidence for an exchange process taking place leading to equilibrium between the four possible complexes. The time dependent experiments (Figs. 1-3 curve c) lead us to conclude that such an equilibrium is attained in less than 2 h at room temperature.

The observed exchange of groups can be explained according to Scheme 1.

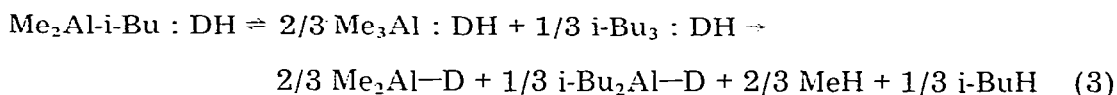
Scheme 1



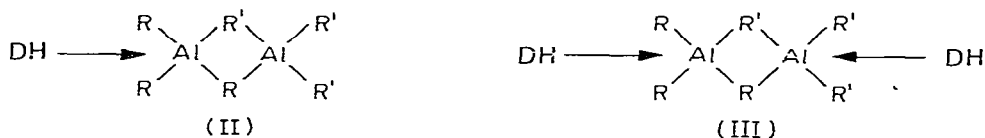
and eq. 2 in which slow exchange between complexes and amines takes place.



This reaction rationalises nearly 100% elimination of methane in all experiments conducted according to method (d). The lack of exchange (2) between substrates and  $R_2Al-D$ , only allows the formation of a maximum of 66% methane in experiment (d).



The path of the exchange is not known but the most probable is the proposal put forward by Mole [12] which involves formation of the intermediates II and III



which each have at least one five-coordinated aluminium atom and can cleave to form exchange products.

In the reactions of dimethylpropynylaluminium with amines we observed only one point of reaction but this does not exclude exchange reactions from proceeding. The variation of the composition of gases with time suggests that an equilibrium exists between the groups. The most probable way for this to occur is by the exchange between substrates and  $RR'Al-D$  formed according to the eq. 2.

## Experimental

All operations were carried out under dry, oxygen-free nitrogen. Solvents were dried using 4A molecular sieves followed by distillation from benzophenone/potassium.

Trimethylaluminium and triisobutylaluminium were purified by vacuum

transfer. Dimethylisobutylaluminium was prepared by mixing 13.90 mmol (10.0 g) of trimethylaluminium and 6.95 mmol (13.7 g) of triisobutylaluminium.

Dimethylpropynylaluminium was prepared from dimethylaluminium chloride and propynylsodium. To a 100 ml two-necked flask equipped with a dry ice condenser containing a vigorously stirred dispersion of 161 mmol (10 g) of propynylsodium in 25 ml isopentane, 146 mmol (13.5 g) of dimethylaluminium chloride in 15 ml of isopentane was added dropwise. After 20 h the dimethylpropynylaluminium prepared was purified by vacuum distillation ( $5 \times 10^{-4}$  mmHg). Yield about 78%.

*N*-methylaniline, di-*n*-butylamine and octylamine were dried over 4A molecular sieves and distilled at atmospheric pressure from zinc powder.

Complexes were prepared at dry ice temperature. A stoichiometric amount of amine was added dropwise to a 10% solution of the aluminium compound in isopentane. Mixtures were stirred by magnetic stirrer. After complexation the solvent was removed under vacuum.

Both solvent-free complexes and approximately 20% solutions of all complexes in cyclohexane and toluene were heated in an oil bath with rates of increasing temperature of either 1–2 or 3–4 deg/min. Neither the temperature nor the rate of gas elimination were affected by the presence of solvents in heated samples. Gases evolved during the reaction were collected in a gas burette system and analysed using gas chromatography.

## Acknowledgements

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## References

- 1 T.R. Crompton and V.W. Reid, *Analyst*, **88** (1963) 713.
- 2 T.R. Crompton, *Anal. Chem.*, **39** (1967) 1464.
- 3 J.K. Gilbert and J.D. Smith, *J. Chem. Soc. A*, (1968) 233.
- 4 K. Gosling and R.E. Bowen, *J. Chem. Soc. Dalton Trans.*, (1974) 1961.
- 5 K. Gosling, G.M. McLaughlin, A.G. Sim and J.D. Smith, *J. Chem. Soc., Chem. Commun.*, (1973) 1617.
- 6 K. Gosling, J.D. Smith and D.H.W. Wharby, *J. Chem. Soc. A*, (1969) 1738.
- 7 A.W. Laubengayer, K. Wade and C. Lengnick, *Inorg. Chem.*, **1** (1962) 632.
- 8 N. Davidson and H.C. Brown, *J. Amer. Chem. Soc.*, **64** (1942) 316.
- 9 E.G. Hoffmann, *Bull. Soc. Chim. Fr.*, (1963) 1467.
- 10 T. Mole, *Austr. J. Chem.*, **18** (1965) 1183.
- 11 M. Skowrońska-Ptasińska, K.B. Starowieyski, S. Pasynekiewicz and M. Carewska, *J. Organometal. Chem.*, **160** (1978) 403.
- 12 N.S. Ham, E.A. Jeffery and T. Mole, *Austr. J. Chem.*, **21** (1968) 2687.