122. Formation and Reactivity of 1,3-Dialuminium Alkanes

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Summary. The formation of 1,3-dialuminium alkanes by auto-addition or by hydro-alumination of methallyl-aluminium derivatives is reported. Some aspects of their thermal decomposition and of their reactivity are discussed.

Although several dialuminium alkanes have been synthesized [1] and some of them rather thoroughly investigated, very little is known about 1,3-dialuminium alkanes. Their existence, however, was demonstrated in the auto-addition products of allyl-aluminium derivatives [2] and in the hydro-alumination products of allene [2] and of hex-1-en-5-yne [3]. To obtain more information on the chemical properties of this type of compounds we attempted their synthesis through auto-addition of methallyl-diethyl-aluminium (**1**) and hydro-aluminium of **1** and of the stable methallyl-dimethyl-aluminium (**2**) recently prepared [4]. No pure 1,3-dialuminium compounds could be isolated, but their existence in solution was proved, and some aspects of their thermal decomposition and of their reactivity have been investigated.

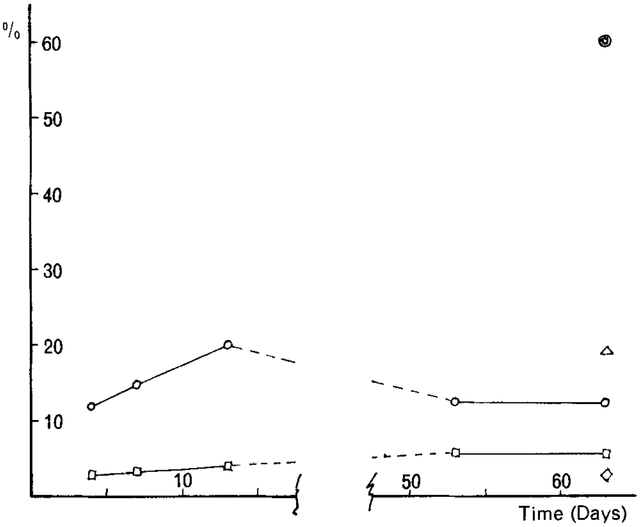
1. Auto-addition of 1. – In toluene solution **1** is not stable even at room temperature, in fact, the ratio of ethane to isobutene in the hydrolysis products increased progressively at a rate dependent on the initial concentration of **1**. At the same time the formation of increasing amounts of different hydrocarbons was noticed after hydrolysis. To obtain a better understanding of these decompositions, the solvolysis was carried out with O-d$_1$-methanol, and the positions, previously bound to aluminium, labelled by deuterium in each hydrocarbon, were determined by mass spectroscopy. The products obtained upon solvolysis of an aged solution of **1** are reported in Table 1. Traces of unidentified hydrocarbons, ranging from C$_6$ to C$_{12}$, were also detected among the products.

Table 1. *Hydrocarbons produced by methanolysis of an aged solution of methallyl-diethyl-aluminium*

Methanolysis: hydrocarbons produced	Deutero-methanolysis: D atoms in the products
Methane	2
Ethane	1
Isobutene	1
2,4-Dimethyl-1,4-pentadiene (**3**)	0
2,4,4-Trimethyl-1-pentene (**4**)	2 [a]
2,4,4,6-Tetramethyl-1,6-pentadiene (**5**)	1
2,4,4,6,6-Pentamethyl-1-heptene (**6**)	3

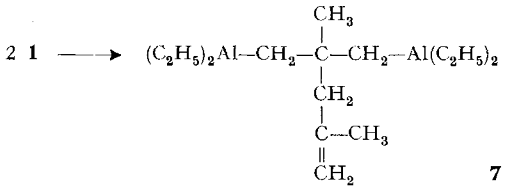
[a] Mono- and tri-deuterated olefins were present in minor amounts (~10% each).

The variation of composition of the hydrolysis products with time is reported in the Figure.



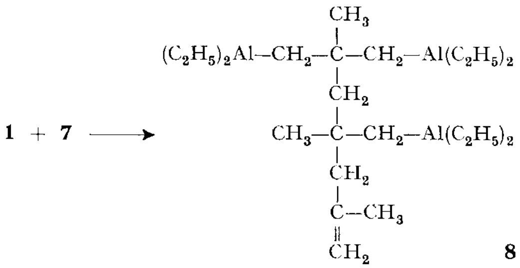
Distribution percent of the methallyl groups among the different methanolysis products as a function of time ◎ Isobutene, □ **3**, ○ **4**, ◇ **5**, △ **6**

Some of the solvolysis products, *i.e.* **4** and **6**, are in keeping with the auto-addition reactions, (1) and (2) (cf. [2]):



$$2\,\mathbf{1} \longrightarrow (C_2H_5)_2Al{-}CH_2{-}\overset{\displaystyle CH_3}{\underset{\displaystyle \underset{\displaystyle \underset{\displaystyle CH_2}{\|}}{\overset{|}{CH_2}{-}}\!}{C}}{-}CH_2{-}Al(C_2H_5)_2 \qquad (1)$$

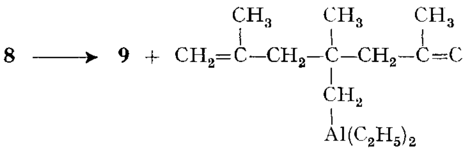
$$(C_2H_5)_2Al{-}CH_2{-}C(CH_3)(CH_2{-}C(CH_3){=}CH_2){-}CH_2{-}Al(C_2H_5)_2 \qquad \mathbf{7}$$



$$\mathbf{1} + \mathbf{7} \longrightarrow (C_2H_5)_2Al{-}CH_2{-}C(CH_3)(CH_2{-}Al(C_2H_5)_2){-}CH_2{-}C(CH_3)(CH_2{-}Al(C_2H_5)_2){-}CH_2{-}C(CH_3){=}CH_2 \qquad \mathbf{8} \qquad (2)$$

Others, *i.e.* ethane and isobutene, are clearly due to unreacted starting material; the presence of methane, **3** and **5**, however, was rather surprising. In fact, the presence simultaneously of the three products, their ratio (see Fig.), and the extent of their deuteration, seem to indicate that they originate from **7** and **8** according to equations (3) and (4), and that a 1 → 3 shift of aluminium atoms with elimination of olefin occurs easily even at room temperature:

$$\mathbf{7} \longrightarrow \underset{\mathbf{9}}{(C_2H_5)_2Al{-}CH_2{-}Al(C_2H_5)_2} + \mathbf{3} \qquad (3)$$



$$\mathbf{8} \longrightarrow \mathbf{9} + CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2{-}\underset{\underset{Al(C_2H_5)_2}{\underset{|}{\underset{CH_2}{|}}}}{\overset{CH_3}{\overset{|}{C}}}{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH_2 \quad \mathbf{10} \qquad (4)$$

As expected, at higher temperature the whole process is accelerated, but a number of collateral reactions occur as well, and the results appear much more complicated. By refluxing a 1 M toluene solution of **1**, a gas evolution took place during the first 3 h. After 4 h the solution was treated either with methanol or with deuteriomethanol, and the solvolysis products were investigated by VPC. and mass spectroscopy. Tables 2 and 3 summarize the results obtained from the treatment of 0.16 moles of **1**. About 1 g of unidentified material in the liquid portion of the mixture is not shown in the tables.

Table 2. *Composition of the gas evolved by refluxing a toluene solution of* **1** *(0.16 moles)*

Product	mmoles
Ethane	0.2
Propylene	1.1
Isobutene	8.7

Table 3. *Methanolysis products after refluxing a toluene solution of* **1** *(0.16 moles)*

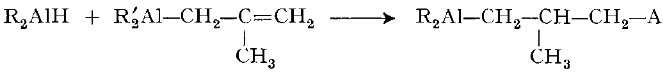
Products	mmoles	Deuterated products
Hydrogen	4.3	not determined
Methane	28.5	d_2
Ethane	245	d_1
Isobutene	57.6	d_1
3	20.1	–
4	8.4	1,5,5'-d_3[a])
5	5.0	d_1
6	0.5	d_3

[a]) *Mono- and di-deuterated products were present in minor amounts (~10% each).*

No immediate explanation can be provided for the evolution of ethane, propylene, and isobutene; the extent of the evolution is not compatible, however, with the accidental presence of traces of water. Furthermore, among the deuteriolysis products, the presence of **4**-d_3, with the third deuterium atom specifically located in position 1, and the fact that the yield of **4** can be closely correlated to the amount of ethane and isobutene evolved, seem to indicate that the hydrogen atoms necessary for the formation of ethane and isobutene probably are provided through an intramolecular mechanism, occurring by an unusual metallation reaction of **7**, or of the corresponding product in which ethyl groups are substituted by isobutenyl groups.

As far as the formation of propylene is concerned, taking into account the presence of d_2-methane among the deuterated products, a possible explanation is illustrated as follows:

$$R_2Al{-}C_2H_5 \longrightarrow R_2AlH + C_2H_4 \qquad (5)$$



$$R_2AlH + R'_2Al{-}CH_2{-}\underset{\displaystyle CH_3}{C}{=}CH_2 \longrightarrow R_2Al{-}CH_2{-}\underset{\displaystyle CH_3}{CH}{-}CH_2{-}AlR'_2 \quad \mathbf{11} \qquad (6)$$

$$\mathbf{11} \longrightarrow CH_2{=}CH{-}CH_3 + R_2Al{-}CH_2{-}AlR'_2 \qquad (7)$$

Reaction (5) is very likely to occur to a certain extent in boiling toluene; the absence of ethylene in the evolved gas could be due to its rapid addition to allyl-aluminium bonds [5]. Reaction (7) is formally analogous to the reaction (3) already discussed.

2. Hydro-alumination of 1 and 2. – The relative stability of **1**, and particularly of **2**, induced us to attempt the synthesis of 1,3-dialuminium-2-methyl-propane through the hydro-alumination reaction (6) (R = ethyl or isobutyl; R′ = methyl or ethyl).

Carrying out this reaction between room temperature and 75°, two interesting facts have been ascertained: first, the hydro-alumination of the methallyl groups cannot be completed, but seems to reach an equilibrium (see Table 4), in which large amounts of hydride and double bonds are still present. This fact is rather surprising, as the hydro-alumination of terminal olefins in similar conditions easily goes to completion [6].

Table 4. *Hydroalumination reaction (6) in toluene*

R	R′	Hydride: methallyl g=groups	Temperature	Time	Hydro-alumination %[a]
Isobutyl	Ethyl	1:1	room	12 h	18
Isobutyl	Ethyl	1:1	room	3 d	18
Isobutyl	Ethyl	1:1	50°	12 h	15
Isobutyl	Ethyl	1:1	75°	12 h	14
Ethyl	Methyl	1:1	room	12 h	0
Ethyl	Methyl	1:1	70°	8 h	15
Ethyl	Methyl	3:1	70°	24 h	40
Ethyl	Methyl	3:1	70°	5 d	50
Ethyl	Methyl	3:1	70°	12 d	66
Ethyl	Methyl	3:1	reflux	12 h	39

[a] Determined from the ratio isobutene:isobutane in the hydrolysis products.

The second fact is that the presence of dialkyl-aluminium hydride, at least in equimolar amount, prevents the auto-addition reactions (1) and (2) not only at room temperature, but also at 75°. The decrease in concentration of monomeric species in solutions of **1** in presence of aluminium hydride, due to the higher stability of electron deficient hydride bridges between aluminium atoms, with respect to the alkyl bridges, could possibly be responsible for the suppression of the auto-addition. When the reaction (6) (R = ethyl, R′ = methyl; ratio hydride: methallyl, 3:1) was carried out in refluxing toluene, a gas evolution took place during twelve hours; its composition is reported in Table 5.

Table 5. *Gas evolved during reaction (6) in boiling toluene*

Product	mmoles	% [a]
Methane	0.27	0.6
Ethylene	0.30	0.2
Ethane	1.0	0.75
Propylene	0.85	3.8
C_4-hydrocarbons	traces	

[a] Based on the starting alkyl groups (propylene is based on methallyl groups).

While the origin of ethylene and propylene can be ascribed to reactions (5) and (7) respectively, the formation of methane and ethane can only be connected either to accidental presence of traces of water or to some still unknown metallation reactions.

Conclusions. – 1,3-Dialuminium alkanes, whose existence in solution has been proved on the basis of their solvolysis products, are prone to decomposition either by a reversible process of 1–2 aluminium hydride elimination, or by a 1, 3 aluminium shift with olefin elimination. This second process, apparently the reverse of an olefin addition to a carbon-aluminium bond, occurs particularly easily when a quaternary carbon atom is present in the 2-position, thus lacking the concurrence of the hydride elimination. This peculiar behaviour appears even more remarkable considering the extremely mild conditions under which it is exhibited.

Experimental. – Organometallic materials were handled in a dry nitrogen atmosphere. Solvents were distilled over sodium. VPC. analyses of gaseous products were performed with a 4 m × 3.1 mm column packed with 100–120 mesh Porapak Q; for quantitative evaluations, calibration with a standard gaseous mixture was used. Mass spectra were taken at 70 eV with a *Hitachi Perkin-Elmer* RMU-6L mass spectrometer; pure samples were introduced through an all glass indirect inlet, and the components of hydrocarbon mixtures were analyzed using a direct combination gas chromatograph/mass spectrometer.

Materials. The preparation of **1** and **2** is described in a previous paper [4]. Commercial diethylaluminium hydride (*K & K* Laboratories) was used without further purification. The hydride content was about 98%, as determined by gas-volumetric analysis. Di-isobutyl-aluminium hydride was prepared according to [7].

Methanolysis of organometallic materials. Methanol (or O-d_1-methanol), in at least tenfold excess, was placed in a two necked flask fitted with dropping funnel and connected, through a reflux condenser, to a gasometer. The organometallic material was added dropwise, under stirring, into the vessel cooled at –70°. The temperature was allowed to rise and the mixture was heated under reflux until gas evolution ceased. The gas evolved was completely swept into the gasometer with a slow stream of nitrogen. The reaction mixture was treated with an equal volume of diluted sulfuric acid and the organic layer containing the liquid portion of the solvolysis products was collected and subsequently investigated.

Thermal decomposition of **1**. A) A 1.5 M toluene solution of **1**, containing 0.15 equivalents of methylcyclopentane as an internal standard, was left standing at room temperature for two months. 2 ml aliquots were periodically withdrawn from the solution and hydrolized either with methanol or with O-d_1-methanol. Gaseous and liquid products were separately analyzed for identification, quantitative evaluation and deuterium content determination.

B) A solution of **1** (0.16 moles) in toluene (150 ml) was heated under reflux in an apparatus connected with a gasometer. 226 ml (at normal conditions) of gas, the composition of which is shown in Table 2, were evolved in 3 h. Refluxing was continued for a further 1 h. A portion of the solution was then treated with methanol, the other with O-d_1-methanol, and the products separately analyzed (see Table 3).

Hydro-alumination reactions. Analogous procedures were used for the hydro-alumination of **1** and **2**. The following description refers to the reaction between diethylaluminium hydride and **2**. A solution of diethylaluminium hydride (25 mmoles) in toluene (20 ml) was added to a cooled (– 70°) solution of **2** (25 mmoles) in toluene (20 ml). The cooling bath was removed and the mixture was left standing, first at room temperature and then at 70°. After 2 d, additional diethylaluminium hydride (50 mmoles) was added and the temperature was maintained at 70° for 12 d more. The course of the reaction was periodically checked on 1 ml aliquots of the solution by VPC. analysis of the methanolysis products (see Table 4); no appreciable amounts of hydrocarbons other than toluene were ever found in the liquid portion of the methanolysis products. The solution was finally heated under reflux: 55 ml (at normal conditions) of gas, the composition of which is shown in Table 5, were evolved in 12 h.

Identification of the products. The components of gaseous mixtures were identified by combined VPC./mass spectroscopy; their retention times and mass spectra were compared with those of authentic samples. **1** and **2** were isolated from the reaction mixture and purified by fractional distillation. Their VPC. retention times, NMR., and mass spectra were identical with those of authentic samples. The structure of **5** was assumed on the basis of its mass spectrum: *m/e* 55 (100), 97 (64), 69 (45), 41 (41), 96 (33), 81 (25), 39 (20), 29 (18), 56 (16), 57 (14); 152 (*M*, <1). An authentic sample of **6** was prepared according to [8]: a comparison of VPC. retention times and mass spectra gave identical results.

Deuterated materials. The extent of deuteration was determined by mass spectroscopy. The position of the deuterium atoms was determined in **4**-d_3 by the comparison of its NMR. spectrum with that of the undeuterated olefin:

4, NMR. (CCl_4, 60 MHz): τ_A 9.07, *s*, 9H; τ_B 8.25, *q*, 3H; τ_C 8.10, *s*, 2H; τ_D 5.43, *m*, 1H; τ_E 5.23, *m*, 1H; $J_{(B-D)\,trans}$ 1 Hz, $J_{(B-E)\,cis}$ 1.5 Hz, J_{D-E} 2.5 Hz. – **4**-1,5,5′-d_3, NMR. (CCl_4, 60 MHz): τ_A 9.08, *s* (broad), 7H; τ_B 8.26, *d*, 3H; τ_C 8.10, *s*, 2H; τ_E 5.21, *q*, 1H; J_{B-E} 1.5 Hz.

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