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COMPLEXATION BETWEEN α-ALKENYLALUMINUM COMPOUNDS AND DIISOBUTYLALUMINUM HYDRIDE: THE NATURE OF ORGANO-ALUMINUM INTERMEDIATES RESPONSIBLE FOR THE INHIBITED HYDRALUMINATION OF ALKYNES*

JOHN J. EISCH and SUE GOO RHEE

Department of Chemistry, State University of New York at Binghamton, Binghamton, New York 13901 (U.S.A.)

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Summary

In order to understand the nature of organoaluminum intermediates encountered in the hydralumination of alkynes, NMR spectral and kinetic studies have been carried out on the alkenyl(dialkyl)aluminum systems (I) resulting from the addition of diisobutylaluminum hydride to 4-octyne and to di-t-butylacetylene. A kinetic study of the reaction of a 1/1 mixture of I and diisobutylaluminum hydride with 5-decyne at 50° followed the rate expression $v = k(\text{5-decyne})^{1.0}$ $(\text{Al—H})^{0.5}$. The $E^{\ddagger}$ (apparent) was 23.0 kcal/mole.

The aluminum adducts of 4-octyne with one or two equivalents of diisobutylaluminum hydride did not show any temperature-dependence in their NMR spectra. However, those derived from di-t-butylacetylene did reveal the existence of several components, both for the alkenyl(dialkyl)aluminum itself, as well as for the 1/1 admixture of the alkenyl(dialkyl)aluminum with diisobutylaluminum hydride. However, in the temperature range of hydralumination, namely 50°, the diisobutyl(*E*-4-octenyl)aluminum was shown to be in equilibrium with triisobutylaluminum.

A proposed rationale for the NMR spectral data, formulated with the aid of data from model systems such as bis(*E*-4-octenyl)aluminum hydride, also offers an insight into the nature and kinetic behavior of organoaluminum intermediates in the hydralumination reaction.

Introduction

Recent NMR spectroscopic studies have demonstrated that dialkylaluminum hydrides form complexes of varying stoichiometry with trialkylaluminum

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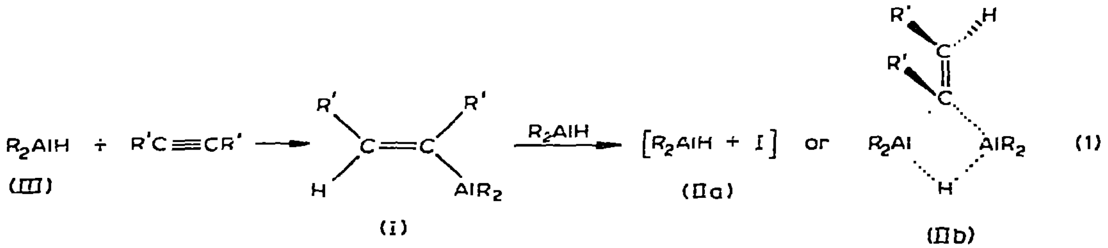
* Part XXVIII of the series Organometallic Compounds of Group III; see ref. 6 for previous related parts.

compounds [1] and with dialkylaluminum chlorides [2]. Complexation also was observed between the α-alkenyl(dialkyl)aluminum compound (I) and the dialkylaluminum hydride (III) during the course of the hydralumination reaction of alkynes by dialkylaluminum hydrides (eqn. 1, IIa) [3, 4]. An NMR spectroscopic monitoring of the reaction uncovered evidence of a 1/1 interaction between the hydralumination product, alkenyl(dialkyl)aluminum (I), and the unreacted dialkylaluminum hydride, for which interaction a mixed-bridge configuration was proposed (IIb) [3]. A contemporaneous kinetic study of the hydralumination of alkynes showed that the product, alkenyl(dialkyl)aluminum (I), retards the rate of hydralumination due to a 1/1 interaction of I with the hydride reagent [4]. Whether the rate retardation was exclusively ascribable to the previously proposed mixed-bridge complex IIb was considered an open question [4]. For not only could a 1/1 admixture of $R_2R''Al$ and R_2AlH lead to a mixture of complexes having different stoichiometries [1, 2], but group exchange could produce different organoaluminum units, such as $RR''AlH$ and R_3Al.



In order to understand the role of such complexation and group exchange in the hydralumination reaction, further kinetic and NMR spectroscopic studies were performed. First, the hydralumination characteristics of a 1/1 mixture of R_2AlH and I toward an alkyne were determined in a kinetic study. Secondly, the tendency of such a mixture to undergo group exchange in the temperature range, 50-70°, was examined. Thirdly, a variable-temperature NMR spectroscopic study was made of this $R_2AlR'' \cdot R_2AlH$ mixture, and of related hydralumination reaction mixtures with reference to model compounds, such as bis-(*E*-4-octenyl)aluminum hydride. This last aspect had as its goal the detection of organoaluminum complexes that might be in dynamic equilibrium with R_2AlH and I.

Results and discussion

A 1/1 mixture of I and R_2AlH was prepared by allowing two equivalents of diisobutylaluminum hydride (III) to react with one equivalent of 4-octyne at 50-55°. Spectral examination of the adduct (IIa, $R = i\text{-}C_4H_9$; $R' = n\text{-}C_3H_7$) and GLC analysis of a hydrolyzed aliquot showed that the mixture was formed in >95% yield. When this mixture was heated under reduced pressure in the temperature range, 40-50°, 25% of the triisobutylaluminum was collected which could result theoretically from the disproportionation shown in eqn. 2. The NMR

$$\underset{\text{(IIa)}}{[(i\text{-}C_4H_9)_2AlH + (i\text{-}C_4H_9)_2AlR'']} \rightarrow (i\text{-}C_4H_9)_3Al + (i\text{-}C_4H_9)R''AlH \qquad (2)$$

$R'' = E$-4-octenyl

spectrum of the remaining adduct was essentially unchanged when compared with the absorptions at 7.18 and 3.75 ppm in the starting adduct. After further heating at 70°, up to 65% of the available triisobutylaluminum was isolated, but additional NMR absorptions at 6.07 and 3.2 ppm were now present. Hydrolysis of an aliquot now led to the detection of both *cis*- and *trans*-4-octenes. These results demonstrate that, at the temperature of the hydralumination of alkynes (50°), triisobutylaluminum is in equilibrium with adduct IIa.

Furthermore, an adduct of I (R = i-C_4H_9 and R′ = *n*-C_3H_7) and III was prepared, in which the ratio of I/III was 1.09/1.0. In this way the possibility of any uncomplexed III, which could complicate the kinetic measurements, was minimized. The kinetic behavior of this adduct as a hydraluminating reagent toward 5-decyne was investigated, since a measurement of initial rates was easier with an alkyne giving a different *cis*-alkene than the *cis*-4-octene the reagent itself (I + III) would yield upon hydrolysis. Separate rate measurements have already shown that 5-decyne is only slightly more reactive (10%) than 4-octyne toward III [5].

By the method of initial rates, which minimizes the difficulties of complex equilibria arising during the latter stage of the reaction, the kinetic order of the hydraluminating reagent, I + III, was shown to be 0.52 ± 0.02 and that of the 5-decyne to be 0.97 ± 0.02 at 50.0° (Tables 1 and 2; Fig. 1). Over the temperature range of 30° to 60° the observed activation energy of the reaction, $E^{\ddagger}$, was 23.0 ± 0.2 kcal/mole (Fig. 2).

It should first be noted that the $E^{\ddagger}$ of this hydralumination is the same, within experimental error, as that for the hydralumination of either 4-octyne or 5-decyne by III, namely 22.8 kcal/mol. However, here the order dependence in the hydride source is essentially one-half, in contrast with the one-third order in III observed in previous kinetic studies of hydraluminating alkynes with diisobutylaluminum hydride [4,6].

Although it has already been shown that an alkenyl(dialkyl)aluminum retards the rate of hydralumination of 4-octyne by III [4], it was of interest to learn whether triisobutylaluminum would also cause retardation. Therefore, the initial rates of adding III to 4-octyne were measured at 30°, with and without the presence of one equivalent of triisobutylaluminum. Indeed, it was found that the aluminum alkyl retarded the initial rate by ca. 40%. Presumably, the known complexes of triisobutylaluminum with III [1] are responsible for this kinetic inhibition.

An NMR spectral examination at 25° of the adduct between I (R′ = n-C_3H_7) and III (R = i-C_4H_9) revealed a spectrum of the same general pattern previously reported for mixtures of I and III [3], namely a vinylic triplet (7.18 ppm, J = 6.0 Hz) and an Al-H broad singlet (3.75 ppm), shifted downfield from its position in III. Even when this neat adduct was examined at a 100 MHz field and at temperatures down to —50°, no new absorption but only broadening of the peaks was observed.

The assignment of the 1-alkenyl group to a bridging position in the dimer of I [3] is supported by the highly associated character of such aluminum [7] and similar gallium [8] derivatives. But it was important to gain firm assurance of this assumption by a study of model compounds. To this end, the preparation of bis(*E*-4-octenyl)aluminum hydride was carried out by the hydralumi-

TABLE 1

REACTION ORDER DEPENDENCE ON A 1/1 MIXTURE OF DIISOBUTYLALUMINUM HYDRIDE AND DIISOBUTYL(*E*-4-OCTENYL)ALUMINUM IN THE HYDRALUMINATION OF 5-DECYNE AT 50°[a]

Run no.	Stock soln. of $(i\text{-}C_4H_9)_2AlH$ and $E\text{-}4\text{-}C_8H_{15}(i\text{-}C_4H_9)_2Al$ (ml)	Available Hydride (mol/l)	log[Al-H] + 2	log[d[5-decene]/dt]$_0$ + 6[b]
1	20	0.3751	1.5741	1.017
2	20	0.3751	1.5741	1.025
3	20	0.3751	1.5741	1.009
4	15	0.2813	1.4492	0.954
5	10	0.1876	1.2732	0.845
6	8	0.1500	1.1761	0.809
7	6	0.1125	1.0511	0.762
8	5	0.0938	0.9722	0.680
9	4	0.0750	0.8751	0.655
10	4	0.0750	0.8751	0.652

[a] Plot of relation, log [d[5-decene]/dt]$_0$+ 6 = n log [Al-H]+2 gives (Fig. 1) a value of n = 0.52 ± 0.02. [b] [5-decene]$_0$ = 0.3750 mol/l.

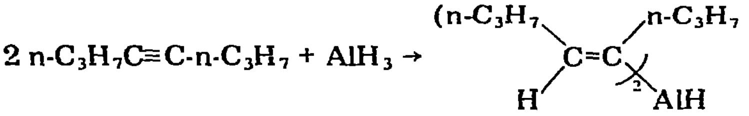
TABLE 2

REACTION ORDER DEPENDENCE ON 5-DECYNE FOR THE HYDRALUMINATION OF 5-DECYNE BY A 1/1 MIXTURE OF DIISOBUTYL ALUMINUM HYDRIDE AND DIISOBUTYL-(*E*-4-OCTENYL)ALUMINUM AT 50°[a]

Run no.	5-Decyne g	log[5-decyne] + 1	log[d[5-decene]/dt]$_0$ + 6
11	0.425	0.1750	0.666
12	0.709	0.3894	0.857
1,2,3	1.112	0.5740	1.045
13	1.990	0.8042	1.270

[a] Admixture of 20 ml of $[(i\text{-}C_4H_9)_2AlH + E\text{-}4\text{-}C_8H_{15}(i\text{-}C_4H_9)_2Al]_0$ = 0.375 ml/l in Al-H with the given amounts of 5-decyne. Plot of relation, log[d[5-decene]dt]$_0$ + 6 = n log[5-decyne] + 1 gives a value of n = 0.97 ± 0.02.

nation of 4-octyne with partially etherated aluminum hydride (eqn. 3).



$$2\ n\text{-}C_3H_7C{\equiv}C\text{-}n\text{-}C_3H_7 + AlH_3 \rightarrow [(n\text{-}C_3H_7)(H)C{=}C(n\text{-}C_3H_7)]_2AlH \qquad (3)$$

(IV)

By reduced pressure the bulk of the ether could be removed from IV. The NMR

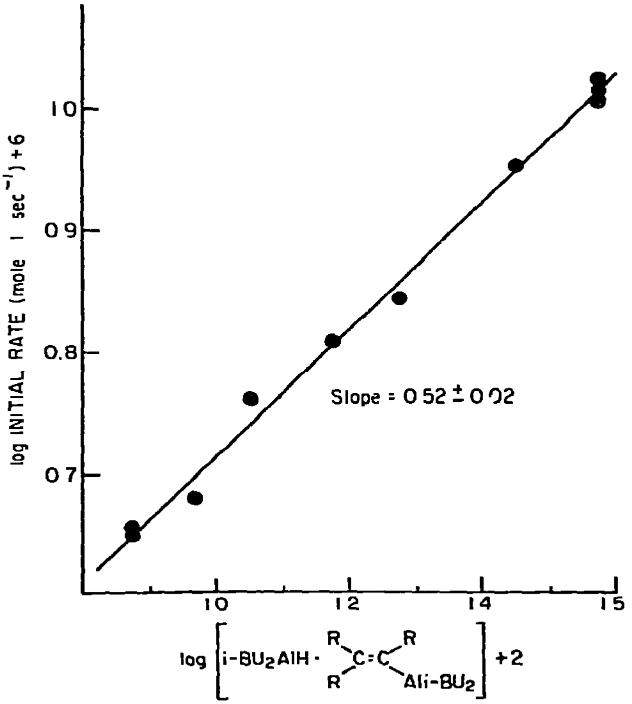


Fig. 1. Logarithmic plot of the initial rate versus the concentration of $(i\text{-}C_4H_9)_2AlH \cdot (i\text{-}C_4H_9)_2(E\text{-}4\text{-}C_8H_{15})Al$ in the hydralumination of 5-decyne.

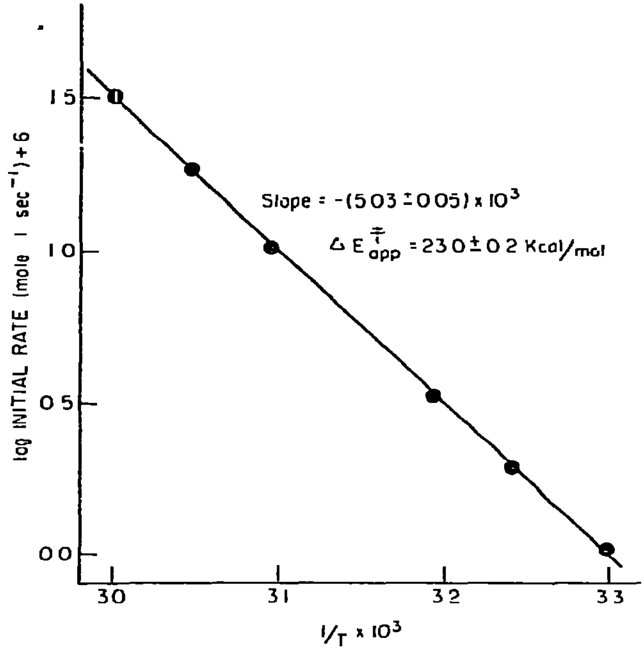


Fig. 2. Plot of the logarithm of the initial rate versus 1/*T* X 10^3 in the hydralumination of 5-decyne by $(i\text{-}C_4H_9)_2AlH \cdot (i\text{-}C_4H_9)_2(E\text{-}4\text{-}C_8H_{15})Al$.

spectrum of neat IV displayed its Al-H signal at 3.32 ppm and its vinylic triplet at 5.72 ppm. Since the superior bridging tendency of the hydride surely places it between the aluminum atoms, the vinylic signal at 5.72 ppm can be taken as that displayed by a non-bridging alkenyl group. The vinylic resonances observed for dimeric I and the 1/1 mixture of I and III thus indeed seem to be shifted downfield (∿7.2 ppm) because of alkenyl bridging.

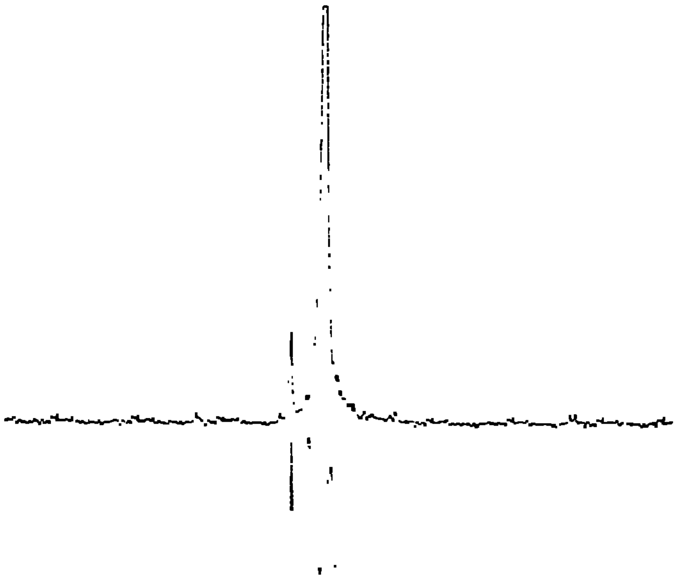
Although an NMR spectral monitoring of the hydralumination of 4-octyne by III was not informative concerning the nature of intermediate complexes, a

TABLE 3

EFFECT OF TEMPERATURE ON THE INITIAL RATE OF HYDRALUMINATING 5-DECYNE WITH A 1/1 MIXTURE OF DIISOBUTYLALUMINUM HYDRIDE AND DIISOBUTYL(*E*-4-OCTENYL) ALUMINUM[a]

Run no.	*T* (°C)	1/*T* X 10^3	[d[5-decene]/d*t*]$_0$	log[d[5-decene]/d*t*]$_0$ + 6
14	60.1	3.0006	3.14 X 10^{-5}	1.4969
15	55.3	3.0445	1.88 X 10^{-5}	1.2742
1,2,3	50.1	3.0934	1.04 X 10^{-5}	1.0170
16	40.1	3.1922	3.23 X 10^{-6}	0.5092
17	35.5	3.2398	1.90 X 10^{-6}	0.2788
18	30.1	3.2975	1.03 X 10^{-6}	0.0128

[a] Admixture of 20 ml of $[(i\text{-}C_4H_9)_2AlH \cdot (i\text{-}C_4H_9)_2(E\text{-}4\text{-}C_8H_{15})Al]$ = 0.3751 mol/l (Al-H), with 1.112 g of 5-decyne. A plot of log[d[5-decene]/d*t*]$_0$ versus 1/*T* X 10^3 gave a slope of −(5.03 ± 0.05) X 10^3 or $E^{\ddagger}_{app}$ = 23.0 ± 0.2 kcal/mol.



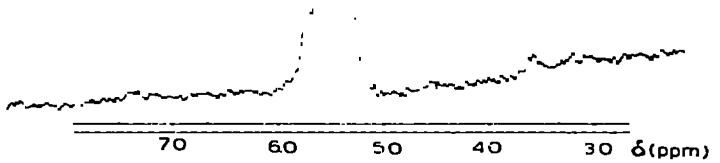
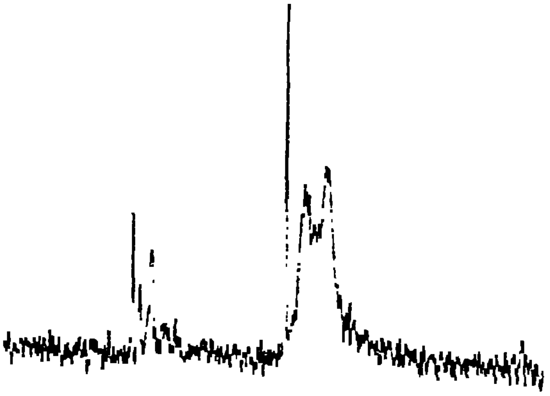


Fig. 3 (upper). NMR spectrum of neat diisobutyl(*E*-2,2,5,5-tetramethyl-3-hexenyl)aluminum (VI) at 70° (60 MHz).

Fig. 4 (lower). NMR spectrum of neat diisobutyl(*E*-2,2,5,5-tetramethyl-3-hexenyl)aluminum (VI) at −16° (60 MHz).

corresponding study of di-t-butylacetylene (V) was most revealing. Interaction of III and V in a 1/1 equivalent ratio readily led to the adduct, diisobutyl(*E*-2,2,5,5-tetramethyl-3-hexenyl)aluminum (VI). (Comparative rate studies have shown that di-t-butylacetylene is 24 times more reactive than 4-octyne toward III at 35° [5]). An NMR spectrum of a neat sample of VI displayed: (a) between 10° and 70°, two vinylic signals at 5.38 and 5.62 ppm (Fig. 3); and (b) at −16°, three vinylic signals at 5.32, 5.48 and 5.62 ppm (Fig. 4). When VI was dissolved in toluene, the NMR spectrum at 30° exhibited three distinct signals in the 7 ppm range (Fig. 5) and three in the 5.5 ppm range. At 0° the group at 7 ppm began to resolve into four resonances and those at 5 ppm sharpened into three clean singlets. At −60° this pattern was clearly discernible (Fig. 6).

When compound VI was then admixed with one equivalent of diisobutylaluminum hydride (III) (the resultant VII being of the composition IIa, where R = i-C_4H_9 and R′ = t-C_4H_9), the NMR spectrum of a neat sample at 25° was that shown in Fig. 7. A rounded vinylic signal at ca. 7.0 ppm, one rounded and two sharp vinylic absorptions at ca. 5.7 ppm and two rounded Al-H signals at



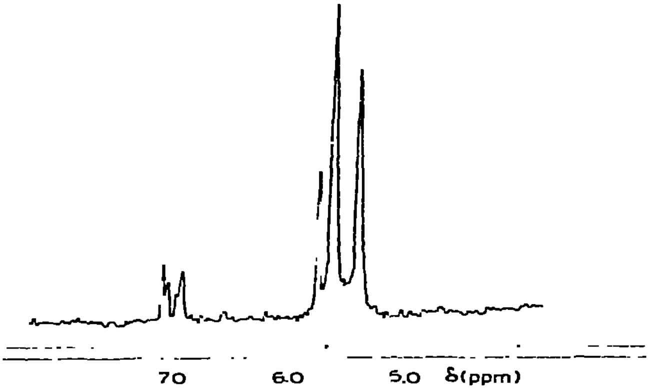


Fig. 5 (upper). NMR spectrum of diisobutyl(*E*-2,2,5,5-tetramethyl-3-hexenyl)aluminum dissolved in toluene-d_8 (40% W/W) at 30° (100 MHz).

Fig. 6 (lower). NMR spectrum of diisobutyl(*E*-2,2,5,5-tetramethyl-3-hexenyl)aluminum (VI) dissolved in toluene-d_8 (40% w/w) at −60° (100 MHz).

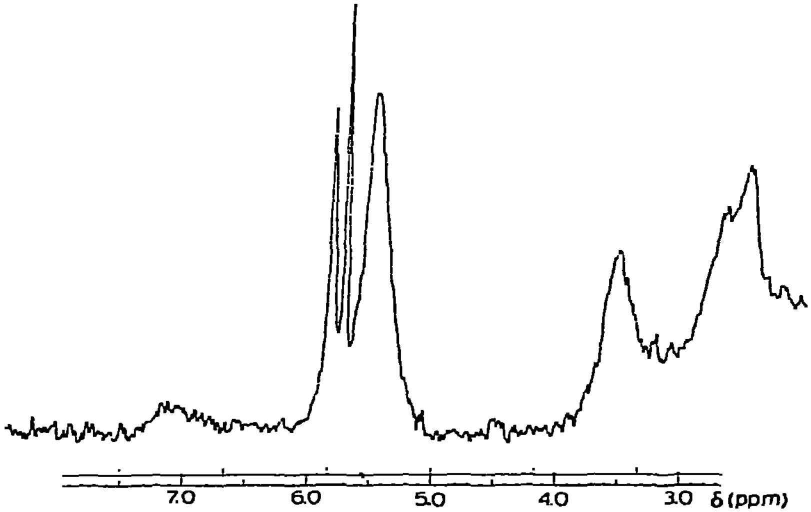


Fig. 7. NMR spectrum (neat) of VI admixed with 1 equiv. of $(i\text{-}C_4H_9)_2AlH$ at 35° (60 MHz).

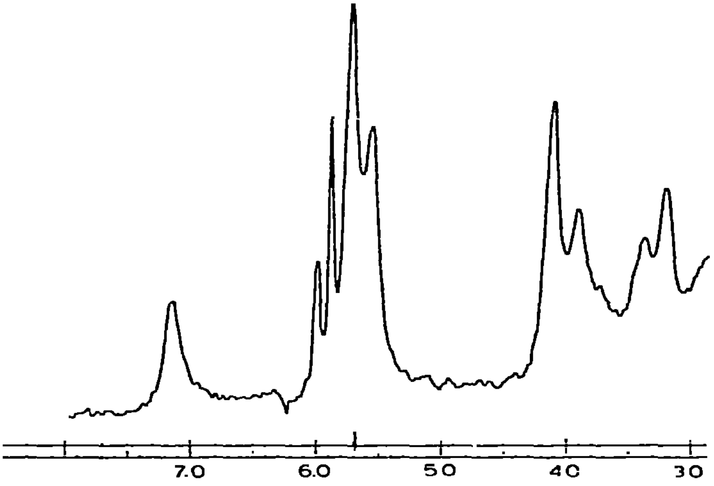


Fig. 8. NMR spectrum of VI admixed with 1 equiv. of $(i\text{-}C_4H_9)_2AlH$, when measured neat at 0° (100 MHz).

ca. 3.0 and 4.0 ppm were then discernible. At lower temperatures (—25°), especially in hexane solution or neat (Fig. 8 and 9), the number of sharp vinylic resonances around 5.7 ppm had risen to four, as had the number of distinct Al-H bands.

The number of distinct vinylic bands in VI and VII, as well as the multiple Al-H bands in VII, clearly requires that more than the single dimer of type I be present in VI and that more than the single 1/1 adduct of type II be present in VII. In proposing structures to account for the multiple vinylic bands observed in the regions of 5.5 and 7.0 ppm at lower temperatures,

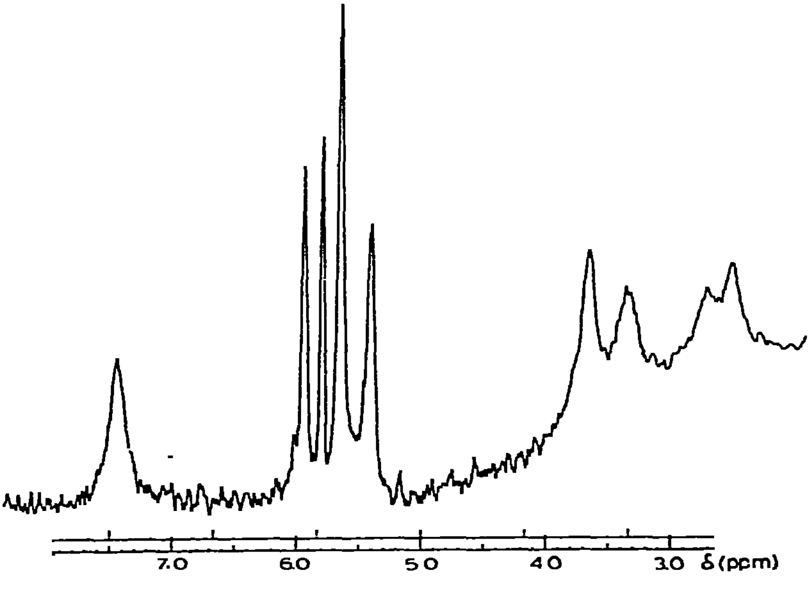
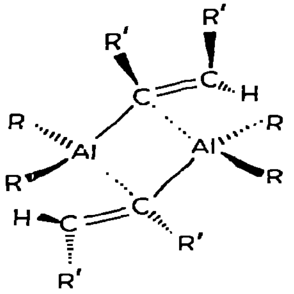
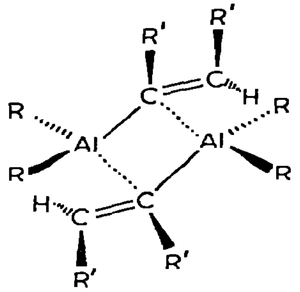


Fig. 9. NMR spectrum of VI admixed with 1 equiv. of $(i\text{-}C_4H_9)_2AlH$, when dissolved in hexane at —25° (60 MHz).

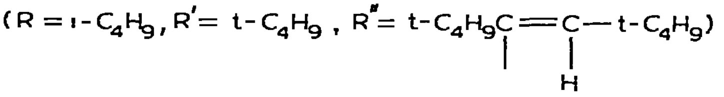
it is well to bear in mind that bridging α-alkenyl groups display their NMR signal at ca. 7.2 ppm [3, 7, 8] and non-bridging α-alkenyl groups at ca. 5.8 ppm (cf. IV). Thus, the low-temperature NMR spectrum of VI requires components having at least three different non-bridging di-t-butyl-*E*-vinyl groups and four different bridging ones. Because of the bulkiness of the alkenyl groups, two effects might be more prominent in this case: (1) in the dimer of VI with both alkenyl groups in the bridges, *syn*- and *anti*-isomers of the dimer can arise due to the alkenyl group's orientation in the bridge (VIII and IX); and (2) the ordinarily weaker isobutyl bridge can begin to compete with the alkenyl group.



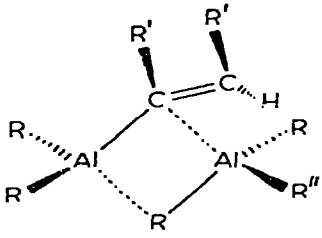
(VIII)



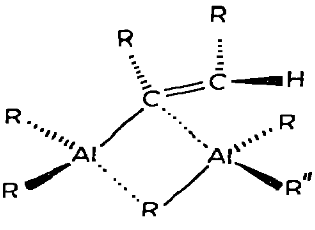
(IX)



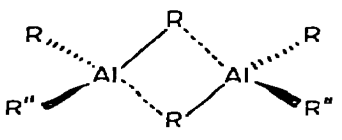
$(R = i\text{-}C_4H_9,\ R' = t\text{-}C_4H_9,\ R'' = t\text{-}C_4H_9\underset{|}{C}{=}\underset{\underset{H}{|}}{C}{-}t\text{-}C_4H_9)$



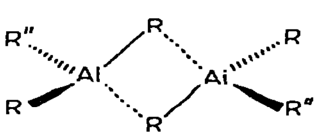
(X)



(XI)



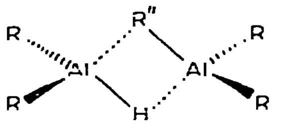
(XII)



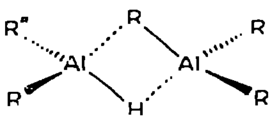
(XIII)

The mixed alkenyl—isobutyl bridged system can again have the alkenyl group enter the bridge in two orientations with respect to R" (X and XI) and the bis-isobutyl-bridged system can exist as *syn*- and *anti*-isomers with respect to the non-bridging alkenyl groups (XII and XIII): Although the scheme portrayed in VIII-XIII accounts rationally for the observed vinylic signals in the NMR spectrum of VI, the explanation may not be unique. Other rationalizations of the data, such as mobile equilibria among components such as R_3Al, RR''_2Al, R''_2RAl and R'''_3Al, and their dimers, could also account for the observed signals. But such disproportionation seems to run counter to the known stability of (α-alkenyl)dialkylaluminum dimers, $(R_2AlR'')_2$, with respect to R_3Al and R''_3Al; only at higher temperatures (>50°) do such group exchanges tend to occur readily (see below and ref. 7).

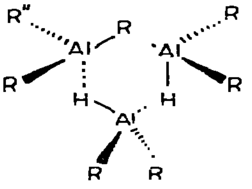
Moreover, the rationale developed to explain the NMR spectrum of VI can be used, with modest changes, to account for the low-temperature spectrum of VII. The single bridging vinylic resonance, the four non-bridging vinylic signals and four Al-H bands can be explained by the presence of 1/1, 1/2 and 2/1 adducts of diisobutylaluminum hydride and VI, similar to the types of adducts already shown to be present in mixtures of this hydride with either triisobutylaluminum [1] or diisobutylaluminum chloride [2]. It need only be further observed that, in one of these complexes, *syn*- and *anti*-isomers could arise due to alkenyl group orientation (XVII) and XVIII):



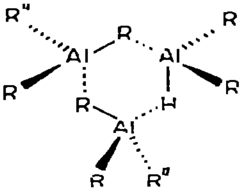
(XIV)



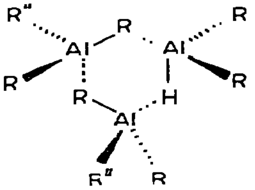
(XV)



(XVI)



(XVII)

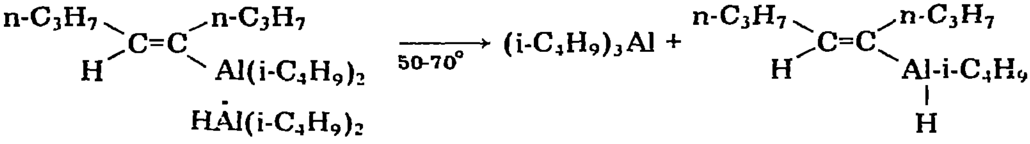


(XVIII)

The single bridging group in XIV, the four non-bridging groups in XV, XVI, XVII and XVIII and the four distinct Al-H in the environments, XIV, XV, XVI and XVII (or XVIII) are thus explicable in a straightforward, if not unique (see above), manner.

Whatever irreducible uncertainties remain in assigning the NMR signals in the adducts of di-t-butylacetylene with III, it is clear that VI and VII are multi-component systems, even at low temperatures. The failure of the adducts of 4-octyne with III to show any temperature-dependence in their NMR spectra down to −50° does not rule out the occurrence of similar equilibria between components similar to VIII-XIII and XIV-XVIII, respectively. Although clearly the t-butyl group changes the structural requirements of the dimers of type I or adducts of type IIa and permits the detection of other components, the corresponding adducts from 4-octyne would not be expected to be radically different in their structural character. Thus, ever though such complexity was not observed down to —50°, it is judged that the (*E*-4 octenyl)diisobutylaluminum and its adduct with III probably also display equilibration between many components, whose NMR signals may not be resolved at —50°.

The existence of other complex equilibria for the adduct of (*E*-4-octenyl)-diisobutylaluminum with diisobutylaluminum hydride does become apparent from the foregoing thermal and kinetic investigations. The disproportionation of this adduct at 50-70° to yield triisobutylaluminum demonstrates the ease of group exchange. Of necessity, the other product would be expected to be an (isobutyl)-4-octenylaluminum hydride; hydrolysis showed that the *E*-4-octenyl group had partly isomerized to the *Z*-4-octenyl configuration:


(4)

(IIa) (XIX)

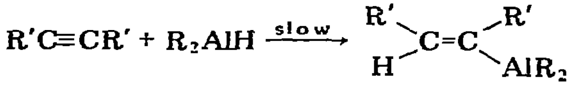
Moreover, the rate expression for IIa acting as a hydraluminating agent toward 5-decyne,

$v(50°) = k(\text{5-decyne})^{1.0}\ (\text{IIa})^{0.5}$ and $E^{\ddagger} = 23$ kcal/mole

requires a reaction scheme, in which a pre-equilibrium exists between a hydride source yielding two R_2AlH and where R_2AlH attacks 5-decyne in the rate-determining step:

$$[(R_2AlH)_2 \cdot Z] \rightleftharpoons 2R_2AlH + Z \qquad (5)$$

(XX)


(6)

As has been previously remarked [6], the observed $E^{\ddagger}$ is only an apparent value, since it embraces an enthalpy contribution for the dissociation equilibrium. The observed value of 23 kcal/mole for 5-decyne is the same as that measured for the hydralumination of 4-octyne by III. Since the two alkynes have about the same reactivity, the enthalpy required to cause dissociation of III into monomer is about the same as that needed for the hydride source in this case, $[(R_2AlH)_2 \cdot Z]$, where R and Z remain to be defined.

The question then is raised as to the nature of XX. From the rate law, it is clear that XX is not a simple 1/1 adduct of I and III. If such an adduct were responsible for hydralumination, a first-order dependence in II would be expected. If II were to dissociate into I and III and the latter trimer were to serve as XX (Z = R_2AlH), then a one-third order in hydride should result.

An explanation for these kinetic results can be fashioned in two different ways: (a) at 50°, group exchange could cause the formation of XIX (eqn. 4) and such a bulky hydride could exist preferentially as a dimer*; or (b) at 50° II could exist as an equilibrium of structures XIV-XVIII, but XVI might be the most reactive hydraluminating agent. Thus, according to the view chosen, XX in eqn. 5 would either be XVI or dimeric XIX. Because of the same activation energies for the action of III on 4-octyne and of XX on 5-decyne, structure XVI is favored as the hydraluminating agent in eqn. 5. The dissociation energy required for XVI to form 2 R_2AlH and R_2AlR'' should be equal to or less than that for trimeric III; dissociation of XIX would appear to be more difficult because of the presence of two good bridging groups, vinyl and hydride.

In conclusion, the foregoing studies have shown that α-alkenyl(dialkyl)-aluminum systems can exist in a variety of structurally distinct dimers at lower temperatures. Furthermore, interaction of these alkenyl(dialkyl)aluminums with dialkylaluminum hydride can form an array of distinct dimeric and trimeric associations at room temperature or lower. At higher temperatures (>50°) exchange of groups attached to aluminum becomes clearly discernible. The existence of such equilibria involving different molecular associations or group exchange is required to understand both the structural and the kinetic properties of alkenylaluminum compounds.

Experimental

General procedures

The experimental procedures for the purification, transfer and analysis of aluminum alkyls and dialkylaluminum hydrides have been described in previous articles [10, 11]. All such reactions were conducted in an atmosphere of dry, oxygen-free nitrogen. The alkynes, 4-octyne and 5-decyne, were purchased in 99% purity from the Farchan Chemical Co.; they were further purified by storage over phosphorus pentoxide and final distillation, under dry nitrogen, through a 0.4 × 30 cm column filled with glass helices. Di-t-butylacetylene was prepared in accordance with published procedures [12]. Just before use, all alkynes were checked for homogeniety by NMR and gas chromatographic methods. The details of the analytical instrumentation adhered closely to those reported previously except that a Hewlett—Packard gas chromatograph, F and M model 720 was used, equipped with 0.60 × 400 cm columns of 10% Silicone SF-96 on Chromosorb P.

Reaction of aluminum hydride diethyl etherate with 4-octyne

Preparation of aluminum hydride diethyl etherate [13]. Depending upon the procedure, the resulting product, $(AlH_3)_n \cdot Et_2O$, varied in composition from n = 2.2-5.7. The following method yielded a product with the smallest n.

A solution of 7.959 g (21.0 mmol) of $LiAlH_4$ in 200 ml of anhydrous ethyl ether was placed in a three-necked flask fitted with a nitrogen inlet tube, a Friedrichs reflux condenser and a pressure-equalized addition funnel. Then a solution of 9.310 g (7.0 mmol) of aluminum chloride in 120 ml of dry ether was added in a dropwise manner. The resulting suspension was filtered through

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* According to ref. 9, dialkylaluminum hydrides with bulky substituents in the α-position tend to be dimeric.

a glass frit of fine porosity with aid of a slightly reduced pressure. The ether was evaporated from the filtrate by slowly raising the temperature to 90° at a pressure of 0.02 Torr. Gasometric analysis [14]: 332 mg yielded, after hydrolysis and chelation with 8-hydroxyquinoline, 3.727 g of aluminum 8-quinolinolate. This corresponds to $(Al_{1.0}\ H_{2.80})_{5.7} \cdot Et_2O$ (70% of AlH_3 by weight).

Reaction of aluminum hydride with 4-octyne in a 1/2 ratio. A mixture of 936 mg (22.8 mmol) of aluminum hydride (70%) and 6.7 ml (45.6 mmol) of 4-octyne was heated at 50-53° for 2.5 h. Since hydrolysis of an aliquot showed that only 83% of the alkyne had been consumed, the viscous and colorless mixture was stirred at 60° for an additional 2.5 h. Gas chromatographic, infrared spectral and NMR analyses of a hydrolyzed portion showed the presence of 97.5% of *cis*-4-octene and 2.5% of n-octane; no trace of *trans*-4-octene or the reductive dimer, *E,E*-5,6-di-n-propyl-4,6-decadiene, could be detected.

The NMR spectrum of the colorless, turbid adduct displayed, in a 2.0/1.0 ratio, a vinylic C-H triplet at 5.72 ppm (J = 7.0 Hz) and a sharp Al-H singlet at 3.32 ppm. The ether quartet at 3.73 ppm indicated that there was about a 10/1 ratio of Al-H to Et_2O. Thus, the product is essentially pure, unsolvated bis(*E*-4-octenyl)aluminum hydride (IV).

The residual ether was removed from IV by heating at 110° under 0.02 Torr for 1 h. The NMR spectrum of the resulting product now had a quintet in the vinylic C-H region, analyzable into overlapping triplets: the original one at 5.72 and a new one at 5.92 ppm. The total C-H/Al-H ratio, however, was still 1.0/2.0.

Further heating of this dialkenylaluminum hydride at 90-100° for 9 h led to a growth of the vinylic C-H peak at 5.92 ppm. Hydrolysis and a combined GC and IR analysis showed that 60% of *cis*-4-octene and 40% of *trans*-3-(-4-)-octene were now present.

Reaction of aluminum hydride with 4-octyne in a 1/1 ratio. A mixture of 825 mg (20 mmol) of aluminum hydride (70%), 2.96 ml (20 mmol) of 4-octyne and 4 ml of hexane was stirred at 55° for 5 h. Since the cloudy solution was too viscous, it could not be filtered through a glass frit. Accordingly, it was clarified by passing through a column of glass wool and then centrifuging. The NMR spectrum of the mixture showed only the signals at 5.72 and 3.32, which were characteristic of IV. Hydrolysis and NMR analysis of the hydrocarbons showed the presence of 57% of n-octane and 43% of *cis*-4-octene.

Reaction of diisobutylaluminum hydride with 4-octyne in a 2/1 ratio. A mixture of 80 mmol of diisobutylaluminum hydride and 40 mmol of 4-octyne was heated at 50-55° for 24 h. Hydrolysis showed that the alkyne was completely consumed and that *cis*-4-octene had been formed in >95% yield. The NMR spectrum of the diisobutylaluminum hydride/diisobutyl(*E*-4-octenyl)-aluminum mixture (IV) showed the vinylic CH triplet at 7.18, the Al-H at 3.75 and the CH_2Al at 0.20 ppm in a 1/1/8 ratio. Heating of the mixture at 70° for 32 h at 0.02 Torr caused the evolution of 65% of the theoretically available triisobutylaluminum, whose identity was secured by IR and NMR spectral comparison. The NMR spectrum of the residual aluminum compound still had broad =C-H and Al-H signals at 7.18 and 3.75 ppm, respectively. New signals, however, had appeared at 6.07 and 3.20 ppm. Hydrolysis now showed the presence of *cis*- and *trans*-3-(-4-)octenes.

Reactions of diisobutylaluminum hydride with di-t-butylacetylene

A 1/1 molar mixture of the hydride and alkyne (25 mmol) in 10 ml of hexane was stirred for 4 h at 20-25° and then hydrolyzed. A combined GC-, IR- and NMR-analysis established that only *cis*-di-t-butylacetylene was formed.

To ensure that no *trans*-adduct was formed at lower temperatures but then isomerized to the *cis*-adduct at 25°, trapping of any intermediate *trans*-adduct was attempted by low-temperature solvolysis. A solution of 3.0 g (21.8 mmol) of the alkyne and 4.5 ml (25.4 mmol) of the hydride in 10 ml of cyclopentane was stirred for 6 h at 25° to permit complete hydralumination. The solution of the adduct was divided into four portions, which were individually solvolyzed with methanol at −60°: (1) directly; (2) after dilution with 2 ml of cyclopentane; (3) after addition of 1 ml of diisobutylaluminum hydride; and (4) after addition of both 2 ml of cyclopentane and 1 ml of the hydride. Gas chromatographic analysis showed only the *cis*-alkene and a trace of the alkyne.

Various 1/1 and 1/2 mixtures of the alkyne and hydride were prepared, either neat or in a hydrocarbon solvent (40% W/W in hexane or toluene). After consumption of the alkyne, the NMR spectra were recorded at various temperatures (Figs. 3-9).

Kinetics of the hydralumination of 5-decyne with a 1/1 mixture of diisobutylaluminum hydride and diisobutyl(E-4-octenyl)aluminum

The stock solution of the 1/1 mixture of $(i\text{-}C_4H_9)_2AlH \cdot (i\text{-}C_4H_9)_2/Al(E\text{-}4\text{-}C_8H_{15})$ was prepared by diluting 30.0 ml of diisobutylaluminum hydride (>98% pure) and 9.80 g of 4-octyne up to a total volume of 200.0 ml. After the solution was heated for 48 h at 40-45°, an analysis of a hydrolyzed portion by gas chromatography showed only 1.2% of residual 4-octyne. Accordingly, the concentration of unreacted $(i\text{-}C_4H_9)_2AlH$ was 0.4023 mol/l and that of $(i\text{-}C_4H_9)_2Al(E\text{-}4\text{-}C_8H_{15})$ was 0.4394 mol/l. The ratio of $[(i\text{-}C_4H_9)_2Al(E\text{-}4\text{-}C_8H_{15})]$ to $[(i\text{-}C_4H_9)_2AlH]$ was thus 1.09/1.0.

The concentration of the available hydride, calculated as $(i\text{-}C_4H_9)_2AlH$, was changed by diluting x ml of the hydride stock solution with 20.0—x ml of hexane distilled directly into the solution. To each 20.0 ml hydride solution in hexane, which had been brought to temperature-equilibrium at 50.0° beforehand, was added 1.112 g of 5-decyne by means of a gas-tight syringe. Thus, the initial concentration of the 5-decyne was 0.3750 mol/l. The kinetic data for the various runs performed at 50° were obtained by the gas chromatographic analysis of hydrolyzed aliquots for *cis*-5-decene (Table 1). By extrapolation of each run to zero time, the initial rate, d[5-decene]/d*t*, could be obtained. A plot of the log d[5-decene]/d*t* versus log $[(i\text{-}C_4H_9)_2AlH]$ yielded a linear relation, whose slope, as determined by the method of least squares, was 0.52 ± 0.02 (Fig. 1).

Similarly, 20.0 ml portions of the original $(i\text{-}C_4H_9)_2AlH \cdot AlR'$ stock solution (0.4023 mol/l) were admixed with different amounts of 5-decyne. Each kinetic run at 50.0° was followed by gas chromatographic analysis of hydrolyzed aliquots for *cis*-5-decene. The resulting kinetic data and the initial rates, d[5-decene]/d*t*, are summarized in Table 2. A plot of the log [d[5-decene]/d*t*] versus log [5-decyne] yielded a linear relation, whose slope was 0.97 ± 0.02.

The temperature-dependence of this hydralumination was determined from the initial rates observed on stock solutions prepared from 20.0 ml of the original $(i\text{-}C_4H_9)_2AlH \cdot R_2AlR'$ solutions and 1.112 g of 5-decyne. The results given in Table 3 were plotted (Fig. 2) versus $1/T \times 10^3$ to yield a value of $E^{\ddagger}$ (apparent) of 23.0 ± 0.2 kcal/mol.

Hydralumination of 4-octyne with diisobutyaluminum hydride in the presence of equivalent amounts of triisobutylaluminum

The rates of two reaction systems were compared at 30.0° by the method of initial rates: (a) a mixture of 0.607 g (265 mmol) of 4-octyne, 1.0 ml (284 mmol) of $(i\text{-}C_4H_9)_2AlH$, 1.5 ml (284 mmol) of $(i\text{-}C_4H_9)_3Al$ and 17.5 ml of hexane; and (b) the same mixture, except that 1.5 ml of additional hexane took the place of the $(i\text{-}C_4H_9)_3Al$. The initial rate of mixture b was 1.37 that of mixture a; that is, the hydralumination is slowed down by the presence of $(i\text{-}C_4H_9)_3Al$.

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