

Kinetic, Stereochemical, and Molecular Association Factors in the Hydralumination of Alkynes. An Inquiry into the Intermediacy of π Complexes¹

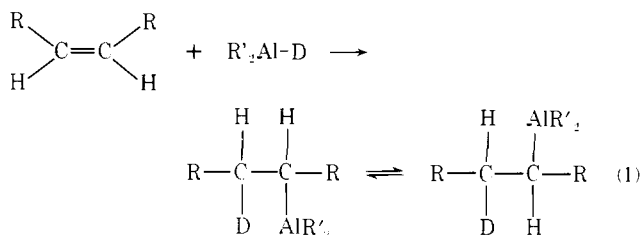
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Abstract: The kinetics, mechanism, and molecular association factors for the addition of diisobutylaluminum hydride to 4-octyne were studied in the temperature range of 0 to 70°. By applying the differential method to the initial rates, the hydralumination was found to obey four-thirds order (n_c) kinetics, first order in the acetylene and one-third order in the hydride, indicating that the monomeric hydride is involved in the rate-determining step. The Arrhenius relationship, $k = (4.5 \pm 0.6) \times 10^{10} e^{-20,840 \pm 50/RT} \text{ mol}^{-1/3} \text{ sec}^{-1}$, and the apparent activation entropy, $-11.0 \pm 0.3 \text{ eu}$ at 30°, were determined; the kinetic deuterium isotope effect was $k_{\text{Al-H}}/k_{\text{Al-D}} = 1.68$ (30°). In mesitylene as a π base, $k_{\text{M}}/k_{\text{hexane}} = 1.2$, and in THF as a π base, $k_{\text{hexane}}/k_{\text{THF}} = 2 \times 10^3$. Since the kinetic order with respect to time (n_t) increased and the rate followed the law, $dx/dt = k(a_0 - x)(a_0 - 2x)^{1/3}$, through 50% of the 1:1, and through 85% of the 1:2, octyne-hydride reaction, the reaction was shown to be retarded by the stoichiometric complexation of the resulting diisobutyl(*E*)-4-octenylaluminum with diisobutylaluminum hydride. However, in the temperature range 25 to 100°, this complexation was shown to involve at least three different kinds of complexes, namely, hydride-alkenyl, alkyl-alkenyl hydride, and saturated dialuminoalkanes. These findings are interpreted to mean that monomeric diisobutylaluminum hydride attacks 4-octyne electrophilically, and that the transition state can be envisaged as approximating a π complex. The subsequent association of the resulting diisobutyl(*E*)-4-octenylaluminum with a unit of diisobutylaluminum hydride can be viewed as leading to π complexation, hydride-alkyl group exchange, or diadduct formation by a mechanistic pathway similar to the original hydralumination.

The addition of the aluminum-hydrogen bond to carbon-carbon unsaturation is the pivotal reaction in the ready synthesis of aluminum alkyls on a large scale.² This hydralumination process has been the gateway to a fascinating region now known as Ziegler chemistry:³ the reduction, oligomerization, or polymerization of unsaturated hydrocarbons by means of organoaluminum reagents, with or without transition metal cocatalysts.⁴ Up to the present, however, definitive studies have been lacking on the mechanism of hydralumination. Nevertheless, circumstantial evidence, such as the stereochemical course with alkynes⁵⁻⁷ and the retarding effect of ethers or amines,⁸ has led to the view⁶⁻⁹ that the hydraluminating agent acts as an electrophile toward the hydrocarbon π base.

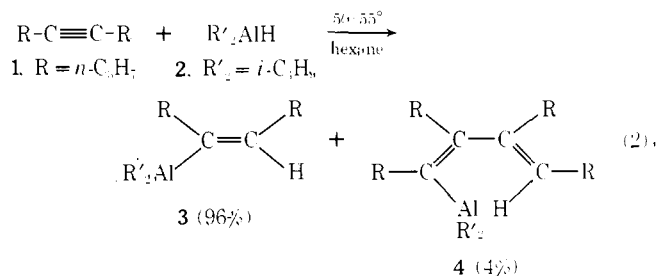
A kinetic study of the reaction of $(\text{AlH}_3)_n$ with unsaturated hydrocarbons is beset with difficulties: (a) pure, unsolvated aluminum hydride is polymeric and insoluble;¹⁰ (b) as usually prepared, the hydride is not free of ether;¹¹ and (c) aluminum hydrides and aluminum alkyls tend to complex¹² and to undergo redistribution reactions² with each other. For these reasons, diisobutylaluminum hydride, a pure, hydrocarbon-soluble, well-defined trimer,¹³ was chosen to interact with a typical internal alkyne, 4-octyne. The hydrocarbon substrate was not prone to the metalation that 1-alkynes sometimes undergo,¹⁴ while the triple bond offered the possibility of monitoring the *cis* or *trans* course of the hydralumination. By comparison, olefinic substrates would be expected to yield alkylaluminum adducts, in which any stereochemical preference of *cis* or *trans* addition would be hidden by the known tendency for such systems to undergo rapid inversion at the C-Al bonds^{15,16} (e.g., eq 1).



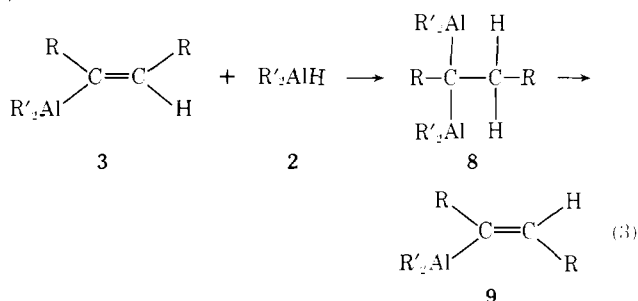
Results

Stoichiometry and Stereochemistry of Hydralumination.

The addition of diisobutylaluminum hydride (**2**) to neat 4-octyne (**1**) proceeded at 50° to yield only the *cis* monoadduct, diisobutyl(*E*)-4-octenylaluminum (**3**), and small amounts of diisobutyl[*(E,E)*-5,6-dipropyl-4,6-decadienyl-4]aluminum¹⁷ (**4**) (eq 2). The amount of **4** could be sup-



pressed almost completely by reaction in hexane solution or with shorter reaction times below 50°. The monoadduct **3** tended to dissociate into **1** and **2** at higher temperatures, for heating a sample of **3** (free of **1** and **4**) at 95–100° and then hydrolyzing led to a mixture of *cis*-4-octene (**5**, 67%), *trans*-4-octene (**6**, 20%), and (*E,E*)-5,6-dipropyl-4,6-decadiene (**7**, 13%). Apparently, the alkyne **1** set free underwent reductive dimerization,^{5,6,18} and the hydride combined with **3** to yield a dialumino adduct **8**^{6,18} which led to **9** (eq 3).



Support for this isomerization pathway was obtained by

heating a sample of **3** with diisobutylaluminum deuteride at 65–70° for 2 days. Hydrolysis of an aliquot and combined gas chromatographic, infrared, nmr, and mass spectral analyses showed the mixture to consist of *cis*- (56%) and *trans*- (2%) 4-octenes, *cis*- (28%) and *trans*- (1%) 4-octene-*d*₁, *n*-octane (11%), and *n*-octane-*d*₁ (2%). The detection of deuterated **5** and **6**, as well as deuterated octane (**10**), is consistent with the participation of diisobutylaluminum deuteride, along with **2** formed by dissociation of **3**, in the isomerization scheme depicted in eq 3.

Initial Rates of Reaction in Hexane. For these determinations, the method of initial rates was employed, namely, the plot of reaction rate vs. time and the extrapolation to zero time. This procedure avoided the complexities of hydride association equilibria encountered as the reaction proceeded to completion. Three series of kinetic experiments with **1** and **2** in hexane solution were performed to determine the apparent activation energy and the kinetic order dependences of each reactant. In Table I, the effect of temperatures

Table I. Effect of Temperature on the 1:1 Hydralumination of 4-Octyne^a by Diisobutylaluminum Hydride

Run no.	Temp, °C	1/T × 10 ⁻³	{([ene]/[yne]) ₀ /t} _{av} ^b	Rate (v), ^c mol l. ⁻¹ min ⁻¹	Log v + 5
1	44.85	3.1446	6.13 × 10 ⁻³	8.27 × 10 ⁻⁴	1.9176
2	44.85	3.1446	6.11	8.25	1.9165
3	34.95	3.2456	2.17	2.93	1.4664
4	34.95	3.2356	2.16	2.92	1.4665
5	30.00	3.2986	1.23	1.66	1.2206
6	24.95	3.3545	6.84 × 10 ⁻⁴	9.23 × 10 ⁻⁵	0.9653
7	19.95	3.4117	3.72	5.05	0.7029
8	15.00	3.4703	2.02	2.72	0.4352

^a [4-Octyne]₀ = [(i-C₄H₉)₂AlH]₀ = 0.138 mol/l. ^b ene = *cis*-4-octene; yne = 4-octyne. ^c Rate (v) = {([ene]/[yne])₀/t}_{av} × 0.135 mol/l.

between 15 and 45° upon the initial rate, v, is tabulated for runs where initial concentrations of **1** and **2** were 0.138 mol/l. A plot of log v vs. 1/T and a computed least-squares analysis of the slope yielded:

$$\text{slope} = -(4.5534 \pm 0.0115) \times 10^3 = \frac{\Delta E^*_{\text{app}}}{(2.303)(1.987)}$$

$$\Delta E^*_{\text{app}} = 20.84 \pm 0.05 \text{ kcal/mol}$$

The kinetic true-order dependences of 4-octyne and diisobutylaluminum hydride were obtained from initial rates (v) for runs where the initial concentration of **1** was varied from 0.0498 to 0.2357 mol/l. and that of **2** held at 0.138 mol/l. (calculated as monomeric **2**) (Table II), or where the

Table II. Reaction Order Dependence on 4-Octyne in the Hydralumination of 4-Octyne^a

Run no.	[Octyne] ₀ , mol/l.	Log [octyne] ₀ + 2	{([ene]/[yne]) ₀ /t} _{av} ^b	Rate (v), ^c mol l. ⁻¹ sec ⁻¹	Log v + 6
9	0.0498	0.6972	1.23 × 10 ⁻³	1.02 × 10 ⁻⁶	0.0086
10	0.1005	1.0021	1.23	2.06	0.3135
5	0.1350	1.1303	1.23	2.76	0.4412
18	0.1350	1.1303	1.23	2.76	0.4412
11	0.1343	1.1281	1.23	2.76	0.4412
12	0.2357	1.3724	1.24	4.86	0.6861

^a [(i-C₄H₉)₂AlH]₀ = 0.138 mol/l.; t = 29.95°. ^b ene = *cis*-4-octene; yne = 4-octyne. ^c Rate (v) = {([ene]/[yne])₀/t}_{av} × [yne]₀/60. Slope (m) = 1.004 ± 0.001; intercept (C_I) = -4.684 ± 0.03.

Table III. Reaction Order Dependence on Diisobutylaluminum Hydride in the Hydralumination of 4-Octyne^a

Run no.	[i-Bu ₂ AlH] ₀ , mol/l.	Log [i-Bu ₂ AlH] + 2	{([ene]/[yne]) ₀ /t} _{av}	Rate (v), ^c mol l. ⁻¹ sec ⁻¹	Log v + 6
13	0.02751	0.4395	6.63 × 10 ⁻⁴	1.49 × 10 ⁻⁶	0.1735
14	0.04127	0.6156	7.97	1.79	0.2539
15	0.05502	0.7406	8.98	2.02	0.3056
16	0.06878	0.8375	9.50	2.14	0.3300
17	0.09629	0.9836	1.11 × 10 ⁻³	2.48	0.3952
18	0.1376	1.1386	1.23	2.76	0.4412
5	0.1376	1.1386	1.23	2.76	0.4412
11	0.1376	1.1386	1.23	2.76	0.4412
19	0.2063	1.3145	1.41	3.16	0.4998
20	0.2751	1.4395	1.60	3.59	0.5555

^a [4-Octyne]₀ = 0.135 mol/l.; t = 30.00°. ^b ene = *cis*-4-octene; yne = 4-octyne. ^c Rate (v) = {([ene]/[yne])₀/t} (min)_{av} × [yne]₀/60. Slope (n) = 0.370 ± 0.008; intercept (C_{II}) = -5.238 ± 0.024.

concentration of **2** was varied from 0.02751 to 0.2751 mol/l. and that of **1** kept at 0.135 mol/l. (Table III). A double-logarithmic plot of the initial rates against the initial concentration of 4-octyne (R'₂AlH) gave the slopes (m and n) and the intercepts (C_I and C_{II}) for the relationships

$$\log v = m \log [4\text{-octyne}]_0 + C_I$$

$$\log v = n \log [R'_2\text{AlH}] + C_{II} \quad (4)$$

$$C_I = \log k + n \log [R'_2\text{AlH}]_0$$

$$C_{II} = \log k + m \log [4\text{-octyne}]_0$$

The kinetic true orders, m and n, and the empirical reaction rate constants, k_{emp}, for this hydralumination at 30.00° are

$$m \text{ for 4-octyne, } 1.004 \pm 0.001$$

$$n \text{ for diisobutylaluminum hydride, } 0.370 \pm 0.008$$

$$k_{\text{emp}} = (4.31 \pm 0.10) \times 10^{-5} \text{ l.}^{1/3} \text{ mol}^{-1/3} \text{ sec}^{-1} \quad (5)$$

From the usual Arrhenius expression, k_{emp} = A exp [-ΔE*/RT], the frequency factor A was calculated as (4.5 ± 0.6) × 10¹⁰ l.^{1/3} mol^{-1/3} sec⁻¹. From the relationship, ΔS*_{app}/4.576 = log A - 10.573 - log T, ΔS*_{app} = -11.0 ± 0.3 eu. Thus,

$$k_{\text{emp}} = (4.5 \pm 0.6) \times 10^{10} \exp[-(20,840 \pm 50)/RT] \text{ l.}^{1/3} \text{ mol}^{-1/3} \text{ sec}^{-1} \quad (6)$$

In a similar manner to the foregoing, the initial rates for the interaction of equimolar concentrations of 4-octyne and R'₂AlH or R'₂AlD were determined at 30.0° (Table IV). The average values of v_{Al-H} and v_{Al-D} yielded a kinetic isotope effect of k_H/k_D = 1.68.

Solvent Effects. Since it is well known that electron-deficient aluminum has a tendency to coordinate with n¹⁸ and π¹⁹ Lewis bases, it was important to learn what effect such complexation might have on the kinetics of hydralumination. As candidate π bases, both mesitylene and neat 4-octyne were examined as solvents; tetrahydrofuran was chosen as a typical n-donor medium.

In a THF solution that was 0.678 M in **1** and 0.561 M in **2**, only 1.54% of **1** was hydralumination after 10 hr at 65°. With the assumption of first-order dependence both on **1** and **2**,²⁰ k_{THF} was calculated as 7.7 × 10⁻⁷ l.⁻¹ sec⁻¹ at 65°. From eq 6, k_{hexane} = 1.53 × 10⁻³ l.^{1/3} mol^{-1/3} sec⁻¹ at 65°. Hence, for initial rates,²¹ v_{hexane}/v_{THF} = 2 × 10³ at 65°.

The initial reaction rates in mesitylene at 20.00, 25.05, 29.95, and 39.95° were then compared with those for hexane solution (Table V). The average k_{hexane}/k_{mesitylene} =

Table IV. Kinetic Isotope Effect for the Hydralumination of 4-Octyne with Diisobutylaluminum Hydride or Deuteride

Run no.	[<i>i</i> -Bu ₂ AlH]		Av ((ene)/[yne] ₀)/t ^a	v _{av}
	[Octyne] ₀	[<i>i</i> -Bu ₂ AlD]		
21	0.135	0.137	7.33 × 10 ⁻⁴	7.33 × 10 ⁻⁴
22	0.135	0.137	7.32 × 10 ⁻⁴	(Al-D)
5	0.135	0.138	1.23 × 10 ⁻³	1.23 × 10 ⁻³
11	0.135	0.138	1.23 × 10 ⁻³	(Al-H)
18	0.135	0.138	1.23 × 10 ⁻³	

$$(d/dt)[ene] = v = k[i\text{-Bu}_2\text{AlH(D)}]^{1/3}[yne]^{1.0}$$

$$\frac{v_{\text{Al-H}}}{v_{\text{Al-D}}} = \frac{k_{\text{Al-H}}[i\text{-Bu}_2\text{AlH}]^{1/3}[yne]^{1.0}}{k_{\text{Al-D}}[i\text{-Bu}_2\text{AlD}]^{1/3}[yne]^{1.0}}$$

$$= \frac{k_{\text{Al-H}}[0.138]^{1/3}[0.135]^{1.0}}{k_{\text{Al-D}}[0.137]^{1/3}[0.135]^{1.0}}$$

$$= \frac{1.23 \times 10^{-3}}{7.33 \times 10^{-4}}$$

$$\frac{k_{\text{Al-H}}}{k_{\text{Al-D}}} = \frac{1.23 \times 10^{-3} [0.137]^{1/3}}{7.33 \times 10^{-4} [0.138]^{1/3}} = 1.68 \text{ at } 30.0^\circ$$

^a ene = *cis*-4-octene; yne = 4-octyne.

Table V. Effect of Mesitylene as Solvent on the Initial Rate of the 4-Octyne-Diisobutylaluminum Hydride Reaction^a

Run no.	Temp. °C	Solvent	Rate (v), mol l. ⁻¹ min ⁻¹	v _{mesitylene} / v _{hexane} ^b
24	29.95	Mesitylene	2.04 × 10 ⁻⁴	1.23
5	30.00	Hexane	1.66 × 10 ⁻⁴	
25	25.05	Mesitylene	1.06 × 10 ⁻⁴	1.15
6	24.95	Hexane	9.23 × 10 ⁻⁵	
26	20.00	Mesitylene	5.79 × 10 ⁻⁵	1.15
7	19.95	Hexane	5.05 × 10 ⁻⁵	

^a For all runs, [4-octyne]₀ = 0.135 mol/l.; [*i*-Bu₂AlH]₀ = 0.138 mol/l. ^b k_{mesitylene}/k_{hexane} = 1.18 at 20–30°.

1.18 over this range. The E*_{app} between 20.0 and 40.0° was found to be 21.03 ± 0.50 kcal/mol.

The effect of 4-octyne (intrinsic concentration (neat), 5.65 mol/l.) as a possible π-donor solvent on the hydralumination at 0° was evaluated. First of all, by varying the concentration of the hydride **2** from 0.0469 to 0.313 mol/l., a kinetic true-order dependence on **2** was found to be 0.366 ± 0.010 (Table VI). The rate constant, k_{4-octyne}, was calculated and compared with the calculated (eq 6) k_{hexane} at 0°: k_{4-octyne}/k_{hexane} = 1.1 ± 0.2.

Kinetics of Hydralumination Reactions Monitored to High Conversion. The reaction of equimolar concentrations (0.518 mol/l.) of 4-octyne and the hydride in hexane at 50.0° was followed until 60% consumption of the 4-octyne (Table VII). The constancy of the ratio of [4-octyne] + [4-octene] to the *n*-nonane included as internal standard en-

Table VI. The Effect of 4-Octyne as Solvent on the Initial Rate of the 4-Octyne-Diisobutylaluminum Hydride Reaction^a

Run no.	[<i>i</i> -Bu ₂ AlH] ₀ , mol/l.	Log [<i>i</i> -Bu ₂ AlH] ₀ + 2	Rate (v), mol l. ⁻¹ sec ⁻¹	Log v + 6
28	4.69 × 10 ⁻²	0.6710	1.96 × 10 ⁻⁶	0.2932
29	6.51	0.8136	2.24	0.3502
30	9.46	0.9757	2.46	0.3907
31	1.59 × 10 ⁻¹	1.2011	3.03	0.4818
32	2.41	1.3816	3.54	0.5494
33	3.13	1.4949	3.97	0.5982

^a Slope (n) = 0.366 ± 0.010; intercept (C₁₁) = -5.223 ± 0.01; temp = 0.0°; [4-octyne]₀ = 5.65 mol/l.

Table VII. Integrated Rate Constants of the 1:1 Reaction of 4-Octyne with Diisobutylaluminum Hydride, Calculated According to Different, Assumed Rate Laws^a

Time, min	[ene]/ [yne] ₀	x, mol/l.	k ₁ ^b × 10 ²	k ₁₁ ^c × 10 ²	k ₁₁₁ ^d × 10 ²
7.66	0.1202	0.0623	2.40	2.13	2.21
9.97	0.1552	0.0804	2.45	2.17	2.28
20.04	0.2736	0.1417	2.40	2.10	2.34
30.04	0.3631	0.1880	2.35	2.02	2.42
40.00	0.4199	0.2175	2.17	1.86	2.40
50.05	0.4601	0.2383	2.00	1.70	2.40
60.00	0.4845	0.2509	1.82	1.54	2.37
70.00	0.4942	0.2559	1.61	1.36	2.25
80.16	0.4984	0.2581	1.42	1.20	2.12
100.06	0.5175	0.2680	1.22	1.03	e
120.00	0.5237	0.2712	1.04	0.87	e
139.92	0.5236	0.2758	0.92	0.77	e
160.78	0.5375	0.2784	0.81	0.68	e
246.5	0.5625	0.2913	0.58	0.48	e
411.0	0.5973	0.3093	0.39	0.32	e

Av 2.32 × 10⁻²

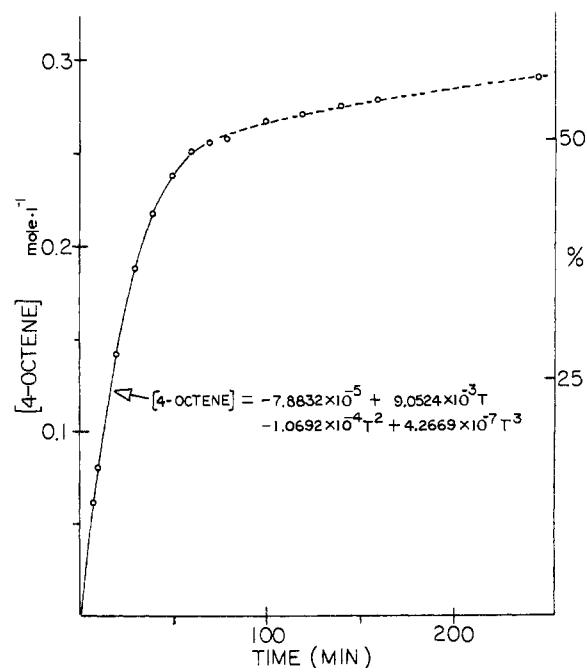
^a [yne]₀ = [(*i*-C₄H₉)₂AlH]₀ = 0.518 mol/l.; t = 50.0°, yne = 4-octyne; ene = *cis*-4-octene. ^b k₁, l.^{1/2} mol^{-1/2} min⁻¹. ^c k₁₁, l.^{1/3} mol^{-1/3} min⁻¹. ^d k₁₁₁, l.^{1/3} mol^{-1/3} min⁻¹. ^e dx/dt = k₁₁₁·(a₀ - x)(a₀ - 2x) has no meaning when 2x > a₀.

sures that no 4-octyne was consumed in side reactions, such as reductive dimerization (eq 2). By the method of initial rates

$$k_{\text{emp}} = 3.52 \times 10^{-4} \text{ l.}^{1/3} \text{ mol}^{-1/3} \text{ sec}^{-1} \text{ at } 50.0^\circ \quad (7)$$

This value agrees well with that obtained from eq 6: k_{emp} = 3.69 × 10⁻⁴ l.^{1/3} mol^{-1/3} sec⁻¹.

When the concentration of 4-octene (formed upon hydrolysis) was plotted against time, however, a pronounced rate retardation was observed after 50% reaction (Figure 1). That retardation was not caused by consumption of hydride by oxidative or hydrolytic side reactions was shown by hydrolyzing a 1:1 hydralumination run that had gone 74% to completion. The hydrogen gas evolved accounted for 87% of that expected from unreacted **2**. Thus, **2** would still have been available for continued reaction.

**Figure 1.** Plot of *cis*-4-octene formation vs. time in the reaction of 4-octyne with diisobutylaluminum hydride in a 1:1 ratio at 50°.

Since the rate retardation was not due to destruction of hydride, the hydride must have been made less reactive in some manner. As a measure of the rate after 50% reaction, the change of 4-octene/time, $\Delta x/\Delta t$, was plotted vs. time; extrapolation to $\Delta t = 0$ (50%) gave the initial rate constant at 50% reaction (due consideration being given to the observed kinetic order dependencies of first order in alkyne and half-order in hydride³¹):

$$k_{emp} = 3.45 \times 10^{-5} \text{ l.}^{1/2} \text{ mol}^{-1/2} \text{ sec}^{-1} \quad (8)$$

Thus, the rate at 50% conversion (eq 8) is *ca.* one-tenth that observed initially (eq 7).²¹

Another measure of the retardation is to compare the overall kinetic true order n_c ($m + n = 1.37$) with the order with respect to time, n_t . The order with respect to time was obtained from the relationships

$$dx/dt = k(a_0 - x)^{m+n} \quad [1] = [2], \quad m + n = n_t \quad (9)$$

$$\log dx/dt = \log k + (m + n) \log (a_0 - x) \quad (10)$$

The instantaneous rate before 50% reaction, dx/dt , was calculated from an empirical polynomial equation

$$[4\text{-octyne}] = \sum_{p=0} C_p t^p$$

so as to fit the curve generated by a plot of [4-octyne] vs. t .²² By comparing computer-generated values (where $p = 0-2, 0-3, 0-4$) with experimental values, the cubic equation was found to give the best fit

$$[4\text{-octyne}] = -7.8832 \times 10^{-5} + 9.0524 \times 10^{-3} t - 1.069 \times 10^{-4} t^2 + 4.2669 \times 10^{-7} t^3$$

If there were no inhibition, a plot of $\log dx/dt$ vs. $\log (a_0 - x)$ should be linear. The curved nature of the plot shows that $m + n$ is always increasing: 1.6 at 20.04 min, 6.1 at 50.05 min, and 67 at 80.16 min. The difference in n_c and n_t shows that the mechanism is changing, and the increase in n_t clearly points to reaction inhibition.

Since the most pronounced change in rate seemed to occur after 50% conversion (Figure 1), it appeared that one-half of the hydride was being rendered less active. Accordingly, a kinetic study of **1** and **2** taken in a 1:2 molar ratio was undertaken (Table VIII). Again, an internal standard of *n*-nonane lent assurance that no 4-octyne was consumed in side reactions up to a reaction conversion of 87%. How-

Table VIII. Integrated Rate Constants of the 1:2 Reaction of 4-Octyne with Diisobutylaluminum Hydride, Calculated According to Different, Assumed Rate Laws^a

Time, min	[ene]/ [yne] ₀	x , mol/l.	$k_I^b \times 10^2$	$k_{II}^c \times 10^2$	$k_{III}^d \times 10^2$
5.33	0.0866	0.0232	2.02	2.06	2.21
9.95	0.1573	0.0422	2.08	2.10	2.18
14.97	0.2270	0.0608	2.10	2.11	2.21
19.98	0.2884	0.0773	2.10	2.10	2.22
30.00	0.3926	0.1052	2.09	2.06	2.23
40.72	0.4819	0.1291	2.06	2.01	2.22
50.01	0.5455	0.1462	2.04	1.97	2.22
59.99	0.5982	0.1603	1.99	1.91	2.19
70.00	0.6469	0.1734	1.97	1.87	2.19
80.14	0.6896	0.1848	1.95	1.84	2.20
89.92	0.7200	0.1930	1.91	1.79	2.17
99.87	0.7500	0.2010	1.89	1.76	2.17
109.94	0.7754	0.2078	1.86	1.72	2.17
169.5	0.8742	0.2343	1.75	1.57	2.17

$$Av \ 2.19 \times 10^{-2}$$

^a [yne]₀ = 0.268 mol/l.; [(*i*-C₄H₉)₂AlH]₀ = 0.537 mol/l.; $t = 50.0^\circ$, yne = 4-octyne; ene = *cis*-4-octene. ^b k_I , $l^{1/2} \text{ mol}^{-1/2} \text{ min}^{-1}$, ^c k_{II} , $l^{1/3} \text{ mol}^{-1/3} \text{ min}^{-1}$, ^d k_{III} , $l^{1/3} \text{ mol}^{-1/3} \text{ min}^{-1}$.

ever, since gas chromatographic analysis would not have separated 4-octene from any *n*-octane, the possibility of some diaddition (eq 3) was not ruled out by the constancy of the octene:nonane ratio. But a separate 1:2 hydralumination run under even more severe conditions (32 hr at 70° and 16 hr at 40°) resulted in only 6% of *n*-octane. Diaddition was thus insignificant in the reported kinetic measurements.

The rate data for both the 1:1 (Table VII) and the 1:2 (Table VIII) kinetic runs at 50.0° were used to calculate the rate constants, k_I , k_{II} , and k_{III} (*vide supra*), derived from the integrated forms of probable rate expressions

$$dx/dt = k_I(a_0 - x)(a_0 - x)^{1/2} \quad (11)$$

$$dx/dt = k_{II}(a_0 - x)(a_0 - x)^{1/3} \quad (12)$$

$$dx/dt = k_{III}(a_0 - x)(a_0 - 2x)^{1/3} \quad (13)$$

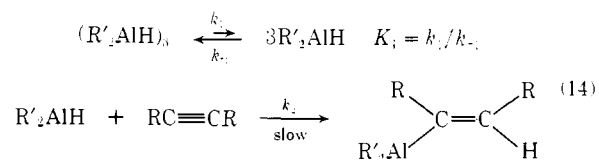
Despite the four-thirds order of the initial kinetics (eq 5), eq 12 did not give constant k_{III} values, nor did eq 11, assuming half-order dependence on **2** (as claimed for the hydralumination of 1-butene²³), give any better fit. However, if one assumes that the product **3** renders **2** unavailable by forming a 1:1 complex, then eq 13 would be appropriate. Indeed, this equation fits the kinetic data best for the first half of the 1:1 reaction (Table VII) and for all the observed points in the 1:2 run (Table VIII). The calculated k_{III} values are reasonably constant and show no discernible drift. From Table VII, $k_{III} = 3.87 \times 10^{-4} \text{ l.}^{1/3} \text{ mol}^{-1/3} \text{ sec}^{-1}$. In good agreement with this value is that obtained from the 1:2 study: $k_{III} = 3.65 \times 10^{-4} \text{ l.}^{1/3} \text{ mol}^{-1/3} \text{ sec}^{-1}$.

Interaction of Diisobutyl(*E*)-4-octenylaluminum and Diisobutylaluminum Hydride. As previously reported for other alkynes,²⁴ interaction of a 1:1 ratio of 4-octyne and hydride **2** to *ca.* 50% reaction gives a mixture whose nmr spectrum displays a vinylic triplet at 7.18 ppm ($J = 6.5$ Hz) and a complexed Al-H peak at 3.74 ppm. Even at 100 Hz, no new absorptions were observed down to -50° . These data are consistent with a 1:1 interaction of **2** and **3** to give a discrete chemical system.

Another 1:1 mixture of **2** and **3**, made by heating a 1:2 mixture of 4-octyne and hydride at 40° and then pumping off the residual 4-octyne, had an identical spectrum. Heating this mixture at 40–70° under 0.01 mm pressure led to the evaporation of 40% of the theoretical triisobutylaluminum. The nmr spectrum of the residue still showed peaks at 7.16 and 3.72 ppm but now had weak peaks at 5.9 and 3.2 ppm (intensity 7.16/5.9 and 3.72/3.2 \approx 8:1). Hydrolysis showed the presence of small amounts of *trans*-4-octene in the *cis*-4-octene.

Discussion

Basic Mechanism of Hydralumination. Since diisobutylaluminum hydride is known to be trimeric¹³ in hydrocarbon solvents under these experimental conditions, the reaction scheme most consistent with the observed initial rate constant and kinetic true order dependencies is the following



With the assumption of a relatively rapid trimer-monomer equilibrium and the steady-state approximation for the monomer as the reactive intermediate

$$d[3]/dt = k_2(K_1)^{1/3}[(R'_2AlH)_3]^{1/3}[RC \equiv CR] \quad (15)$$

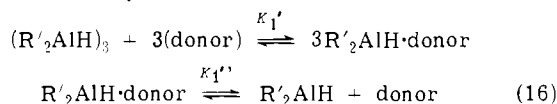
Other mechanisms having preequilibria between hydride trimer, dimer, and monomer will also give one-third order dependence in **2**, so long as only the monomer reacts with the acetylene.²⁵ On the other hand, a mechanism allowing both the dimer (*cf.* ref 23) and monomer to react with the acetylene could display a kinetic order between 0.33 and 0.67.²⁵

From transition state theory, the apparent activation energy (eq 15) includes kinetic and thermodynamic contributions:

$$\Delta E^* = RT + \frac{1}{3}\Delta H_1 + \Delta H_2^*$$

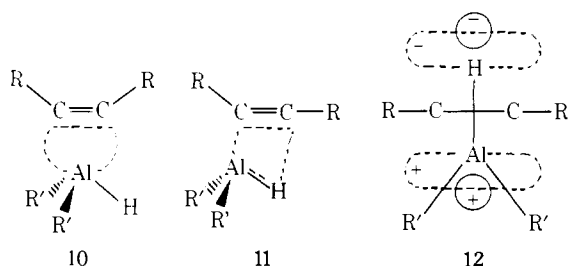
ΔH_1 = enthalpy of hydride trimer \rightarrow monomer, ΔH_2^* = enthalpy of activation for eq 14, and $RT = ca.$ 0.6 kcal at 25°. Now, although no experimental value of ΔH_1 for **2** is available, kinetic estimates of 15–20 kcal and 16.4 kcal²⁸ per Al–H bridge have been made. Hence, a minimum value of $\frac{1}{3}\Delta H_1 = 15$ kcal seems reasonable. Therefore, with an observed $\Delta E^* = 20.84$ kcal/mol, $\Delta H_2^* = 5$ kcal/mol. In a similar fashion, ΔS_2^* for eq 14 can be estimated, if one assumes values for the unknown K_1 . For 0.33% dissociation at 30°, $K_1 = 10^{-6}$ and $S_2^* = -52$ eu.

The effect of π -donor solvents, mesitylene and neat 4-octyne, on the hydralumination was, at most, small. In the preequilibrium of hydride trimer and monomer



any rate acceleration could be accounted for if $(K_1')^{1/3}$, $(K_1'') > (K_1)$ of eq 15. With an *n* donor, however, the rate retardation with THF was striking ($\nu_{\text{hexane}} \approx 10^3 \nu_{\text{THF}}$). Tetrahydrofuran is known to form a strong 1:1 complex with monomeric **2**.¹⁸ This effect is consistent with the importance of tricoordinate hydride monomer in eq 14 ($K_1' \gg 1$ and $K_1'' \ll 1$ in eq 16).

The observed isotope effect, $k_{Al-H}/k_{Al-D} = 1.68$ at 30.0°, cannot be considered as a primary effect, for the overall rate embraces a preequilibrium whose $\Delta H_1 \approx 45$ kcal/trimer. Hence, it is to be expected that the actual isotope effect on k_2 in eq 14 is even smaller.²⁹ Thus, in the attack of unsolvated, monomeric R'_2AlH on 4-octyne, there is not much stretching of the Al–H bond in the transition state. Three models could be considered, in which R'_2AlH attacks the acetylenic π cloud electrophilically: a transition state resembling a π complex (**10**), a σ complex (**11**) (where

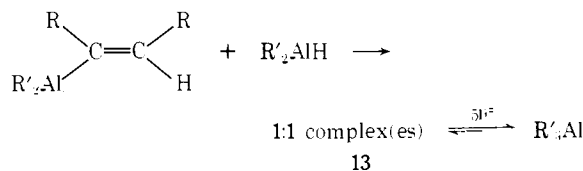


the reacting bonds are in a plane), or a π complex where the Al–H bond is perpendicular to the $C\equiv C$ bond (**12**). Structure **11** is acceptable, if the Al–H bond is not stretched much. A rectangular variant of **11** (“four-centered” concerted making and breaking of bonds) is unfavorable on several counts: (a) a larger isotope effect would be expected; (b) severe steric interactions between R and R' would be encountered with bulky α -substituted alkynes (actually, *tert*-butylacetylene hydraluminates 24 times faster than 4-octyne);^{1b} and (c) such a configuration of orbitals should be partly forbidden on orbital-symmetry grounds (*cf.* analo-

gous considerations for hydroboration).³⁰ Indeed, some of these criticisms against a symmetrical four-center state are validly lodged, to some extent, against **11** itself. Consequently, the π models **10** and **12** are more appealing. Structure **12** not only minimizes the nonbonded interactions between R and R' but permits the LUMO of R'_2AlH ($3p_z$ of Al) to overlap with the one π HOMO of the acetylene (out of the plane) and also the antibonding orbital of the Al–H σ bond to overlap with the other π HOMO of the triple bond (in plane of **12**). Since **12** could collapse to product largely in a concerted, symmetry-allowed process, it seems to be the best choice of a transition state for hydralumination.

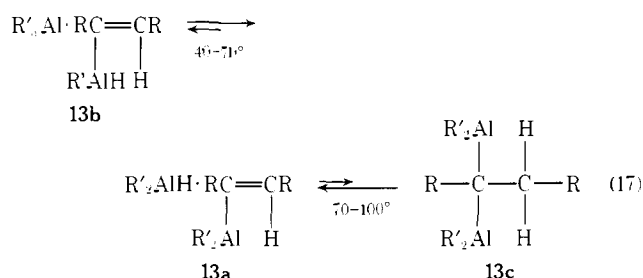
Mechanistic Complexities and Molecular Association.

The sharp drop in rate observed after 50% reaction with 1:1 mixtures of 4-octyne and hydride **2** demands that the product, diisobutyl(*E*)-4-octenylaluminum (**3**), complex with **2** in a 1:1 fashion. When this autoinhibition (eq 16) is taken into account (eq 13), a completely satisfying rate description can be obtained for the first half of the 1:1 reaction (Table VII) and for almost the entire extent of the 1:2 reaction (Table VIII). Although there is no doubt about the stoichiometry of eq 16, nor that K_{eq} is large, a completely satisfying description of the inhibiting intermediate is not straightforward. Such intermediates, first detected by nmr studies of hydralumination, have been described as mixed hydride–alkenyl bridged complexes.²⁴ However, in the temperature range of hydralumination (40–70°) such adducts clearly are in equilibrium with triisobutylaluminum, for this alkyl can be selectively evaporated from the complex



Furthermore, if the 1:1 complex were simply described as an associated union of **2** and **3**, then it would be expected to display first-order hydride dependence in any hydralumination reaction (essentially, source of monomeric R'_2AlH). In fact, this complex shows 0.5 order dependence in the hydralumination of 4-octyne.³¹ Thus, in the temperature range 20–50°, **13** possesses more structural variation than has been supposed.

These apparently divergent structural and kinetic properties can be made consonant by recognizing that the nature of **13** is temperature dependent,³¹ over 40°, triisobutylaluminum and a vinylaluminum hydride (**13b**) are in equilibrium with any mixed hydride–alkenylaluminum complex (**13a**). Indeed, as the isomerization studies of **3** make clear, in the range of 70–100° geminal dialumino adducts (**13c**) must also be taken into account in any complete description of system **13**.^{5,6,32}



Experimental Section

General Techniques. Techniques for the preparation, handling, and storage of organoaluminum alkyls and hydrides have already been described.^{6,33} In these kinetic studies, all glassware coming

into contact with an organoaluminum reagent was washed sequentially with chromic acid solution, water, and acetone and then dried overnight at 150°. Reaction assemblies were set up with warm glassware and purged thoroughly with dry nitrogen.

All reactions, measurements and transfers of organometallic compounds were conducted under an atmosphere of high-purity (99.995%) nitrogen, which was further purified in the reported manner. The organoaluminum samples were prepared for infrared spectral recording by use of a small desiccator modified by the attachment of a three-way stopcock to one port in the lid and of a serum cap to the other, centrally situated, port. The stopcock port permitted the desiccator (charged with granular phosphorus pentoxide at the bottom) to be alternately evacuated and flushed with dry nitrogen; the serum port permitted the parts of the infrared cell to be assembled by means of long forceps (with the serum cap removed and a purging stream of nitrogen) or permitted the introduction of an organoaluminum sample with a gas-tight syringe (with the serum cap in place). The sodium chloride infrared cell, equipped with Teflon spacer and gaskets, yielded infrared spectra that did not change over a period of a day. This observation gave assurance of an air-tight cell. The spectra themselves were recorded on a Perkin-Elmer spectrophotometer, Model 137.

For recording the nmr spectra of air- and moisture-sensitive compounds, a standard nmr tube was equipped with a rubber septum (i.d. 4 mm, o.d. 7 mm). A needle (attached to a three-way stopcock, which in turn led to a nitrogen line and to the vacuum system) was inserted through the serum cap, in order to evacuate and flush the tube. Then the organoaluminum sample was introduced through the serum cap by means of an air-tight Teflon syringe. This method was more rapid and safer than sealing the nmr tube where pressure buildup can lead to explosion. Moreover, the air tightness of such serum-capped samples is shown in the reproducibility of spectra even after standing a few days.

The foregoing nmr spectra were recorded on a Varian spectrometer, Model A-60. In those cases where spectra were required at various temperatures, a Varian V-6040 control unit was used to regulate the sample temperature in the range of -60 to +40 to within $\pm 2^\circ$. The chemical shift (in hertz) between the OH and CH₃ absorptions of methanol was measured and the temperature calculated ($^\circ\text{K}$) from available empirical equations. The compressed air for spinning the sample was dried thoroughly (P₂O₅) to prevent frost formation.

For glc analysis either an F&M dual-column gas chromatograph, Model 720, or a Varian-Aerograph unit, Model 1200, was used. The latter, highly sensitive unit (limit, 10⁻¹⁰ g), equipped with a flame-ionization detector, was employed for the analysis of most reaction mixtures in the kinetic measurements. Both chromatographs were connected to a Honeywell recorder, Model Elektronik 15, which in turn was provided with a disk-chart integrator, Model 201-B. Three types of columns were used: (a) 6 ft or 12 ft \times 0.25 in. column of 10% silicone gum rubber on Chromosorb W (60-80 mesh); (b) a coupled column of 6 ft \times 0.125 in. length of 8% silicone DC-703 and 12 ft \times 0.125 in. length of 8% silicone SE-30, both on siliconized Chromosorb P (100-120 mesh); and (c) 9 ft \times 0.125 in. length of 10% silicone SF-96 on Chromosorb P (100-120 mesh). Response factors for the 4-octyne, *n*-octane, and the *cis*- and *trans*-4-octenes were determined, relative to 1.00 for 4-octyne for both thermal-conductivity and flame-ionization detectors. *n*-Nonane and *n*-hexadecane were used as internal standards for the octane and dimeric octane derivatives, respectively.

Preparation and Purification of Reagents. Solvents. All hydrocarbon solvents used with organoaluminum compounds were of high initial purity (99+%) and were dried by heating them to reflux over sodium metal slices (heptane, nonane, and mesitylene) or over sodium metal with added benzophenone (hexane and benzene) under nitrogen in a specially designed flask to avoid contamination by grease. Tetrahydrofuran was purified and dried in the usual manner,³⁴ the final distillation being from LiAlH₄. For the kinetic and nmr studies, all solvents were distilled directly from the aforementioned solvent still into the stock-solution vessel or into the reaction flask (or nmr tube) *via* a needle-tipped buret. The stock-solution vessels were standard volumetric flasks to which a side tube bearing a three-way stopcock had been fused above the calibration mark. The needle-tipped burets, suitable for introducing controlled amounts into septa-capped vessels, were provided with a standard-taper joint at their top, so that the buret could be

joined directly to the solvent still for filling. Only ungreased or Teflon joints were allowed to come into contact with the pure solvent distillate.

Hydrocarbon Reagents and Products. The 4-octyne (obtained from the Farhan Chemical Co. as 99% pure) used for kinetic runs was dried over granular phosphorus pentoxide for 4 hr and then distilled under nitrogen through a 30 \times 0.75 cm column packed with glass helices. By glc analysis with column b, the resulting 4-octyne had <0.2% contamination and was stored in the dark under nitrogen.

Authentic *cis*-4-octene was isolated from the hydralumination of 4-octyne by preparative glc of the hydrolysate by use of column a. It was shown to be pure by infrared and nmr spectral data. Authentic *trans*-4-octene was obtained from the Aldrich Chemical Co. in 99% purity. The reductive dimer of 4-octyne, (*E,E*)-5,6-dipropyl-4,6-decadiene,¹⁷ was isolated and identified by infrared, nmr, and mass spectral measurements.

Aluminum Alkyls. The diisobutylaluminum hydride obtained from Texas Alkyls, Inc., contained 94% of the hydride, 4.5% of triisobutylaluminum, 0.5% of tributylaluminum, and 1.0% of tripropylaluminum. A careful fractional distillation could readily remove these impurities. Commercially available triisobutylaluminum (95%) and diisobutylaluminum chloride (97%) were redistilled before use. The purified triisobutylaluminum was stored at <0°, since it decomposes slowly at room temperature into the hydride and isobutene. Before use, its purity was checked by an nmr spectral scan at high amplitude of the region, δ 2.5-4.5 ppm.

The preparation of diisobutylaluminum deuteride was accomplished by modifying the procedure for diethylaluminum hydride.^{2,11} Into a 1000-ml, three-necked flask fitted with a Friedrichs reflux condenser, a motor-driven sealed stirrer, and a pressure-equalized addition funnel was distilled 300 ml of ethyl ether (from LiAlH₄). To this solvent was added 8.6 g (1.07 mol) of lithium deuteride (Alfa, 97% pure), and the suspension was placed in a cooling bath at 0° (direct coolant, mineral oil, in the event of flask rupture). Then 146 ml (0.75 mol) of diisobutylaluminum chloride was added dropwise to the vigorously stirred suspension. The mixture was thereafter stirred at the reflux temperature for 48 hr. Since hydrolysis of 0.5 ml of the supernatant solution still gave a positive Cl test with AgNO₃ solution, 0.5 g more of lithium deuteride was added and an additional 40-hr heating period undertaken. The test for soluble chloride was now negative. Under nitrogen, the reaction mixture was filtered through a glass frit of medium porosity. Most of the ether was removed from the filtrate to leave a turbid liquid, which was refiltered. The resulting crude filtrate of diisobutylaluminum deuteride was heated at 75° under 2 mm for 4 hr, in order to remove the coordinated ether. The clear, viscous product was distilled through a 25 \times 1.5 cm Vigreux column, bp range 110-123° (0.6 mm), which by nmr spectral analysis was shown to contain 8.3% of ether. A careful redistillation gave *ca.* 80 ml of ether-free diisobutylaluminum deuteride (bp 112-118° at 0.6 mm).

The isotopic purity of the deuteride was determined by solvolysis of a sample on a vacuum line with ethanol and mass spectral analysis of the hydrogen evolved: *m/e* 3, 95.5%; *m/e* 2, 3.7%; and *m/e* 4, 0.4%. The diisobutylaluminum deuteride was thus 96.7% pure.

The hydride content of diisobutylaluminum hydride samples can be determined in the presence of contaminants such as triisobutylaluminum and diisobutylaluminum isobutoxide by means of the isoquinoline titration procedure.³⁵ The procedures of Hagen³⁶ and of Mitchen³⁷ were modified in the present study. Absorbance measurements were made in a special Pyrex cell of 0.1-cm path length with a Cary spectrophotometer, Model 14. The Pyrex cell was fused to a 45-ml reservoir closed with a rubber septum and the whole cell assembly purged by needle inlets with dry nitrogen. A standard solution of known volume of highly pure isoquinoline in dry benzene was placed in the cell and then the hydride sample in an amount judged to be somewhat in excess of what is necessary for a 1:1 hydride-isoquinoline complex. Increments of isoquinoline in benzene were added with a needle-tipped, pressure-equalized buret, while the absorbance of the resulting 1:2 hydride-isoquinoline complex at 450 nm was recorded. A plot of absorbance vs. volume of isoquinoline added showed a rounded break at a ratio of 1:2. Titrations of redistilled diisobutylaluminum hydride samples gave purities of 99.1 \pm 0.4%.

Kinetics of the Addition of Diisobutylaluminum Hydride to 4-

Octyne. General Procedure. With scrupulous adherence to the exclusion of moisture and oxygen, the kinetic studies were conducted in a 100-ml flask fitted with a three-way nitrogen inlet and a 10-mm tube sealed with a rubber serum cap. The flask was provided with a magentic stirring bar, and an air-driven magnetic stirrer was immersed in the constant temperature bath ($\pm 0.01^\circ$). Because the high reactivity and viscosity hindered the exact transfer of the hydride, a stock solution of the hydride in *n*-hexane (or mesitylene) was prepared for each series of experiments. In some cases *n*-nonane was added as an internal glc analytical standard. Such analyzed stock solutions were prepared in 200-ml volumetric flasks fitted with a side-arm, three-way stopcock for nitrogen purging. Dried *n*-hexane of the Baker Gas Chromatographic Quality was used as diluent, since it showed minimal tailing interference with the 4-octyne peak.

In a typical experiment, 20.0 ml of the hydride stock solution was placed in the reaction vessel. The vessel was thermally equilibrated in the constant-temperature oil bath for 10 min; then the 4-octyne was introduced with vigorous stirring. The 4-octyne was loaded into a Hamilton gas-tight syringe equipped with a Chaney adapter, and the amount used was determined by weight loss. This procedure allowed reproducible transfer of 4-octyne from one run to the next (e.g., 0.304 ± 0.02 g). The reaction flask was under a positive pressure from the nitrogen line, so that no air could enter through small leaks. (Also the stirrer platform was kept 1 cm away from the flask to prevent local temperature fluctuations.) Samples of 0.3 ml were removed with a gas-tight syringe at appropriate intervals. (The needle was inserted through the serum cap just after nitrogen had been expelled from the syringe.) The contents of the withdrawn syringe were injected into a deaerated aqueous solution of dilute hydrochloric acid. After standing for 1 hr, the organic layer of each hydrolyzed sample was analyzed for 4-octyne and *cis*-4-octene.

Two methods were employed for the calculation of the initial rate of hydride addition to 4-octyne: (a) below 35° , the rate was sufficiently slow (5% after 25 min) to allow for good mixing of the 4-octyne and direct initial rate determination before 7% of reaction (product formation was linear with time within experimental error); and (b) at higher temperatures, there was inadequate time for proper mixing, and hence a plot of rate against time had to be extrapolated to zero time.

Kinetic Studies in Hexane. The stock solutions in hexane were prepared by diluting 5.0 ml of diisobutylaluminum hydride to a total volume of 200.0 ml. For runs 1-8 (Table I), a 20.0-ml aliquot of this solution was mixed with 0.304 g of 4-octyne (total volume = 20.4 ml); for runs 9-12 (Table II), the concentration of 4-octyne was varied; and for runs 13-20 (Table III), 10 ml of the pure hydride was diluted up to 200.0 ml with hexane. Then, for these runs, varying amounts of the stock solution ($x = 2.0$ to 20.0 ml) were diluted with hexane (20.0 to x ml), which was added from a needle-tipped buret. The kinetic data presented in Tables I-III were obtained by glc analysis using a type b column on the Varian Aerograph apparatus, Model 1200.

Kinetic Isotope Effect. A stock solution of diisobutylaluminum deuteride was prepared by diluting 2.5 ml of the deuteride up to a volume of 100.0 ml with hexane. To 20.0 ml of this stock solution was added 0.304 g of 4-octyne at 29.94° . The kinetic data given in Table IV were gathered by the same glc method cited directly above.

Solvent Effects. (a) Mesitylene. Stock solutions of diisobutylaluminum hydride were prepared by diluting a 5.0-ml sample up to a volume of 200.0 ml with mesitylene. Individual 20.0-ml aliquots were each mixed with 0.304 g of 4-octyne and the kinetic data measured in the usual way for temperatures of 20.00, 25.05, 29.95, and 39.95° (Table V).

(b) Tetrahydrofuran. To 20.0 ml of pure tetrahydrofuran was added, first 2.0 ml of the hydride and, then, 2.0 ml of 4-octyne. The reaction mixture, $[i\text{-Bu}_2\text{AlH}]_0 = 0.561$ mol/l. and $[4\text{-octyne}]_0 = 0.678$ mol/l., was stirred at 65° for 1 hr. Gas chromatography showed a $[cis\text{-}4\text{-octene}]:[4\text{-octyne}]_0$ ratio of 1.54×10^2 and assured the absence of 1-butanol, a possible cleavage product of THF.

(c) 4-Octyne. To 10.0 ml of 4-octyne were added $(2.0 - x)$ ml of hexane, and the resulting solution was equilibrated at 0.0° . A stock solution of diisobutylaluminum hydride was prepared by mixing 5.0 ml of the hydride with 10.0 ml of *n*-nonane. Then x ml of this

solution was added to the foregoing equilibrated octyne solution. The presence of the *n*-nonane as an internal glc standard eliminated the inaccuracy of measuring the area of the 4-octyne. Instead, the reaction rates were derived from measuring the ratio of the 4-octene and *n*-nonane areas (Table VI).

Kinetics of the Hydralumination of 4-Octyne by Diisobutylaluminum Hydride at 50.0° . (a) Reagent Ratio, 1:1. A stock solution was prepared by diluting 10.0 ml of the hydride and 5.0 ml of *n*-nonane with hexane to a total volume of 100.0 ml. A 30.0-ml aliquot of this solution was equilibrated at 50.0° , and then 1.855 g (2.50 ml) of 4-octyne was added. The reaction was followed by a glc type a analysis with the F&M chromatograph, Model 720, until 60% completion (411 min). The data are offered in Table VII. *n*-Nonane was used to check on the material balance and thereby to ensure that no octyne was consumed in competing reactions, such as reductive dimerization. Column 2 indicates that the ratio of areas, $[4\text{-octyne}] + [4\text{-octene}]$, remains a constant (1.9000 ± 0.02), within experimental error. However, this ratio decreased slightly as the hydralumination rate slackened.

(b) Reagent Ratio 1:2. This kinetic run formed an important contrast with the foregoing run for two reasons: first, it allows the reaction to be followed to an extent $>87\%$ in a shorter period of time; and, secondly, the integrated rate equation describing the kinetics becomes much simpler.

To 20.0 ml of the hydride stock solution, prepared as in part a above, was added 0.617 g of 4-octyne. The reaction was followed by the same glc method as above. The ratio, $[4\text{-octyne}] + [4\text{-octene}]$, remained constant at 0.8973 ± 0.013 through 87% of the reaction (Table VIII).

Nonkinetic Studies of Hydralumination. (a) Determination of Active Al-H Bonds. An equimolar mixture of 4-octyne (0.3056 g) and diisobutylaluminum hydride (4.0 g) in 25 ml of hexane was allowed to react for 29 hr at 50° and then for 24 hr at room temperature. The reaction vessel was then attached to a vacuum line and the whole vessel cooled in a Dry Ice-acetone bath. Then 5.0 ml of water was slowly added for hydrolysis, and the gas evolved was collected after passage through two liquid nitrogen traps. Mass spectrometric analysis (Consolidated Electrodynamics, Model 21-620A) showed the collected gas to be $>98\%$ hydrogen, and manometric measurements revealed that it amounted to 87% of the hydride expected to have remained. Thus, a glc analysis of the liquid hydrolysate showed it to be a mixture of 73.6% of 4-octene, 22.8% of 4-octyne, and 3.6% of reduced dimer. The 24.6% of remaining $R_2\text{AlH}$ ($22.8 + 3.6/2$) should give an observed H_2 pressure at 25° (760 mm) of 35.7 cm; the observed value was 31 cm.

(b) Determination of the Ratio of *cis*-4-Octene:*trans*-4-Octene by Infrared Spectroscopy. Since the relative amounts of *cis*- and *trans*-4-octenes could not be determined by gas chromatography, the internal standard method of infrared spectroscopy³⁸ was employed. Two inseparable peaks arising from the asymmetric methyl bending vibration [$\delta_{as}(\text{CH}_3)$, 1460 cm^{-1}] and the methylene scissoring deformation [$\delta_s(\text{CH}_2)$, 1468 cm^{-1}] were used as the internal standard. Then the absorbance of the *trans* olefinic C-H out-of-plane bending vibration [$\gamma(\text{CH})$, 970 cm^{-1}] was the measure of the *trans* isomer in the mixture, with the reasonable assumption that δ_{as} and δ_s for both isomers in the region is the same. From the equation

$$\frac{A_\gamma/A_{\delta_{\text{mixture}}}}{2.08} = \frac{C_1}{C_1 + C_2}$$

where A_δ and A_γ are the total absorbances at $1460\text{-}1468\text{ cm}^{-1}$ and at 970 cm^{-1} , respectively, for the isomeric mixture, and C_1 and C_2 are the concentrations of the *trans* and the *cis* isomer, respectively, the relative percentages of the isomers can be calculated.

(c) Study of the Nature of Diisobutyl(4-octenyl)aluminum. When equimolar portions of diisobutylaluminum hydride and 4-octyne (56.1 mmol) were stirred at $50\text{-}55^\circ$ for 22 hr, a colorless solution resulted. An aliquot of the mixture was diluted with 20 ml of anhydrous ethyl ether and then treated carefully with dilute HCl. Work-up of the organic layer and glc analysis with a type a column showed a 79.8, 16.6, and 3.6 molar mixture of 4-octene, 4-octyne, and (*E,E*)-5,6-dipropyl-4,6-decadiene, respectively. After most of the ether was removed by fractional distillation, the 4-octene was separated by preparative glc with a type a column. Infrared spectroscopy showed it to be only the *cis*-4-octene, and mass spectrom-

etry at 70 eV indicated the absence of any detectable *n*-octane.

The 16.6% of unreacted 4-octyne was removed at 25° *in vacuo* from the original organoaluminum mixture (glc test for 4-octyne on a hydrolyzed sample was negative). Then 5.0 ml of the crude diisobutyl(4-octenyl)aluminum was treated with 3.0 ml of diisobutylaluminum deuteride (96.4% pure, 0.0167 mol) and the mixture stirred at 65–70° for 2 days to yield a pale orange-colored liquid. Usual hydrolytic work-up and infrared analysis of the glc-collected liquid showed the presence of *trans*-4-octene-*d*₀, but a quantitative measure was vitiated by the presence of deuterated octenes and octanes. A mass spectral analysis at 70 eV showed the presence of 4-octene (*m/e* 112), 4-octene-*d*₁ (113), *n*-octane (114), and *n*-octane-*d*₁ (115) in parent peak ratios of 7.9:4.5:1.5:0.3. Since at 70 eV *n*-octane does not give fragmentation for P – 1 (*m/e* 113, (P – 1)/P = 0), and only a negligible amount of P – 2 (*m/e* 112, (P – 2)/P = 0.07) and 4-octene does not show any P – 1, only the C₁₃ abundances for a C₈H₁₈ hydrocarbons must be allowed for in the calculations. With consideration for the mass ratios of C₈H₁₈, 113/112 = 0.0890, and 114/112 = 0.0035, the proportions of 4-octene and 4-octene-*d*₁ are found to be 67:33. Although the exact calculation of the *n*-octane would require the knowing of the sensitivity ratio, P(octane)/P(octene), the following rough estimate can be made: 58% of 4-octene, 29% of 4-octene-*d*₁, 11% of *n*-octane, and 2% of *n*-octane-*d*₁.

The nmr spectrum of the neat liquid collected above showed distinct aliphatic (CH₃, CH₂), allylic, and vinylic signals. Comparison of the integration ratios of the three kinds of protons, 6.25:2.35:1.00, with those expected for various octene-octane mixtures permits one to calculate a 4-octene:4-octene-*d*₁ ratio of 70:30, in good agreement with the mass spectral analysis.

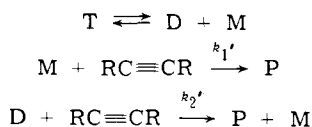
The remaining crude diisobutyl(4-octenyl)aluminum (*ca.* 8 ml) was stirred at 95–100° for 15 hr. Usual hydrolysis of the reddish solution and glc analysis with a type a column showed the presence of 86.9% of 4-octene and 13.1% of (*E,E*)-5,6-dipropyl-4,6-decadiene. By preparative glc, the 4-octene was collected and with infrared spectroscopy the *A_v/A_δ* shown to be 0.482. Thus, 23% of the 4-octene was the *trans* isomer or an overall analysis of 66.9% of *cis*-4-octene, 20% of *trans*-4-octene, and 13.1% of dimer.³⁹

(d) **Nuclear Magnetic Resonance Spectrum of Mixtures of Diisobutyl(*E*)-4-octenylaluminum and Diisobutylaluminum Hydride.** An equimolar mixture of the hydride (3.19 g, 0.0224 mol) and 4-octyne (2.47 g, 0.0224 mol) in 5.0 ml of hexane was allowed to react at 25° for 24 hr. A glc analysis of a hydrolyzed sample with a column of type a indicated the occurrence of 58% of hydralumination. The nmr spectrum of the remaining organoaluminum portion displayed a fairly well-resolved triplet at 7.18 ppm (*J* = 6.5 Hz) and a broad singlet at 3.74 ppm, the ratio of the two peaks being *ca.* 6:4. After 3 further days at 25°, the organoaluminum mixture showed 72% of hydralumination by glc and now displayed a quartet in its nmr spectrum, owing to the overlap of two triplets at 7.08 and 7.18 ppm, respectively, and a broad singlet at 3.74 ppm.

Finally, when 0.4 ml of the above organoaluminum sample (0.73 mM in both hydride and 4-octyne) was treated with 1.1 mmol of diisobutylaluminum hydride, the resulting nmr spectrum taken after 12 hr at 50° showed a clean triplet at 7.18 ppm and two broad singlets at 2.94 and 3.74 ppm, respectively (intensity ratio of *ca.* 4:11). The latter spectrum was also recorded at 100 MHz at various temperatures. Down to –50°, no new peaks but only broadening of the peaks was observed.

Integrations of Possible Rate Expressions for the Addition of Diisobutylaluminum Hydride to Alkynes. The derivations of the following equations can be found elsewhere.⁴⁰ In the mere tabulation given here the following abbreviations are used: *a*₀ = initial concentration of diisobutylaluminum hydride calculated as monomeric species; *b*₀ = initial concentration of the alkyne; T = *i*-Bu₂AlH as trimer; D = *i*-Bu₂AlH as dimer; M = *i*-Bu₂AlH as monomer; *x* = concentration of product.

Case I, *a*₀ = *b*₀. Ia: Three-halves order kinetics without formation of an inhibiting intermediate



When $k_1' = 2k_2'$, $D = M$

$$\begin{aligned} dx/dt &= k_I(a_0 - x)^{3/2} \\ k_I &= \frac{2}{l} \left[\frac{1}{(a_0 - x)^{1/2}} - \frac{1}{a_0^{1/2}} \right] \end{aligned}$$

Ib: Four-thirds order kinetics without an inhibiting intermediate

$$\begin{aligned} T &\rightleftharpoons 3M \\ M + RC\equiv CR &\longrightarrow P \\ dx/dt &= k_{II}(a_0 - x)^{4/3} \\ k_{II} &= \frac{3}{l} \left[\frac{1}{(a_0 - x)^{1/3}} - \frac{1}{a_0^{1/3}} \right] \end{aligned}$$

Ic: Four-thirds order kinetics with an inhibiting intermediate

$$\begin{aligned} T &\rightleftharpoons 3M \\ M + RC\equiv CR &\longrightarrow P \\ P + nM &\longrightarrow \text{inhibiting intermediate(s)}, m = n + 1 \\ dx/dt &= k_{III}(a_0 - x)(a_0 - mx)^{1/3} \\ k_{III} &= -\frac{1}{la} \left[\frac{1}{2} \log \frac{4(a^2 - ay + y^2)}{(a + y)^2} + \sqrt{3} \tan^{-1} \frac{(2y - a)}{\sqrt{3a}} - 0.9069 \right] \\ y &= (a_0 - x)^{1/3} \end{aligned}$$

Case II, *a*₀ = 2*b*₀.

$$\begin{aligned} \frac{dx}{dt} &= \frac{k_{III}}{2}(a_0 - 2x)^{2/3} \\ k_{III} &= \frac{3}{l} \left[\frac{1}{(a_0 - 2x)^{1/3}} - \frac{1}{a_0^{1/3}} \right] \end{aligned}$$

Acknowledgments. The authors express their appreciation to the Public Health Service for support of these kinetic studies through Grants GM-13421 and GM-20304. Structural studies of 13 were aided by Grant GP-28209 from the National Science Foundation.

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$$\frac{r_{\text{hexane}}}{r_{\text{THF}}} = \frac{k_{\text{hexane}} (0.138)^{1/3}}{k_{\text{THF}} (0.561)} = \frac{1.53 \times 10^{-3} (0.517)}{7.7 \times 10^{-5} (0.561)} = 2 \times 10^3$$

Likewise, for comparing the initial $v_0\%$ with $v_{50\%}$ (eq 8), one notes that

$$\frac{v_{50\%}}{v_0} = \frac{k_{0.259}}{k_{0.502}} \frac{(0.259)^{1/3}}{(0.259)^{1/2}} = \frac{3.52 \times 10^{-4} (0.637)}{3.45 \times 10^{-5} (0.502)} = 13$$

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Reaction of *N,N*-Dichlorourethane and of Diethyl Azodicarboxylate with Alkoxide¹

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Abstract: Exposure of *N,N*-dichlorourethane (**1**) to sodium methoxide gave high yields of ethyl methyl carbonate (**2**) and nitrogen gas. Several mechanistic possibilities were considered, including (A) generation of chloronitrene (**4**) via NCl_2^- , (B) attack of base on the chlorine site, and (C) formation of an *N*-chloro nitrogen radical. Diethyl azodicarboxylate (**14**), a proposed intermediate in both (B) and (C), was rapidly decomposed by ethoxide to diethyl carbonate, nitrogen, and diethyl hydrazine-1,2-dicarboxylate. Possibility B was eliminated since treatment of **1** with potassium monochlorourethane did not yield **14**. A labeling experiment involving $1-^{15}N$ and isopropyl *N,N*-difluorocarbamate yielded $^{15}N \equiv N$, in accord with (A) but not with (C).

N-Chlorocarbamates are versatile reagents which can react with a variety of substrates by either radical or polar pathways.

Good yields of adducts were obtained from *N,N*-dichlorourethane (DCU) and unsaturated substrates, such as styrene.^{4,5} A similar, facile reaction occurred with conjugated dienes.⁶ In a number of cases, a metal ion redox system was employed, as in the addition of *N*-monochlorocarbamates to cyclohexene.⁷ Uv light has also been used as the initiator.⁸ For these examples, evidence pointed to the involvement of radical intermediates. In the presence of aluminum chloride, apparently DCU, styrene, and acetonitrile participate in ionic processes leading to an imidazoline product.⁹

Various transformations entail halogenation. For example, *N*-monochlorourethane (MCU) converted benzylamine to the *N*-mono- or *N,N*-dichloro derivative.¹⁰ Exposure of ethyl ether to DCU resulted in chlorination and scission of the ether, presumably *via* a homolytic mechanism.¹¹ An intriguing result, involving formation of 3,3,5-trichlorooxindole, was observed on interaction of DCU and indole-2-carboxylic acid.^{12,13}

With triphenylphosphine, replacement of the halogen in DCU gave rise to ethyl triphenylphosphazocarboxylate.¹⁴ A similar pathway was followed with the sodium salt of

MCU.¹⁴ The amide proton of MCU is fairly acidic, giving rise to salts on exposure to strong base.^{15,16}

The principal aim of our work was to determine the response of DCU to alkoxide ion. Of interest was the nature of the reaction pathway, particularly in relation to the possible generation of dichloroamide ion and chloronitrene. In connection with this study, the behavior of diethyl azodicarboxylate toward alkoxide was also examined.

Results and Discussion

N,N-Dichlorocarbamates have been prepared by passing chlorine into a solution of the carbamate in buffered acetic acid.⁵ Our procedure for *N,N*-dichlorourethane (DCU, **1**) entailed treatment of the carbamate with calcium hypochlorite in hydrochloric acid. A reverse disproportionation reaction was employed for the synthesis of *N*-monochlorourethane (MCU) from DCU and urethane.¹⁷ The anhydrous potassium salt of MCU was obtained by exposure to 1 equiv of potassium hydroxide in methanol.¹⁶

In the presence of 1.5 equiv of sodium methoxide in methanol at 0°, DCU decomposed rapidly and cleanly to ethyl methyl carbonate (**2**), nitrogen, and sodium chloride (eq 1).

Identification of the ester was accomplished by compari-