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Preliminary communication

Organometallic compounds of Group III
XX*. Kinetics and mechanism of the hydralumination of 4-octyne

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Although various investigations have been made of the kinetic[1,2] and thermodynamic[3] factors in the hydralumination of alkenes, mechanistic studies with alkynes thus far have been confined to the stereochemistry[4,5] and regioselectivity[6,7] of hydralumination. Our recent examination of the stereochemistry[8] and kinetics[9] of the carbalumination of alkynes prompted us to undertake a complementary kinetic analysis of the hydralumination of alkynes, in order to understand the *cis*-[4,5] and *trans*-[6] stereochemistry of this reaction and to probe the electronic nature of any reaction intermediates.

We now wish to report our results on the kinetics of hydraluminating a symmetrical alkyne of convenient reactivity, 4-octyne, with diisobutylaluminum hydride in hexane and in mesitylene solutions over the temperature range of 0° to 50°. By comparing the kinetic true order[10], n_c, with respect to the 4-octyne and the diisobutylaluminum hydride, with n_t, the order with respect to time, and by following the rate of the reaction for 1/1 and 1/2 mixtures of the alkyne–hydride reagents, we were able to establish the operation of an hydralumination reaction occurring with inhibition[10]. This communication analyzes the mechanistic implications of our kinetic data for the hydralumination proper of alkynes, both in terms of reactive intermediates and in terms of suitable transition-state models. A subsequent communication will deal with the nature of the inhibition in hydralumination and the mechanistic consequences of such a process.

The interaction of 4-octyne with diisobutylaluminum hydride in hexane solution was followed of hydrolyzing aliquots and analyzing the octene–octyne content by GLPC with a n-nonane internal standard**. Results of typical 1/1 and 1/2 alkyne–hydride runs at 50° are given in Tables 1 and 2, respectively. The data points were fitted to an empirical expression relating the 4-*cis*-octene concentration with time by a least-squares, curve-fitting program[11] and this expression differentiated to give the instantaneous rate, d[4-octene]/dt. The data in Table 1 were tested with various empirical rate expressions suggested by our measurements of the kinetic true order[10], n_c. By holding one concentration of reagent constant (4-octyne or the hydride) while varying the other, the measurement of initial rates (< 7% conversion) at

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*Previous related parts, see ref. 7.

**The n-nonane was used to check on the material balance and thereby to assure ourselves that no octyne was consumed in competing reactions, such as reductive dimerization (*cf.* ref. 4,5).

TABLE 1

KINETIC DATA FOR THE DIISOBUTYLALUMINUM HYDRIDE–4-OCTYNE REACTION (1/1) [a] AT 50.0° IN HEXANE

Time (min)	4-Octene (%)	k_I ($l^{1/2} \cdot mole^{-1/2} \cdot min^{-1}$)	k_{II} ($l^{1/3} \cdot mole^{-1/2} \cdot min^{-1}$)	k_{III} ($l^{1/3} \cdot mole^{-1/3} \cdot min^{-1}$)	slope [b] ($mole \cdot l^{-1} \cdot min^{-1}$)
9.97	15.52	3.5×10^{-2}	3.1×10^{-2}	3.3×10^{-2}	7.05×10^{-3}
20.04	27.36	3.4	3.0	3.4	5.28
30.04	36.31	3.3	2.9	3.5	3.78
40.00	41.99	3.1	2.7	3.5	2.55
50.05	46.01	2.8	2.5	3.4	1.56
60.00	48.45	2.6	2.2	3.4	0.83
70.00	49.42	2.3	2.0	3.2	0.35
80.16	49.84	2.0	1.7	3.1	0.14
100.2	51.75	1.7	1.5	2.0	
120.0	52.37	1.4	1.3	1.6	
139.9	53.26	1.3	1.1	1.3	
160.8	53.75	1.2	1.0	1.1	
246.5	56.25	0.8	0.7	0.6	
411.0	59.73	0.6	0.5	0.3	

[a] [Diisobutylaluminum hydride] = [4-octyne] = 0.5179 mole · l^{-1}. [b] First ten data points were used for the curve fitting to give an empirical expression: [4-octene] = $-7.8831668 \times 10^{-5} + 9.0524271 \times 10^{-3} T + -1.0691553 \times 10^{-4} T^2 + 4.2668906 \times 10^{-7} T^3$

TABLE 2

REACTION RATE CONSTANTS CALCULATED FROM THE DIISOBUTYLALUMINUM HYDRIDE–4-OCTYNE REACTION (2/1) AT 50.0° [a] IN HEXANE

Time (min)	4-Octene (%)	k_{III} ($l^{1/3} \cdot mole^{-1/3} \cdot min^{-1}$)
9.95	15.73	3.1×10^{-2}
14.97	22.70	3.2
19.98	28.84	3.2
30.00	39.26	3.2
40.72	48.19	3.2
50.01	54.55	3.2
59.99	59.82	3.2
70.00	64.69	3.2
80.14	68.96	3.2
89.92	72.00	3.1
99.87	75.00	3.1
109.94	77.54	3.1
169.5	87.42	3.1

[a] $[(C_4H_9)_2AlH]$ = 0.5368 mole · l^{-1}; [4-Octyne] = 0.2680 mole · l^{-1}

30.0° gave n_c (diisobutylaluminum hydride) = 0.37 ± 0.01 and n_c (4-octyne) = 1.00 ± 0.01. Thus, from the four-third order dependence the initial rate can be expressed accurately by the equation★:

$$k_{\text{empirical}} = 4.5 \times 10^{10}\, e^{-20.800/RT}\, l^{1/3} \cdot \text{mole}^{-1/3} \cdot \text{sec}^{-1}$$

From initial rate studies over the temperature range of 15.0° to 45.0°, an apparent activation energy of 20.8 ± 0.1 kcal · $mole^{-1}$ and an activation entropy of −11.8 e.u. were obtained. The hydralumination of 4-octyne by diisobutylaluminum deuteride was also examined at 30° and was found to give k(Al–H)/k(Al–D) = 1.68.

Despite the four-third order of the initial kinetics, the expression★★,

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★The hydralumination was 1.2 times faster in mesitylene solution than in hexane and exhibited $\Delta E^{\dagger} = 21.0 \pm 0.5$ kcal · $mole^{-1}$;

★★Integrated forms:

$$k_I = \frac{2\sqrt{2}}{t}\left[\frac{1}{\sqrt{a_o - x}} - \frac{1}{\sqrt{a_o}}\right]$$

$$k_{II} = \frac{3\sqrt[3]{3}}{t}\left[\frac{1}{(a_o - x)^{1/3}} - \frac{1}{(a_o)^{1/3}}\right]$$

$$k_{III} = -\frac{3\sqrt{3}}{t}\left[1/2 \log \frac{4(a^2 - ay + y^2)}{(a + y)^2} + \sqrt{3}\tan^{-1}\frac{2y - a}{\sqrt{3}a} - \frac{\pi}{2\sqrt{3}}\right]$$

$$y = (a_o - 2x)^{1/3} \qquad a = a_o^{\ 1/3}$$

$\text{rate} = \dfrac{d[\text{4-octene}]}{dt} = \dfrac{1}{\sqrt[3]{3}}\; k_{II}\,(a_o - x)^{4/3}$, where a_o = initial conc. of reagents,did not fit the data well (Table 1). Nor did an expression assuming half-order dependence on the hydride, as reported for the hydralumination of 1-butene[1], give any better fit:

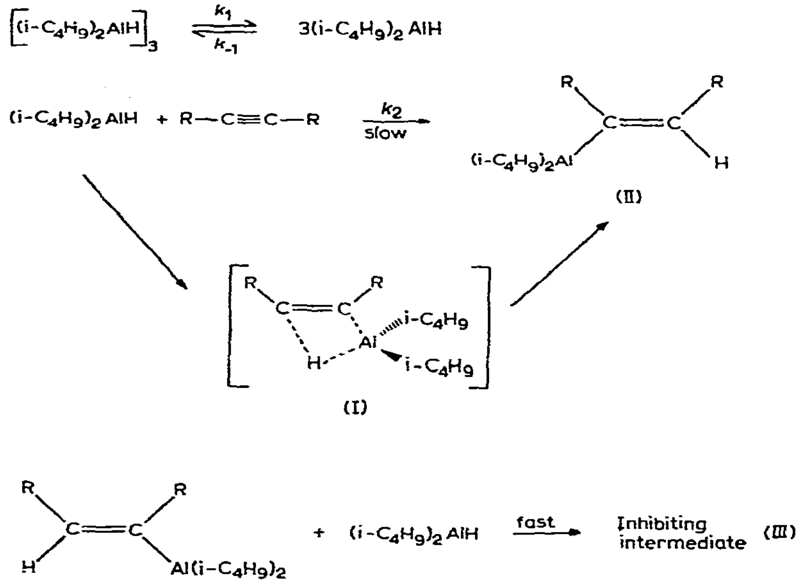
$$\text{rate} = \frac{1}{\sqrt{2}}\, k_I\, (a_o - x)^{3/2}.$$

However, the reason that neither k_I nor k_{II} could be made to fit the data was shown to be the occurrence of rate retardation (inhibition) due to the product. The order with respect to time, n_t, was determined from the slope of a plot of the logarithms of the instantaneous rates against the logarithms of the reagent concentrations. The trend in n_t values (1.9 (30 min 3.2 (60 min), 4.7 (80 min)) can only mean that the product is inhibiting the hydralumination[1] Since the data in Table 1 show the most pronounced deviation from constancy in k_I and k_{II} after 50% consumption of 4-octyne, we assume that the product is inhibiting the rate stoichiometrically. Therefore, we tested the suitability of the expression:

$$\text{rate} = \frac{d[\text{4-octene}]}{dt} = k_{III}\,(a_o - x)\,(a_o - 2x)^{1/3}, \text{ for fitting the data.}$$

As shown in Table 1, this equation gives the best fit of the first half of the reaction; as reveale in Table 2, when a 1/2 stoichiometry is chosen, the expression fits the observed rate through at least 90% of the reaction.

These kinetic data demonstrate that the initial rate of hydralumination involves the attack of monomeric diisobutylaluminum hydride, formed reversibly from the trimer[12], on the alkyne in the rate-determining step:



The kinetic isotope effect, suggestive of only a modest stretching of the aluminum–hydrogen bond in the rate-determining step (k_2), is better compatible with electrophilic attack by the aluminum center on the π-bond of the alkyne (I), than with hydridic nucleophilic attack. Our next report will deal with the nature of the "inhibiting intermediate", III, formed from product II and diisobutylaluminum hydride. Although a recent interesting NMR study has led to the suggestion that alkenylalanes and dialkylaluminum hydrides form complexes via mixed alkenyl–hydride bridges[13], other structural models for III merit consideration.

EXPERIMENTAL

Materials

The diisobutylaluminum hydride, as received from Texas Alkyls, was 94 ± 1% pure. The major impurity, triisobutylaluminum, and any oxidized contaminants were removed by distillation under reduced pressure. The distilled hydride (b.p. 114° at 0.3 mm) was assayed as 100 ± 1% pure by the isoquinoline titration procedure[14]. Diisobutylaluminum deuteride was prepared from diisobutylaluminum chloride (Texas Alkyls) and lithium deuteride (> 97%) in diethyl ether solution. Repeated fractional distillation of the product was necessary to remove all traces of ether. Mass spectrometric analysis of the gas from a hydrolyzed sample showed the diisobutylaluminum deuteride to be 96.4% pure and the balance to be diisobutylaluminum hydride. The 4-octyne (Farchan) contained < 1% of impurities as received; careful fractional distillation gave a pure sample.

Kinetic analysis

Experimental details for the proper handling and sampling of air- and moisture-sensitive organometallic solutions have been published[7-9]. After hydrolyzing 0.5 ml aliquots with calculated amounts of cooled hydrochloric acid, the 4-octyne and *cis*-4-octene were analyzed against a n-nonane standard by means of either a Varian Aerograph model 1200 gas chromatograph equipped with a coupled column of 8% Silicone DC-703 and 8% Silicone SE-30 on Chromosorb P, or a F & M model 720 unit equipped with columns of 10% Silicone gum rubber on Chromosorb W. The response factors of 4-octyne, *cis*-4-octene and n-nonane to the thermal conductivity (F & M) and to flame ionization (Varian) detectors were obtained and the reproducibility of the GC analyses was generally within ± 1%.

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