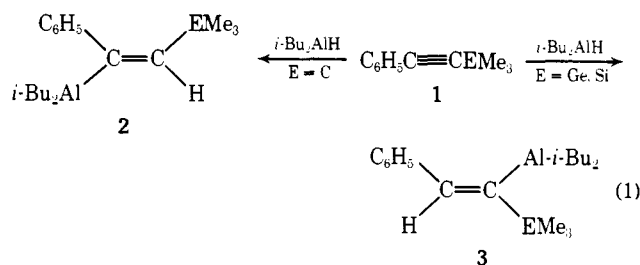# Kinetic, Stereochemical, and Molecular Association Factors in the Hydralumination of Group IV Substituted Alkynes. The Role of p_π–d_π Conjugation in the Addition of Diisobutylaluminum Hydride to Trimethyl(phenylethynyl)silane[1]

John J. Eisch* and Sue-Goo Rhee

*Contribution from the Department of Chemistry.
State University of New York at Binghamton. Binghamton. New York 13901.
Received October 23, 1974*

Abstract: The kinetic, stereochemistry, and molecular association factors for the addition of diisobutylaluminum hydride to trimethyl(phenylethynyl)silane were studied in the temperature range of −10 to 38°. By means of the differential method applied to initial rates, the hydralumination was found to have a kinetic true order of essentially one in the alkyne and one-third in the hydride. Although the trans adduct is the predominating product (~99%) after completion of the hydralumination, the variation of the proportion of cis adduct and the initial rate law are consistent with a kinetically controlled cis hydralumination by monomeric R'_2AlH, followed by a rapid isomerization to the trans adduct. The Arrhenius relationship, $k = (1.1 \pm 0.4) \times 10^{10} e^{-17,330 \pm 220/RT} l^{1/3}$ $mol^{-1/3}$ sec^{-1}, and the apparent activation entropy, -13.4 ± 0.1 eu at $-5.2°$, were determined; the kinetic deuterium isotope effect is $k_H/k_D = 1.71$ ($-5.2°$); and the equilibrium constant for the trans:cis adducts is 120 at $-5.2°$ and has an enthalpy of isomerization of -2.1 ± 0.3 kcal/mol. Bishydralumination was a minor side reaction under these conditions and was shown not to be responsible for the facile cis,trans isomerization. The trans adduct formed a complex with 1 equiv of the hydride, but only to an extent of ca. 30% at $-10°$. However, this complexation had to be taken into account, in order to explain the observed rate retardation and to obtain satisfactory integrated rate expressions for hydraluminations monitored to high conversion. Since in hydralumination this silylacetylene shows a stereospecificity and regiospecificity exactly opposite that of *tert*-butyl(phenyl)acetylene, as well as a heightened reactivity, a critical consideration of possible p_π–d_π electronic effects was undertaken. Although such an effect can be invoked in explaining these differences, this conclusion is not compelling. The unusually facile isomerization of the resulting silyl-substituted vinylalanes, however, does seem more persuasive evidence for a p_π–d_π effect, which promotes isomerization by electrophilic attack of R'_2AlH on the carbon α to the Me_3Si group.

The cis hydralumination of alkyl- and aryl-substituted acetylenes, leading to vinylalanes, constitutes a versatile method for the stereospecific synthesis of *cis*-alkenes,[2] acrylic acids,[3] vinylic halides,[4] or vinylic carbinols.[3a,4a] Although the mechanism and stereochemistry of such cis Al–H bond additions are now reasonably well understood,[5,6] the behavior of germyl- and silylacetylenes upon hydralumination is not. The contrasting results with *tert*-butyl(phenyl)acetylene,[7] on the one hand, and the analogous germanium or silicon derivative,[8] on the other, are shown in eq 1. Thus, both hydraluminations are regiospeci-

fic, but with opposite orientations. In addition, the reaction of *tert*-butyl(phenyl)acetylene is stereospecifically cis, while that of the silyl- or germylacetylene (**1**, E = Ge, Si) occurs in a highly stereoselective (>99%) trans fashion. When, however, the hydraluminations of these silyl- or germylacetylenes are conducted with an amine complex, *i*-Bu₂AlH·NR₃, essentially only cis hydralumination is observed (>98%)[8] (eq 2). Abstraction of the amine from **4** with a stronger Lewis acid leads to rapid isomerization to the trans hydralumination adduct **3**. The similar orientation and stereochemistry observed for the hydralumination of
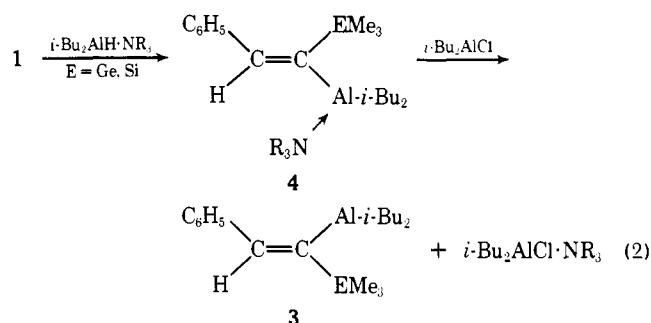
other 1-alkynylsilanes[8] show that this behavior is not restricted to phenylethynylsilanes.

Therefore, a detailed kinetic and thermodynamic investigation of the hydralumination of trimethyl(phenylethynyl)silane (**5**) was undertaken, in order to understand: (a) this unusual trans addition (**1 → 3**, eq 1); (b) the unexpected regiospecificity (cf. **2** and **3**); and (c) the extraordinarily ready cis,trans isomerization of the vinylic aluminum adducts (**4 → 3**, eq 2). In addition to determining the rate laws, it was considered equally important to learn about the role of molecular complexes[6] in the rate of formation and the equilibration of such vinylic aluminum compounds. Furthermore, since the presence of a silyl (or germyl) substituent seemed responsible for the unusual behavior of these alkynes (**1**, E = Si, Ge) and the derived alkenes (**3** and **4**), these studies looked promising in learning more about the importance of p_π–d_π conjugation in chemical reactivity.[9] The relative weights of canonical structures (e.g., **6**), based on a p_π–d_π effect, should be different for the ground state and the transition state of a reaction:
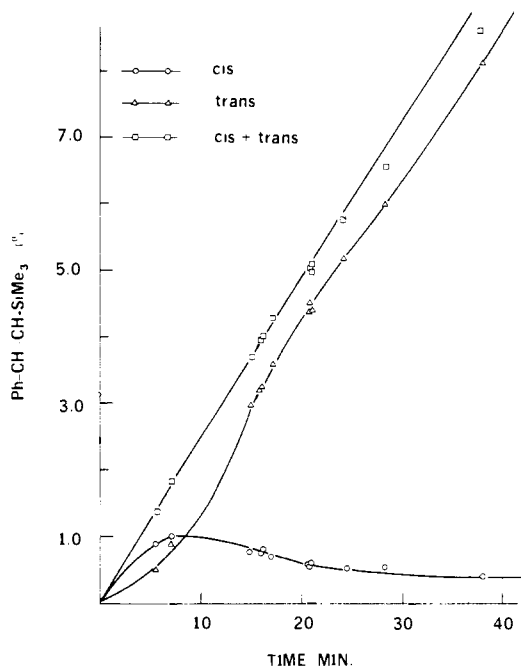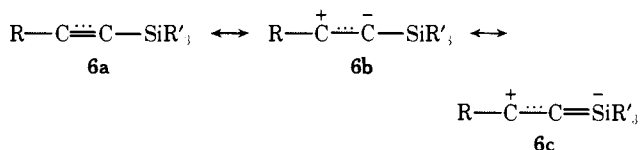
Figure 1. Percentage of conversion of trimethyl(phenylethynyl)silane into the respective trimethyl(β-styryl)silanes by hydralumination vs. reaction time at $-5.2°$.

$$R—C\equiv\!\!\equiv C—SiR'_3 \quad \longleftrightarrow \quad R—\overset{+}{C}\!=\!\!=\!\overset{-}{C}—SiR'_3 \quad \longleftrightarrow$$
$$\underset{\textbf{6a}}{} \qquad\qquad \underset{\textbf{6b}}{}$$

$$R—\overset{+}{C}\!=\!\!=\!C\!=\!\!=\overset{-}{SiR'_3}$$
$$\underset{\textbf{6c}}{}$$

Hence, the relative reactivity, stereochemistry, and isomerizability of α,β-unsaturated silanes were expected to reflect such electronic effects.

Results

Stoichiometry and Stereochemistry of Hydralumination. The complete conversion of trimethyl(phenylethynyl)silane (**5**) into exclusively the regioisomer **7** by 1.4 equiv of diisobutylaluminum hydride at 15° was accompanied by only 1.4% of the bisalumino adduct **8** (eq 3). There was no trace of any bimolecular reduction involving 2 equiv of the alkyne with 1 equiv of the hydride **9**.[2c,6-8] Hence, by studying the kinetics with a 1:1 ratio of silylacetylene:hydride at temperatures below 15°, a clean formation of **7** was obtained, with negligible interference from the diadduct **8**.

Under these conditions, the resultant ratio of *cis*-**7a** and *trans*-**7b** adducts was 1.0:98.6. But this cis:trans ratio was found to be subject to both kinetic and thermodynamic control. Thus, a study of this ratio vs. time for the first 10% of conversion at $-5.2°$ showed that the cis isomer is the major product (maximum of 1.0%) during the first 8 min of reaction (Figure 1); this then dropped rapidly to ca. 0.4% and thereafter slowly increased to a final value of ca. 0.8% (Figure 2). On the other hand, the final composition of **7a** and **7b** was temperature dependent (Table V); over the temperature range of -5.0 to $+15.0°$, equilibration of the isomers **7a** and **7b** could be achieved and the equilibrium constant, $K_3 = [\text{7b}]/[\text{7a}]$, measured. From a plot of K_3 vs. $1/T$ (Figure 3, slope $= 0.45 \pm 0.06$), the enthalpy change for the isomerization was calculated to be -2.1 ± 0.3 kcal/mol.

The small amounts of the bisalumino adduct **8** formed during the trans monohydralumination (eq 3) raised the possibility that the equilibration of **7a** and **7b** took place via the bisalumino adduct **8**. Accordingly, a mixture of **7a** and
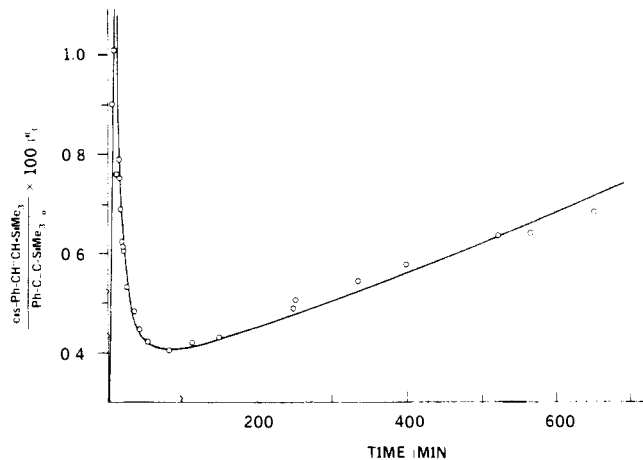

Figure 2. Percentage of conversion of trimethyl(phenylethynyl)silane into trimethyl(*cis*-β-styryl)silane by hydralumination vs. reaction time at $-5.2°$.
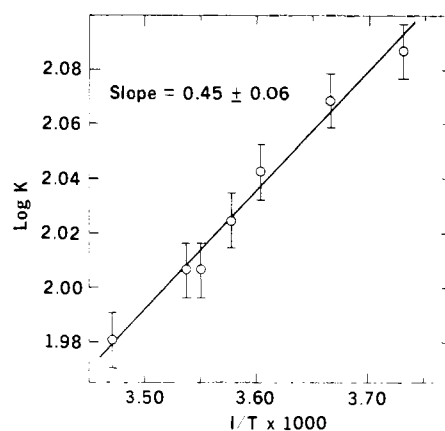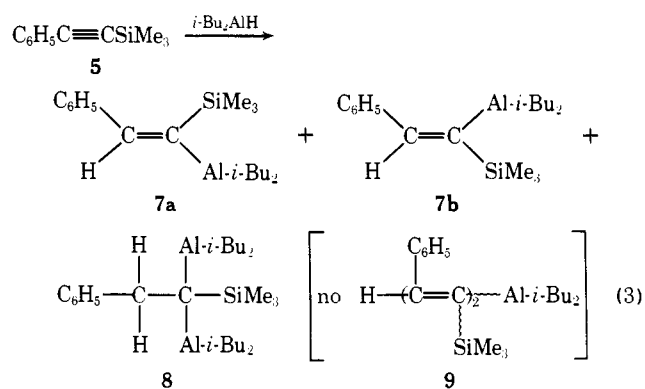

Figure 3. Plot of the equilibrium constant, $K_3 = [\text{7b}]/[\text{7a}]$, vs. the reciprocal of the absolute temperature.

$$C_6H_5C\equiv\!\!\equiv CSiMe_3 \xrightarrow{i\text{-Bu}_2\text{AlH}}$$
$$\underset{\textbf{5}}{}$$

$$\begin{matrix} C_6H_5 \\ \diagdown \\ H \end{matrix} C\!=\!C \begin{matrix} SiMe_3 \\ \diagup \\ Al\text{-}i\text{-}Bu_2 \end{matrix} \quad + \quad \begin{matrix} C_6H_5 \\ \diagdown \\ H \end{matrix} C\!=\!C \begin{matrix} Al\text{-}i\text{-}Bu_2 \\ \diagup \\ SiMe_3 \end{matrix} \quad +$$
$$\underset{\textbf{7a}}{} \qquad\qquad\qquad \underset{\textbf{7b}}{}$$

$$C_6H_5—\overset{\overset{\displaystyle H}{|}}{C}—\overset{\overset{\displaystyle Al\text{-}i\text{-}Bu_2}{|}}{\underset{\underset{\displaystyle Al\text{-}i\text{-}Bu_2}{|}}{C}}—SiMe_3 \qquad \left[no \quad H\!-\!(C\!=\!C)_2\!-\!Al\text{-}i\text{-}Bu_2 \right] \quad (3)$$
$$\underset{\textbf{8}}{} \qquad\qquad\qquad\qquad\qquad \underset{\textbf{9}}{}$$

7b was allowed to be in contact with an excess of diisobutylaluminum deuteride for 25 hr at 8°. If eq 4 were the

$$\begin{matrix} C_6H_5 \\ \diagdown \\ H \end{matrix} C\!=\!C \begin{matrix} Al\text{-}i\text{-}Bu_2 \\ \diagup \\ SiMe_3 \end{matrix} \overset{?}{\rightleftharpoons} C_6H_5—\overset{\overset{\displaystyle D}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}—\overset{\overset{\displaystyle Al\text{-}i\text{-}Bu_2}{|}}{\underset{\underset{\displaystyle Al\text{-}i\text{-}Bu_2}{|}}{C}}—SiMe_3 \overset{?}{\rightleftharpoons}$$
$$\underset{\textbf{7a} \ + \ \textbf{7b}}{} \qquad\qquad\qquad\qquad \underset{\textbf{10}}{}$$

$$\begin{matrix} C_6H_5 \\ \diagdown \\ D \end{matrix} C\!=\!C \begin{matrix} Al\text{-}i\text{-}Bu_2 \\ \diagup \\ SiMe_3 \end{matrix} \qquad (4)$$
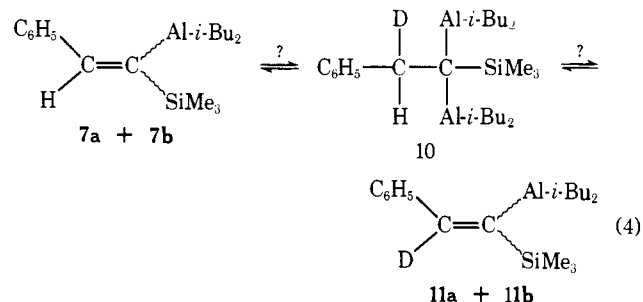$$\underset{\textbf{11a} \ + \ \textbf{11b}}{}$$

Table I. Initial Rates for the Hydralumination of Trimethyl(phenylethynyl)silane at Various Temperatures

Run no.	T, °C	$(1/T) \times 10^3$	$\left(\dfrac{[cis] + [trans]}{[PhC\equiv CSiMe_3]_0}\Big/t\right)_{av}$	Rate (v), mol/l. sec[a]	Log v + 6
1	−10.30	3.8036	1.41×10^{-3}	3.19×10^{-6}	0.5038
3, 4, 5	−5.20	3.7319	2.44	5.54	0.7435
6	−1.00	3.6743	4.03	9.13	0.9605
7	2.10	3.6329	5.73	1.30×10^{-5}	1.1139
8	8.00	3.5567	1.14×10^{-2}	2.58	1.4116
9	15.00	3.4703	2.55	5.78	1.7619

[a] Rate (v), mol/l. = $[\{([cis] + [trans])/[PhC\equiv CSiMe_3]_0\}/t]_{av} \times (0.136 \text{ mol/l.})/60$.

route of isomerization, then the vinyl adducts should incorporate deuterium during this treatment (eq 4). However, subsequent treatment of the vinylic aluminum compounds with H_2O showed that no deuterium was present in the resulting trimethyl(β-styryl)silanes. Conversely, when the adducts **11a** and **11b** formed from **5** and diisobutylaluminum deuteride were equilibrated in the presence of diisobutylaluminum hydride, subsequent hydrolysis with H_2O yielded only the trimethyl(α-deuterio-β-styryl)silanes.

Therefore, intermediates **8** and **10** play no role in the equilibration of either **7a** and **7b** or **11a** and **11b**.

Initial Rates of Reaction in Hexane. As in the previous study,[6] the method of initial rates could be used to avoid the complexities of mixed hydride association equilibria, which became prominent as the hydralumination went to completion. Although plots of concentration vs. time for the cis or trans adduct did not give straight lines, a plot of the sum of their concentrations was linear during the early stages of the reaction (Figure 1).

In Table I, the effect of temperatures between −10.2 and +15.2° upon the initial rate (v) is tabulated for runs where initial concentrations of **5** and hydride were 0.136 ml/l. A plot of log v vs. $1/T$ and a computed least-squares analysis of the slope yielded: slope = $-(3.788 \pm 0.047) \times 10^3 = \Delta E^*_{app}/(2.303)(1.987)$; and $\Delta E^*_{app} = 17.33 \pm 0.22$ kcal/mol.

The kinetic true order dependences of the silylacetylene **5** and the hydride were obtained from double-logarithmic plots of the initial rates (Tables II and III) against the initial concentrations of the varying reagents; the intercepts and the kinetic true orders were given as the slopes m and n (eq 5). The kinetic true orders (m and n) and the empirical

$$\log v = m \log [5]_0 + C_I$$

$$\log v = n \log [\text{hydride}]_0 + C_{II}$$

$$C_I = \log k + n \log [\text{hydride}]$$

$$C_{II} = \log k + m \log [5] \quad (5)$$

reaction rate constants, (k_{emp}) for this hydralumination at −5.2° are given in eq 6. From the Arrhenius equation, k_{emp}

$$m \text{ for } C_6H_5C\equiv CSiMe_3 = 0.991 \pm 0.011$$

$$n \text{ for diisobutylaluminum hydride} = 0.380 \pm 0.007$$

$$k_{emp} \text{ (average from } C_I \text{ and } C_{II}) = (8.12 \pm 0.74) \times$$

$$10^{-5} \text{ l.}^{1/3} \text{ mol}^{-1/3} \text{ sec}^{-1} \quad (6)$$

$= A \exp[-\Delta E^*_{app}/RT]$, the frequency factor A was calculated as $(1.1 \pm 0.4) \times 10^{10}$ l.$^{1/3}$ mol$^{-1/3}$ sec^{-1} and, from the relationship $\Delta S^*_{app}/4.576 = \log A - 10.573 - \log T$. $\Delta S^*_{app} = -13.4 \pm 1.0$ eu. Thus:

$$k_{emp} = (1.1 \pm 0.4) \times$$

$$10^{10} \exp[-17,330 \pm 220/RT]\text{l.}^{1/3} \text{ mol}^{-1/3} \text{ sec}^{-1} \quad (7)$$

Table II. Kinetic Order Dependence on Trimethyl(phenylethynyl)silane Based upon Initial Hydralumination Rates at −5.2°

Run no.	$[PETS]_0$, mol/l.	Log $[PETS]_0$, + 2	$\{([STS]/[PETS]_0)/t\}_{av}$	Rate (v), mol/l. sec[a]	Log v + 6
10	0.0468	0.6702	2.50×10^{-3}	1.95×10^{-6}	0.2900
11	0.0675	0.8293	2.45	2.76	0.4409
12	0.0989	0.9952	2.48	4.09	0.6117
3, 4, 5	0.1360	1.1335	2.44	5.53	0.7427

[a] Rate (v) (mol/l. sec) = $\{([STS]/[PETS]_0) \div t\}_{av} \times [PETS]_0/60$. Slope ($m$) = 0.99 ± 0.01. Intercept (C_I) = -4.395 ± 0.031.

Table III. Kinetic Order Dependence on Diisobutylaluminum Hydride Based upon Initial Rates of Addition to Trimethyl(phenylethynyl)silane at −5.2°

Run no.	$[i\text{-}Bu_2AlH]_0$, mol/l.	Log $[i\text{-}Bu_2AlH]_0$ + 2	$\{([STS]/[PETS]_0)/t\}_{av}$	Rate (v), mol/l. sec[a]	Log v + 6
13	0.0345	0.5378	1.42×10^{-3}	3.22×10^{-6}	0.5079
14	0.0345	0.5378	1.44	3.27	0.5145
15	0.0690	0.8388	1.87	4.24	0.6274
16	0.0690	0.8388	1.83	4.15	0.6180
17	0.0690	0.8388	1.89	4.29	0.6325
18	0.1035	1.0149	2.13	4.83	0.6839
19	0.1035	1.0149	2.15	4.94	0.6937
20	0.1035	1.0149	2.15	4.87	0.6875
3	0.1380	1.1399	2.43	5.50	0.7404
4	0.1380	1.1399	2.44	5.53	0.7427
5	0.1380	1.1399	2.44	5.53	0.7427

[a] Rate (v) (mol/l. sec) = $\{([STS]/[PETS]_0)/t\}_{av} \times [PETS]_0/60$. Slope ($n$) = 0.380 ± 0.007. Intercept (C_{II}) = -4.394 ± 0.021.

In an analogous manner to the foregoing, the initial rates for the interaction of equimolar concentrations of the silylacetylene **5** and diisobutylaluminum hydride or deuteride were determined at −5.2° (Table IV). The average values of v_{Al-H} and v_{Al-D} yielded a kinetic isotope effect of $k_H/k_D = 1.71$.

Complexation between Diisobutylaluminum Hydride and Diisobutyl((Z)-β-trimethylsilyl-β-styryl)aluminum (7b). Complexation of unreacted hydride with the vinylic aluminum product has been shown to be the cause of the pronounced rate retardation encountered as the hydralumination of ordinary alkynes proceeds to completion.[6,10-12] At room temperature, such complexation occurs with a 1:1 stoichiometry and, in the case of adducts from disubstituted acetylenes, the equilibrium strongly favors the complexed hydride **12**, $RCH=CHAlR'_2 \cdot R'_2AlH$.[10,11] The formulation of this 1:1 complexation as **12** intentionally leaves its exact structure unspecified since recent NMR and chemical studies[12,13] have shown such complexes to possess more structural variety than had been initially supposed.[10]

In the case of the trans adduct of **5**, namely diisobutyl((Z)-β-trimethylsilyl-β-styryl)aluminum (**7b**), (Figure 4) complexation with diisobutylaluminum hydride in a 1:1 ratio did occur, but the reaction went to an extent of ca. 30% at −10° and ca. 20% at 38°. The hydride-alkenylalu-

Table IV.[a] Hydrogen–Deuterium Kinetic Isotope Effect for the Hydralumination of Trimethyl(phenylethynyl)silane at $-5.2°$

Run no.	$[PETS]_0$, mol/l.	$[i\text{-}Bu_2AlH]_0$ or $[i\text{-}Bu_2AlD]_0$	$\{([STS]/[PETS]_0)/t\}_{av}$	Rate (v), mol/l. sec	Rate$_{av}$, mol/l. sec
21 (D)	0.135	0.137	1.44×10^{-3}	3.26×10^{-6}	3.22×10^{-6}
22 (D)	0.136	0.137	1.40	3.17	
3 (H)	0.136	0.138	2.43×10^{-3}	5.50×10^{-6}	5.52×10^{-6}
4 (H)	0.136	0.138	2.44	5.53	
5 (H)	0.136	0.138	2.44	5.53	

^{a} $d[PhCH{=}CHSiMe_3]/dt = v = k[i\text{-}Bu_2AlH(D)]^{1/3}[PhC{\equiv}CSiMe_3]^{1.0}$; $v_{Al-H}/v_{Al-D} = k_{Al-H}[0.138]^{1/3}[0.136]^{1.0}/k_{Al-D}[0.137]^{1/3}[0.136]$ $[0.136]^{1.0} = (5.52 \times 10^{-6})/(3.22 \times 10^{-6})$; $k_{Al-H}/k_{Al-D} = 1.71$.

minum complex 13 displayed its hydride signal at δ 3.90 ppm and the methyl protons of its isobutyl groups at 0.98 ppm (eq 8; Figure 5).

$$7b$$

$$13$$
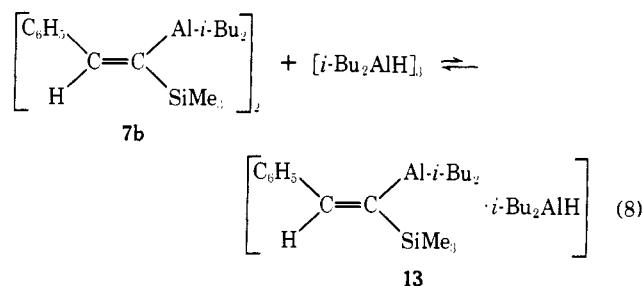
Kinetics of Hydralumination Reactions Monitored to High Conversion.

As with the hydralumination of 4-octyne, this reaction also showed rate retardation, but to a lesser extent. The aforementioned NMR study revealed that 7b does not complex with the hydride quantitatively in a 1:1 manner, as do other vinylaluminum systems (eq 8).

Thus, in applying the method of integration to such reactions displaying rate inhibition, it was assumed that m would have fractional values in eq 9, where dx/dt is the

$$\frac{dx}{dt} = k_{III}(a_0 - x)(a_0 - mx)^{1/3} \qquad (9)$$

rate of forming 7b, a_0 are the initial, equal concentrations of 5 and hydride, and m is >1.0 but <2.0. Where $m = 1.0$, no inhibition of rate would be found and, where $m = 2.0$, the equilibrium shown in eq 8 would have to lie far to the right.

The integrated forms of eq 9,[6] where $m = 1.0$–2.0, were used to test for the constancy of k_{III} for runs followed to high conversion (Tables VI–VIII). For all three temperatures, -5.2, 8.0, and $15.0°$, the value of k_{III}, where $m = 1.0$, decreased with time. On the other hand, the values of k_{III}, where $m = 1.4$, 1.6, or 2.0, increased with time. It is difficult to choose between k_{III} ($m = 1.2$) and k_{III} ($m = 1.3$), for both were essentially constant. At $-5.2°$, k_{III} ($m = 1.2$) showed a slight decrease in value with time, compared with k_{III} ($m = 1.3$). Thus, at this temperature, k_{III} ($m = 1.3$) seems to be the best choice. This value of m also agrees well with the NMR analysis of equilibrated 13 at $-5.2°$, which shows that ca. 30% of the hydride reactant was consumed by complexation with 7b.

Discussion

Mechanism for the Hydralumination of Trimethyl(phenylethynyl)silane (5).

Because of the preponderantly trans stereochemistry of this reaction, the most immediate question is whether the rate law is the same as that observed for the cis hydralumination of ordinary alkynes.[6] Now, although the trans adduct is present to the extent of $\geq 99\%$ after complete consumption of the silylacetylene, the relative amount of the cis adduct predominates early in the reaction (Figure 1). Furthermore, only a plot of the sum of

the cis and trans adduct concentrations against time gives a straight line for this early stage of reaction; the concentration of either adduct alone against time yields a curved plot (Figure 1). Such a finding is consistent with a kinetically controlled cis hydralumination, whose product (7a) then isomerizes to the more stable trans adduct 7b (Table V; Figure 2).

By the method of initial rates, then, the observed rate law at $-5.2°$ has essentially a first-order dependence on the silylacetylene 5 and a 0.38-order dependence on diisobutylaluminum hydride. These values are comparable to the first-order dependence on alkyne and a 0.37-order dependence on the hydride observed for the cis hydralumination of 4-octyne at $30.0°$.[6] The ΔE^*_{app} for the silylacetylene 5, namely 17.33 kcal/mol, is considerably lower than the 20.84 kcal/mol measured for 4-octyne. It follows that the reaction scheme most consistent with the initial fluctuation in the cis:trans adduct ratio (Figures 1–3) and the kinetic true order dependences would be:

$$[R'_2AlH]_3 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 3R'_2AlH \quad K_1 = k_1/k_{-1} \qquad (10)$$
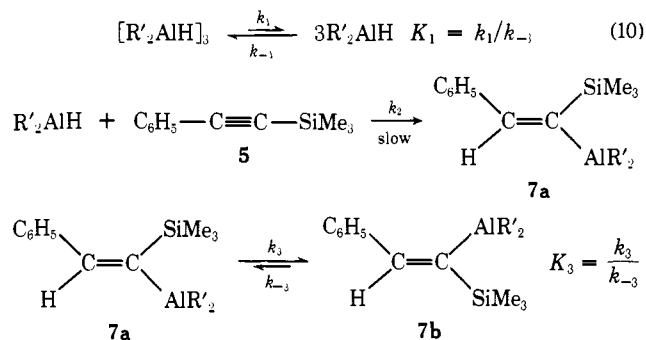
With the assumption of a relatively rapid trimer–monomer hydride equilibrium and a cis,trans equilibration of 7a and 7b, the steady-state approximation, applied to the monomer as the reactive intermediate, gives eq 11. Although K_3 was

$$v = d[7b]/dt =$$
$$k_2(K_1)^{1/3}(K_3)[(R'_2AlH)_3]^{1/3}[R{-}C{\equiv}C{-}R] \qquad (11)$$

found to be 120 at $-5.0°$ (Table V), no direct measure of K_1 has been possible. Since the monomeric, unsolvated hydride has never been detected by various spectral measurements, it is reasonable to assume that K_1 is very small (e.g., 0.33% dissociation would correspond to $K_1 = 10^{-6}$).

As a competing or alternative pathway from 5 to 7b, the direct trans hydralumination of 5 should be considered. First of all, the observed rate law argues against more than one R'_2AlH unit being involved in the rate-determining step. If then direct trans hydralumination is to be significant, a maximum of one R'_2AlH must be active in the slow step. With this restriction, such addition could result only via a rectangular approach of 5 and monomeric hydride (eq 12). Such a perpendicular approach, as in 14a and 14b, has
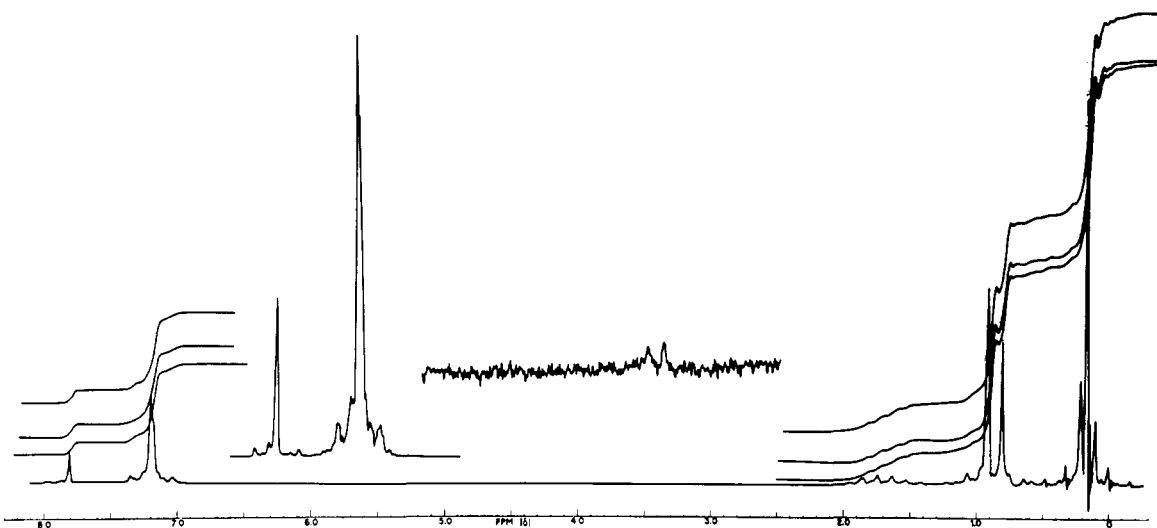
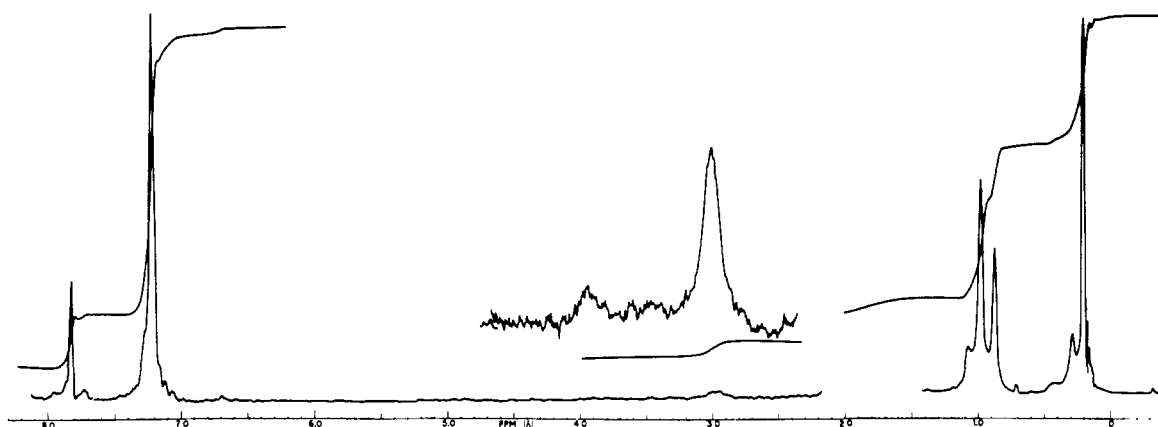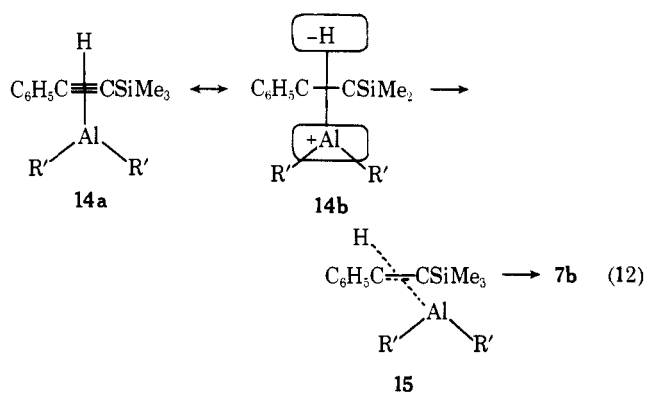Figure 4. The NMR spectrum of a neat sample of diisobutyl((Z)-β-trimethylsilyl-β-styryl)aluminum (7b).

Figure 5. The NMR spectrum of a neat, 1:1 mixture of diisobutyl((Z)-β-trimethylsilyl-β-styryl)aluminum and diisobutylaluminum hydride at $-10°$.

$$C_6H_5C\!\equiv\!CSiMe_3 \longleftrightarrow \underset{\underset{R'}{\overset{|}{\overset{}{Al}}}{\scriptstyle R'}}{C_6H_5C\!-\!CSiMe_2} \longrightarrow$$

14a $\qquad$ 14b

$$C_6H_5C\!\cdots\!CSiMe_3 \longrightarrow 7b \quad (12)$$

15

a certain appeal in rationalizing, by means of orbital symmetry rules, how a π complex can collapse smoothly to the cis adduct.[6] However, in attaining the trans adduct via 14, the aluminum–hydrogen bond must eventually undergo much stretching (15). Accordingly, a pronounced kinetic isotope effect would be expected if diisobutylaluminum deuteride were used. Actually, however, the k_H/k_D ratio at $-5.2°$ was found to be 1.71. As previously argued,[6] this isotope effect should be considered as modest since the overall rate embraces a preequilibrium of trimeric and monomeric hydrides (eq 10), whose $\Delta H = 45$ kcal/trimer. Hence, it is probable that the actual $k_{2(H)}/k_{2(D)}$ in eq 10 is even smaller. All these considerations lead to the conclusion that the

Table V. Equilibrium between Diisobutyl((Z)-β-trimethylsilyl-β-styryl)aluminum (7a) and Diisobutyl((E)-β-trimethylsilyl-β-styryl)aluminum (7b) at Various Temperatures

Run no.	Temp, °C	$(1/T) \times 10^3$	$[7b]/[7a]$, K	K_{av}	Log K_{av}
23	-5.0	3.731	118	120	2.0792
23			119		
23			121		
23			122		
23	0.0	3.663	110	113	2.0531
23			113		
23			115		
24	1.0	3.650	109	113	2.0531
25			112		
24			114		
24			115		
25			116		
25			117		
25	3.0	3.623	108	109	2.0374
25			109		
24	5.0	3.597	100	104	2.0170
24			101		
23			106		
23			107		
25	10.0	3.534	94	98	1.9912
25			98		
24			102		
25	15.0	3.472	86	94	1.9731
25			92		
23			92		
23			97		
25			101		

Table VI. Kinetic Data for Hydraluminations of Trimethyl(phenylethynyl)silane at $-5.2°$ Monitored to High Conversions and Rate Constants Calculated from Integrated Forms of Equation 11 (Runs 3, 4, and 5)

Time, min	X, mol/l.	k_{III} ($m = 1.2$)	k_{III} ($m = 1.3$)	k_{III} ($m = 1.4$)	k_{III} ($m = 1.6$)	k_{III} ($m = 2.0$)
5.66	0.0019	4.3×10^{-3}	4.4×10^{-3}	4.5×10^{-3}	4.6×10^{-3}	4.9×10^{-3}
7.20	0.0025	4.4	4.6	4.7	4.8	5.1
16.33	0.0054	4.3	4.4	4.5	4.7	4.9
16.45	0.0055	4.3	4.5	4.6	4.7	5.0
21.22	0.0068	4.2	4.3	4.4	4.6	4.8
21.37	0.0069	4.2	4.4	4.5	4.6	4.8
37.97	0.0117	4.2	4.3	4.4	4.6	4.8
42.14	0.0127	4.1	4.2	4.3	4.5	4.7
53.52	0.0158	4.1	4.2	4.3	4.5	4.7
83.37	0.0231	4.0	4.1	4.2	4.4	4.7
113.96	0.0303	4.0	4.2	4.3	4.5	4.9
149.14	0.0374	4.0	4.2	4.3	4.5	4.9
248.68	0.0540	4.0	4.2	4.3	4.6	5.4
249.70	0.0540	4.0	4.1	4.3	4.6	5.4
337.40	0.0653	4.0	4.2	4.4	4.8	6.4
401.57	0.0722	4.0	4.2	4.4	5.0	a
523.85	0.0817	3.9	4.2	4.5	5.6	a
585.32	0.0873	4.0	4.4	4.8	5.3	a
654.20	0.0910	4.0	4.4	4.9	a	a
Average with standard deviation:		4.1 ± 0.12	4.3 ± 0.11	4.5 ± 0.15	4.7 ± 0.20	5.0 ± 0.28

$^a dx/dt = k_{III}(a_0 - X)(a_0 - mX)$ has no meaning when $mX > a_0$. k_{III}, $1.^{1/3}$ $mol^{-1/3}$ min^{-1}.

Table VII. Kinetic Data for Hydraluminations of Trimethyl(phenylethynyl)silane at $8°$ Monitored to High Conversions and Rate Constants Calculated from Integrated Forms of Equation 11 (Run 8)

Time, min	X, mol/l.	k_{III} ($m = 1.2$)	k_{III} ($m = 1.3$)	k_{III} ($m = 1.4$)	k_{III} ($m = 1.6$)	k_{III} ($m = 2.0$)
4.34	0.0066	2.0×10^{-2}	2.1×10^{-2}	2.1×10^{-2}	2.2×10^{-2}	2.3×10^{-2}
10.23	0.0144	1.9	2.0	2.0	2.1	2.2
17.82	0.0235	1.9	2.0	2.0	2.1	2.3
31.60	0.0373	1.9	2.0	2.0	2.1	2.3
52.83	0.0539	1.9	1.9	2.0	2.2	2.5
104.00	0.0804	1.9	2.0	2.2	2.6	a
184.55	0.101	1.9	2.0	2.3	a	a
Average with standard deviation:		1.9 ± 0.01	2.0 ± 0.03	2.1 ± 0.1	2.2 ± 0.12	2.3 ± 0.06

$^a dX/dt = k_{III}(a_0 - X)(a_0 - mX)$ has no meaning when $mX > a_0$. k_{III}, $1.^{1/3} mol^{-1/3} min^{-1}$.

Table VIII. Kinetic Data for Hydraluminations of Trimethyl (phenylethynyl)silane at $15°$ Monitored to High Conversions and Rate Constants Calculated from Integrated Forms of Equation 11 (Run 9)

Time, min	X, mol/l.	k_{III} ($m = 1.2$)	k_{III} ($m = 1.3$)	k_{III} ($m = 1.4$)	k_{III} ($m = 1.6$)	k_{III} ($m = 2.0$)
1.96	0.0067	4.5×10^{-2}	4.6×10^{-2}	4.7×10^{-2}	4.9×10^{-2}	5.1×10^{-2}
6.07	0.0186	4.3	4.4	4.6	4.7	5.0
10.91	0.0303	4.2	4.4	4.5	4.7	5.1
18.44	0.0453	4.2	4.3	4.5	4.8	5.3
33.88	0.0675	4.2	4.4	4.6	5.1	7.5
61.26	0.0906	4.2	4.6	5.3	a	a
Average with standard deviation:		4.3 ± 0.28	4.5 ± 0.14	4.7 ± 0.24	4.8 ± 0.12	5.6 ± 0.76

$^a dx/dt = k_{III}(a_0 - X)(a_0 - mX)$ has no meaning when $mX > a_0$. k_{III}, $1.^{1/3} mol^{-1/3} min^{-1}$.

observed isotope effect is too small to be in accord with the pathway illustrated in eq 12. On the other hand, this isotope effect is essentially the same as that of the cis hydralumination of 4-octyne, namely 1.68.

Therefore, there is no reasonable doubt that the hydralumination of trimethyl(phenylethynyl)silane occurs predominantly in a kinetically controlled cis manner, and that the trans adduct results from a subsequent isomerization of the cis adduct.

Thermodynamic Parameters. The observed activation parameters, ΔE^*_{app} and ΔS^*_{app}, are actually apparent values which embrace both kinetic and thermodynamic contributions (cf. preequilibrium in eq 10). Up to now, no direct experimental value was available for ΔH_1. But it is obvious that $1/3\Delta H_1$ must be less than 16.8 kcal/mol (eq 13). Since

$$\Delta E^*_{app} = RT + 1/3\Delta H_1 + \Delta H_2^*$$

$$17.33 = 0.5 + 1/3\Delta H_1 + \Delta H_2^*$$

ΔH_1 = enthalpy of hydride trimer $\longrightarrow$ monomer

ΔH_2^* = enthalpy of activation for eq 12

$$RT = \text{ca. 0.5 kcal at } -5° \qquad (13)$$

kinetic estimates of $1/3\Delta H_1$ have ranged from 15 to 20 kcal,[14] the minimum value of $1/3\Delta H_1 = 15$ kcal/Al-H bridge seems reasonable. Then, $\Delta H_2^* = 2$ kcal/mol.

In a similar fashion, ΔS_2^* for eq 12 can be estimated as -60 eu at $-5.2°$ if K_1 is assumed to be ca. 10^{-6}.

The equilibration of the cis and trans adducts, **7a** and **7b**,

permitted the determination of K_3 (eq 10) as equaling 120 at $-5.2°$. This value corresponds to a Gibbs free energy change, $\Delta G = -2.55$ kcal/mol. The variation of K_3 with temperature led to $\Delta H = -2.1$ kcal/mol. The greater stability of the trans adduct **7b′** can be ascribed to the steric anisotropy of the diisobutylalumino group, compared with the grossly spherical, isotropic trimethylsilyl group (cf. eq 14); in this way, nonbonded atom repulsions are minimized for the syn groups.


(14)
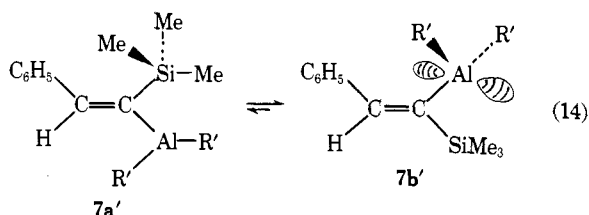
Role of Complexation between Diisobutylaluminum Hydride and Diisobutyl ((*Z*)-β-trimethylsilyl-β-styryl)aluminum (7b). The 1:1 interaction of R′$_2$AlH with vinylalanes can be viewed in several ways: (a) mixed alkenyl–hydride bridging[10] (**16**); (b) π complexation of R′$_2$AlH with the vinylic bond[15] (**17**; n.b., asymmetry of the R′$_2$Al group with respect to Al centers; cf. **16**, where the R′$_2$Al group is symmetrically bridged); and (c) isobutyl–hydride exchange, accompanied by association of the resulting R′$_3$Al with the vinylic aluminum hydride **18**:[12]
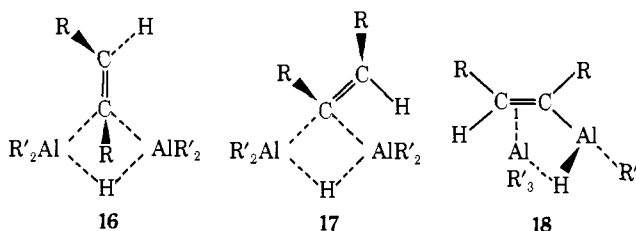
There is a structural precedent for the π interaction in **17** that has been revealed in the crystallographic structure determination of the diphenylphenylethynylaluminum dimer.[15] Also, heating the system, RCH=CRAlR′$_2$/R′$_2$AlH, causes the evolution of R′$_3$Al, which observation supports the possible presence of structure **18**.[12]

The initially formed cis adduct **7a** should be able to interact with R′$_2$AlH more readily than the trans adduct, and rapidly isomerize to the trans adduct. Especially for the silyl-substituted vinylalane, **7b′**, it is readily apparent that the requisite $3p_z$ orbital on aluminum, necessary for complexation of the type shown in **16** and **17**, is less accessible than in **7a′**. The incomplete complexation of **7b** was readily evident from the NMR spectrum of a mixture of **7b′** and R$_2$AlH, from which an equilibrium constant of $K_4 \simeq 0.2$ at $-10°$ was determined (eq 15). This equilibrium should then

$$7b + i\text{-Bu}_2\text{AlH} \rightleftharpoons (7b)(i\text{-Bu}_2\text{AlH}) \qquad (15)$$
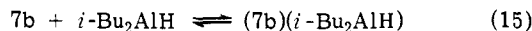
$$K_4 = \frac{[7b \cdot (i\text{-Bu}_2\text{Al} \cdot \text{H})]}{[7b][i\text{-Bu}_2\text{AlH}]}$$

Concentrations are considered for formulas as written, disregarding molecular association.

be included with those equations defining the kinetic behavior of this hydralumination, namely eq 10. The kinetic necessity of eq 15 is seen from those kinetic measurements made on hydraluminations conducted to high conversion. The integrated forms of the rate expression shown in eq 10 gave empirical rate constants (k_{emp}) that showed the least drift when m was set equal to 0.30. A comparison of this

Table IX.

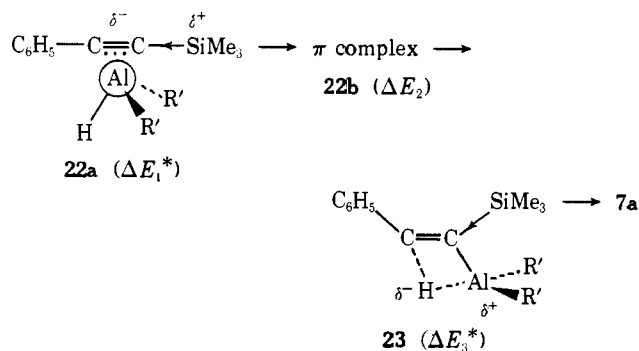|	$-0.5°$	$8.0°$	$15°$
k_{emp}(integration)[a]	7.2×10^{-5}	3.3×10^{-4}	7.5×10^{-4}
k_{emp}(intercept)[a]	8.1×10^{-5}	3.7×10^{-4}	7.9×10^{-4}
k_{emp}(initial rate)[a]	7.9×10^{-5}	3.7×10^{-4}	8.3×10^{-4}

[a] In $\text{mol}^{-1/3}$ l. $^{+1/3}$ sec^{-1}

k_{emp}(integration) with the k_{emp}(intercept), obtained from initial rates by eq 5, or with the k_{emp}(initial rate), obtained from the equation, initial rate $= k(0.136)^{4/3}$, gives a very satisfactory agreement (Table IX).

Electronic Factors in the Reactivity, Stereochemistry, and Isomerizability of α,β-Unsaturated Silanes. These results show that trimethyl(phenylethynyl)silane (**5**) actually undergoes an initial cis hydralumination, just like its carbon analog, *tert*-butyl(phenyl)acetylene. But the relative reaction rate[5] of the silyl compound is 16 times faster at 35°. Furthermore, the relative rates for typical aryl- and alkyl-substituted acetylenes ($C_6H_5C≡CC_6H_5$, 1.0; $C_6H_5C≡CCH_3$, 1.2; $n\text{-}C_3H_7C≡C\text{-}n\text{-}C_3H_7$, 6.3; $C_6H_5C≡CH$, 12; $C_6H_5C≡C\text{-}t\text{-}C_4H_9$, 28; **5**, 431) clearly demonstrate that the trimethylsilyl group enhances the reactivity of the C≡C linkage toward attack by the electrophilic R′$_2$AlH monomer.[5,6,11] Now several studies of the electronic character of the Me$_3$Si group have concluded that it is modestly electron withdrawing when attached to acetylenic carbon centers.[9,16] Toward saturated carbon centers, where only an inductive effect could be operative, the Me$_3$Si group seems to be electron donating (e.g., σ^* of Me$_3$Si $= -0.73$).[17] The reactivity of **5** and other alkynes toward hydralumination seems to require that the Me$_3$Si group be electron donating. But a further aspect of such relative reactivities is unusual; those alkynes having branched groups adjacent to the C≡C site are actually more reactive, even though such branching might cause some F or B strain during hydralumination.[5] Thus, consider the relative rates: $n\text{-}C_4H_9C≡C\text{-}n\text{-}C_4H_9$, 6.9, vs. $t\text{-}C_4H_9C≡C\text{-}t\text{-}C_4H_9$, 151; $C_6H_5C≡CCH_3$, 1.2, vs. $C_6H_5C≡C\text{-}t\text{-}C_4H_9$, 28. The argument has been advanced that the transition state must occur early in the configurational change involved, namely near a structure resembling a π complex (**19**), so as to avoid the F and B strains involved in later transition states (e.g., **20** or **21**).[5]
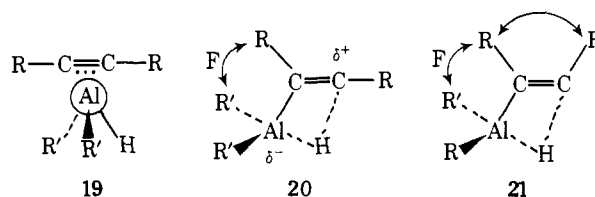

Applying these views to the silylacetylene **5**, we would ascribe its heightened reactivity to ground-state electron donation by the Me$_3$Si group, which fosters the formation of the π-complex-like transition state **22a**. Any actual π-complex intermediate (**22b**) would presumably occur after transition state **22a** and would lie in a high-energy trough ($\Delta E_1^* > \Delta E_2 < \Delta E_3^*$). Collapse of **22b** would ensue via a second transition state (**23**), which is not rate determining ($\Delta E_1^* > \Delta E_3^*$) but is product determining (regiospecific). Collapse of the transition state to yield product **7a**, however, involves rapid transfer of the hydride to unsaturated carbon. Again, by virtue of electron release by the Me$_3$Si group, the carbon α to it should be less recep-

Eisch, Rhee / Hydralumination of Group IV Substituted Alkynes

tive to hydride attack. Hence, the carbon β to it is attacked (23) and 7a results:

$$C_6H_5\overset{\delta^-}{—}C\overset{\varepsilon^+}{≡}C\text{—}SiMe_3 \longrightarrow \pi \text{ complex} \longrightarrow$$

22a ($\Delta E_1{}^*$)

22b (ΔE_2)

23 ($\Delta E_3{}^*$)

In this way, the high reactivity, the lack of steric hindrance, and the regiospecificity of this silylacetylene are explained by means of the recognized electron release of the Me_3Si group, without recourse to controversial p_π-d_π effects. In fairness, however, it should be noted that an alternative explanation could be developed based upon the latter view. Resonance structure 6b could be made an important contributor by such p_π-d_π interactions, whereby the silicon does not so much withdraw electron density, as it does polarize the π bond. From this argument would follow an equally satisfactory accounting for the ease of attaining 22a and for its specific collapse via 23.

On the other hand, a more persuasive case for the role of a p_π-d_π effect can be made in explaining the ready cis,trans equilibration of 7a and 7b. That such rapid equilibration at temperatures as low as $-5.0°$ is extraordinary is shown by the configurational stability of ordinary vinylalanes to long heating at $50°$. Attempted exchange experiments (eq 4) permit us to dismiss diadduct formation, such as 8, as a significant pathway in this isomerization. But three other pathways remain to be considered: (a) a lowered barrier to $C≡C$ bond rupture because of synergistic p_π-Sid_π (24) and p_π-Alp_π (25) effects in 7a; (b) a lowered barrier at the

24

25
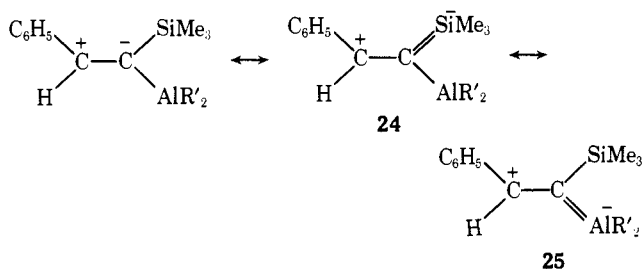
$C≡C$ bond, as in a, but with the isomerization proceeding via the dimer of 7a (25); and (c) the Lewis acid catalyzed attack of R'_2AlH on 7a, leading to lowered $C≡C$ character (26). Regardless of which pathways are actually responsible

25

26
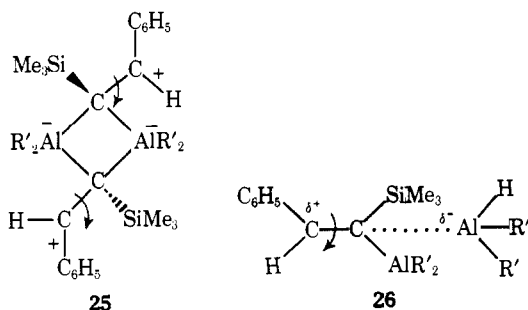
for this facile isomerization, in all three, the buildup of negative charge α to the Me_3Si group in the transition state

must be invoked. For this situation, a p_π-d_π polarization, expressed by 6b and 6c, forms the most suitable interpretation. Also, coordination of the tertiary amine at the aluminum center should stabilize the cis isomer 7a by hindering such buildup of negative charge on the α carbon. As to which pathway is the most important under our experimental conditions, we conclude that pathway c (26) is the most likely for several reasons. First of all, the observed isomerization and equilibration always occur in the presence of excess R'_2AlH. Such hydride is well recognized as able to break up homodimers, such as 25, and form more stable heterocomplexes (cf. 16-18). Secondly, vinylalanes have a strong dimerizing tendency[2b] so there is little likelihood that monomeric 7a (or 24) is even present is solution. Thirdly, when actual bishydralumination is forced to occur, the adduct has geminal dialumino groups (cf. 8). This finding supports the formulation of 26, where the σ-complex intermediate has the R'_2AlH electrophile attached α to the Me_3Si group.

Experimental Section

General Techniques. Techniques for the purification and handling of organoaluminum compounds, especially in kinetics and measurements, have already been described.[6,18]

Gas-liquid chromatographic analyses of mixtures containing the trimethyl(cis- and trans-β-styryl)silanes and trimethyl(phenylethynyl)silane were performed with the highly sensitive (10^{-10} g) Varian-Aerograph unit, Model 1200, which was equipped with a flame-ionization detector. The chromatograph was connected to a Honeywell recorder, Model Electronik 15, which in turn was provided with a disk-chart integrator, Model 201-B. The chromatographic column was of 9 ft × 0.125 in. size, packed with 10% silicon SF-96 on Chromosorb P of 100-120 mesh (the Chromosorb P having previously been acid-washed and siliconized to reduce tailing). Several repeated GLC analyses, using known concentrations of the starting alkynylsilane and the products under the conditions of the kinetic analysis (flow rate of He 30 ml/min; detector 205°; injector 180°; column 120°), showed all three compounds to have the same response factor (1.00 ± 0.01).

Preparation and Purification of Reagents. Silanes. Trimethyl(phenylethynyl)silane, trimethyl(cis-β-styryl)silane, trimethyl(trans-β-styryl)silane, and trimethyl(β-phenylethyl)silane were all prepared according to published procedures.[8] Just before use, fractional distillation of trimethyl(phenylethynyl)silane was carried out under dry nitrogen through a 30 × 0.75 cm column packed with glass helices. Since this silane had a GLC retention time identical with that of trimethyl(β-phenylethyl)silane, the characteristic NMR spectrum of the latter was used, together with its mass spectral detection, to measure the amount of the saturated silane formed: (neat) δ -0.04 (s, 9 H); 0.65-0.94 (sextet, 2 H); 2.41-2.70 (sextet, 2 H); 7.11(s, 5 H).

Aluminum Alkyls. The purification and analysis of diisobutylaluminum hydride, suitable for kinetic investigations, have already been described in detail, as has a reliable synthesis of diisobutylaluminum deuteride.[6]

Solvents. The principal reaction medium, hexane, was of the highest commercially available grade, which was then dried by prolonged reflux over sodium metal in the presence of benzophenone. The drying was conducted under nitrogen in an apparatus especially designed to avoid contaminating the solvent with grease. Thereupon, the purified hexane was distilled into the previously described stock-solution vessels or dispensing buret.[6]

Kinetics of the Addition of Diisobutylaluminum Hydride to Trimethyl(phenylethynyl)silane. General Procedure. The same procedures described for the kinetics of the hydralumination of 4-octyne were used here, except that the hydrolysis method had to be changed. Because of the rapidity with which the hydride reacts with the alkynylsilane, most of the kinetic runs were conducted at lower temperatures. Although it took only ca. 2 sec to withdraw a reaction mixture aliquot (0.3 ml) and to inject it into the hydrolysis solution, the time lag for quenching was long enough to change the relative amounts of the alkynylsilane and the alkenylsilane, as well as the cis,trans ratio of the latter. To avoid these errors, a 1-ml

hypodermic syringe was fused with a glass jacket, which covered two-thirds of the syringe tube starting from the needle exit. A current of ethanol, chilled to constant temperature by a circulating cooling bath, was passed through the jacket of the vertically mounted syringe during a transfer of an organoaluminum aliquot. The piston and the upper part of the syringe barrel were maintained uner dry nitrogen by a removable cap, in order to prevent condensation of moisture and freezing of the barrel. The rapid hydrolysis of each organoaluminum sample was achieved by injecting the sample (collected into the jacketed syringe at a constant low temperature), through a septum, into 1 ml of deoxygenated, dilute HCl in 10% v/v mixture of ethanol–water. The aqueous, ethanolic HCl samples were contained in broad-bore test tubes (to increase contact of the organic and aqueous phases) and maintained at a constant, low temperature by a cooling bath. After hydrolysis, more water was added, and the supernatant organic phase could be removed, dried, and subjected to GLC analysis.

Possible Effect of Experimental Variables on Analytical Results. To investigate the possible isomerization of the cis olefin to the trans isomer during hydrolysis, 10 ml of 0.5 N HCl solution was added to a hexane solution containing 0.30 g (1.7 mmol) of trimethyl(cis-β-styryl)silane. After 5 hr at 25°, a GLC analysis indicated essentially no cis,trans isomerization.

In determining the initial rate of hydralumination for trimethyl-(phenylethynyl)silane at −10.2° [i-Bu$_2$AlH]$_0$ = [PhC≡CSiMe$_3$]$_0$ = 0.136 mol/l., three different hydrolysis procedures were compared: (a) the reaction mixture was collected into a jacketed syringe cooled to −10.2° (vide supra) and thereupon hydrolyzed by injection into the cold 0.5 HCl (10% EtOH); (b) the same conditions as in procedure a, except that no acid was employed; and (c) the reaction mixture was withdrawn with a syringe that was at room temperature, but the rest of the procedure was that used in a. The average values for the initial rates obtained by these three procedures were: (a) 3.19 × 10^{-6}; (b) 3.22 × 10^{-6}; and (c) 3.64 × 10^{-6} mol/l. sec. Thus, little variation in the observed values results when water–ethanol replaces dilute HCl as the hydrolyzing medium, but the apparent reaction rate can increase by 15% when the sampling syringe is at room temperature.

Effect of Temperature on the Initial Rate. The stock solutions were prepared by diluting 5.0 ml of diisobutylaluminum hydride with hexane to a total volume of 200.0 ml (apparatus previously described).[6] To 20.0 ml of such a stock solution was added 0.473 g (0.40 ml) of trimethyl(phenylethynyl)silane, giving a concentration of [i-Bu$_2$AlH]$_0$ = [PhC≡CSiMe$_3$]$_0$ = 0.136 mol/l. The hydralumination rate was measured at six different temperatures: −10.3 (run 1); −5.2 (runs 2, 3, 4, and 5); −1.0 (run 6); 2.1 (run 7); 8.0 (run 8); and 15.0° (run 9) (Table I). For runs 1–7 the initial rates were calculated from the average values of the analytical results before 7% conversion. At 8.0 and 15.0° (runs 8 and 9), the addition reaction was too fast to permit the analysis of 3–4 samples before 7% conversion. Consequently, the initial rates were obtained by a graphical extrapolation of the first four values to t = 0. Thus, for run 8,

$$\left(\frac{[\text{cis olefin}] + [\text{trans olefin}]}{[\text{PhC≡CSiMe}_3]_t}\right)_{t\to 0} = 1.14 \times 10^{-2} \text{ min}^{-1}$$

and for run 9, 2.55 × 10^{-2} min^{-1}, by intercept.

Kinetic Order Dependence of the Reactants. For the kinetic true order in the silylacetylene, 20.0 ml of the aforementioned hydride solution in hexane were mixed with varying amounts of the silylacetylene (0.163 g in run 10, 0.235 g in run 11, and 0.344 g in run 12) at −5.2° (Table II).

For the kinetic true order in the hydride (runs 13–20), the concentration of diisobutylaluminum hydride was varied by using different amounts of the same stock solution (x = 5.0, 10.0, or 15.0 ml) and then distilling hexane into the hydride aliquot, via a needle-tipped buret,[6] up to a final volume of 20.0 ml. After the hydride solutions had been equilibrated at −5.2°, 0.473 g of the silylacetylene was added to each solution (Table III).

Kinetic Hydrogen–Deuterium Isotope Effect. The reactivity of diisobutylaluminum deuteride in hydraluminating trimethyl(phenylethynyl)silane (runs 21 and 22) at −5.2° was compared with that of diisobutylaluminum hydride (runs 3, 4, and 5). A stock solution of the deuteride in hexane, containing 2.50 ml of deuteride

in a total volume of 100.0 ml, was first prepared. Then a 20.0-ml aliquot of this solution was equilibrated at −5.2°, after which 0.473 g of the silylacetylene was introduced (Table IV).

Study of the Equilibrium between the Cis and Trans Hydralumination Adducts, Diisobutyl((Z)-β-trimethylsilyl-β-styryl)aluminum and Diisobutyl((E)-β-trimethylsilyl-β-styryl)aluminum. Not only the apparent extent of hydralumination, but also the ratio of the trimethyl(cis-β-styryl)silane to the trimethyl(trans-β-styryl)silane, obtained by the hydrolysis of the hydralumination adducts, is very sensitive to the method of hydrolytic work-up. Accordingly, the method of using a jacketed syringe and a cooled hydrolysis medium, both of which were held at constant temperature with a cooling bath (procedure a) under the aforementioned kinetic measurements, was used in the present equilibrium measurements. By means of this reliable hydrolysis method, any observed variations in the cis:trans ratio of the styrylsilanes obtained could then be ascribed to a change in the cis:trans ratio of the hydralumination adducts themselves. By means of triplicate analyses of organoaluminum samples and by random selection of the temperature (by raising or lowering), the determination of the cis:trans ratio sought to eliminate errors inherent in a single hydrolytic analysis.

To 25.0 ml of the previously described stock solution of diisobutylaluminum hydride in hexane was added 0.473 g of the silylacetylene, giving [i-Bu$_2$AlH] = 0.138 mol/l. and [PhC≡CSiMe$_3$]$_0$ = 0.107 mol/l. For runs 23, 24, and 25, the hydralumination of the silylacetylene was complete when the temperature was held at 0 to +1° for 18–25 hr. When a similar sample was allowed to react for 12 hr at 15°, hydrolysis yielded 98.87% of the trans-β-styrylsilane, 0.92% of the cis isomer, and 0.21% of the residual silylacetylene. After a total of 43.5 hr, hydrolysis revealed a composition of 97.62% trans- and 0.99% cis-β-styrylsilanes; little silylacetylene was left, but the remaining 1.39% was now trimethyl(β-phenylethyl)silane (MS: P (m/e) 178).

After one or two samples were withdrawn from runs 23, 24, and 25 at one temperature and then analyzed, the temperature was raised or lowered, in a random fashion, to a new temperature. The solutions were allowed to equilibrate for 2–3 hr and samples again withdrawn for the special hydrolytic analysis (Table V).

Study of the Bisalumino Adduct Formation in the Reaction of Diisobutylaluminum Hydride with Trimethyl(phenylethynyl)silane. As mentioned in the previous section, a 1.4:1.0 ratio of hydride and silylacetylene (run 23) gave ca. 1% of trimethyl(β-phenylethyl)silane after 43.5 hr at 15°. When 1.5 g of the silylacetylene (8.6 mmol) was allowed to react with 4.5 ml (25.0 mmol) of the hydride in 100 ml of hexane for 40 hr at 25°, hydrolysis yielded only 2.7% of the phenylethylsilane. Further heating for 15 hr at 40° now gave 12.4% of the phenylethylsilane and 82.5% of the trans- and 5.1% of the cis-β-styrylsilanes, as determined both by GLC and NMR analyses. In the latter analysis, the integration of the distinct Me$_3$Si peaks (trans, δ 0.14; cis, 0.03; and PhCH$_2$CH$_2$, −0.04 ppm) served as the criterion.

Treatment of the remaining organoaluminum solution with D$_2$O and GLC separation (13 ft × 0.25 in. 15% silicone SF-96 on Chromosorb W at a column temperature of 140°) provided a sample shown to be essentially pure trimethyl(α,α-dideuterio-β-phenyl)silane by NMR (vanishing small absorption in the 0.65–0.94 ppm region) and mass spectral (P, m/e 180) analyses.

Attempted Exchange of Hydrogen (Deuterium) for Deuterium (Hydrogen) in the Trans Hydralumination Adduct of Trimethyl(phenylethynyl)silane. In the first case, 0.783 g (4.5 mmol) of the silylacetylene was allowed to react with a 22% excess (1.0 ml, 5.5 mmol) of diisobutylaluminum deuteride in 30 ml of hexane for 20 hr at 25–30°. Hydrolysis of a 13-ml aliquot gave a composition of 98.7% of trans- and 1.2% of cis-styrylsilane with 0.1% of starting material. NMR spectrum of the crude trans-PhCD=CHSiMe$_3$ (neat) showed: 0.14 (Me$_3$Si), 6.40 (t, 1-CH, J = 3.0 Hz), and 7.10–7.45 (m, 5 H) ppm.

To the remaining reaction mixture (ca. 17 ml) was added 0.7 ml (3.9 mmol) of diisobutylaluminum hydride and the resulting solution allowed to stir for 36 hr at 25–30°. Hydrolytic work-up yielded a crude product, whose NMR spectrum was identical with that obtained before the (i-Bu$_2$AlH)$_3$ had been added, namely, that of trans-PhCD=CHSiMe$_3$.

In the second attempt, 0.473 g (2.7 mmol) of the silylacetylene was allowed to react first with diisobutylaluminum hydride (0.63 ml, 3.4 mmol) for 15 hr at 8° (hydrolysis giving 98.8% of the

trans-styrylsilane) and then with diisobutylaluminum deuteride (1.0 ml, 5.4 mmol) for 25 hr at 8°. However, in the final hydrolysis product (>98% of trans-β-styrylsilane), no deuterium was incorporated [NMR (neat) δ 0.14 (s, Me₃Si); 6.38 (d, CH=, J = 19 Hz), 6.88 (d, CH=, J = 19 Hz), 7.07-7.41 (m, 5 H)].

Infrared and NMR Spectral Study of Mixtures of Diisobutylaluminum Hydride and Trimethyl(phenylethynyl)silane. In 1:1 Ratio. By means of a gas-tight syringe, the silylacetylene (1.90 g, 10.9 mmol) was added dropwise to the neat hydride (1.50 g, 10.5 mmol) at 0°. After ca. 5 min of reaction, the C=C stretch at 1530 cm⁻¹, characteristic of the trans hydralumination adduct, was already prominent. As the reaction progressed, the Al–H and C≡C bands at 1760 and 2160 cm⁻¹, respectively, slowly disappeared, but these bands did not appear to be shifted from their usual positions in the pure components.

The NMR spectrum of the neat trans adduct displayed peaks at (δ, ppm): 0.17 (d, 4 H, J = 6.5 Hz), 0.18 (s, 9 H), 0.88 (d, 12 H, J = 6.5 Hz), 1.70 (m, 2 H), 7.23 (s, 5 H), and 7.84 (s, 1 H) (Figure 4).

In 2:1 Ratio. Admixture of 0.515 g (3.0 mmol) of the silylacetylene with 0.80 g (5.6 mmol) of the hydride was performed slowly and carefully in an NMR tube (Caution: exothermic reaction). The progress of the hydralumination was then monitored by NMR spectroscopy at a probe temperature of 0°. After ca. 15 min, new sharp singlets appeared at δ 7.84 and 0.18 ppm because of the vinylic proton and the Me₃Si group, respectively, of the trans adduct. Also, a new, broad singlet centered at 3.90 ppm developed because of a mixed 1:1 complex of the trans adduct with diisobutylaluminum hydride. When the starting acetylene was consumed, the peak at 7.84 bore a 1:5 ratio to the now sharp singlet at 7.23 ppm (C₆H₅). The methyl protons of the isobutyl groups gave rise to a triplet, which seemed to be due to the overlap of two different doublets centered at 0.98 and 0.88 ppm, respectively. The ratio of broad peaks at 3.90 and 2.93 ppm, arising from the hetero- and homohydride complexes of i-Bu₂AlH, varied with tempera-

ture. At −10°, the ratio of the heterocomplex absorption [PhCH=C(SiMe₃)Al(i-Bu₂) with i-Bu₂AlH] to that of the homocomplex, (i-Bu₂AlH)₃, was 29:71 and became 19:81 at 38° (Figure 5).

References and Notes

(1) Part XXX of the series, "Organometallic Compounds of Group III"; for previous part, cf. J.J. Eisch and K. C. Fichter, *J. Am. Chem. Soc.*, **96**, 6815 (1974).
(2) (a) H. Lehmkuhl, K. Ziegler, and H.-G. Gellert in "Houben-Weyl Methoden der Organischen Chemie", Vol. III/4, E. Müller, Ed., Georg Thieme Verlag, Stuttgart, West Germany, 1970, pp 204–258; (b) G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629**, 222 (1960); (c) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966).
(3) (a) G. Zweifel and R. B. Steele, *J. Am. Chem. Soc.*, **89**, 2754 (1967); (b) J. J. Eisch and M. W. Foxton, *J. Organomet. Chem.*, **11**, P7 (1968).
(4) (a) G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 2753 (1967); (b) G. Zweifel and R. B. Steele, *ibid.*, **89**, 5085 (1967).
(5) J. J. Eisch and S.-G. Rhee, *Justus Liebigs Ann. Chem.*, 565 (1975).
(6) J. J. Eisch and S.-G. Rhee, *J. Am. Chem. Soc.*, **98**, 7276 (1974).
(7) J. J. Eisch and R. Amtmann, *J. Org. Chem.*, **37**, 3410 (1972).
(8) J. J. Eisch and M. W. Foxton, *J. Org. Chem.*, **36**, 3520 (1971).
(9) C. J. Attridge, *Organomet. Chem. Rev., Sect. A*, **5**, 323 (1970).
(10) G. M. Clark and G. Zweifel, *J. Am. Chem. Soc.*, **93**, 527 (1971).
(11) J. J. Eisch and S.-G. Rhee, *J. Organomet. Chem.*, **31**, C49 (1971).
(12) J. J. Eisch and S.-G. Rhee, *J. Organomet. Chem.*, **86**, 143 (1975).
(13) J. J. Eisch and M. Boleslawski, unpublished studies.
(14) K. W. Egger, *J. Am. Chem. Soc.*, **91**, 2867 (1969).
(15) G. D. Stucky, A. M. McPherson, W. E. Rhine, J. J. Eisch, and J. L. Considine, *J. Am. Chem. Soc.*, **96**, 1941 (1974).
(16) H. Bock and H. Seidl, *J. Chem. Soc. B*, 1158 (1968).
(17) Cf. R. W. Taft, Jr., in M. S. Newman, Ed., "Steric Effects in Organic Chemistry", Wiley, New York, N.Y., 1956, pp 595–596.
(18) J. J. Eisch and C. K. Hordis, *J. Am. Chem. Soc.*, **93**, 2974 (1971).

Intramolecular Cycloaddition Reactions of Vinyl-Substituted 2H-Azirines[1]

Albert Padwa,* Joel Smolanoff, and Alan Tremper

Contribution from the Department of Chemistry, State University of New York at Buffalo, Buffalo, New York 14214. Received October 30, 1974

Abstract: The scope of the thermal and photochemical ring expansion reactions of a number of 2-vinyl-substituted 2H-azirines has been examined. The azirine derivatives undergo photochemical rearrangement to 2,3-disubstituted pyrroles via transient nitrile ylide intermediates which can be trapped with external dipolarophiles. The thermal reactions proceed by a different pathway involving rupture of the azirine C–N single bond giving a butadienyl nitrene which cyclizes to a 2,5-disubstituted pyrrole. That the photocycloadditions proceed via the excited singlet state of the azirine is indicated by the failure of triplet sensitizers and quenchers to sensitize or quench the reaction. Photolysis of 3-phenyl-2-styryl-2H-azirine proceeds by a seven-membered transition state and gives 1-phenyl-3H-2-benzazepine as the major product. A study of the quantum yield for product formation as a function of added dipolarophile shows that the photocyclization to give a seven-membered azepine is significantly faster than cyclization to the five-membered pyrrole ring.

Several in-depth studies from these laboratories have demonstrated that arylazirines undergo photocycloaddition with electron-deficient olefins to give Δ¹-pyrroline derivatives.[2-4] The formation of the adducts was interpreted as proceeding by way of irreversible ring opening of the azirine ring to form a nitrile ylide intermediate. As a 1,3-dipole, this species can be intercepted with a variety of dipolarophiles to form five-membered heterocyclic rings.[5-9] The cleavage of the C–C bond of the azirine ring was shown to proceed from the n-π* singlet state[2] and was rationalized in

terms of an electrocyclic transformation[10-12] analogous to the cyclopropyl → allyl cation rearrangement.[13] That the photocycloadditions proceed via the excited singlet state of the azirine was indicated by our inability to quench or sensitize the cycloaddition with a variety of triplet quenchers and sensitizers.[2,6] In the cases reported previously, the nitrile ylide intermediate generated from the azirine was trapped by an external dipolarophile. As a continuation of our investigations in this area, we were particularly interested in determining whether the cycloaddition reaction