

$\log k_i$  vs.  $pK_a$  of the various bases has a slope,  $\beta$ , of about 0.4 for both azulene and azulene-1,3- $d_2$ ; however, water and especially 2,4,6-trimethylpyridine deviate considerably from the linear relationship and are less effective catalysts than predicted from their basic strengths. The low catalytic activity of 2,4,6-trimethylpyridine can reasonably be attributed<sup>8</sup> to a steric effect involving the 2,6-dimethyl groups on approach of the basic nitrogen to the iodoazulenium cation. Paralleling the decrease in  $(k_i)_H$  there is a still larger decrease in  $(k_i)_D$  such that with 2,4,6-trimethylpyridine the isotope effect  $(k_i)_H/(k_i)_D$  is over three times as great as in the case of pyridine. We believe that the large increase in the isotope effect here is due in good part to proton tunneling in the transition state for the same reasons which Funderburk and Lewis<sup>9</sup> have advanced to explain the 2.5-fold greater isotope effect  $(k_H/k_D)$  upon ionization of 2-nitropropane by 2,4,6-trimethylpyridine as compared to pyridine. Lewis and Funderburk<sup>11</sup> have recently pointed out that steric effects may also increase the isotope effect by bringing about a larger than usual loss of zero-point vibrational energy in a more stretched transition state.

In contrast to the nitrogen bases, the oxygen bases of Table I give an almost constant isotope effect  $(k_i)_H/(k_i)_D$  in spite of 7  $pK$  units difference in basicity over the range of bases examined. In the ionization of aliphatic C-H bonds by bases of various strength Bell and co-workers<sup>10</sup> found a maximum in the isotope effect when the ionizing acid and the attacking base had about equal  $pK_a$ . In terms of this correlation and the likely approximation that iodoazulenium cation is some 2  $pK$  units more acidic than azulonium cation, the bases of Table I should give decreasing isotope effects with increasing  $pK_a$  of the base (*i.e.*, in going from water to 2,4,6-trimethylpyridine). The trend in isotope effect from water to pyridine is in qualitative accord with this expectation; however, the near constancy in isotope effect among the oxygen bases suggests that a factor is operating here in opposition to the basicity effect of Bell. We suggest that this is a steric effect, qualitatively like that mentioned earlier for 2,4,6-trimethylpyridine, which increases about in proportion to the basicity of the base and which has its possible origin in the increased solvation of the ions of greater basicity.

We think that the phenomenon of steric amplification of isotope effects<sup>12</sup> may prove a useful tool in chemistry especially in cases where the normal isotope

effect is either too small to detect or so small that it might be confused with a secondary isotope effect.

**Acknowledgment.** This research was supported by generous grants from the National Science Foundation. A grant from the Charles F. Kettering Foundation aided in purchase of the Cary spectrophotometer.

Erling Grovenstein, Jr., Frank C. Schmalstieg

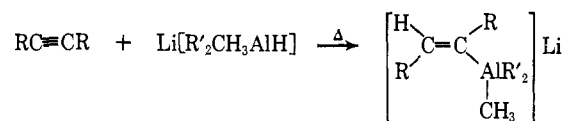
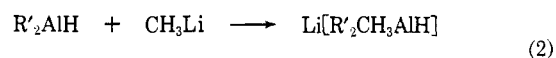
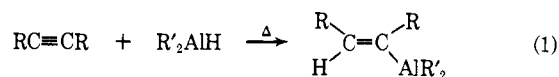
School of Chemistry, Georgia Institute of Technology  
Atlanta, Georgia 30332

Received July 14, 1967

### A Novel Method for the Synthesis of *cis*- $\alpha,\beta$ -Unsaturated Derivatives via *trans*-Hydroalumination of Disubstituted Alkynes with Lithium Diisobutylmethylaluminum Hydride<sup>1</sup>

Sir:

The hydroalumination of disubstituted alkynes with diisobutylaluminum hydride is a highly stereoselective process giving excellent yields of *cis*-vinylalanes (1)<sup>2</sup> which may readily be converted into a variety of isomerically pure  $\alpha,\beta$ -unsaturated derivatives.<sup>3</sup> In view of the increasing interest in vinylalanes as synthetically useful intermediates we have been investigating possible routes for the preparation of *trans*- as well as *cis*-vinylaluminum derivatives. We now wish to report that the hydroalumination of disubstituted alkynes with lithium diisobutylmethylaluminum hydride<sup>4</sup> in ether solvents apparently results in a *trans* addition of the aluminum-hydrogen bond to the triple bond (2). Evidence for the *trans* addition was obtained by hydrolysis of the intermediate vinylalanes which revealed the formation of *trans*-olefins.<sup>5</sup>



The possibility that the hydroalumination of disubstituted alkynes with lithium diisobutylmethylaluminum hydride produces initially the *cis*-vinylalanes, which subsequently isomerize on heating to the *trans* compounds,<sup>6</sup> was ruled out on the basis of the following experiment. The *cis*-vinylalane derived from the reaction of 3-hexyne with diisobutylaluminum hydride was treated with methyllithium and the *cis*-vinylalane thus formed was heated under conditions similar to the one used for the preparation of the *trans*-vinylalane. Hy-

(8) H. Zollinger [*Helv. Chim. Acta*, **38**, 1623 (1955)] has noted similarly that 2-methylpyridine and especially 2,6-dimethylpyridine are less effective catalysts than expected from their base strengths in the azo coupling of 2-naphthol-6,8-disulfonic acid with *p*-chlorobenzenediazonium ion, and he has attributed this result to steric effects involving the methyl groups. While the factor appears not to have been studied, we would anticipate that these catalysts would show larger isotope effects in azo coupling than the unhindered pyridine bases, in accord with the present observations on iodination.

(9) L. Funderburk and E. S. Lewis, *J. Am. Chem. Soc.*, **86**, 2531 (1964); see also ref 10.

(10) R. P. Bell and D. M. Goodall, *Proc. Roy. Soc. (London)*, **A294**, 273 (1966); R. P. Bell and J. E. Crooks, *ibid.*, **A286**, 285 (1965); see also J. L. Longridge and F. A. Long, *J. Am. Chem. Soc.*, **89**, 1292 (1967).

(11) E. S. Lewis and L. H. Funderburk, *ibid.*, **89**, 2322 (1967).

(12) The effect under discussion is different from another type of steric effect where, in a complex mechanism, a bulky substituent may shift the rate-determining step from one not directly involving the isotope to one involving the isotope, *e.g.*, nitration of 2,4,6-tri-*t*-butylnitrobenzene [P. C. Myhre and M. Beug, *ibid.*, **88**, 1569 (1966)]; however, even here direct steric effects in the rate-determining step may be responsible in part for the isotope effects observed.

(1) This work was supported by the National Science Foundation, Grant No. GP-6633.

(2) G. Wilke and H. Müller, *Ann.*, **629**, 222 (1960).

(3) G. Zweifel and R. B. Steele, *J. Am. Chem. Soc.*, **89**, 2754 (1967).

(4) The reagent is readily prepared by adding methyllithium to diisobutylaluminum hydride.

(5) The progress of the reaction was followed by withdrawing samples at different time intervals and quenching them in dilute sulfuric acid. Glpc analysis of the upper phase formed indicated that only the *trans* olefin was formed.

(6) The isomerization of *cis*-vinylalanes to the corresponding *trans* compounds has been reported by J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88**, 2213 (1966).

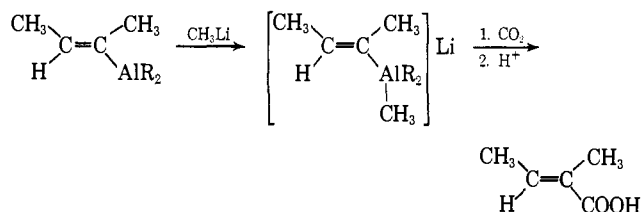
**Table I.** Products from *cis*- and *trans*-Vinylalanes with Various Reagents

Alkyne	Vinylalane	Reagent	Product <sup>c</sup>	Yield, %
2-Butyne	<i>cis</i> <sup>a</sup>	CO <sub>2</sub>	Tiglic acid	76
	<i>trans</i> <sup>b</sup>	CO <sub>2</sub>	Angelic acid	72
3-Hexyne	<i>cis</i> <sup>a</sup>	H <sub>2</sub> O	<i>cis</i> -3-Hexene	90 <sup>d</sup>
		CO <sub>2</sub>	<i>trans</i> -2-Ethyl-2-pentenoic acid	78
		HCHO	<i>trans</i> -2-Ethyl-2-penten-1-ol	73
		I <sub>2</sub>	<i>cis</i> -3-Iodo-3-hexene	57
	<i>trans</i> <sup>b</sup>	H <sub>2</sub> O	<i>trans</i> -3-Hexene	88 <sup>d</sup>
		CO <sub>2</sub>	<i>cis</i> -2-Ethyl-2-pentenoic acid	67
		HCHO	<i>cis</i> -2-Ethyl-2-penten-1-ol	68
		I <sub>2</sub>	<i>trans</i> -3-Iodo-3-hexene	60

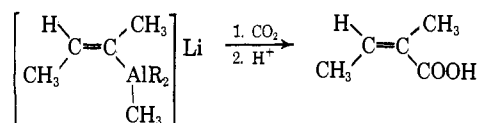
<sup>a</sup> From diisobutylaluminum hydride followed by treatment of the vinylalane with methyllithium. <sup>b</sup> From hydroalumination with lithium diisobutylmethylaluminum hydride. <sup>c</sup> All products gave satisfactory elemental analyses and infrared and pmr spectra in agreement with the assigned structures. <sup>d</sup> Yield by glpc analysis.

hydrolysis of the reaction mixture with dilute sulfuric acid yielded only *cis*-3-hexene, indicating that the *cis*-vinylalane had not isomerized. Thus, in contrast to the observed *cis* addition of the aluminum-hydrogen bond in the hydroalumination of alkynes with diisobutylaluminum hydride, lithium diisobutylmethylaluminum hydride must directly add *trans*.<sup>7</sup>

We have recently shown that *cis*-vinylalanes, derived from the hydroalumination of alkynes with diisobutylaluminum hydride, upon treatment with methyllithium yield the corresponding ate complexes, which react readily with a variety of Grignard coreagents to give isomerically pure *trans*- $\alpha,\beta$ -unsaturated derivatives.<sup>3,8</sup> This is shown as follows.



Correspondingly, carbonation of the *trans*-vinylalanes derived from the hydroalumination of alkynes with lithium diisobutylmethylaluminum hydride yields *cis*- $\alpha,\beta$ -unsaturated acids in high yields.



Paraformaldehyde reacts with the *trans*-vinylalanes to produce *cis*- $\alpha,\beta$ -unsaturated alcohols, and iodination of the *trans*-vinylalanes affords the *trans*-vinyl iodides.<sup>9</sup> Since vinylaluminum compounds are readily hydrolyzed to olefins when treated with diluted acid, it is also now possible to convert disubstituted acetylenes *via* hydroalumination into either *cis*- or *trans*-olefins, depending on the nature of the hydroaluminating agent used. These reactions are essentially free from side products, since the alkyl moieties on aluminum are converted to the volatile hydrocarbons methane and/or isobutane in the

(7) It has been reported that lithium aluminum hydride is a catalyst for the selective *trans*-hydrogenation of 2-pentyne: L. H. Slaugh, *Tetrahedron*, **22**, 1741 (1966).

(8) Direct carbonation of *cis*-vinylalanes gives lower yields (50–60 %) of the corresponding carboxylic acids.

(9) G. Zweifel and C. C. Whitney, *J. Am. Chem. Soc.*, **89**, 2753 (1967).

hydrolysis step. A summary of the experimental results of these reactions is given in Table I.

It is evident that the feasibility for preparing both *cis*- and *trans*-vinylaluminum compounds from disubstituted alkynes should greatly increase the synthetic versatility of the hydroalumination reaction. The general procedure for the preparation of *trans*- $\alpha,\beta$ -unsaturated derivatives from *cis*-vinylalanes was reported earlier.<sup>3</sup> The simplicity of the present procedure for the conversion of alkynes into *cis*- $\alpha,\beta$ -unsaturated compounds *via trans*-hydroalumination with lithium diisobutylmethylaluminum hydride is illustrated by the following example.

To 0.10 mole of diisobutylaluminum hydride in 30 ml of monoglyme was added 0.10 mole of methyllithium in ether while maintaining the temperature below 25°. The diethyl ether was then removed under reduced pressure and 0.05 mole of 3-hexyne was added.<sup>10</sup> The reaction mixture was heated at 100–130° for 6 hr and cooled to 60° and 0.10 mole of paraformaldehyde was added at a rate such that the temperature was maintained between 60 and 70°. After standing for an additional hour at 65° the reaction mixture was poured slowly into a mixture of ice and concentrated hydrochloric acid, and the alcohol produced was extracted with ether. The ether extract was washed with sodium carbonate and distilled to give 3.9 g of *cis*-2-ethyl-2-penten-1-ol (68%), bp 40° (1 mm),  $n_D^{20}$  1.4467.

(10) A lower ratio of lithium diisobutylmethylaluminum hydride to alkyne may be used; however, longer reaction times or higher temperatures are required to achieve high yields of products.

(11) National Institutes of Health Predoctoral Fellow, 1965–1967.

George Zweifel, Roger B. Steele<sup>11</sup>

Department of Chemistry, University of California  
Davis, California 95616

Received June 28, 1967

### $\alpha$ -Halovinylboranes. Their Preparation and Conversion into *cis*-Vinyl Halides, *trans*-Olefins, Ketones, and *trans*-Vinylboranes<sup>1</sup>

Sir:

The hydroboration of 1-bromo- and 1-iodo-1-alkenes with dicyclohexylborane results in the formation of  $\alpha$ -haloboranes which undergo migration of one alkyl group from boron to the adjacent carbon atom. Oxidation of the reaction mixture with alkaline hydrogen peroxide

(1) This research was supported by the National Science Foundation Grant No. GP-6633.