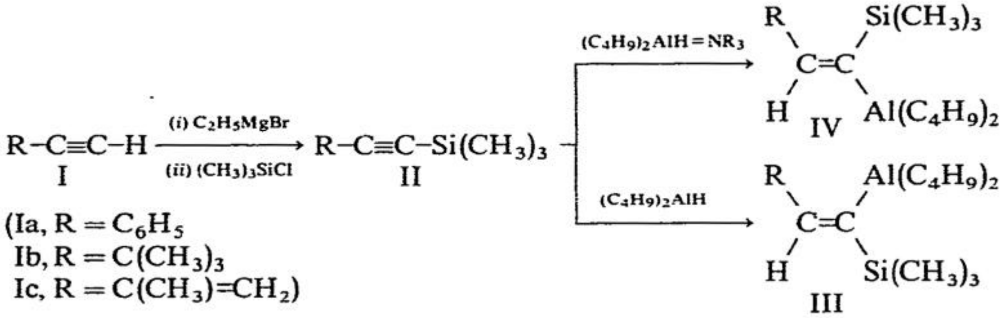
Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

PRELIMINARY COMMUNICATION

Facile *trans*- and *cis*-hydraluminations of certain alkynyl derivatives of Group IV elements

The stereospecific *cis*-addition of aluminum hydrides[1,2] and boron hydrides[3] to alkynes has been well established. The resulting *cis*-vinylaluminum products have been found to undergo a rather slow thermal isomerization to the *trans*-vinylaluminum systems via a *geminal*-dialumina-alkane intermediate[2]. Recently, the *trans*-hydralumination of alkynes in donor solvents by use of lithium aluminum hydride[4,5] or by lithium diisobutylmethylaluminum hydride[6] has been achieved. We now wish to report that certain terminal alkynes, as their trimethysilyl or trialkylgermyl derivatives can be reduced easily and stereospecifically in a *cis*- or a *trans*- fashion by diisobutylaluminum hydride.



(Ia, $R = C_6H_5$
Ib, $R = C(CH_3)_3$
Ic, $R = C(CH_3){=}CH_2$)

Thus, in hydrocarbon media the alkynylsilane (II) is converted to the *trans*-alkenylsilane (III) containing $< 5\%$ of the *cis*-adduct (IV). However, in the presence of one equivalent of a strong donor, *e.g.*, *N*-methylpyrrolidine, the addition of hydride occurs stereospecifically *cis*, giving IV which contains 4% III. Use of a weaker donor, such as ethyl ether, results in a 65 : 35 mixture of *cis* and *trans* products. Almost complete conversion of the *cis*-alkenylaluminum compound (IV) to the *trans*-isomer (III) (final ratio 1 : 18) could be achieved by heating IV (presumably as amine complex) with a small amount of diisobutylaluminum hydride at 100° for 66 h[2]. Attempted isomerization of III under similar conditions failed.

The structures of the styryl-silanes of -germanes obtained upon hydrolysis, as well as those of the various olefinic products from related hydraluminations (see Table 1), were assigned on the basis of the NMR coupling constants[7] and the C–H out-of-plane deformations in the infrared spectra[8]. With the assumption of no change of configuration upon hydrolysis*, the position of the aluminum attachment in III and IV was shown, by treatment with deuterium oxide and NMR analysis of the resulting deuterated silanes, (*trans* V; *cis* VI) to be exclusively on the same carbon as the trimethylsilyl (or triethylgermyl) group.

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* *Cf.* Ref. 9 for the support for this assumption.

TABLE 1

HYDRALUMINATION OF PHENYLETHYNYL DERIVATIVES WITH DIISOBUTYLALUMINUM HYDRIDE

$$C_6H_5{-}C{\equiv}C{-}E \xrightarrow[(ii)\ H_2O(D_2O)]{(i)\ (C_4H_9)_2AlH} C_6H_5\underset{\alpha}{C}H{=}\underset{\beta}{C}HE$$

E	Position of deuteron	Geometry	R_3N[a]	NMR data		
				δ(ppm)		J(cps)
				α	β	
H	β	*cis*[b]		6.69[c]	5.69	17.5
Br		[d]				
$C(CH_3)_3$	α	*cis*		6.43	5.57	12.5
$Si(CH_3)_3$	β	*cis*	+	7.36	5.83	15
$Si(CH_3)_3$	β	*trans*		6.88	6.33	19
$Ge(C_2H_5)_3$	β	*cis*	+	7.50	5.92	14
$Ge(C_2H_5)_3$	β	*trans*		6.84	6.57	18.5

[a] *N*-Methylpyrrolidine. [b] In a competing metallation reaction a phenylethynylaluminum derivative is formed to an extent of 29% (isolation of $C_6H_5C{\equiv}C{-}D$ upon hydrolysis with D_2O). [c] Center of triplet, $J = 1.5$ cps. [d] Only cleavage occurs to give phenylacetylene upon hydrolysis.

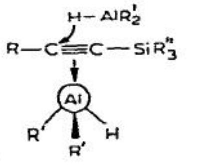
In a typical experiment, phenylacetylene was converted via the Grignard reagent to phenylethynyltrimethylsilane[10] (IIa). A solution of 0.056 mole of IIa and 0.056 mole of diisobutylaluminum hydride in 25 ml of heptane was allowed to stand at room temperature for 15 h. Hydrolytic work-up yielded the *trans*-olefin Va (b.p. 90–91°/13 mm) in 96% yield. Alternatively, adding one equivalent of *N*-methylpyrrolidine to the diisobutylaluminum hydride and mixing this complex[11] with the alkynylsilane (IIa) at 60° for 15 h and then at 100° for 4 h resulted in the *cis*-olefin VIa (b.p. 43–45°/0.53 mm) in 96% yield (containing *ca.* 4% of IIIa). Similar results were obtained with IIb and IIc.

In order to test whether the *trans*-isomer IIIa might be formed by a rapid conversion of the *cis*-isomer IVa in a thermodynamically controlled process, the hydralumination reaction without amine was run at −10°. However, even after 5% of conversion the amount of *trans*-olefin (Va) predominated in a ratio 19 : 1. This finding tends to rule out a *cis-trans* isomerization[2] for *trans*-hydralumination.

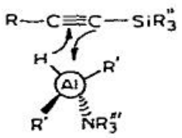
As a further test of possible steric requirements for *trans*-addition, the carbon analog of II, 3,3-dimethyl-1-phenylbutyne-1 (VII), was treated with diisobutylaluminum hydride. In sharp contrast to II, however, the hydrolysis product was solely the *cis*-olefin, 3,3-dimethyl-1-phenylbutene-1 and work-up with deuterium oxide showed the aluminum to be attached exclusively to the same carbon as the phenyl group.

In the light of previous evidence indicating an electrophilic attack of aluminum alkyls and hydrides on unsaturated hydrocarbons[2,12], we suggest that initially alkynylsilanes (or alkynylgermanes) form a π-complex with the Lewis acidic diisobutylaluminum hydride. Subsequent attack by R_2AlH from the opposite side leads to *trans*-hydralumination (VIII). In the presence of an amine the alane forms a complex ($R'_2AlH{-}NR''_3$) which attacks the alkynylsilane in a nucleophilic fashion (IX).

The alternative mechanistic possibility, that *trans*-hydralumination of alkynylsilanes by diisobutylaluminum hydride results from initial nucleophilic attack



VIII



IX

by hydride, is disfavored by the following experiment. When IIa was treated with a recognized hydride source, namely lithium aluminum hydride, only silicon–carbon cleavage leading to phenylacetylene resulted.

The change in the orientation and stereochemistry for the hydralumination of the silyl and germyl derivatives of Ia, compared with that of the carbon analog VII, may be related to differences in the polarization of the C≡C bond. The shift of the C≡C stretch in these alkynyl-silanes[13] and -germanes to higher frequencies (*ca.* 2160 cm^{-1}) and the enhanced intensity of this absorption can be interpreted in terms of dative bonding (d_π–p_π) in the ground state[13]*: $R''_3E{-}C{\equiv}C{-}R \leftrightarrow R''_3E{-}\bar{C}{=}\overset{+}{C}{-}R$. We now suggest that such polarization is also operative in the transition state of hydralumination of silyl- and germyl-alkynes, thereby promoting π-complex formation (VIII) and directing the orientation of the R'_2Al group to the carbon adjacent to the R''_3E group (VIII and IX).

Additional studies in progress promise to elucidate the mechanisms of hydrometallations under various conditions, and to provide flexible methods for the stereospecific reduction of alkynes and the preparation of vinyl derivatives.

We wish to express our appreciation to the Public Health Service for support of this research under Grant GM-13421.

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1 G. WILKE AND H. MÜLLER, *Chem. Ber.*, 89 (1956) 444.
2 J. J. EISCH AND W. C. KASKA, *J. Amer. Chem. Soc.*, 88 (1966) 2213.
3 H. C. BROWN AND G. ZWEIFEL, *J. Amer. Chem. Soc.*, 81 (1959) 1512.
4 J. J. EISCH AND M. W. FOXTON, *Amer. Chem. Soc. Maryland Meeting-in-Miniature, May 5, 1967, Baltimore, Md.; Third Intern. Symp. on Organometallic Chemistry, Sept. 1, 1967, Munich (Germany).*
5 L. H. SLAUGH, personnel communication.
6 G. ZWEIFEL AND R. STEELE, *J. Amer. Chem. Soc.*, 89 (1967) 5085.
7 R. SUMMITT, J. J. EISCH, J. T. TRAINOR AND M. T. ROGERS, *J. Phys. Chem.*, 67 (1963) 2362.
8 W. J. POTTS AND R. A. NYQUIST, *Spectrochim. Acta*, 15 (1959) 679.
9 G. WILKE AND H. MÜLLER, *Ann. Chem.*, 618 (1958) 267.
10 A. D. PETROV, L. L. SHCHUKOVAKAYA AND YU P. EGOROV, *Doklady Akad. Nauk SSSR*, 93 (1953) 293.
11 E. G. HOFFMANN AND G. SCHOMBURG, *Z. Elektrochem.*, 61 (1957) 1101, 1110.
12 J. J. EISCH, C. K. HORDIS, *152nd Amer. Chem. Soc. Meeting Abstr., New York, Sept. 13, 1966*, p. S-68.
13 R. WEST AND C. S. KRAIHANZEL, *Inorg. Chem.*, 1 (1962) 967.
14 J. J. EISCH AND J. T. TRAINOR, *J. Org. Chem.*, 28 (1963) 487.

Received September 29th, 1967

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* *Cf.* Ref. 14 for a study of dative bonding in vinylsilanes.