was separated and dried with KOH pellets. To this solution was added 50 ml (0.52 mol) of ethyl vinyl ether, and the mixture was kept in the dark at room temperature. A small sample was withdrawn after 27 days and submitted for GC–MS. Conditions were 3% OV-101, 3 mm i.d. by 8 ft, column and injector block at 60 °C. Only two sharp, well-separated peaks were seen, solvent and product, with <1% of anything else. The MS of early, middle, and late portions of the product peak were all identical with that of pure II; thus the peak was homogeneous.

After 38 days, the yellow color was still strong. The reaction mixture was concentrated to a small volume by slowly distilling through a 5-in. helix-packed column, heating with a water bath at 40–44 °C, overhead temperature 34 °C. The initial distillate was very yellow; the final distillate and pot residue were colorless. The residue was further slowly concentrated to constant weight, 4.82 g (29% based on NMU) at <25 °C, 130 mm pressure. The ir and NMR spectra of the crude product were identical with those of pure II.

Samples were distilled at 120 °C (130 mm) and 27 °C (0.2 mm), giving pure II in both cases in >81% yield from crude. Thus the overall yield from NMU to pure II was >24%. Anal. Calcd: C, 52.6; H, 8.77; N, 24.6. Found: C, 52.6; H, 8.56; N, 24.9. ^{1}H NMR ($CDCl_3$) δ 1.31 t, J = 7 Hz, CH_3; 1.30 m, 1.90 m, 4-CH_2; 4.1 m, CH_2O; 4.0 m, 5-CH_a; 4.65 m, J = 17.5, 9.1, 4.0, 1.7 Hz,[21] 5-CH_b; 5.47 m, J = 7.8, 6.3, 1.5 Hz,[21] 3-CH. Integrals (mm, from a T-60 spectrum): CH_3 and 4-CH_a, 39; 4-CH_b, 12; CH_2O and 5-CH_2, 42; 3-CH, 9. The ^{1}H NMR spectrum is provided (Figure 1), as it is complex; further scan to δ 11.6 shows nothing more. ^{13}C NMR ($CDCl_3$) 113.4 d, J = 156 Hz, C-3; 75.0 t, J = 144 Hz, C-5; 66.4 t, J = 141 Hz, and 15.5 q, J = 127 Hz, ethyl group; 23.9 ppm t, J = 134 Hz, C-4. The ir has a weak band and the Raman a strong one at 1552 cm^{-1}, N=N stretch; other peaks are in accord with II. MS *m/e* 114 weak, 86 strong, 57, 58 very strong.

In another experiment, ca. 0.3 g (7.13 mmol) of diazomethane was prepared from 2.15 g of Diazald with 0.5 g of KOH in 0.8 ml of H_2O and 2.5 ml of EtOH, distilling with 24 ml of ether. To the distillate was added 6.8 ml (71.3 mmol) of ethyl vinyl ether, total volume 27.5 ml. Half of this was diluted to 25 ml with ether, and the other half to 25 ml with acetonitrile. Both solutions were kept in the dark at room temperature for 2 weeks. Over this period there was no noticeable difference between them in color.

Acknowledgment. Although much invaluable assistance was received from several of Merck's analytical experts, a special debt is owed to Dr. Byron H. Arison for his definitive interpretation of the ^{1}H NMR and ^{13}C NMR spectra.

Registry No.—II, 58832-35-2; ethyl vinyl ether, 109-92-9; diazomethane, 334-88-3.

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Stereospecific Reductive Alkylation of Acetylenes by Successive Hydralumination and Carbodemetalation[1]

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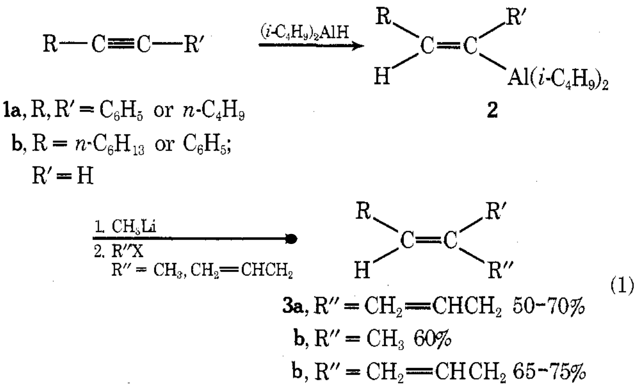
The widespread natural occurrence of substituted olefinic groups having a preferred geometrical configuration, such as those in terpenes, antibiotics, and pheromones, has stimulated the search for stereospecific olefin syntheses.[2] We wish to present here a potentially general and flexible method that is based on the stereospecific cis hydralumination of acetylenes[3] and the alkylation of the aluminate complexes[4] of the resulting vinylalanes (eq 1).[5]



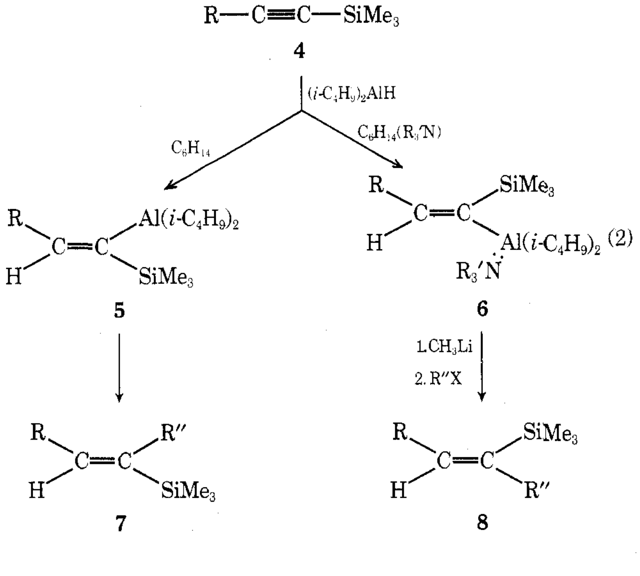
1a, R, R' = C_6H_5 or n-C_4H_9
b, R = n-C_6H_{13} or C_6H_5; R' = H

2

3a, R'' = CH_2=$CHCH_2$ 50–70%
b, R'' = CH_3 60%
b, R'' = CH_2=$CHCH_2$ 65–75%

The direct hydralumination of mono- or disubstituted acetylenes (eq 1) provides a convenient and direct route to stereoregular di- and trisubstituted olefins, respectively. Drawbacks lie in (1) the slow rate with which certain disubstituted acetylenes hydraluminate;[7] (2) the regioisomeric mixtures resulting when R ≠ R';[3a,6b,7] and (3) the contamination of **2** with small amounts of R—C≡C—AlR_2' formed from the metalation of terminal alkynes by aluminum alkyls.[8] This method appears feasible, however, for symmetrical or terminal acetylenes and for reactive alkylating agents, such as methyl iodide and allylic or benzylic halides.

Since the trimethylsilyl derivatives of monosubstituted acetylenes can be hydraluminated selectively in a cis or trans manner (by conducting the addition in the presence or absence of a Lewis base[6]), this same alkylation method can lead to the stereospecific synthesis of either the *Z* or the *E* alkenylsilane[5] (eq 2).



4

5

6

7

8

Hydralumination of the trimethylsilyl derivative of terminal acetylenes, followed by complexation of the vinylalane with methyllithium and subsequent alkylation, has several advantages over direct reaction, as in eq 1. First of all, no metalative displacement of the silicon occurs and hence no $R{-}C{\equiv}C{-}AlR_2'$ is formed. Secondly, the silyl group activates the triple bond to hydralumination[7] and no regioisomers are formed.[6a] Thirdly, the cis or trans nature of the adduct (**5** or **6**) can be almost exclusively determined by use of a donor cosolvent. Fourthly, the silyl group in **7** or **8** can be quantitatively and stereospecifically removed by acid, with retention of configuration,[9] to yield *Z*- or *E*-disubstituted olefins, respectively. Finally, such silyl derivatives can also be stereospecifically bromodesilylated[10] to provide stereoregular vinylic bromides. The latter could be alkylated, for example, with π-allylic nickel reagents,[11] to form heterotrisubstituted olefins stereospecifically.

Our present drawback in the alkylation of the cis adduct of the silyl derivative is the yield: allyl iodide must be used at 25 °C to avoid partial loss of configuration, but the yield of **8** is ca. 40%. If allyl bromide is used, the mixture must be heated. A yield of allyl product >80% is then obtained, but, where $R = C_6H_5$, the product is an 80:20 mixture of **8**:**7**. Further variations in the solvent and the Lewis base may remove this difficulty.

Experimental Section

Procedures and techniques for conducting the following hydraluminations and related organometallic reactions under a nitrogen atmosphere were those described previously.[3a,6,7] The preparation and hydralumination of diphenylacetylene,[3a] phenylethynyl(trimethyl)silane,[6a] and 1- and 4-octynes[7] have already been reported. All starting acetylenes and halides, as well as reaction solvents, were dried and distilled under a nitrogen atmosphere before use.

Three typical experimental procedures will convey the ease of the transformation.

1,4(*E*)-Undecadiene. A solution of 9 mmol of 1-octyne in 20 ml of hexane was treated with 10 mmol of $(i\text{-}C_4H_9)_2AlH$ in 15 ml of hexane over a 30-min period. After several hours 9 mmol of CH_3Li in ethyl ether and 35 ml of THF were added, followed by 11 mmol of allyl bromide. After reflux overnight hydrolytic workup and distillation provided 68% of the olefin [bp 37–38 °C (0.2 mm)]: NMR (neat, internal Me_4Si, δ scale) 5.25–6.10 (br m, 3 H), 4.63–5.20 (m, 2 H), 2.5–2.9 (m, 2 H), 1.75–2.25 (m, 2 H), 1.07–1.65 (br s, 6 H), and 0.6–1.0 (m, 3 H); ir (neat) sharp bands 915 and 990 ($CH{=}CH_2$) and 970 cm^{-1} (trans $CH{=}CH$).

(*E*)-1-Phenyl-2-trimethylsilyl-1,4-pentadiene.[12] Treatment of 3 mmol of phenylethynyl(trimethyl)silane with 3 mmol of $(i\text{-}C_4H_9)_2AlH$ in 20 ml of hexane, stirring for 4 h, and then the successive addition of 3 mmol of CH_3Li in ether, 15 ml of THF, and 3.5 mmol of allyl bromide gave a solution that was heated at reflux overnight. Hydrolytic workup and distillation gave 90% of the product, bp 72–73 °C (0.2 mm).

(*Z*)-1-Phenyl-2-trimethylsilyl-1,4-pentadiene.[12] As in the foregoing, 3 mmol of the silane was treated with 3 mmol of $(i\text{-}C_4H_9)_2AlH$, but here the hydride also contained 3 mmol of *N*-methylpyrrolidine. After heating at 55 °C for several hours, the flask was cooled and treated successively with 3 mmol of CH_3Li in ether, 30 ml of THF, and 6 mmol of allyl iodide. After standing at room temperature for 36 h a GLC analysis showed ca. 40% yield of product, which was separated by preparative GC. This isomer possessed an NMR spectrum [0.0, s, Me_3Si; 3.05, m with d ($J = 7.0$ Hz), CH_2; 5.1, m, $={CH_2}$; 5.6–6.4, m, $CH{=}$; 7.28, s, aromatic + 1 H] different from that of the *E* isomer [0.2, s, Me_3Si; 3.05, m with d ($J = 5.5$ Hz), CH_2; 5.0, m, appearing as d ($J = 13$ Hz); 5.56–6.12, m, $CH{=}$; 6.85, s, vinyl H; 7.15, s, aromatic].

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Registry No.—**1b** ($R = C_6H_{13}$), 629-05-0; **3b** ($R = C_6H_{13}$, $R'' = CH_2{=}CHCH_2$), 55976-13-1; **4** ($R = C_6H_5$), 2170-06-1; **7** ($R = C_6H_5$; $R'' = CH_2{=}CHCH_2$), 58784-44-4; **8** ($R = C_6H_5$; $R'' = CH_2{=}CHCH_2$), 58784-45-5; $(i\text{-}C_4H_9)_2AlH$, 1191-15-7; allyl bromide, 106-95-6.

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(13) The authors appreciate the willingness of Dr. Kiitiro Utimoto of Kyoto University to have our work published simultaneously with his.

Stereospecific 1,2-Dialkylvinylsilane Synthesis via Reductive Alkylation of Trialkylsilylacetylene

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Recent progress of desilylative transformation has rendered vinylsilanes of even more importance as a synthetic intermediate leading to ketones and olefins as well as vinyl halides of rigorous stereochemistry.[1] We describe herein a novel procedure for the stereoselective synthesis of the *E* or *Z* isomer of 1-alkyl-1-trialkylsilyl-1-octene which utilizes reductive alkylation of 1-trimethylsilyl- or 1-triethylsilyl-1-octyne. This unprecedented procedure is a key for the selective synthesis of 1,2-dialkylvinylsilanes.[2]

Reaction of 1-trimethylsilyl-1-octyne (I) with diisobutylaluminum hydride in heptane afforded a mixture of diisobutyl[1-trimethylsilyl-1-(*Z*)-octenyl]aluminum (II) and the *E* isomer.[3] Treatment of the reaction mixture with methyllithium and then with methyl iodide at room temperature afforded a mixture of 2-trimethylsilyl-2(*Z*)-nonene (III, $R = CH_3$) and the *E* isomer. The isomer ratio was dependent upon the hydralumination conditions and was not affected by the alkylation conditions. Remarkably, however, 2-triethylsilyl-2(*E*)-nonene (VI) was obtained in 68% yield (*E*:*Z* 93:7) from the reaction of the triethylsilylacetylene IV proceeding via V.[5] These results suggest following: (1) the primary cis adduct[6] isomerizes to give a thermally equilibrated (*E*, *Z*) mixture; (2) the bulky triethylsilyl group influences the equilibrium so as to favor the *E* isomer (V) as anticipated from the reported cases;[4] and (3) alkylation of the ate complex is