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].

Acknowledgment. The authors are grateful to the Public Health Service for support of this research by Grant GM-20304.[13]

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.

References and Notes

(1) (a) Part 35 of the series "Organometallic Compounds of Group III", devoted to carbometalation and hydrometalation. Previous part: J. J. Eisch, N. E. Burlinson, and M. Boleslawski, *J. Organomet. Chem.*, in press. (b) Results drawn, in part, from the Master of Arts Thesis of G. A. Damasevitz, accepted by the State University of New York at Binghamton in May 1975.

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(3) (a) J. J. Eisch and W. C. Kaska, *J. Am. Chem. Soc.*, **88,** 2213 (1966); (b) G. Wilke and H. Müller, *Justus Liebigs Ann. Chem.*, **629,** 222 (1960).

(4) (a) G. Zweifel and R. B. Steele, *J. Am. Chem. Soc.*, **89,** 2754 (1967); (b) K. F. Bernadry and M. J. Weiss, *Tetrahedron Lett.*, 4083 (1972), have successfully used such lithium *trans*-1-alkenylalanates to add a vinylic group to the β position of 2-(6-carbethoxylhexyl)-2-cyclopentenone.

(5) All yields are given for the isolated product but the experimental conditions have not yet been varied for optimum yields.

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(9) K. E. Koenig and W. P. Weber, *J. Am. Chem. Soc.*, **95,** 3416 (1973).

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(12) The stereochemistry of these and other *E* and *Z* silylalkenes was assigned by recourse to photochemical isomerization at 254 nm of the *E* isomer into an *E,Z* mixture or by protodesilylation into the known cis- or trans-disubstituted ethylenes. Moreover, NMR data from compounds of known configuration provided chemical shift parameters useful in calculating the expected position of the vinylic protons: C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49,** 164 (1966).

(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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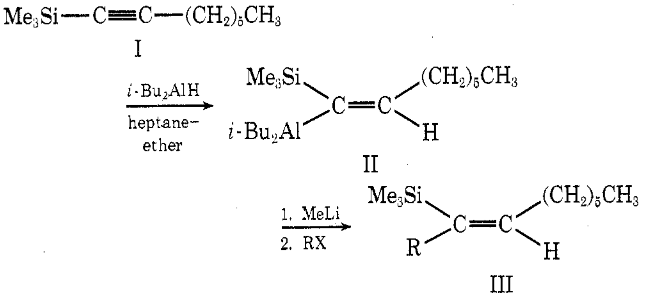
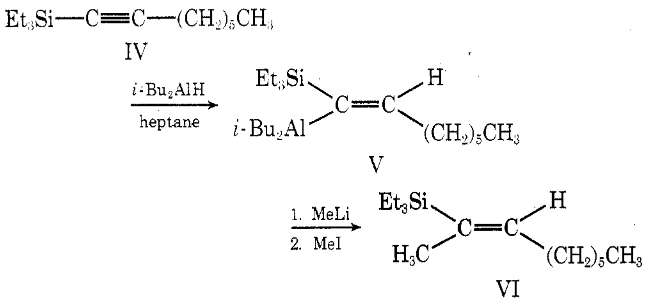
Recent progress of desilylative transformation has rendered vinylsilanes of even more importance as a synthetic intermediate leading to ketones and olefins as well as vinyl halides of rigorous stereochemistry.[1] We describe herein a novel procedure for the stereoselective synthesis of the *E* or *Z* 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





believed to proceed with the strict retention of configuration at the olefinic carbon.[7]

In contrast to the above described cases, hydralumination of I in heptane–ether (1:1) gave stereoselectively 2-trimethylsilyl-2(*Z*)-nonene (III, R = CH_3) in 88% yield (purity > 99%). This result is explained by assuming that ether oxygen coordinates aluminum of the initial product (II) to fix the stereochemistry.[8]

Allyl halides such as allyl chloride, methallyl chloride, and 2,3-dichloropropene afforded analogous allylated products (III, $Z > 99\%$: R = $CH_2CH{=}CH_2$, yield 77%; $CH_2C(CH_3){=}CH_2$, 84; $CH_2CCl{=}CH_2$, 77).[9] On the other hand, such alkyl halides as ethyl iodide and butyl iodide reacted with the ate complex in only poor yield. Irrespective of these limitations, the above described procedure for reductive alkylation of 1-trialkylsilyl-1-alkynes promises general utility for stereospecific synthesis of alkenylsilanes.

A strictly selective synthesis of 1,4(*E*)-undecadiene[10] is illustrating the synthetic utility. The previously reported procedure[1d] for exchange of Me_3Si to H proceeded with rigorous retention and therefore 4-trimethylsilyl-1,4(*Z*)-undecadiene (III, R = $CH_2CH{=}CH_2$) was converted into 1,4(*E*)-undecadiene in quantitative yield.

Experimental Section

Infrared spectra were obtained using a Shimadzu IR-27G grating spectrophotometer. NMR spectra were determined on a Varian Associates EM-360 or a JEOL JNM-PMX60 with Me_4Si as internal standard. Mass spectra were measured with a Hitachi RMU-6L spectrometer at a chamber voltage of 70 V.

1-Trimethylsilyl-1-octyne. 1-Trimethylsilyl-1-octyne was prepared from 1-octyne (0.1 mol) by successive treatment with ethylmagnesium bromide (0.11 mol) in THF (reflux for 15 min) and trimethylchlorosilane (0.11 mol, reflux for 1 h) in 88% yield, bp 62–66 °C (15 mm), lit.[11] 98–108 °C (26 mm).

1-Triethylsilyl-1-octyne. Replacement of trimethylchlorosilane by triethylchlorosilane in the above described procedure gave 1-triethylsilyl-1-octyne in 98% yield, bp 86–90 °C (3 mm), lit.[12] 93–94 °C (3 mm).

2-Trimethylsilyl-2(*Z*)-nonene (III, R = CH_3). A. Hydralumination in Heptane. To a heptane solution of diisobutylaluminum hydride (3.3 mmol, 4.2 ml of 0.79 M solution), 1-trimethylsilyl-1-octyne (0.55 g, 3.0 mmol) was added and the resulting mixture was stirred for 16 h at room temperature. The reaction mixture was added with an ether solution of methyllithium (3.3 mmol, 3.9 ml of 0.85 M solution) at 0 °C, stirred for 20 min at 0 °C, and treated with methyl iodide (1.46 g, 10.0 mmol) at room temperature. The whole mixture was stirred at room temperature for 20 h, diluted with ether, and poured onto dilute HCl and crushed ice. After washing ($NaHCO_3$ solution, brine), drying (Na_2SO_4), and evaporation, chromatography of the ethereal extract on silica gel–hexane gave a mixture of silylated hydrocarbons. GLC analysis indicated that 2-trimethylsilyl-2-nonene was obtained in 70% yield (*E* isomer, III, R = CH_3, 74%; *Z* isomer, 26%).

E isomer[13] exhibited ir (neat) 1621, 1250, 837, 751, 691 cm^{-1}; NMR (CCl_4) δ 0.03 (9 H, s), 0.89 (3 H, t, $J = 6$ Hz), 1.1–1.6 (8 H, m), 1.64 (3 H, broad s), 1.8–2.3 (2 H, m), 5.63 (1 H, q-t, $J = 2, 6$ Hz); MS *m/e* (rel intensity) 198 (M^+, 2), 183 (26), 124 (15), 123 (8), 99 (10), 74 (9), 73 (100), 59 (30).

Z isomer (III, R = CH_3): ir (neat) 1621, 1246, 837, 754, 688, 650 cm^{-1}; NMR (CCl_4) δ 0.10 (9 H, s), 0.88 (3 H, t, $J = 6$ Hz), 1.1–1.6 (8 H, m), 1.72 (3 H, broad s), 1.8–2.3 (2 H, m), 5.92 (1 H, q-t, $J = 2, 8$ Hz); MS *m/e* (rel intensity), 198 (M^+, 1), 184 (4), 183 (22), 124 (15), 113 (9), 99 (10), 74 (9), 73 (100), 59 (28). Anal. Calcd for $C_{12}H_{26}Si$: C, 72.64; H, 13.21. Found: C, 72.49; H, 13.21.

B. Hydralumination in Heptane–Ether. To a stirred solution of 3.3 mmol of diisobutylaluminum hydride in heptane (4.1 ml of 0.81 M solution) and 2.0 ml of dry ether, 1-trimethylsilyl-1-octyne (0.55 g, 3.0 mmol) was added at room temperature. The mixture was stirred for 17 h at room temperature, treated with 4.0 ml of methyllithium (0.83 M ethereal solution containing 3.3 mmol of methyllithium) at 0 °C, stirred for 20 min, and then added with 8.0 mmol of methyl iodide at 0 °C. The whole mixture was stirred for 20 h at room temperature and then poured onto crushed ice (HCl). Workup gave a mixture of silylated hydrocarbons [0.55 g, mainly III (R = CH_3) with some contamination of 1-trimethylsilyl-1-octyne, 1-trimethylsilyl-1-octene, and *E* isomer of III], whose GLC showed that 2-trimethylsilyl-2(*Z*)-nonene (III, R = CH_3) was obtained in 88% (containing <1% *E* isomer).

2(*E*)-Nonene. A solution of 2-trimethylsilyl-2(*Z*)-nonene was treated with constant boiling hydriodic acid analogously to the reported procedure.[1d] 2(*E*)-Nonene was obtained in almost quantitative yield.

2-Triethylsilyl-2(*E*)-nonene (VI). Hydralumination of 1-triethylsilyl-1-octyne (IV, 0.45 g, 2.0 mmol) was performed with 2.7 ml of diisobutylaluminum hydride solution (0.81 M in heptane containing 2.2 mmol of diisobutylaluminum hydride) for 20 h at room temperature. Successive treatment with methyllithium (2.8 ml of 0.78 M ethereal solution containing 2.2 mmol of methyllithium) at 0 °C and with methyl iodide (1.42 g, 10 mmol) at 0 °C was followed by hydrolytic workup to give 0.41 g of a mixture of silylated hydrocarbons. GLC analysis of the oil showed that 2-triethylsilyl-2(*E*)-nonene (containing 7% of the *Z* isomer) was obtained in 68% yield: ir (neat) 1618, 1234, 1016, 718 cm^{-1}; NMR (CCl_4) δ 0.3–1.1 (18 H, m), 1.1–1.6 (8 H, m), 1.64 (3 H, broad s), 1.9–2.4 (2 H, m), 5.64 (1 H, q-t, $J = 2, 7$ Hz); MS *m/e* (rel intensity), 240 (M^+, 2), 212 (20), 211 (100), 184 (10), 183 (58), 155 (9), 141 (10), 127 (15), 123 (17), 115 (12), 113 (25), 101 (45), 99 (22), 87 (55), 85 (15), 83 (10), 73 (39), 59 (13). Anal. Calcd for $C_{15}H_{32}Si$: C, 74.91; H, 13.41. Found: C, 74.83; H, 13.64.

4-Trimethylsilyl-1,4(*Z*)-undecadiene (III, R = $CH_2CH{=}CH_2$). Methyl iodide was replaced with allyl chloride in the procedure for the preparation of 2-trimethylsilyl-2(*Z*)-nonene by hydralumination in heptane–ether. GLC analysis of the crude product indicated that 4-trimethylsilyl-1,4(*Z*)-undecadiene (III, R = $CH_2CH{=}CH_2$) was obtained in 77% yield (<1% *E* isomer). Distillation [Kugelrohr, 105–110 °C (2 mm)] gave a pure sample: ir (neat) 3100, 1640, 1614, 1250, 998, 911, 836, 759, 691 cm^{-1}; NMR (CCl_4) δ 0.12 (9 H, s), 0.91 (3 H, t, $J = 6$ Hz), 1.1–1.7 (8 H, m), 1.8–2.4 (2 H, m), 2.8 (2 H, broad d, $J = 6$ Hz), 4.74–5.18 (2 H, m), 5.5–6.0 (1 H, m), 5.97 (1 H, broad t, $J = 8$ Hz); MS *m/e* (rel intensity) 224 (M^+, 2), 209 (2), 150 (5), 125 (9), 74 (10), 73 (100), 59 (22). Anal. Calcd for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 75.09; H, 12.70.

2-Methyl-4-trimethylsilyl-1,4(*Z*)-undecadiene [III, R = $CH_2C(CH_3){=}CH_2$]. Treatment of 0.55 g (3.0 mmol) of 1-trimethylsilyl-1-octyne (I) with 0.54 g (6.0 mmol) of methallyl chloride gave 2-methyl-4-trimethylsilyl-1,4(*Z*)-undecadiene (containing <1% *E* isomer) in 84% yield (GLC). Preparative GLC gave a pure sample: ir (neat) 3100, 1650, 1615, 1250, 891, 837, 758, 690 cm^{-1}; NMR (CCl_4) δ 0.10 (9 H, s), 0.89 (3 H, t, $J = 6$ Hz), 1.1–1.6 (8 H, m), 1.68 (3 H, broad s), 1.9–2.5 (2 H, m), 2.71 (2 H, broad s), 4.67 (2 H, m), 5.90 (1 H, broad t, $J = 7$ Hz); MS *m/e* (rel intensity), 238 (M^+, 3), 223 (3), 164 (12), 74 (10), 73 (100), 59 (20). Anal. Calcd for $C_{15}H_{30}Si$: C, 75.54; H, 12.68. Found: C, 75.30; H, 12.68.

2-Chloro-4-trimethylsilyl-1,4(*Z*)-undecadiene (III, R = $CH_2CCl{=}CH_2$). Reaction with 2,3-dichloropropene gave 2-chloro-4-trimethylsilyl-1,4(*Z*)-undecadiene (<1% *E* isomer) in 77% yield (GLC): ir (neat) 1631, 1615, 1250, 1113, 881, 839, 761, 692 cm^{-1}; NMR (CCl_4) δ 0.14 (9 H, s), 0.90 (3 H, t, $J = 6$ Hz), 1.1–1.7 (8 H, m), 1.9–2.4 (2 H, m), 3.12 (2 H, broad s), 5.03 (1 H, broad s), 5.14 (1 H, broad s), 5.99 (1 H, broad t, $J = 7$ Hz); MS *m/e* (rel intensity), 245 (M − 15, 2), 243 (M − 15, 7), 149 (8), 95 (37), 93 (100), 79 (22), 73 (56). Anal. Calcd for $C_{14}H_{27}ClSi$: C, 64.95; H, 10.51. Found: C, 65.04; H, 10.44.

1,4(*E*)-Undecadiene. A solution of 4-trimethylsilyl-1,4(*Z*)-undecadiene (III, R = $CH_2CH{=}CH_2$, 0.27 g, 1.2 mmol) in 1.2 ml of benzene was treated with constant boiling hydriodic acid (51 μl, 0.60 mmol) at room temperature for 1 h as previously reported procedure.[1d] The reaction mixture was diluted with 20 ml of pentane and quenched with 2 ml of saturated aqueous solution of $NaHCO_3$. The combined pentane extracts were washed (10% $Na_2S_2O_3$), dried (Na_2SO_4), and distilled (Kugelrohr) to afford 183 mg of 1,4(*E*)-undecadiene (quantitative), bp (bath temperature) 120–125 °C (120 mm).

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Registry No.—I, 15719-55-8; III (R = CH_3), 58801-94-8; III (R = CH_3) *E* isomer, 58801-95-9; III (R = $CH_2CH{=}CH_2$), 58801-96-0; III [R = $CH_2C(CH_3){=}CH_2$], 58801-97-1; III (R = $CH_2CCl{=}CH_2$), 58801-98-2; IV, 18408-64-5; VI, 58801-99-3; VI *Z* isomer, 58802-00-9; 1-octyne, 629-05-0; trimethylchlorosilane, 75-77-4; triethylchlorosilane, 994-30-9; methyl iodide, 74-88-4; allyl chloride, 107-05-1; methallyl chloride, 563-47-3; 2,3-dichloropropene, 78-88-6; 1,4(*E*)-undecadiene, 55976-13-1.

References and Notes

(1) (a) G. Stork and M. E. Jung, *J. Am. Chem. Soc.*, **96**, 3682 (1974); (b) G. Stork, M. E. Jung, E. Colvin, and Y. Noel, *ibid.*, **96**, 3684 (1974), and references cited therein; (c) B. Miller and T. Reichenbach, *Tetrahedron Lett.*, 543 (1974); (d) K. Utimoto, M. Kitai, and H. Nozaki, *ibid.*, 2825 (1975), and references cited therein.

(2) Analogous reaction has been studied by J. J. Eisch and G. A. Damasevitz, *J. Org. Chem.*, preceding paper in this issue. We thank Professor Eisch for communicating his results to us in advance of publication.

(3) The aluminum compound was neither isolated nor identified by spectrometry. The reaction mixture was quenched by deuterium oxide affording 1-deuterio-1-trimethylsilyl-1-octene. The regioselectivity is in harmony with the analogous reported case[4] and with the consideration of electronic characteristic of silicon atom.

(4) Hydralumination of trimethylsilylphenylacetylene was studied: (a) J. J. Eisch and M. W. Fixton, *J. Org. Chem.* **36**, 3520 (1971); (b) J. J. Eisch and S.-G. Rhee, *J. Am. Chem. Soc.*, **97**, 4673 (1975), and references cited therein

(5) Quenched with water gave 1-triethylsilyl-1(*E*)-octene (purity 94%).

(6) Hydralumination and isomerization have reviewed: J. J. Eisch, *Ind. Eng. Chem., Prod. Res. Dev.*, **14**, 11 (1975).

(7) The hydralumination product of trimethylsilylphenylacetylene was subjected first to treatment with methyllithium and then with methyl iodide affording (*E*)-1-phenyl-2-trimethylsilylpropene (isolated yield 98%, purity >99%) and analogous reaction with allyl chloride gave 1-phenyl-2-trimethylsilyl-1(*E*),4-pentadiene (isolated yield 98%, purity >99%). These results also suggested the retention of configuration during alkylation.

(8) Lewis bases such as tertiary amines and ethers coordinate to aluminum and prohibit *Z*–*E* isomerization; see also ref 6.

(9) Hydralumination and successive allylation of acetylenes via organocopper compounds were reported.[10]

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(13) Several attempts at obtaining a pure sample was fruitless. A sample obtained by preparative GLC was sufficiently pure for spectral analyses, but not for elemental analyses.

Steric Effects. 7. Additional υ Constants

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We have previously defined[1] and successfully applied[2–7] the υ steric parameters to a number of different reactions and substrates. Thus, it seems to us that the utility of the υ parameters has been established. It therefore seemed useful to determine as many additional υ values as possible. To this end, we have correlated 11 sets of rate constants for esterification and acid-catalyzed ester hydrolysis with the modified Taft equation.

$$\log k_X = \psi \upsilon_X + h \qquad (1)$$

Table I. Data Used in Correlations

29. *k*, $XCO_2H + EtOH$ in EtOH at 25 °C, catalyzed by HCl[a]
i-Pr, 0.156; *sec*-Bu, 0.038; Et_2CH, 0.0031; c-C_6H_{11}, 0.081
30. *k*, $XCO_2H + EtOH$ in EtOH at 25 °C catalyzed by HCl[b]
Bu, 0.268; $BuCH_2$, 0.267; $C_2H_3CH_2CH_2$, 0.274; $PhCH_2CH_2$, 0.321; *i*-Bu, 0.0518; *i*-$BuCH_2$, 0.247; Pr_2CH, 0.00285; c-$C_6H_{11}CH_2$, 0.0809; c-$C_6H_{11}CH_2CH_2$, 0.141; Et, 0.550; *i*-Pr, 0.156; Pr, 0.270
31. *k*, $XCO_2H + MeOH$ in equimolar MeOH–H_2O at 15 °C catalyzed by HCl[c]
H, 0.128; Me, 0.00955; Et, 0.00965; Pr, 0.00531; Bu, 0.00567; $BuCH_2$, 0.00532; $BuCH_2CH_2$, 0.00544; CH_2OH, 0.00723
32. *k*, $XCO_2H + MeOH$ in equimolar MeOH + H_2O at 25 °C, catalyzed by HCl[c]
H, 0.273; Me, 0.0221; Et, 0.0221; Pr, 0.0122; Bu, 0.0133; $BuCH_2$, 0.0134; $BuCH_2CH_2$, 0.0125; CH_2OH, 0.0181; $EtOCH_2$, 0.00954; $EtSCH_2$, 0.00872; $ClCH_2$, 0.0101
33. *k*, $XCO_2H + MeOH$ in equimolar MeOH–H_2O at 35 °C catalyzed by HCl[c]
H, 0.603; Me, 0.0484; Et, 0.0493; Pr, 0.0274; Bu, 0.0294; $BuCH_2$, 0.0295; $BuCH_2CH_2$, 0.0272; CH_2OH, 0.0409
34. *k*, $XCO_2Me + H_2O$ in equimolar MeOH–H_2O at 15 °C catalyzed by HCl[c]
H, 0.0347; Me, 0.00169; Et, 0.00167; Pr, 0.00094; Bu, 0.00106; $BuCH_2$, 0.00100; $BuCH_2CH_2$, 0.00087; CH_2OH, 0.00205
35. *k*, $XCO_2Me + H_2O$ in equimolar MeOH–H_2O at 25 °C catalyzed by HCl[c]
H, 0.0810; Me, 0.00445; Et, 0.00423; Pr, 0.00239; Bu, 0.00254; $BuCH_2$, 0.00249; $BuCH_2CH_2$, 0.00225; CH_2OH, 0.0056; $EtOCH_2$, 0.00302; $EtSCH_2$, 0.00228; $ClCH_2$, 0.00356
36. *k*, $XCO_2Me + H_2O$ in equimolar MeOH–H_2O at 35 °C catalyzed by HCl[c]
H, 0.193; Me, 0.0102; Et, 0.00985; Pr, 0.00563; Bu, 0.00617; $BuCH_2$, 0.00595; $BuCH_2CH_2$, 0.00541; CH_2OH, 0.0133
37. *k*, $XCO_2Me + H_2O$ in H_2O at 25 °C catalyzed by HCl[d]
Pr, 0.00423; Bu, 0.00441; $BuCH_2$, 0.00410; $BuCH_2CH_2$, 0.00412; *i*-Bu, 0.00151; *sec*-Bu, 0.00138; *t*-Bu, 0.000709
38. *k*, $XCO_2H + MeOH$ in MeOH at 60.0 °C catalyzed by TsOH[e]
Me, 22.1; $PhCH_2$, 9.43; Ph_2CH, 0.825
39. *k*, $XCO_2Et + H_3O^+$ in 70% MeAc–H_2O (v/v) at 25 °C[f]
Me, 4.30; CH_2Cl, 2.65; $PhCH_2$, 1.50

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The data used in the correlations are set forth in Table I. Results of the correlations are reported in Table II. The υ constants required for correlation with eq 1 are taken from the first paper in this series[1] or from this work.

Of the 11 sets correlated with eq 1, nine gave excellent, one gave very good, and one gave good results. The two sets which did not give excellent correlations (as determined by the confidence level of the *F* test) had only three points. We believe that these sets are useful for the calculation of new υ values. Of the six sets, 31–36, the best results were obtained with set 35, which was therefore chosen for the calculation of new υ values. In Table III new υ values are presented, with the set from which they were calculated. Set numbers less than 29 refer to the first paper of this series.[1]

It is now possible to draw certain conclusions regarding structural effects upon υ values.

A comparison of υRCHOH with υRCHMe shows (Table IV) that when R is alkyl there is a considerable decrease in υ for the oxygen containing groups. In the case of the substitution of OMe for Et, a comparison of υRCHOMe with υRCHEt