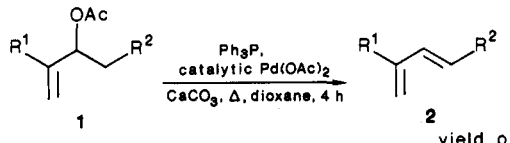
Scheme I



	yield of 2, %
a: $R^1 = CH_3$; $R^2 = CH_2CH(OCH_2CH_2CH_2O)$	91
b: $R^1 = CH_2CH_3$; $R^2 = CH_2CH(OCH_2CH_2CH_2O)$	96
c: $R^1 = CH_3$; $R^2 = (CH_2)_2CH_3$	73
d: $R^1 = CH_2CH_3$; $R^2 = (CH_2)_2CH_3$	81
e: $R^1 = CH_3$; $R^2 = CH_2Ph$	77
f: $R^1 = CH_2CH_3$; $R^2 = CH_2Ph$	71
g: $R^1 = CH_3$; $R^2 = CH_2CH_2SPh$	91
h: $R^1 = CH_2CH_3$; $R^2 = CH_2CH_2SPh$	78

a general, high-yield route for selective syntheses of *E* isomers of 1,3-disubstituted dienes. The reaction conditions are mild and compatible with a variety of functional groups elsewhere in the molecule. Currently, we are applying these results to other synthetic work, which will be reported shortly.

Experimental Section

General Procedures. A magnetically stirred mixture of the allyl acetate 1 (36 mmol), palladium acetate (0.4 mmol), calcium carbonate (40 mmol), and triphenylphosphine (4 mmol) in dioxane (15 mL) was heated at reflux. The progress of the reaction was followed by GLC and was usually complete in 4 h. The bright yellow mixture[8] was cooled and then filtered, and the precipitate was washed with ether (3 × 5 mL). Ether (20 mL) was added to the filtrate, and the organic layer was separated and washed successively with saturated bicarbonate (2 × 10 mL) and water (10 mL). The solution was dried ($MgSO_4$), filtered, and evaporated at reduced pressure. Distillation of the residue furnished the pure (*E*)-1,3-diene **2**.

(*E*)-2-(4-Methylene-2-pentenyl)-1,3-dioxane (2a). The diene **2a**, prepared from the allyl acetate **1a** in 91% yield, had bp 45–46 °C (0.15 mm): ^{1}H NMR ($CDCl_3$) δ 1.34 (m, 1 H, OCH_2CH), 1.84 (s, 3 H, CH_3), 2.10 (m, 1 H, OCH_2CH), 2.43 (dd, 2 H, *J* = 6.6 and 5.5 Hz, CH_2), 3.77 (dt, 2 H, *J* = 12.6 and 2.2 Hz, OCHH), 4.12 (dd, 2 H, *J* = 11.4 and 5.3 Hz, CHH), 4.57 (t, 1 H, *J* = 5.5 Hz, CH), 4.90 (s, 2 H, $=CH_2$), 5.65 (dt, 1 H, *J* = 15.5 and 6.6 Hz, =CH), 6.21 (d, 1 H, *J* = 15.5 Hz, =CH); MS, *m/z* 168 (M^+).

(*E*)-2-(Methylene-2-hexenyl)-1,3-dioxane (2b). The diene **2b**, prepared from the allyl acetate **1b** in 96% yield, had bp 80–81 °C (0.25 mm): ^{1}H NMR ($CDCl_3$) δ 1.08 (t, 3 H, *J* = 7 Hz, CH_3), 2.05 (m, 2 H, CHH), 2.20 (q, 2 H, *J* = 7 Hz, CH_2), 2.41 (dd, 2 H, *J* = 5.9 and 6.4 Hz, CH_2), 3.76 (m, 2 H, OCHH), 4.10 (m, 2 H, OCHH), 4.56 (t, 1 H, *J* = 5.5 Hz, CH), 4.91 (s, 2 H, $=CH_2$), 5.70 (dt, 1 H, *J* = 16 and 6.5 Hz, =CH), 6.16 (d, 1 H, *J* = 16 Hz, =CH); MS, *m/z* 182 (M^+).

(*E*)-2-Methyl-1,3-heptadiene (2c). The diene **2c**, prepared from the allyl acetate **1c** in 73% yield, had bp 54 °C (59 mm): ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3 H, *J* = 7 Hz, CH_3), 1.43 (m, 2 H, CH_2), 1.84 (s, 3 H, CH_3), 2.08 (q, 2 H, *J* = 7 Hz, CH_2), 4.86 (s, 2 H, $=CH_2$), 5.66 (dt, 1 H, *J* = 15.6 and 7 Hz, =CH), 6.14 (d, 1 H, *J* = 15.6 Hz, =CH).

(*E*)-2-Ethyl-1,3-heptadiene (2d). The diene **2d**, prepared from the allyl acetate **1d** in 81% yield, had bp 62 °C (37 mm): ^{1}H NMR ($CDCl_3$) δ 0.91 (t, 3 H, *J* = 7 Hz, CH_3), 1.09 (t, 3 H, *J* = 7 Hz, CH_3), 1.42 (m, 2 H, CH_2), 2.05 (q, 2 H, *J* = 7 Hz), 2.21 (q, 2 H, *J* = 7 Hz, CH_2), 4.87 (s, 2 H, $=CH_2$), 5.71 (dt, 1 H, *J* = 15.6 and 7 Hz, =CH), 6.08 (d, 1 H, *J* = 15.6 Hz, =CH).

(*E*)-2-Methyl-5-phenyl-1,3-pentadiene (2e). The diene **2e**, prepared from the allyl acetate **1e** in 77% yield, had bp 38 °C (0.12 mm): ^{1}H NMR ($CDCl_3$) δ 1.83 (s, 3 H, CH_3), 3.45 (d, 2 H, *J* = 6.8 Hz, CH_2), 4.91 (s, 2 H, $=CH_2$), 5.80 (dt, 1 H, *J* = 15.6 and 6.8 Hz, =CH), 6.22 (d, 1 H, *J* = 15.6 Hz, =CH), 7.18–7.33 (m, 5 H, Ar H).

(*E*)-2-Ethyl-5-phenyl-1,3-pentadiene (2f). The diene **2f**, prepared from the allyl acetate **1f** in 71% yield, had bp 54 °C (0.1 mm): ^{1}H NMR ($CDCl_3$) δ 1.08 (t, 3 H, *J* = 6.9 Hz, CH_3), 2.21 (q, 2 H, *J* = 6.9 Hz, CH_2), 3.44 (d, 2 H, *J* = 6.9 Hz, CH_2), 4.92 (s, 2 H, $=CH_2$), 5.84 (dt, 1 H, *J* = 15.6 and 6.9 Hz, =CH), 6.16 (d, 1 H, *J* = 15.6 Hz, =CH), 7.18–7.32 (m, 5 H, Ar H).

(*E*)-2-Methyl-6-(phenylthio)-1,3-hexadiene (2g). The diene **2g**, prepared from the allyl acetate **1g** in 91% yield, had bp 90 °C (0.1 mm): ^{1}H NMR ($CDCl_3$) δ 1.81 (s, 3 H, CH_3), 2.46 (dt, 2 H, *J* = 7.5 and 7 Hz, CH_2), 2.99 (t, 2 H, *J* = 7.5 Hz, CH_2S), 4.90 (s, 2 H, $=CH_2$), 5.66 (dt, 1 H, *J* = 15.6 and 7 Hz, =CH), 6.18 (d, 1 H, *J* = 15.6 Hz, =CH), 7.15–7.36 (m, 5 H, Ar H).

(*E*)-2-Ethyl-6-(phenylthio)-1,3-hexadiene (2h). The diene **2h**, prepared from the allyl acetate **1h** in 78% yield, had bp 97 °C (0.14 mm): ^{1}H NMR ($CDCl_3$) δ 1.08 (t, 3 H, *J* = 7.2 Hz, CH_3), 2.19 (q, 2 H, *J* = 7.2 Hz, CH_2), 2.44 (dt, 2 H, *J* = 7.5 and 6.6 Hz, CH_2), 3.00 (t, 2 H, *J* = 7.5, CH_2S), 4.91 (s, 2 H, $=CH_2$), 5.72 (dt, 1 H, *J* = 15.6 and 6.6 Hz, =CH), 6.13 (d, 1 H, *J* = 15.6 Hz, =CH), 7.17–7.36 (m, 5 H, Ar H).

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(8) Red solutions were obtained with the sulfur compounds **1g** and **1h**.

Convenient Alternative Approach to 2-(Acetoxymethyl)-3-(trimethylsilyl)propene

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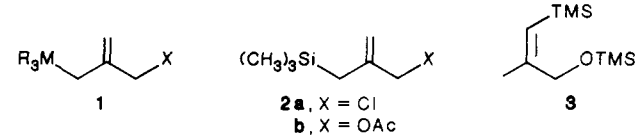
Bifunctional conjunctive reagents like **1** which possess both nucleophilic and electrophilic centers are useful annulating agents.[1] The silicon derivatives **2** have proven to be especially valuable in metal-catalyzed cycloaddition.



The preparation of **2** by metalation of methallyl alcohol is very direct, but always produces some amount of an alternative product **3** which relates to the amount of hexane present during the metalation step.[2] We report an alternative approach that produces these silicon bifunctional conjunctive reagents free of any isomeric contaminants.

We previously noted a sharp rate retardation for S_N2 displacements with compounds of general structure **2**

(1) For some illustrative examples, see: Trost, B. M. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1. Cossy, J.; Belotti, D.; Pete, J. P. *Tetrahedron Lett.* **1987**, *28*, 4547. vanderLouw, J.; vanderBaan, J. L.; Bickelhaupt, F.; Klumpp, G. W. *Tetrahedron Lett.* **1987**, *28*, 2889. Molander, G. A.; Schubert, D. C. *J. Am. Chem. Soc.* **1987**, *109*, 6877; **1986**, *108*, 4683. Heathcock, C. H.; Smith, K. M.; Blumenkopf, T. A. *J. Am. Chem. Soc.* **1986**, *108*, 5023. Molander, G. A.; Andrews, S. W. *Tetrahedron Lett.* **1986**, *27*, 3115. Jones, M. D.; Kemmitt, R. D. W. *J. Chem. Soc., Chem. Commun.* **1986**, 1201. Molander, G. A.; Shubert, D. C. *Tetrahedron Lett.* **1986**, *27*, 787. Jones, M. D.; Kemmitt, R. D. W. *J. Chem. Soc., Dalton Trans.* **1986**, 1411. Baker, R.; Keen, R. B. *J. Organomet. Chem.* **1985**, *285*, 419. Tiner-Harding, T.; Ullrich, J. W.; Chiu, F.-T.; Chen, S. F.; Mariano, P. S. *J. Org. Chem.* **1982**, *47*, 3360. Trost, B. M.; Adams, B. R. *J. Am. Chem. Soc.* **1983**, *105*, 4849. Trost, B. M.; Vincent, J. E. *J. Am. Chem. Soc.* **1980**, *102*, 5680. Knapp, S.; O'Connor, V.; Mobilio, D. *Tetrahedron Lett.* **1980**, *21*, 4557.

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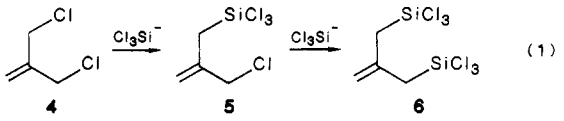
0022-3263/88/1953-4887$01.50/0

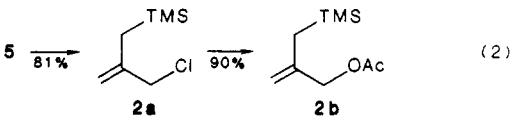
compared to the corresponding methallyl analogue.[3] This observation suggests that there may be a significant rate difference between the first and second alkylations with the bifunctional allylating agent 2-(chloromethyl)-3-chloropropene (eq 1). Indeed, reacting the dichloride **4**



4 5 6 (1)

with 1.25 equiv of trichlorosilane in the presence of triethylamine and cuprous chloride in ether[4] smoothly gives the monosilyl compound **5** in yields as high as 97% although a yield of distilled material of approximately 60% is more common. The disubstitution product **6**, which forms upon using 2.1 equiv of trichlorosilane under otherwise identical conditions,[5] does not form to a detectable extent.

Reaction of the trichlorosilane **5** with 3.5 equiv of commercially available methylmagnesium bromide in ether at −78 °C provides the chloro bifunctional conjunctive reagent **2a** (eq 2). Since the chloride **2a** requires the presence of



2a **2b** (2)

acetate ion to participate in palladium-catalyzed cycloadditions,[6] the acetoxy analogue **2b**, which also is much more chemically stable than the chloride for storage, is the preferred reagent. Warming (55–60 °C) of a DMF solution of **2a** with potassium acetate effects virtually quantitative substitution to give the bifunctional conjunctive reagent **2b** completely pure. This three-step process provides the useful bifunctional conjunctive reagent in 43% overall yield from commercially available materials.

Experimental Section

2-(Chloromethyl)-3-(trichlorosilyl)propene. A solution of freshly distilled trichlorosilane (27.09 g, 20 mL, 0.2 mol) and 3-chloro-2-(chloromethyl)propene (20 g, 18.6 mL, 0.16 mol) in anhydrous ether (50 mL) was added dropwise to a mechanically stirred green solution–suspension of cuprous chloride (0.158 g, 1.6 mmol) and triethylamine (20.22 g, 28 mL, 0.2 mol) in anhydrous ether (300 mL) over a period of 4 h. The reaction mixture was stirred at room temperature for 14 h and then filtered under argon. Ether was removed by distillation at atmospheric pressure. The residue was fractionally distilled at reduced pressure by using a 15-cm Vigreux column, affording 21.83 g (61%) of product, bp 50–54 °C at 2 mmHg (lit.[7] bp 78 °C at 10 mmHg): ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.3 (s, 1 H), 5.1 (s, 1 H), 4.1 (s, 2 H), 2.6 (s, 2 H).

2-(Chloromethyl)-3-(trimethylsilyl)propene. To a −78 °C solution of 2-(chloromethyl)-3-(trichlorosilyl)propene (35 g, 0.156 mol) in anhydrous ether (700 mL) was added dropwise a solution of methylmagnesium bromide in ether (183 mL of a 3 M solution, 0.55 mol). The reaction mixture was stirred at −78 °C for 1 h and then at room temperature for 10 h. The reaction mixture was poured slowly into an ice-cooled solution of saturated aqueous ammonium chloride (~500 mL), the ether layer separated, and the resulting aqueous solution again extracted with ether (~200 mL). The combined ether layers were washed with brine (~300 mL) and dried ($MgSO_4$). The mixture was filtered and the ether removed by rotatory evaporator using a 0 °C ice-cooled bath to afford 23.29 g of crude product as a pale yellow oil, which was fractionally distilled through a 15-cm Vigreux column under reduced pressure using a water aspirator at 45–50 °C, affording 20.41 g (81%) of a colorless oil. Distillation may also be performed at 158 °C at atmospheric pressure (lit.[8] bp 162–163 °C at 768 mmHg): ^{1}H NMR (60 MHz, $CDCl_3$) δ 5.0–5.1 (m, 1 H), 4.9–4.8 (m, 1 H), 4.0 (s, 2 H), 0.1 (s, 9 H).

2-(Acetoxymethyl)-3-(trimethylsilyl)propene. A mixture of 2-(chloromethyl)-3-(trimethylsilyl)propene (20.4 g, 0.125 mol) and potassium acetate (49 g, 0.5 mol) in 200 mL of dry DMF was heated at 55–60 °C for 48 h. After being cooled to room temperature, the reaction mixture was poured into water (~500 mL) and extracted twice with ether (~300 mL × 2). The combined ether layers were washed twice with water (~400 mL × 2) and dried ($MgSO_4$). After filtration and removal of the solvent via a rotatory evaporator, the residue was distilled at 6.5 mmHg by using a short-path column and the product was collected at 68–70 °C (lit.[2] bp 95 °C at 7 mm) to give 20.97 g (90%) of a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.84 (apparent q, J = 1.5 Hz, 1 H), 4.69–4.67 (m, 1 H), 4.40 (br s, 2 H), 2.06 (s, 3 H), 1.51 (apparent d, J = 0.9 Hz, 2 H), 0.000 (s, 9 H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 170.63, 141.58, 109.54, 67.81, 23.81, 23.49, 20.90, −1.49.

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Registry No. **2a**, 18388-03-9; **2b**, 72047-94-0; **4**, 1871-57-4; **5**, 18147-84-7; Cl_3SiH, 10025-78-2.

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