kin-Elmer 782 spectrophotometer, and optical rotations were measured on Perkin-Elmer 141 and 241 polarimeters. Mass spectra were recorded on a Kratos MS 80 RFA instrument. NMR spectra including the 2D experiments were recorded on a Bruker AM-500 FT NMR spectrometer interfaced with an Aspect 3000 computer. Standard pulse sequences were used for proton–proton[10] and proton–carbon[11] cosy spectra. 2D *J*-resolved[12] NMR experiment was carried out using the pulse sequence RD – $\pi/2$ – $t_1/2$ – π – $t_1/2$ – FID.

Isolation of Isobongkrekic Acid (IIa). Approximately 250 L of the clarified broth filtrate (pH 7.3) was passed through a column of 8 L of Diaion HP-20. The column was first washed with demineralized water and then eluted with 40 L of 50% aqueous MeOH. Concentration in vacuo followed by lyophilization gave 670 g of the crude antibiotic as a dark brown mass. This was subjected to medium-pressure liquid chromatography (MPLC) over SiO_2 (230–400 mesh, 3 kg), and the antibiotic was eluted with 10 L of 5:95 MeOH–$CHCl_3$ at a flow rate of 150 mL min^{-1}. Concentration gave 100 g of a dark brown oil, which on repeated trituration with petroleum ether (60–80 °C) gave 16 g of a brown powder. This was subjected to three MPLC's over dimethyl octadecylsilyl SiO_2 (RP 18) with aqueous MeOH as the eluant. The antibiotic eluted out with 30% aqueous MeOH in the first case, 40% aqueous MeOH in the second case, and with 50% aqueous MeOH in the third column. Concentration followed by lyophilization gave 1.0 g of a very pale yellowish powder. Final purification on Sephadex G-10 column using double-distilled water afforded isobongkrekic acid as a white powder: HPLC retention time 1.8 min on a 4 × 120 mm ODS-hypersil (5 μm) column, eluant 30% aqueous MeOH, flow rate 0.5 mL min^{-1}, detection at 268 nm; FAB-MS 487 $(M + H)^+$; UV λ_{max} (aqueous MeOH) 234, 268 (254 with alkali) nm; IR (KBr) 3400, 3200, 1670–1560 (broad), 1400, 1345, 1090, 980, 945, 770 cm^{-1}; ^{13}C NMR (D_2O) δ 183.13 (s), 180.83 (s), 179.12 (s), 143.95 (s), 143.80 (d), 143.57 (s), 139.17 (d), 136.11 (s), 134.64 (d), 133.72 (d), 132.16 (d), 131.15 (d), 129.02 (d), 128.41 (d), 128.26 (d), 127.96 (d), 127.38 (d), 81.34 (d), 58.39 (q), 46.06 (t), 42.12 (t), 39.71 (d), 34.81 (t), 34.30 (t), 34.11 (t), 21.62 (q), 20.24 (q), 15.77 (q); ^1H NMR (D_2O, DSS) δ 7.26 (1 H, d, J = 12 Hz), 6.92 (1 H, d, J = 16 Hz), 6.47 (1 H, d, J = 12 Hz), 6.42 (1 H, dd, J = 11, 16 Hz), 6.09 (1 H, t, J = 11 Hz), 5.92 (1 H, dd, J = 7.5, 16 Hz), 5.81 (1 H, dt, J = 16, 7 Hz), 5.71 (1 H, s), 5.55 (2 H, m), 5.30 (1 H, dt, J = 11, 7 Hz), 4.58 (1 H, t, J = 7.9 Hz), 3.25 (3 H, s), 3.15 (2 H, s), 2.65–2.40 (2 H, ddd, J = 6, 8, 16 Hz), 2.32 (1 H, septet, J = 6 Hz), 2.38–1.98 (6 H, m), 1.90 (3 H, s), 1.80 (3 H, s), 1.05 (3 H, s).

Preparation of Trimethyl Ester of Isobongkrekic Acid (IIb). IBA (IIa, 100 mg) was esterified with 4–5-fold excess of CH_2N_2 in a mixture of MeOH, diethyl ether, and water at 0 °C for 1 h. The crude ester was purified by preparative TLC (20 × 20 cm SiO_2 plates; 0.5 mm thickness; solvent for developing 1.5% MeOH in $CHCl_3$; solvent for elution 5% MeOH in $CHCl_3$). The ester was obtained as a colorless oil (IIb, 59 mg): R_f 0.54 (SiO_2, 1.5% MeOH in $CHCl_3$); $[\alpha]^{20}_D$ +27.78° (*c* 1.4, $CHCl_3$); EIMS, m/z 528 (M^+); UV λ_{max} (MeOH) 236, 268 (no alkali shift) nm; IR (neat) 3020, 2950, 2920, 2840, 1745, 1715, 1635, 1615, 1435, 1380, 1320, 1260, 1190, 1160, 1110, 1020, 970, 945, 915, 870, 830, 780, 750 cm^{-1}. Anal. Found: C, 69.95; H, 8.50. Calcd for $C_{31}H_{44}O_7$: C, 70.45; H, 8.33.

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Registry No. IIa, 60132-21-0; **IIb**, 60132-22-1.

(10) Aue, W. P.; Bartholdi, E.; Ernst, R. R. *J. Chem. Phys.* **1976**, *64*, 2229.
(11) Bax, A.; Murris, G. *J. Magn. Reson.* **1981**, *42*, 501.
(12) Turner, D.; Freeman, R. *J. Magn. Reson.* **1978**, *29*, 587.

Stereospecific Syntheses of (*E*)-1,3-Disubstituted Dienes

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(*E*)-1,3-dienes, unlike the *Z* isomers, are useful components in Diels–Alder reactions.[2,3] We have found a straightforward method for stereospecific preparation of (*E*)-1,3-dialkyl-substituted 1,3-dienes from allylic acetates and describe herein our findings.

Tsuji and co-workers[4] have reported that treatment of allylic acetates with triphenylphosphine and a catalytic amount of palladium acetate in refluxing dioxane or toluene furnishes *E,Z* mixtures of 1,3-dienes. Although a variety of allylic acetates were examined in that study, none of the starting materials had a substitution pattern that would lead to 1,3-disubstituted 1,3-dienes.

Our interest in the use of dienes such as **2a** and **2b** as intermediates to 1,4(*H*)-naphthalenones led us to explore the palladium-catalyzed elimination of **1a** and **1b**. Under the Tsuji conditions, the allylic acetates[5] **1a** and **1b** were converted exclusively to the (*E*)-dienes **2a** and **2b** in 91 and 96% yield, respectively. Since the stereochemical result was unexpected and the procedure appeared especially promising as a method for stereospecific synthesis of (*E*)-1,3-disubstituted 1,3-dienes, additional examples were performed, and these are shown in Scheme I.

Stereospecific conversion of **1c** and **1d** to the (*E*)-1,3-dienes **2c** and **2d** established that the oxygens in the acetal were not a factor in the stereochemical outcome. Moreover, the fact that conversion of **1e** and **1f** to the (*E*)-1,3-dienes **2e** and **2f** proceeded without isomerization to the conjugated compound indicated that subsequent isomerization of the initially formed diene was probably not occurring. Finally, in order to establish the compatibility of other functionality in the reaction, the conversion of allylic acetates with terminal thiophenyl groups was examined. Here again we observed that **1g** and **1h** produced the (*E*)-1,3-dienes **2g** and **2h** exclusively. In all cases, yields were uniformly very good to excellent.

It is well known that palladium(II) acetate reacts with triphenylphosphine to give a palladium(0) complex.[6] In a subsequent step, the palladium(0) species displaces the acetate group to furnish a π-allyl intermediate, which is in equilibrium with the σ-bonded species.[7] Although it is unknown whether the π-allyl or the σ-bonded intermediate is the species undergoing reaction or whether the elimination step is a syn or anti process, *it is clear that the transition state is highly ordered and that the 2-alkyl substituent on the vinyl moiety is a controlling feature, since systems devoid of this group furnish E,Z mixtures.*[3,4]

In summary, the palladium-catalyzed conversion of allyl acetates with a 2-alkyl group on the vinyl moiety provides

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(2) Onishchenko, A. S. *Diene Synthesis*; Davey: New York, 1964; pp 13–15. Craig, D. *J. Am. Chem. Soc.* **1950**, *72*, 1678.
(3) Hauser, F. M.; Mal, D. *J. Am. Chem. Soc.* **1984**, *106*, 1098.
(4) Tsuji, J.; Yamakawa, T.; Mitsumasa, K.; Mandai, T. *Tetrahedron Lett.* **1978**, 2075.
(5) The allylic acetates 1 were prepared through Grignard addition of an alkyl halide with 2-methyl- and 2-ethylacrolein, followed by acetylation of the alcohol intermediate.
(6) Tsuji, J. *Organic Synthesis with Palladium Complexes*; Spriger-Verlag: Berlin, 1980; p 81.
(7) Vrieze, K. *Dynamic Nuclear Magnetic Resonance Spectroscopy*; Jackman, L. M., Cotton, F. A., Eds.; Academic: New York, 1975; p 441.

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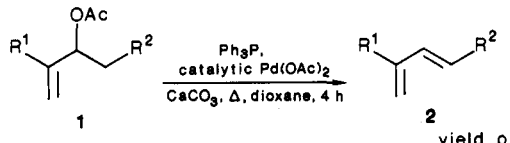
Scheme I



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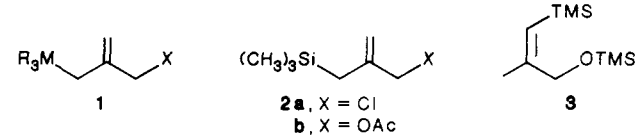
Bifunctional conjunctive reagents like **1** which possess both nucleophilic and electrophilic centers are useful annulating agents.[1] The silicon derivatives **2** have proven to be especially valuable in metal-catalyzed cycloaddition.



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.

(2) Trost, B. M.; Chan, D. M. T.; Nanninga, T. N. *Org. Synth.* **1984**, *62*, 58.

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