Application of (α-Phosphonoacyl)silane Reagents to the Synthesis of α,β-Unsaturated Acylsilanes†

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An efficient and convergent synthetic route to α,β-unsaturated acylsilanes has been developed based on the Horner–Wadsworth–Emmons reaction of (α-phosphonoacyl)silanes. The Arbuzov reaction of the (α-iodoacyl)silane **1c** with trimethyl phosphite provides access to the phosphonate **2**, which can be alkylated by treatment with potassium *tert*-butoxide and methyl iodide to afford **3**. These (α-phosphonoacyl)silane reagents combine smoothly with a variety of aldehydes to furnish α,β-unsaturated acylsilanes **5–13** in good to excellent yield.

In this paper we report on the application of the Horner–Wadsworth–Emmons modification of the Wittig reaction as a convergent and efficient synthetic route to *α,β-unsaturated acylsilanes*. The chemistry of α,β-unsaturated acylsilanes has attracted considerable attention recently. Scheller, Iwasaki, and Frei[2] have described interesting thermal and photochemical transformations of these compounds, while other studies have established the utility of α,β-unsaturated acylsilanes as building blocks for the synthesis of a variety of complex organic compounds. For example, these acylsilanes react as α,β-unsaturated carbonyl derivatives in organocuprate conjugate additions,[3] $TiCl_4$-promoted conjugate allylations,[4] 1,4-additions with silylated nucleophiles,[5] Diels–Alder reactions,[3] 1,3-dipolar cycloadditions,[6] and [3 + 2] annulations with allenylsilanes.[6] These interesting compounds also participate in various transformations unique to the acylsilane moiety including Brook rearrangements,[7,8] oxidation to carboxylic acids,[9] and fluoride-promoted conversion to ketones and aldehydes.[9] Recently novel polymers with potential utility in microlithographic applications have been prepared by the free-radical-initiated polymerization of α,β-unsaturated acylsilanes.[10]

A number of different synthetic routes to α,β-unsaturated acylsilanes have been developed since the first representative of this class was prepared in 1971.[11] The silylation of α,β-unsaturated "acyl anion" equivalents constitutes the most popular strategy employed thus far. Among the acyl anion synthons used in this approach are metalated allenyl ethers,[3,7a,11] 1,3-enynes,[12] propargylic selenides,[13] 1-methoxy-1,3-butadienes,[14] 1,3-bis(phenylseleno)propenes,[15] vinyl[16] and allenyl thioethers,[17] and dithiane derivatives.[4,10,18] Recently we have developed an efficient two-step method for the conversion of allylic alcohols to α,β-unsaturated acylsilanes based on an application of the silyl-Wittig rearrangement.[19,20] The elimination of heteroatom substituents from saturated acylsilanes provides an alternative approach to α,β-unsaturated derivatives.[6,21] Another attractive strategy involves the 1,2-addition of trialkylsilyl metal compounds to certain α,β-unsaturated carbonyl compounds. For example, Reich has reported the preparation of a (2-methylpropenoyl)silane via the addition of (phenyldimethylsilyl)lithium to acrolein followed by Swern oxidation,[7b] and Degl'Innocenti and co-workers have recently described the synthesis of (3-methylbutenoyl)trimethylsilane by the addition of $(Me_3Si)_2CuLi$ to 3-methylbutenoyl chloride.[22,23]

Retrosynthetic analysis suggests that a particularly attractive and *convergent* way to assemble α,β-unsaturated acylsilanes would involve disconnection of the C_2–C_3 bond. In a synthetic sense, this could be achieved by the condensation of an α-functionalized acylsilane reagent with a ketone or aldehyde. Miller and Zweifel in fact utilized this strategy to prepare α,β-unsaturated acylsilanes in 1981.[9] In their approach, [(trimethylsilyl)acetyl]trimethylsilane is first alkylated (via its lithium enolate) and then combined with an aldehyde in a variant of the Peterson olefin synthesis. Although $Me_3SiCOCH_2SiMe_3$ is readily available by the hydroboration–oxidation of bis(trimethylsilyl)acetylene, this key synthon unfortunately is rather unstable and is reported to isomerize to the corresponding silyl enol ether even when stored at low temperature.[9]

† This paper is dedicated to our colleague Professor Frederick D. Greene in appreciation of his years of service as Editor of *The Journal of Organic Chemistry*.

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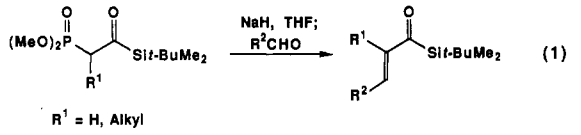
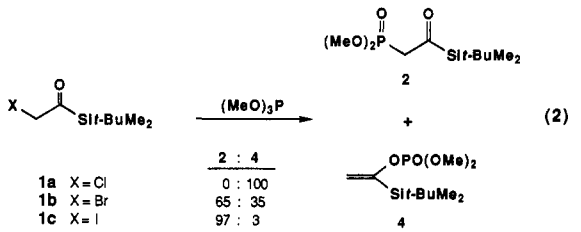
In connection with our ongoing investigation of the chemistry of certain functionalized and unusual acylsilane derivatives,[4,6,19b,24] we required a general and efficient method for the synthesis of α,β-unsaturated acylsilanes. We have been particularly interested in convergent strategies that would permit the preparation of acylsilanes with bulky trialkylsilyl groups and that would employ aldehydes as starting materials. In this paper we describe the preparation of *stable* (α-phosphonoacyl)silane reagents and their application to the synthesis of a variety of α,β-unsaturated acylsilanes via the Horner–Wadsworth–Emmons (HWE) reaction (eq 1).



Results

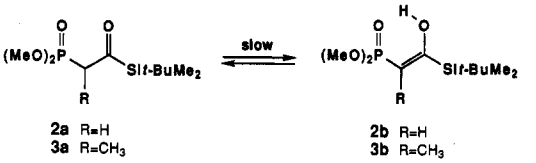
The Arbuzov reaction[25] is generally regarded as the most efficient method for the synthesis of α-phosphono carbonyl compounds. We therefore initially attempted to use (α-haloacetyl)silanes **1a** and **1b** as starting materials for the preparation of the proposed HWE reagent **2**. Previously we have reported that the requisite (α-haloacyl)silanes can be prepared conveniently in two steps (60–70% overall yield) from ethyl vinyl ether by silylation (*t*-BuLi, THF; then *t*-BuMe$_2$SiCl) followed by treatment with 1 equiv of NBS or NCS in aqueous acetonitrile.[24] Unfortunately, as summarized in eq 2, the reaction of both **1a** and **1b** with



trimethyl phosphite is complicated by the formation of substantial quantities of the undesired Perkow reaction product **4**.[26] In contrast to the behavior of the chloro and bromo compounds, the corresponding *(iodoacyl)silane* **1c** reacts almost completely in the desired fashion to afford the phosphonate **2** and the Perkow side product in a ratio of 97:3. The (iodoacyl)silane itself is easily obtained in quantitative yield by the reaction of **1b** with sodium iodide in acetone (0 °C, 15 min).

The optimal procedure for the preparation of the (α-phosphonoacyl)silane **2** involves the slow addition of **1c** to a large excess of trimethyl phosphite with the simultaneous distillation of methyl iodide from the reaction mixture as it forms. The efficient removal of this byproduct is necessary since it catalyzes the exothermic isomerization of trimethyl phosphite to dimethyl methylphosphonate. When this procedure is used, the (α-phosphonoacyl)silane can be prepared on a 20-g scale in 96% overall yield from **1b**. The phosphonate is generally obtained as a 1:1 mixture of slowly interconverting keto and enol tautomers (**2a** and **2b**) and can be stored indefinitely in the dark at room temperature or (preferably) 0 °C without detectable decomposition.

A variety of 2-substituted HWE reagents should be available by alkylation of **2**. For example, exposure of the

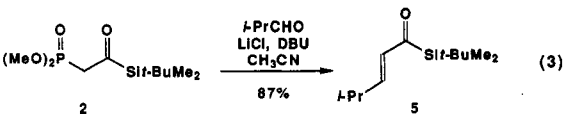


(α-phosphonoacyl)silane to 1 equiv of potassium *tert*-butoxide and 3 equiv of methyl iodide in *tert*-butyl alcohol at room temperature for 15 h smoothly provided **3** as an 8:1 mixture of keto and enol tautomers (**3a** and **3b**) in 84% yield after chromatographic purification. Interestingly, methylation using sodium hydride in THF proved less satisfactory, leading to the formation of a mixture of unreacted **2**, the desired product **3**, and a dimethylated side product.

As summarized in Table I, the (α-phosphonoacyl)silane reagents **2** and **3** smoothly combine with a variety of aldehdyes in excellent yield under standard Horner–Wadsworth–Emmons reaction conditions.[27] In a typical reaction, a solution of the phosphonate is allowed to react with 1.0 equiv of sodium hydride at room temperature until H_2 evolution ceases, and the aldehyde is then added in one portion. When the reaction is performed on volatile, low-molecular-weight aldehydes, it is generally most convenient to employ 1.5 equiv of the carbonyl substrate; however, reactions involving valuable aldehydes are best carried out by using a slight excess (1.1–1.2 equiv) of the phosphonate reagent. It should also be noted that reactions carried out on a large scale (as well as those involving reactive aldehydes such as *p*-nitrobenzaldehyde and acetaldehyde) are best performed with external cooling. The course of the HWE reaction (disappearance of phosphonate reagent and formation of acylsilane product) is easily monitored by thin-layer chromatography; reaction times range from 10 min (*p*-nitrobenzaldehyde, entry 8) to 42 h (pivaldehyde, entry 3).

We have also employed an alternative procedure for the HWE reaction, which is particularly suited for small-scale experiments since it avoids the need to accurately weigh out small quantities of sodium hydride. In this procedure the phosphonate reagent is allowed to react with an excess of NaH, and the resulting suspension is then transferred via cannula through a small sintered-glass filter funnel into a second flask. The aldehyde is added to the filtered solution, and the reaction is then allowed to proceed as described above.

Other modified HWE reaction procedures should also prove applicable for reactions involving our (α-phosphonoacyl)silane reagents. For example, addition of **2** to isobutyraldehyde using the mild conditions introduced by Masamune and Roush[28] furnished the α,β-unsaturated acylsilane **5** in 87% yield (eq 3). Although the HWE reaction proceeds considerably more slowly under these conditions (24 h as compared to 90 min when using NaH in THF), the Masamune–Roush procedure should prove advantageous for reactions involving base-sensitive aldehydes.



As expected, the HWE reactions of **2** and **3** proceed with high stereoselectivity to produce trans-substituted α,β-

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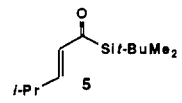
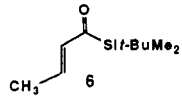
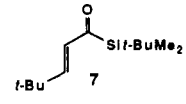
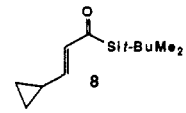
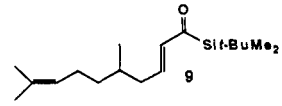
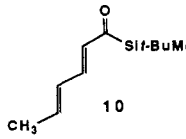
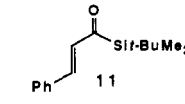
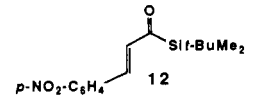
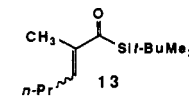
Table I. Synthesis of α,β-Unsaturated Acylsilanes

entry	aldehyde	phosphonate reagent	product(s)[a]	yield,[b] %
1	*i*-PrCHO	2	 5	86
2	CH_3CHO	2	 6	81
3	*t*-BuCHO	2	 7	84
4	cyclopropane-carboxaldehyde	2	 8	89
5	citronellal	2	 9	97
6	(*E*)-$CH_3CH{=}CHCHO$	2	 10	54
7	PhCHO	2	 11	86
8	*p*-nitrobenzaldehyde	2	 12	90
9	*n*-PrCHO	3	 13 *E*/*Z* = 93:7	74

[a] Products were determined to contain <2% of the *Z* isomer by ^1H NMR analysis of the purified reaction products unless otherwise indicated. [b] Isolated yields of products purified by column chromatography.

unsaturated carbonyl compounds. In the case of reactions involving the parent reagent **2**, none of the *Z* isomers could be detected by ^1H NMR examination of the crude reaction products (>95:5 *E* stereoselectivity). The reaction of the substituted reagent **3** with *n*-butanal similarly led to the predominant (93:7) formation of the *E* olefin.

To date, our efforts to extend the HWE reaction of (α-phosphonoacyl)silanes to ketones have proved disappointing. Little reaction is observed to take place at 25 °C, and reaction at elevated temperature leads to the desired α,β-unsaturated acylsilanes in low yield. For example, treatment of the sodium salt of phosphonate **2** with excess acetone in THF at reflux for 24 h gave 1-(*tert*-butyldimethylsilyl)-3-methyl-2-buten-1-one in only 20% yield.

The Horner–Wadsworth–Emmons approach described in this paper should prove to be the most expedient route to a variety of α,β-unsaturated acylsilanes. We anticipate that this new methodology will facilitate the further investigation of the chemistry of these interesting compounds as well as their exploitation in synthesis.

Experimental Section

Instrumentation. Low-resolution mass spectra (MS) were determined by using a reduced ionization voltage (24–40 V) or a GCMS system at 70 eV. Melting points and boiling points are uncorrected.

Materials. Commercial grade reagents and solvents were used without further purification except as indicated below. Trimethyl phosphite was distilled from calcium hydride. Sodium hydride was obtained as a dispersion in mineral oil, washed with pentane, and dried by argon purge. The resulting oil-free solid was stored in tightly capped bottles and weighed rapidly in air. Methyl iodide and *tert*-butyl alcohol were passed through a short plug of flame-dried neutral Al_2O_3 prior to use. Tetrahydrofuran was distilled from sodium benzophenone ketyl or dianion. All liquid aldehydes were distilled before use; sufficient foreruns were discarded to ensure removal of water azeotropes. Acetaldehyde was dried over $MgSO_4$ prior to distillation. Citronellal was purified by column chromatography on silica gel after distillation under reduced pressure. (Bromoacyl)silane **1b** was prepared as described previously[24] and purified by low-temperature (−78 °C) recrystallization from pentane (19 g of crude **1b** from 2 × 50 mL of pentane) to afford pure **1b**, mp 19.5–20 °C.

General Procedures. All reactions were performed in oven-dried glassware under a positive pressure of argon. Reaction mixtures containing α,β-unsaturated acylsilanes were routinely protected from excessive exposure to light. Reaction mixtures were stirred magnetically unless otherwise indicated. Reaction product solutions were concentrated by using a Büchi rotary evaporator at 1–30 mmHg. Column chromatography was performed on Merck or Baker silica gel (230–400 mesh).

1-(*tert*-Butyldimethylsilyl)-2-iodo-1-ethanone (1c). A 250-mL, three-necked, round-bottomed flask equipped with an argon inlet adapter, addition funnel, and a thermometer was charged with NaI (15.79 g, 105.4 mmol) and 150 mL of acetone and cooled in an ice bath while (bromoacyl)silane **1b** (16.66 g, 70.24 mmol) was added over the course of 5 min. The resulting yellow suspension of white precipitate was stirred for 10 min and then partitioned between 1500 mL of H_2O and 300 mL of pentane. The aqueous phase was separated and washed with an additional 300 mL of pentane, and the combined organic phases were dried over $MgSO_4$, filtered, and concentrated to give 19.90 g (100%) of (iodoacyl)silane **1c** as a dark yellow oil, which was used immediately for the preparation of phosphonate **2** without further purification. (During the course of its preparation and handling, the (iodoacyl)silane was protected from prolonged exposure to light and air.) Compound **1c**: IR (film) 2956, 2932, 2888, 2860, 1658, 1636, 1470, 1465, 1409, 1393, 1376, 1367, 1251, 1191, 1148, 1080, 1008, 993, 942, 842, 825, 813, 781, and 678 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 4.14 (s, 2 H), 0.95 (s, 9 H), and 0.30 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 232.3 (s), 26.3 (q), 18.5 (t), 16.6 (s), and −5.9 (q).

Dimethyl [2-(*tert*-Butyldimethylsilyl)-2-oxoethyl]-phosphonate (2a) and Dimethyl (*E*)-[2-(*tert*-Butyldimethylsilyl)-2-hydroxyethenyl]phosphonate (2b). A 500-mL, three-necked, round-bottomed flask was equipped with a magnetic stirring bar, glass stopper, addition funnel, and a distillation head fitted with a vacuum distillation adapter connected to an argon inlet and a receiving flask. The reaction flask was charged with 200 mL of $(MeO)_3P$ and then heated until the phosphite began to slowly distill. The (iodoacyl)silane **1c** (19.90 g, 70.02 mmol) was then added dropwise over the course of 15 min while distillation was maintained (the addition funnel was rinsed with ca. 5 mL of Et_2O). **CAUTION**: the reaction of the (iodoacyl)silane with trimethyl phosphite is exothermic, and careful control of the rate of heating is necessary. Efficient removal of methyl iodide

is important since this byproduct catalyzes the exothermic isomerization of trimethyl phosphite to dimethyl methylphosphonate. After an additional 15 min of distillation, heating was terminated, the reaction mixture was allowed to cool to room temperature, and volatile materials were then removed by distillation under reduced pressure. The pale yellow residue was transferred to a 50-mL round-bottomed flask with the aid of ca. 10 mL of Et_2O and then distilled at 62–66 °C (ca. 0.0005 mmHg) to afford 17.95 g (96%) of **2** as a very pale yellow oil (1:1 mixture of keto **2a** and enol **2b** tautomers as determined by ^1H NMR analysis): IR (film) 2500–3700 (br), 2950, 2928, 2890, 2854, 1639, 1551, 1463, 1408, 1391, 1363, 1293, 1252, 1198, 1032, 941, 835, 780, 744, and 677 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) keto tautomer **2a** δ 3.76 (d, J_{P-H} = 11.2 Hz, 6 H), 3.30 (d, J_{P-H} = 22.0 Hz, 2 H), 0.94 (s, 9 H), and 0.25 (s, 6 H), enol tautomer **2b** δ 10.72 (s, 1 H), 4.57 (d, J_{P-H} = 16.0 Hz, 1 H), 3.71 (d, J_{P-H} = 11.8 Hz, 6 H), 0.96 (s, 9 H), and 0.15 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) keto tautomer **2a** δ 230.8, 52.5 (d, J_{P-C} = 6 Hz), 46.0 (d, J_{P-C} = 123 Hz), 26.2, 16.6, and −7.1, enol tautomer **2b** δ 187.3 (d, J_{P-C} = 8 Hz), 89.7 (d, J_{P-C} = 168 Hz), 52.0 (d, J_{P-C} = 4 Hz), 26.3, 16.1, and −7.3; MS, *m/e* 266 (M^+, 1.1) 251, 223, 210, 209, 197, 196, 195 (100), 184, 183, 182, 181, 169, 167, 163, 153, 152, 151, 139, 137, 123, 121, 119, 115, 110, 109, 105, 99, 91, 89, 75, 73, 59. Anal. Calcd for $C_{10}H_{25}O_4PSi$: C, 45.09; H, 8.70. Found: C, 44.83; H, 8.57.

Dimethyl [2-(*tert*-Butyldimethylsilyl)-1-methyl-2-oxoethyl]phosphonate (3a) and Dimethyl (*E*)-[2-(*tert*-Butyldimethylsilyl)-2-hydroxy-1-methylethenyl]phosphonate (3b). A 10-mL, two-necked, pear-shaped flask equipped with an argon inlet adapter and a rubber septum was charged with KO-*t*-Bu (0.337 g, 3.00 mmol) and 5 mL of *tert*-butyl alcohol. To the resulting clear solution was added rapidly, via syringe, phosphonate **2** (0.799 g, 3.00 mmol) and then CH_3I (0.56 mL, 9.0 mmol). After 15 h, the reaction mixture was poured into 20 mL of H_2O and extracted with three 20-mL portions of CH_2Cl_2. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated to afford 0.833 g of a yellow oil. Column chromatography on silica gel (repeated six times, elution with ethyl acetate–hexanes) furnished 0.705 g (84%) of **3** as a pale yellow oil (8:1 mixture of keto **3a** and enol **3b** tautomers as determined by ^1H NMR analysis): IR (film) 3300–3700 (br), 2960, 2934, 2888, 2860, 1641, 1567, 1465, 1414, 1393, 1366, 1252, 1189, 1032, 943, 829, 809, 784, and 778 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) keto tautomer **3a** δ 3.81 (dq, J_{P-H} = 22.8 Hz, J_{H-H} = 7.2 Hz, 1 H), 3.76 (d, J_{P-H} = 10.7 Hz, 3 H), 3.73 (d, J_{P-H} = 10.7 Hz, 3 H), 1.25 (dd, J_{P-H} = 18.5 Hz, J_{H-H} = 7.4 Hz, 3 H), 0.92 (s, 9 H), 0.32 (s, 3 H), and 0.21 (s, 3 H), enol tautomer **3b** δ 10.71 (s, 1 H), 3.70 (d, J_{P-H} = 11.3 Hz, 6 H), 1.68 (d, J_{P-H} = 14.7 Hz, 3 H), 0.97 (s, 9 H), and 0.24 (s, 6 H); ^{13}C NMR (125 MHz, $CDCl_3$) keto tautomer **3a** δ 242.7, 52.8, 49.6 (d, J_{P-C} = 125 Hz), 26.2, 16.8, 9.8 (d, J_{P-C} = 6 Hz), −6.7, and −7.1, enol tautomer **3b** δ 178.9, 97.8 (d, J_{P-C} = 158 Hz), 51.8, 26.5, 17.3, 13.0 (d, J_{P-C} = 9 Hz), and −4.7; MS, *m/e* 280 (M^+, 0.2), 237, 224, 223, 209, 197, 196, 195, 169, 168 (100), 167, 43; HRMS *m/e* calcd for $C_{11}H_{25}O_4PSi$ 280.1260, found 280.1259.

General Procedure A for the Addition of Phosphonate Reagents 2 and 3 to Aldehydes. Preparation of (*E*)-1-(*tert*-Butyldimethylsilyl)-4-methyl-2-penten-1-one (5). A 50-mL, two-necked, round-bottomed flask equipped with an argon inlet adapter and a rubber septum was charged with NaH (0.117 g, 4.89 mmol) and 25 mL of THF. The phosphonate reagent **2** (1.302 g, 4.89 mmol) was added over the course of ca. 1 min via a gas-tight syringe (rapid gas evolution), and after 15 min, isobutyraldehyde (0.666 mL, 7.34 mmol) was added in one portion. The reaction mixture was stirred at room temperature for 1.5 h and then quenched with 25 mL of half-saturated NH_4Cl solution. The resulting mixture was partitioned between 100 mL of H_2O and 100 mL of diethyl ether, and the organic phase was separated and extracted with 100 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to afford a yellow oil. Column chromatography on silica gel (elution with ethyl acetate–hexanes) provided 0.890 g (86%) of **5** as a brilliant yellow oil: IR (film) 3018, 2958, 2930, 2882, 2856, 1645, 1585, 1464, 1408, 1389, 1365, 1337, 1290, 1251, 1185, 1112, 1040, 1006, 982, 941, 838, 825, 811, 776, and 675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.64 (dd, *J* = 16.2, 6.9 Hz, 1 H), 6.30 (dd, *J* = 16.2, 1.6 Hz, 1 H), 2.40–2.52 (m, 1 H), 1.07 (d, *J* = 6.8 Hz, 6 H), 0.93 (s, 9 H), and 0.23 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 235.3, 152.5, 133.3, 31.0, 26.4, 21.2, 16.4, and −6.1; UV max (isooctane) 227 (ε 9800) and 426 nm (129); MS, *m/e* 213 ($[M + H]^+$, 41), 212 (M^+, 1.7), 115, 113, 97, 75, 73 (100), 44, 43. Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.84; H, 11.48.

General Procedure B for the Addition of Phosphonate Reagents 2 and 3 to Aldehydes. Preparation of (*E*)-1-(*tert*-Butyldimethylsilyl)-3-(*p*-nitrophenyl)-2-propen-1-one (12). A 10-mL, two-necked, pear-shaped flask equipped with an argon inlet adapter and a rubber septum was charged with NaH (0.095 g, 4.0 mmol) and 6 mL of THF. The phosphonate reagent **2** (0.879 g, 3.30 mmol) was added over the course of ca. 1 min via a gas-tight syringe, and when gas evolution ceased, the walls of the flask were rinsed with 1 mL of THF. After 15 min, the resulting suspension was transferred via cannula to a 2-mL sintered-glass filter funnel (10–20-μm porosity) fitted with a rubber septum and bearing a ground-glass joint and argon inlet upon its lower portion and was filtered (with the aid of slight suction) into a 25-mL, two-necked, round-bottomed flask which was also equipped with a rubber septum; 3 mL of THF was used to ensure complete transfer of the phosphonate solution into the round-bottomed flask. The filtrate was cooled to 0 °C, and a solution of *p*-nitrobenzaldehyde (0.453 g, 3.00 mmol) in 5 mL of THF was added via a gas-tight syringe. (For aldehdyes other than *p*-nitrobenzaldehyde and acetaldehyde, the reaction was performed at room temperature. Liquid aldehydes were added neat.) The resulting mixture was stirred for 10 min at 0 °C and then for an additional 10 min at room temperature. The resulting mixture was quenched with 15 mL of half-saturated NH_4Cl solution and then poured into 50 mL of H_2O and 50 mL of diethyl ether. The organic phase was separated, extracted with 50 mL of saturated NaCl solution, dried over $MgSO_4$, filtered, and concentrated to afford a dark orange solid. Column chromatography on silica gel (elution with ethyl acetate–hexanes) provided 0.787 g (90%) of **12** as dark orange crystals: mp 101.5–103.5 °C; IR ($CHCl_3$) 3024, 3006, 2950, 2926, 2880, 2856, 1637, 1598, 1567, 1518, 1492, 1469, 1462, 1410, 1363, 1345, 1324, 1297, 1271, 1251, 1153, 1110, 1029, 1004, 980, 960, 853, 830, and 689 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (apparent d, *J* = 9.7 Hz, 2 H), 7.71 (apparent d, *J* = 8.7 Hz, 2 H), 7.33 (d, AB pattern, J_{AB} = 16.1 Hz, 1 H), 7.12 (d, AB pattern, J_{AB} = 16.1 Hz, 1 H), 0.98 (s, 9 H), and 0.32 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 235.4, 148.4, 141.3, 136.3, 133.0, 128.8, 124.1, 26.5, 16.8, and −6.4; UV max (isooctane) 198 (ε 16 000), 218 (11 000), 305 (28 000), and 468 nm (129). Anal. Calcd for $C_{15}H_{21}NO_3Si$: C, 61.82; H, 7.26; N, 4.80. Found: C, 61.75; H, 7.20; N, 4.77.

(*E*)-1-(*tert*-Butyldimethylsilyl)-2-buten-1-one (6). A solution of the sodium salt of phosphonate **2** was generated by reaction of **2** (5.371 g, 20.17 mmol) with NaH (0.484 g, 20.17 mmol) in 40 mL of THF at 0 °C as described in general procedure A. Acetaldehyde (2.25 mL, 40.3 mmol) was added via a chilled syringe, and the reaction mixture was stirred at 0 °C for 30 min and then at room temperature for 30 min. The resulting mixture was quenched by the addition of 40 mL of half-saturated NH_4Cl solution and then poured into 100 mL of H_2O and 100 mL of pentane. The organic phase was separated and extracted with 100 mL of H_2O, dried over $MgSO_4$, and concentrated to yield 3.985 g of a brilliant yellow oil. Column chromatography on silica gel (elution with ether–pentane) afforded 3.022 g (81%) of **6** as a brilliant yellow oil: IR (film) 3024, 2950, 2928, 2884, 2862, 1640, 1583, 1469, 1463, 1441, 1408, 1391, 1375, 1363, 1282, 1248, 1184, 1115, 1041, 1005, 975, 940, 914, 840, 798, 776, and 675 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.69 (dq, *J* = 15.5, 6.9 Hz, 1 H), 6.39 (dq, *J* = 15.5, 1.7 Hz, 1 H), 1.90 (dd, *J* = 6.9, 1.4 Hz, 3 H), 0.90 (s, 9 H), and 0.22 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 235.3, 141.2, 138.0, 26.6, 18.4, 16.6, and −6.1; UV max (isooctane) 226 (ε 9400) and 429 nm (118). Anal. Calcd for $C_{10}H_{20}OSi$: C, 65.15; H, 10.93. Found: C, 64.93; H, 10.64.

(*E*)-1-(*tert*-Butyldimethylsilyl)-4,4-dimethyl-2-penten-1-one (7). Reaction of phosphonate **2** (2.661 g, 9.99 mmol) with NaH (0.31 g, 12.9 mmol) and pivaldehyde (1.63 mL, 1.50 mmol) for 42 h according to general procedure B afforded 1.891 g (84%) of **7** as a brilliant yellow oil: IR (film) 3028, 2960, 2930, 2900, 2882, 2860, 1644, 1589, 1465, 1409, 1394, 1366, 1289, 1250, 1199, 1151, 1046, 1007, 984, 943, 927, 838, 825, 810, 777, 727, 691, and 676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.68 (d, *J* = 16.0 Hz, 1 H), 6.25 (d, *J* = 16.0 Hz, 1 H), 1.09 (s, 9 H), 0.93 (s, 9 H), and 0.23

(s, 6 H); ^{13}C NMR (68 MHz, $CDCl_3$) δ 235.8, 156.7, 131.5, 33.7, 28.7, 26.6, 16.5, and −5.9; UV max (isooctane) 226 (ϵ 9700) and 424 nm (126); MS, m/e 227 ($[M + 1]^+$, 0.1), 113 (100), 111, 75, 73, 59, 57, 41. Anal. Calcd for $C_{13}H_{26}OSi$: C, 68.96; H, 11.57. Found: C, 69.12; H, 11.69.

(*E*)-1-(*tert*-Butyldimethylsilyl)-3-cyclopropyl-2-propen-1-one (8). Reaction of phosphonate **2** (0.266 g, 1.00 mmol) with NaH (0.05 g, 2 mmol) and cyclopropanecarboxaldehyde (0.112 mL, 1.50 mmol) for 4 h according to general procedure B afforded 0.187 g (89%) of **8** as a brilliant yellow oil: IR (film) 3086, 3008, 2954, 2930, 2884, 2860, 1641, 1569, 1471, 1463, 1430, 1408, 1391, 1364, 1252, 1194, 1142, 1096, 1051, 1024, 1008, 980, 953, 941, 896, 868, 842, 829, 810, 777, and 676 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 6.56 (d, J = 15.7 Hz, 1 H), 6.13 (dd, J = 15.2, 10.0 Hz, 1 H), 1.49–1.60 (m, 1 H), 0.94–1.02 (m, 2 H), 0.93 (s, 9 H), 0.62–0.68 (m, 2 H), and 0.20 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 233.1, 150.7, 132.8, 26.4, 16.5, 14.6, 9.0, and −6.3; UV max (isooctane) 252 (ϵ 12 000) and 428 nm (114). Anal. Calcd for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54. Found: C, 68.67; H, 10.63.

(*E*)-1-(*tert*-Butyldimethylsilyl)-5,9-dimethyl-2,8-decadien-1-one (9). Reaction of phosphonate **2** (0.336 g, 1.26 mmol) with NaH (0.030 g, 1.26 mmol) and (+)-citronellal (0.162 g, 1.05 mmol) for 4 h according to general procedure A afforded 0.300 g (97%) of **9** as a brilliant yellow oil: IR (film) 3022, 2954, 2926, 2856, 1640, 1584, 1464, 1411, 1378, 1365, 1296, 1250, 1182, 1115, 1006, 982, 946, 839, 776, and 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.66 (dt, J = 15.8, 7.4 Hz, 1 H), 6.33 (apparent d, J = 15.9 Hz, 1 H), 5.08 (apparent t, J = 7.1 Hz, 1 H), 2.20–2.26 (m, 1 H), 2.05–2.09 (m, 1 H), 1.93–2.05 (m, 2 H), 1.69 (s, 3 H), 1.63–1.67 (m, 1 H), 1.60 (s, 3 H), 1.32–1.39 (m, 1 H), 1.16–1.24 (m, 1 H), 0.93 (s, 9 H), 0.91 (d, J = 6.7 Hz, 3 H), and 0.23 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 235.2, 145.6, 137.9, 131.3, 124.3, 40.0, 36.7, 32.2, 26.6, 25.6, 25.4, 19.5, 17.6, 16.6, and −5.9; UV max (isooctane) 196 (ϵ 11 000), 229 (13 000), and 428 nm (129). Anal. Calcd for $C_{18}H_{34}OSi$: C, 73.40; H, 11.63. Found: C, 73.49; H, 11.70.

(*E,E*)-1-(*tert*-Butyldimethylsilyl)-2,4-hexadien-1-one (10). Reaction of phosphonate **2** (0.266 g, 1.00 mmol) with NaH (0.05 g, 2 mmol) and crotonaldehyde (0.124 mL, 1.50 mmol) for 7 h according to general procedure B afforded 0.114 g (54%) of **10** as a brilliant orange oil (contaminated with 6 mol % of a by-product, which was tentatively assigned as the isomeric (*E,Z*)-2,4-diene): IR (film) 3020, 2948, 2924, 2880, 2852, 1644, 1619, 1603, 1573, 1554, 1470, 1462, 1442, 1407, 1390, 1376, 1362, 1320, 1289, 1248, 1224, 1180, 1141, 1085, 1026, 995, 939, 837, 777, and 675 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 6.97 (dd, J = 15.5, 9.8 Hz, 1 H), 6.38 (d, J = 15.6 Hz, 1 H), 6.15–6.26 (m, 2 H), 1.87 (d, J = 5.8 Hz, 3 H), 0.93 (s, 9 H), and 0.23 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 235.3, 140.6, 140.5, 132.6, 130.7, 26.5, 18.8, 16.6, and −6.3; UV max (isooctane) 196 (ϵ 6500), 281 (22 000), and 453 nm (91); MS, m/e 210 (M^+, 0.3), 75, 73 (100), 67, 59, 41, 39; HRMS m/e calcd for $C_{12}H_{22}OSi$ 210.1440, found 210.1439.

(*E*)-1-(*tert*-Butyldimethylsilyl)-3-phenyl-2-propen-1-one (11). Reaction of phosphonate **2** (0.266 g, 1.00 mmol) with NaH (0.05 g, 2 mmol) and benzaldehyde (0.152 mL, 1.50 mmol) for 95 min was performed according to general procedure B to afford 0.282 g of an orange oil. Excess benzaldehyde was removed by Kugelrohr distillation (85 °C, 3 mmHg). Column chromatography on silica gel (elution with ethyl acetate–hexanes) afforded 0.212 g (86%) of **11** as orange crystals: mp 52.5–53.5 °C; IR ($CHCl_3$) 3082, 3058, 3006, 2954, 2930, 2882, 2856, 1636, 1624, 1577, 1560, 1494, 1468, 1463, 1448, 1407, 1392, 1364, 1324, 1300, 1274, 1252, 1165, 1156, 1131, 1114, 1072, 1042, 1005, 999, 987, 978, 941, 893, 839, 824, 811, and 690 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.55–7.58 (m, 2 H), 7.38–7.41 (m, 3 H), 7.37 (d, J = 16.1 Hz, 1 H), 7.02 (d, J = 16.1 Hz, 1 H), 0.98 (s, 9 H), and 0.30 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 234.8, 140.5, 134.8, 130.8, 130.2, 128.8, 128.2, 26.5, 16.6, and −6.3; UV max (isooctane) 195 (ϵ 12 000), 225 (10 000), 291 (22 000), and 454 nm (116). Anal. Calcd for $C_{15}H_{22}OSi$: C, 73.11; H, 9.00. Found: C, 72.77; H, 8.81.

1-(*tert*-Butyldimethylsilyl)-2-methyl-2-hexen-1-one (13). Reaction of phosphonate **3** (0.280 g, 1.00 mmol) with NaH (0.05 g, 2 mmol) and *n*-butanal (0.132 mL, 1.50 mmol) for 3.5 h according to general procedure B afforded 0.167 g (74%) of **13** as a brilliant yellow oil (93:7 mixture of *E* and *Z* isomers as determined by ^1H NMR analysis): IR (film) 3046, 2958, 2930, 2882, 2858, 1642, 1588, 1463, 1410, 1381, 1363, 1317, 1250, 1207, 1065, 1032, 1007, 940, 904, 840, 823, 808, 777, 690, and 665 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *E* isomer δ 6.57 (tq, J = 7.2, 1.6 Hz, 1 H), 2.30 (apparent q, J = 7.0 Hz, 2 H), 1.66 (apparent q, J = 1.3 Hz, 3 H), 1.53 (sextet, J = 7.5 Hz, 2 H), 0.98 (t, J = 7.2 Hz, 3 H), 0.91 (s, 9 H), and 0.25 (s, 6 H), *Z* isomer (partial data) δ 5.30 (tq, J = 7.8, 1.7 Hz, 1 H), 1.96 (apparent qq, J = 6.9, 1.7 Hz, 2 H), 1.83 (q, J = 1.6 Hz, 3 H), 1.35 (sextet, J = 7.4 Hz, 2 H), and 0.21 (s, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) *E* isomer δ 235.0, 148.9, 145.2, 30.9, 26.7, 21.9, 16.6, 13.7, 9.6, and −4.1, *Z* isomer (partial data) δ 247.3, 143.3, 129.7, 26.4, 23.0, 18.7, 17.0, 13.6, and −6.2; UV max (isooctane) 236 (ϵ 11 000) and 413 nm (130); MS, m/e 226 (M^+, 3.3), 183, 170, 169, 155, 141, 128, 127 (100), 115, 113, 99, 75, 74, 73, 43; HRMS m/e calcd for $C_{13}H_{26}OSi$ 226.1753, found 226.1753.

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