Cross-Coupling of Enol Phosphates with Trimethylsilylmethylmagnesium Halides Catalyzed by Nickel or Palladium Complexes; A Selective Synthesis of Allylsilanes

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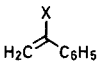
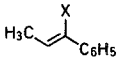
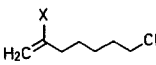
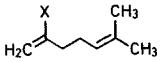
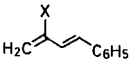
Allylsilanes (2-alkenylsilanes) are useful intermediates in organic synthesis[1]; they react with a wide range of electrophiles in a regiospecific manner. Although allylsilanes have generally been prepared by silylation of allylmetal compounds, this method may suffer from lack of regioselectivity when the allylmetal compound is unsymmetrical[2]. An alternative method for the synthesis of 2-alkenylsilanes is the catalytic cross-coupling of 1-alkenyl halides with silylmethylmagnesium halides[3,4], but the mostly difficult accessibility of alkenyl halides with desired regio- and stereochemical structure limits the use of the method to the synthesis of only a few 2-alkenylsilanes.

We now report that enol phosphates **(2)** can be converted into 2-alkenylsilanes (**4**, allylsilanes) in high yields by reaction with 1-(trimethylsilyl)-alkylmagnesium halides **(3)** in the presence of a nickel or palladium catalyst. This method provides an efficient selective synthesis of 2-alkenylsilanes **(4)**; the enol phosphates **(2)** used can be prepared regio- and stereoselectively by phosphorylation of enolate anions generated from ketones **(1)** under kinetically or thermodynamically con-

Table 1. Diethyl Enol Phosphates **(2)**

2 X = $-O-P(=O)(OC_2H_5)_2$	Yield [%]	b.p. [°C]/torr	Molecular formula[a] or Lit. b.p. [°C]/torr	^{1}H-N.M.R. (CCl_4/TMS) δ [ppm]
a 	90	90°/0.05	105°/0.15[11]	1.35 (t, 6H, J=7 Hz); 1.5-1.9, 2.0-2.3 (m, 8H); 4.10 (double q, 4H, J_{P-H}=8 Hz); 5.42 (m, 1H)
b 	61	77-80°/0.04	85-87°/0.1[7]	1.37 (t, 6H, J=7 Hz); 1.97 (quin, 2H, J=7 Hz); 2.2-2.6 (br m, 4H); 4.12 (double q, 4H, J_{P-H}=8 Hz); 5.2 (m, 1H)
c 	80	143-146°/0.05	$C_{16}H_{31}O_4P$ (318.4)	1.32 (t, 6H, J=7 Hz); 1.0-1.7 (br, 16H); 2.0-2.4 (br, 4H); 4.06 (double q, 4H, J_{P-H}=8 Hz); 4.85 (t, 1H, J=8 Hz)
d 	87	90-95°/0.04	101-103°/0.005[12]	1.32 (t, 6H, J=7 Hz); 4.13 (double q, 4H, J_{P-H}=8 Hz); 5.24 (d, 2H, J_{P-H}=2 Hz); 7.2-7.65 (m, 5H)
e 	91	110-112°/0.04	114-116°/0.005[12]	1.22 (t, 6H, J=7 Hz); 1.88 (double d, 3H, J_{H-H}=7 Hz, J_{P-H}=3 Hz); 4.06 (m, 4H); 5.71 (double q, 1H, J_{P-H}=2 Hz); 7.3-7.7 (m, 5H)
f 	68	100-103°/0.05	$C_{12}H_{25}O_4P$ (264.3)	0.90 (br t, 3H); 1.14-1.6 (br, 8H); 1.34 (t, 6H, J=7 Hz); 2.15 (br t, 2H); 4.15 (double q, 4H, J_{P-H}=8 Hz); 4.39 (br s, 1H); 4.75 (m, 1H)
g 	66	120-125°/0.06	$C_{12}H_{23}O_4P$ (262.3)	1.30 (t, 6H, J=7 Hz); 1.60, 1.67 (pair of s, 6H); 2.13, 2.16 (pair of s, 4H); 4.04 (double q, 4H, J_{P-H}=8 Hz); 4.36 (br s, 1H); 4.7 (m, 1H); 4.9-5.15 (br m, 1H)
h 	68	83-92°/0.03	100-103°/0.07[9]	1.08 (d, 3H, J=7 Hz); 1.33 (t, 6H, J=7 Hz); 1.4-2.6 (m, 7H); 4.07 (double q, 4H, J_{P-H}=8 Hz); 5.45 (m, 1H)
i 	57	—[b]	$C_{14}H_{19}O_4P$[c] (282.3)	1.35 (t, 6H, J=7 Hz); 4.15 (double q, 4H, J_{P-H}=8 Hz); 4.73, 5.15 (pair of br m, 2H); 6.58 (ABX, 2H, J_{HA-HB}=16 Hz, J_{HA-P}=3 Hz, $\Delta\nu$=34 Hz); 7.0-7.4 (m, 5H)

[a] The microanalyses of **2c, f, g** were in satisfactory agreement with the calculated values: C, ±0.23; H, ±0.17; P, ±0.21.
[b] Isolated by column chromatography using ethyl acetate as eluent.
[c] Reproducible microanalyses could not be obtained because of the instability of **2i**. M.S.: m/e of M^+ =282.1015 (calc. 282.1022).

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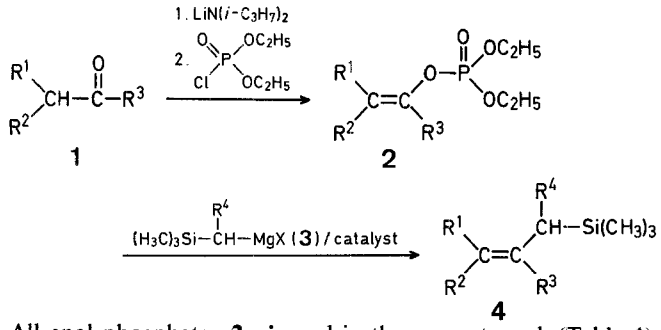
trolled conditions[5,6,7], or by the Perkow reaction of α-haloketones with trialkyl phosphites[7,8,9].



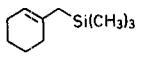
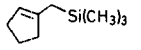
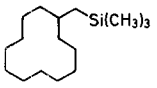
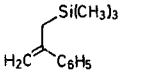
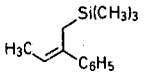
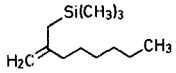
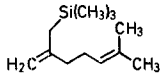
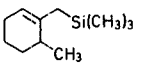
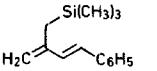
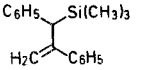
All enol phosphates **2a–i** used in the present work (Table 1) were prepared by adding diethyl phosphorochloridate to the lithium enolates generated from ketones **1a–i** and lithium diisopropylamide under kinetically controlled conditions.

Several transition metal complexes were tested for their catalytic activity in the reaction of diethyl 1-phenylvinyl phosphate **(2d)** with trimethylsilylmethylmagnesium chloride. Nickel acetylacetonate, nickel bromide, and nickel(II) complexes with tertiary phosphines such as triphenylphosphine or 1,3-bis[diphenylphosphino]-propane were all effective, giving the coupling product 2-phenyl-3-trimethylsilylpropene **(4d)** in ~90% yield under mild conditions (room temperature, 20 h). Tetrakis[triphenylphosphine]-palladium(0) exhibit almost the same catalytic activity[10]; palladium chloride was not effective.

As shown in Table 2, various kinds of enol phosphates **(2a–i)** could be selectively converted into the corresponding allylsilanes **(4a–i)** in satisfactory yields by cross-coupling with trimethylsilylmethylmagnesium chloride in the presence of a nickel or palladium catalyst. The results obtained with **2e–h** demonstrate that the reaction proceeds without isomerization of the C=C double bond. α-(Trimethylsilyl)-benzylmagnesium bromide also reacts with enol phosphate **2d** in the presence of nickel acetylacetonate to give 2,3-diphenyl-3-trimethylsilylpropane **(4j)** in moderate yield.

Diethyl Enol Phosphates (2); General Procedure:
To a solution of diisopropylamine (4.05 g, 40 mmol) in anhydrous tetrahydrofuran (25 ml) is added a 1.5 molar solution of butyllithium in hexane (27 ml, 40 mmol) at 0 °C under a nitrogen atmosphere. The lithium diisopropylamide solution is cooled to −78 °C and the ketone **1** (35 mmol) is added dropwise over a period of 10 min. The mixture is

Table 2. 2-Alkenylsilanes **(4)**[a]

4	Catalyst	Yield[b] [%]	b.p.[c] [°C]/torr	Molecular formula[d]	M.S. (24 eV) *m/e* (rel. int. %)	^{1}H-N.M.R. (CCl_4/TMS) δ [ppm]
a 	$Ni(acac)_2$	81	70°/5	$C_{10}H_{20}Si$ (168.4)	168 (M^+, 19); 94 (14); 73 (100)	0.05 (s, 9H); 1.35 (s, 2H); 1.56 (m, 4H); 1.75–2.1 (br m, 4H); 5.1 (br, 1H)
b 	$Ni(acac)_2$	75	80°/16	$C_9H_{18}Si$ (154.3)	154 (M^+, 49); 139 (13); 80 (12); 73 (100)	−0.02 (s, 9H); 1.49 (br s, 2H); 1.76 (m, 2H); 2.0–2.2 (br m, 4H); 5.05 (br s, 1H)
c 	$Ni(acac)_2$	87	—	$C_{16}H_{32}Si$ (252.5)	252 (M^+, 7); 128 (54); 73 (100)	0.02 (s, 9H); 1.1–1.7 (br m, 18H); 1.8–2.2 (br m, 4H); 5.10 (m, 1H)
d 	$NiBr_2$	82 (91)	100°/16	$C_{12}H_{18}Si$ (190.4)	190 (M^+, 15); 175 (6); 135 (4); 73 (100)	−0.06 (s, 9H); 2.00 (s, 2H); 4.82, 5.07 (pair of br m, 2H); 7.15–7.4 (m, 5H)
e 	$[P(C_6H_5)_3]_4Pd$	78[e]	—	$C_{13}H_{20}Si$ (204.4)	204 (M^+, 6); 189 (1); 135 (1); 73 (100)	−0.14 (s, 9H); 1.70 (d, 3H, J=7 Hz); 1.95 (s, 2H); 5.50 (q, 1H); 7.0–7.3 (m, 5H)
f 	$NiBr_2$	92	84°/5	$C_{12}H_{26}Si$ (198.4)	198 (M^+, 7); 128 (21); 73 (100)	−0.03 (s, 9H); 0.85 (deformed t, 3H); 1.1–1.6 (br, 8H); 1.43 (s, 2H); 1.75–2.0 (br m, 2H); 4.43, 4.51 (pair of br s, 2H)
g 	$NiBr_2$	81	—	$C_{12}H_{24}Si$ (196.4)	196 (M^+, 3); 153 (3); 128 (5); 122 (4); 73 (100)	0.01 (s, 9H); 1.49 (s, 2H); 1.56, 1.66 (pair of s, 6H); 1.85–2.15 (m, 4H); 4.47, 4.54 (pair of br s); 4.9–5.16 (br m, 1H)
h 	$NiBr_2$	48[f]	—	$C_{11}H_{22}Si$ (182.4)	182 (M^+, 35); 108 (42); 73 (100)	−0.07 (s, 9H); 0.95 (d, 3H, J=7 Hz); 1.36 (s, 2H); 1.1–2.1 (m, 7H); 5.09 (br t, 1H)
i 	$NiBr_2$	70	—	$C_{14}H_{20}Si$[g] (216.4)	216 (M^+, 100); 201 (20); 112 (23); 73 (78)	0.05 (s, 9H); 1.80 (s, 2H); 4.80, 4.97 (pair of br s, 2H); 6.53 (AB, 2H, J=16 Hz, $\Delta\nu$=32 Hz); 6.97–7.4 (m, 5H)
j 	$Ni(acac)_2$	47[h]	—	$C_{18}H_{22}Si$ (266.5)	266 (M^+, 84); 251 (9); 192 (6); 73 (100)	−0.21 (s, 9H); 3.15 (s, 1H); 5.01, 5.20 (pair of br s, 2H); 6.8–7.14 (m, 10H)

[a] The coupling reaction was carried out at room temperature for 15 h unless otherwise noted.
[b] Yield of isolated product. G.L.C. yield in parentheses.
[c] Kugelrohr distillation.
[d] The microanalyses were in satisfactory agreement with the calculated values: C, ±0.30; H, ±0.24; except for **3i** (see footnote g).
[e] For 40 h.
[f] At room temperature for 3 days.
[g] Reproducible microanalyses could not be obtained because of the instability of the allylsilane **3i**. M.S.: *m/e* of M^+ = 216.1337 (calc. 216.1335).
[h] Reflux for 8 h.

stirred at −78 °C for 30 min, diethyl phosphorochloridate (7.25 g, 42 mmol) is added, and the mixture is allowed to warm to room temperature over 1 h. It is then diluted with ether (70 ml), and washed successively with water (50 ml), dilute hydrochloric acid (50 ml), and saturated sodium hydrogen carbonate solution (50 ml). The ether layer is dried with sodium sulfate and the solvent is removed using a rotary evaporator. The diethyl enol phosphates **2a–h** are isolated by distillation under reduced pressure and **2i** is isolated by column chromatography using ethyl acetate as eluent.

2-Alkenylsilanes (4); General Procedure:
Into a 50-ml round-bottomed flask equipped with a stirring bar are successively added the catalyst (0.10–0.15 mmol), a solution of trimethylsilylmethylmagnesium chloride (5–9 mmol) in ether, and the enol phosphate **2** (3.0 mmol). The flask is sealed with a serum cap. The mixture is stirred at room temperature for 15 h, and then hydrolyzed with dilute hydrochloric acid (15 ml) under cooling with an ice bath. The organic layer is separated and the aqueous layer extracted with ether (2 × 220 ml). The combined ether phase is washed with saturated sodium hydrogen carbonate solution (30 ml) and with water (30 ml) and is dried with sodium sulfate. The solvent is evaporated and the allylsilane **4** isolated by distillation under reduced pressure **(4a, b, d, f)**, column chromatography on silica gel using hexane as eluent **(4c, e, g, h, i)**, or preparative T.L.C. on silica gel using hexane as eluent **(4j)**.

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