ether (2 × 30 mL). The combined organic layers were washed with water (25 mL) and brine (25 mL), dried ($MgSO_4$), and concentrated in vacuo to give VSP **31** (0.52 g). Final purification by flash chromatography (silica, 30% EtOAc, 70% hexane) afforded pure compound **31** (0.272 g, 80%): $^1H$ NMR $\delta$ 4.12–4.00 (m, 4 H), 2.28 (d, 1 H, $J$ = 3.6 Hz), 1.81–1.76 (m, 1 H), 1.55–1.38 (m, 3 H), 1.32–1.27 (m, 6 H), 0.99 (s, 3 H), 0.81 (s, 3 H), 0.69 (s, 3 H), 0.08 (s, 9 H); $^{31}P$ NMR $\delta$ −7.19. EIMS, $m/z$ (relative intensity) 360 ($M^+$, 1), 345 (29), 317 (20), 227 (14), 183 (20), 155 (100), 91 (30), 73 (57); HRMS calcd for $C_{17}H_{33}O_4PSi$ ($M^+$) 360.1885, found 360.1871.

**Acknowledgment.** We gratefully acknowledge the University of Iowa Faculty Scholars Program for the research leave during which this work was conducted (1985–88) and the Alfred P. Sloan Foundation and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for their financial support.

**Registry No.** **2**, 70-11-1; **5**, 118297-82-8; **6**, 5469-26-1; **7**, 118297-83-9; **8**, 13672-07-6; **9**, 118297-84-0; **10**, 76-29-9; **11**, 118297-85-1; **12**, 43209-86-5; **15**, 118297-86-2; **16**, 83845-70-9; **17**, 118297-87-3; **18**, 72162-99-3; **19**, 118297-88-4; **20**, 118297-89-5; **21**, 118297-90-8; **23**, 7065-46-5; **24**, 118297-91-9; **25**, 118297-92-0; **26**, 13735-78-9; **27**, 96574-65-1; **28**, 118297-93-1; **29**, 65898-11-5; **31**, 118297-94-2; $LiN(TMS)_2$, 4039-32-1; TMSCl, 75-77-4; $TMSCH_2MgCl$, 13170-43-9; diphenyl phosphorochloridate, 2524-64-3; benzoyl chloride, 98-88-4; $p$-anisoyl chloride, 100-07-2.

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# Synthesis of Vinyl Silanes from Vinyl Silane Phosphates

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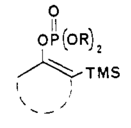
To develop a new synthesis of vinyl silanes, a representative set of vinyl silane phosphates (VSP's) has been treated with several organocuprate reagents. With acyclic VSP's, phosphate substitution proceeds in generally good yields, giving a single stereoisomer of the vinyl silane with retention of the VSP stereochemistry. In the cyclic systems examined, yields are generally somewhat lower under the same reactions conditions. However, this new sequence offers a regiochemistry complementary to other syntheses of cyclic vinyl silanes, and an approach to highly substituted vinyl silanes applicable to both cyclic and acyclic systems.

As vinyl silanes have gained popularity as synthetic intermediates,[2] the need for more general syntheses of this functionality has grown as well.[2,3] Furthermore, while many types of vinyl silanes are readily available, synthesis of certain classes is still problematic. For example, the regiospecific synthesis of cyclic vinyl silanes can be troublesome,[4] and it is difficult to prepare highly substituted vinyl silanes in either cyclic or acyclic systems.[2] In an earlier paper,[5] we described several syntheses of vinyl silane phosphates (VSP's, **1**), a novel juxtaposition of functionality with a variety of potential applications in organic synthesis. In this report, we describe a synthesis of vinyl silanes from representative VSP's.[6]



1

The most straightforward conversion of a VSP into a vinyl silane formally requires displacement of a phosphate ester with concomitant carbon–carbon (or carbon–hydrogen) bond formation. While substitutions of vinyl phosphates by alkyl groups upon treatment with various cuprates are known, in simple systems this is a difficult transformation, which often proceeds in low yield.[7] In contrast, vinyl phosphates in conjugation with a group capable of stabilizing a negative charge, e.g. the vinyl phosphate derivatives of $\beta$-keto esters or $\beta$-diketones, react with alkyl cuprates in an efficient C–C bond forming reaction.[8] Therefore, with respect to the potential for cuprate substitution in VSP's, the central question could be whether or not the trialkylsilyl group provides stabilization in a fashion analogous to the carbonyl group of conjugated vinyl phosphates. While there is evidence to support the view that a trialkylsilyl group can stabilize an $\alpha$-anion,[9] the significance of this fact to cuprate substitutions in VSP's is less apparent.

Preparations of organocuprates are legion,[10] and their reactivity in additions to enones is known to vary with the nature of the copper salt and solvent, as well as the cuprate order.[11] Initially, two representative systems, the VSP derivatives of pinacolone (**2**) and acetophenone (**4**), were treated with several copper-based reagents. With a standard preparation of lower order methyl cuprate[10a] (from CuI and MeLi), the desired vinyl silanes **3a** and **5a**

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[1] Fellow of the Alfred P. Sloan Foundation, 1985–1989.

[2] Fleming, I.; Chan, T. H. *Synthesis* **1979**, 761. Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: Berlin, 1983.

[3] Syntheses of vinyl silanes include the following. (a) Silane additions to acetylenes: Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527. (b) Addition reactions: Burford, C.; Cooke, F.; Roy, G.; Magnus, P. *Tetrahedron* **1983**, *39*, 867. (c) Wurtz-like reactions of vinylic halides: Nagendrappa, G. *Synthesis* **1980**, 704. Fleming, I.; Pearce, A. *J. Chem. Soc., Perkin Trans. 1* **1980**, 2485. Hudrlik, P. F.; Kulkarni, A. K.; Jain, S.; Hudrlik, A. M. *Tetrahedron* **1983**, *39*, 877. (d) From tosylhydrazones: Paquette, L. A.; Fristad, W. E.; Dime, D. S.; Bailey, T. R. *J. Org. Chem.* **1980**, *45*, 3017.

[4] Hudrlik, P. F.; Kulkarni, A. K. *Tetrahedron* **1985**, *41*, 1179.

[5] Koerwitz, F. L.; Hammond, G. B.; Wiemer, D. F. *J. Org. Chem*, preceding paper in this issue.

[6] Portions of this work were reported at the 193rd American Chemical Society National Meeting, Denver, April 1987, and at the 23rd Midwest Regional Meeting, Wichita, November 1987.

[7] Blaszczak, L.; Winkler, J.; O'Kuhn, S. *Tetrahedron Lett.* **1976**, *49*, 4405.

[8] Sum, F. W.; Weiler, L. *Can. J. Chem.* **1979**, *57*, 1431.

[9] Schleyer, P. v. R.; Clark, T.; Kos, A. J.; Spitznagel, G. W.; Rohde, C.; Arad, D.; Houk, K. N.; Rondan, N. G. *J. Am. Chem. Soc.* **1984**, *106*, 6467 and references cited therein.

[10] Among the copper salts often used are the following. (a) CuI: House, H. O.; Respess, W. L.; Whitesides, G. M.; *J. Org. Chem.* **1966**, *31*, 3128. Corey, E. J.; Posner, G. H. *J. Am. Chem. Soc.* **1967**, *89*, 3911. (b) $CuBr{\cdot}SMe_2$: House, H. O.; Chu, C.-y.; Wilkens, J. M.; Umen, M. J. *J. Org. Chem.* **1975**, *40*, 1460. (c) CuCN: Lipshutz, B. H.; Wilhelm, R. S.; Floyd, D. M. *J. Am. Chem. Soc.* **1981**, *103*, 7672. (d) CuOTf: Bertz, S. H.; Dabbagh, G.; Williams, L. M. *J. Org. Chem.* **1985**, *50*, 4414.

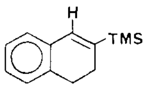
[11] (a) Bertz, S. H.; Gibson, C. P.; Dabbagh, G. *Tetrahedron Lett.* **1987**, *28*, 4251. (b) Lipshutz, B. H. *Synthesis* **1987**, 325. (c) Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A. *Tetrahedron* **1984**, *40*, 5005.

0022-3263/89/1954-0743$01.50/0

were obtained in reasonable yields (52 and 90%, respectively). With a lower order butyl cuprate, the VSP **2** was converted to the vinyl silane **3b** in 38% yield.[12] However, higher order cyano cuprates[10c,11c] ultimately were chosen for further study, for such cuprates combine an ease of preparation and handling with good reactivity.[12]

After these preliminary experiments, a number of VSP's,[5] with varying degrees of $\alpha$-substitution and conjugation, were treated with several higher order cyano cuprates (Table I). Although the yields varied over a wide range, in every case but one (bicyclic VSP **16**) the desired vinyl silane was produced. With the VSP derivatives of acyclic ketones, isolated yields of the vinyl silanes averaged approximately 66%. With the VSP derivatives of cyclic ketones, yields of the vinyl silanes were usually somewhat lower (23–74%). As noted above, the bicyclic, camphor-derived, VSP **16** failed to react under these conditions, although a trace of the methyl substitution product was observed when a lower order methyl cuprate was used.

The ease of vinyl silane formation is dependent upon both the VSP structure and the particular cuprate used. For example, with the methyl cuprate, yields ranged from approximately 20% for the cyclohexyl system to over 70% for substitution in nonconjugated, acyclic cases. With the more reactive butyl cuprate, the substitution products generally were obtained in equal or better isolated yields. However, in one case, with VSP **14**, the desired product **15b** was accompanied by a significant amount of compound **18**, apparently a product of hydride substitution.[13]

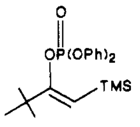
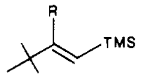
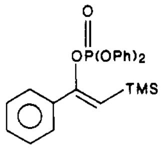
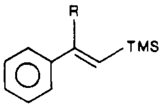
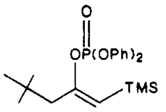
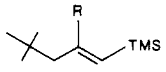
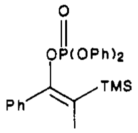
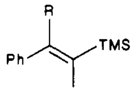
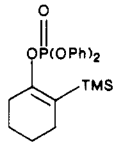
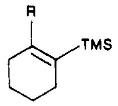
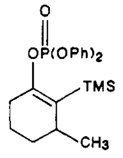
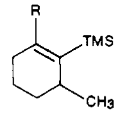
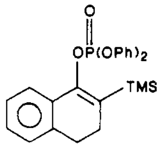
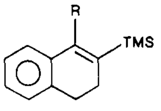
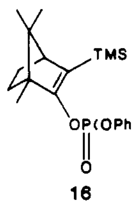
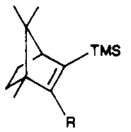


**18**

With the phenyl cuprate, the vinyl silanes were obtained in intermediate yields relative to the methyl and butyl series. While this may be due in part to a lower reactivity of the phenyl cuprate, the formation of significant amounts of biphenyl in these reactions also plays a role because it makes purification of the product more difficult.

Substitution reactions with the cyclic VSP's can give only a single stereoisomer, but the acyclic VSP's **2**, **4**, **6**, and **8** could give two stereoisomers in most of these cases. Only one isomer was detected in each of the reactions examined, however. In several cases, stereochemical assignments could be made by comparisons with known data; in others, difference NOE experiments could be used to assign stereochemistry. For example, VSP **2** reacts with phenyl cuprate to give a known product, compound **3c**,[14] and thus the *Z* stereochemistry could be assigned by comparison with literature data. The vinyl silane **3a** was assigned the *E* stereochemistry, after a difference NOE experiment revealed a 13% enhancement of the vinylic resonance upon irradiation of the signal at 1.03 ppm. With the butyl-substituted product **3b**, an analogous NOE experiment gave a 12% enhancement of the vinylic resonance, again leading to assignment as the *E* stereoisomer. Thus, with all three of these cuprates, VSP **2** undergoes substitution with retention of the original olefin stereochemistry.

**Table I. Conversion of VSP's to Vinyl Silanes by Reaction with Higher Order Cyano Cuprates**

| VSP | ketone | yield, % |
|---|---|---|
|  **2** |  | |
| | **3a**: R = Me | 62 |
| | **b**: R = *n*-Bu | 66 |
| | **c**: R = Ph | 45 |
|  **4** |  | |
| | **5a**: R = Me | 90[a] |
| | **b**: R = *n*-Bu | 70 |
| | **c**: R = Ph | 72 |
|  **6** |  | |
| | **7a**: R = Me | 74 |
| | **b**: R = *n*-Bu | 72 |
| | **c**: R = Ph | 72 |
|  **8** |  | |
| | **9a**: R = Me | 36 |
| | **b**: R = *n*-Bu | 90 |
| | **c**: R = Ph | 46 |
|  **10** |  | |
| | **11a**: R = Me | 23 |
| | **b**: R = *n*-Bu | 74 |
| | **c**: R = Ph | 38 |
|  **12** |  | |
| | **13a**: R = Me | 24 |
| | **b**: R = *n*-Bu | 63 |
| | **c**: R = Ph | 25 |
|  **14** |  | |
| | **15a**: R = Me | 60 |
| | **b**: R = *n*-Bu | –[b] |
| | **c**: R = Ph | 47 |
|  **16** |  | |
| | **17**: R = Me | trace |

[a] Yield obtained with a lower order cuprate. [b] Both the desired product (**15b**) and a reduction product (**18**) were observed, in a 40:60 ratio by GC analysis.

With the acetophenone-derived compounds **5a** and **5b**, stereochemical assignments could be made in an analogous fashion. Both stereoisomers in the methyl series were previously known compounds.[15] Our data for compound **5a** agrees with that previously reported, and observation

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(12) Koerwitz, F. L. Ph.D. Thesis, University of Iowa, 1988.

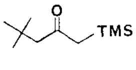
(13) Ashby, E. C.; Coleman, D. *J. Org. Chem.* **1987**, *52*, 4554. Lipshutz, B. H.; Wilhelm, R. S.; Kozlowski, J. A.; Parker, D. *J. Org. Chem.* **1984**, *49*, 3928. Analogous reduction products were not detected in the reactions of butyl cuprate with the other VSP's, not even with the closely related VSP **4** derived from acetophenone. However, substitution is more facile in the acyclic acetophenone case, which may preclude this competing reaction.

(14) Sakurai, H.; Nishiwaki, K.; Kira, M. *Tetrahedron Lett.* **1973**, 4193.

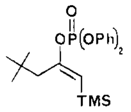
(15) Mitchell, T. N.; Wickenkamp, R.; Amamria, A.; Dicke, R.; Schneider, U. *J. Org. Chem.* **1987**, *52*, 4868. In this paper the data reported for the *Z* and *E* isomers were inadvertently transposed. Mitchell, T. N., personal communication.

of a strong NOE enhancement of the vinylic resonance upon irradiation of the ortho protons confirmed an assignment as the *E* isomer. A similar NOE effect (15%) was observed with the butyl substitution product **5b**, again indicating the *E* stereochemistry and substitution with retention of the VSP stereochemistry in the vinyl silane product.

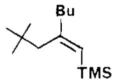
The VSP **6** also was treated with methyl, butyl, and phenyl cuprates, to obtain the expected vinyl silanes **7a–c** in uniformly good yields. These new vinyl silanes were assigned the *E*, *E*, and *Z* stereochemistries, respectively, primarily on the basis of NOE experiments, and all consistent with retention. Because formation of the stereoisomeric VSP **20** from the α-silyl ketone **19** could be favored under slightly different conditions,[5,12] it was possible to test whether substitution proceeds with true retention of the VSP stereochemistry. When an 80:20 mixture of VSP's **20** and **6** was treated with the higher order butyl cuprate, a mixture of the vinyl silanes **21** and **7b** was obtained, in the same ratio. This observation implies that the substitution process is governed by retention of the initial VSP stereochemistry, which is consistent with previous observations of cuprate substitutions in vinyl phosphates.[8]



**19**



**20**



**21**

Stereochemical assignments for the tetrasubstituted vinyl silanes **9a** and **9b** are difficult to make with certainty, for the data from NOE experiments were inconclusive. However, because all of the other acyclic cases proceed with retention of the VSP stereochemistry, it may be reasonable to assume stereochemical retention in these last two cases as well.

In conclusion, this study has shown that it is possible to prepare a variety of vinyl silanes from VSP's with carbon–carbon bond formation. On the basis of the matrix of reactions reported here, it appears that the substitution process works best in acyclic systems, with cuprates that are good nucleophiles, and that the strategy can be used to prepare highly substituted systems. Because the vinyl silane is produced regiospecifically from the VSP, the regiochemistry of the vinyl silane can be controlled by the methods used to prepare VSP's.[5] Thus, this approach offers some advantage in regiocontrol over previous methods for synthesis of cyclic vinyl silanes, as well as a regiochemistry complementary to that of the most general previous synthesis.[3d] Therefore, this new preparation of vinyl silanes from VSP's should be considered along with other approaches to vinyl silanes. Other syntheses of VSP's, and more reactions of this unique functionality, will be reported in due course.

## Experimental Section

To maintain anhydrous conditions, tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use, and all reactions in this solvent were conducted under a positive pressure of an inert gas. Flash column chromatography was done on Merck grade 60 silica gel (230–400 mesh), while radial chromatography was performed with a Chromatotron apparatus and Merck PF254 silica gel with $CaSO_4 \cdot 0.5H_2O$. NMR spectra ($^1H$ and $^{13}C$) were recorded on either a JEOL FX-90Q or a Brucker WM-360 spectrometer, with deuteriochloroform as the solvent. The $^1H$ and $^{13}C$ chemical shifts are reported in parts per million relative to $(CH_3)_4Si$. Low-resolution electron impact (EI) mass spectra were recorded with a Hewlett-Packard 5985B instrument operating at 70 eV; only selected ions are reported here. High-resolution mass spectra were recorded on a VG Instruments ZAB-HF spectrometer at the University of Iowa Mass Spectrometry Facility. Microanalyses were conducted by Desert Analytics, Tucson, AZ, or Galbraith Laboratories, Inc., Knoxville, TN.

**Reaction of $(CH_3)_2CuLi$ with VSP 4. General Procedure for Additions with Lower Order Cuprates.** To a suspension of copper(I) iodide (270 mg, 1.42 mmol) in ether (0.9 mL) was added methyllithium (1.69 M in ether, 2.84 mmol) at −30 °C. After 12 min the solution became transparent, at which point a solution of VSP **4** (150 mg, 0.35 mmol) in ether (1.6 mL) was added dropwise. The resulting yellow mixture was stirred at −30 °C for 4 h and then quenched by addition of a mixture of saturated ammonium chloride (10 mL) and ether (10 mL). The resulting mixture was filtered through a Florisil pad, which was in turn washed with ether. The organic filtrate was washed with a dilute solution of ammonia in brine (20 mL), dried ($MgSO_4$), and concentrated in vacuo to yield vinyl silane **5a** (60 mg, 90%): $^1H$ NMR δ 7.45 (d, 2 H, *J* = 7.0 Hz), 7.32–7.23 (m, 3 H), 5.91 (s, 1 H), 2.21 (s, 3 H), 0.19 (s, 9 H); $^{13}C$ NMR δ 151.6, 144.3, 128.1, 127.3, 125.4, 120.1, 20.9, 0.04; EIMS, *m/z* (relative intensity), 190 ($M^+$, 14), 175 (63), 159 (12), 135 (100), 105 (5), 73 (9), 59 (6). This compound was assigned the *E* stereochemistry on the basis of comparison with $^1H$ NMR data previously reported,[15] and observation of an 8% NOE enhancement of the resonance at 5.91 ppm upon irradiation of the resonance at 7.45 ppm. Irradiation of the resonance at 2.21 ppm gave no enhancement of the vinylic resonance.

**Reaction of $(CH_3)_2CuLi$ with VSP 2.** A solution of VSP **2** in diethyl ether (200 mg, 0.5 mmol, in 2 mL) was treated with $Me_2CuLi$ (1.98 mmol) in ether (4 mL) in a manner analogous to the procedure described above. Purification of the crude product by column chromatography (silica, pentane) produced vinyl silane **3a**[16b] (44 mg, 52%): $^1H$ NMR δ 5.24 (s, 1 H), 1.74 (s, 3 H), 1.03 (s, 9 H), 0.09 (s, 9 H); EIMS, *m/z* (relative intensity) 170 ($M^+$, 5), 155 (24), 113 (13), 99 (7), 96 (21), 83 (5), 73 (100), 59 (10), 45 (10). Anal. Calcd for $C_{10}H_{22}Si$: C, 68.26; H, 13.02. Found: C, 68.14; H, 12.77. Irradiation of the resonance at 1.03 ppm results in a 13% enhancement of the resonance at 5.24 ppm, supporting assignment as the *E* isomer. When VSP **2** was treated with the higher order methyl cuprate according to the general procedure given below, the same product was obtained in 62% yield.

**Reaction of $(CH_3)_2Cu(CN)_2Li_2$ with VSP 6. General Procedure for Vinyl Silane Synthesis via Higher Order Methyl Cuprates.** To a suspension of CuCN (172 mg, 1.92 mmol) in THF (5 mL) was added methyllithium (1.4 M in ether, 3.84 mmol) at −78 °C. The resulting mixture was allowed to warm to −40 °C over 45 min and then cooled to −78 °C before the addition of VSP **6** (200 mg, 0.48 mmol) as a solution in THF (1 mL). After 3 h the reaction was quenched by the addition of a solution of saturated ammonium chloride and concentrated ammonium hydroxide (4:1, 10 mL) and ether (20 mL). The layers were separated, and the ether layer was washed with brine (2 × 20 mL) and dried ($MgSO_4$). Concentration in vacuo and purification by column chromatography (silica, hexane) provided pure vinyl silane **7a** as a colorless oil (66 mg, 74%): $^1H$ NMR δ 5.13 (s, 1 H), 1.97 (s, 2 H), 1.81 (s, 3 H), 0.9 (s, 9 H), 0.09 (s, 9 H); $^{13}C$ NMR δ 153.5, 127.6, 56.6, 31.6, 30.1, 22.7, 0.1; EIMS, *m/z* (relative intensity), 184 ($M^+$, 0.4), 169 (9), 128 (24), 113 (25), 97 (19), 73 (100), 57 (65). Anal. Calcd for $C_{11}H_{24}Si$: C, 71.65; H, 13.12. Found: C, 71.80; H, 13.36. Irradiation of the resonance at 1.97 ppm results in a 4% enhancement of the resonance at 5.13 ppm, supporting assignment as the *E* isomer.

**Reaction of $(CH_3)_2Cu(CN)_2Li_2$ with VSP 8.** Compound **8** (300 mg, 0.68 mmol) in anhydrous THF (2 mL) was treated with the higher order cuprate (2.74 mmol) in THF (10 mL) according to the general procedure. Purification by radial chromatography (silica, hexane) gave pure vinyl silane **9a** (49 mg, 36%): $^1H$ NMR δ 7.33–7.20 (m, 3 H), 7.08 (d, 2 H, *J* = 6.9 Hz), 2.07 (q, 3 H, *J* = 1.5 Hz), 1.55 (q, 3 H, *J* = 1.5 Hz), 0.22 (s, 9 H); $^{13}C$ NMR δ 146.7, 145.6, 130.2, 128.0, 127.7, 125.2, 19.9, 0.28; EIMS, *m/z* (relative intensity) 204 ($M^+$, 11), 189 (53), 173 (5), 135 (95), 115 (18), 91

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(16) (a) Ikenaga, K.; Kikukawa, K.; Matsuda, T. *J. Org. Chem.* **1987**, *52*, 1276. (b) Cunico, R. F.; Han, Y.-k. *J. Organomet. Chem.* **1979**, *174*, 247.

(17), 73 (100), 45 (36); HRMS calcd for $C_{13}H_{20}Si$ 204.1334, found 204.1338.

**Reaction of $(CH_3)_2Cu(CN)_2Li_2$ with VSP 10.** VSP **10** (300 mg, 0.75 mmol) was treated with the higher order cuprate (2.99 mmol) to obtain vinyl silane **11a**[17] (30 mg, 23%): $^1H$ NMR $\delta$ 2.01–1.93 (m, 4 H), 1.71 (s, 3 H), 1.58–1.49 (m, 4 H), 0.09 (s 9 H); EIMS, *m/z* (relative intensity) 168 ($M^+$, 8) 153 (12), 94 (51), 79 (18), 73 (100), 59 (27).

**Reaction of $(CH_3)_2Cu(CN)_2Li_2$ with VSP 12.** Treatment of VSP **12** (200 mg, 0.48 mmol) in THF (2 mL) with the higher order methyl cuprate (1.92 mmol) in THF (5 mL) provided compound **13a** (27 mg, 29%): $^1H$ NMR $\delta$ 2.30 (m, 1 H), 1.97–1.89 (m, 2 H), 1.72 (s, 3 H), 1.68–1.37 (m, 2 H), 0.95 (d, 3 H, $J$ = 6.9 Hz), 0.14 (s, 9 H); $^{13}C$ NMR $\delta$ 142.8, 134.8, 33.1, 31.2, 29.8, 24.3, 21.8, 17.9, 0.8; EIMS, *m/z* (relative intensity) 182 ($M^+$, 2), 167 (2), 108 (20), 93 (19), 73 (100), 58 (29), 45 (39); HRMS calcd for $C_{11}H_{22}Si$ 182.1491, found 182.1485.

**Reaction of $(CH_3)_2Cu(CN)_2Li_2$ with VSP 14.** Compound **14** (300 mg, 0.68 mmol) in THF (2 mL) was allowed to react with the higher order methyl cuprate (2.74 mmol) in THF (10 mL) to obtain compound **15a** (49 mg, 36%): $^1H$ NMR $\delta$ 7.28–7.10 (m, 4 H), 2.62 (t, 2 H, $J$ = 7.0 Hz), 2.21 (t, 2 H, $J$ = 6.9 Hz), 2.18 (s, 3 H), 0.22 (s, 9 H); $^{13}C$ NMR $\delta$ 140.3, 137.1, 136.7, 156.1, 126.9, 126.8, 126.3, 122.8, 28.5, 27.1, 19.6, 0.3; EIMS, *m/z* (relative intensity) 216 ($M^+$, 22), 201 (8), 142 (100), 128 (17), 115 (12), 73 (43), 59 (20). Anal. Calcd for $C_{14}H_{20}Si$: C, 77.71; H, 9.32. Found: C, 77.90; H, 9.30.

**Reaction of $(n\text{-}Bu)_2Cu(CN)_2Li_2$ with VSP 6. General Procedure.** To a slurry of CuCN (172 mg, 1.92 mmol) in THF (5 mL) at −78 °C was added *n*-butyllithium (1.6 M in hexane, 3.84 mmol). The resulting clear tan solution was allowed to warm to −40 °C but was cooled to −78 °C before addition of a solution of VSP **6** (200 mg, 0.48 mmol) in THF (1 mL). After the mixture was stirred for two more hours, the reaction was quenched with 10 mL of 4:1 saturated ammonium chloride–concentrated ammonium hydroxide and diluted with ether (20 mL). The layers were separated, and the ether layer was washed with brine (20 mL) and dried ($MgSO_4$). Evaporation of the solvent in vacuo and purification by column chromatography (silica, hexane) afforded pure vinyl silane **7b** (78 mg, 72%): $^1H$ NMR $\delta$ 5.1 (s, 1 H), 2.1–2.08 (m, 2 H), 1.95 (s, 2 H), 1.35–1.24 (m, 4 H), 0.90–0.87 (m, 12 H); $^{13}C$ NMR $\delta$ 158.5, 127.4, 51.9, 37.6, 32.4, 31.8, 30.1, 23.1, 14.1, 0.5; EIMS, *m/z* (relative intensity) 226 ($M^+$, 1.2), 211 (4), 128 (41), 113 (6), 97 (8), 73 (100), 57 (67); HRMS calcd for $C_{14}H_{30}Si$ 226.2117, found 226.2137. Irradiation of the resonance at 1.95 ppm results in a 13% enhancement of the resonance at 5.1 ppm, supporting assignment as the *E* isomer.

**Reaction of $(n\text{-}Bu)_2Cu(CN)_2Li_2$ with VSP 2.** A solution of VSP **2** (110 mg, 0.27 mmol) in THF (1 mL) was added to the higher order butyl cuprate (1.08 mmol in 5 mL of THF). The crude product, isolated as described above, was purified by radial chromatography (silica, hexane), furnishing vinyl silane **3b** (38 mg, 66%): $^1H$ NMR $\delta$ 5.29 (s, 1 H), 2.14–2.09 (m, 2 H), 1.38–1.28 (m, 4 H), 1.06 (s, 9 H), 0.91 (t, 3 H, $J$ = 7.1 Hz), 0.09 (s, 9 H); $^{13}C$ NMR $\delta$ 167.8, 119.9, 38.5, 35.1, 33.1, 30.1, 23.6, 14.0, 0.6; EIMS, *m/z* (relative intensity) 197 ($M^+ - 15$, 2), 170 (7), 113 (10), 73 (100), 59 (7); HRMS calcd for $C_{13}H_{28}Si$ ($M^+ - 15$) 197.1725, found 197.1705. Irradiation of the resonance at 1.06 ppm results in a 12% enhancement of the resonance at 5.29 ppm, supporting assignment as the *E* isomer.

**Reaction of $(n\text{-}Bu)_2Cu(CN)_2Li_2$ with VSP 4.** According to the general procedure, VSP **4** (250 mg, 0.59 mmol) in THF (2 mL) was converted to the vinyl silane **5b** (95 mg, 70%) by treatment with the higher order butyl cuprate (2.36 mmol) in THF (8 mL): $^1H$ NMR $\delta$ 7.41–7.20 (m, 5 H), 5.71 (s, 1 H), 2.62–2.57 (m, 2 H), 1.33–1.26 (m, 4 H), 0.86 (t, 3 H, $J$ = 6.8 Hz), 0.18 (s, 9 H); $^{13}C$ NMR $\delta$ 157.9, 143.9, 128.1, 127.8, 127.1, 126.2, 34.8, 31.7, 22.9, 14.0, 0.4; EIMS, *m/z* (relative intensity) 232 ($M^+$, 7), 217 (13), 190 (42), 175 (17), 149 (97), 135 (100), 105 (12), 73 (45); HRMS calcd for $C_{15}H_{24}Si$ 232.1647, found 232.1622. Anal. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41. Found: C, 77.98; H, 10.74. Irradiation at 7.39 ppm results in a 15% enhancement of the resonance at 5.71 ppm, supporting assignment as the *E* isomer.

**Reaction of $(n\text{-}Bu)_2Cu(CN)_2Li_2$ with VSP 8.** Treatment of VSP **8** (300 mg, 0.68 mmol in 2 mL of THF) with *n*-butyl cuprate (2.74 mmol) in THF (10 mL) yielded the expected vinyl silane **9b** (151 mg, 90%): $^1H$ NMR $\delta$ 7.33–7.20 (m, 3 H), 7.03 (d, 2 H, $J$ = 7.0 Hz), 2.42–2.38 (m, 2 H), 1.49 (s, 3 H), 1.26–1.15 (m, 4 H), 0.81 (t, 3 H, $J$ = 6.9 Hz), 0.21 (s, 9 H); $^{13}C$ NMR $\delta$ 152.4, 144.0, 129.8, 128.3, 128.0, 125.9, 38.9, 31.2, 22.9, 19.8, 14.1, 0.6; EIMS, *m/z* (relative intensity) 246 ($M^+$, 5), 231 (13), 204 (30), 172 (6), 135 (90), 128 (12), 115 (22), 91 (20), 73 (100); HRMS calcd for $C_{16}H_{26}Si$ 246.1804, found 246.1804.

**Reaction of $(n\text{-}Bu)_2Cu(CN)_2Li_2$ with VSP 10.** The general procedure was repeated with the *n*-butyl cuprate (2.99 mmol) in THF (10 mL) and VSP **10** (300 mg, 0.75 mmol) in THF (2 mL). The usual workup and purification provided vinyl silane **11b** (30 mg, 23%): $^1H$ NMR $\delta$ 2.05–1.95 (m, 6 H), 1.59–1.48 (m, 4 H), 1.37–1.28 (m, 4 H), 0.90 (t, 3 H, $J$ = 7.0 Hz), 0.09 (s, 9 H); $^{13}C$ NMR $\delta$ 148.1, 128.8, 38.3, 31.5, 30.4, 29.2, 23.3, 23.0, 14.2, 0.4; EIMS, *m/z* (relative intensity) 210 ($M^+$, 4), 195 (5), 168 (14), 136 (31), 127 (6), 107 (13), 94 (51), 73 (100). Anal. Calcd for $C_{13}H_{26}Si$: C, 74.20; H, 12.45. Found: C, 74.00; H, 12.07.

**Reaction of $(n\text{-}Bu)_2Cu(CN)_2Li_2$ with VSP 12.** Reaction of VSP **12** (200 mg, 0.48 mmol in 1 mL of THF) with the higher order butyl cuprate (1.92 mmol) in THF (5 mL) gave vinyl silane **13b** (21 mg, 24%): $^1H$ NMR $\delta$ 2.31 (m, 1 H), 2.03–1.92 (m, 4 H), 1.65–1.25 (m, 8 H), 0.93 (d, 3 H, $J$ = 6.9 Hz), 0.90 (t, 3 H, $J$ = 7.1 Hz), 0.12 (s, 9 H); $^{13}C$ NMR $\delta$ 147.6, 134.6, 38.6, 31.4, 30.2, 30.0, 23.1, 22.0, 17.9, 14.2, 1.2; EIMS, *m/z* (relative intensity) 224 ($M^+$, 3), 209 (4), 150 (13), 121 (7), 108 (13), 93 (14), 73 (100), 59 (18). Anal. Calcd for $C_{14}H_{28}Si$: C, 74.91; H, 12.57. Found: C, 75.21; H, 12.70.

**Reaction of $(n\text{-}Bu)_2Cu(CN)_2Li_2$ with VSP 14.** According to the general procedure, VSP 14 (250 mg, 0.55 mmol) in THF (2 mL) was treated with the higher order butyl cuprate (2.22 mmol) in THF (8 mL). Both the substitution product **15b** and the reduction product **18** were formed, in a ratio of 40:60 based on GC analysis. After workup, the standard chromatographic techniques proved incapable of separating these two products. However, pure compound **18** (42 mg, 38%) and a small amount of pure compound **15b** were obtained by radial chromatography on silver nitrate impregnated silica (hexane 65%, ethyl acetate 35%). Compound **18**: $^1H$ NMR $\delta$ 7.16–7.02 (m, 4 H), 6.7 (s, 1 H), 2.72 (t, 2 H, $J$ = 7.8 Hz), 2.29 (dt, 2 H, $J$ = 1.5, 7.8 Hz), 0.15 (s, 9 H); EIMS, *m/z* (relative intensity) 202 ($M^+$, 21), 187 (14), 143 (4), 128 (100), 115 (5), 73 (67), 59 (34); HRMS calcd for $C_{13}H_{18}Si$ 202.1160, found 202.1169. Compound **15b**: $^1H$ NMR $\delta$ 7.34–7.15 (m, 4 H), 2.68–2.61 (m, 4 H), 2.22 (t, 2 H, $J$ = 7.0 Hz), 1.43–1.39 (m, 4 H), 0.95 (t, 3 H, $J$ = 6.8 Hz), 0.25 (s, 9 H); EIMS, *m/z* relative intensity 258 ($M^+$, 12), 243 (4), 216 (37), 142 (52), 129 (20), 115 (11), 73 (100), 59 (25); HRMS calcd for $C_{17}H_{26}Si$ 258.1807, found 258.1806.

**Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 4. General Procedure.** Phenylmagnesium bromide (3.0 M in ether, 6.58 mmol) was added to a suspension of CuCN (295 mg, 3.28 mmol) in THF (15 mL) at 0 °C. After 15 min VSP 4 (400 mg, 0.94 mmol) in THF (3 mL) was introduced, and the mixture was stirred for 2 h. The reaction was then quenched by adding a solution of 4:1 $NH_4Cl$ (saturated)/$NH_4OH$ (concentrated) (15 mL) and ether (20 mL). The layers were separated, and the ether layer was washed with saturated ammonium chloride (30 mL) and brine (30 mL) and dried ($MgSO_4$). Concentration in vacuo and purification by radial chromatography (silica; partitioning conditions, $CH_3CN$/hexane) gave pure vinyl silane **5c**[16] (171 mg, 72%): $^1H$ NMR $\delta$ 7.37–7.30 (m, 10 H), 6.32 (s, 1 H), −0.08 (s, 9 H); $^{13}C$ NMR $\delta$ 157.0, 143.2, 142.6, 129.62, 129.58, 127.9, 127.8, 127.5, 127.3, 127.1, −0.03; EIMS, *m/z* (relative intensity) 252 ($M^+$, 11), 237 (33), 178 (7), 159 (4), 135 (100), 105 (7), 73 (6), 43 (6).

**Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 2.** Treatment of VSP **2** (222 mg, 0.55 mmol) with the higher order diphenyl cuprate (1.93 mmol) in a manner analogous to the general procedure described above gave compound **3c**[14] (58 mg, 45%): $^1H$ NMR $\delta$ 7.25–7.21 (m, 3 H), 7.03–7.00 (m, 2 H), 5.67 (s, 1 H), 1.07 (s, 9 H), −0.31 (s, 9 H); $^{13}C$ NMR $\delta$ 167.6, 142.6, 129.9, 126.9, 126.2, 123.5, 37.9, 29.7, −0.1; EIMS, *m/z* (relative intensity) 232 ($M^+$, 2), 217 (44), 175 (41), 135 (33), 115 (8), 73 (100), 57 (7).

**Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 6.** Phenylmagnesium bromide (3.0 M in THF, 3.84 mmol) was added

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[17] Eaborn, C.; Jackson, R. A.; Pearce, R. *J. Chem. Soc., Perkin Trans. 1* **1975**, 470.

dropwise to a stirred suspension of CuCN (172 mg, 1.92 mmol) in THF (10 mL) at -78 °C. The resulting tan-colored slurry was allowed to warm to -10 °C to produce a clear tan solution. After the mixture was cooled to -78 °C, a solution of VSP **6** (200 mg, 0.48 mmol) in THF (1 mL) was added, and the reaction mixture was left to warm to room temperature overnight. Workup and purification as described above afforded compound **7c** (85 mg, 72%): $^1$H NMR $\delta$ 7.29–7.22 (m, 5 H), 5.57 (s, 1 H), 2.47 (s, 2 H), 0.81 (s, 9 H), -0.13 (s, 9 H); $^{13}$C NMR $\delta$ 157.8, 145.4, 131.9, 128.3, 127.6, 126.8, 56.6, 31.9, 30.1, 0.24; EIMS, *m/z* (relative intensity) 246 ($M^+$, 0.3), 231 (0.5), 135 (8), 73 (32), 57 (100), 41 (46); HRMS calcd for $C_{16}H_{26}Si$ 246.1804, found 246.1798. Irradiation of the resonance at 2.47 ppm results in a 10% enhancement of the resonance at 5.57 ppm, supporting assignment as the *Z* isomer.

**Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 8.** Solutions of VSP **8** (325 mg, 0.74 mmol) and the higher order phenyl cuprate (2.97 mmol) in THF (3 and 15 mL, respectively) were allowed to react via the general procedure above to obtain vinyl silane **9c** (91 mg, 46%): $^1$H NMR $\delta$ 7.26–7.10 (m, 10 H), 1.82 (s, 3 H), -0.14 (s, 9 H); $^{13}$C NMR $\delta$ 152.3, 145.3, 143.5, 135.6, 129.6, 129.2, 127.8, 127.7, 126.8, 126.3, 20.7, -0.2; EIMS, *m/z* (relative intensity) 266 ($M^+$, 27), 251 (57), 135 (100), 115 (9), 105 (4), 91 (6), 73 (27). Anal. Calcd for $C_{18}H_{22}Si$: C, 81.14; H, 8.32. Found: C, 81.43; H, 8.35.

**Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 10.** According to the general procedure, vinyl silane **11c** was prepared from the VSP **10** (250 mg, 0.62 mmol) and the higher order phenyl cuprate (2.48 mmol) with THF as solvent (5 and 10 mL, respectively). The desired vinyl silane **11c** was obtained as a colorless oil (54 mg, 38%): $^1$H NMR $\delta$ 7.27–7.19 (m, 3 H), 7.09 (d, 2 H, $J$ = 8.0 Hz), 2.26–2.22 (m, 2 H), 2.17–2.13 (m, 2 H), 1.73–1.60 (m, 4 H), -0.26 (s, 9 H); $^{13}$C NMR $\delta$ 148.9, 146.7, 133.5, 128.4, 127.7, 126.4, 34.5, 29.0, 23.3, 22.8, -0.4; EIMS, *m/z* (relative intensity) 230 ($M^+$, 8), 215 (21), 156 (53), 135 (11), 91 (11), 73 (100), 59 (21); HRMS calcd for $C_{15}H_{22}Si$ 230.1490, found 230.1490.

**Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 12.** VSP **12** (300 mg, 0.72 mmol) was treated with the higher order phenyl cuprate (2.88 mmol) in THF (12 mL) to obtain vinyl silane **13c** (44 mg, 25%): $^1$H NMR $\delta$ 7.31–7.08 (m, 5 H), 2.50–1.25 (m, 7 H), 1.10 (d, 3 H, $J$ = 6.9 Hz), -0.23 (s, 9 H); $^{13}$C NMR $\delta$ 149.4, 146.7, 138.8, 128.4, 127.7, 126.4, 34.6, 31.9, 30.6, 22.0, 19.0, 1.0; EIMS, *m/z* (relative intensity) 244 ($M^+$, 5), 229 (9), 170 (100), 155 (18), 135 (25), 91 (22), 73 (92); HRMS calcd for $C_{16}H_{24}Si$ 244.1647, found 244.1613.

**Reaction of $(C_6H_5)_2Cu(CN)_2(MgCl)_2$ with VSP 14.** The general procedure was repeated with the higher order phenyl cuprate (1.77 mmol) and VSP **14** (200 mg, 0.44 mmol) in THF (10 mL) to obtain vinyl silane **15c** (57 mg, 47%): $^1$H NMR $\delta$ 7.36–7.01 (m, 8 H), 6.65 (d, 1 H, $J$ = 7.6 Hz), 2.78 (m, 2 H), 2.41 (m, 2 H), -0.18 (s, 9 H); $^{13}$C NMR $\delta$ 147.1, 141.8, 137.7, 136.5, 136.4, 130.4, 127.9, 127.0, 126.96, 126.9, 126.2, 125.8, 28.3, 26.9, -0.4; EIMS, *m/z* (relative intensity) 278 ($M^+$, 5), 204 (29), 189 (5), 128 (5), 73 (100), 59 (40); HRMS calcd for $C_{19}H_{22}Si$ 278.1491, found 278.1498.

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# Chemistry of Cyclic Phosphorus Compounds. 3. Synthesis of Pheromones Having an γ,δ-Unsaturated Ketone System from 1,1-Diphenylphospholanium Perchlorate

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1,1-Diphenylphospholanium perchlorate (**1**) was converted into the sex pheromones **5a,b** of the Japanese female peach fruit moth by use of tandem Wittig reactions. The ylide of **1** formed with potassium *tert*-butoxide reacted with heptanal to give *Z* phosphine oxide **2** with stereoselectivity. The reaction of the anion of **2** with dimethyl disulfide followed by the Horner–Wittig reaction with nonanal or octanal gave the corresponding diene derivatives **4a,b**. Hydrolysis of **4a,b** afforded the desired *Z* γ,δ-unsaturated ketones **5a,b**. On the other hand, the conversion of **9**, which was derived from methylthio-substituted compound **6**, gave an *E* and *Z* isomeric mixture of **5b** (4:5).

Tandem Wittig reactions with the same phosphorous atom from a cyclic phosphonium salt provide a versatile procedure for syntheses of dienes or enones. However, to our knowledge, only few examples of their use have been reported.[1,2] We have previously reported the synthesis of 1,6-diene derivatives by tandem Wittig reactions[3] and application of the method to a synthesis of the sex pheromone of Douglas Fir Tussock moth.[4] In connection with our continuing interest in the utilization of these reactions, we applied the method to a synthesis of γ,δ-unsaturated ketones: the sex pheromones of the Japanese female peach

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