and iodomethane (15 mL, 0.24 mol; 2 equiv). The reaction mixture was heated at 60 °C for 24 h to completely consume 1 according to TLC analysis. The reaction mixture was concentrated to small volume, diluted with water, and extracted three times with ether. The combined extracts were dried ($MgSO_4$) and concentrated to afford 21.2 g (98%) of *S*-6. The spectral characteristics of 6 were identical to those reported;[6a] $[\alpha]^{24}_D$ −18.8° (*c* 4.735, EtOH), lit.[18] for *R*-6, $[\alpha]^{24}_D$ +18.3° (*c* 4.78, EtOH).

Ethyl (*S*)-3-Hydroxy-3-phenylpropanoate (*S*-4). By a similar procedure to that described for 6 above, *S*-1 (337 mg, 2.03 mmol) was treated with potassium bicarbonate (2.0 g, 20 mmol; 10 equiv) and iodoethane (1.6 mL; 20 mmol; 10 equiv) in 2.5 mL of acetone at reflux for 36 h to afford *S*-4 (327 mg; 83%). All achiral properties of 4 are as described previously;[5a] $[\alpha]^{20}_D$ −50.8° (*c* 1.070, $CHCl_3$).

(*S*)-1-Phenyl-1,3-propanediol (*S*-7). Optically pure hydroxy acid *S*-1 (1.66 g, 10.0 mmol) was dissolved in THF (20 mL) and cooled to 0 °C. A 1.0 M solution of borane in THF (21 mL, 21 mmol; 2.1 equiv) was added (frothing) and the reaction mixture was warmed to room temperature for 1 h to completely consume 1 as determined by TLC analysis. Aqueous sodium hydroxide was added and the mixture was heated to 60 °C for 3 h to cleave the borate. The mixture was cooled to room temperature and extracted three times with ether. The combined extracts were dried ($MgSO_4$) and concentrated to afford 1.59 g of crude *S*-(−)-7 that solidified upon chilling (−20 °C). This was dissolved in methylene chloride (7.5 mL, 5 mL/g) and hexanes (7.5 mL, one volume) was added. This resulted in a phase separation which upon cooling (−20 °C) overnight afforded *S*-7 (1.47 g; 97%) as white needles, mp 63–65 °C: ^1H NMR ($CDCl_3$) δ 7.4–7.2 (m, 5 H), 4.869 (dd, 1 H, *J* = 4.04 Hz, *J* = 8.52 Hz), 3.789 (m, 2 H), 3.6 (s, 1 H), 3.14 (s, 1 H), 2.05–1.8 (m, 2 H); IR (KBr, cm^{-1}) 3350 (s, b), 1605 (w), 1485 (w); EIMS *m/e* 152 (M^+), 134 ($M^+ - H_2O$), 107 ($M^+ - CH_2CH_2OH$); $[\alpha]^{21.5}_D$ −70.5° (*c* 1.015, $CHCl_3$), lit.[6h] for *S*-7,[6h] $[\alpha]^{21.5}_D$ −63.0° (*c* 0.958, $CHCl_3$). Anal. Calcd for $C_9H_{12}O_2$: C, 71.03; H, 7.95; N, 0. Found: C, 70.98; H, 7.80; N, <0.3.

Registry No. *S*-1, 36567-72-3; *R*-1, 2768-42-5; (±)-4, 86286-51-3; *R*-4, 72656-47-4; *S*-4, 33401-74-0; *S*-6, 36615-45-9; *S*-7, 96854-34-1; ethyl benzoylacetate, 94-02-0.

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Access to Unstabilized Secondary Vinylphosphines by Chemoselective Reduction of Vinylphosphinates or by P-Alkylation of the Primary Vinylphosphine

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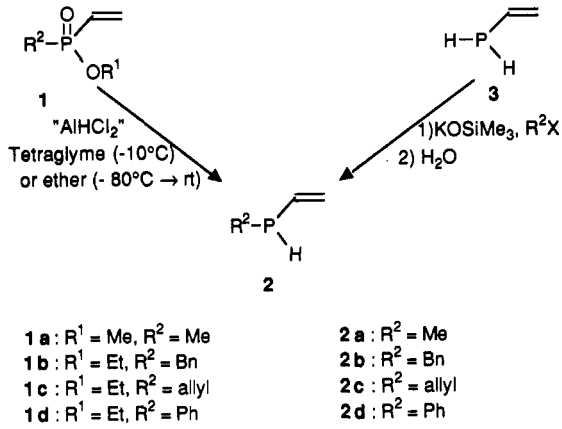
Primary and secondary alkenylphosphines, because of their multifunctionalities, present considerable potential as organophosphine ligands and for hydrophosphorylation reactions.[1,2] Among these derivatives, the vinylphosphines which can be furthermore considered as potential precursors of η^3 phospha-allyl-metal complexes[3] and phosphaalkenes[4] have been very poorly investigated. The lack of development of their chemistry came probably from the fact that they were long thought to be intrinsically unstable because of the high reactivity of the P–H bond toward their own unsaturation. The low yield obtained in the synthesis of some unstabilized derivatives was regarded as a confirmation of this assumption.[5-7] The fact that simple primary vinylphosphines, which were recently obtained by vacuum gas-phase thermolysis[8] from their corresponding anthracenic adducts, show a reasonable stability should encourage further development of their chemistry. We have already reported a preparative-scale synthesis of unstabilized primary vinylphosphines by a chemoselective reduction of the corresponding vinylphosphonic esters.[9] Since only few kinetically stabilized secondary vinylphosphines were described in the literature,[3c,4] a more general approach was needed. We present herein two routes to these species which involve chemoselective reduction of vinylphosphinic esters 1 (method A) or P-alkylation of the free vinylphosphine parent com-

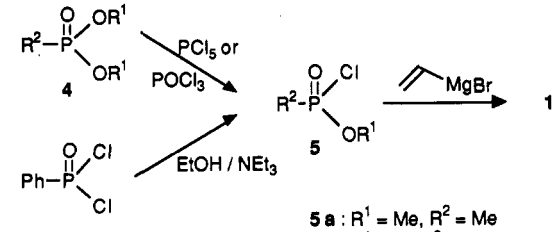
Scheme I



1a: R^1 = Me, R^2 = Me
1b: R^1 = Et, R^2 = Bn
1c: R^1 = Et, R^2 = allyl
1d: R^1 = Et, R^2 = Ph

2a: R^2 = Me
2b: R^2 = Bn
2c: R^2 = allyl
2d: R^2 = Ph

Scheme II



5a: R^1 = Me, R^2 = Me
5b: R^1 = Et, R^2 = Bn
5c: R^1 = Et, R^2 = allyl
5d: R^1 = Me, R^2 = Ph

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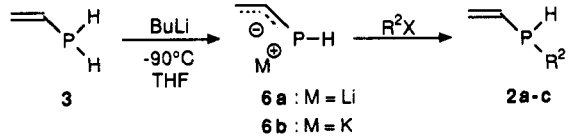
Scheme III



pound 3 (method B) (Scheme I).

Results and Discussion

Chemoselective Reduction of Vinylphosphinic Esters 1 (Method A). Vinylphosphinates 1 were synthesized according to the literature either by a sequence involving P-chlorination of phosphonic esters 4 with PCl_5 for **1a**[10] and $POCl_3$ for **1b–1c**[11] or by monoesterification of phenylphosphonic dichloride for **1d**,[12] followed by nucleophilic addition of vinylmagnesium bromide to the acid chloride intermediate **5**[13] (Scheme II). Compounds 1 were obtained in 50–75% yield and were kept for several months at 0 °C in the presence of hydroquinone without decomposition.

A few secondary vinylphosphines bearing bulky substituents have been recently synthesized by reduction of the *P*-chlorophosphine precursors with lithium aluminum hydride.[3c,4] The reduction of vinylphosphinates 1 with this reagent being not chemoselective, dichloroalane ($AlHCl_2$), which is an electrophilic reducing agent already used for the reduction of vinylphosphonates,[9] has been found to give the best results (Scheme I). The reaction was carried out in tetraglyme or in ether, depending on the volatility of the product. In both cases, we cannot avoid a partial cleavage of the *P*-vinyl bond (<10%), even by lowering the temperature of the reduction and using just a small excess of reducing agent (1.3 equiv). Tetraglyme was used as solvent for the preparation and purification of the volatile phosphine **2a**: the suspension containing the reducing agent was stirred at −10 °C under reduced pressure while the phosphinate **1a** was slowly introduced. Phosphine **2a** was distilled off and condensed into a liquid nitrogen cold trap. The isolated yield after purification by trap to trap distillation was 73%. Other phosphines **2b–2d** were prepared in ether. The reduction slowly occurred on warming the suspension from −80 to −20 °C. Isolated yields were found to be mainly dependent on the volatility of the phosphines **2**, a higher distillation temperature increasing self-condensation reactions. Allyl- and phenylvinylphosphines **2c, 2d** were purified by trap to trap distillation. Benzylvinylphosphine (**2b**) cannot be distilled[14] and must be generated in situ for further purposes. The purified vinylphosphines **2a, 2c, 2d** can be kept for several weeks in a Schlenk flask at −10 °C under nitrogen in the presence of a small amount of hydroquinone.

P-Alkylation of the Free Vinylphosphine 3 (Method B). The reaction of the primary vinylphosphine (**3**) with a stoichiometric amount of *n*-butyllithium in THF at −90 °C leads exclusively to the phosphaallyl anion **6a** which was characterized by low-temperature ^{31}P NMR analysis (−90 °C). The spectrum shows a doublet at $\delta = -125$ ppm. We observe a decrease of the $^1J_{PH}$ coupling constant ($^1J_{PH}$ = 156 Hz, doublet) compared with the corresponding vinylphosphine precursor **3** ($^1J_{PH}$ = 200 Hz, triplet). The corresponding potassium anion **6b** formed by addition of KO^{t}Bu shows a similar coupling constant ($^1J_{PH}$ = 146 Hz) with a chemical shift at lower field ($\delta = -115$ ppm) (Scheme III). The ^{31}P upfield shift observed for phosphaallyl anion **6a** and **6b** compared with **3** takes into account the delocalization of the negative charge. The decrease of the $^1J_{PH}$ values from **3** to **6** can be mainly attributed to the greater s character in the P–H bond as the coordination number decreases.[15]

P-Alkylation of **6** with methyl iodide leads to the formation of methylvinylphosphine (**2a**) and a complex mixture of self-condensed products even under various conditions. In order to improve the selectivity and the yield of the P-alkylation, we searched for a more efficient base. After various unsuccessful trials using pyridine, triethylamine, DBU, and DABCO, a clean reaction was observed using potassium trimethylsilanolate ($KOSiMe_3$) in THF. Since this weak base is compatible with alkylating agents, the conditions of the reaction were simplified: a selective monoalkylation occurred on warming the THF solution containing vinylphosphine (**3**), electrophile (RX) and $KOSiMe_3$ from −90 to −30 °C (Scheme I). To avoid dialkylation, the mixture was hydrolyzed at a temperature which is dependent on the substituent. Vinylphosphines **2** are thus obtained in yields ranging from 62 to 76% and characterized by ^1H, ^{13}C, and ^{31}P NMR and HRMS (Table I).

We have synthesized secondary vinylphosphines **2** by reduction of vinylphosphinates **1** and by P-alkylation of the primary vinylphosphine **3**. The second pathway appears to be the more direct and general route. This work shows that primary vinylphosphine (**3**) and secondary vinylphosphines **2** which were previously mentioned as rather unstable species[6] can be used as starting material in further synthesis.

Table I. Preparation, Yields, and Selected NMR Data for Vinylphosphines 2

2	method[a]	yield[b] (%)	^{31}P NMR ($^1J_{PH}$) (ppm)
2a: R^2 = Me	A	73[c]	−80.5 (208 Hz)
	B	70[d]	
2b: R^2 = $PhCH_2$	A	82[c]	−53.4 (205 Hz)
	B	76[c]	
2c: R^2 = $CH_2CH{=}CH_2$	A	56[e]	−62.5 (209 Hz)
	B	62[c]	
2d: R^2 = Ph	A	20[c]	−48.7 (202 Hz)

[a] Method A: reduction of vinylphosphinates **1**. Method B: P-alkylation of **3**. [b] Determined by ^1H NMR with dimethyl methylphosphonate as internal reference. [c] Purification by trap to trap distillation (purity higher than 95%). [d] Distillation under vacuum; separation from THF was unsuccessful. [e] Yield of crude product.

Experimental Section

Caution: Vinylphosphines are pyrophoric and nauseating smelling compounds. All the reactions must be carried out under nitrogen in a well-ventilated hood.

All glassware was flamed before use. Tetraglyme and THF were purified by refluxing and distillation from sodium/benzophenone. Vinylphosphines **2** have been fully characterized by ^1H, ^{31}P, and ^{13}C NMR analysis and by high-resolution mass spectroscopy (HRMS). Due to their high reactivity, the combustion analysis has not been undertaken.

Preparation of Secondary Vinylphosphines 2 by Reduction of Vinylphosphinates 1 (Method A). Phosphonochloridate 5a was prepared according to Balthazor and Flores[10] by P-chlorination of methylphosphonate **4a** at 0 °C with PCl_5 in benzene solution.

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Phosphonochloridates 5b–5c were prepared by chlorination of **4b–c** with $POCl_3$.[11] Typically, a mixture of alkylphosphonate **4b** or **4c** (0.1 mol) and freshly distilled $POCl_3$ (1.1 equiv, 0.11 mol) were then heated at 60 °C for 4 h. Phosphonochloridate **5b** or **5c** was then distilled under reduced pressure.

Ethyl Benzylphosphonochloridate (5b). Bp 117 °C (0.1 mm). Yield 78%. ^{31}P NMR (32.38 MHz, $CDCl_3$): δ 39.4. ^1H NMR (80 MHz, $CDCl_3$): δ 1.31 (t, 3 H, $^3J_{HH}$ = 7.0 Hz); 3.51 (d, 2 H, $^2J_{PH}$ = 20.5 Hz); 4.20 (m, 2 H); 7.31 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 15.8 (qm, $^3J_{PC}$ = 7.2 Hz, $^1J_{CH}$ = 127 Hz); 41.0 (td, $^1J_{PC}$ = 121 Hz, $^1J_{CH}$ = 131 Hz); 63.6 (tm, $^2J_{PH}$ = 8.6 Hz, $^1J_{CH}$ = 146 Hz); 127.6 ($^5J_{PC}$ = 4.9 Hz); 128.7 ($^4J_{PC}$ = 3.6 Hz); 130.1 ($^3J_{PC}$ = 7.2 Hz); 130.4 ($^2J_{PC}$ = 8.5 Hz). HRMS calcd for $C_9H_{12}Cl^{37}O_2P^{\bullet+}$: 220.023 39. Found: 220.0236. Calcd for $C_9H_{12}Cl^{35}O_2P^{\bullet+}$: 218.026. Found: 218.026.

Ethyl Allylphosphonochloridate (5c). Bp 53 °C (0.1 mm). Yield 79%. ^{31}P NMR (32.38 MHz, $CDCl_3$): δ 39.5. ^1H NMR (80 MHz, $CDCl_3$): δ 1.40 (t, 3 H, ^3J_H = 7.0 Hz); 2.30 (m, 2 H, $^2J_{PH}$ = 21 Hz, $^3J_{PH}$ = 7.0 Hz); 4.29 (m, 2 H); 5.31 (m, 2 H); 5.8 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.0 (qm, $^3J_{PC}$ = 7.0 Hz, $^1J_{CH}$ = 128 Hz); 39.0 (td, $^1J_{PC}$ = 123 Hz, $^1J_{CH}$ = 137 Hz); 63.6 (tm, $^2J_{PC}$ = 8.5 Hz, $^1J_{CH}$ = 149 Hz); 122.3 (tm, $^3J_{PC}$ = 16.3 Hz, $^1J_{CH}$ = 159 Hz); 125.3 (dm, $^2J_{PC}$ = 12.4 Hz, $^1J_{CH}$ = 161 Hz). HRMS calcd for $C_5H_{10}Cl^{35}O_2P^{\bullet+}$: 168.010. Found: 168.009.

Methyl phenylphosphonochloridate (5d) was prepared by addition of 1 equiv of EtOH to phenylphosphonic dichloride in ether at 0 °C in the presence of triethylamine according to Hudson and Keay.[12]

General Procedure for Preparation of Vinylphosphinic Esters 1. The method of Minowa and co-workers[13] was used. To a solution of phosphonochloridate **5** (0.05 mol) dissolved in dry THF (100 mL) and cooled to −70 °C was added dropwise vinylmagnesium bromide (0.05 mol) in dry THF. Stirring was continued for 1 h. The reaction was allowed to warm to room temperature and then quenched with 20 mL of a cooled saturated NH_4Cl solution. After extraction with CH_2Cl_2, washing (2 × 5 mL of water), and drying over $MgSO_4$, the concentrated solution was distilled in the presence of a small amount (≈0.05%) of hydroquinone (66–75% yield).

Methyl Methylvinylphosphinate (1a). Bp 42 °C (2 mm) (lit.[13] 74 °C (14 mm)). Yield 51%. ^{31}P NMR (32.38 MHz, $CDCl_3$): δ 41.5. ^1H NMR (80 MHz, $CDCl_3$): δ 1.50 (d, 3 H, $^2J_{PH}$ = 14.5 Hz); 3.65 (d, 3 H, $^3J_{PH}$ = 11.0 Hz); 6.10 (m, 1 H); 6.30 (m, 2 H). HRMS calcd for $C_4H_9O_2P^{\bullet+}$: 120.034 01. Found: 120.0332.

Ethyl Benzylvinylphosphinate (1b). The product polymerizes during the distillation; the crude product (purity > 90%) is pure enough to be used in the following step. ^{31}P NMR (32.38 MHz, $CDCl_3$): δ 38.35. ^1H NMR (300 MHz, $CDCl_3$): δ 1.28 (t, 3 H, $^3J_{HH}$ = 7.1 Hz); 3.17 (d, 2 H, $^2J_{PH}$ = 18.18 Hz); 4.01 (m, 2 H); 6.13 (m, 3 H); 7.25 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.4 (qm, $^3J_{PC}$ = 6.1 Hz, $^1J_{CH}$ = 128.0 Hz); 37.1 (td, $^1J_{PC}$ = 95.4 Hz, $^1J_{CH}$ = 135 Hz); 60.7 (tm, $^2J_{PC}$ = 6.6 Hz, $^1J_{CH}$ = 149 Hz); 126.8 ($^5J_{PC}$ = 3.2 Hz); 128.2 (dd, $^1J_{PC}$ = 121.1 Hz, $^1J_{CH}$ = 157 Hz); 128.4 ($^4J_{PC}$ = 2.5 Hz); 129.8 ($^3J_{PC}$ = 5.7 Hz); 131.4 ($^2J_{PC}$ = 7.5 Hz); 136.3 (t, $^1J_{CH}$ = 163 Hz). HRMS calcd for $C_{11}H_{15}O_2P^{\bullet+}$: 210.080. Found: 210.080.

Ethyl Allylvinylphosphinate (1c). Bp 53 °C (0.1 mm). Yield 75%. ^{31}P NMR (32.38 MHz, $CDCl_3$): δ 38.70. ^1H NMR (80 MHz, $CDCl_3$): δ 1.3 (t, 3 H, $^3J_{HH}$ = 7.1 Hz); 2.62 (dd, 2 H, $^2J_{PH}$ = 21 Hz, $^3J_{HH}$ = 7.0 Hz); 4.05 (m, 2 H); 5.22 (m, 2 H); 5.78 (m, 1 H); 6.25 (m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 16.2 (qm, $^3J_{PC}$ = 6.0 Hz, $^1J_{CH}$ = 127 Hz); 35.9 (td, $^1J_{PC}$ = 97.0 Hz, $^1J_{CH}$ = 134.0 Hz); 60.4 (tm, $^2J_{PC}$ = 6.3 Hz, $^1J_{CH}$ = 147.2 Hz); 120.0 (tm, $^3J_{PC}$ = 12.9 Hz, $^1J_{CH}$ = 162.0 Hz); 126.9 (dm, $^2J_{PC}$ = 9.2 Hz, $^1J_{CH}$ = 158.0 Hz); 128.0 (dd, $^1J_{PC}$ = 121.2 Hz, $^1J_{CH}$ = 158 Hz); 136.0 (t, $^1J_{CH}$ = 163.0 Hz). HRMS calcd for $C_7H_{13}O_2P^{\bullet+}$: 160.065. Found: 160.065.

Ethyl Phenylvinylphosphinate (1d).[16] Bp 125 °C (0.1 mm). Yield 66%. ^{31}P NMR (32.38 MHz, $CDCl_3$): δ 29.2. ^1H NMR (80 MHz, $CDCl_3$): δ 1.4 (t, 3 H, $^3J_{HH}$ = 7 Hz); 4.4 (dq, 2 H, $^3J_{PH}$ = 10.0 Hz, $^3J_{PH}$ = 7.0 Hz); 7.6 (m, 5 H).

Reduction of Vinylphosphinic Esters 1. Dichloroalane was prepared in tetraglyme or in ether according to the Ashby procedure.[17] Volatile phosphine **2a** was prepared by reduction of methylphosphinate **1a** in tetraglyme. Other phosphines **2b–2d** were prepared by reduction of the corresponding phosphinic esters **1b–1d** in ether at low temperature.

Methylvinylphosphine (2a). The procedure previously described for the preparation of primary vinylphosphines[9] was used. The flask containing the reducing mixture (0.06 g (1.58 mmol) of $LiAlH_4$; 0.63 g (4.74 mmol) of $AlCl_3$ in 10 mL of tetraglyme) was fitted on the vacuum line and then cooled to −10 °C. The solution of phosphinate **1a** (0.29 g, 2.43 mmol) in tetraglyme (5 mL) was slowly cannulated into the flask through a septum over ca. 30 min. Phosphine **2a** was distilled from the mixture as soon as it was formed and condensed into a liquid nitrogen cold trap. The products (**2a** and a small amount of methylphosphine (<5%)) were separated by trap to trap distillation (yield 73%).

General Procedure for Reduction of Phosphinates 1b–1d Using $AlHCl_2$ in Ether. The reducing mixture (0.06 g (1.58 mmol) of $LiAlH_4$; 0.63 g (4.74 mmol) of $AlCl_3$ in ether (10 mL)) was cooled to −80 °C. Phosphinate **1b–1d** (2.43 mmol) in ether (5 mL) was slowly added (20 min). The mixture was vigorously stirred for 15 min and then allowed to warm to room temperature, quenched at −20 °C with 0.3 mL (15.8 mmol) of degassed water, and then stirred for 20 min at room temperature. After this general procedure, the following workup procedures were used.

Benzylvinylphosphine (2b). The etheral suspension was filtered under nitrogen pressure over dried and degassed Celite. All attempts to purify **2b** were unsuccessful, polymerization occurring while the solution was concentrated. Only the ^{31}P NMR spectrum was obtained; the data (δ_P = −53.0 ppm, $^1J_{PH}$ = 205.0 Hz) are in good agreement with a sample synthesized according to method B (see below). The yield (82%) is evaluated by NMR integration using $MePO(OMe)_2$ as internal reference.

Allylvinylphosphine (2c). Allylvinylphosphine (**2c**) was purified by trap to trap distillation (yield 55%, purity >95%). All the NMR data are in good agreement with a sample synthesized according to method B (see below).

Phenylvinylphosphine (2d). The etheral suspension was filtered under nitrogen pressure over dried and degassed Celite. Tetraglyme (0.2 mL) and hydroquinone (0.1 g) were then added to the solution and the flask was fitted on the vacuum line. Phenylvinylphosphine (**2d**) was distilled from the mixture and purified by trap to trap distillation. Yield 20%, purity higher than 95%. ^{31}P NMR (32.38 MHz, $CDCl_3$): δ −48.7. ^1H NMR (300 MHz, $CDCl_3$): δ 4.02 (dm, 1 H, $^1J_{PH}$ = 202 Hz); 5.72 (ddd, 1 H(cis), $^3J_{PHcis}$ = 18.8 Hz, $^3J_{HH}$ = 14.4 Hz, $^2J_{HH}$ = 2.1 Hz); 5.70 (ddd, 1 H(trans), $^3J_{PHtrans}$ = 29.9 Hz, $^3J_{HH}$ = 11.6 Hz, $^2J_{HH}$ = 2.1 Hz); 6.51 (ddd, 1 H, $^3J_{HH}$ = 11.6 Hz, $^3J_{HH}$ = 14.4 Hz, $^2J_{PH}$ = 18.2 Hz); 7.33 (m, 3 H); 7.5 (m, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 129.2 ($^2J_{PC}$ = 20.5 Hz); 132.7 ($^1J_{PC}$ = 13.7 Hz, $^1J_{CH}$ = 157 Hz); 128.5 ($^1J_{CH}$ > 155 Hz); 128.6 (J_{CP} = 8.3 Hz, $^1J_{CH}$ > 155 Hz); 130.4 ($^1J_{CP}$ = 11.9 Hz); 133.6 (J_{CP} = 17 Hz, $^1J_{CH}$ > 160 Hz). HRMS calcd for $C_8H_9P^{\bullet+}$: 136.044. Found: 136.044.

Preparation of Secondary Vinylphosphines 2 by P-Alkylation of Vinylphosphine 3 (Method B). Phosphaallyl anion 6 was formed by addition of 1 equiv of base on vinylphosphine (**3**)[9] and characterized by low-temperature ^{31}P NMR. In an NMR tube fitted with a septum and degassed under nitrogen was placed vinylphosphine (**3**) (0.2 mmol) in freshly distilled THF. The tube was then cooled to −90 °C, and a base (0.22 mmol, *n*-BuLi or KO-*t*-Bu) was slowly added under nitrogen. The mixture was homogenized, and the tube was rapidly introduced into the spinner of the NMR apparatus previously cooled to −90 °C.

Base used: *n*-BuLi. Temperature: −90 °C. **Phosphaallyl Anion 6a.** ^{31}P NMR (121 MHz, C_6D_6): δ −125.0 (d, $^1J_{PH}$ = 156.0 Hz).

Base used: KO-*t*-Bu. Temperature: −90 °C. **Phosphaallyl Anion 6b.** ^{31}P NMR (121 MHz, C_6D_6): δ −115.0 (d, $^1J_{PH}$ = 146.0 Hz).

Secondary Vinylphosphines 2a–2c. $KOSiMe_3$ (4.13 mmol, 0.53 g) in 25 mL of freshly distilled THF was cooled to −90 °C (internal temperature), and the alkylating agent (1.76 mmol) was introduced. Then, a solution of primary vinylphosphine (1.6

(16) (a) For the preparation of **1d** see: Kabachnick, M. I. *Zh. Obshch. Khim* **1962**, *32*, 3351. Mastryukova, T. A.; Mashchenko, N. V.; Odinets, I. L.; Kabachnick, M. I. *Ibid.* **1988**, *58*, 1962.

(17) Ashby, E. C.; Prather, J. *J. Am. Chem. Soc.* **1966**, *88*, 729.

mmol) in THF was slowly added (10 min). A wonderful blue color appeared when the phosphine was added. The mixture was allowed to warm to a temperature depending on the alkylating agent as indicated below. Then, previously degassed water (10 equiv) was added under nitrogen to avoid dialkylation. The solution was decanted and transferred with a flex-needle into a flask containing dried and degassed $MgSO_4$ (0.5 g). The mixture was stirred 15 min under nitrogen and transferred into another flask containing a small amount of hydroquinone (0.05 equiv). Further purification was performed by trap to trap distillation for the volatile compounds **2a**, **2c**, and **2d**.

Methylvinylphosphine (2a). Alkylating agent: methyl iodide. Hydrolysis temperature: −10 °C. Yield: 70%. Purity (>95%). ^{31}P NMR (121 MHz, $CDCl_3$): δ −80.5 (d, $^1J_{PH}$ = 208.7 Hz). ^1H NMR (300 MHz, $CDCl_3$): δ 1.22 (dd, 3 H, $^3J_{HH}$ = 7.5 Hz, $^2J_{PH}$ = 2.6 Hz); 3.80 (dm, 1 H, $^1J_{PH}$ = 208.7 Hz); 5.62 (m, 1 H, $^3J_{PH}$ = 18.5 Hz, $^3J_{HH}$ = 12.6 Hz, $^2J_{HH}$ = 1.7 Hz); 5.70 (ddd, 1 H, $^3J_{PH}$ = 24.3 Hz, $^3J_{HH}$ = 11.8 Hz, $^2J_{HH}$ = 1.7 Hz); 6.41 (ddm, 1 H, $^3J_{HH}$ = 12.6 Hz, $^3J_{HH}$ = 11.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 4.0 (qd, $^1J_{CH}$ = 130.2 Hz, $^1J_{CP}$ = 10.0 Hz); 125.7 (tdm, $^1J_{CH}$ = 156.8 Hz, $^2J_{CP}$ = 14.3 Hz); 135.5 (ddm, $^1J_{CH}$ = 157.0 Hz, $^1J_{CP}$ = 14.2 Hz). HRMS calcd for $C_3H_7P^{\cdot+}$: 74.0285. Found: 74.0284.

Benzylvinylphosphine (2b). Alkylating agent: benzyl bromide. Hydrolysis temperature: −30 °C. Yield: 76%. Purity (>85%). ^{31}P NMR (121 MHz, $CDCl_3$): δ −53.4 ($^1J_{PH}$ = 205.0 Hz). ^1H NMR (300 MHz, $CDCl_3$): δ 2.7 (m, 2 H); 3.9 (dm, $^1J_{PH}$ = 205.0 Hz); 5.5 (m, 2 H); 6.1 (m, 1 H); 7.0 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.8 (td, $^1J_{CH}$ = 129.5 Hz, $^1J_{CP}$ = 10.8 Hz); 126.1 (td, $^1J_{CH}$ = 160.1 Hz, $^2J_{CP}$ = 14.3 Hz); 130.3 (dd, $^1J_{CH}$ = 158.7 Hz, $^1J_{CP}$ = 20.7 Hz). HRMS calcd for $C_9H_{11}P^{\cdot+}$: 150.0598. Found: 150.059.

Allylvinylphosphine (2c). Alkylating agent: allyl bromide. Hydrolysis temperature: −40 °C. Yield: 62%. Purity (>95%). ^{31}P NMR (121 MHz, $CDCl_3$): δ −62.5 (d, $^1J_{PH}$ = 209.0 Hz). ^1H NMR (300 MHz, $CDCl_3$): δ 2.33 (m, 2 H); 3.7 (dm, 1 H, $^1J_{PH}$ = 209.0 Hz); 4.95 (m, 2 H); 5.78 (m, 3 H); 6.36 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.9 (td, $^1J_{CH}$ = 132.0 Hz, $^1J_{CP}$ = 10.7 Hz); 115.4 (td, $^1J_{CH}$ = 161.1 Hz, $^3J_{CP}$ = 6.7 Hz); 128.6 (td, $^1J_{CH}$ = 160.1 Hz, $^2J_{CP}$ = 19.5 Hz); 132.8 (dd, $^1J_{CH}$ = 159.8 Hz, $^1J_{CP}$ = 15.9 Hz); 135.8 (dd, $^1J_{CH}$ = 160.0 Hz, $^2J_{CP}$ = 1.1 Hz). HRMS calcd for $C_8H_9P^{\cdot+}$: 100.044. Found: 100.043.

Registry No. **1a**, 63314-88-5; **1b**, 89222-11-7; **1c**, 77697-52-0; **1d**, 7766-52-1; **2a**, 141850-64-8; **2b**, 141850-65-9; **2c**, 141850-66-0; **2d**, 90006-08-9; **3**, 58436-39-8; **4a**, 756-79-6; **4b**, 1080-32-6; **4c**, 1067-87-4; **5a**, 1066-52-0; **5b**, 41760-95-6; **5c**, 41760-96-7; **5d**, 41761-00-6; **6a**, 141850-67-1; **6b**, 141850-68-2; phenylphosphonic dichloride, 824-72-6; vinylmagnesium bromide, 1826-67-1.

The Isolation of a Bi(2,4,6,8-tetraazabicyclo[3.3.0]octane) from the Reaction of Glyoxal with Benzylamine

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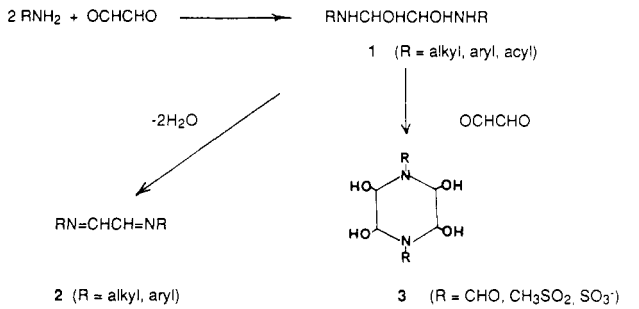
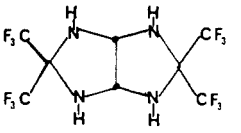
The reactions of primary amines and amides (RNH_2) with glyoxal give a variety of products depending upon the nature of R and, in certain cases, upon the reaction conditions.[1-5] Primary aliphatic amines usually form dicarbinolamines **1** or conjugated diimines **2**, while aromatic primary amines form these and other products.[1,2] Primary aliphatic amides give primarily adducts of type **1**,[6] but in some cases, further reaction with glyoxal occurs to give tetrahydroxypiperazines **3**.[3-5]



Ethylenediamine and N,N′-disubstituted ethylenediamines react with glyoxal to give *cis*- and *trans*-1,4,5,8-tetraazadecalins and 2,2′-biimidazolidines.[7] We have shown that the *gem*-diamine 2,2-diaminohexafluoropropane reacts with glyoxal to give the 2,4,5,8-tetraazabicyclo[3.3.0]octane **4** in high yield.[8]



4

Recently, Nielsen and co-workers have reported, in this journal, the facile condensation of glyoxal with benzylamine (and certain phenyl-substituted benzylamines) to produce the new polyazapolycyclic caged ring system **5**, to which they have assigned the semisystematic name hexabenzylhexaazaisowurtzitane.[1] In this report, we describe the isolation of another compound produced in this reaction as a byproduct in low but significant yield, whose structure was determined to be that of **6**. The production of **6**, a bi(2,4,6,8-tetraazabicyclo[3.3.0]octane), further illustrates the diversity of products formed in amine–glyoxal reactions and is consistent with the mechanism of formation of **5**, as proposed by Nielsen.[1]

Our experimental conditions for the condensation of glyoxal with benzylamine were essentially the same as those reported (procedure A in ref 1), with the exception of some variations in solvent volume (800 mL CH_3CN vs 1100 mL), added water (40 mL vs 100 mL), and time of addition of glyoxal (30 min vs 1 h).[9] The crude reaction product, mp 149–152 °C, was recrystallized from a large volume of CH_3CN to give colorless needles of almost pure **5**, mp 153–155 °C. Repeated recrystallizations (5×) of a sample gave pure **5**, mp 155–157 °C. Pure **6**, mp 174–175 °C, was isolated from the original CH_3CN recrystallization

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(9) We thank Dr. A. T. Nielsen for providing us with technical reports on the preparation of **5** prior to his publication.