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Preparative synthesis of primary vinylphosphines by chemoselective reduction of the corresponding vinylphosphonates

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Abstract

Primary vinylphosphines which were described as highly polymerisable compounds in the literature are prepared on gram scale in one step by a chemoselective reduction of the corresponding vinylphosphonates. They exhibit a surprising stability.

Introduction

Alkenylphosphines are valuable intermediates in coordination chemistry [1]. However, whereas tertiary vinylphosphines can be synthesized readily by several routes, only few examples of secondary and primary analogues have been reported [2]. Because of the high reactivity of the P–H bond towards multiple bonds, primary vinylphosphines are described as highly polymerisable compounds [3]. Some theoretical data for the parent compound have recently been published [4,5]. Some primary vinylphosphines have been synthesized by [4 + 2] cycloreversion reactions under FVT * conditions [2]. Divinylphosphines have been characterized as their tungsten complexes [6]. We recently prepared α-chloroalkylphosphines by a chemoselective reduction of the corresponding phosphonates [7], and we now describe straightforward synthesis of primary vinylphosphines by chemoselective reduction of the corresponding vinylphosphonates.

Results and discussion

The most direct route to vinylphosphines involves the reduction of the corresponding vinylphosphonates. We first optimized the conditions of the reduction

* FVT = Flash Vacuum Thermolysis

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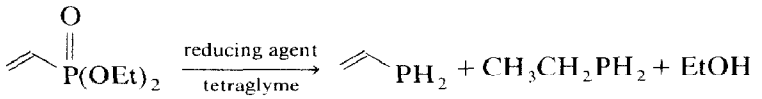
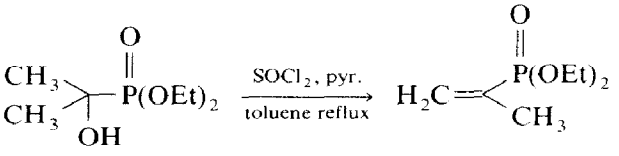
with the parent compound **1** and then applied them to the synthesis of substituted derivatives. So that the pure phosphines could be isolated easily tetraglyme was used as the solvent in all the reductions. The suspension containing the reducing agent was stirred under vacuum during the reduction and the volatile phosphines were condensed on a liquid nitrogen cooled trap. Under these conditions lithium aluminium hydride (LAH) reduction of the vinylphosphonate **1** affords a mixture of ethylphosphine (**3**) and EtOH without any trace of the vinylphosphine (**2**).



(1) (2) (3) (1)

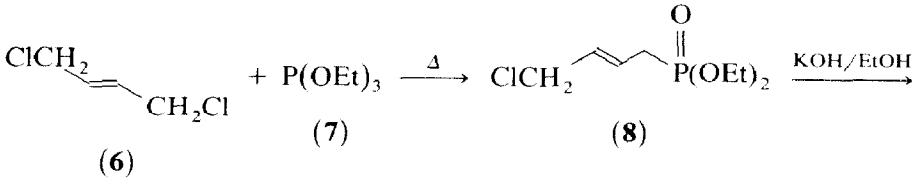
Aluminium hydride (AlH_3), which gave satisfactory results in the reduction of chloroalkylphosphonates, was also tested for the reduction of vinylphosphonates. It gave the expected vinylphosphine (**2**) in a poor yield (20%) accompanied by ethylphosphine (**3**) and ethanol. A long reaction time was necessary to achieve this reduction (12 h), and purification of **2** by trap to trap distillation was impossible. Finally a chemoselective reduction was achieved by use of dichloroalane ($AlHCl_2$), but a large excess (8 molar ratio) of this was necessary to obtain a good yield (76%). Enhancement of the electrophilic character at the phosphorus by complexation of the phosphonate group with $AlHCl_2$, which behaves as a strong Lewis acid, could account for this selectivity [8].

We then extended this reduction to other vinylphosphonates. The compound **5** was prepared by a thionyl chloride/pyridine induced dehydration [9] of the α-hydroxyphosphonate (**4**) (eq. 2).

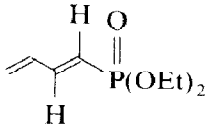


(4) (5) (2)

The phosphonate **9** was prepared by thermal condensation of **6** and **7** followed by potassium hydroxide induced 1,4-dehydrohalogenation [10] (eq. 3).

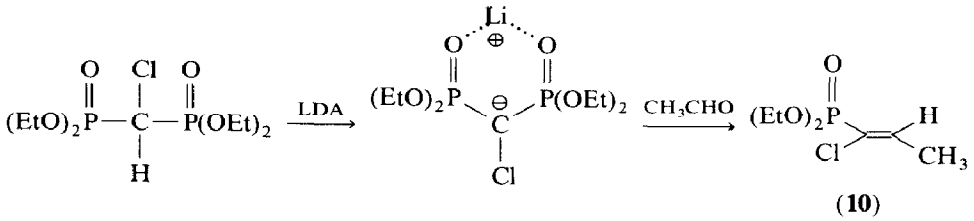


(6) (7) (8)



(9) (3)

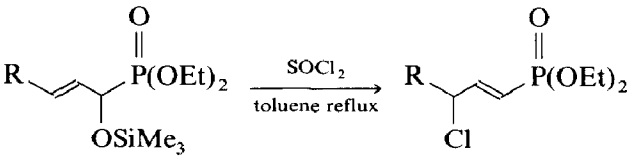
The derivative **10** was prepared by the procedure described by Savignac [11] (eq. 4).



(**10**)

(4)

The silylated phosphonates **12**, prepared as described by Evans [12], were directly chlorinated in refluxing toluene by use of thionyl chloride without any base. An allylic rearrangement occurs, and the only product observed is **13** (*E* isomer) (eq. 5). The overall yield is very high (> 90%).



(5)

(**12**) (**13a**: R = H; **13b**: R = CH_3)

We reduced these phosphonates under the experimental conditions as used for the parent compound. The results and the main spectroscopic data for the products are summarized in Table 1. The vinylphosphines **2, 14, 16, 17, 18a** and **18b** can be synthesized on a gram scale. Polymerization occurs slowly at room temperature in condensed phase, but the compounds can be kept in a Schlenk tube at $-10\,^{\circ}C$ under nitrogen in the presence of a small amount of hydroquinone without any decomposition. No by-product was observed by ^{1}H and ^{31}P NMR spectroscopy in these reductions.

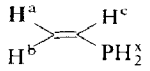
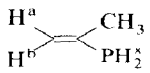
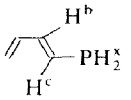
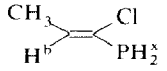
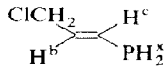
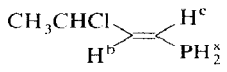
It is clear that vinylphosphines can be prepared on a gram scale by reduction of the corresponding phosphonates. These compounds are surprisingly stable, and are likely to be as useful synthons in coordination chemistry.

Experimental

All the reactions were carried out under dry nitrogen in a two necked round-bottom flask equipped with a gas-inlet tube, a rubber septum, and a stirring bar. All glassware was flamed before use. Tetraglyme was purified by refluxing over and distillation from sodium/benzophenone under reduced pressure (0.01 mmHg). The ^{1}H, ^{31}P, ^{13}C NMR spectra of the phosphines were recorded on a Bruker WP 80 DS or a WP 80 spectrometer. Chemical shifts are given in ppm relative to internal $SiMe_4$ for ^{1}H and ^{13}C spectra, and to external H_3PO_4 85% for ^{31}P NMR spectra. Chemical shifts upfield to the standard are defined as negative. High resolution mass spectra were recorded on a Varian MAT 311 spectrometer. The vinylphosphines are too reactive to be characterized by combustion analysis, but the mass spectra confirm their identities.

Table 1

Selected spectroscopic data for the vinylphosphines **2, 14, 16, 17, 18a, 18b** and yields of the reductions.

	Yield (%)	$\delta(^{31}P)$ (ppm)	$^1J(PH^x)$ (Hz)	$^2J(PH^c)$ (Hz)	$^3J(PH^a)$ (Hz)	$^3J(PH^b)$ (Hz)
 **(2)** [a]	76	−133	199	5.5	13.5	6.5
 **(14)** [a]	82	−116	191		31.4	16
 **(16)**	63	−140	202	12		12
 **(17)**	72	−98	206			13
 **(18a)**	57	−141	203	13		13
 **(18b)**	72	−143	202	13		13

[a] Reference 2.

Caution: Vinylphosphines are pyrophoric compounds and induce nausea. All preparations and handling must be carried out with appropriate precautions under a well ventilated hood.

The phosphonates **4–10, 12** were prepared as described previously [9–12]

Preparation of diethyl-3-chloro-prop-1-enylphosphonate (13a)

To a solution of the phosphonate **12a** (14 g, 0.05 *M*) in toluene (120 ml) in a 500 ml round-bottom flask, was added thionyl chloride (9.5 g, 0.08 *M*) at room temperature during 5 min. The mixture was heated under reflux for 4 h and then allowed to cool to room temperature. The toluene was evaporated off under reduced pressure (2 mmHg, 60 °C) and the residue distilled (b.p. 52 °C/0.05 mmHg) to give 9.8 g of **13a** (87% yield).

^1H NMR ($CDCl_3$) δ 1.3 (t, 6H, $^3J(HH)$ 7 Hz); 4.1 (m, 4H); 4.15 (dd, 2H, $^3J(HH)$ 5.2 Hz, $^4J(HP)$ 1.8 Hz); 6.0 (m, 1H, $^3J(HH)$ 17 Hz; $^2J(HP)$ 18 Hz); 6.8 (m, 1H, $^3J(HH)$ 5.2 Hz, $^3J(HP)$ 16 Hz). ^{31}P NMR (THF/C_6D_6): δ 15. Analysis Found: C, 38.25; Cl, 16.89; P, 15.14. $C_7H_{14}ClO_3P$ calcd.: C, 38.52; Cl, 16.70; P, 14.59%.

*Diethyl-3-chloro but-1-enylphosphonate (**13b**)*

The phosphonate **13b** was prepared according to the procedure described for **13a** (bp 66 °C/0.05 mmHg) 91% yield. ^{1}H NMR ($CDCl_3$) δ 1.3 (t, 6H, ^3J(HH) 7Hz); 1.65 (d, 3H, ^3J(HH) 7Hz); 4.1 (m, 4H); 4.65 (m, 1H, ^3J(HH) 6Hz, ^4J(HP) 2Hz); 5.9 (m, 1H, ^3J(HH) 17 Hz, ^3J(HP) 16 Hz); 6.8 (m, 1H, ^2J(HP) 15Hz). ^{31}P NMR (THF): 8.7. Analysis Found: C, 41.91; Cl, 15.42; P, 14.14. $C_8H_{16}ClO_3P$ calcd.: C, 42.38; Cl, 15.67; P, 13.69%.

Preparation of dichloroalane ($AlHCl_2$)

$AlHCl_2$ was prepared by modification of the procedure described by Ashby [13]. LAH in 200 ml of tetraglyme in a 500 ml flask was cooled to −20 °C and $AlCl_3$ (20 g, 0.16 *M*) was added in portions during 10 min under a nitrogen blanket. The mixture was then stirred for 30 min at room temperature and used immediately for reductions.

*Preparative reduction of the vinylphosphonate **1** by $AlHCl_2$ (gram scale general procedure)*

The flask containing the reducing mixture described above was attached to the vacuum line (Fig. 1) and the phosphonate **1** (4 g, 0.025*M*) in 30 ml of tetraglyme was added slowly (30 min) at room temperature with a flex-needle through a septum to flask A. The vacuum was maintained for 12 h. During and after the addition the vinylphosphine and any tetraglyme carried away were condensed in a trap B cooled in liquid nitrogen. When the reaction was complete this cold trap was allowed to warm to room temperature and the cooled vinylphosphine evolved was condensed in a second trap C cooled to −90 °C; the more volatile fraction carried away and the tetraglyme stays in B. The cold finger D was then cooled with liquid nitrogen and the trap C was allowed to warm to room temperature so that the vinylphosphine **2** condensed on the cold finger. Subsequently the liquid nitrogen was removed from D and the product was collected under vacuum in the Schlenk flask E (equipped with a "Young" tap and containing 0.1 g of hydroquinone). The whole apparatus,

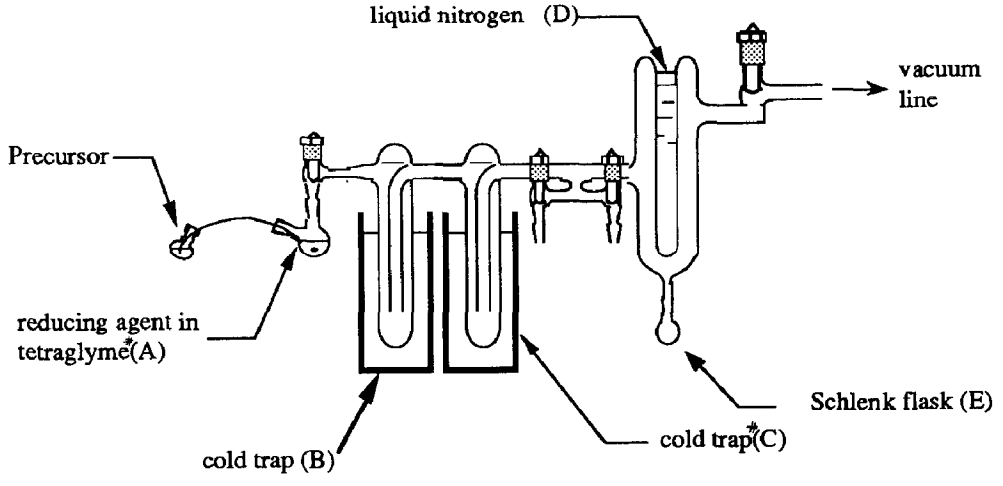


Fig. 1. Apparatus used.

including the Schlenk flask, was then filled with dry nitrogen. (Under these conditions the vinylphosphine **2** can be kept for several weeks in a refrigerator. The vinylphosphine (1.1 g, 76% yield) was identified by comparison of the ^{1}H and ^{31}P NMR data with those in the literature [2].

*Isopropenylphosphine (**14**)*

The phosphine **14** was prepared by the same procedure and was obtained in 82% yield (purity > 95%) and identified by comparison of its spectroscopic data with those in the literature [2].

*Buta-1,3-dienylphosphine (**16**)*

The phosphine **16** was prepared by the same procedure and obtained in 63% yield (purity > 95%). It was identified by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. ^{1}H NMR ($CDCl_3$) δ 3.4 (dd, 2H, ^{1}J(PH) 202 Hz, ^{3}J(HH) 6 Hz); 5.1 (m, 1H, ^{3}J(HH) 10 Hz, ^{2}J(HH) 2 Hz); 5.2 (m, 1H, ^{3}J(HH) 11 Hz); 6.1 (m, 1H, ^{3}J(HH) 11 Hz); 6.3 (m, 1H, ^{3}J(HH) 11 Hz); 6.6 (mm, 1H, ^{3}J(HP) 12 Hz). ^{31}P NMR (THF/C_6D_6) δ −140. ^{13}C NMR ($CDCl_3$) δ 118 (t, ^{1}J(CH) 156 Hz); 119.7 (d, ^{1}J(CH) 156 Hz, J(CP) 10 Hz); 137.3 (d, J(CP) 11 hz); 144.8 (d, ^{1}J(CH) 159 Hz, ^{1}J(CP) 21 Hz). Mass calc. for C_4H_7P: 86.0285; found: 86.0286.

*1-Chloroprop-1-enylphosphine (**17**)*

The phosphine **17** was prepared by usual procedure, but in this case trap C was cooled to −80 °C. The phosphine **17** was obtained in 72% yield (purity > 95%) ^{1}H NMR ($CDCl_3$) δ 1.9 (d, 3H, ^{3}J(HH) 7 Hz, ^{4}J(HP) 2 Hz); 4.0 (d, 2H, ^{1}J(PH) 206 Hz, ^{3}J(HH) 2 Hz); 6.3 (m, 1H, ^{2}J(PH) 10 Hz). ^{31}P NMR (THF/C_6D_6) δ −98. ^{13}C NMR ($CDCl_3$) δ 16 (q, ^{3}J(CP) 10 Hz, ^{1}J(CH) 129 Hz); 125 (d, ^{1}J(CH) 150 Hz, ^{2}J(CP) 28.6 Hz); 148.5 (d, ^{1}J(CP) 36 Hz). Mass calc. for C_3H_6ClP: 107.9895; found: 107.9891.

*3-Chloroprop-1-enylphosphine (**18a**) (E isomer)*

The phosphine **18a** was prepared as described for the derivative **17** and obtained in 57% yield (purity > 90%). It was identified by ^{1}H, ^{31}P, ^{13}C NMR spectroscopy. The vinylic protons cannot be distinguished even with a 300 MHz NMR spectrometer, and are equivalent at the NMR scale ($CDCl_3$). ^{1}H NMR ($CDCl_3$) δ 3.4 (d, 2H, ^{1}J(PH) 203 Hz); 4.05 (m, 2H, ^{3}J(HH) 2.8 Hz, ^{4}J(HH) 2.8 Hz, ^{4}J(HP) 2 Hz); 6.2 (dt, 2H, J(HP) 13 Hz). ^{31}P NMR (THF/C_6D_6) δ −141. ^{13}C NMR ($CDCl_3$) δ 45.2 (t, ^{1}J(CP) 151 Hz, ^{3}J(CP) 9.7 Hz); 121.5 (d, ^{1}J(CH) 164 Hz, J(CP) 12 Hz); 140 (d, ^{1}J(CH) 160 Hz, J(CP) 19 Hz). Mass calc. for C_3H_6ClP: 107.9895; found: 107.9896.

*3-Chlorobut-1-enylphosphine (**18b**) (E isomer)*

The phosphine **18b** was prepared by the procedure described for **17** and obtained in 72% yield. The coupling between the vinylic protons cannot be seen even with a 300 MHz NMR spectrometer. ^{1}H NMR ($CDCl_3$): 1.5 (d, 3H, ^{3}J(HH) 7 Hz); 3.1 (d, 2H, ^{1}J(HP) 203 Hz); 4.5 (m, 1H, ^{3}J(HH) 12 Hz, ^{4}J(HH) 6 Hz); 6.14 (m 1H, ^{3}J(HP) 13 Hz); 6.17 (m, 1H, ^{2}J(HP) 13 Hz). ^{31}P NMR (THF/C_6D_6) δ −143. ^{13}C NMR ($CDCl_3$) δ 24 (q, ^{1}J(CH) 129 Hz); 57,8 (d, ^{1}J(CH) 153 Hz, ^{3}J(CP) 11 Hz); 118 (d, ^{1}J(CH) 158 Hz, J(CP) 12 Hz); 146 (d, ^{1}J(CH) 160 Hz, J(CP) 20 Hz). Mass calc. for $C_4H_{10}ClP$: 122.0052; found: 122.005.

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