Lewis Base-induced Rearrangement of Primary Ethyn-1-ylphosphines, a New and Efficient Route to Phosphaalkynes

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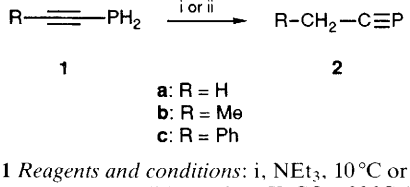
Phosphaalkynes bearing primary carbon substituents are prepared in good yield by low-temperature Lewis base-induced rearrangement of primary ethyn-1-ylphosphines; the mechanism involves a *P*-unsubstituted phosphaallene intermediate.

Phosphaalkynes are very important building blocks in synthetic chemistry.[1] They are used in the formation of various heterocyclic compounds. Their potential as ligands in transition-metal complexes has recently been reviewed.[2] The most efficient method of formation of the C≡P triple bond involves hexamethyldisiloxane elimination.[1,3] However, although phosphaalkyne derivatives with tertiary or secondary carbon substituents have been thus prepared, this method generally failed for compounds bearing primary carbon substituents. We have recently prepared volatile derivatives such as MeC≡P by bis-dehydrohalogenation of the corresponding α-dichlorophosphines using vacuum gas–solid elimination.[4] The most significant feature comes from the unexpected stability of these compounds: they can be kept for several days in solution at room temp. Consequently, more general routes are now required to accede to such species which must be considered as useful starting materials in organic synthesis. We have recently described the preparation of primary ethyn-1-ylphosphines **1** by chemoselective reduction of the corresponding phosphonates.[5] We present here their rearrangement into phosphaalkynes.

Low temperature treatment of **1a–1c** with a catalytic amount (<5%) of a Lewis base {NEt_3 or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene)} leads [in very good yield (>90%)] to the formation of phosphaalkynes **2a–2c**. The volatile products **2a** and **b** were also obtained by room temperature base-induced rearrangement of **1a** and **b** on solid potassium carbonate in VGSR (vacuum gas–solid reaction) conditions[6] (Scheme 1).

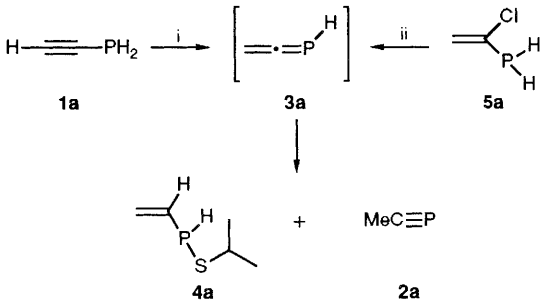


Scheme 1 *Reagents and conditions*: i, NEt_3, 10 °C or DBU, −90 °C in THF; ii, vacuum gas–solid reaction, K_2CO_3, 20 °C (for **1a** and **1b**)

The structures of **2a** and **b** were determined by ^1H, ^{13}C, ^{31}P NMR and IR spectroscopy and HRMS (high resolution mass spectrometry) analysis and comparison with an authentic sample;[4] compound **2c**† was obtained for the first time. The stability of phosphaalkynes **2a** and **b** is apparently not reduced by the presence of the Lewis base catalyst: the crude solution can be kept for several days at room temp.[4] The new compound **2c** decomposes in several hours under these conditions.

Since secondary ethynylphosphines bearing bulky substituents have been reported to rearrange to the corresponding *P*-substituted phosphaallenes in the presence of sodium hydroxide,[7] a plausible mechanism for the rearrangement **1** → **2** involves the phosphaallene R–CH=C=PH **3** as intermediate. All attempts to characterize this species by low-temperature NMR analysis were unsuccessful. However, the presence of **3a** was unambiguously proved by chemical trapping with propane-2-thiol: thus adduct **4a**† was observed by low-temperature NMR analysis (Scheme 2); however, the formation of **2a** cannot be completely avoided. Obtention of the same adduct

† *Selected data* for **2c**, **4a** and **5a**: **2c**: ^1H NMR (300 MHz, $CDCl_3$, room temp.) δ 3.65 (d, 2H, $^3J_{PH}$ 14.8 Hz); 7.24–7.26 (m, 5H). ^{31}P NMR (121 MHz, $CDCl_3$, room temp.) δ −53.2. ^{13}C NMR (75.5 MHz, $CDCl_3$, room. temp.) δ 35.4 ($^2J_{CP}$ 19.6 Hz, d, $^1J_{CH}$ 129.7 Hz, t); 125.5; 126.7 ($^1J_{CH}$ 159.8 Hz, d); 127.8 ($^1J_{CH}$ 161.3 Hz, d); 128.5 ($^1J_{CH}$ 159.7 Hz, d); 170.6 ($^1J_{CP}$ 46.2 Hz, d).
4a: ^1H NMR (300 MHz, CD_2Cl_2–CCl_3F, −80 °C) δ 1.32 (dd, 6H, $^3J_{HH}$ 7.0, $^3J_{PH}$ 2.1 Hz); 2.90 (d.hept, 1H, $^3J_{HH}$ 7.0, $^2J_{PH}$ 5.3 Hz); 4.70 (dd, 1H, $^1J_{PH}$ 222.5, $^3J_{HH}$ 6.3 Hz); 5.63–5.83 (m, 2H); 6.20–6.40 (m, 1H). ^{31}P NMR (121 MHz, CD_2Cl_2–CCl_3F, −80 °C) δ −39.5. ^{13}C NMR (75.5 MHz, CD_2Cl_2, CCl_3F, −80 °C) δ 25.6 ($^1J_{CH}$ 126.6, q, $^1J_{CP}$ 7.7 Hz); 37.6 ($^1J_{CH}$ 140.6, d, $^2J_{CP}$ 18.4 Hz, d); 127.2 ($^1J_{CH}$ 158.1, t, $^2J_{CP}$ 9.6 Hz, d); 133.2 ($^1J_{CH}$ 156.5 Hz, d, $^1J_{CP}$ 24.7 Hz, d).
5a: ^1H NMR (300 MHz, $CDCl_3$, room temp.) δ 4.00 (ddd, 2H, $^1J_{PH}$ 206.1, $^4J_{HH}$ 1.5, $^4J_{HH}$ 1.4 Hz); 5.80 (ddt, 1H, $^3J_{PH}$ 24.1, $^2J_{HH}$ = $^4J_{HH}$ 1.5 Hz); 5.80 (ddt, 1H, $^3J_{PH}$ 9.2; $^4J_{HH}$ 1.4, $^2J_{HH}$ 1.5 Hz). ^{31}P NMR (121 MHz, $CDCl_3$, room temp.) δ −100.1. ^{13}C NMR (75.5 MHz, $CDCl_3$, room temp.) δ 127.9 ($^1J_{CH}$ 162.5 Hz, t; $^2J_{PH}$ 24.6 Hz, d; $^3J_{CH}$ 5.2 Hz, t); 133.4 ($^1J_{PH}$ 30.8 Hz, d).



Scheme 2 *Reagents and conditions*: i, DBU (cat.), THF, −90 °C, Pr^{i}SH; ii, DBU (1 equiv.), THF, −90 °C, Pr^{i}SH

by dehydrohalogenation of chlorovinylphosphine **5a**†‡ with DBU at −90 °C evinces phosphaallene **3a** as the same intermediate in both sequences.

The high P–H acidity of the ynephosphines **1** can explain the mild conditions needed for the rearrangement. It was recently claimed[8] that an adjacent carbon–carbon triple bond makes alcohol of phenylethynol 13 pK_a units more acidic than EtOH and amine of phenylethynylamine at least 17 pK_a units more acidic than NH_3. A similar effect should exist with phosphorus analogues: to explain isomerization of **1** into **2** with a Lewis base like Et_3N, we estimate ethynylphosphine **1** to be more acidic than PH_3 (pK_a 28)[9] by at least 17 pK_a units. The P–H acidity of phosphaallene **3a** should have a value of the same order (p$K_a \approx 11$).

The rearrangement of ynephosphines **1** into phosphaalkynes **2** is unprecedented. Since primary ynephosphines bearing various substituents are easily available in gram quantities,[5] their use as starting materials for the synthesis of stable phosphaalkynes is especially attractive: volatile phosphaalkynes like **2a** and **b** can be easily synthesized without special equipment; more heavily substituted derivatives like **2c** can now also be prepared.

‡ Prepared by reduction of the corresponding phosphonate with $AlHCl_2$.

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