Formation under High-dilution Conditions of Transient Phosphaalkenes by Lewis-base-induced Rearrangement of Vinylphosphines, a Useful Entry to Cyclic Phosphines

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Transient phosphaalkenes are formed under high-dilution conditions by Lewis-base induced rearrangement of vinylphosphines. They lead to cyclic phosphines in high yields in the presence of dienes.

The impressive development of the phosphaalkene chemistry can be mainly attributed to the high reactivity of the P=C double bond.[1] In recent years, phosphalkenes have received attention as reagents in the synthesis of unusual organophosphorus derivatives. Thus, a great variety of cyclic phosphines whose chemisty is concerned in particular with metal complexation, have recently been prepared.[2] However, steric protection or electronic stabilization is usually required to keep the chemistry of the free phosphaalkenes under control. For synthetic purposes, it is of interest to extend these cycloaddition reactions to unhindered derivatives which are known to be highly reactive species. Unfortunately, to our knowledge, only two approaches dealing with their synthetic potential have been described in the literature. They respectively involve low-temperature dehydrochlorination of α-chlorophosphines[3] and thermal fragmentation of a bicyclic adduct at temperatures below 40 °C.[4] The former approach allows characterization of phosphaalkenes in the gas phase and leads to formation of the corresponding cycloadducts when the reaction occurs in solution; however, the formation of byproducts cannot be avoided with the simplest members. In the later approach, simple phosphaalkenes like CH_2=PHMe are efficiently trapped with dienes but generalization of this approach to compounds bearing various substituents seems difficult since the synthesis of the precursors is time consuming. We present here a two-step synthesis of cyclic phosphines which involves a base-induced rearrangement of unhindered vinylphosphines to the corresponding phosphaalkenes followed by *in situ* [4+2] cycloaddition of these intermediates with dienes.

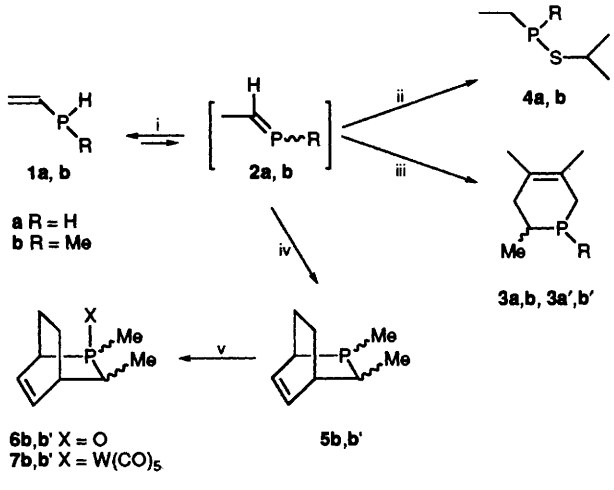
It has been widely demonstrated that rearrangement of compounds bearing an ethenyl function directly bonded to an heteroatom like O, N, or S into the corresponding heteroalkenes plays a fundamental role in organic systhesis. For the analogous phosphorus derivatives, the sole example related in the literature deals with the formation of a kinetically stabilized phosphaalkene upon heating the corresponding vinylphosphine precursor.[5] We have also to mention the reverse rearrangement which allows the transformation of phosphaalkenes bearing an –OSiMe$_3$ or –OBR$_2$ substituent on the carbon into the corresponding thermodynamically more stable vinylphosphines (1,3-hydrogen shift).[6]

We first tried to extend the thermal rearrangement to unhindered primary and secondary vinylphosphines, which are now readily available,[7] in order to use the corresponding phosphaalkenes as synthetic intermediates. Upon heating the primary vinlyphosphine **1a** at 50 °C† for 2 d in the presence of a large excess of 2,3-dimethylbutadiene, only *ca.* 2% of the corresponding cycloadduct **3a** was obtained, products of self-condensation being mainly observed. This result seems to indicate that the thermal rearrangement cannot be extended to unhindered vinylphosphines.

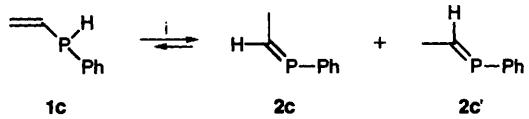
Since tautomerism is an acid–base catalysed process, we then allowed the primary vinylphosphine **1a** to react with a diene in the presence of a catalytic amount of Lewis base. After various unsuccessful trials using pyridine or triethylamine, a clean rearrangement was observed with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU); tetrahydrophosphinine **3a** was formed in good yield (>75%) at room temperature in the presence of an excess of 2,3-dimethylbutadiene. Secondary thiophosphine **4a** was also prepared in a nearly quantitative yield when the rearrangement occurred in the presence of a thiol (Scheme 1).

We supposed that the remarkable acidifying effect induced by the carbon–carbon double bond, already observed for ethenol and ethenamine,[8] is sufficient to induce a 1,3 hydrogen shift, the phosphaallyl anion intermediate then undergoing a C-protonation leading to the transient phosphaalkene **2a**. Whatever the conditions, we never detected (by low-temperature ^{31}P NMR experiments) the presence of the phosphaallyl anion‡ or the phosphaalkene **2a**. Only a slow polymerization was observed in the absence of chemical trapping agents. The high yield of the cycloadducts was rather suprising since we have already observed that **2a** polymerizes in solution at *ca.* −120 °C when it was generated by elimination of HCl starting from the α-chlorophosphine.[3a] This can be explained by the very low concentration of the transient species in the medium. This result is a consequence of the tautomeric equilibrium, the vinylphosphine being thermodynamically more stable than the phosphaalkene, in a good agreement with theoretical calculations.[9]

The same rearrangement was also observed with the secondary alkyl- and aryl-vinylphosphines **1b** and **1c**. However, the required conditions depend on the P–H acidity; the isomerization of the PMe derivative **1b** slowly occurred at 50 °C (3 d) while isomerization of the phenyl derivative **1c** was observed as low as 0 °C. The presence of the transient phosphaalkene **2b** was proved by chemical trapping. Thus, in the presence of an excess of 2,3-dimethylbutadiene or cyclohexadiene (Aldrich), a mixture of the two tetrahydro-



Scheme 1 *Reagents and conditions:* i, DBU (catalyst), THF (R = H, 20 °C; R = Me, 50°C); ii, Pr^{i}SH; iii, 2,3-dimethylbutadiene; iv, R = Me, cyclohexa-1,3-diene; v, O_2 or [W(CO)$_5$(THF)]



Scheme 2 *Reagents and conditions:* i, DBU, THF, 20 °C

phosphinines **3b,b'** and 7-phosphanorbornene **5b,b'** isomers were respectively obtained in *ca.* 97:3 molar ratio in both cases (yield > 70%). With propane-2-thiol the formation of the corresponding thiophosphine **4b** was observed in high yield (> 75%). The cyclic phosphines were found to be very sensitive to oxygen (formation of **6**). We could not determine the stereochemistry of the cycloadducts **3**, **5**, or **6** (^{1}H, ^{13}C and NOE experiments). Treatment of **5** with [W(CO)$_5$(THF)] led after purification by chromatography to the oily complex **7b** (Scheme 1).

Rearrangement of the *P*-phenylvinylphosphine **1c** led to a mixture of the *Z*- and *E*-isomers **2c** (Scheme 2) identified by ^{31}P NMR analysis (20 °C). According to the '*cis*-rule',[10] *Z*-sterochemistry was attributed to the compound having the larger $^2J_{PH}$ coupling constant (**2c**, δ_P 236, $^2J_{PH} \geqslant 30$ Hz; **2c'**, δ_P 241 $^2J_{PH} < 20$ Hz). All attempts to obtain the corresponding cycloadducts with 2,3-dimethylbutadiene or cyclohexadiene in reasonable yield were unsuccessful. We believe that the conjugation of the P=C bond with the phenyl group[11] may make the phosphaalkene **2c** more stable than the vinylphosphine isomer **1c**. Consequently, when the Lewis base is introduced, the concentration of **2c** becomes high; the self-condensation is, in these conditions, the major process. This result is in good agreement with theoretical calculations[11,12] and reactivity of analogous P-aryl derivatives.[5,13]

To summarize we have shown that conditions allowing the use of unstabilized phosphaalkenes in the field of organic synthesis are fullfilled when the transient species are formed under high-dilution conditions at a temperature which preserves their reactivity; the high yield and the good purity observed in the [4+2] cycloadditions with phosphaalkenes **2a**, **2b** demonstrates the synthetic potential of this approach. A limitation is however observed with P–phenyl substituted phosphaalkene **2c** for which self-condensation is the main process.

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Footnotes

† Only products of self-condensation were observed heating **1a** at higher temperature.

‡ We have recently characterized the phosphaallyl anion when using a strong base such as butyllithium by low-temperature ^{31}P NMR analysis[7].

§ All new compounds gave satisfactory spectroscopic data. *Selected spectroscopic data:* **3a** (2 isomers in a 67:33 molar ratio): ^{31}P NMR ($CDCl_3$), δ −64.6 (d, $^1J_{PH}$ 183.2 Hz), −75.3 (d, $^1J_{PH}$ 187.0 Hz). ^{1}H and ^{13}C NMR data (*J*/Hz) are only given for the major adduct. NMR ($CDCl_3$:^{1}H, δ 1.1 (3H, dd, $^3J_{PH}$ 16.5, $^3J_{HH}$ 7.1), 1.5–1.6 (6H, m), 2.7 (1H, d, $^1J_{PH}$ 183.2); ^{13}C, δ 20.7 (q, $^1J_{CH}$ 122.0), 21.1 (qd, $^1J_{CH}$ 124.2, $^2J_{CP}$ 11.5), 21.4 (q, $^1J_{CH}$ 125.0), 23.0 (dd, $^1J_{CH}$ 126.0, $^1J_{CP}$ 5.6), 24.2 (td, $^1J_{CH}$ 125.6, $^1J_{CP}$ 11.0), 43.5 (td, $^1J_{CH}$ 122.6, $^2J_{CP}$ 5.7), 123.9 (m), 127.4 (m).

4a NMR ($CDCl_3$): ^{31}P, δ −30.7 (d, $^1J_{PH}$ 204.1); ^{1}H, δ 1.30 (3H, dq, $^3J_{PH} \approx {}^3J_{HaHb}$ 7.2), 1.44 (6H, d, $^3J_{HH}$ 6.8), 1.76 (2H, m), 3.06 (1H, d spt d, $^3J_{PH} \approx 6.8$, $^5J_{HH}$ 1.5), 4.5 (1H, ddd, $^1J_{PH}$ 206.4, $^3J_{HaH}$ 6.7, $^3J_{HHb}$ 6.71); ^{13}C, δ 12.6 (qdt, $^1J_{CH}$ 126.8, $^2J_{CP}$ 9.0, $^2J_{CH}$ 4.0), 18.5 (tdq, $^1J_{CH}$ 130.0, $^2J_{CP}$ 15.9, $^2J_{CH}$ 4.1), 25.2 (q, $^1J_{CH}$ 126.9), 37.9 (ddd spt, $^1J_{CH}$ 141.6, $^2J_{CP}$ 21.3, $^3J_{CH}$ 5.9, $^2J_{CH}$ 4.4).

3b (2 isomers in a 97:3 molar ratio), ^{31}P NMR ($CDCl_3$), δ −53.3 (m) and −49.6 (m). ^{1}H and ^{13}C NMR are given only for the major adduct. NMR ($CDCl_3$): ^{1}H, δ 0.73 (3H, d, $^2J_{PH}$ 3.4), 1.0 (3H, dd, $^3J_{PH}$ 15.5, $^3J_{HH}$ 7.1), 1.47–1.55 (6H, m), 2.19–2.30 (2H, m), 3.30–3.35 (2H, m); ^{13}C, δ 2.6 (qdm, $^1J_{CH}$ 127.0, $^1J_{CP}$ 20.7), 18.8 (qdm, $^1J_{CH}$ 124.5, $^2J_{CP}$ 15.4), 20.5 (q, $^1J_{CH}$ 124.5), 21.8 (q, $^1J_{CH}$ 126.6), 24.1 (dd, $^1J_{CH}$ 120.8, $^1J_{CP}$ 7.1), 30.4 (td, $^1J_{CH}$ 120.3, $^1J_{CP}$ 12.7), 36.1 (tdm, $^1J_{CH}$ 123.0, $^2J_{CP}$ 4.0), 120.6 (q, $^2J_{CH}$ 4.7), 124.3 (d, $^2J_{CP}$ 18.4).

4b NMR ($CDCl_3$): ^{31}P, δ 12.6 (m); ^{1}H, δ 1.1 (3H, m), 1.28 (6H, dd, $^3J_{HH}$ 6.7, $^4J_{PH}$ 3.3), 1.29 (3H, d, $^2J_{PH}$ 6.6), 1.56 (2H, m), 2.98 (1H, spt, $^3J_{HH} \approx {}^3J_{PH}$ 6.7, $^5J_{HH}$ 1.3); ^{13}C, δ 9.95 (qdt, $^1J_{CH}$ 127.0, $^1J_{CP}$ 13.0, $^3J_{CH}$ 4.1), 15.8 (qdt, $^1J_{CH}$ 129.4, $^2J_{CP}$ 20.2, $^3J_{CH}$ 3.2), 25.1 (tdm, $^1J_{CH}$ 127.6, $^1J_{CH}$ 15.8), 25.7 (qd, $^1J_{CH}$ 127.1, $^3J_{CP}$ 27.0), 37.8 (ddm, $^1J_{CH}$ 142.0, $^2J_{CP}$ 20.2).

6b and **6b'** (2 isomers in a 97:3 molar ratio). ^{31}P, ^{1}H and ^{13}C NMR data are only given for the major adduct. NMR ($CDCl_3$): ^{31}P, δ 56.2; ^{1}H, δ 1.1 (dd, 3H, $^3J_{PH}$ 15.2, $^3J_{HH}$ 7.4), 1.4 (d, 3H, $^2J_{PH}$ 12.6), 1.7 (m, 2H), 2.0 (m, 2H), 2.45 (m, 1H), 2.6 (dm, 1H, $^3J_{PH}$ 26.0), 2.7 (m, 1H), 6.1 (m, 1H), 6.2 (m, 1H); ^{13}C, δ 11.4 (qd, $^1J_{CH}$ 130.0, $^1J_{CP}$ 67.3), 17.5 (dq, $^1J_{CH}$ 125.0, $^2J_{CP}$ 3.8), 17.6 (td, $^1J_{CH}$ 122.5, $^2J_{CP}$ 6.0), 26.0 (td, $^1J_{CH}$ 124.5, $^3J_{CP}$ 12.0), 35.7, (dd, $^1J_{CH}$ 135.5, $^3J_{CP}$ 5.1), 36.3 (d, $^1J_{CH}$ 126.5), 38.4 ($^1J_{CH}$ 139.5, $^2J_{CP}$ 3.5), 128.2 (dd, $^1J_{CH}$ 165.5, $^2J_{CP}$ 6.2), 134.8 (dd, $^1J_{CH}$ 163.5, $^3J_{CP}$ 13.9).

7b and **7b'** (2 isomers in a 97:3 molar ratio). ^{31}P and ^{1}H NMR data are only given for the major adduct. NMR ($CDCl_3$): ^{31}P, δ −2.2 ($^1J_{PW}$ 113.2); ^{1}H, δ 0.9 (dd, 3H, $^3J_{PH}$ 13.2, $^3J_{HH}$ 7.4), 1.4 (d, 3H, $^2J_{PH}$ 6.3), 1.5 (m, 2H), 1.9 (m, 2H), 2.2 (dqd, 1H, $^2J_{PH}$ 9.5, $^3J_{HH}$ 7.4, $^3J_{HH}$ 2.2), 2.5 (dm, 1H, $^3J_{PH}$ 18.6), 2,7 (dm, 1H, $^2J_{PH}$ 4.9), 6.1 (m, 1H), 6.4 (m, 1H) (chemical shift of the C*H*–CH_3 was attributed by spin decoupling).

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