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Unstabilized 1-Phosphaallenes : Synthesis and Characterization

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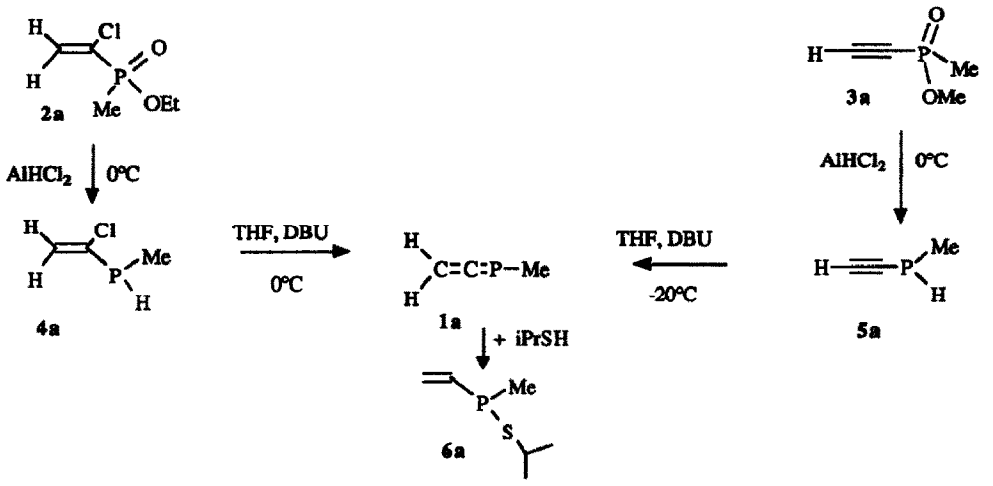
Abstract : *Unstabilized P-methyl-1-phosphaallenes 1 are prepared by a base-induced dehydrohalogenation of 1-chlorovinyl-methylphosphines or rearrangement of 1-alkynyl-methylphosphines.*

Although 1-phosphaallenes have been widely studied, only sterically stabilized derivatives have been described so far.[1-3] Such compounds are prepared either by a base-induced rearrangement of P-aryl-1-alkynylphosphine intermediates [2] or through reaction of phosphaketenes with methylenephosphoranes [3a] or silylated phosphines.[3b] Efforts to apply the latter approach to the generation of 1-phosphaallenes with a less bulky substituent at the P atom lead to the corresponding dimer.[3b] The synthetic utility of the reported methods is restricted by hardly accessible unshielded starting materials. We have recently prepared unstabilized phosphaalkynes by dehydrohalogenation of the corresponding dichloroalkylphosphines [4] and by base-induced rearrangement of primary 1-alkynylphosphines.[5] In the latter approach, the presence of a phosphaallene intermediate has been demonstrated. In this paper, we show that unstabilized P-methyl-1-phosphaallenes **1** can be prepared by dehydrohalogenation of 1-chlorovinyl-methylphosphines and by rearrangement of 1-alkynyl-methylphosphines.

Secondary 1-chlorovinyl- and ethynylphosphines **4a-c** and **5a,b** are prepared by chemoselective reduction at 0°C of the corresponding phosphinic esters **2a-c**[6] and **3a,b**[7] respectively using $AlHCl_2$ in tetraglyme (Scheme 1).[8] In both cases, formation of by-products resulting from C-P bond cleavage cannot be avoided. Phosphines **4** and **5** are purified by trap-to-trap distillation, and may be kept for several days in solution at room temperature in the presence of a small amount of hydroquinone. The structures are assigned on the basis of ^{1}H, ^{31}P, ^{13}C NMR and IR spectroscopy and mass spectrometry.[9-11]

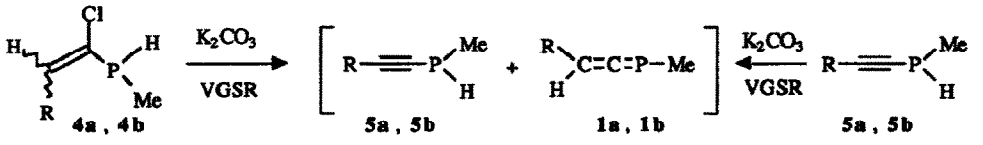
Reactions in solution. Using DBU, dehydrochlorination of the phosphine **4a** is observed at 0°C, but the 1-phosphaallene **1a** is too unstable in these conditions to be characterized by ^{31}P NMR. Presence of this intermediate is proved by addition of 2-propanethiol and formation of the 1,2-thiophosphine adduct **6a**.[12] Compound **1a** can be however detected by low temperature ^{31}P NMR in the base-induced rearrangement of phosphine **5a** : the chemical shift of the phosphorus atom of **1a** is observed at δ 42.0 ppm by warming up a THF

solution of **5a** from -78 to -20°C in the presence of a catalytic amount of DBU. When 2-propanethiol is added, the ^{31}P NMR signal of **1a** disappears while the signal corresponding to **6a** is observed (Scheme 1). In both approaches, we failed in our attempts to isolate the phosphaallene **1a**.



Scheme 1

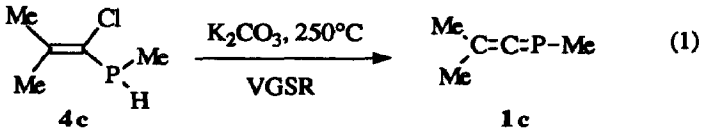
Reactions in the gas-phase (VGSR). The two liquid-phase approaches to 1-phosphaallene **1a** precedently described can also be performed in the gas-phase (VGSR)[4,5] using K_2CO_3 heated to 250°C as a solid base. Whatever the precursor (**4a** or **5a**), a mixture of phosphaallene **1a** and 1-alkynylphosphine **5a** is observed in the same molar ratio (92 : 8 respectively). A mixture of **1b**, **5b** in a 55 : 45 molar ratio is also observed starting from **4b** or **5b** (Scheme 2). A tautomeric equilibrium between **5** and **1** rationalizes these results. The structures of compounds **1a-b** are determined from their low temperature (-50°C) ^1H, ^{13}C and ^{31}P NMR, IR and mass spectra.[13] The observed values are in good agreement with those reported for bulky substituted derivatives.[2,3] As an example, the ^{13}C NMR signals of **1a** at δ 95.2 and 250.4 ppm are characteristic of the chemical shifts of the two allenic carbons. The IR absorptions at 1715 and 869 cm^{-1} have been tentatively attributed to $\nu_{C=C}$ and $\nu_{C=P}$ stretching respectively.[14] Phosphaallenes **1** slowly oligomerize on warming to -20°C.



a : R= H
b : R= Me

Scheme 2

The gas-phase dehydrohalogenation of secondary chlorovinylphosphines provides an efficient synthesis of C-disubstituted 1-phosphaallenes : thus, starting from the 1-chloro-2-methylpropenyl-methylphosphine **4c**, the 1-phosphaallene **1c** is obtained in a nearly pure state in 38% yield (Equation 1).[15]



4c 1c (1)

The two approaches, basic dehydrohalogenation of secondary 1-chlorovinylphosphines and base-induced rearrangement of secondary 1-alkynylphosphines, which are effective in solution and in the gas-phase, provide two efficient and convenient routes to unstabilized 1-phosphaallenes.

References and Notes

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

1. For a review see : Apple, R; Knoll, F. *Advances in Inorganic Chemistry* **1989**, *33*, 313-321.

2. Märkl, G.; Reitinger, S. *Tetrahedron Lett.* **1988**, *29*, 463-466. Märkl, G.; Herold, U. *Tetrahedron Lett.* **1988**, *29*, 2935-2938. Märkl, G.; Kreitmeier, P.; Nöth, H.; Polborn, K. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 927-929.

3. a) Yoshifuji, M.; Toyota, K; Shibayama, K.; Inamoto, N. *Tetrahedron Lett.* **1984**, *25*, 1809-1812. b) Appel, R.; Fölling, P.; Josten, F.; Knoch, M.; Siray, M.; Winkhaus, V. *Angew. Chem., Int. Ed. Engl.* **1984**, *25*, 619-620; Appel, R.; Winkhaus, V; Knoch, F. *Chem. Ber.* **1986**, *119*, 2466-2472.

4. Guillemin, J.C.; Janati, T.; Guenot, P.; Savignac, P.; Denis, J.M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 196-198.

5. Guillemin, J.C.; Janati, T; Denis, J.M. *J. Chem. Soc., Chem. Commun.* **1992**, 415-416.

6. Compounds **2** are prepared by P-chlorination of the corresponding phosphonates followed by alkylation using a Grignard reagent. Teulade, M.P.; Savignac, P. *J. Organomet. Chem.* **1988**, *338*, 295-303; Morise, X.; Savignac, P.; Guillemin, J.C.; Denis, J.M. *Synth. Commun.* **1991**, *21*, 793-798; Minowa, N; Fukatu, S.; Niida, T.; Takada, M.; Sato, K. *Tetrahedron Lett.* **1983**, *24*, 2391-2392.

7. Balthazor, T.M.; Flores, R.A. *J. Org. Chem.* **1980**, *45*, 529-531.

8. Cabioch, J.L.; Denis, J.M. *J. Organomet. Chem.* **1989**, *377*, 227-233; Guillemin, J.C.; Savignac, P.; Denis, J.M. *Inorg. Chem.* **1991**, *30*, 2170-2173.

9. All new compounds exhibit physical and spectroscopic properties consistent with their proposed structure.

10. *Selected spectroscopic data :* **4a** : (yield : 52%) ^{1}H NMR ($CDCl_3$) δ : 1.34 (dd, 3H, $^3J_{HH}$ = 7.4 Hz, $^2J_{PH}$ = 3.5 Hz); 4.05 (dq, 1H, $^1J_{PH}$ = 197.0 Hz, $^3J_{HH}$ = 7.4 Hz); 5.77 (dd, 1H, $^3J_{PH}$ = 13.3 Hz, $^2J_{HH}$ = 1.4 Hz); 5.82 (dd, 1H, $^3J_{PH}$ = 13.3 Hz, $^2J_{HH}$ = 1.4 Hz); ^{31}P NMR ($CDCl_3$) δ : -53 ($^1J_{PH}$ = 197.0 Hz); ^{13}C NMR ($CDCl_3$) δ : 4.45 (qd, $^1J_{CH}$ = 131 Hz, $^1J_{CP}$ = 11 Hz); 125.3 (td, $^1J_{CH}$ = 162.4 Hz, $^2J_{CP}$ = 25.8 Hz); 141.1 (d, $^1J_{CP}$ = 36.6 Hz). HRMS calcd. for $C_3H_6{}^{35}ClP$: 107.9896; found : 107.990. **4b** (2 stereoisomers) (yield : 57%): ^{1}H NMR ($CDCl_3$) δ : 1.30 (d, 3H, $^3J_{HH}$ = 7.6 Hz); 1.89 (dd, 3H, $^4J_{PH}$ = 0.5 Hz, $^3J_{HH}$ = 7.0 Hz); 3.90 (dq, 1H, $^1J_{PH}$ = 207.9 Hz, $^3J_{HH}$ = 7.6 Hz); 6.39 (qd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 14.2 Hz) and 1.30 (d, 3H, $^3J_{HH}$ = 7.6 Hz); 1.86 (dd, 3H, $^4J_{PH}$ = 0.8 Hz, $^3J_{HH}$ = 6.5 Hz); 3.90 (dq, 1H, $^1J_{PH}$ = 214.8 Hz, $^3J_{HH}$ = 7.6 Hz); 6.33 (qd, $^3J_{HH}$ = 7.0 Hz, $^3J_{PH}$ = 7.0 Hz) ; ^{31}P NMR ($CDCl_3$) δ : -49.6 ($^1J_{PH}$ = 207.9 Hz) and -71.6 ($^1J_{PH}$ = 214.8 Hz, $^2J_{PH}$ = 14.2 Hz); ^{13}C NMR ($CDCl_3$) δ : 4.35 (qd, $^1J_{CH}$ = 130.9 Hz, $^1J_{CP}$ = 9.7 Hz); 15.6 (qd, $^1J_{CH}$ = 125.6 Hz, $^3J_{CP}$ = 9.7 Hz); 132.9 (d, $^1J_{CP}$ = 34.6 Hz); 138.8 (dd, $^1J_{CH}$ = 150.O Hz, $^2J_{CP}$ = 24.1 Hz) and 3.64

(qd, $^1J_{CH}$ = 131.7 Hz, $^1J_{CP}$ = 9.7 Hz); 16.8 (qd, $^1J_{CH}$ = 128.2 Hz, $^3J_{CP}$ = 21.5 Hz); 131.0 (d, $^1J_{CP}$ = 39.5 Hz); 136.8 (dd, $^1J_{CH}$ = 157 Hz, $^2J_{CP}$ = 37.8 Hz). HRMS calcd for $C_4H_8{}^{35}ClP$ 122.0052; found : 122.005. **4c** : (yield : 65%) ^1H NMR ($CDCl_3$) δ : 1.29 (d, 3H, $^2J_{PH}$ = 4.2 Hz); 1.94 (s, 3H); 2.07 (s, 3H); 3.82 (d, 1H,$^1J_{PH}$ = 217.5 Hz); ^{31}P NMR ($CDCl_3$) δ : -61.4 ($^1J_{PH}$ = 217.5 Hz); ^{13}C NMR ($CDCl_3$) δ : 4.39 (qd, $^1J_{CH}$ = 131.2 Hz, $^1J_{CP}$ = 9.7 Hz); 22.9 (qd, $^1J_{CH}$ = 131.7 Hz, $^3J_{CP}$ = 3.6 Hz); 23.4 (qd, $^1J_{CH}$ = 131.7 Hz, $^3J_{CP}$ = 29.1 Hz); 124.7 (d, $^1J_{CP}$ = 37.0 Hz); 145.9 (d, $^2J_{CP}$ = 25.7 Hz). HRMS calcd. for $C_5H_{10}{}^{35}ClP$: 136.0209; found : 136.021.

11. *Selected spectroscopic data :* **5a** : (yield : 31%) ^1H NMR ($CDCl_3$) δ : 1.35 (dd, 3H, $^3J_{HH}$ = 7.6 Hz, $^2J_{PH}$ = 4.2 Hz); 2.71 (d, 1H, $^4J_{HH}$ = 3.3 Hz); 3.96 (ddq, 1H, $^1J_{PH}$ = 221.4 Hz, $^4J_{HH}$ = 3.3 Hz, $^3J_{HH}$ = 7.6 Hz); ^{31}P NMR ($CDCl_3$) δ : -115 ($^1J_{PH}$ = 221.4 Hz) ; ^{13}C NMR ($CDCl_3$) δ : 4.6 (qd, $^1J_{CH}$ = 131.6 Hz, $^1J_{CP}$ = 7.0 Hz); 80.8 (d, $^1J_{CP}$ = 21.0 Hz); 92.0 (dd, $^1J_{CH}$ =245.0 Hz, $^2J_{CP}$ = 1.8 Hz). IR (film; 77K, cm^{-1}) : ν_{PH} : 2280 (m); $\nu_{C\equiv C}$: 2025(w). HRMS calcd for C_3H_5P : 72.0128 ; found : 72.0130. **5b** : (yield : 35%) ^1H NMR ($CDCl_3$) δ : 1.30 (dd, 3H, $^3J_{HH}$ = 7.3 Hz, $^2J_{PH}$ = 4.1 Hz); 1.93 (d, 3H, $^4J_{PH}$ = 1.0 Hz); 3.63 (dq, 1H, $^1J_{PH}$ = 213.0 Hz, $^3J_{HH}$ = 7.3 Hz,); ^{31}P NMR ($CDCl_3$) δ -114 ($^1J_{PH}$ = 213.0 Hz) ; ^{13}C NMR ($CDCl_3$) δ : 5.1 (q, $^1J_{CH}$ = 131.6 Hz); 5.3 (qd, $^1J_{CH}$ = 131.4 Hz; $^1J_{CP}$ = 6.5 Hz); 73.7 (d, $^1J_{CP}$ = 12.2 Hz); 101.3. IR (film; 77K, cm^{-1}) : ν_{PH} : 2260 (m); $\nu_{C\equiv C}$: 2178 (w). HRMS calcd. for C_4H_7P : 86.0285; found : 86.0286.

12. *Selected spectroscopic data :* **6a** : ^1H NMR ($CDCl_3$) δ : 1.22 (dd, 6H, $^4J_{PH}$ = 1.8 Hz, $^3J_{HH}$ = 6.7 Hz); 1.25 (d, 3H, $^2J_{PH}$ = 6.7 Hz); 2.93 (d.hept, 1H, $^3J_{PH}$ = $^3J_{HH}$ = 6.7 Hz); 5.47 (ddd, 1H, $^3J_{PH}$ = 26.0 Hz, $^3J_{HHcis}$ = 11.7 Hz, $^2J_{HH}$ = 1.7 Hz); 5.58 (ddd, 1H, $^3J_{HHcis}$ = 12.0 Hz, $^3J_{HHtrans}$ = 18.2 Hz, $^2J_{HH}$ = 1.7 Hz); 6.34 (ddd, 1H, $^2J_{PH}$ = 20.6 Hz, $^3J_{HH}$ = 18.2 Hz, $^3J_{HH}$ = 11.7 Hz). ^{31}P NMR ($CDCl_3$) δ : 3.2. ^{13}C NMR ($CDCl_3$) δ : 16.0 (qd, $^1J_{CH}$ = 130.0 Hz, $^1J_{CP}$ = 19.3 Hz); 27.1 (qd, $^1J_{CH}$ = 126 Hz, $^3J_{CP}$ = 3.0 Hz); 39.1 (dd, $^1J_{CH}$ = 142 Hz, $^2J_{CP}$ = 20.6 Hz); 125.4 (dd, $^1J_{CH}$ = 157.5 Hz, $^1J_{CP}$ = 17.2 Hz); 142.5 (td, $^1J_{CH}$ = 150 Hz, $^2J_{CP}$ = 25.9 Hz). HRMS : calcd for $C_6H_{13}PS$: 148.0476; found: 148.047. IR : $\nu_{C\equiv C}$: 1610 cm^{-1} (w).

13. **Ethenylidene-methylphosphine 1a** : (yield : 28% from **3a** and 26% from **4a**) ^1H NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 1.49 (td, 3H, $^5J_{HH}$ = 2.9 Hz, $^2J_{PH}$ = 0.5 Hz); 5.46 (dq, 2H, $^3J_{PH}$ = 26.0 Hz, $^5J_{HH}$ = 2.9 Hz); ^{31}P NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 42.0 ($^3J_{PH}$ = 26 Hz (d)); ^{13}C NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 10.4 (qd, $^1J_{CH}$ = 132.8 Hz, $^1J_{CP}$ = 40.3 Hz); 95.2 (td, $^1J_{CH}$ = 168 Hz, $^2J_{CP}$ = 13.6 Hz); 250.4 (d, $^1J_{CP}$ = 24.6 Hz). IR (film, 77 K, cm^{-1}) : 2970 (s); νC=C : 1715 (s); 1255 (m); 950 (s); $\nu_{C\equiv P}$: 869 (s); 653 (m). HRMS calcd for C_3H_5P : 72.0128 ; found : 72.0130. **Propenylidene-methylphosphine 1b** : (yield : 26% from **3b** and 32% from **4b**) ^1H NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 1.42 (d, 3H, $^5J_{HH}$ = 2.6 Hz); 1.81 (d, 3H, $^3J_{HH}$ = 1.3 Hz,); 5.85 (dqq, 1H, $^3J_{PH}$ = 23.3 Hz, $^5J_{HH}$ = 2.6 Hz, $^3J_{HH}$ = 1.3 Hz); ^{31}P NMR (CD_2Cl_2/CCl_3F, -80°C) δ 45.3 ($^3J_{PH}$ = 23.0 Hz) ; ^{13}C NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 11.3 (qd, $^1J_{CH}$ = 132.0 Hz, $^1J_{CP}$ = 41.3 Hz); 17.5 (qd, $^1J_{CH}$ = 127.8 Hz, $^3J_{CP}$ = 25.2 Hz); 107.6 (dd, $^1J_{CH}$ = 157.3 Hz, $^2J_{CP}$ = 11.3 Hz); 247.2 (d, $^1J_{CP}$ = 24.5 Hz).

14 These values can be compared with the calculated $\nu_{C\equiv C}$ and $\nu_{C\equiv P}$ values of the parent compound : Nguyen, M. T.; Hegarty, A. F. *J. Chem. Soc., Perkin Trans II* **1985**, 1999-2004.

15. **2-Methylpropenylidene-methylphosphine 1c** : (yield : 38%) ^1H NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 1.34 (s, 3H); 1.81 (d, 6H, $^4J_{PH}$ = 9.8 Hz); ^{31}P NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 39; ^{13}C NMR (CD_2Cl_2/CCl_3F, -80°C) δ : 12.5 (qd; $^1J_{CH}$ = 131.6 Hz, $^1J_{CP}$ = 42.4 Hz); 22.1 (qd, $^1J_{CH}$ = 128.6 Hz, $^3J_{CP}$ = 11.4 Hz); 118.6 (dhept, $^2J_{CP}$ = 10.0 Hz, $^3J_{CH}$ = 6.7 Hz); 209.0 (d, $^1J_{CP}$ = 23.8 Hz). HRMS calcd for C_5H_9P : 100.0442 ; found : 100.044.

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