Pergamon

Tetrahedron Letters, Vol. 36, No. 25, pp. 4421-4424, 1995
Elsevier Science Ltd
Printed in Great Britain
0040-4039/95 $9.50+0.00

0040-4039(95)00761-X

First Synthesis of Secondary P-Alkenyl and P-Alkynyl Phosphine Oxides

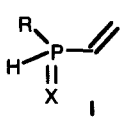
Gnon Baba, Jean-François Pilard, Khalid Tantaoui, Annie-Claude Gaumont and Jean-Marc Denis*

Groupe de Physicochimie Structurale associé au CNRS - Université de Rennes I, 35042 - Rennes, France.

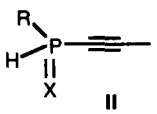
Abstract : A general method for preparing secondary P-alkenyl and P-alkynyl phosphine oxides, compounds unknown so far, involves the condensation of the vinyl Grignard reagent or lithium acetylide on P-chloroaminophosphines followed by acidic hydrolysis of the corresponding vinyl- or ethynylaminophosphines on a solid acid (Amberlyst 15). The few reported chemical properties are mainly related to the strong *PH* bond activation. Of special interest is the addition of a secondary vinylphosphine oxyde derivative on methyl acrylate which occurs at room temperature without any catalyst.

P- alkyl and P-aryl secondary phosphine oxides ($R_1R_2PO(H)$) are useful intermediates in organophosphorus chemistry. They can be P-alkylated *via* hydrogen/metal exchange. However, the main synthetic potential is related to their addition to unsaturated functions like aldehydes, ketones, imines or various Michael acceptors[1,2]. Intramolecular additions to aldehydes have also been reported[3]. Several examples of optically active derivatives are also known[2b,4,5].

As part of our continuing study on reactive phosphines, we present here the preparation of P-vinyl- and P-ethynylphosphine oxides I and II. If these derivatives are completly unknown so far, on the contrary, there has been considerable effort spent in studying their free or complexed counterparts I_f, I_c and II_f, II_c which present interesting properties related to the *PH* activation induced by the presence of the unsaturated group[6,7]. We can for example point out the base-induced rearrangement of vinylphosphines I_f and ethynylphosphines II_f into phosphaalkenes[8,9] and phosphaalkynes[9,10] respectively, and for I_c derivatives, the hydrophosphorylation of an ethynyl group[11] and the formation of η^3 complexes[12]. Considering these results, a promising reactivity should be expected for unsaturated phosphine oxides I and II.

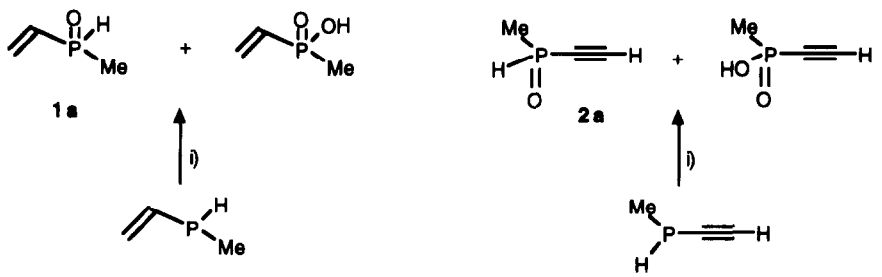


I X=O
I_f X = lone pair
I_c X = MLn



II X=O
II_f X = lone pair
II_c X = MLn

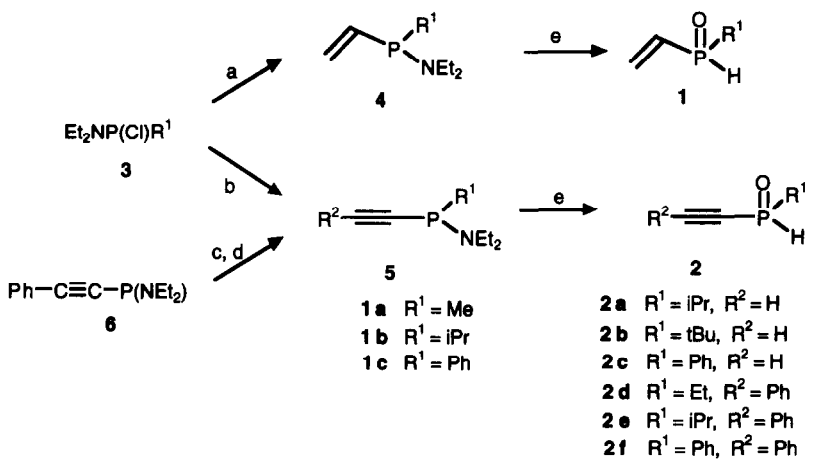
Secondary dialkylphosphine oxides are usually prepared by oxidation of free phosphines or by hydrolysis of P-aminophosphines[2a,13]. First, we have prepared the simple vinylphosphine oxide **1a** and ethynylphosphine oxide **2a** by oxidation of the corresponding free phosphine[14a,14b] with oxygen, H_2O_2 or ^tBuOOH (Scheme 1). This approach is however only of analytical significance due to the low selectivity of the oxidation (presence of the corresponding phosphinic acid (20 %)) and to the unsolved purification.



Reagents : i) O_2, H_2O_2 or tBuOOH

Scheme I

Unsaturated phosphine oxides **1** and **2** were easily prepared in good yields by hydrolysis of aminophosphines **4** and **5** (Scheme II). The P-chloroaminophosphine intermediates **3** were formed by condensation of the Grignard reagent onto diethylaminodichlorophosphines (R^1 = iPr, t.Bu) or by monoamination of $PhPCl_2$ (R^1=Ph). Condensation of vinylmagnesiumbromide or lithium acetylide on **3** has allowed the access to aminophosphines **4** and **5** respectively[15]. Approach for **5d** (R^1 = Et) involves the P-chlorination of ethynylaminophosphine **6** with PCl_3 followed by addition of EtMgBr[15,16].

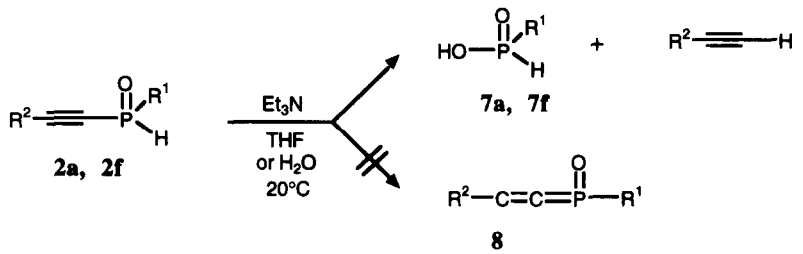


Reagents : a) CH_2=CH-MgBr, TMEDA; b) R_2-C≡C-Li ; c) PCl_3, d) EtMgBr, e) Amberlyst 15, H_2O (5 eq), THF.

Scheme II

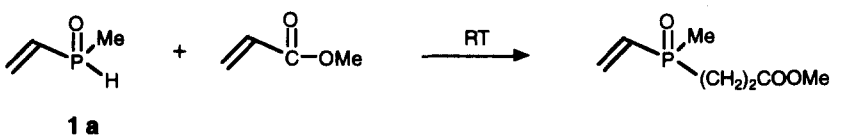
The key step of the overall sequence is the acidic cleavage of unsaturated aminophosphines **4** and **5**. Application of the procedure described in the literature[17] for saturated derivatives gave a complexe mixture, the main products corresponding to the clivage of the P-C bond. However, when using a solid acid (Amberlyst® 15) in a THF solution with 4 equivalents of H_2O at room temperature, secondary phosphine oxides **1** and **2** were obtained very easily and in good yields[18,19] (*ca* 80%). These compounds present however a weak stability. Purification by liquid chromatography gave very poor yield. The crude products (purity > 90%) can however be used further without purification. If necessary, they can also be stored few weeks in solution (THF, H_2O) under neutral gas in the refrigerator.

First studies dealing with the reactivity of **1** and **2** have been performed. Alkynyl- phosphine oxides **2a**, **2e** are rapidly decomposed in the presence of a catalytic amount of triethylamine : clivage of the P-C bond and formation of the corresponding alkylphosphinic acids **7a**, **7f** is mainly observed. The mechanism probably involves the formation of the conjugated base of the secondary hydroxyphosphine[4b], the tautomeric form of phosphine oxide. The phosphaallene oxide derivatives **8** which might be expected in a rearrangement involving a 1,3-hydrogen shift[10,14b] were never observed (Scheme III).



Scheme III

Activation of the *PH* bond is evidenced by addition of the vinylphosphine oxide **1a** on methylacrylate ; the reaction occurs at room temperature without any activation agent.



Further studies including the reactivity of secondary vinyl and ethynylphosphine oxides with various Michael acceptors or electrophiles are currently underway.

References and Notes

1. Review : Edmundson, R.S., *"The chemistry of organophosphorus compounds"*, Vol. 2, Hartley, F.R. editor, **1992** , John Wiley and son.
2. a) Kleiner, H.J., *Liebigs Ann. Chem.*, **1974**, 751-764 ; b) Emmick, T.L. ; Letsinger, R.L., *J. Am. Chem. Soc.*, **1968**, *90*, 3459-3465.
3. Musierowicz, S. ;Waszkuc, W.T.; Krawczyk, H.W, *Phosphorus and Sulfur*, **1979**, *5*, 377-379.
4. a) Skrzypczynski, Z. and Michalski J., *J. Org. Chem.*, **1988**, *53*, 4549-4551. b) Emmick, T.L. ; Letsinger, R.L., *J. Am. Chem. Soc.*, **1968**, *90*, 3459-3465 and references therein.
5. Pietrusiewicz, K.M. and Zablocka, M., *Chem. Rev.*, **1994**, *94*, 1375-1411.
6. For acid-strengthening effects of carbon-carbon double and triple bond of enols and ynols see ref[7].
7. Kresge, A.J., *Acc. Chem. Res.*, **1990**, *23*, 43-48.
8. Gaumont, A.C. ; Guillemin, J.C. ; Denis, J.M., *J. Chem. Soc., Chem. Commun.*, **1994**, 945-946.
9. Gaumont, A.C. ; Denis, J.M., *Chem. Rev.*, **1994**, *94*, 1413-1439.
10. Guillemin, J.C. ; Janati, T. ; Denis, J.M., *J. Chem. Soc., Chem. Commun.*, **1992**, 415-416.
11. Lang, H. ; Lay, U. and Imhof, W., *J. Organomet. Chem.*, **1993**, *444*, 53-59.
12. Mercier, F. ; Hugel-Le Goff, C. and Mathey, F., *Organometallics*, **1988**, *7*, 955-963.

13. Review : Bhattacharya, A.K. ; Roy, N.K., *The chemistry of organophosphorus compounds*, Vol. 2, Hartley, F.R. editor, **1992**, John Wiley and son.

14. a) Cabioch, J.L. ; Denis, J.M., *J. Organomet. Chem.*, **1989**, *377*, 227-233 ; b) Guillemin, J.C. ; Janati, T. ; Denis, J.M. ; Guenot, P. ; Savignac, P., *Tetrahedron Lett.*, **1994**, *35*, 245-248.

15. All new compounds gave consistent ^{1}H, ^{31}P and ^{13}C NMR spectra and analytical or mass spectrometric data.

16. Galindo, A. ; Mathieu, R. ; Caminade, A.M. ; Majoral, J.P., *Organometallics*, **1988**, *7*, 2198-2202.

17. Krech, F. ; Issleib, K. ; Zschunke, A. ; Mügge, C. ; Skvorcov, S., *Z. Anorg. Allg. Chem.*, **1991**, *594*, 66-76.

18. Example of the hydrolysis procedure : To a cold (-40°C) stirred and degassed suspension of Amberlyst® 15 (6.40g, 30 mmol) in THF (30mL) was added degassed water (720 µL). Aminophosphine **5b** (10 mmol) in a THF solution (10mL) was then added dropwise under neutral gas. The mixture was stirred 10 mn at this temperature and allowed to warm to room temperature where the stirring is maintained for 1 h. After filtration, the solid acid was washed twice with THF. The crude phosphine oxide **2b** was obtained with good yield (84%) after evaporation of the solvent.

19. Spectral data of representative compounds : **1b.** ^{31}P NMR (121 MHz, $CDCl_3$) : δ -10 (d, $^{1}J_{PH}$ = 482 Hz). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.10 (m, 6H), 2.05 (m, 1H), 6.10-6.40 (m, 3H), 6.75 (d, $^{1}J_{PH}$ = 482 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 16 (qd, $^{1}J_{CH}$ = 125 Hz, $^{2}J_{CP}$ = 40 Hz), 28.7 (ddm, $^{1}J_{CH}$ = 140 Hz, $^{1}J_{CP}$ = 71 Hz), 128 (dd, $^{1}J_{CH}$ = 162 Hz, $^{1}J_{CP}$ = 90 Hz), 140 (td, $^{1}J_{CH}$ = 154 Hz, $^{2}J_{CP}$ = 31.6). Hz). **1c.** ^{31}P NMR (121 MHz, $CDCl_3$) : δ 15.8 (d, $^{1}J_{PH}$ = 465.8 Hz). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 5.4 (m, 3H), 7.0 (m, 3H), 7.45 (d, $^{1}J_{PH}$ = 465.8 Hz, 1H), 7.5 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 130 (ddm, $^{1}J_{CH}$ = 146 Hz, $^{1}J_{CP}$ = 94 Hz), 130.5, 131.2, 131.8, 132.0 (m, C_{ar}), 139 (td, $^{1}J_{CH}$ = 170 Hz, $^{2}J_{CP}$ = 10 Hz). **2a.** ^{31}P NMR (121 MHz, $CDCl_3$) : δ 11.5 (ddhd, $^{1}J_{PH}$ = 507.5 Hz, $^{2}J_{PH}$ = 20.8 Hz, $^{3}J_{PH}$ = 13.3 Hz, $^{3}J_{PH}$ = 9.5 Hz). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 1.15 (dd, $^{3}J_{PH}$ = 13.9 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H), 1.2 (dd, $^{3}J_{PH}$ = 12.8 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H), 2.1 (dhd, $^{2}J_{PH}$ = 20.8 Hz, $^{3}J_{HH}$ = 7.1 Hz, $^{3}J_{HH}$ = 2.4 Hz, 1H), 3.37 (dd, $^{3}J_{PH}$ = 9.5 Hz, $^{4}J_{HH}$ = 0.5 Hz, 1H), 6.6 (dd, $^{1}J_{PH}$ = 507.5 Hz, $^{3}J_{HH}$ = 2.4 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 14.9 (qdm, $^{1}J_{CH}$ = 128.8 Hz, $^{2}J_{CP}$ = 13.9 Hz), 14.1 (qdm, $^{1}J_{CH}$ = 128.8 Hz, $^{2}J_{CP}$ = 12.6 Hz), 28.7 (ddm, $^{1}J_{CH}$ = 129.4 Hz, $^{1}J_{CP}$ = 80 Hz), 75.6 (dddd, $^{1}J_{CP}$ = 139 Hz, $^{2}J_{CH}$ = 45.8 Hz, $^{2}J_{CH}$ = 16.1 Hz, $^{3}J_{CH}$ = 2.9 Hz), 93.9 (ddd, $^{1}J_{CH}$ = 252 Hz, $^{2}J_{CP}$ = 23.8 Hz, $^{3}J_{CH}$ = 4.8 Hz). **2c.** ^{31}P NMR (121 MHz, $CDCl_3$) : δ -14.0 (d, $^{1}J_{PH}$ = 529 Hz). ^{1}H NMR (300 MHz, $CDCl_3$) : δ 3.4 (d, $^{3}J_{PH}$ = 9.3 Hz), 7.2 (m, 3H), 7.8 (d, $^{1}J_{PH}$ = 529 Hz, 1H), 7.9 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) : δ 77 (d, $^{1}J_{CP}$ = 20 Hz), 98 (dd, $^{1}J_{CH}$ = 260 Hz, $^{2}J_{CP}$ = 8 Hz), 127.7, 128.0, 128.2, 129.2, 129.4 (m, Car), 132.3 (d, $^{1}J_{CP}$ = 16 Hz).

(*Received in France* 14 *February* 1995; *accepted* 25 *April* 1995)