Tetrahedron Letters,Vol.27,No.47,pp 5723-5726,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

# UNHINDERED PHOSPHAALKENES AND PHOSPHAALKYNES IN STABLE CONDITION FROM A VACUUM MULTISTEP SEQUENCE.

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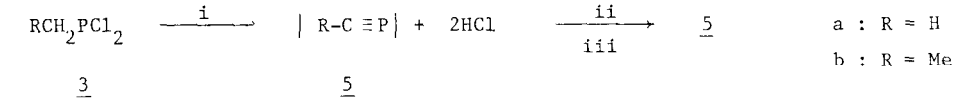
ABSTRACT. Unhindered low coordinated phosphines 5-6 are obtained in stable condition starting from dichlorophosphines 3 and 4 by a Flash Vacuum Thermolysis/Gas Solid Reaction sequence (FVT/GSR) and fully characterized by $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopy.

The chemistry of low coordinated trivalent phosphorus compounds is of current interest. Only species stabilized by bulky substituents or delocalization are well known[1]. Recent formation of a stable metal complex $\eta^2(CH_2{=}PCl)W(CO)_5$ 1 by rearrangement of a transient phosphinidene isomer, constitutes a promising approach to stabilize the low coordinated unhindered phosphines[2]. Some reactive phosphaalkenes and alkynes have been spectroscopically characterized. Thus, the parent compound methylidynephosphine 5a formed by passage of phosphine through a carbon arc[3], was analysed by microwave and photoelectron spectroscopy in the gas phase pyrolysis decomposition products of the corresponding dichlorophosphines[5,6]. However this approach cannot be easily extended to the preparation of these low coordinated phosphines in stable condition since addition of HCl occurs even at low temperature, leading to the corresponding dichlorophosphines precursors[3]. We show in this paper that Flash Vacuum Thermolysis (FVT) of dichlorophosphines 3 and 4 and subsequent removal of the HCl on solid base, according to a vacuum multistep sequence (FVT/GSR)[7], allowed us to isolate and fully characterize by $^{1}H$, $^{13}C$ and $^{31}P$ NMR spectroscopy the corresponding unhindered unsaturated phosphines 5-6 respectively, depending on the temperature[8].

The one-coordinated phosphines 5a and 5b are obtained in ca. 30 % yield by a FVT/GSR sequence starting from dichlorophosphines 3a and 3b respectively (scheme 1). Phosphine 5a is contaminated by phosphaalkene 6a (30 %) ; purity of 5b is higher than 90 %. Stability of 5a (half-life 5 mn at -10°C) is higher than previously reported[3,4] ; 5b can be kept three days in solution at room temperature without significant decomposition.

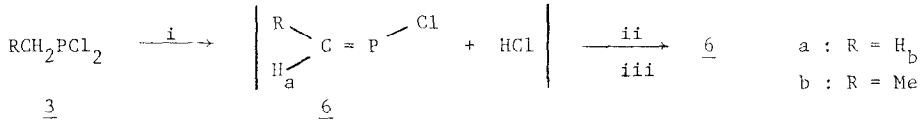



3 5

Scheme 1

Reagents and conditions : i, $10^{-3}$ torr, 3.5 cm i.d. x 90 cm quartz tube, 900°C (R = H), 750°C (R = Me) ; ii, horizontal half-filled 3.5 i.d. x 20 cm column of 1,3,5-tricylohexylhexahydro-s-triazine 2 at room temperature ; iii, cold trap at -120°C.

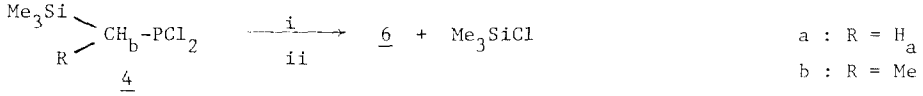
The two-coordinated phosphines 6a and 6b are obtained at lower temperature by the same multistep sequence starting from dichlorophosphines 3a and 3b or by FVT of silylated dichlorophosphines 4a and 4b, respectively[10] (Scheme 2 and 3). Using this latter approach, better yields are obtained and the two isomers 6b and 6b' can be observed. However the stability of unsaturated phosphines is highly depending on the medium : half-lives of 6a and 6b are respectively 5 mn at room temperature and 3 mn at -20°C, but decomposition of the two compounds occurs at lower temperature (-40°C) when $ClSiMe_3$ is present. The P=C double bond is furthermore confirmed by a controlled addition of dry HCl to 6a, leading to the dichlorophosphine 3a precursor[3,11,12]. The failure to obtain 6b using FVT technique, starting from dichlorophosphine 3b[6], illustrates the utility of removing HCl before condensation of the gaseous flow.




3 6

Scheme 2

Reagents and conditions : i, $10^{-3}$ torr, 1.0 cm i.d. x 20 cm quartz tube, 850°C (R = $H_a$), 700°C (R = Me) ; ii, horizontal half-filled 3.5 i.d. x 20 cm column of 2 at room temperature ; iii, cold trap at -120°C.




4

Scheme 3

Reagents and conditions : i, $10^{-3}$ torr, 1.0 i.d. x 20 cm quartz tube, 700°C (R = $H_a$), 600°C (R = Me) ; ii, cold trap at -120°C.

The $^1H$, $^{13}C$ and $^{31}P$ NMR data of unsaturated phosphines 5-6 are in good agreement with the structure[13] and particularly allow us to identify the geometry of 6b (table I). As it has been noted for a similar structure, the high value of the $^2J_{PH}$ coupling constant is attributed to the proton at the syn position to the lone pair[14,15]. Consequently, the Z configuration is attributed to the single product 6b resulting from FVT/GSR of 3b ($^2J_{PH}$ = 56 Hz) ; a small amount of the E isomer 6b' is also detected in the FVT of 4b ($^2J_{PH}$ = 15 Hz).

Free unhindered phosphaalkynes and -alkenes were obtained from easily available dichlorophosphines. Absence of reagents (HCl or $ClSiMe_3$) reveals their surprising stability. Thus, steric hindrance or delocalisation is not always required to stabilize low coordinated phosphorus derivatives ; consequently their direct utilisation in synthesis seems possible.

Table I. $^{1}H$, $^{13}C$ and $^{31}P$ NMR data of unsaturated phosphines 5-6[a].

| | $\delta^{1}H$ ($J_{HH}$) | $\delta^{31}P$ | $\delta^{13}C$ | $J_{PH}$ | $J_{PC}$ | $J_{CH}$ | Yield |
|---|---|---|---|---|---|---|---|
| 5a[bc] | 2.90 | -32.0 | 158.0 | $^{2}J_{PH}$ = 44.0 | $^{1}J_{PC}$ = 56.0 | $^{1}J_{CH}$ = 210.0 | 30 % |
| 5b[b] | 2.20 | -60.0 | 170.8<br>15.6 (Me) | $^{3}J_{PH}$ = 15.0 | $^{1}J_{PC}$ = 49.0<br>$^{2}J_{PC}$ = 20.0 | $^{1}J_{CH}$ = 127.0 | 30 % |
| 6a[d] | 7.83 ($H_a$)<br>7.97 ($H_b$)<br>($^{2}J_{HH}$ = 9.1) | 300.4 | 163.0 | $^{2}J_{PH_a}$ = 44.9<br>$^{2}J_{PH_b}$ = 14.4 | $^{1}J_{PC}$ = 58.1 | $^{1}J_{CH_a}$ = 165.0<br>$^{1}J_{CH_b}$ = 154.0 | 35 %<br>60 %[f] |
| 6b[b] | 7.90 ($H_a$)<br>2.40 (Me)<br>($^{3}J_{HH}$ = 7.8) | 265.0 | 174.9<br>17.6 (Me) | $^{2}J_{PH_a}$ = 56.0<br>$^{3}J_{PH}$ = 15.5 | $^{1}J_{PC}$ = 60.6<br>$^{2}J_{PC}$ = 56.0 | $^{1}J_{CH_a}$ = 146.4<br>$^{1}J_{CH}$ = 130.3 | 15 %<br>30 %[f] |
| 6b'[de] | 8.78 ($H_b$)<br>2.14 (Me) | 266.5 | 184.3 | $^{2}J_{PH_b}$ = 15.0<br>$^{3}J_{PH}$ = 23.0 | $^{1}J_{PC}$ = 56.3 | | 0 %<br>5 %[f] |

[a] 10 % solution in $CD_2Cl_2$ at -80°C, internal $Me_4Si$ or external 85 % $H_3PO_4$ as reference.

[b] recorded on a Brucker WP 80 spectrometer.

[c] $^{31}P$ and $^{13}C$ NMR data are consistant with previous results[4].

[d] recorded on a Brucker AM 300 spectrometer.

[e] low concentration prevents obtention of all NMR data.

[f] obtained by FVT of silylated dichlorophosphines 4a and 4b respectively.

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(Received in France 23 July 1986)