Tetrahedron Letters,Vol.27,No.46,pp 5611-5614,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

NEW ACCESS TO FUNCTIONALIZED DICHLOROPHOSPHINES : SYNTHESIS OF TWO COORDINATED PHOSPHORUS HETEROCYCLES.

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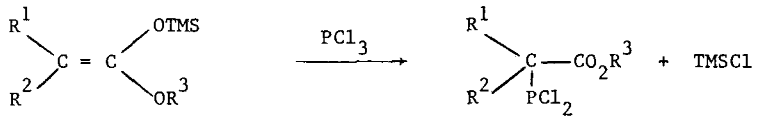
Summary : An easy access to functionalized dichlorophosphines 2, 4, 5, 7 is described, and these compounds are dehydrochlorinated in situ with DABCO and trapped by a diene or a diazocompound to give phosphabenzenes or diazaphospholes.

Dichlorophosphines bearing a functional group and an hydrogen on the α-carbon atom are scarce in the litterature(1). By dehydrochlorination, these compounds may lead to functionalized phosphaalkenes which may be used as dienophiles or dipolarophiles for the synthesis of new two coordinated phosphorus heterocycles. We report now a new and general access to functionalized dichlorophosphines.

Silylated ketene acetals 1(2) react at -30° in THF or Et_2O with PCl_3 under nitrogen during three hours to give dichlorophosphines 2 with a quantitative yield after removal of the solvent at room temperature under vacuum (Scheme 1).



1

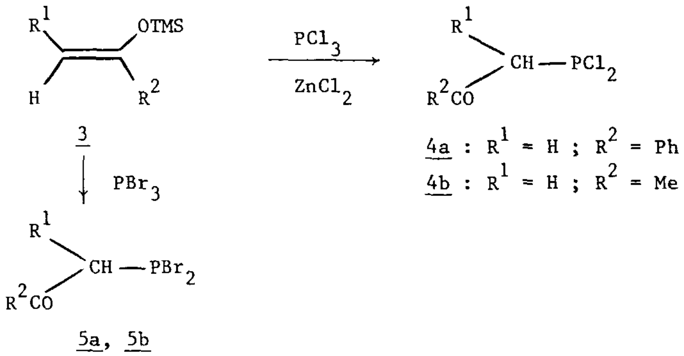
2a : R^1 = TMS ; R^2 = H ; R^3 = Et
2b : R^1 = TMS ; R^2 = H ; R^3 = TMS
2c : R^1 = CN ; R^2 = H ; R^3 = Me
2d : R^1 = R^2 = R^3 = Me

Scheme 1

These compounds are characterized by ^1H and ^{31}P NMR. For instance 2a : (^{31}P NMR external 85 % H_3PO_4) 185 ppm, d, J^2_{PH} = 10 Hz. ^1H NMR (TMS, lock, CH_2Cl_2) : 3.31 (d, 1H, 10 Hz). 2a is rather unstable and leads to $Cl_2P\text{-}CH_2\text{-}CO_2Et$

on standing 5 days in $CDCl_3$ at 0° ; 2b is very unstable and could not be characterized but as we will see it may be trapped "in situ" ; 2c and 2d are fairly stable.

The reaction was extended to ketodichlorophosphines 4 starting from silyl enol ethers 3 (Scheme 2) but in this case PCl_3 alone does not react at -30°C nor at room temperature. Nevertheless if the reaction is catalyzed by $ZnCl_2$ at room temperature in THF or Et_2O, 4 is obtained with a 70 % yield together with 30 % of the corresponding ketone.



4a : R^1 = H ; R^2 = Ph
4b : R^1 = H ; R^2 = Me

Scheme 2

The reaction with PBr_3 needs no catalyst and leads to 5 in the same conditions with the same yield. The use of two equivalents of PBr_3 gives 5 with a quantitative yield. These compounds are also characterized by NMR (^1H and ^{31}P) for example :

4a : ($^{31}P/H_3PO_4$) : 176 ppm, J^2_{PH} = 12 Hz ; (^1H, $CDCl_3$, TMS) : 4.2 (d, 2H, J^2_{PH} = 12 Hz).

5b : (^{31}P) : 167 ppm, J^2_{PH} = 14 Hz ; (^1H, $CDCl_3$, TMS) : 4.07 (d, 2H, J^2_{PH} = 14 Hz) ; 2.33 (s, 3H, J = 0.9 Hz).

In the case of the amide function, the lithium carbanion of NN-dimethyl acetamide treated with TMSCl leads to an exclusive C-silylation to give 6 which on treatment in THF at room temperature with an equimolar amount of PCl_3, gives the dichlorophosphine 7 with a quantitative yield (Scheme 3).

$$\underset{6}{TMS\text{-}CH_2\text{-}CONMe_2} \xrightarrow{PCl_3} \underset{7}{Cl_2P\text{-}CH_2\text{-}CONMe_2} + TMSCl$$

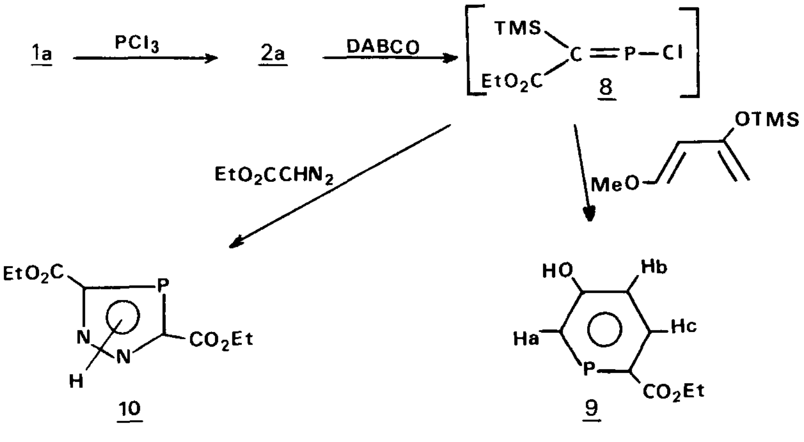
Scheme 3

7 (^{31}P) : 166 ppm, J^2_{PH} = 10 Hz ; (^1H, $CDCl_3$, TMS) : 4.08 (d, 2H, J^2_{PH} = 10 Hz).

Starting from these readily available dichlorophosphines, we thought that their dehydrochlorination with a base would lead to the corresponding functionalized phosphaalkenes. After various unsuccessful attempts with Et_3N, DBU, we could succeed only in the case of 2a with DABCO in the following way : the ether solution of 2a at -80° is treated with an equimolar amount of DABCO and the reaction is followed by ^{31}P NMR, at -60° it appears a signal at 213 ppm which may be attributed to 8 TMS $(EtO_2C)C{=}PCl$ according to the litterature(3), then at -40° this signal disappears.

Owing to this instability, we decided to trap the phosphaalkenes in situ by a diene or ethyl diazoacetate according to the litterature which reports examples of Diels Alder and 1,3-dipolar cycloadditions(4,5,6).

The overall reaction is realized in one pot starting from the silylated derivative ; we will take for example 1a (Scheme 4). 1a is treated at -30° in ether with an equimolar amount of PCl_3 during 3 hours, then the mixture is cooled to -70° and an equivalent of DABCO in ether is added. After 15 mn, a stoechiometric quantity of the Danishefsky's diene(7) or ethyl diazoacetate is added and the temperature is set to -50° for 5 hours, then to room temperature during 12 hours. After addition of water, the crude product is extracted with ether, to give the phosphabenzene 9 or the diazaphosphole 10.



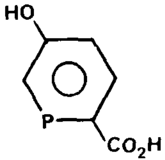
Scheme 4

These compounds are characterized by NMR (^1H, ^{31}P) and mass spectrometry.

9(8) F = 135°, 70 % yield, ^{31}P (THF/C_6D_6) : 217 ppm, J^2_{PH} = 38 Hz ; ^1H $(CD_3)_2CO$: 8.1 (dd, H_a, J^2_{PH} = 38 Hz, J^4_{HH} = 2.6 Hz) ; 7.02 (dt, H_b, J^4_{PH} = 2.6 Hz, J^3_{HH} = 9.2 Hz ; J^4_{HH} = 2.6 Hz) ; 8.47 (dd, H_c, J^3_{PH} = 4.2 Hz, J^3_{HH} = 9.2 Hz). Mass spectrometry $C_8H_9O_3P$ calculated 184.0289, found 184.0294.

10 F = 125°, 80 % yield, ^{31}P (THF/C_6D_6) : 118 ppm. Mass spectrometry $C_8H_{11}N_2O_4P$ calculated 230.0456, found 230.0455.

In the same way we prepared and isolated the heterocycles 11 and 12 but the compounds 13 and 14 were only characterized by ^{31}P and ^1H NMR.



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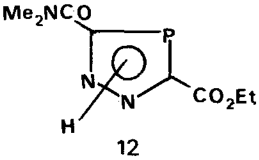

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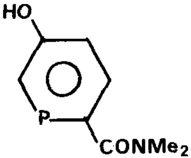

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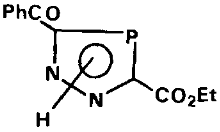

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11 F = 172°, 70 % yield, ^{31}P (D_2O) : 231 ppm, J^2_{PH} = 38 Hz ; ^1H $(CD_3)_2CO$: 8.05 (dd, H_a, J^2_{PH} = 38 Hz, J^4_{HH} = 2.6 Hz) ; 7.03 (dt, H_b, J^4_{PH} = 2.6 Hz, J^3_{PH} = 9.2 Hz, J^4_{HH} = 2.6 Hz) ; 8.42 (dd, H_c, J^3_{PH} = 4.2 Hz, J^3_{HH} = 9.2 Hz). Mass spectrometry : $C_6H_5O_3P$ calculated 155.9976, found 155.9974.
12 F = 150°, 60 % yield, ^{31}P (THF/C_6D_6) : 113 ppm. Mass spectrometry : $C_8H_{12}N_3O_3P$ calculated 229.0616, found 229.0615.
13 ^{31}P (THF/C_6D_6) : 225 ppm, J^2_{PH} = 38 Hz ; ^1H ($CDCl_3$) : 8.0 (dd, H_a, J^2_{PH} = 38 Hz, J^4_{HH} = 2.5 Hz) ; 7.0 (dt, H_b, J^4_{PH} = 2.5 Hz, J^3_{HH} = 9.2 Hz, J^4_{HH} = 2.5 Hz) ; 7.7 (dd, H_c, J^3_{PH} = 5.0 Hz, J^3_{HH} = 9.2 Hz).
14 ^{31}P (THF/C_6D_6) : 122 ppm.

It has not been possible to isolate primary adducts so the real mechanism of aromatization is not established. We thank Dr. Y.Y.C. Yeung Lam Ko for helpful discussions.

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(Received in France 23 July 1986)