Tetrahedron Letters,Vol.27,No.39,pp 4725-4726,1986 0040-4039/86 $3.00 + .00
Printed in Great Britain Pergamon Journals Ltd.

FIRST SYNTHESIS OF 1,2-DIHYDRO 1,2-λ^3-AZAPHOSPHORINES

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Abstract - 1,2-dihydro 1,2- λ^3-azaphosphorines were prepared by reaction of dichlorophenylphosphine with two equivalents of imines derived from propanal. In some cases, 2-oxo 1,2-azaphospholenes were also obtained.

A few examples of 1,4-dihydro 1,4- λ^3-azaphosphorines are known [1-3] ; they are precursors of 1,4-λ^3-azaphosphorines [2]. The 1,2-dihydro 1,2- λ^3-azaphosphorines are not yet known. We describe here the first preparation of these compounds.

In 1981, Nurtdinov et al. [4] reported that the reaction of dichlorophosphines with aliphatic N-butylimines led to the 2-oxo 1,2-azaphospholenes. We have reexamined this reaction and we have found that the reaction of $PhPCl_2$ with imines **1** gave the azaphosphorines **2** [5] when R^1 = t.Bu or t.Bu.CH_2CMe_2- or a mixture of **2** and 2-oxo 1,2-azaphospholenes **3** when R^1 = iPr, $PhCH_2$ or iPr-CH_2 (table). Treatment of **2** with H_2O_2 resulted in good yields of **4**. The azaphosphorines **2** were converted into the crystalline sulfides **5** by reaction with sulfur. The structures of the products were deduced from their spectral properties (^1H, ^{31}P, ^{13}C NMR and mass spectra).

4, R^1 = t.Bu, m.p. 142°C (AcOEt), $\delta^{31}P$ = 18.0 ; **4**, R^1 = iPr, m.p. 120°C (AcOEt) $\delta^{31}P$ = 19.0.

5, R^1 = t.Bu, m.p. 130°C (AcOEt/EtOH), $\delta^{31}P$ = 51.3 ; **5**, R^1 = iPr, m.p. 115°C (AcOEt/EtOH) $\delta^{31}P$ = 55.8.

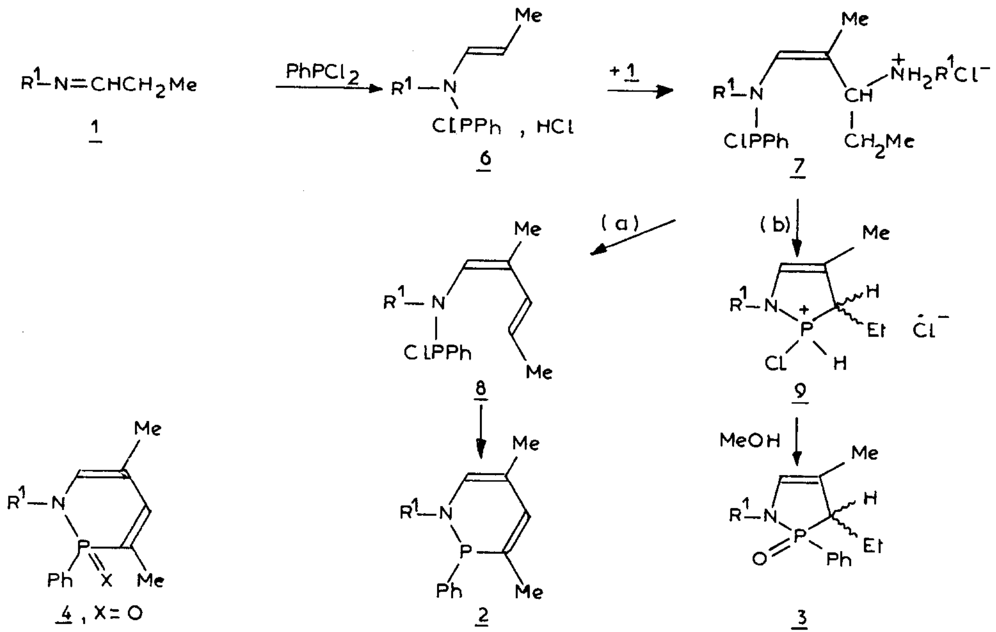
The formation of **2** and **3** can be visualized as represented in scheme I. In a first step, the nucleophilic attack of **1** on $PhPCl_2$ gave an enamine **6** which can add on a second mole of imine **1** to yield **7**[5]. When R^1 provided a sufficient steric hindrance, the elimination of R^1NH_2 from **7**, with formation of **8** was fast. The dienamine **8** cyclized into **2** (pathway (a)). When the pathway (a) was slow, the displacement of R^1NH_2 by nucleophilic attack of the phosphorus atom occured (pathway (b)). The intermediate **9** was obtained ; treated with MeOH, **9** gave the azaphospholene **3**.

Table - Selected NMR spectral data of azaphosphorines **2**.

R^1	$bp_{0.02}$,°C	Yield,%	^1H NMR,($CDCl_3$)δ(J_{PH},Hz) Me-3	H-4	Me-5	H-6	^{31}P NMR ($CDCl_3$, δ)
t.Bu	120-125	64	2.11 (16)	6.36 (9.6)	1.81	6.12	4.4
t.Bu.CH_2.CMe_2	138-140	47	2.07 (16)	6.31 (9.6)	1.83	6.12	
i.Pr[a]	115-118	41	2.10 (16)	6.38 (10)	1.80	5.93	15.4
$PhCH_2$[a]	150-153	30	2.04 (14)	6.44 (11)	1.73	5.77	
i.Pr.CH_2[a]	125-130	10	2.03 (11)	6.39 (10)	1.80	5.78	5.4

a. Yield of **2** : 20-30 %.

Scheme I



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5 - A solution of $PhPCl_2$ (15 mmol) in dry benzene was added to a solution of imine **1** (30 mmol) in benzene (30 ml). The mixture was stirred for 5 h at 20°C. NEt_3 (30 mmol) and MeOH (30 mmol) in benzene were added, the mixture was stirred for 5 h, then filtered and the solution was washed with 1M HCl. **2** was purified by distillation.

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(Received in France 6 July 1986)