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SYNTHESIS OF THE 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. 2-Oxo 1,2-azaphospholenes were also obtained in some cases.

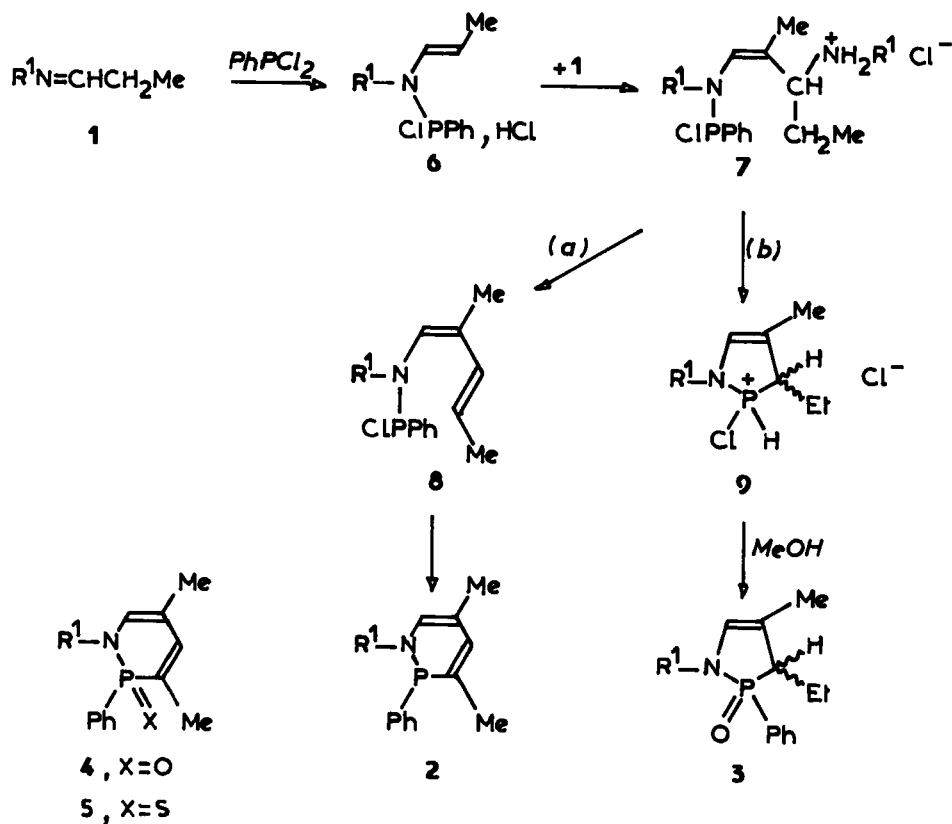
A few examples of 1,4-dihydro 2-oxo 1,4-azaphosphorines and 1,4-dihydro 1,4- λ^3 -azaphosphorines are known.¹⁻³ The 1,4-dihydro 1,4- λ^3 -azaphosphorines are precursors of 1,4- λ^3 -azaphosphorines.² The 1,2-dihydro 1,2- λ^3 -azaphosphorines are not yet known. We report here the first preparation of these compounds. In 1981, Nurtdinov *et al.*⁴ have 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 dichlorophenylphosphine reacted with two equivalents of imines 1, then with methanol, to give the azaphosphorines 2 when R¹ = t.Bu or t.Bu-CH₂-CMe₂, or a mixture of 2 and 2-oxo 1,2-azaphospholenes 3 when R¹ = i.Pr, Ph-CH₂ or i.Pr-CH₂ (table I).

Treatment of azaphosphorines 2 with hydrogen peroxide resulted in good yields of 2-oxo 1,2-azaphosphorines 4. The azaphosphorines 2 were converted into crystalline sulfides 5 by reaction with sulfur. The structures of these products were deduced from their spectral properties (¹H, ³¹P, ¹³C NMR and mass spectra).

TABLE I NMR Spectral data of 1,2-Dihydro 1,2 azaphosphorines and yields of 2 and 3.

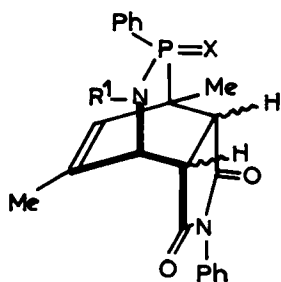
R ¹	2 yield,%	3 yield,%	¹ H NMR of 2 : δ(J _{PH} ,Hz)				³¹ P NMR of 2 δ
			Me-3	H-4	Me-5	H-6	
t.Bu	64	0	2.11(16)	6.36(9.6)	1.81	6.12	4.4
t.Bu.CH ₂ CMe ₂	47	0	2.07(16)	6.31(9.6)	1.83	6.12	
i.Pr	41	10	2.10(16)	6.88(10)	1.80	5.93	15.4
PhCH ₂	30	30	2.04(14)	6.44(11.2)	1.73	5.77	
iPrCH ₂	10	40	2.03(11)	6.39(10.4)	1.80	5.78	5.4

SCHEME I



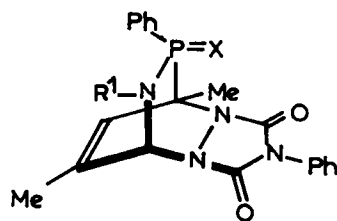
A mechanism which might explain the formation of **2** and **3** is presented in scheme I. In the first step, the nucleophilic attack of the imine **1** on PhPCl_2 gives an enamine **6** which can add on a second mole of imine **1** to yield the intermediate **7**. The reaction of an enamine with an imine is known.⁵ When R^1 provides a sufficient steric bulk, the elimination of R^1NH_2 from **7**, to give **8**, is fast. The intermediate **8** cyclizes into **2** by a nucleophilic attack of the dienamine moiety on the phosphorus atom (pathway (a)). When the elimination of R^1NH_2 from **7** is slow, the displacement of R^1NH_2 by a nucleophilic attack of the phosphorus atom occurs (pathway (b)). The intermediate **9** which is formed, treated with methanol, gives the 2-oxo 1,2-azaphospholene **3**.

The adducts **10** and **11** have been prepared by the Diels Alder reactions of **4** and **5** with N-phenyl maleimide and the adducts **12** and **13** by the Diels Alder reactions of **4** and **5** with 4-phenyl 3,5-dihydro 4H-1,2,4-triazoldione.^{3,5} However, dimethyl acetylene dicarboxylate does not react with **4** and **5**.



10, X = O

11, X = S



12, X = O

13, X = S

The study of the chemistry of the compounds **2** is in progress, particularly the preparation of transition metal complexes of **2**.

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