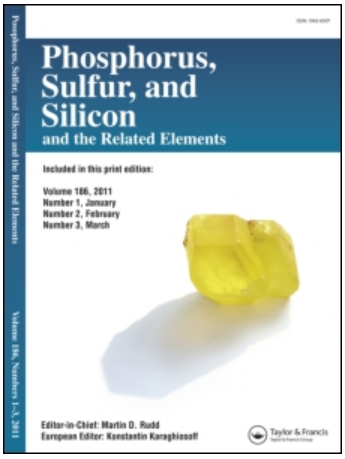


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# Synthesis of the 1,2-Dihydro 1,2-$\Delta^3$-azaphosphorines

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# SYNTHESIS OF THE 1,2-DIHYDRO 1,2- $\lambda^3$-AZAPHOSPHORINES

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Abstract 1,2-Dihydro 1,2- $\lambda^3$- azaphosphorines were prepared by reaction of dichlorophenylphosphine with two equivalents of imines. 2-Oxo 1,2-azaphospholenes were also obtained in some cases.



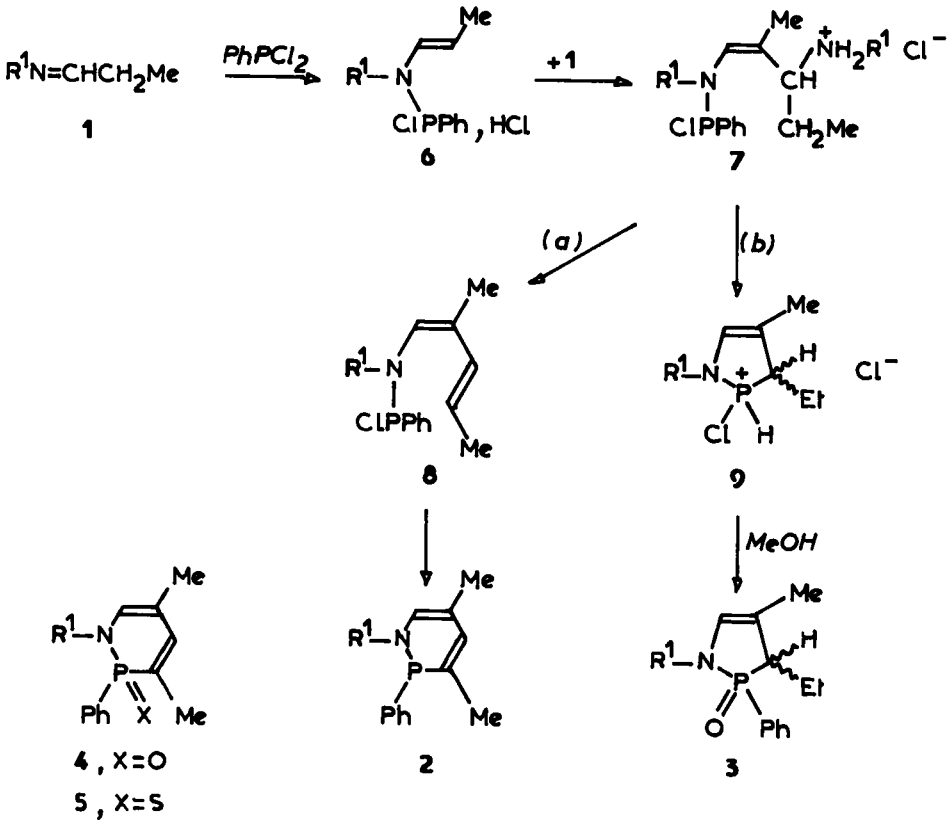
A few examples of 1,4-dihydro 2-oxo 1,4-azaphosphorines and 1,4-dihydro 1,4-$\lambda^3$-azaphosphorines are known.[1-3] The 1,4-dihydro 1,4- $\lambda^3$-azaphosphorines are precursors of 1,4-$\lambda^3$-azaphosphorines.[2] The 1,2-dihydro 1,2- $\lambda^3$-azaphosphorines are not yet known. We report 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 $R^1$ = t.Bu or t.Bu-$CH_2$-$CMe_2$, or a mixture of **2** and 2-oxo 1,2-azaphospholenes **3** when $R^1$ = i.Pr, Ph-$CH_2$ or i.Pr-$CH_2$ (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 cristalline sulfides **5** by reaction with sulfur. The structures of these products were deduced from their spectral properties ($^1H$, $^{31}P$, $^{13}C$ NMR and mass spectra).

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

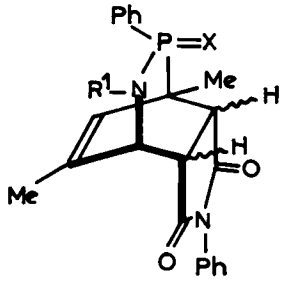
| $R^1$ | **2** yield,% | **3** yield,% | $^1H$ NMR of **2** : δ ($J_{PH}$,Hz) Me-3 | H-4 | Me-5 | H-6 | $^{31}P$ NMR of **2** δ |
|---|---|---|---|---|---|---|---|
| t.Bu | 64 | 0 | 2.11(16) | 6.36(9.6) | 1.81 | 6.12 | 4.4 |
| t.Bu.$CH_2CMe_2$ | 47 | 0 | 2.07(16) | 6.31(9.6) | 1.83 | 6.12 | |
| i.Pr | 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

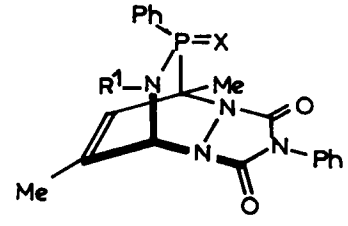


A mechanism which might explain the formation of **2** and **3** is presented in scheme I. In the first step, the nucleophilic attack of the imine **1** on $PhPCl_2$ gives an enamine **6** which can add on a second mole of imine **1** to yield the intermediate **7**. The reaction of an enamine with an 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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