

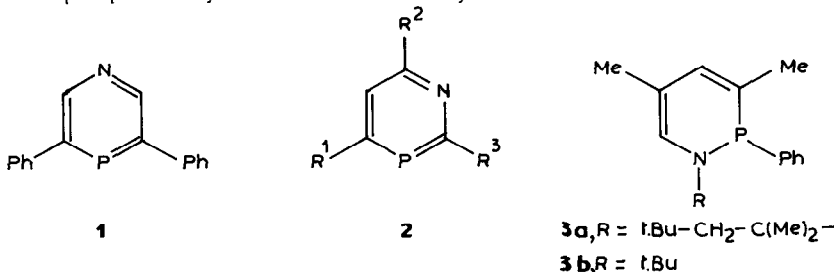
1,2- λ^3 AZAPHOSPHININE BY FLASH VACUUM THERMOLYSIS.

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Abstract - 1,2- λ^3 Azaphosphinine **4** is prepared for the first time by flash vacuum thermolysis of 1-tert.octyl 2-phenyl 1,2-dihydro 1,2- λ^5 azaphosphinine. The reaction of **4** with water gives the 1,2-dihydro 1,2- λ^5 azaphosphinine 2-oxide.

1,4- λ^3 Azaphosphinine **1** has been prepared from 1,4-dihydro 1,4- λ^3 azaphosphinine.¹ This compound is extremely electrophilic because of the electronegativity of the nitrogen atom and the electronegativity difference between nitrogen and phosphorus. Recent reports^{2,3} describe the formation of 1,3- λ^3 azaphosphinine **2**, which is much less electrophilic than **1**. The properties of the 1,2- λ^3 azaphosphinine ring system are unknown. We have previously reported the preparation of several 1,2-dihydro 1,2- λ^3 azaphosphinines **3**.⁴ We now describe herein an efficient generation of 1,2- λ^3 azaphosphinine by flash vacuum thermolysis of **3a**.

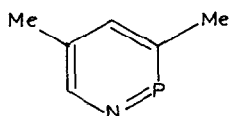
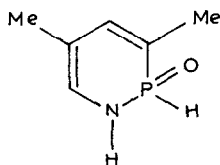
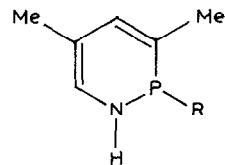


As expected, the dihydroazaphosphinine **3a** was cleaved at 600°C, benzene, isobutene and 1,2- λ^3 azaphosphinine **4** distilling off in vacuo.

4, yellow oil. ¹H NMR (CDCl₃) δ 2.38 (s, Me-5) ; 2.51 (d, J_{PH} = 12 Hz, Me-3) ; 7.58 (d, J_{PH} = 9 Hz, H-4) ; 9.11 (d, J_{PH} = 21 Hz, H-6) ; ³¹P NMR δ = 263.3. The strongly low field shifted ³¹P NMR resonance is in good agreement with that of 1,4- λ^3 azaphosphinine.¹ As 1,4- λ^3 azaphosphinines, 1,2- λ^3 azaphosphinine **4** is very sensitive to moisture. The reaction of **4** with water gave the 1,2-dihydro 1,2- λ^5 azaphosphinine 2-oxide **5**.

5, oil ; ¹H NMR (CDCl₃) δ : 1.81 (s, Me-5) ; 2.12 (d, J_{PH} = 16 Hz, Me-3) ; 6.40 (d, J_{PH} = 16.8 Hz, H-6) ; 6.69 (d, J_{PH} = 29.6 Hz, H-4) ; 8.20 (d, J_{PH} = 56.4 Hz, H-2). ¹³C NMR δ = 18.2 (J_{PC} = 16 Hz, Me-3) ; 18.3 (s, Me-5) ; 117.7 (J_{PC} = 114 Hz, C-3) ; 126.8 (J_{PC} = 7 Hz, C-4) ; 141.8 (J_{PC} = 4 Hz, C-6). ³¹P NMR δ = 1.8 ; MS (70 eV) m/z (relative intensity) 143

(35, M⁺) ; 119 (16) ; 105 (10) ; 95 (16) ; 94 (19) ; 85 (16) ; 78 (19) ; 71 (36) ; 43 (100) ; 41 (39) ; high-resolution mass spectral analysis for C₆H₁₀NPO, calcd 143.0492 ; found 143.0500.

**4****5****6**, R = MeS**7**, R = iPr-NH

Azaphosphinines **6** and **7** were obtained by trapping **4** with MeSH and iPrNH₂.

6, oil. ¹H NMR δ : 1.79 (s) ; 2.06 (d, J_{PH} = 15 Hz) ; 2.16 (d, J_{PH} = 6.4 Hz) ; 6.03 (d, J_{PH} = 6.4 Hz) ; 6.43 (d, J_{PH} = 9.6 Hz) ; ³¹P NMR δ = 59.

7, oil. ¹H NMR δ : 0.99 (d, J_{PH} = 6 Hz) ; 1.80 (s) ; 2.08 (d, J_{PH} = 13 Hz) ; 3.05 (m) ; 6.10 (s) ; 6.55 (d, J_{PH} = 12 Hz). ³¹P NMR δ : 21.

In the presence of water, the hydrolysis of **6** and **7** gave the azaphosphinine 2-oxide **5**. Fast hydrolysis of six membered cyclic phosphonites has previously been observed.⁵ The thermolysis of **3b** also can give the azaphosphinine **4**.

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