

5-Thio- or 5-Oxo-dihydro-1,2,4,3-triazaphosphole: Novel and Stable Cyclic Dicoordinated Phosphorus Compounds: Synthesis and Properties

Y. Kandri Rodi, L. Lopez, C. Malavaud, M. T. Boisdon and J. Barrans

Laboratoire de Synthèse, Structure et Réactivité de Molécules Phosphorées, Unité Associée au CNRS 454, Université Paul Sabatier, 118 route de Narbonne, 31062 Toulouse Cédex, France

Novel, stable cyclic dicoordinated phosphorus compounds, 5-thio- and 5-oxo-dihydro-1,2,4,3-triazaphosphole have been prepared and characterized.

Although the chemistry of dicoordinated phosphorus compounds has been extensively investigated in recent years, the number of heterocycles with P=X (X = CR, N, P) double bonds remains scarce.¹ In the reported examples, the heterocycles are normally stabilised by several intracyclic double bonds.² Thus, triazaphosphole³ and diazaphosphole⁴ heterocyclic systems with two double bonds are stabilised by conjugation, whereas dihydroazaphospholes are not stable and readily oligomerise to tetraphosphazanes, even at low temperatures.⁵

We have found that the novel 5-thio- and 5-oxo-dihydro-1,2,4,3-triazaphospholes **4** and **8** can be prepared readily from the corresponding semicarbazide **2** or thiosemicarbazide **1**. These compounds are the first stable dicoordinated phosphorus heterocycles containing only one intracyclic double bond. Compounds **4** and **8** can be methylated or silylated to give new functionalised triazaphospholes substituted at the 5 position with an SMe or OSiMe₃ group respectively.

Thus, reaction of stoichiometric amounts of tris(dimethylamino)phosphine with **1** in boiling toluene gave, after three molecules of dimethylamine had been evolved, 1-methyl-5-thioxodihydro-1,2,4,3-triazaphosphole **4** in 60% yield as a solid which can formally exist as various isomers depending upon the position of the proton.†

Addition of diethylamine or triethylamine to **4** gave in quantitative yield the salt **3a** (B = HNEt₂) or **3b** (B = NEt₃), analogues of a diazaphospholium salt,⁶ which could be methylated with methyl iodide to give the 1-methyl-5-methylthio-1,2,4,3-triazaphosphole **5** (Scheme 1).†

The ³¹P and ¹⁵N NMR data for **5** agree with those of 1,2,4,3-triazaphospholes.⁷ The ³¹P NMR signal of **4** is less deshielded than those of triazaphospholes owing to less electron delocalization. Note that ²J_{CP} is smaller for **4** (6.25 Hz) than for triazaphosphole **5** (16 Hz). ν_{C=S} (1430 cm⁻¹) is not observed in the IR spectrum of **5**.

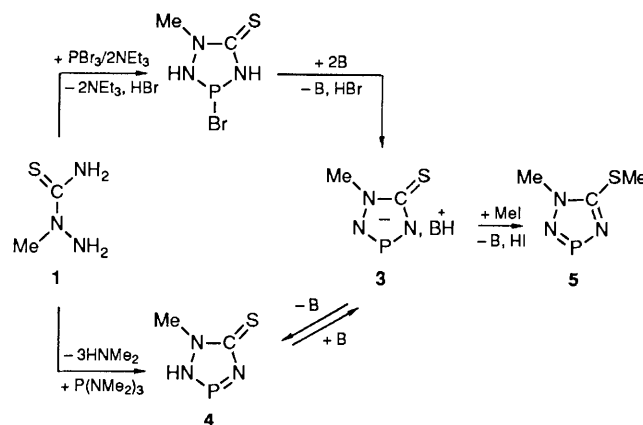
The conversion of **4** to **3a** is readily reversible: solvent

evaporation of a solution of **3a** under low pressure at room temperature evolves diethylamine and affords **4** in quantitative yield.

The salts of general structure **3** can be also prepared by an alternative route shown in Scheme 1. Reaction of **1** with PBr₃ in dichloromethane at 0 °C followed by the addition of two equivalents of triethylamine gave a bromotriazaphospholidine intermediate (³¹P NMR δ 144) which with a further two equivalents of base (HNEt₂ or NEt₃) gave the salt **3a** or **3b**.† The ³¹P NMR spectrum of the reaction solution shows only one signal at δ 245 attributed to **3**.

Compounds **3a** and **3b** were not isolated; the ³¹P chemical shifts (244) of these anions are nearer than those of the dihydrotriazaphosphole **4** (208) to triazaphosphole chemical shifts (255). For this reason we propose a semi-delocalised structure (X).

The 5-oxodihydrotriazaphosphole **8** (Scheme 2) was prepared in one step by the reaction of 1-phenylthiosemicarbazide



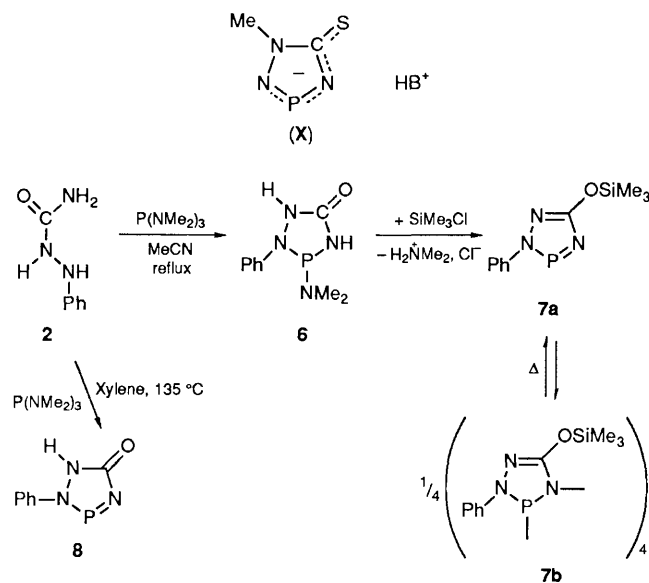
† **4**: m.p. 161–163 °C; ³¹P NMR (32.44 MHz, C₅D₅N): δ 208; ¹H NMR (80 MHz, C₅D₅N): δ 3.56 (s, 3H, CH₃), 13.26 (br, NH); ¹³C NMR (20.15 MHz, C₅D₅N): δ 176.9 (d, ²J_{CP} 6.25 Hz, C=S), 41.3 (s, CH₃); IR (CH₂Cl₂) ν/cm⁻¹ 3380 (NH), 1430.4 (C=S).

5: b.p. 35 °C (10⁻² Torr); ³¹P NMR (C₆D₆): δ 257.6; ¹H NMR (C₆D₆): δ 2.67 (s, CH₃S), 3.86 (d, ⁴J_{HP} 0.9 Hz, CH₃N); ¹³C NMR (C₆D₆): δ 160.4 (d, ¹J_{HP} 15.9 Hz, C=N), 39.6 (s, CH₃N), 16.42 (s, CH₃S); ¹⁵N NMR (C₆D₆): δ -10.4 (d, ¹J_{NP} 85.6 Hz, P=N), -87 (d, ¹J_{NP} 85.6 Hz, P=N), -156 (s, N-CH₃).

3a: ³¹P NMR (C₅D₅N): δ 244.5; ¹³C NMR (C₅D₅N): δ 177.92 (d, ²J_{CP} 14.5 Hz, C=S), 42.95 (s, CH₂N), 41.97 (s, CH₃N), 12.69 (s, CH₃CH₂); **3b**: ³¹P NMR [C₅D₅N]: δ 245.8; ¹³C NMR (C₅D₅N): δ 177.73 (d, ²J_{CP} 9.9 Hz), 46.02 (s, CH₂N), 41.47 (s, CH₃N), 9.42 (s, CH₃CH₂).

8: ³¹P NMR (xylene): δ 242; ¹³C NMR (C₆D₆): δ 169.5 (d, ²J_{CP} 13.9 Hz), 150–110 (m, Ph); ¹⁵N NMR (C₆D₆): δ -106 (d, ¹J_{NP} 90 Hz, N₄), -135 (d, ¹J_{NP} 79 Hz, N₂), -99.9 (s, N₁); IR ν/cm⁻¹ (CH₃CN) 3334 (NH), 1671 (C=O).

7a: b.p. 85 °C (10⁻² Torr); ³¹P NMR (C₅D₅N, 102 °C): δ 244; ¹H NMR (C₅D₅N, 102 °C): δ 0.34 [s, OSi(Me₃)₃], 7–7.4 (m, Ph); ¹³C NMR (C₅D₅N, 102 °C): δ 1.50 [s, OSi(CH₃)₃], 110–150 (m, Ph), 170.63 (d, ²J_{CP} 14.7 Hz, C=N); ¹⁵N NMR (C₇D₈, 75 °C): δ 83.1 (d, ²J_{NP} 2.2 Hz, N₁), -105.1 (d, ¹J_{NP} 85.9 Hz, N₄), -123.6 (d, ¹J_{NP} 91.8 Hz, N₂).



Scheme 2

ide **2** with tris(dimethylamino)phosphine in xylene at 135 °C. Attempts to remove the xylene completely from the solid resulted in decomposition.† The spectral data for **8** agree with a dihydrotriazaphosphole structure and not with a 5-hydroxy-1,2,4,3-triazaphosphole structure.

If the same reaction is carried out in boiling acetonitrile, an intermediate cyclic aminophosphine **6** [³¹P NMR (MeCN) 93.3] is obtained. Treatment of **6** with trimethylsilyl chloride afforded a mixture of the triazaphosphole **7a** and its oligomer **7b** (³¹P NMR δ 74–100, m). A temperature controlled equilibrium exists between **7a** and **7b**, as for the dicoordinated phosphorus derivatives of diamines.⁵

The trimethylsilyloxy group position was determined from the ¹⁵N NMR spectrum of **7a**, analogous to 2,5-disubstituted triazaphospholes.^{7†}

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