5-Thioxo- 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-thioxo- 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, triazaphosphole[3] and diazaphosphole[4] 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-thioxo- 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 $OSiMe_3$ 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 = $HNEt_2$) or **3b** (B = NEt_3), 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).†

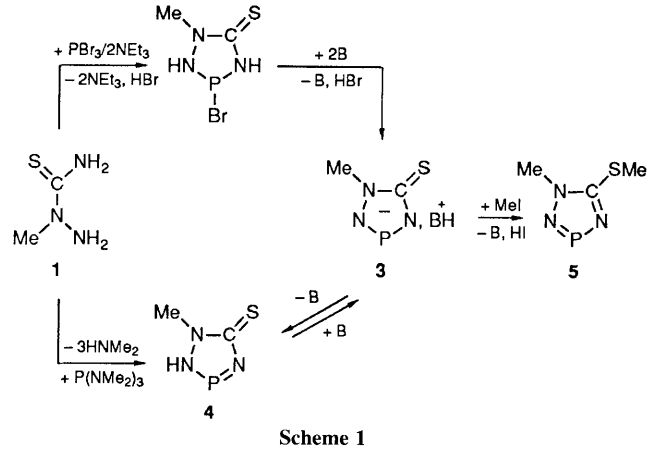
The ^{31}P and ^{15}N NMR data for **5** agree with those of 1,2,4,3-triazaphospholes.[7] The ^{31}P NMR signal of **4** is less deshielded than those of triazaphospholes owing to less electron delocalization. Note that $^2J_{CP}$ is smaller for **4** (6.25 Hz) than for triazaphosphole **5** (16 Hz). $\nu_{C=S}$ (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.

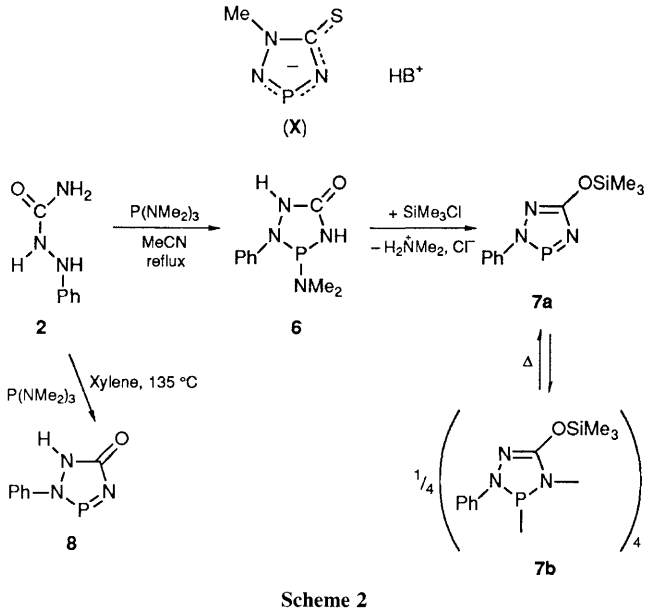
The salts of general structure **3** can be also prepared by an alternative route shown in Scheme 1. Reaction of **1** with PBr_3 in dichloromethane at 0 °C followed by the addition of two equivalents of triethylamine gave a bromotriazaphospholidine intermediate (^{31}P NMR δ 144) which with a further two equivalents of base ($HNEt_2$ or NEt_3) gave the salt **3a** or **3b**.† The ^{31}P NMR spectrum of the reaction solution shows only one signal at δ 245 attributed to **3**.

Compounds **3a** and **3b** were not isolated; the ^{31}P 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-phenylthiosemicarbaz-



Scheme 1



Scheme 2

† **4**: m.p. 161–163 °C; ^{31}P NMR (32.44 MHz, C_5D_5N): δ 208; ^1H NMR (80 MHz, C_5D_5N): δ 3.56 (s, 3H, CH_3), 13.26 (br, NH); ^{13}C NMR (20.15 MHz, C_5D_5N): δ 176.9 (d, $^2J_{CP}$ 6.25 Hz, C=S), 41.3 (s, CH_3); IR (CH_2Cl_2) ν/cm^{-1} 3380 (NH), 1430.4 (C=S).

5: b.p. 35 °C (10^{-2} Torr); ^{31}P NMR (C_6D_6): δ 257.6; ^1H NMR (C_6D_6): δ 2.67 (s, CH_3S), 3.86 (d, $^4J_{HP}$ 0.9 Hz, CH_3N); ^{13}C NMR (C_6D_6): δ 160.4 (d, J_{HP} 15.9 Hz, C=N), 39.6 (s, CH_3N), 16.42 (s, CH_3S); ^{15}N NMR (C_6D_6): δ −10.4 (d, $^1J_{NP}$ 85.6 Hz, P=N), −87 (d, $^1J_{NP}$ 85.6 Hz, P–N), −156 (s, N-CH_3).

3a: ^{31}P NMR (C_5D_5N): δ 244.5; ^{13}C NMR (C_5D_5N): δ 177.92 (d, $^2J_{CP}$ 14.5 Hz, C=S), 42.95 (s, CH_2N), 41.97 (s, CH_3N), 12.69 (s, CH_3CH_2); **3b**: ^{31}P NMR [C_5D_5N): δ 245.8; ^{13}C NMR (C_5D_5N): δ 177.73 (d, $^2J_{CP}$ 9.9 Hz), 46.02 (s, CH_2N), 41.47 (s, CH_3N), 9.42 (s, CH_3CH_2).

8: ^{31}P NMR (xylene): δ 242; ^{13}C NMR (C_6D_6): δ 169.5 (d, $^2J_{CP}$ 13.9 Hz), 150–110 (*m*, Ph); ^{15}N NMR (C_6D_6): δ −106 (d, $^1J_{NP}$ 90 Hz, N_4), −135 (d, $^1J_{NP}$ 79 Hz, N_2), −99.9 (s, N_1); IR ν/cm^{-1} (CH_3CN) 3334 (NH), 1671 (C=O).

7a: b.p 85 °C (10^{-2} Torr); ^{31}P NMR (C_5D_5N, 102 °C): δ 244; ^1H NMR (C_5D_5N, 102 °C): δ 0.34 [s, $OSi(Me_3)_3$], 7–7.4 (m, Ph); ^{13}C NMR (C_5D_5N, 102 °C): δ 1.50 [s, $OSi(CH_3)_3$], 110–150 (m, Ph), 170.63 (d, $^2J_{CP}$ 14.7 Hz, C=N); ^{15}N NMR (C_7D_8, 75 °C): δ 83.1 (d, $^2J_{NP}$ 2.2 Hz, N_1), −105.1 (d, $^1J_{NP}$ 85.9 Hz, N_4), −123.6 (d, $^1J_{NP}$ 91.8 Hz, N_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** [^{31}P NMR (MeCN) 93.3] is obtained. Treatment of **6** with trimethylsilyl chloride afforded a mixture of the triazaphosphole **7a** and its oligomer **7b** (^{31}P 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 ^{15}N NMR spectrum of **7a**, analogous to 2,5-disubstituted triazaphospholes.[7]†

Received, 31st July 1990; Com. 0/03502E

References

1 R. Karaghiosoff and A. Schmidpeter, *Phosphorus and Sulfur*, 1988, **36**, 217–259, and references therein.

2 J. P. Legros, Y. Charbonnel, J. Barrans and J. Galy, *C. R. Acad. Sci.*, 1978, **286**, 319; J. P. Legros, Y. Charbonnel and J. Barrans, *C. R. Acad. Sci.*, 1980, **291**, 271.

3 Y. Charbonnel and J. Barrans, *C. R. Seances Acad. Sci.*, 1974, **278**, 355; *Tetrahedron*, 1976, **32**, 2039; A. Schmidpeter, J. Luber and H. Tautz, *Angew. Chem., Int. Ed. Engl.*, 1977, **16**, 546; A. Schmidpeter and H. Tautz, *Z. Naturforsch., Teil B*, 1980, **35**, 1222; L. Lopez, J. P. Majoral, A. Meriem, T. N'Gando M'Pondo, J. Navech and J. Barrans, *J. Chem. Soc., Chem. Commun.*, 1984, 183.

4 V. G. Andrianov, Yu. T. Struchkov, N. I. Shvetsov-Shilovskii, N. P. Ignatova, R. G. Bobkova and N. N. Mel'Nikov, *Dokl. Akad. Nauk SSSR*, 1973, **211**, 1101; J. Luber and A. Schmidpeter, *Angew. Chem., Int. Ed. Engl.*, 1976, **15**, 111.

5 C. Malavaud, M. T. Boisdon, Y. Charbonnel and J. Barrans, *Tetrahedron Lett.*, 1979, **20**, 447; C. Malavaud, T. N'Gando M'Pondo, L. Lopez, J. Barrans and J. P. Legros, *Can. J. Chem.*, 1984, **62**, 43.

6 A. Schmidpeter and K. Karaghiosoff, *Z. Naturforsch., Teil B*, 1981, **36**, 1273; K. Karaghiosoff, J. P. Majoral, A. Meriem, J. Navech and A. Schmidpeter, *Tetrahedron Lett.*, 1983, **24**, 2137; K. Karaghiosoff, H. Klehr and A. Schmidpeter, *Chem. Ber.*, 1986, **119**, 410.

7 M. Haddad, M. T. Boisdon, L. Lopez, C. Malavaud, G. Pelletier, J. Barrans, G. Pfister-Guillouzo and J. P. Legros, *J. Chem. Res.*, 1989, (*S*) 250; (*M*) 1815.