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Phosphorus *Closo*-Oxymide $P_4(NCH_3)_6O_4$

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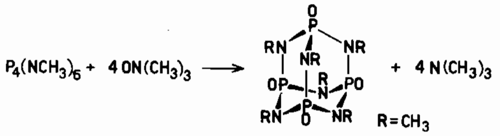
Phosphorus is known to form *closo*-type oxides, sulphides and imides. The molecular phosphorus oxysulphides, $P_4O_6S_4$ and $P_4S_6O_4$, are also known,[1] as well as the whole series of thioimides $P_4(NCH_3)_6S_n$ (n = 1–4).[2,3] On the other hand, all previous attempts to obtain the related *closo*-oxyimides by reacting the parent tetraphosphus hexaimide, $P_4(NCH_3)_6$,[4] with oxidising agents such as oxygen gas,[4] metal oxides,[3,5] *etc.,* have so far failed to give definite molecular compounds.

We have found that the hexaimide may be oxidised smoothly by trimethylamine-N-oxide at room temperature to form tetraphosphorus hexa-N-methylimide tetraoxide, I, in 96% yield, according to:



I

The oxyimide is a white, sublimable, air-sensitive compound which is soluble in common organic solvents including pentane, benzene, chloroform and ether.

The formulation as a phosphoryl compound is supported by the appearance of a strong intensity band in the infrared at 1280 cm^{-1} which we attribute to $\nu(P{=}O)$.

The molecular *closo*-structure of T_d symmetry is confirmed by the very characteristic second-order ^1H nmr spectrum similar to that observed for previous *closo*-imides (δ = 2.93 ppm *vs.* TMS, $N = 2(J_{AX} + J_{AX'})$ = 20.1 Hz).[2,3] The ^{31}P nmr spectrum is also second order as expected. Only one type of phosphorus was observed, with a chemical shift δ = 2.6 ppm (*vs.* H_3PO_4), which is characteristic of a phosphoryl group bonded to nitrogen.[6]

The mass spectrum also supports the molecular formulation. We observe that the P=O bond is largely preserved on fragmentation, whereas the thioanalogue loses sulphur showing the expected difference in bond energies.[7]

A similar reaction with the thioimide $P_4(NCH_3)_6S_3$ has given the expected oxythioimide $P_4(NCH_3)_6S_3O$ in 82% yield.

Experimental

A suspension of $(CH_3)_3NO$ (1.55 g, 20.7 mmol) and $P_4(NCH_3)_6$ (1.54 g, 5.17 mmol) in 20 ml benzene was stirred under nitrogen for 12 h at 25 °C to give a clear solution. The solvent was removed *in vacuo* and the crude product sublimed (100 °C, 10^{-2} mm Hg) to give 1.7 g, 4.95 mmol of tetraphosphorus hexa-N-methylimide tetraoxide (m.p. 175 °C decomp.). *Anal.* Found: C 19.20, H 5.01, N 23.20, P 34.21%. Calc. for $P_4O_4N_6C_6H_{18}$: C 20.03, H 4.98, N 23.08, P 33.99%.

$(CH_3)_3N$ (0.197 g, 3.34 mmol) was recovered from a similar experiment carried out with $(CH_3)_3NO$ (0.306 g, 4.08 mmol) and $P_4(NCH_3)_6$ (0.276 g, 0.93 mmol) in benzene in a sealed tube *in vacuo.*

References

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