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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

Unusual Nucleophilic Degradation of The Phosphorus(III) Oxide Cage

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To cite this Article Kant, Michael , Neumann, Peter and Meisel, Manfred(1994) 'Unusual Nucleophilic Degradation of The Phosphorus(III) Oxide Cage', Phosphorus, Sulfur, and Silicon and the Related Elements, 93: 1, 371 — 372

To link to this Article: DOI: 10.1080/10426509408021862

URL: <http://dx.doi.org/10.1080/10426509408021862>

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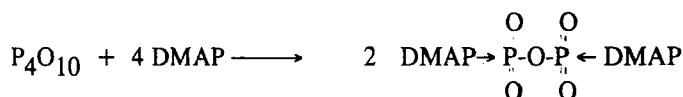
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UNUSUAL NUCLEOPHILIC DEGRADATION OF THE PHOSPHORUS(III) OXIDE CAGE

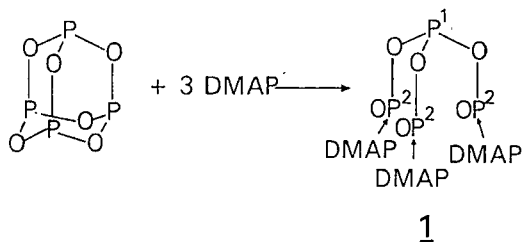
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Abstract Reaction of dimethylaminopyridine (DMAP) with P_4O_6 leads under unusual splitting of three P-O-P bonds to $(DMAP)_3P_4O_6$ (**1**). Further reactions of **1** are discussed.

Phosphorus chalcogenides with adamantane-like structure react with tertiary aromatic amines like pyridine or quinoline to dimeric compounds^{1,2}. Thus, phosphorus(V) oxide reacts with dimethylaminopyridine (DMAP) quantitatively to $(DMAP)_2P_2O_5$ ³:

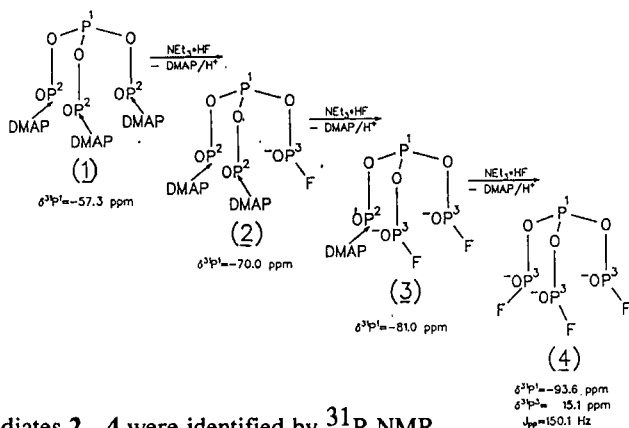


The attempt to prepare the corresponding compound with trivalent phosphorus starting from P_4O_6 leads surprisingly to a donor-stabilized non-caged phosphorus(III) oxide of the formula $(DMAP)_3P_4O_6$ (**1**) formed by breaking of the three P-O-P bonds of the trimeric ring base of the P_4O_6 cage:



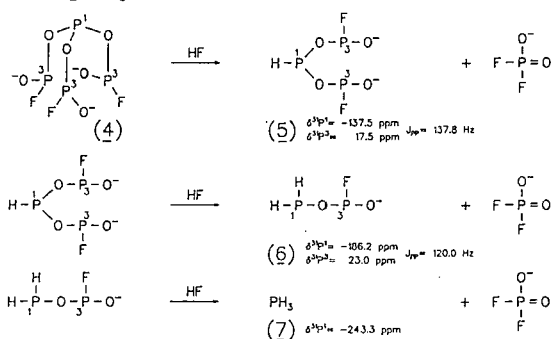
The NMR spectrum of **1** shows a quadruplet and a doublet with $\delta^{31}\text{P}^1$ -55.8 to -65.2 ppm (depending on the solvent) and $\delta^{31}\text{P}^2$ 10.7 to 12.0 ppm, respectively. Remarkable is the very large coupling constant $^2J_{\text{P}^1-\text{O}-\text{P}^2}$ which is found between 172.3 and 180.9 Hz. At room temperature the compound **1** is quite stable under inert conditions. It reacts with protic nucleophiles like water, alcohols, amines, and HF, respectively, in a multi-step process in the end under formation of PH_3 and the corresponding substituted phosphates.

As exemplary shown with the fluoridolysis the reaction proceeds in two main reaction sequences. In the first one **1** reacts with the fluorinating reagent under stepwise substitution of DMAP by fluoride:



The intermediates **2** - **4** were identified by ^{31}P -NMR.

In the second sequence compound **4** reacts with fluoride under disproportionation to difluorophosphate and phosphane:



The intermediates **5** and **6** were also clearly identified by NMR just as the final products PH_3 and difluorophosphate.

REFERENCES

1. H. Grunze, M. Meisel, *Z. anorg. allg. Chem.* **360** (1968) 277
2. G.-U. Wolf, M. Meisel, *Z. Chem.* **22** (1982) 52 and unpublished results
3. M. Meisel, M. Kant, unpublished