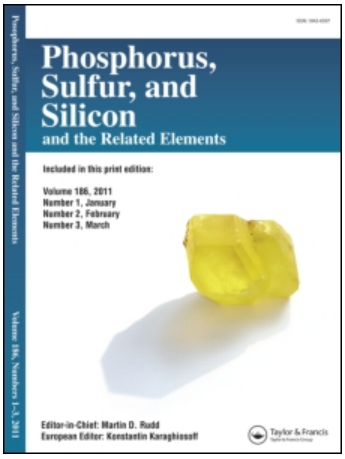

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Unusual Nucleophilic Degradation of The Phosphorus(III) Oxide Cage

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UNUSUAL NUCLEOPHILIC DEGRADATION OF THE PHOSPHORUS(III) OXIDE CAGE

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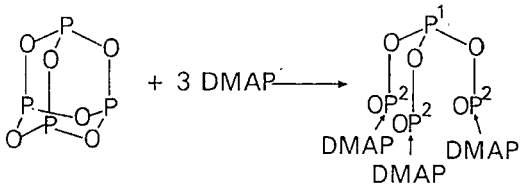
Abstract Reaction of dimethylaminopyridine (DMAP) with P_4O_6 leads under unusual splitting of three P-O-P bonds to $(DMAP)_3P_4O_6$ (1). Further reactions of 1 are discussed.

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]:

$$P_4O_{10} + 4\,DMAP \longrightarrow 2\,DMAP \rightarrow \underset{\underset{O\quad O}{}}{\overset{\overset{O\quad O}{}}{P\text{-}O\text{-}P}} \leftarrow DMAP$$

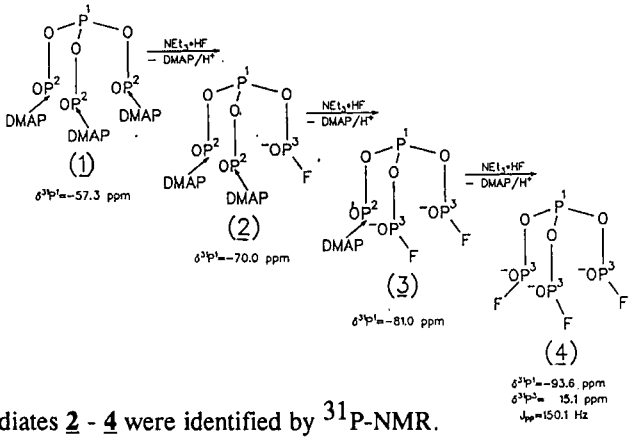
The attempt to prepare the corresponding compound with trivalent phosphorus starting from P_4O_6 leads surprisingly to a donor-stabilized non-caged phosphorus(III) oxide of the formula $(DMAP)_3P_4O_6$ (1) formed by breaking of the three P-O-P bonds of the trimeric ring base of the P_4O_6 cage:



1

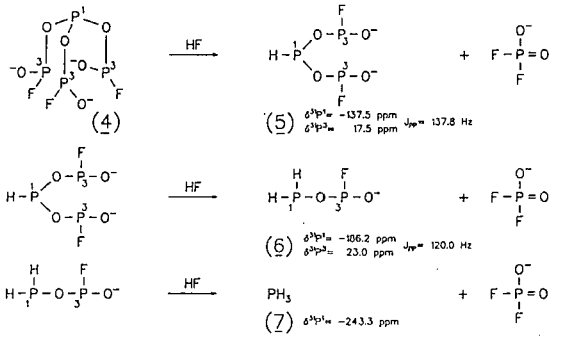
The NMR spectrum of **1** shows a quadruplet and a doublet with $\delta^{31}P^1$ -55.8 to -65.2 ppm (depending on the solvent) and $\delta^{31}P^2$ 10.7 to 12.0 ppm , respectively. Remarkable is the very large coupling constant $^2J_{P1\text{-}O\text{-}P2}$ which is found between 172.3 and 180.9 Hz. 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 clear identified by NMR just as the final products PH_3 and difluorophosphate.

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