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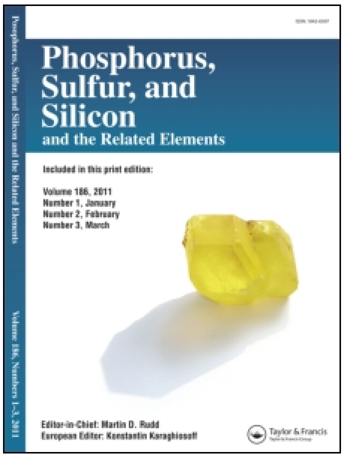

Phosphorus, Sulfur, and Silicon and the Related Elements

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Phosphonylation by Tetraphosphorus Hexoxide

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PHOSPHONYLATION BY TETRAPHOSPHORUS HEXOXIDE

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Abstract The general usefulness of P_4O_6 as starting material for the preparation of inorganic and organic phosphorus compounds is demonstrated by reactions of P_4O_6 with nucleophilic and elektrophilic compounds.

Tetraphosphorus hexoxide, P_4O_6, is a colorless hygroscopic compound with an adamantane-like structure, a melting point of 23,8 °C and a boiling point of 175,4 °C. It is soluble in most of the inert organic solvents. P_4O_6 was prepared by oxidation of phosphorus vapour with oxygen in the molar ratio $P_4:O_2=1:3$ (yield 85 %).[1]
Above 400 °C P_4O_6 is quickly decomposed to phosphorus(III/V)-oxides, P_4O_{7-9}, phosphorus suboxide, P_4O, and phosphorus. P_4O_6 reacts with donor and acceptor compounds. The reactivity is due to the branched and three-fold co-ordinated phosphorus atoms in the P_4O_6 cage.

NUCLEOPHILIC DEGRADATION OF P_4O_6

The hydrolysis of P_4O_6 depends on the molar ratio $P_4O_6:H_2O$ as shown in the following equations:

$$P_4O_6 \quad + \quad 6H_2O \qquad 4H_3PO_3 \qquad (1)$$

$$P_4O_6 \quad + \quad 4H_2O \qquad 2H_4P_2O_5 \qquad (2)$$

$$nP_4O_6 \quad + \quad 2nH_2O \qquad (HPO_2)_{4n} \qquad (3)$$

In this way prepared phosphorous acid and diphosphorous acid are of high purity. The polymeric phosphorous acid,

$(HPO_2)_n$, is a mixture of oligomers thermically unstable. The alcoholysis of P_4O_6 is a vigorous reaction, which leads via oligomeric esters to an equivalent mixture of mono- and diesters (4).

$$P_4O_6 \quad + \quad 6ROH \qquad 2(RO)_2PHO \quad + \quad 2ROPH(O)OH \qquad (4)$$

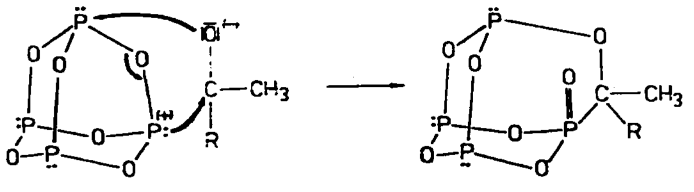
Amines react in a similar way to an equivalent mixture of mono- and diamides (5)

$$P_4O_6 \quad + \quad 8R_2NH \qquad 2(R_2N)_2PHO + 2R_2NPH(O)O^- H_2NR_2^+ \qquad (5)$$

ELECTROPHILIC DEGRADATION OF P_4O_6

As indicated by ^{31}P-NMR data the electronic environment of the phosphorus atoms in trialkylphosphites (=128-142) and P_4O_6 (=112) are comparable. Therefore it is not unexpected, that P_4O_6 like trialkylphosphites will be attacked by electrophiles as carbonyl compounds under formation of C-P bonds.

In contrast with trialkylphosphite the phosphorus atoms in the P_4O_6 cage are branched by P-O-P bonds. This result in the formation of polymeric intermediates in the reaction of P_4O_6 and carbonyl compounds containing P-O-P and C-O-P bonds as shown for the first electrophilic attack of a carbonyl compound at the P_4O_6 cage (6).



(6)

Aldehydes: The reaction of aldehydes with P_4O_6 in an inert solvent leads to condensed 1-hydroxy-phosphonic acids and, after hydrolysis, to the corresponding monomers (7).

$$4RCHO \quad + \quad P_4O_6 \quad + \quad 6H_2O \qquad 4RCH(OH)PO_3H_2 \qquad (7)$$

R=H,COOH,Phenyl,Alkyl C_1-C_5; yield 70-98 %

In Table I the results of the phosphonylation of benzaldehyde with P_4O_6 and phosphorous acids are summerized. The yields of 1-hydroxy-1-phenyl-methane phosphonic acid indicate that polymeric phosphorous acid is alo an useful phosphonylation agent. Furthermore it is shown, that the yields directly depend on the degree of polymerisation of the phosphorous acids.

TABLE I Phosphonylation of benzaldehyde by P_4O_6 and phosphorous acids

carbonyl compound	phosphonylation agent	reaction condition	yield $-CH(HO)PO_3H_2$
4 CHO	P_4O_6	dioxane	95 %
	$4(HPO_2)_n$	80 °C	88 %
	$2\ H_4P_2O_5$	1 h	63 %
	$4\ H_3PO_3$		32 %

Ketones: The reaction of ketones with P_4O_6 leads in high yields to 1-hydroxy-phosphonic acids and starting from methylorganyl ketones to vinylorganyl phosphonic acids, $CH_2{=}C(PO_3H_2)R$.

Mono- and dicarboxylic acids: On heating a mixture of carboxylic acids and P_4O_6, 1-hydroxy-alkane-1,1-diphosphonic acids, $RC(OH)(PO_3H_2)_2$ R=alkyl C_1-C_{17}, yield 70-98 % and dihydroxyalkane tetraphosphonic acids, $(H_2O_3P)_2(HO)C(CH_2)_nC(OH)(PO_3H_2)_2$ n=3-4; yield 70-90 % are formed, respectively.

Carboxylic acid amides, lactames: Amides of carboxylic acids react on heating with P_4O_6 under formation of 1-amino-alkane-1,1-diphosphonic acids (8)

$$2RCONH_2 + P_4O_6 + 4H_2O \qquad 2RC(NH_2)(PO_3H_2)_2 \qquad (8)$$

R=H, alkyl C_1-C_5; yield 70-98 %

Formamide first reacts with P_4O_6 to formamidomethanediphosphonic acid (9), which is hydrolysed in alkaline solution to give aminomethanediphosphonate.

$$4HCONH_2 + P_4O_6 + 2H_2O \qquad 2H_2NCH{=}NCH(PO_3H_2)_2 \qquad (9)$$

yield 98 %

Caprolactam and P_4O_6 react to hexamethyleneimino-2,2-diphosphonic acid, yield 90 %.

<u>Substituted carboxylic acids:</u> The phosphonylation of amino acids, as glycine, and ß-alanine, -aminocaproic acid leads to amino-1-hydroxy-alkane-1,1-diphosphonic acids e.g. (10).

$$2H_2NCH_2CH_2COOH + P_4O_6 + 4H_2O \qquad 2H_2NCH_2CH_2C(OH)(PO_3H_2)_2$$

yield 70 % (10)

Phosphonoacetic acid first reacts with P_4O_6 to 1-hydroxy-ethane-1,1,2-triphosphonic acid, which is dehydrated and phosphonylated by P_4O_6 to ethane-1,1,2,2-tetraphosphonic acid.

<u>Compounds with C=C double bonds:</u> P_4O_6 is only attacked by activated C=C double bonds. Thus the reaction of acrylic acid with P_4O_6 leads to 3-phosphonoproionic acid (yield 95 %) and, in a secondary reaction to 1-hydroxy-propane-1,1,3-triphosphonic acid (yield 70 %).

Unsaturated aldehydes like acrolein first react at the carbonyl group yielding unsaturated hydroxyphosphonic acids and, in a secundary reaction at the double bond yielding vic. diphosphonic acids.

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