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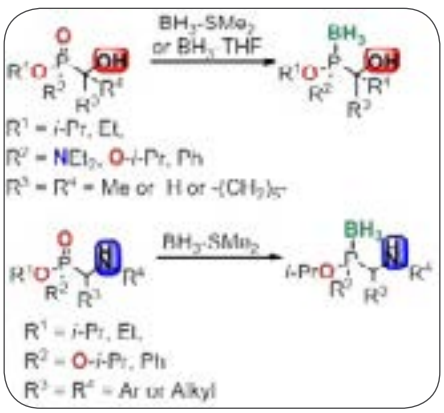
### Making BH3 to cleave strong chemical bonds with an added chemoselectivity gain

The P=O bond is one of the strongest of those commonly encountered. The large amount of energy released during its formation acts as the driving force for many important transformations in organic chemistry; the Wittig, Mitsunobu, and Appel reactions being classic examples. Conversely, this same bond strength causes considerable difficulties in the deoxygenation of P=O-containing species; the conversion being highly desirable, enabling access to their PIII counterparts serving very often as valuable ligands and organo catalysts. Due to the inert nature of P-C bonds, options do exist for the reduction of most tertiary phosphine oxides, which are successfully deoxygenated with strong reducing agents such as metal hydride and silanes. In contrast to tertiary phosphine oxides, the deoxygenation of phosphorus(V) acid esters and amides by these agents is effectively impossible due to the need to break the immensely strong and inert P=O bond in the presence of relatively weak and more reactive P-O and P-N bonds. This long-standing problem in organophosphorus synthesis is solved by use of BH3, a mild reducing agent, which chemo selectively cleaves the P=O bond in phosphinate and phosphonate derivatives leaving the P-O and/or P-N bonds intact. The success is owed to the assistance of the α-heteroatom group present in the P=O containing species which is directing the chemoselective action of BH3. The P=O bond is deoxygenated with clean inversion of configuration at P. A mechanistic picture of the reduction process coherent with all the observations is proposed. This simple one-pot procedure was applied for a wide range of P-O and P-N-containing phosphinate/phosphonate compounds to produce the corresponding borane-protected PIII products in good yields. The P-BH3 product can be easily deprotected to produce the free PIII ester or amide derivative. The availability of this methodology opens up previously unavailable synthetic options in organophosphorus chemistry, some of which are exemplified.



## Recent Publications

1. Sowa S and Pietrusiewicz K M (2019) Chemoselective reduction of the P=O bond in the presence of P–O and P–N bonds in phosphonate and phosphinate derivatives. Eur. J. Org. Chem. 2019(5): 923-938.
2. Sowa S, Stankevic M, Flis A and Pietrusiewicz K M (2018) Reduction of tertiary phosphine oxides by BH3 assisted by neighboring activating groups. Synthesis 50(10):2106-2118.
3. Frynas S, Łastawiecka, Kozioł A E and Pietrusiewicz K M (2019) [4+2] Cycloaddition of Vinylphosphine Oxides to α-Oxy-o-xylylene as a Route to Phosphorylated Naphthyl and Biaryl Scaffolds. J. Org. Chem. 84(4):1818-1832.
4. Demchuk O M, Jasiński R and Pietrusiewicz K M (2015) Mechanism of reduction of tertiary phosphine oxides by means of phenylsilane. Heteroatom Chem. 26(6):441-448.
5. Pietrusiewicz K M and Zabłocka M (1994) Preparation of scalemic P-chiral phosphines and their derivatives. Chem. Rev. 94(5):1375-1411.

## Biography

K Michał Pietrusiewicz has his expertise in the field of organic chemistry, stereochemistry, stereoselective synthesis, organophosphorus synthesis and use of organophosphorus compound as synthetic reagents as well as ligands in asymmetric processes catalyzed by transition metal complexes.

**Notes:**