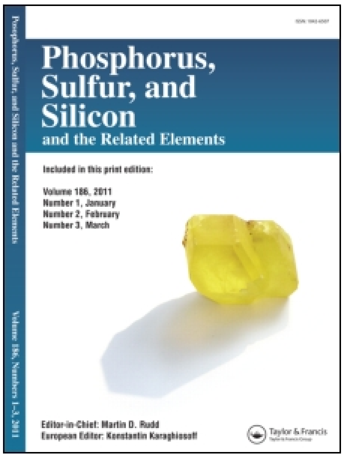

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Silylperoxides as Selective Oxygenation Reagents in Phosphorus Chemistry

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SILYLPEROXIDES AS SELECTIVE OXYGENATION REAGENTS IN PHOSPHORUS CHEMISTRY

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Abstract Bis(trimethylsilyl)peroxide (BSPO) can be used for chemo- and stereoselective generation of P=O group by oxygenation of P(III) centre and transformation of P=S and P=Se groups.

INTRODUCTION

Silyl peroxides, which constitute a broad and well known class of organosilicon compounds[1] and in particular $Me_3SiOOSiMe_3$ (BSPO), are very promising reagents for the generation of oxyphosphoryl group. Their ability to oxidize P(III) centre was recognized earlier[2], however, the potential of BSPO as the reagent for selective oxygenation under mild conditions in the chemistry of phosphorus has been demonstrated only recently[3,4].

RESULTS AND DISCUSSION

BSPO shows an exceptionally high reactivity towards P(III) centre. Variety of compounds of tricoordinate phosphorus may be transformed to their P=O derivatives with theoretical yield, under very mild conditions using stoichiometric amounts of the peroxide.

TABLE I Oxidation of P(III) compounds with BSPO

$$R^1R^2R^3P \xrightarrow[CH_2Cl_2]{BSPO} R^1R^2R^3P{=}O$$

R^1	R^2	R^3	Temp.	Yield(^{31}P NMR)
Ph	Ph	Ph	-20	100
Ph	Ph	Cl	-20	100
Ph	Ph	OMe	-30	100
Ph	Cl	Cl	-50	60
Ph	Ph	$(CH_2)_2SiMe_2(OPh)$	0	100
Ph	Ph	$CH_2CH{=}CH_2$	r.t.	100
n-Bu	n-Bu	n-Bu	r.t.	100
t-Bu	Ph	Cl	-20	100
EtO	EtO	EtO	-20	100
Cl	Cl	Cl	-70	50
NMe_2	NMe_2	OMe	-20	100

BSPO undergoes homolytic cleavage less easily than its carbon analogue $(t\text{-}BuO)_2$. In consequence, some organic groups which are reactive towards free radicals are preserved in the course of oxygenation. Some phosphines having olefinic bond are found to give the corresponding oxides with theoretical yields. A competitive oxidation at nitrogen, sulfur and some other centres usually goes much slower and can be avoided.

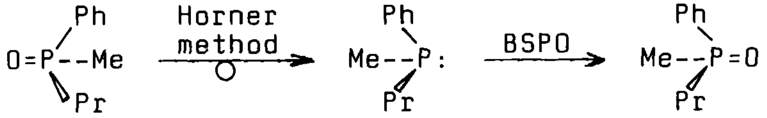
Compounds of tetracoordinate phosphorus, even those being formally at P oxidation level III undergo oxidation with BSPO slowly. In consequence the oxidation of secondary phosphines may be carried out in two separate stages:

$$Ph_2PH \xrightarrow[-40^{o}]{BSPO\ 1:1} Ph_2P(O)H \xrightarrow[25^{o}]{BSPO\ excess} Ph_2P(O)OSiMe_3$$

The first step product may be obtained with theoretical yield.

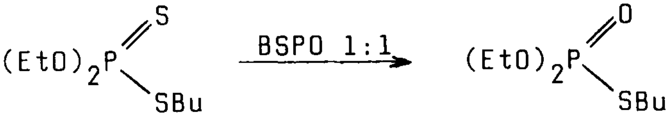
BSPO being soluble in organic solvents may be used in non-hydroxylic systems to generate P=O group in compounds hydrolytically unstable, like phosphorus silyl ester.

The oxygenation of P(III) compounds with BSPO proceeds in a highly stereospecific manner leading to full retention of configuration at the phosphorus centre, which was demonstrated for both acyclic and cyclic models[3].

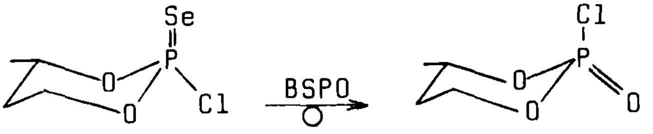


(+)R $|\alpha|_D^{25}=7.6^o$ (−)R $|\alpha|_D^{25}=-8.2^o$ (−)S $|\alpha|_D^{25}=-7.2^o$

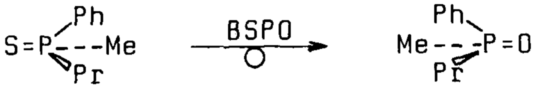
BSPO proved also to be effective in the transformation of the P=S and the P=Se to the P=O function. The reaction may be effectively accelerated by electrophiles such as $AlCl_3$, $SnCl_4$ and others. During the oxygenation of ditiophosphoric acid esters, the mercapto group is not oxidized.



The P=S, or P=Se to P=O transformation proceeds in a stereospecific manner leading to inversion at phosphorus:

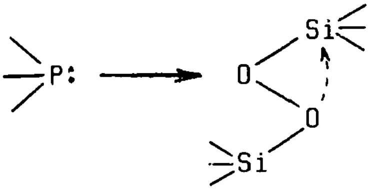


trans, ^{31}P δ=51.0 ppm cis, ^{31}P δ=−5.7 ppm



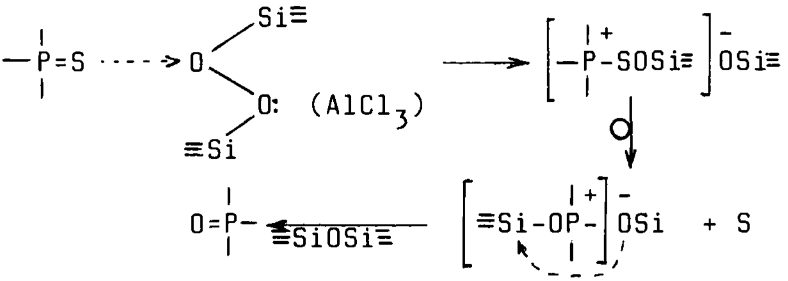
(+)R $|\alpha|_D^{25}=10.8^o$ (−)S $|\alpha|_D^{25}=-7.1^o$

The oxygenation of phosphorus compounds with BSPO presumably proceeds according to a non-free radical pathway. The oxidation of trivalent phosphorus involves perhaps the nucleophilic attack of the phosphorus at oxygen atom of BSPO:



The mechanism may be synchronous or stepwise with the transient formation of phosphonium salt.

The mechanism of the P=S, or P=Se to P=O transformation is probably more complex, and involves several steps. Again, it is possible that the reaction begins with a nucleophilic attack at the peroxide. A variant of such pathway which could be considered is shown below:



Further works on this subject are in progress.

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