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BIS(TRIMETHYLSILYL)PEROXIDE AS A VERSATILE REAGENT FOR SELECTIVE GENERATION OF OXYPHOSPHORYL GROUP

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Abstract: Bis(trimethylsilyl)peroxide, $Me_3SiOOSiMe_3$, (BSPO) oxidizes phosphines and phosphites to respective oxyphosphoryl derivatives with retention of the configuration at the phosphorus atom. It also converts thiophosphoryl function to oxyphosphoryl function with inversion of the configuration at phosphorus. High yields and high stereoselectivities of these processes render them useful for the synthetic application.

Considerable attention has been recently paid to the oxygenation of organophosphorus compounds as a method of the generation of oxyphosphoryl function, particularly in connection with fast development of the chemistry of bioactive phosphorus containing products. During multistep synthesis of these products chemists often encounter the problem how to perform the oxygenation at the phosphorus centre in chemo- regio- and/or stereoselective way to obtain the intended product with a high yield and a high degree of purity [1-4]. Although a variety of oxygenation methods exists many of them suffer from deficiencies giving by-products and showing a poor selectivity. We present in this paper synthetic results indicating that BSPO meets requirements of versatile oxygenation reagent for the selective generation of oxyphosphoryl group. It is able both, to transfer oxygen to trivalent phosphorus as well as to convert the thiono phosphoryl compounds into the corresponding oxo derivatives, in a highly selective way. Bissilyl peroxides are relatively easily accessible [5-7] and they were shown to oxidize readily triorgano phosphines and triorgano phosphites [8]. In contrast to the reaction of organic peroxides the mechanism of oxygenation with BSPO is ionic rather than free radical [9] what makes it even more promising as agent for selective oxygenations. It may be easily purified by distillation and it is soluble in many organic non-hydroxylic solvents. During oxygenation, BSPO is reduced to hexaorganodisiloxane, which being chemically inert, does not react with the phosphorus product.

A good example of the utility of BSPO in the P(III) $\longrightarrow$ P(IV) oxidation is the conversion of (dimethylphenoxysilylalkyl)diphenyl phosphines to the corresponding phosphine oxides.

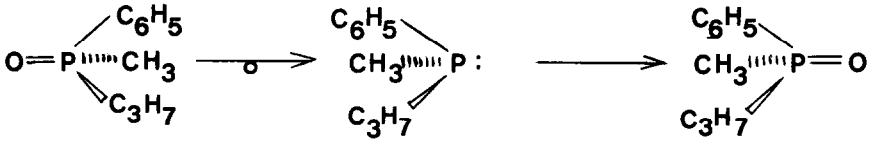
(1) $$(PhO)Me_2Si(CH_2)_nPPh_2 \xrightarrow[n = 2,3]{BSPO} (PhO)Me_2Si(CH_2)_nP(O)Ph_2$$

These phosphines have very reactive phenoxy groups bound to the silicon atom, which may be easily cleaved by a nucleophile. This excludes the possibility of using oxidizing reagents having hydroxy groups. On the other hand, the application of such reagents as gaseous oxygen, ozone, nitrogen oxides or organic peroxides leads to by-products which lower the yield of the desired phosphine oxide and complicate its purification. Such a result might have been expected taking into account well-known instability of P-C bond towards free radical reagents.

Using BSPO as the oxygenation reagent enables obtaining the respective phosphine oxides with theoretical yields as checked by ^{31}P NMR. In a typical procedure 1.1 molar equivalent of BSPO was slowly introduced to 0.01 mol of [β-(dimethylphenoxysilyl)ethyl]diphenyl phosphine in 20 ml of benzene (or methylene chloride). The reaction vessel was cooled to $0^{o}C$. ^{31}P NMR spectrum showed only one phosphorus-containing product. The distillation gave the respective phosphine oxide (b.p. 182-186/2 x 10^{-2} mmHg) with 94% yield.

The stereoselective oxygenation of P(III) compounds with BSPO was performed in the following reduction-oxidation cycle. First, optically active R(+) methylpropylphenyl phosphine oxide (optical purity 38%) was reduced using Horner method [11] and then the produced phosphine was oxidized adding of 1,2 molar equivalent of BSPO in the room temperature. S(-) methylpropylphenyl phosphine oxide was obtained with 95% stereospecificity. Since the reduction step is known to proceed with inversion of the configuration at phosphorus centre [11], the oxidation occurs with the retention.

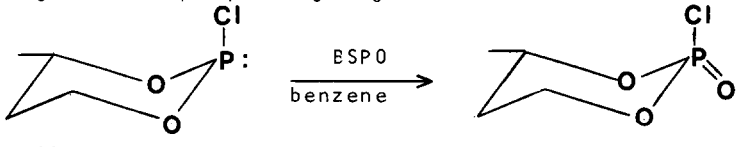
(2)



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

P(III) esters can also be stereoselectively oxidized by BSPO as it was demonstrated by the transformation of 2-chloro-4-methyl-1,3-dioxaphosphorinane to its oxygen derivative. The reaction of trans isomer proceeds very fast in benzene solution in the r.t. with full retention of the configuration at phosphorus giving 100% of cis isomer as monitored by ^{31}P NMR.

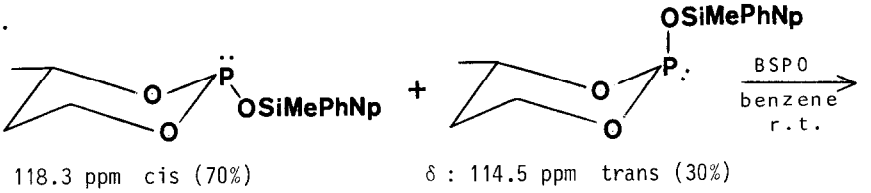
(3)



^{31}P δ: 150.4 ppm trans δ : -5.5 ppm cis

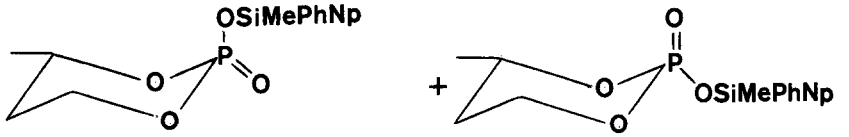
Another illustration of the stereospecific oxygenation of cyclic phosphorus esters is provided by the reaction of 2-naphtylphenylmethylsililoxy-4-methyl-1,3-dioxaphosphorinane with BSPO. The mixture of cis and trans isomers in the molar ratio 70:30 gives cis and trans

isomers of the respective product in the ratio 30:70 as ascertained by ^{31}P NMR spectrum taken immediately after the reaction, indicating again the stereospecific course of the reaction (retention).



^{31}P δ : 118.3 ppm cis (70%) δ : 114.5 ppm trans (30%)

(4)



^{31}P δ : -17.5 ppm cis (30%) δ : -13.5 ppm trans (70%)

kinetic products

The fast oxygen transfer to P(III) compounds and the high stereospecifity can be explained by the ionic character of the process. The retention of configuration at the phosphorus atom, as well as the observation that phosphines are oxidized faster than phosphites both indicate that phosphorus acts as a nucleophile centre in this process, which probably proceeds according to scheme (5).

(5)

$\longrightarrow$ P = O + $Me_3SiOSiMe_3$

We have found that BSPO also converts P=S and P=Se groups in P(IV) compounds into the P=O group. Some of these reactions can be used in the synthetic chemistry.

Triphenylsulphide, as well as triphenylselenide were converted to triphenyl phosphine oxide with almost theoretical yield.

(6) $Ph_3P{=}Z \xrightarrow{BSPO} Ph_3PO$ Z = S, Se

In the room temperature the reaction proceeds slowly, but cleanly. With an excess of BSPO the selenide is converted in several hours, while several days are required to convert the sulphide. The reaction may be effectively accelerated by Lewis acids. In the presence of $AlCl_3$ the full conversion of the sulphide is attained with one hour and the yield of the oxide is almost 100% as monitored by ^{31}P NMR.

The stereochemistry of the conversion of the thiophosphoryl group with BSPO was studied using cyclic thionochlorophosphates as model compounds. Trans isomer (100% isomeric purity) of 2-thio-2-chloro-5-chloromethyl-5-methyl-1,3-dioxaphosphorinane was oxidized in the presence of $AlCl_3$ giving the cis isomer of the corresponding product of the oxygenation accompanied by less than 5% of the trans isomer. The reaction occurs with inversion of the configuration at phosphorus.

(7)

^{31}P δ : 55.5 ppm
trans

δ : -5.8 ppm (more than 95%)
cis

In a typical experiment, the trans isomer 1 mmol of the thiono phosphorinane was added to 1.5 mmol of BSPO and 0.1 mmol of $AlCl_3$ in 5 ccm of benzene. The full conversion was obtained after 1 hour at the room temperature. $AlCl_3$ and traces of the hydrolysis product of the oxyphosphoryl compound were separated on a short column filled with Merck neutral Al_2O_3 gel.

The oxygenation of cyclic phosphorochloridoselenoates with BSPO in the room temperature leads to by-products, thus is less promising as the synthetic method.

By contrast to the oxidation of P(III) compounds, the conversion of P=S and P=Se compounds proceeds with the inversion of the configuration at phosphorus. Evidently phosphorus is electrophilic centre in this reaction, though the mechanism is probably more complex.

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