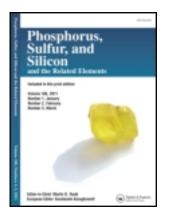
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# Phosphorus, Sulfur, and Silicon and the Related Elements

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# Selective Functional Transformation of 1,2-Diols Via Organophosphorus Reagents

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## Selective Functional Transformation of 1,2-Diols Via Organophosphorus Reagents

### JEAN-LUC PIRAT, MICHEL CARTERON, ANNIE-FRANCOISE MAGGIO, STEPHANIE BOT and HENRI-JEAN CRISTAU

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A new synthesis of  $1,3,2\lambda^5$ -dioxaphospholanes was realized by direct reaction of dibromotriphenylphosphorane with 1,2-diols. Ring opening studies were performed with or without electrophilic activation (Lewis acids or hydrogen bonding) in order to substitute selectively one of the hydroxy function.

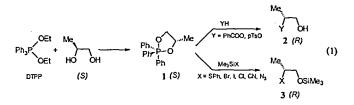
Keywords:  $1,3,2\lambda^5$ -dioxaphospholanes; 1,2-diols; electrophilic activation

#### INTRODUCTION

 $1,3,2\lambda^5$ -dioxaphospholanes 1 exhibit a broad range of applications in organic synthesis : first of all, they are widely used for cyclodehydratation reaction under mild thermolysis conditions to prepare a variety of heterocycles, including ethers<sup>[1a]</sup>, sulfides<sup>[1b]</sup> and aziridines<sup>[1e]</sup>.

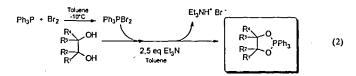
More, recently, Evans and al. demonstrated that (S)-4-methyl-2,2,2-triphenyl-1,3,2 $\lambda^5$ -dioxaphospholanes 1, prepared from diethoxytriphenylphosphorane (DTPP) and (S)-propane-1,2-diol, underwent a highly regioselective ring opening and a subsequent stereospecific substitution in the presence of organic acids<sup>[1d],[1e]</sup>, or trimethylsilyl reagents<sup>[1f]</sup> (scheme 1).

In these transformations, nucleophilic substitutions occur mainly on the most sterically-hindered carbon to afford, with essentially complete inversion of stereochemistry, derivatives 2 and 3 (scheme 1).

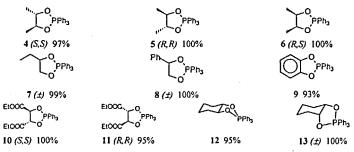


#### **RESULTS AND DISCUSSION**

So far, almost all the synthetic methods used for the formation of  $1,3,2\lambda^5$ dioxaphospholanes require the preliminary preparation of DTPP from diethyl peroxide<sup>[1f],[1g]</sup>. Therefore, to avoid this peroxide route, we described a new procedure for the synthesis of  $1,3,2\lambda^5$ -dioxaphospholanes in near quantitative yield<sup>[2]</sup> from dibromotriphenylphosphorane (scheme 2).



Primary and secondary diols are more reactive than cyclic diols (cyclohexane-1,2-diol), or diols containing electron-withdrawing groups (diethyl tartrate) and, of course, diphenol (pyrocatechol). During the transformation no racemisation takes place and the synthesis of the dioxaphospholanes 4, 5 and 6 always occurs with the formation of only one dioxaphospholane for each transphosphoranylation. By this method, various 1,3,2 $\lambda^5$ -dioxaphospholanes were prepared; some of them (5-8 and 10-12) have been described for the first time.



The functional transformation of 1,2-diols, using the P=O formation as driving force, can afford the substituted alcohol 14 (scheme 3), and it must be pointed out that it is possible to recover the starting Ph<sub>3</sub>P by reduction of the by-product Ph<sub>3</sub>PO<sup>[3]</sup>.

Such a sequence of reactions was investigated on the example of compound 8 (2,2,2,4-tetraphenyl-1,3,2 $\lambda^5$ -dioxaphospholane) with several nucleophilic species. The ring opening studies were performed with or without electrophilic activation.

$$\begin{pmatrix} OH & a) Ph_3PBr_2 \\ OH & & OH \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & & & \\ & & & & &$$

Evans has shown<sup>[4]</sup> that addition of Lewis acids (ZnCl<sub>2</sub> or LiBr) allows a dynamic and preferential coordination to one of the ethercal oxygens, activating the  $1,3,2\lambda^5$ -dioxaphospholane and promoting its decomposition into epoxide. Protic or polar solvents promote also decomposition<sup>[5]</sup> of  $1,3,2\lambda^5$ -dioxaphospholanes.

Accordingly we first studied the stability of 2,2,2,4-tetraphenyl- $1,3,2\lambda^5$ dioxaphospholane in pure toluene or with addition of ZnCl<sub>2</sub> or LiBr. The transformation % ratio of dioxaphospholanes, monitored by <sup>31</sup>P NMR as a function of time showed that the dioxaphospholane is :

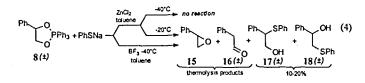
- stable at 4°C in toluene, without activating agents, during one month.
- quite stable, in presence of LiBr, during one week (25% transformation) at -40°C.
- stable only few hours after the addition of ZnCl<sub>2</sub>, at -40°C.

So, all the experiments were then carried out at  $-40^{\circ}$ C to avoid the formation of epoxide.

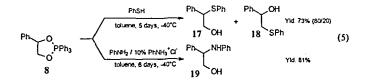
Soft nucleophiles as PhSNa, Ph<sub>2</sub>PNa, NaBH<sub>4</sub>, Ph<sub>3</sub>P were used first without electrophilic activation for the functional transformation of the  $1,3,2\lambda^5$ -dioxaphospholane : no reaction occurs and the dioxaphospholane is totally recovered. With electrophilic activation (ZnCl<sub>2</sub> or BF<sub>3</sub>), PhSNa reacts to give the substituted alcohols **17**, **18** (10-20%) together with "thermolysis" products **15**, **16** (scheme 4).

With electrophilic activation (LiBr), nucleophiles as PhSNa, Et<sub>3</sub>SiH, Ph<sub>2</sub>NH give only thermolysis products. Only NaBH<sub>4</sub>, in presence of LiBr, gives the corresponding alcohol PhCH<sub>2</sub>CH<sub>2</sub>OH with 10% yield.

So the use of Lewis acids often lead to "thermolysis" products.



Hard nucleophiles as Ph<sub>2</sub>NH, PhNH<sub>2</sub>, Et<sub>2</sub>NH, PhCH<sub>2</sub>OH do not react with 1,3,2 $\lambda^5$ -dioxaphospholanes in spite of electrophilic activation by hydrogen-bonding. Among soft nucleophiles (PhSH, Ph<sub>2</sub>PH), only PhSH gives the corresponding functional transformation with a 73% yield (scheme 6).



To reinforce the nucleophilicity of NuH we used either Nu or H<sup>+</sup>, both in catalytic amounts. No reaction occurs with the pairs Ph<sub>2</sub>PH / 0,1 Ph<sub>2</sub>PLi or  $CH_2(COOEt)_2$  / 0,1 NaCH(COOEt)\_2. However, the pair PhNH<sub>2</sub> / 0,1 PhNH<sub>3</sub><sup>+</sup>Cl affords the corresponding substituted alcohol with 81% yield (scheme 5).

#### Regioselectivity

With PhSH two regio-isomers 17 and 18 were obtained (70% yield) but only one 19 with PhNH<sub>2</sub> / 0,1 PhNH<sub>3</sub><sup>+</sup>Cl<sup>'</sup>. As it was expected the nucleophilic substitutions occur on the most sterically-hindered carbon to afford derivatives 17 and 19 (table 1) except in the case of 4-ethyl-2,2,2-triphenyl-1,3,2 $\lambda^5$ -dioxaphospholane.

TABLE 1	Ring opening of 1,3,2	<sup>5</sup> -dioxaphospholanes.
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Dioxaphospholane	Nucleophile NuH	HO Nu Prod	ucts	YId (%)
Ph_O PPh_O	PhSH PhNH <sub>2</sub> / 0,1 PhNH <sub>3</sub> Cl	80% (17) 100% (19)	20% (18)	73% 81%
O, PPha	PhSH	40% (20)	60% (21)	76%

PhSH does not react with epoxide in the same experimental conditions. With PhNH<sub>2</sub> / 0,1 PhNH<sub>3</sub><sup>+</sup>Cl<sup>-</sup>, the reaction with epoxide occurs with the same regioselectivity but with only 20% yield.

#### CONCLUSION

We worked out a new procedure for the synthesis of dioxaphospholanes from different 1,2-diols. The ring opening by various nucleophiles occurs with PhSH and PhNH<sub>2</sub> / 0,1 PhNH<sub>3</sub>  $^{+}$ Cl<sup>-</sup>. These transformations occur with some regioselectivity.

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