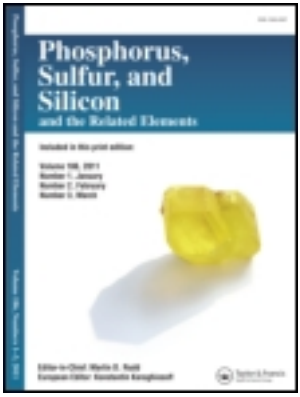

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A new synthesis of 1,3,2λ^5-dioxaphospholanes was realized by direct reaction of dibromotriphenylphosphorane with 1,2-diols. Ring opening studies were performed with or without electrophilic activation (Lewis acids or hydrogen bonding) in order to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

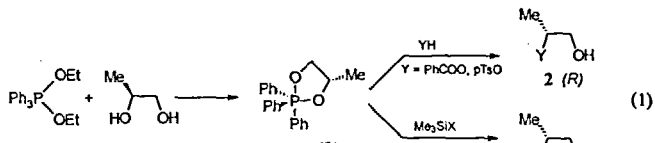
Keywords: 1,3,2λ^5-dioxaphospholanes; 1,2-diols; electrophilic activation

INTRODUCTION

1,3,2λ^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[1a], sulfides[1b] and aziridines[1c].

More, recently, Evans and al. demonstrated that (S)-4-methyl-2,2,2-triphenyl-1,3,2λ^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[1d],[1e], or trimethylsilyl reagents[1f] (scheme 1).

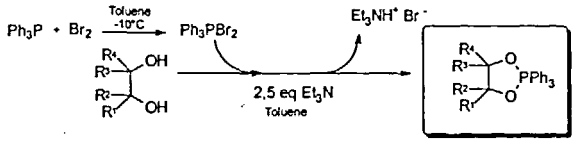
In these transformations, nucleophilic substitutions occur mainly on the most sterically-hindered carbon to afford, with essentially complete inversion of stereochemistry, derivatives **2** and **3** (scheme 1).



(1)

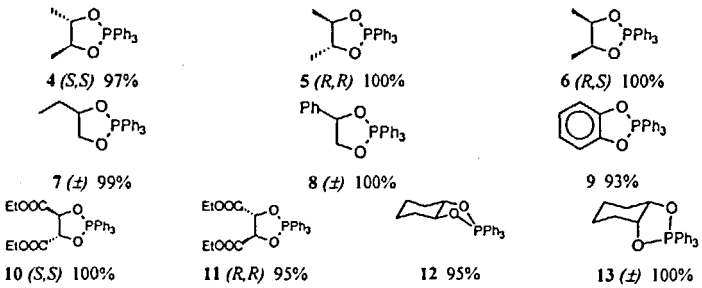
RESULTS AND DISCUSSION

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



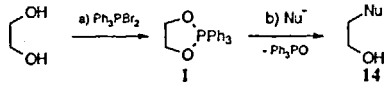
(2)

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 1,3,2λ^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_3P by reduction of the by-product Ph_3PO[3].

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



(3)

Evans has shown[4] that addition of Lewis acids ($ZnCl_2$ or LiBr) allows a dynamic and preferential coordination to one of the ethereal oxygens, activating the 1,3,2λ^5-dioxaphospholane and promoting its decomposition into epoxide. Protic or polar solvents promote also decomposition[5] of 1,3,2λ^5-dioxaphospholanes.

Accordingly we first studied the stability of 2,2,2,4-tetraphenyl-1,3,2λ^5-dioxaphospholane in pure toluene or with addition of $ZnCl_2$ or LiBr. The transformation % ratio of dioxaphospholanes, monitored by ^{31}P NMR as a function of time showed that the dioxaphospholane is :

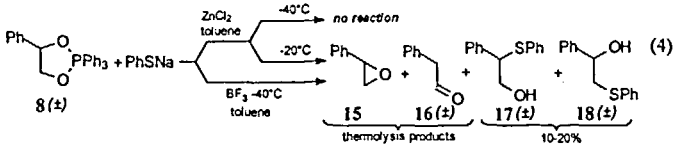
- stable at 4°C in toluene, without activating agents, during one month.
- quite stable, in presence of LiBr, during one week (25% transformation) at –40°C.
- stable only few hours after the addition of $ZnCl_2$, at –40°C.

So, all the experiments were then carried out at –40°C to avoid the formation of epoxide.

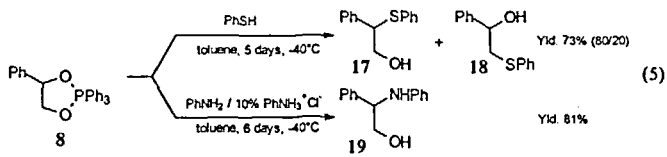
Soft nucleophiles as PhSNa, Ph_2PNa, $NaBH_4$, Ph_3P were used first without electrophilic activation for the functional transformation of the 1,3,2λ^5-dioxaphospholane : no reaction occurs and the dioxaphospholane is totally recovered. With electrophilic activation ($ZnCl_2$ or BF_3), PhSNa reacts to give the substituted alcohols **17, 18** (10-20%) together with "thermolysis" products **15, 16** (scheme 4).

With electrophilic activation (LiBr), nucleophiles as PhSNa, Et_3SiH, Ph_2NH give only thermolysis products. Only $NaBH_4$, in presence of LiBr, gives the corresponding alcohol $PhCH_2CH_2OH$ with 10% yield.

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



Hard nucleophiles as Ph_2NH, $PhNH_2$, Et_2NH, $PhCH_2OH$ do not react with 1,3,2λ^5-dioxaphospholanes in spite of electrophilic activation by hydrogen-bonding. Among soft nucleophiles (PhSH, Ph_2PH), only PhSH gives the corresponding functional transformation with a 73% yield (scheme 6).

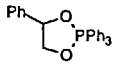
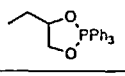


To reinforce the nucleophilicity of NuH we used either Nu^- or H^+, both in catalytic amounts. No reaction occurs with the pairs Ph_2PH / 0,1 Ph_2PLi or $CH_2(COOEt)_2$ / 0,1 $NaCH(COOEt)_2$. However, the pair $PhNH_2$ / 0,1 $PhNH_3^+Cl^-$ affords the corresponding substituted alcohol with 81% yield (scheme 5).

Regioselectivity

With PhSH two regio-isomers **17** and **18** were obtained (70% yield) but only one **19** with $PhNH_2$ / 0,1 $PhNH_3^+Cl^-$. 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-1,3,2λ^5-dioxaphospholane.

TABLE 1 Ring opening of 1,3,2λ^5-dioxaphospholanes.

Dioxaphospholane	Nucleophile NuH	Products HO–CH(R)–CH$_2$–Nu	Products Nu–CH(R)–CH$_2$–OH	Yld (%)
	PhSH	80% **(17)**	20% **(18)**	73%
	$PhNH_2$ / 0,1 $PhNH_3^+Cl^-$	100% **(19)**	-	81%
	PhSH	40% **(20)**	60% **(21)**	76%

PhSH does not react with epoxide in the same experimental conditions. With $PhNH_2$ / 0,1 $PhNH_3^+Cl^-$, 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 $PhNH_2$ / 0,1 $PhNH_3^+Cl^-$. These transformations occur with some regioselectivity.

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