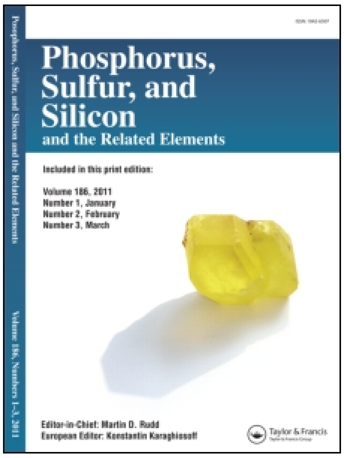

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SHORT COMMUNICATION

Annulation of Secondary Phosphine Oxides Containing δ-Oxoalkyl Group. 1-Phenyl-2-Hydroxyphospholane 1-Oxides

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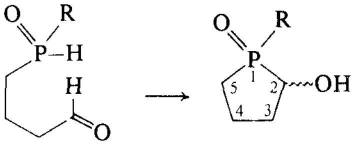
A simple synthesis of δ-oxoalkyl (phenyl) phosphine oxides has been described. δ-Oxoalkyl (phenyl) phosphine oxides have been found to cyclize in the presence of acid to afford 1-phenyl-2-hydroxyphospholane 1-oxides being precursors of phosphafuranoses.

In a previous paper[1] we have published the results of studies on the addition of chiral sec-phosphine oxides to prochiral carbonyl compounds, leading to diastereomeric α-hydroxy-tert-phosphine oxides.

In the present communication we show preliminary results concerning the intramolecular addition of secondary phosphine oxides containing δ-oxoalkyl group resulting in the formation of 2-hydroxyphospholane 1-oxide system.



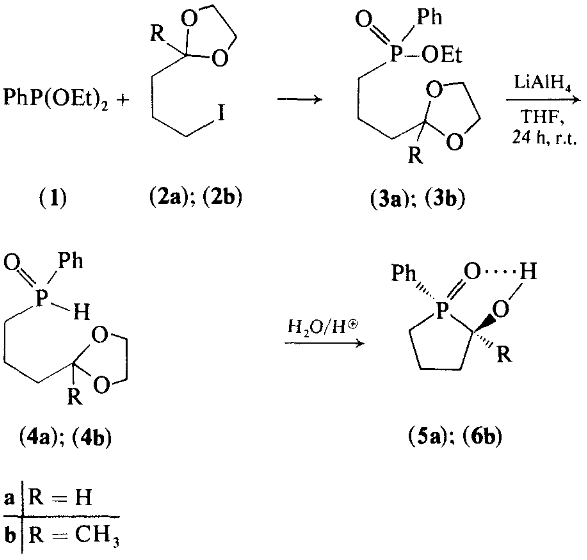
2-Hydroxyphospholane 1-oxides are phosphorus analogues of 2-hydroxytetrahydrofurans, and from this point of view they can be considered as precursors of phosphafuranoses.

It is worth while to note that Inokawa *et al.*[2] have recently obtained some pyranoses with hemiacetal phosphorus by modifying the appropriate furanoses.

For obvious reasons we focused our attention on the syntheses of the simplest compounds, i.e. 1-phenyl-2-hydroxyphospholane 1-oxide (**5a**) and 1-phenyl-2-hydroxy-2-methylphospholane 1-oxide (**6b**). The realized reaction sequence is shown in Scheme 1.

Phosphinates (**3a**) and (**3b**) were obtained in the reaction between phosphonite (**1**) and the corresponding suitably blocked γ-iodocarbonyl compounds (**2a**) or (**2b**); (**3a**): bp 125–8°/0.05 mmHg in 72% yield, (**3b**): 130–2°/0.05 mmHg in 68% yield.

Reduction of (**3a**) and (**3b**) ($LiAlH_4$, THF, 24 h, room temp.) led to the formation of phosphine oxides: (**4a**) ir (film): $\nu_{P-H} = 2320\ cm^{-1}$; ^1H-nmr(C_6D_6): $\delta_{P-H} = 7.23$ ppm, $^1J_{P-H} = 464$ Hz and (**4b**): ir(film): $\nu_{P-H} = 2320\ cm^{-1}$; ^1H-nmr(C_6D_6): $\delta_{P-H} = 7.18$ ppm, $^1J_{P-H} = 462$ Hz, respectively. However, the phosphine oxides (**4a**) and (**4b**) were not isolated in a pure state.



SCHEME 1

Heating of the crude (**4a**) and (**4b**) in diluted HCl or H_2SO_4 yielded the final cyclic products: (**5a**) cis in 45% yield, mp 120–1°, ^{31}P-nmr($CHCl_3$): δ = −55.11 ppm (H_3PO_4); ir(KBr): ν_{OH} = 3150 cm^{-1}, $\nu_{P=O}$ = 1170 cm^{-1}; ^{1}H-nmr($CDCl_3$): $\delta_{C}2_{-H}$ = 4.2 ppm (dt), $^3J_{H-C-C-H}$ = 5.5 Hz, $^2J_{P-C-H}$ = 8.5 Hz and (**6b**) cis in 58% yield, mp 149–50°, ^{31}P-nmr($CHCl_3$): δ = −59.8 ppm (H_3PO_4); ir(KBr): ν_{OH} = 3200 cm^{-1}, $\nu_{P=O}$ = 1180 cm^{-1}; ^{1}H-nmr($CDCl_3$): $\delta_{C}7_{-H}$ = 1.13 ppm (d), $^3J_{P-C-C-H}$ = 14.0 Hz. The ^{13}C-nmr data of (**5a**) cis and (**6b**) cis are given in Table I.

TABLE I

The ^{13}C-nmr data of: (**5a**) cis, (**6b**) cis and (**11**)

Compound	C-2	C-3	C-4	C-5	C-6	C-7
(5a) cis δ (ppm)	69.38	33.77	20.25	26.59	—	—
J_{C-P} (Hz)	72.07	16.18	7.35	64.71	—	—
(6b) cis δ (ppm)	73.00	39.31	19.70	25.03	—	22.56
J_{C-P} (Hz)	73.54	23.53	5.88	64.71	—	8.82
(11a) δ (ppm)	67.04	26.24	19.42	34.17	55.46	—
J_{C-P} (Hz)	75.00	14.70	8.38	67.40	0.00	—

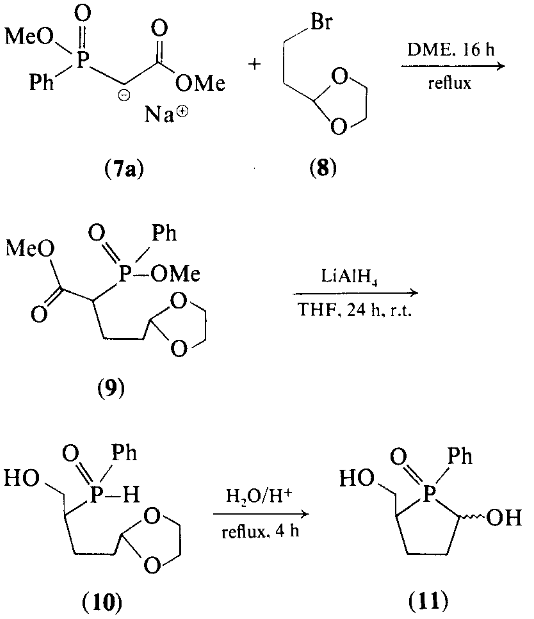
Spectra were taken: (a) in $CDCl_3$, (b) in CD_3OD solutions. Chemical shifts were measured from TMS.

When cyclization of (**4b**) was carried out at room temperature, formation of both isomers (**6b**) cis and (**6b**) trans has been observed with the thermodynamically more stable isomer (**6b**) cis dominating ($\Delta\delta$ = 0.4 ppm for protons of the methyl groups attached to the phospholane ring).

Looking for a synthetic approach to phenylphospholane 1-oxides containing hydroxymethylene group at C-5 position we turned our attention to the racemic phosphinylacetic ester (7) as the one of the suitable substrates. Both enantiomers of this compound are accessible[3] and could be used for asymmetric induction in the synthesis of polyhydroxyphospholane 1-oxides.

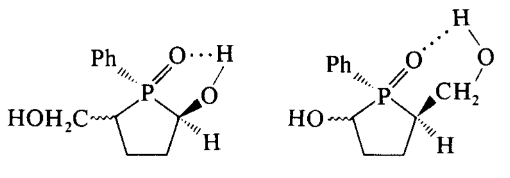
The synthesis of 1-phenyl-2-hydroxy-5-hydroxymethylenephospholane 1-oxide (11) is shown in Scheme 2.

Alkylation of sodium phosphinylacetate (**7a**) with bromoacetal (**8**) (DME, reflux, 16 h) results in the formation of diastereomeric esters (**9**) in the ratio 55:45 in 35% yield, bp 165–8°/0,05 mmHg; ^{31}P-nmr($CHCl_3$): δ = −39.07 ppm and δ = −38.59 ppm (H_3PO_4), respectively. The esters (**9**) treated with $LiAlH_4$ under standard conditions afforded diastereomeric alcohols (**10**). The crude alcohols (**10**) were cyclized in the presence of HCl aq. to give the phospholane 1-oxides (**11**). The final product (**11**) appeared to be a mixture of anomers. One of them (**11a**) has been isolated, mp 170–72°, ^{31}P-nmr(CH_3OH): δ= −53.9 ppm (H_3PO_4); ir(KBr): ν_{OH} = 3185 cm^{-1}, ν_{OH} = 3135 cm^{-1}, $\nu_{P=O}$ = 1155 cm^{-1}.



SCHEME 2

We believe that both the anomers (**11**) have the same configuration at phosphorus and carbon C-5 and opposite configurations at carbon C-2. This situation seems to be likely if the following assumptions are taken into account: (i) the cyclization is reversible; (ii) secondary phosphine oxides can change their configuration in acidic medium[4]; (iii) the stabilization of (11) by intramolecular hydrogen bonding is more effective for a six-membered than a five-membered ring.



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