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ANALOGIES BETWEEN SILICON AND PHOSPHORUS STEREOCHEMISTRY—I

INFLUENCE OF THE LEAVING GROUP ON THE STEREOCHEMISTRY OF NUCLEOPHILIC DISPLACEMENT AT PHOSPHORUS

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Abstract—Stereochemistry of cyclic halogenophosphates has been studied by adding aryloxides, in THF. All extra parameters being equal, the fluoro substituent which is of the more electronegative (and the more apicophilic) is displaced with the more predominant retention F > Cl ≈ Br. Such behaviour cannot be explained with the usual concepts of phosphorus stereochemistry and, in particular, the generally accepted view of apical attack giving the more stable P^V intermediate. By contrast, strong analogies with the stereochemistry observed at silicon are clearly evidenced. Like for silicon compounds, front-side attack could explain predominant retention, particularly in P–F bond cleavage. Trigonal bipyramidal intermediates with the entering group in equatorial position and the leaving group in apical position, or square-pyramidal geometries may be envisaged.

Strong analogies found in racemisation and hydrolysis of chlorosilicon and chlorophosphorus compounds, both activated by external nucleophiles[1,2] prompt us to report additional results emphasing the similar stereochemical behaviour between the two series.

Extensive studies on the nucleophilic substitution of organosilane[3,4] allowed to emphasise "chief factors" governing the stereochemistry at silicon:

(i) the lability of the leaving group
(ii) the electronic character of the nucleophile.

Stereochemical studies have been carried out on a large variety of organosilicon derivatives by different research groups.[5–7,8–10] Nucleophilic displacements are highly stereoselective, proceeding either with retention or inversion of configuration. Strong nucleophiles which have a concentrated charge promote retention with poor leaving groups attached at silicon. On the other hand, good leaving groups are generally displaced with predominant inversion by weak nucleophiles, having a delocalised negative charge.

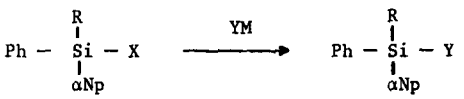
Functional substituents at silicon have been classified on the basis of the stereochemical behaviour corresponding to changes in nature of the leaving group. An empirical order was proposed for predominant inversion.[4]

$$(RET)\quad H < OR < F \approx SR < Cl \approx Br \quad (INV).$$

Interpretations based on the physical properties of the reactant species, such as pKa of the conjugate acid[8] or polarisability of the leaving group, were dismissed on the consideration of high similarity between bromide and chloride, or even better between fluoride and thioalkoxides. The last two substituents, which are completely different in electronic character or basicity, promote a similar degree of stereoselectivity. Conclusive experiments are described below (Table 1).

The more interesting point in relation to the present study was the displacement towards retention from chlorine to fluorine as leaving group, a general

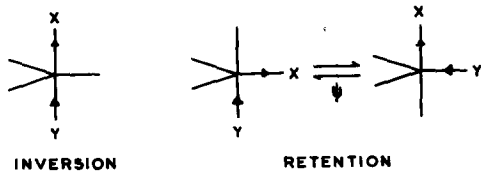
Table 1.



YM \ X	R=neoPen Br	R = Me or Et Cl	SPh	F	OMe	H
iBu_2AlH-hexane	RN	RN	RN	RN	RN	-
EtLi-TMDA	IN	IN	RN	RN	RN	RN
$LiAlH_4$-Et_2O	IN	IN	IN	IN	RN	-
$PhCH_2Li$	-	IN	IN	IN	IN	RN
CH_2=CH-CH_2MgBr	-	IN	IN	IN	IN	-

phenomenon which was observed whatever the other substituents at silicon or possible geometric constraints.[5,7]

In the case of phosphorus compounds, stereochemistries of nucleophilic substitutions are usually explained with the accepted view of apical attack and apical departure,[11] via trigonal bipyramidal five coordinate intermediates or transition states. Since both retention and inversion of configuration at phosphorus can proceed, the retention pathway, which can be predominant in certain reactions has been rationalised on the basis of possible pseudorotations of the different T.B.P. intermediates.[11a]



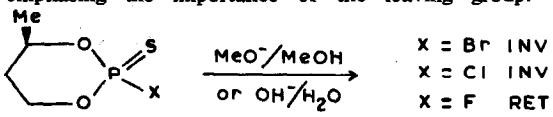
The main factor governing the stereochemistry is the formation of the most stable P^V intermediate or transition state, in terms of apicophilicity of the different substituents at phosphorus. Tripett has been able to establish a scale of apicophilicity from dynamic NMR studies on stable pentacovalent phosphoranes.[11c]

$$\text{INV} \xleftarrow{\text{F} \quad \text{H} \quad \text{Cl} \quad \text{Br} \quad \text{OPh} \quad \text{OR} \quad \text{SPh} \quad \text{R}} \text{RET}$$

Fluorine is much more apicophilic than chlorine or bromine on the basis of electronegativity or NMR studies. Interestingly some literature data concerning the stereochemistry of nucleophilic displacements of halogeno-phosphorus compounds do not agree with these considerations.

For instance, striking results have been presented by Inch on carbohydrate derivatives.[12] Despite of their high apicophilicity, chloro and fluoro derivatives are displaced by methyl Grignard reagent with predominant retention. Also, alkaline solvolysis shows a general displacement towards retention changing the leaving group from chloride to fluoride or oxygen derivative (Table 2). These results can be significantly compared with the stereochemistry of the reaction of functional organosilanes with alkoxides.[13,14]

The stereochemical crossover observed by Mikolajczyk in the alkaline solvolysis of 2-halogeno-4-methyl-2-thio-1,3,2-dioxaphosphorinans is even more significant, emphasing the importance of the leaving group.[15]



Nucleophilic displacement of the fluoro derivative with predominant retention contrary to the chloro or bromo compounds which display more inversion is not in accord with the concept of apicophilicity as predominant factor governing the stereochemistry at phosphorus. On the other hand, the good parallelism with the order of selectivity F > Cl ≥ Br observed for predominant retention at silicon justifies a systematic study of the different parameters which could affect the stereochemical behaviour of functional phosphorus derivatives, taking in mind the general pattern of similarity between silicon and phosphorus species.

In the present paper, we consider the effect of halogens as leaving groups in the case of 2-halogeno 5-halogenomethyl 5-methyl 2-oxo (or thio) 1,3,2-dioxaphosphorinan system. Our choice of such a model was primarily directed by experimental considerations. Starting materials and products are known, or easily prepared. Stereochemical investigations by means of NMR spectra are simple and quite sensitive.

Moreover, stereochemical data reported by Wadsworth showed this model to be an interesting borderline case, where small modifications in the leaving group and the nucleophile can completely change the stereochemical pathway.[16–18]

We have prepared five cyclic halogenophosphorus derivatives, and studied their stereochemical outcome by reaction with nucleophiles.

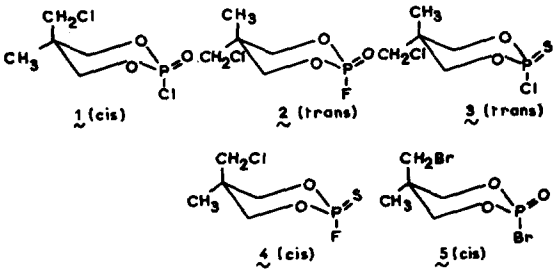
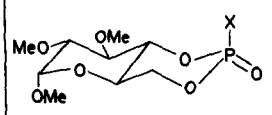
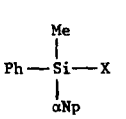


Table 2.

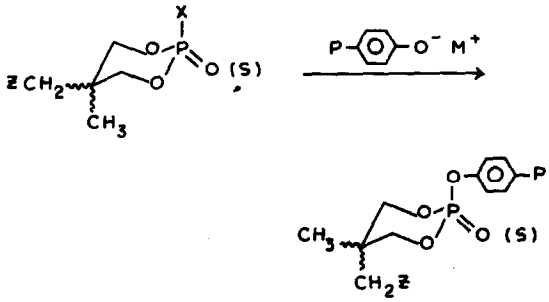
	X	Nu	Stereoselectivity
	- Cl	EtONa/EtOH	56 % RN
	- F	"	74 % RN
		"	100 % RN

	X	RONa	Solvent	% S.S	Ref.
	- Cl	tBuONa 1.2 eq	tBuOH	100 % IN	13
	- SMe	nBuONa 1.2 eq	3%nBuOH-PhH	58 % IN	14
	- F	nBuONa 1.16 eq	2%nBuOH-PhH	94 % RN	14

The two chlorides 1, 3 and the bromide 5 have been already described.[16,17,19] The conformation of the bromide had been determined by X-ray structure.[20]

The fluoro compounds 2, 4 are prepared from the chlorophosphates by exchange with NH_4F, in acetonitrile, followed by fractional crystallisation of the *cis/trans* mixture in the appropriate solvent.

Nucleophilic substitutions have been carried out in THF, using stoechiometric amounts of aryloxide and halogenophosphorus compound with described subsequent work-up.



Products have been isolated and the *cis-trans* isomer ratios determined from integration of ^1H NMR spectra (Table 3). In some instances, duplicated reactions gave similar results. Moreover, in typical experiments, the nucleophilic reactivity has been also checked by means of proton-decoupled Fourier transform ^{31}P NMR spectroscopy (Table 4).

The only products obtained were 2-*p*substituted phenoxy-5-halogeno-methyl-2-oxo (or thio)-1,3,2-dioxaphosphorinans. Stereochemistries reported in the Table 3 are indicative of a good comparison between the two methods. Moreover, in control experiments, we have shown that:

(1) Cyclic halogenophosphates are not epimerised under reaction conditions, when they are mixed in NMR tubes with 1/2 equivalent of aryloxide.

(2) Final products are stable in reaction conditions, except *p*-nitrophenoxy derivatives which epimerise slowly in such medium.

(3) Isomer ratios of *cis-trans* products are constant along the reaction process when they are measured *in situ* by means of ^1H NMR integrated spectra.

Therefore, we must consider that the stereochemistries reported in Table 3 are kinetic evidence of the stereochemical behaviour of P–X bonds.

DISCUSSION

We have initially to mention that the purpose of the present paper is the comparison of halogens as leaving groups in 2-halogeno-2-oxo-(or thio)1,3,2-dioxaphosphorinans. In the homogeneous series concerned, the only important variable parameter is the nature of that leaving group. All the other possible factors are the same. In particular, geometrical constraints of 6-membered rings or angular torsions are of similar magnitude order. Moreover, it is important to note that in all the 6-membered ring compounds 1–5 here studied, the halogen atom lies in axial position and the thio or oxo substituent in equatorial site of chair conformers.[19–21]

Preliminary comments can be made from the experimental data reported in Table 3.

(i) The stereochemical outcome is strongly dependent on the leaving group lability. Bromine and chlorine are close, and both give more inversion than fluorine, whatever the nucleophile

$$(INV)\quad Br \simeq Cl > F\quad (RET)$$

(ii) A similar general displacement, F vs Cl, is observed in both 2-oxo and 2-thio derivatives, with compared results in the two series.

(iii) Analogous experimental data obtained respectively with chlorides 1-*cis* and 3-*trans* or with fluorides 2-*trans* and 4-*cis* show that the *cis-trans* geometry of the starting material has little or no influence on the stereochemical outcome.[12]

If we consider the stereochemical behaviour of halogenophosphorus compounds by analogy with halogenosilicon derivatives, we observe a good parallelism between the two series. In both cases, we note a general displacement towards retention in the case of fluorine, despite the high electronegativity of that leaving group.

Now, concerning the possible geometries of the trigonal bipyramidal intermediates (TBP) corresponding to an apical approach of the nucleophile, two possibilities exist (Fig. 1). In the first one, 1a, back-side attack opposite to the leaving group left the 6-membered ring in

Table 3. Stereoselectivity of aryloxides in THF

Z Retention	Y = O						Y = S			
	F trans	Cl cis		Br cis		F cis		Cl trans	
	^1H	^1H	^{31}P	^1H	^{31}P d	^1H	^{31}P	^1H	^{31}P
p-MeO-C_6H_4-O^- Na^+	100	72[a]	68	65[a]	62	90	91	56	60
p-Me-C_6H_4-O^- Na^+	82	53	54	50	51	93	94	52	55
C_6H_5-O^- Na^+	74	50[c]	47	48[a]	44	98	96	50[a]	46
pNO_2-C_6H_4-O^- Na^+ [b]	(50)	(12)	5[e]	(30)	-	-	-	(12)	3[e]
pMeO-C_6H_4-O^- Li^+	100	79	85	68	63	87	90	84	89
pMe-C_6H_4-O^- Li^+	79	82	82		77	100	100	76	84

a - duplicated reaction

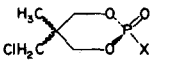
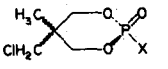
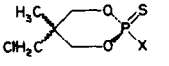
b - homogeneous conditions are generally considered, except in the case of sodium p-nitrophenoxide which is sparingly soluble in THF

c - ref 16 - duplicated reaction gave 49% retention

d - relative integrations of cis-trans mixtures by means of ^{31}P proton-decoupled spectra.

e - slow epimerization of the p-nitrophenoxide derivative was observed after completion of the reaction, explaining the different stereochemical values obtained depending on the two methods. Values in brackets probably refer to partially epimerized products.

Table 4. ^{31}P NMR values (δ)

	X	Br –	Cl –	F –	CH_3O-⟨⟩-O-	CH_3-⟨⟩-O-	⟨⟩-O-	NO_2-⟨⟩-O-
	cis	-	- 5.25	- 18.53	- 15.00	- 15.35	- 15.56	- 16.11
	trans	-	-	- 18.20	- 14.06	- 14.41	- 14.66	- 15.43
	cis	- 15.85	-	-	- 15.14	- 15.30	- 15.51	- 15.47
	trans	-	-	-	- 14.18	- 14.57	- 14.74	- 15.38
	cis	-	56.74	51.41	54.25	53.54	53.24	52.24
	trans	-	57.04	52.18	57.12	56.40	56.01	54.42

Chemical shifts are in ppm with positive values downfield, relative to H_3PO_4 in D_2O, as external standard. All spectra were recorded under similar conditions (0.2M in THF).

diequatorial position, which corresponds to an inversion pathway. The second possibility is the formation of a TBP with the 6-membered ring in equatorial-axial positions corresponding to attack of the nucleophile opposite to one of the ring O atoms, **1b**. The leaving group can depart directly from equatorial position, B, or leave from an apical site, C, after one pseudorotation. The overall result is retention at phosphorus.

On the basis of electronegativity (and apicophilicity), the preference for the geometry **1-A** (inversion) would be in the order Br > Cl > F. At the opposite, the geometry **1-B** would be more favored as X is less electronegative, so in the order Br > Cl > F.

In fact, experimental data are clearly in the opposite direction to the stereochemical crossover which could be reasonably expected from the consideration of apical attack of the nucleophile and apical preference for electronegative substituents as determining factors of the stereoselectivity at phosphorus, since these two parameters would induce more inversion at phosphorus in the order:

$$F > Cl > Br$$

Moreover, the evidence we have recently presented on equatorial nucleophilic attack at silicon reassess the question of the exact nature and geometry of pentacoordinate phosphorus intermediates. Permutational isomerisations were postulated by Westheimer for explaining the rate enhancement and product distribution in the hydrolysis of cyclic phosphorus esters.[11a,29] By application of the principle of microscopic reversibility (PMR), the concept of apical entry as a consequence of an apical departure (or vice versa) implied a symmetric energy profile. In the case of hydrolysis of P–O bonds, such extended application appeared correct since leaving

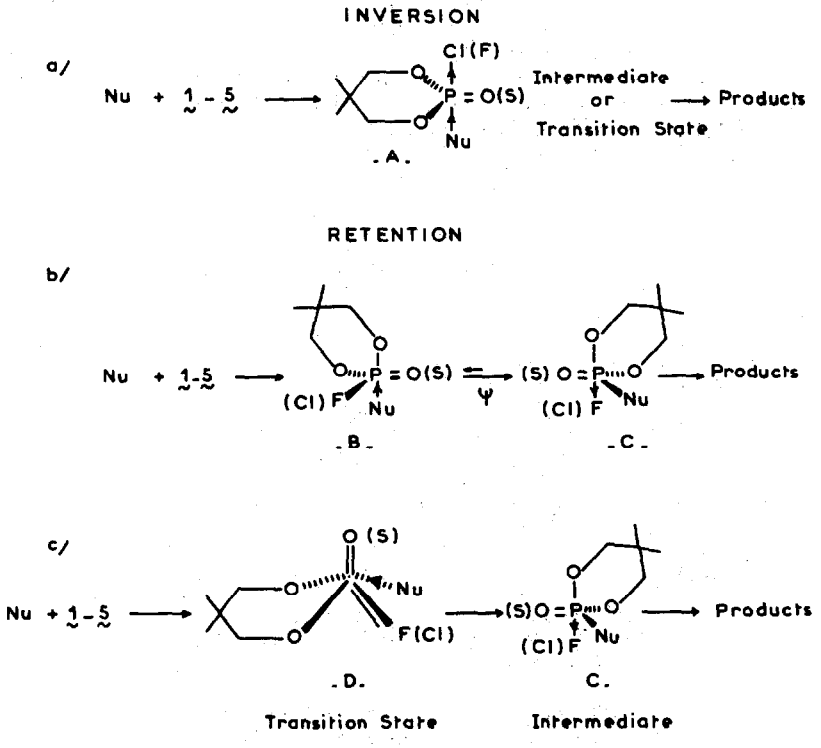


Fig. 1.

group and attacking nucleophile were both O atoms. But, when the entering and leaving groups are different, this application of the PMR is not necessary since the reaction energy profile does not admit a mirror symmetry. In such cases, as Mislow pointed out,[23] an apical attack followed by an equatorial departure (or equatorial attack, apical departure) cannot be dismissed on the only consideration of violating the PMR.

Interpretation of the retentive mechanism could be the formation of the more stable P^V intermediate **1-C**, corresponding to an equatorial entry of the nucleophile[6] with the halogen in apical position. The preference for such a geometry is in accord with the consideration of high electronegativity of halogens in the order F > Cl > Br. As proposed by Hudson for alkaline hydrolysis of cyclic phosphonamidates,[24] front-side attack relative to X could give initially (Fig. 1c), the intermediate or transition state of square pyramidal geometry, **D**. Such species could then rearrange to the more stable TBP intermediate, **C**.

Inversion of configuration could be simply explained by back-side attack of the nucleophile relative to the leaving group, giving an intermediate or transition state of type **1-A**. The more labile the group X (Br, Cl > F), the more important the S_N-2 process corresponding to an inversion pathway.

CONCLUSION

Strong analogies we have observed between the nucleophilic displacement on halogenosilanes and halogenophosphorus compounds emphasises the importance of such comparison between the two series. In both cases, we can reasonably admit that "chief factors" governing the stereochemistry are a fine balance between leaving group lability and strong or weak character of the nucleophile; studies on the latter effect are under present investigations.[25]

EXPERIMENTAL

All the reactions have been carried out in Schlenk tubes, under dry N_2. THF "Baker quality" was refluxed and distilled under calcium hydride, just prior to use. Starting materials and products are characterised by proton NMR spectroscopy (Varian EM 390); isomer ratios are calculated from the relative integrations of both methyl-5 and methylene-5 protons. The chemical purity is checked by tlc on Kieselgel PF 254 eluting with chloroform or ethyl acetate.

In some instances, mass spectrometry or ^{31}P NMR spectra (Jeol JNM-PS-100 or Brucker WP-80) confirmed the quality of isolated materials.

cis - 2 - *Chloro* - 5 - *chloromethyl* - 5 - *methyl* - 2 - *oxo* - 1,3,2 - *dioxaphosphorinan* **1**. A procedure, identical with that reported by Wadsworth,[16] was followed.

trans - 2 - *Chloro* - 5 - *chloromethyl* - 5 - *methyl* - 2 - *thio* - 1,3,2 - dioxaphosphorinan **3** was prepared as recorded,[17] the *trans* phosphorochloridothionate crystallised from petroleum ether from the 1:2 *cis/trans* mixture.

cis - 2 - *Bromo* - 5 - *bromomethyl* - 5 - *methyl* - 2 - *oxo* - 1,3,2 - *dioxaphosphorinan* **5**. Following a modified version of the procedure of Verkade *et al.*[19] 4-methyl-2,6,7-trioxal-1-phosphabicyclo-2,2,2-octane was first extracted with CCl_4 to eliminate 4-methyl-2,6,7-trioxa-1-phosphabicyclo-2,2,2-octane-1-oxide. The soln piped in a Schlenk tube under N_2 pressure was concentrated *in vacuo*. To the bicyclic phosphite dissolved in benzene was slowly added a benzene soln of Br_2. Benzene was removed *in vacuo*, and the crude material dissolved in hexane-ether. *Cis* **5** precipitated *in vacuo*, along with the removal of hexane–ether (m.p. 77°).

trans - 2 - *Fluoro* - 5 - *chloromethyl* - 5 - *methyl* - 2 - *oxo* - 1,3,2 - *dioxaphosphorinan* **2**. The fluoro compound was obtained from *cis*-chloride(1) and ammonium fluoride by the halogen exchange reaction carried out in acetonitrile.[15] The solvent was added at once on the pre-mixed reactants at 35°. The heterogeneous mixture was heated for 20 min at 70°, under N_2 flow. Petroleum ether was added. The ppt was quickly filtered off and the filtrate concentrated *in vacuo*. Crystallisation from CCl_4 gave a poor yield (15%) of diastereomerically pure *trans*-fluoride (m.p. 85–86°) (mass spectrometry: M = 202) δ^{31} P_{trans}—18.20 ppm (THF, H_3PO_4 in D_2O), $J_{P-F_{trans}}$ = 1006 Hz

$\delta_{H(methyle)}$	$\delta_{H(methylene)}$
2-*trans* 1.38 ppm	2-*trans* 3.41 ppm

The same reaction carried out for a longer period of reflux (3 hr) gave a *cis–trans* mixture of fluoride (73/27). Separation of the diastereoisomers by fractional crystallisation from CCl_4, petroleum ether or anhydrous ether could not be accomplished.

Cis **2** in the epimerized mixture $\delta^{31}P_{cis}$: − 18.52 (THF, H_3PO_4 in D_2O)

$J_{P-F_{cis}}$ = 1111 Hz.

$\delta_{H_{cis}}$(methyle) 0.97 ppm; $\delta_{H_{cis}}$(methylene) 3.78 ppm.

cis - 2 - *Fluoro* - 5 - *chloromethyl* - 5 - *methyl* - 2 - *thio* - 1,3,2, - *dioxaphosphorinan* **4**. In 200 ml acetonitrile, were mixed 14.1 g (0.06 mole) *trans*-2chloro-5-chloromethyl-5-methyl-2-thio-1,3,2-dioxaphosphorinan and 2.46 g (0.066 mole) ammonium fluoride. The heterogeneous mixture was magnetically stirred under N_2 at 70° for 6 hr. The ppt was filtered off. The filtrate was evaporated *in vacuo* to leave a residue of *cis–trans* fluoride in the 2/1 ratio (91% yield). The thermodynamically more stable *cis*-isomer was isolated by recrystallisations from n-hexane—(m.p. 62–63°).

$\delta^{31}P_{cis}$: + 51.36 ppm (THF, H_3PO_4 in D_2O) $J_{P-F_{cis}}$ = 1111 Hz

$\delta^{31}P_{trans}$: + 52.20 ppm $J_{P-F_{trans}}$ = 1108 Hz

$\delta_H$methyle =	$\delta_H$methylene =
4*cis* = 0.96 ppm	4*cis* = 3.77 ppm
trans = 1.36 ppm	*trans* = 3.40 ppm.

Reactions of 2-halogeno-2-oxo (or thio)1,3,2-dioxaphosphorinan with aryloxides. In general, we used the method described.[16–18] Sodium *p*-substituted phenoxides were prepared from the corresponding phenols and sodium hydride dispersion, in ether. Sodium salts were washed with ether, and dried *in vacuo* just prior to use.

Lithium *p*-methoxyphenoxide was synthesised by the exchange reaction of *p*-methoxyphenol with n-BuLi in ether.

In a typical experiment, *cis*-**1** (1.1 g; 0.005 mole) and sodium *p*-methoxyphenoxide (0.65 g; 0.005 mole) were dissolved in 20 ml of freshly distilled THF. The mixture was stirred at room temp for 2 hr. Water was added (60 ml). The ppt was filtered off and dried. NMR spectrum of the residual material was recorded in $CDCl_3$ as solvent. Integrations of different protons showed the presence of only one product 2-*p*-methoxyphenoxy 5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan. The spectrum corresponded to a *cis-trans* mixture of diastereoisomers in a 53.47 ratio.

Recrystallisation of the solid material in n-hexane did not change the isomer ratio. When the mixture failed to precipitate by adding water, even after multiple triturations, a second method was used to work-up the mixture. THF was removed *in vacuo*, water was added and the product extracted with $CHCl_3$. Isomer ratios were obtained by integration of the NMR spectra of crude materials. In a typical experiment, the two methods of subsequent work-up gave identical results.

In the case of phosphorobromidate (**5**) with aryloxides removal of THF led a solid material which was washed with water and thoroughly dried. In some cases, the solid material was recrystallised from n-hexane.

All the data reported in Table 3 have been obtained in a similar manner using the appropriate substrates.

^{31}P NMR data. Spectra were recorded by Fourier transform method (200 scans) on a Bruker WP 80 at 32.37 MHz, with a D_2 decoupling frequency of 5900 Hz using 8 mm high resolution spinning tubes with H_3PO_4 as external standard.

In a typical experiment, 131 mg (0.6 mmole) of *cis*-2-chloro-5-chloro-methyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan and 87 mg (0.6 mmole) of sodium *p*-methoxyphenoxide were dissolved in 2.5 ml of freshly distilled THF.

The signal at −5.25 ppm, corresponding to **1**, had completely disappeared. Only two peaks were present at −15.14 ppm and −14.18 ppm, relative to H_3PO_4, respectively *cis*- and *trans* - 2 - *p* - methoxyphenoxy - 5 - chloromethyl - 5 - methyl - 2 - oxo - 1,3,2 - dioxaphosphorinan.

All the other reactions followed by ^{31}P NMR have been carried out in the same way. In the case of bromo-derivatives, unidentified materials were observed in a relatively low yield ($\delta_{^{31}P} \approx -22$ to -20 ppm).

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