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ANALOGIES BETWEEN SILICON AND PHOSPHORUS STEREOCHEMISTRY—II

INFLUENCE OF THE ATTACKING ANION UPON THE STEREOCHEMISTRY OF NUCLEOPHILIC DISPLACEMENT AT TETRAHEDRAL PHOSPHORUS

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Abstract—The stereochemistry of reactions of cyclic halogenophosphates with a representative series of *p*-substituted aryloxides emphasizes the relative influence of the attacking anion. For a given leaving group, the stereochemistry depends essentially upon the electronic character of the *p*-substituent and the ion-pair dissociation of the nucleophile. Both stereochemical and kinetic data rule out a cation-assisted mechanism to explain retention at phosphorus. Meanwhile, a comparison between $S_N2(P)$ and $S_N2(Si)$ suggests similar mechanisms in the two series. Retention and/or inversion are the consequence of two competing reactions of similar energies. The stereochemistry is determined by the factors which affect the approach of the nucleophile to give two initial intermediates of different geometries.

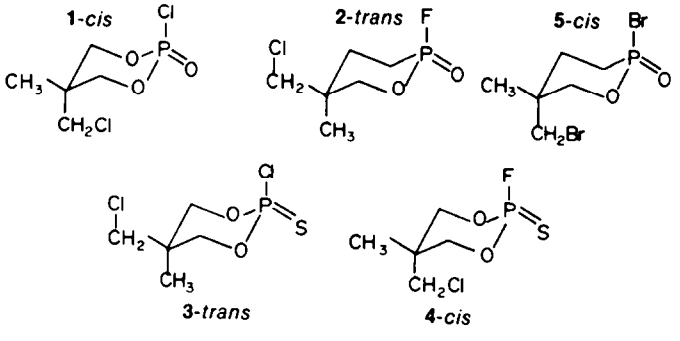
We have presented evidence that the stereochemistry of nucleophilic substitution at the phosphorus atom of 2-halogeno-2-oxo (or thio)-1,3,2-dioxaphosphorinans is highly dependent upon the nature of the leaving group.[1] The predominant stereochemistry increases towards retention in the order F > Cl > Br which was not in accord with the generally accepted view of backside attack giving the more stable P(5) intermediate and/or transition state.[2] On the other hand, close analogies were found between silicon and phosphorus stereochemistries.[3] These results prompted us to extend the comparison, and especially, to examine the influence of the attacking nucleophile on possible changes of stereochemistry.

In nucleophilic displacements at silicon, the more delocalized the negative charge of the nucleophile, the more inversion observed.[4] Similar careful examination of the data reported by Wadsworth shows a close relationship between the nucleophilicity of the attacking anion and the stereochemical behaviour of the 2-oxo-1,3,2-dioxaphosphorinan system.[5] The present results for the reactions of a representative series of aryloxides at tetrahedral phosphorus extends the comparison between Si and P derivatives. Meanwhile, the high sensitivity of cyclic compounds to closed nucleophiles[6] makes this model very useful to study the stereochemical reactivity in terms of the stereoelectronic character of the reactive species.[7]

RESULTS

Since the framework was a general comparison Si-P, our original effort has been the extension of Wadsworth's studies[5] in order to differentiate the effective parameters which affect the stereochemical outcome. We have studied the reactions of compounds **1–5** (Scheme 1) with stoichiometric amounts of aryloxides. The techniques used have been previously described.[1,5] As mentioned earlier, the reactions are highly specific. Homogeneous mixtures are generally obtained, but in some heterogeneous conditions, duplicate reactions checked *in situ* by ^{31}P NMR, or measured after usual work-up by isolation of residual material, gave identical results. The constant isomer ratios along the reaction coordinate are kinetic evidence for two competing reactions giving retention and/or inversion at phosphorus.

Three predominant factors are considered concerning the attacking anion (i) the electronic character of the *p*-substituted aryloxides, (ii) specific counterion interactions, (iii) solvent effects upon the dissociation of the aryloxides.



Scheme 1.

Electronic character of p-*substituents*

Previously, the predominant formation of retentive product has been observed, in an order parallel to the basicity of the phenolates:[5a] pNO$_2$- < pBr- < H- < pMe- < p-MeO. In the present paper, the same stereochemical crossover is observed (Table 1), independently of reaction conditions (benzene, THF or acetonitrile) or leaving groups concerned (F, Cl, Br). In both series, oxo or thio compounds **1–5**, we observe a dramatic change in stereochemistry depending on the electronic nature of the p-substituents. Electron-donating groups, like MeO or Me, promote retention, whereas with electron-withdrawing substituents, we observe predominant inversion. Thus, when p-MeO-C$_6$H$_4$ONa is added to a THF solution of chlorophosphate **1**-*cis*, the amount of *cis*-p-methoxyphenylphosphorus ester rises to 72% retention, whereas under the same conditions, C$_6$H$_5$ONa gives a 50/50 *cis*–*trans* mixture of phenylesters, and p-NO$_2$-C$_6$H$_4$ONa gives essentially *trans*-product (88% inversion).

Specific counterion interactions

When the reactions were carried out in the presence of added salts, dramatic effects of extraneous cations were also reported. For instance, the influence of LiClO$_4$, generally diverted the substitution towards retention.[5b] Addition of NMe$_4^+$Cl$^-$ had an opposite effect, leading to predominant inversion (i.e. the chloride **3**-*trans*, which gave 40% retention with pCH$_3$-C$_6$H$_4$O$^-$Na$^+$ in acetonitrile, rose to 87% retention with added LiClO$_4$, but changed to 94% inversion with added NMe$_4^+$Cl$^-$).

Instead of this, we studied coupling reactions of **1–5** with p-substituted aryloxides, by changing the associated cation from Li$^+$ to Na$^+$, NBu$_4^+$ and Na$^+$-K$_{221}$. (K$_{221}$ is a specific cryptand for Na$^+$). Typical results are presented for p-methylphenoxides (Table 2).

In the case of the chloro and bromo compounds, changing Na$^+$ to Li$^+$ favours retention, whereas p-CH$_3$-C$_6$H$_4$O$^-$NBu$_4^+$ gives essentially inversion. Moreover, the naked anion (addition of 2-2-1 cryptand) affords the almost pure trans isomer of the cyclic p-methyl-

Table 1. Influence of the electronic character of p-substituents

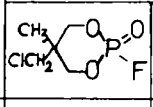
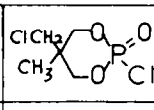
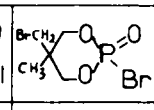
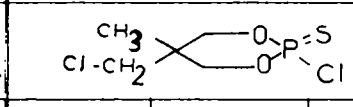
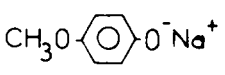
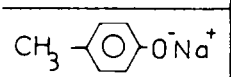
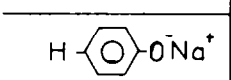
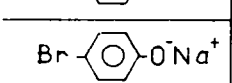
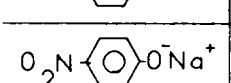
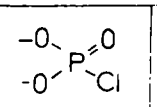
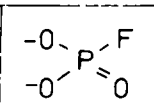
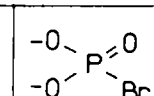
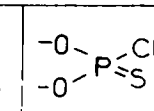
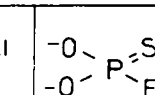
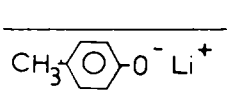
% Retention	THF			PhH	THF	CH_3CN
						
	100	72	65	86	56	50
	82	53	50	82	52	40
	74	50	48	85	50	39
	-	42	-	70	45	24
	(50)	(12)	(30)	18	12	5

Table 2. Influence of the associated cation (coupling reaction of **1–5** with CH$_3$-C$_6$H$_4$O$^-$M$^+$, in THF)

% retention					
	82	79	88	76	100
〃 Na$^+$	53	82	50	56	93
〃 NBu$_4^+$ [a]	5	93	7	0	(60)
〃 Na$^+$/221	0	(45)	0	0	(56)

a - For the preparation, see ref. 19.

phenoxyphosphate (100% inversion). This trend is observed independently of double-bond phosphoryl (P=O) or thiophosphoryl (P=S) substituents.

In the case of fluoro compound **2**, results are somewhat different. Naked anions obtained by addition of specific 2-2-1 cryptand to sodium aryloxides do not react in the same manner. Fast isomerisation of the fluoride prior to substitution probably involves the formation of symmetric species.[8] We noted that the dependence of the product ratio upon the electronic character of *p*-substituted aryloxides is reinforced by increasing the size of the counterion. With electron-donating *p*-substituents, changing Na^+ to NBu_4^+ increases the percentage of retention, whereas the same changes from Na^+ to NBu_4^+ for electron-withdrawing substituents divert the substitution to more inversion (Table 3).

Table 3. Coupling reactions of **2** with various aryloxides, in THF

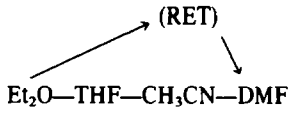
% Retention	Na^+	NBu_4^+
pCH_3-C_6H_4-O^-	82	93
pNO_2-$C_6H_4O^-$	50	16

Solvent effects upon the dissociation of aryloxides

Some changes in the stereochemistry were observed by increasing the basicity of the solvent.[5b] Thus, stoichiometric amounts of **1**-*cis* with C_6H_5ONa in benzene, THF and DMF gave respectively 14%, 50% and 83% inversion.

The study has been extended to other nucleophiles and phosphorus species. In the case of Ar-ONa with **1–3**, the preference for inversion is exhausted by increasing the nucleophilic capability of the solvent (Table 4). The continuous variation of the stereochemical outcome is valid for all five concerned aryloxides: (Ret) PhH > Et_2O > THF > CH_3CN (Inv).

Less conclusive are the experiments performed in the case of ArOLi (Table 5). The preference for a retentive substitution falls in the order:



In the case of fluoride **2**, only slight variations are observed (Table 6). As earlier shown in Table 2, the stereochemical crossover of this model is very sensitive to small modifications of the reaction conditions. We reasonably suppose simultaneously occuring opposite effects.

Kinetics

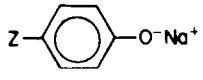
Despite the large differences between reactivities, some kinetic experiments have been also performed and proton NMR results are summarized in Table 7.

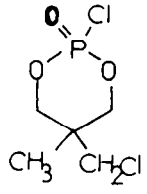
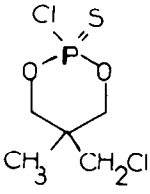
Reactions are much slower with ArOLi than with ArONa, both in CD_3CN and (d_6) acetone. On the other hand, no large rate differences are observed between chloro-**3** and fluoro-**4**.

^{31}P Fourier transform NMR spectroscopy was used to monitor the reaction mixtures after only 2 mn (Table 8). Half-time reactions in THF are twice the values compared with those observed in CD_3CN or (d_6) acetone. Again, fluoro-**4** is somewhat more reactive (1.5) than chloro-**3**.

Quantitative rate values are not significant in the case of the oxo derivatives, which give reactions which are too fast. However, from a qualitative analysis the fol-

Table 4. Solvent dissociation of aryloxides Z-$C_6H_4O^-Na^+$



Z	% Inversion	CH_3O	CH_3	H	Br	NO_2
	C_6H_6*	12	10	15	-	60
	Et_2O	21	17	30	45	-
	THF	28	47	50	58	88
	CH_3CN*	43	50	52	64	94
	C_6H_6	14	18	-	30	82
	Et_2O	20	35	36	50	-
	THF	44	48	50	55	88
	CH_3CN*	50	60	61	76	95

* Wadsworth et al. (ref. 5)

Table 5. Action of ArOLi with 1 and 3 in various solvents

% inversion	1 + Z-C6H4O⁻Li⁺			3 + Z-C6H4O⁻Li⁺		
solvent \ Z	MeO	Me	H	MeO	Me	H
Et_2O	34	33	36	+	+	-
THF	21	18	17	16	24	+
CH_3CN	6	15	11	13	23	-
DMF	25	45	73	⁂	⁂	-

⁂ Secondary reactions give oxo derivatives (5)

\+ No reaction

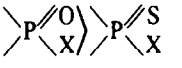
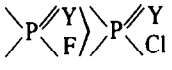
Table 6. Action of ArONa with 2 in various solvents

% Retention	pMeO	pMe	H	pNO_2
PhH	90	90	77	(35)
Et_2O	-	90	-	-
THF	100	82	74	50
CH_3CN	100	90	73	45

Table 7. Kinetic constant ratios of 3 and 4 with pMe-$C_6H_4O^-M^+$

Influence of X			Influence of M^+		
k_{F}/k_{Cl}	CD_3CN	$(CD_3)_2CO$	k_{Na^+}/k_{Li^+}	CD_3CN	$(CD_3)_2CO$
Na^+	1.1	1.4	Cl	300	250
Li^+	2.5	2.3	F	150	150

lowing reactivity order can be deduced:

(1)  (2) 

(3) $Li^+ \ll Na^+ < NBu_4^+ < Na^+, K_{221}$

(4) $THF < CD_3CN < (CD_3)_2CO$

Such a behaviour essentially reflects the relative influence of the electrophilic character of phosphorus and the nucleophilic properties of aryloxides. However, no direct correlation may be deduced between rate increases and stereochemical crossovers.

DISCUSSION

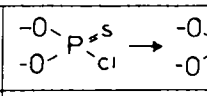
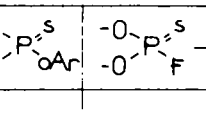
In the preceding paper, we had shown that the lability of the leaving group in the order $F < Cl \leq Br$ is essential for predominant inversion.[1] The same relative order had been largely characterized at silicon.[4,6] Now a similar parallel can be established between $S_N2(P)$ and $S_N2(Si)$, concerning the relative influence of the attacking anion upon the stereochemistry.

Some results obtained with organosilanes are relevant for the present discussion (Table 9). Nucleophilic substitutions of R_3Si^*F and R_3Si^*SPh have been studied with different aryloxides. The stereochemistry essentially depends on (a) the electronic character of p-substituents Z; (b) the relative dissociation of the ion-pair. The latter effect has been studied by changing the basicity of the solvent and/or the size of the associated cation.

At phosphorus, the data show that these factors also influence the stereochemical outcome. We observe (a) variations depending on the p–Z substituents; (b) variations depending on the ion-pair dissociation.

Solvent effects and cation interactions are particularly effective. Therefore, the different parameters may be analyzed in the same manner for the two series. The relative scale of pZ for predominant retention parallels the order of electronic properties of the p-substituents: $MeO > Me > H > Br > NO_2$. Electron-donating groups on the phenoxy moiety displace the stereochemistry towards retention. By contrast, electron-withdrawing substituents favour predominant inversion.

Table 8. Yield of substitution product from 3 and 4 with pMeC$_6$H$_4$O$^-$M$^+$, in THF after 2'

yield ⁂ % / M^+		
Na^+/221	100	-
NBu_4^+	70	95
Na^+	53	80
Li^+	3	-

⁂ Checked by ^{31}P nmr integration

Table 9. Coupling of (+) MePhNpSiX with $pZC_6H_4O^-M^+$ (Ref. 7)

X	Z	M^+	Solvent	$[\alpha]_D$	Predominant Stereochemistry
SPh	MeO	Na^+	C_6H_6	+ 4°	Retention
		"	THF	+ 6°	"
		NBu_4^+	"	+ 8°	"
		$Na^+/K^{\not}$	"	+ 9°	"
	NO_2	Na^+	C_6H_6	+ 2.5°	Inversion
		"	THF	+ 3°	"
		NBu_4^+	"	+ 5°	"
		$Na^+/K^{\not}$	"	+ 8°	"
F	MeO	Na^+	THF	- 4.5°	Retention
		$Na^+/K^{\not}$	"	- 6°	"
	H	Na^+	"	+ 3°	"
		$Na^+/K^{\not}$	"	- 2.5°	
	NO_2	Na^+	"	+ 0.5°	Retention
		$Na^+/K^{\not}$	"	- 4°	Inversion

$K^{\not}_{221}$ specific cryptand for Na^+

Any change to the dissociation of the ion-pair modifies the stereochemical outcome. In the case of P-F (or Si-F) bond breaking, specific effects of the *pZ* substituents of aryloxides are magnified by increasing the size of the counterion (more retention with *p*-donors from Na^+ to NBu_4^+, more inversion with *p*-acceptors). By contrast, P-Cl bonds are more sensitive to the dissociation itself, all factors diverting the stereochemistry towards more inversion. Despite these facts, we note that the specific effect of *pZ* always produces the same ordering of increased retention: $p\text{MeO} > p\text{Me} > p\text{NO}_2$.

In fact, if only from the point of view of the stereochemical variation as a function of the ion-pair dissociation, we can say that in both series, Si and P, the process is highly dependent upon the electronic nature of the attacking nucleophile.

Elimination of a cation-assisted retention mechanism

Electrophilic assistance by M^+ cation had been envisaged to explain the cleavage of Si-X bonds with retention at Si.[9] But, the $S_Ni(Si)$ mechanism was ruled out on the basis of solvent effects.[10] Increasing solvation of the associated cation favoured retention and accelerated the substitution process.[11] Similarly, in the case of phosphorus compounds, two possibilities may be envisaged (i) association of M^+ with the leaving group; (ii) association of M^+ with the phosphoryl double-bond.

The $S_Ni(P)$ process (A) would correspond to the earlier proposed $S_Ni(Si)$ mechanism. As an example of cation association with the phosphoryl, intermediate formation of square pyramidal structure (B) has been recently proposed with the anion–cation complex spanning the phosphoryl oxygen bond[5] in apical position (Fig. 1).

In these two hypotheses, the driving force of the retention process would be an initial complexation of the associated cation with the phosphorus species.

Any effect capable of reducing the complexation (e.g. bulky cations) would simultaneously displace the stereochemistry towards inversion and slow down the rate of substitution.

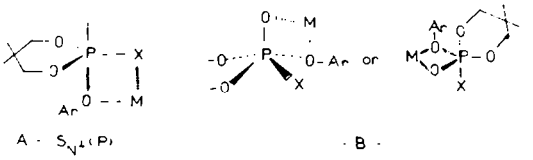


Fig. 1.

Experimental data show an opposite trend. In the reaction of **2** with $p\text{Me-C}_6\text{H}_4\text{O}^-\text{Na}^+$, retention is favoured with more bulky cations (Table 2). Moreover, in the reaction of $p\text{MeO-C}_6\text{H}_4\text{O}^-\text{M}^+(\text{M}^+ = \text{Li}^+, \text{Na}^+)$ with the fluorothiophosphate **4**, both stereochemical and kinetic data may be compared: (a) rate increase ($k_{Na}/k_{Li} = 100$); (b) predominant retention (Li^+: 87%; Na^+: 90%).

Obviously, electrophilic assistance is not a controlling factor governing the stereochemical outcome. The relative influences of the anion–cation interactions only exist with slight modifications to the electronic character of the nucleophiles.

Thus, the analogy with nucleophilic substitution at Silicon is obvious. We are faced with the same factors affecting the stereochemistry (i.e. for predominant retention): (a) lability of the leaving group (F > Cl > Br); (b) electronic character of $\text{Nu}(p\text{MeO} > p\text{MeO} > \text{H} > p\text{NO}_2)$. The relative influence of the nucleophile can be rationalized on the basis of HSAB concepts.[13] (a) *p*-electron withdrawing substituents (NO_2) delocalize the negative charge on the nucleophile; the aryloxide may be considered as "soft" in terms of Pearson theory.[13] Such nucleophiles give essentially inversion of configuration at Si, P. (b) *p*-electron-donating substituents (MeO) in-

crease the negative charge on the oxygen atom; these "hard" reagents prefer a different approach relative to P- (or Si-X) in such a manner that overall retention is observed on the heteroatom. The general parallelism P-F/Si-F is well established, since all the external parameters which affect the electronic character of Nu correspond to the same stereochemical crossover in the two series. The particular case of the P-Cl bond is more difficult to rationalize, since we observe that any effect upon the dissociation of the ion-pair increases inversion at phosphorus. Comparison with the Si-Cl bond is not possible since the latter undergoes substitution with almost exclusive inversion at Silicon. Nevertheless, if we focus on the effect of *p*-substituents, general conclusions derived from the data on fluoro derivatives also apply to P-Cl. Two effects are essential, X and Nu, but we have no direct comparison in Silicon chemistry.

The present conclusions are original compared to the earlier proposals, based on the Westheimer concepts, in the sense that we eliminate the initial formation of the P(5) as essential to describe the stereochemical outcome.

The predominant stereochemistry is the consequence of a fine balance between two possible mechanisms of similar energies.

In the preceding paper, we had presented some conclusions concerning different geometries which are able to rationalize the stereochemical outcome. The preferential apical position of X for the retentive mechanism was discussed on the basis of the electronegativity (apicophilicity) of the leaving group.[2d,14] Similar arguments may be used here. *Ab initio* electronic structure calculations for the super molecule $H_3PO + H^{(-)}$ showed the distorted trigonal bipyramid with the phosphoryl oxygen equatorial being the most stable one (Fig. 2-A).

Applying these results to the preferred geometries corresponding to approach a nucleophile, we have to suppose a basal position of the phosphoryl on the distorted TBP. Therefore, if X occupies an apical site two TBP geometries are relevant: the nucleophile will span either an apical site (B), or an equatorial site (C).

Inversion can be easily explained by initial formation of the intermediate B. The entering and leaving groups are in apical positions, at 180°. The mechanism would correspond to apical entry, followed by direct departure of X.

The same TBP geometry, B, could be also *a priori* considered to explain the retention at P. The mechanism would involve 3 pseudorotations before departure of the leaving group.[15] In fact, such a process would not be stereoselective; moreover, it can be ruled out on the comparison between F and Cl as leaving groups.[1] Similarly, for a given leaving group, for instance Cl, it is difficult to rationalize why *p*MeO-C_6H_4ONa, which gives predominant retention in THF, would undergo 3 pseudorotations before P-Cl bond breaking, whereas *p*NO_2-C_6H_4ONa, which gives essentially inversion would directly displace the leaving group. The two aryloxides are oxygenated nucleophiles.

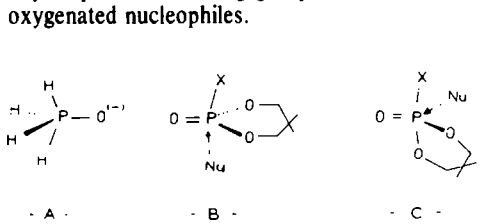


Fig. 2.

Thus, the only reasonable assumption for the retention process is the formation of the intermediate (C), with the attacking nucleophile in an equatorial position (square pyramidal structure may be envisaged as transition state).

Summarizing the above discussion, the mechanism can be viewed as two competing reaction schemes giving two initial intermediates of different geometries. The stereochemistry of $S_N2(P)$ or $S_N2(Si)$ must be discussed in terms of factors which affect the concurrent formation of the intermediates B or C, or more rigorously, the factors which affect the approach of the nucleophile to give the intermediates B or C.

In the case of $S_N2(Si)$ theoretical approach to the problem has been recently outlined.[16] Assuming frontier orbital approximation, Nguyen and Minot have calculated the HOMO-LUMO overlap map for H^- as nucleophile approaching H_3SiX. When X is fluoride, the HOMO-LUMO interaction in frontside approach is stronger than in backside attack leading to possible retention of configuration. On the other hand, in the case of chloride, HOMO-LUMO interactions are close in energy for the two geometrical models, and electronic and/or steric repulsions favor the attack of H^- at the opposite side to the leaving group. Hitherto, such calculations only point out the relative tendency of F^- to be substituted with retention, compared with Cl^-. But this view can explain all the stereochemical data observed at silicon.[7] It would be of interest to extend such a rationalization to phosphorus compounds. However, the question of $S_N2(P)$ mechanism is probably more complicated, since the antibonding orbital σ^*_{P-X} is also affected by the antipleriplanar lone pairs of the ring oxygens.[17,18] Moreover, steric interactions or repulsive terms are perhaps more effective than hitherto recognized.

EXPERIMENTAL

Detailed descriptions of the preparations of the many compounds studied in the course of this work will be found in Refs. 1 and 5.

Tetrabutylammonium aryloxides were prepared from the corresponding sodium salts and nBu$_4$Br, in THF, according to Ref. 19. Specific cryptand K_{221} was purchased from Merck, and used without delay.

Kinetic runs were monitored by ^{31}P Fourier transform NMR techniques (100 scans) with 0.2% solutions in the appropriate solvent.

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