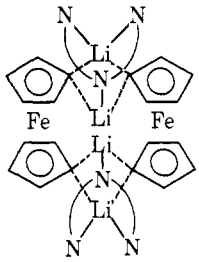

We have attempted to investigate the ^7Li NMR spectrum but could not obtain any signal at room temperature, although one resonance was observed at higher temperatures. The absence of a signal at room temperature could be due to quadrupolar relaxation of the nitrogen atoms on the PMDT molecule.

Acknowledgment. The financial support of the National Science Foundation under DMR-77 2-3999 and CHE 77 24964 is gratefully acknowledged. A NSF departmental equipment grant to the University of Illinois made the NMR studies possible and is also appreciated.

Supplementary Material Available: Structure factor tables (Table 6) for $[(\eta^5\text{-}C_5H_4)_2Fe(N_3C_9H_{23})Li_2]_2$ (4 pages). Ordering information is given on any current masthead page.

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Nucleophilic Substitution at Phosphorus. The Effect of Ion Association on the Stereochemistry and Rate of Substitution at Phosphorus in a Six-Membered Ring Phosphate[1]

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Abstract: The *cis*- and less stable *trans*-2-*p*-nitrophenyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinans undergo substitution with an oxy anion to give both inversion and retention products. The product isomer ratio is highly dependent upon the degree of anion–cation association which in turn is dependent upon the nature of the cation and solvent. A high degree of ion association favors the retention pathway. The results are interpreted by assuming a square pyramidal intermediate with the anion–cation complex spanning the phosphoryl oxygen bond.

Nucleophilic substitution at tetravalent phosphorus, e.g., phosphate triesters, is presently discussed in terms of trigonal bipyramidal (TBP) transition states or intermediates.[2] Hydrolysis studies with ^{18}O have ruled out an addition–elimination mechanism.[3a-c] A TBP intermediate has been invoked, however, to explain, by means of suitable pseudorotational permutations, retention at phosphorus,[4a-d] a route which often accompanies the assumed normal inversion path.[5]

Difficulties arise in devising mechanisms which adhere to the principle of microscopic reversibility and meet the requirement that ligands prefer to enter and leave from apical positions. The choice between retention and inversion is assumed to rest with the relative apicophilicity of the ligands in the intermediate TBP phosphorane.[6] However, recent variable temperature NMR studies[7a-c] indicate similar apicophilicities for groups which normally are displaced by different pathways.

Owing to its conformationally rigid ring, the 2-substituted

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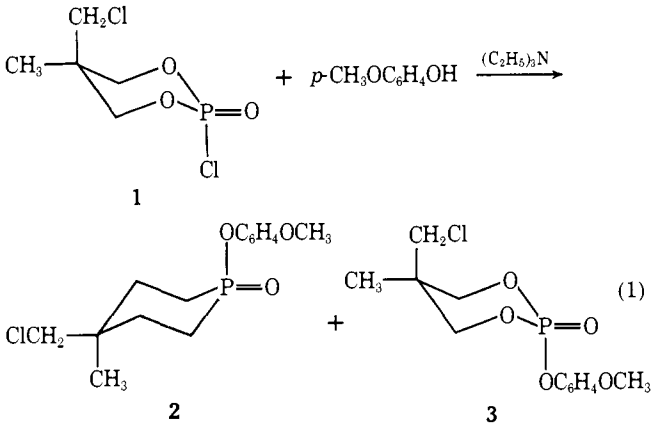
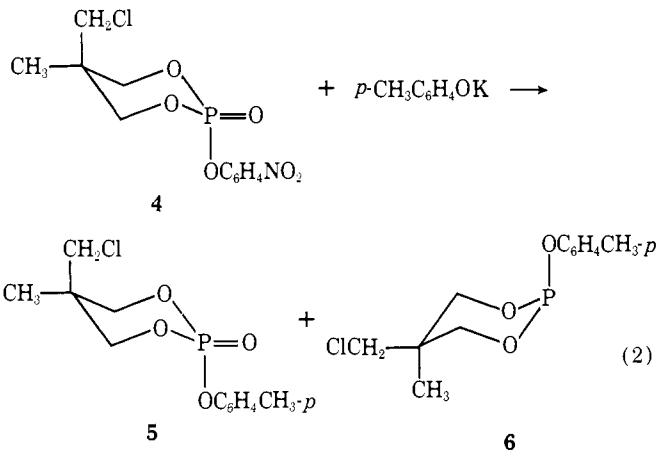
5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan system affords by NMR measurements a simple means with which to follow the course of substitutions. The system has been outlined in detail in previous publications.[8a-c] Substitution at phosphorus in a 1,3,2-dioxaphosphorinan system proceeds by both retention and inversion. Particularly striking is the effect of added cations on the reaction pathway.

In a previous communication, the ability of lithium ion to divert substitution from inversion to retention was discussed.[9] Thus, *cis*-2-chloro-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan (**1**), when added to an acetonitrile solution of *p*-methoxyphenol and triethylamine, gives 91% of the inversion produ the *trans*-*p*-methoxyphenyl ester, **2**. In contrast, the same reaction when repeated in the presence of 1 equiv of lithium perchlorate gives 96% of the retention product, the *cis*-*p*-methoxyphenyl ester, **3**, a result which was not duplicated with other added cations (eq 1). To better understand the phenomenon, we have extended our studies to other systems and as a result have had to revise our original conclusions.



1 **2** **3**

Owing to their ease of preparation, ability to be separated into pure isomeric forms by simple fractional crystallization, and stability, we resorted to the isomeric 2-*p*-nitrophenyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinans. Treatment of the cis isomer, **4**, with 1 equiv of potassium *p*-methylphenoxide, with dimethylformamide (DMF) as solvent, yields a mixture of isomeric products (eq 2). The product ratio



4 **5** **6**

is dependent upon added salts (Table I), with the lithium ion, as in the case of the phosphorochloridate, directing substitution to the retention pathway. The opposite effect, substitution directed toward inversion, is observed when 18-crown-6-ether, capable of entraining potassium ion, is present. Replacement of potassium ion by a quaternary ion has an effect similar to the crown ether, although its effect is greater.

A similar study was carried out with the isomeric *trans*-2-*p*-nitrophenyl ester, **7**. Again, lithium ion has a decided tendency to divert substitution to retention (Table II). The final isomer ratios do not match those in Table I owing to the different thermodynamic stabilities of the inversion and retention products and reactant. In both the cis and trans cases, potassium ion typifies ions other than lithium in its lack of influence on the product ratio. The products, the *p*-methylphenyl esters, with their poor leaving group are stable under the reaction conditions.

A further example of the salt effect is provided by substitutions carried out in a protic solvent, methanol, to which salts are added. Whereas both inversion and retention are observed, the amount of substitution by retention is increased upon addition of lithium ion. Thus, a 0.2 M solution of the chloridate, **1**, in methanol, when treated with 1 equiv of triethylamine as HCl scavenger, gives methyl esters in an inversion-retention ratio of 3.04. In the presence of 1 equiv of lithium perchlorate the ratio falls to 2.08 and in the presence of 4 equiv, equal quantities of the two esters are obtained.

Our data indicate that association between the nucleophile and its counterion is a determining factor. The greater the degree of association the greater the tendency to substitute by retention. The effect of 18-crown-6 ether, which entrains potassium ion, supports the conclusion (Table I). Substitution in the presence of the ether and in the absence of ion association reverts predominantly to inversion. The ability of lithium ion to strongly associate with oxy anions is well known, an ability which normally exceeds that of other cations.[10a-c] We conclude that diversion of substitution to retention is a consequence of association between a cation and negatively charged nucleophile.

We find that lithium ion (ion association) retards the rate of substitution (Table I), and in particular the inversion pathway. Further evidence of its effect was provided by a study

Table I. Reaction of *cis*-2-*p*-Nitrophenyl Ester (**4**, 0.1 M) with 1 equiv of Potassium *p*-Methylphenoxide, DMF as Solvent

added salt	½ reaction min[d]	retention (cis)/ inversion (trans)[a]
0	3	1.0
$KClO_4$ (4 equiv)	1	1.0
$LiClO_4$ (1 equiv)	14	4.0
$LiClO_4$ (2 equiv)	21	10.0
$LiClO_4$ (6.6 equiv)	36	10.0
18-crown-6 ether (2 equiv)[b]		0.47
$CH_3C_6H_4O^-$ $N(CH_3)_4^+$ (1 equiv)[b,c]		0.25

[a] Ratios were obtained by integration of product NMR spectra. The axial and equatorial 5-methyl hydrogens have different chemical shifts. [b] To assure completion, reaction mixtures were allowed to stand for 15 min before workup. [c] Used in place of $CH_3C_6H_4OK$. [d] Reactions were followed by integration of NMR spectra with time. The 5-methyl hydrogens were compared to *p*-methyl hydrogens.

Table II. The Effect of Salts on the Product Ratio Formed by Adding 1 equiv of *trans*-*p*-Nitrophenyl Ester (**7**) to 2 equiv of Potassium *p*-Methylphenoxide, DMF as Solvent

added salt	retention (trans)/ inversion (cis)[a]
0[b]	0.091
$(C_2H_5)_3N^+CH_2C_6H_5$ Cl^- (2 equiv)	0.088
$KClO_4$ (2 equiv)	0.14
$LiClO_4$ (2 equiv)	0.55
$LiClO_4$ (4 equiv)	2.27

[a] Ratios were obtained by integration of product NMR spectra. [b] Solutions were 0.1 M in phosphate. Reaction mixtures were allowed to stand for 15 min before workup.

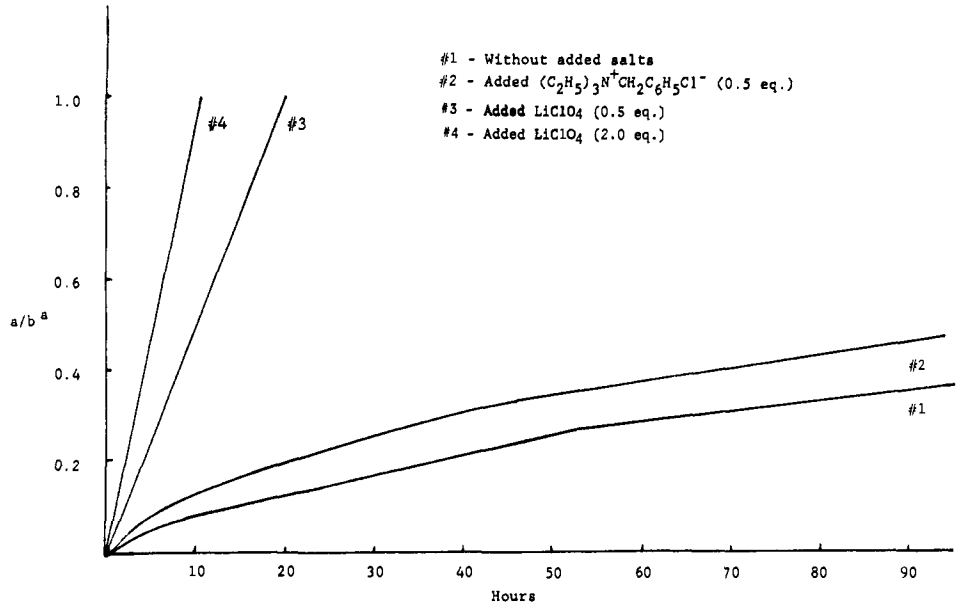
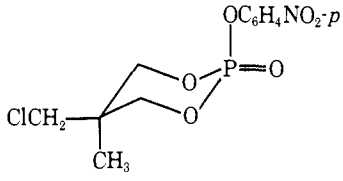


Figure 1. Treatment of *trans*-*p*-nitrophenyl ester (7, 0.2 M) with *p*-cresol and triethylamine (0.4 M), acetonitrile as solvent. Ratios were obtained by comparing absorption due to *p*-methyl hydrogens of product with that due to 5-methylphosphorinan hydrogens of both product and reactant.

of the influence of lithium ion on the rate of isomerization of the *trans*-*p*-nitrophenyl ester (eq 3). At equilibrium the cis



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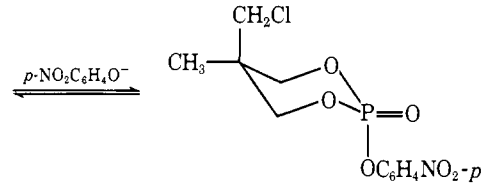
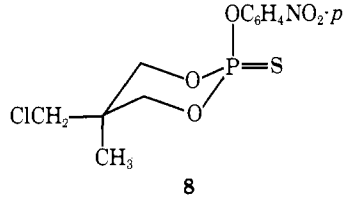


4

(3)

isomer, **4**, is favored over the trans by a factor of 2.8. The isomerization of **7**, 0.05 M in DMF, by sodium *p*-nitrophenoxide, 0.01 M, is half complete in 210 min in the absence of added salts but requires 550 min in the presence of 1 equiv of lithium perchlorate and 875 min in the presence of 2 equiv. Other salts such as potassium and sodium perchlorate do not depress the rate of isomerization and indeed at high concentrations, 0.2 M, have a slight accelerating effect.

The isomerization of the analogous but less reactive 2-thioester, **8**, is likewise depressed by added lithium ion (eq 4).



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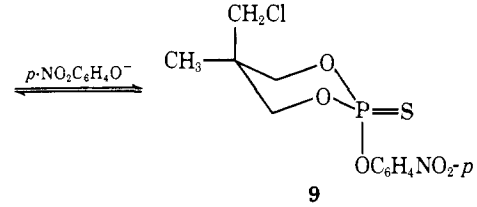
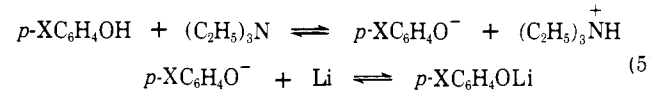


9

(4)

It requires 70 h for a 0.05 M DMF solution of the ester which is 0.1 M in sodium *p*-nitrophenoxide to reach equilibrium and 400 h with 2 equiv of lithium perchlorate. Clearly, the rate of substitution by inversion is retarded by ion association.

Whether the retention rate is aided or depressed by association of the attacking nucleophile with a cation is difficult to determine and unknown. In one system, we have found a dramatic increase in rate which may, however, be merely a consequence of the medium employed. Addition of *trans*-2-*p*-nitrophenyl ester, **7**, to an acetonitrile solution of *p*-cresol and triethylamine gives a low overall yield of both isomeric *p*-methylphenyl esters. In contrast, when conducted in the presence of lithium ion, but not other cations, a high yield, close to theoretical, of *trans*-*p*-methylphenyl ester is obtained (Figure 1). Perhaps the best explanation for the high yield of retention product and its rapid rate of formation lies in the assumption that, owing to ion association and a shift in equilibrium, the concentration of nucleophile in the form of an associated ion is increased while the concentration of triethylamine is decreased (eq 5). Ion association is particularly



(5)

favorable in dipolar aprotic solvents whose ability to solvate cations is low, e.g., acetonitrile.[11] The low yield in the absence of lithium ion is due to competitive C–O cleavage of the starting ester brought about by attack of triethylamine at carbon. Cleavage is particularly fast in the presence of alkali metal ions for insoluble phosphate salts are formed. With lithium ion and *p*-cresol, substitution is fast enough to make salt precipitation negligible. It is known that addition of amines, soft bases, to *p*-nitrophenyl phosphate esters gives products arising from C–O bond cleavage.[12]

The behavior of the *p*-nitrophenyl–triethylamine–acetonitrile system is not unique. *trans*-2-Thiophenyl ester (**10**), as well as other thioesters, normally undergoes substitution with retention. Lithium perchlorate has a decided accelerating affect when substitution by *p*-methylphenol is catalyzed by triethylamine (Figure 2). Only the product of retention is formed (eq 6).

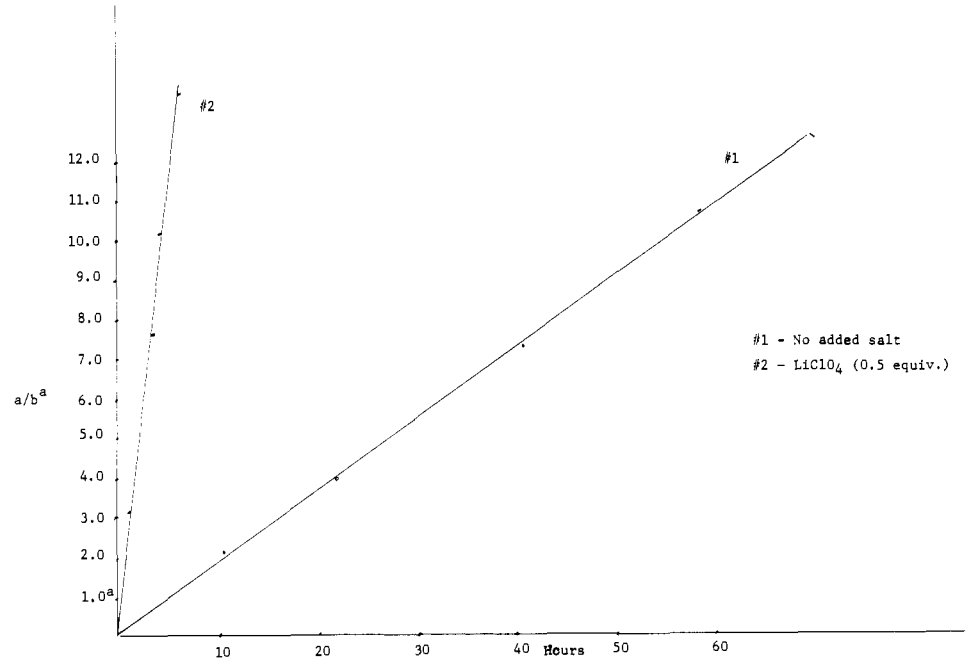
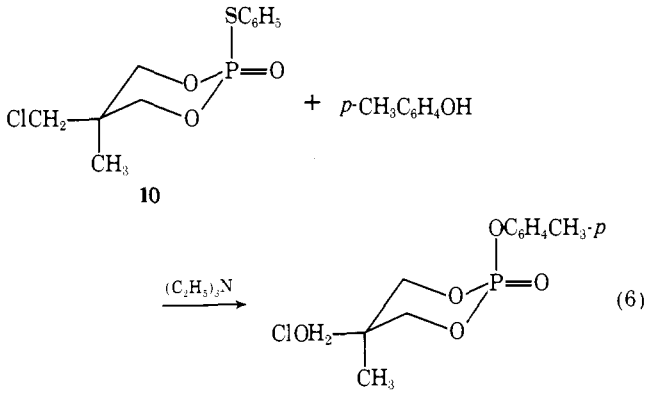


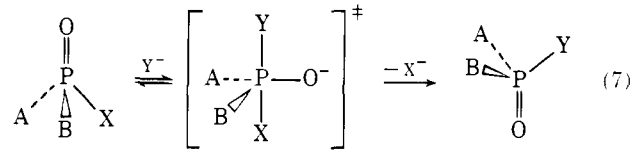
Figure 2. Treatment of *trans*-2-thiophenyl ester (0.2 M) with *p*-cresol (0.4 M) and triethylamine (0.4 M), acetonitrile as solvent. Ratios were obtained by comparing 5-methylphosphorinan hydrogen absorption of product (δ 1.25) with that of reactant (δ 1.10).



(6)

Mechanism of Substitution

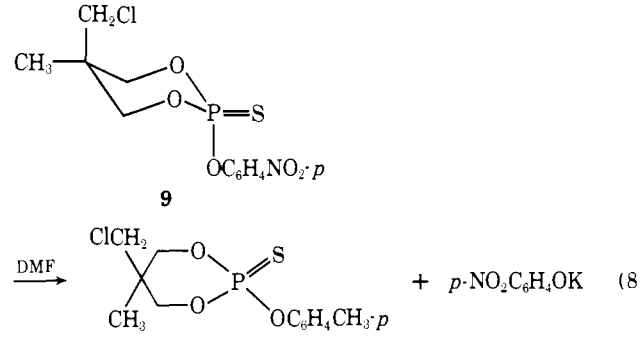
Substitution at phosphorus in phosphate systems has traditionally been presented as proceeding through pentacoordinated intermediates or transition states. Our evidence supports the inversion process as proceeding through a trigonal bipyramidal transition state in an S_N2 fashion (eq 7). In accordance with this mechanism, the decrease in rate of inversion by added lithium ion is easily explained. Ion association would be expected to decrease the nucleophilicity of the negatively charged attacking species.



(7)

Other evidence points to electrophilic catalysis which also supports the mechanism. Thus upon treatment of the cis chloridate, **1**, with *p*-methoxyphenol and triethylamine in acetonitrile, the product isomer ratio goes from 91% inversion without added salt to 100% inversion in the presence of 1 equiv of magnesium perchlorate. *trans*-*p*-Nitrophenyl ester (**7**) gives only the retention product, *trans*-methyl ester, when added to methanol containing 1 equiv of triethylamine. The identical procedure carried out in the presence of 1 equiv of magnesium perchlorate yields both inversion and retention products in a ratio of 0.7. Finally, methanolysis of *trans*-2-thiophenyl ester (**10**) proceeds in the absence of salts by 100% retention but by partial inversion in the presence of cations capable of coordinating with sulfur.[13]

It would appear safe to assume that an associated ion in the form of an ion pair would add to the phosphoryl (P=O) group. Indeed, that an oxy anion with a quarternary counterion substitutes almost exclusively by inversion (Table 1) may be collaborative evidence. The degree of ion association in such cases is unknown, but at any rate, the ion pair, owing to steric reasons, would not be expected to easily add across the phosphoryl-oxygen bond. Other evidence for a phosphoryl addition is provided by *cis*-2-thio-2-*p*-nitrophenyl ester (**9**), which undergoes substitution in DMF by both inversion and retention with the isomer ratio unaffected by added lithium ion (eq 8).



(8)

No rate enhancement occurs by addition of lithium ion to an acetonitrile solution of the ester, *p*-cresol, and triethylamine (Figure 3). Sulfur being less electronegative than oxygen renders a thiophosphoryl (P=S) group less polar than a phosphoryl group. As a result, one might expect an associated ion to have less tendency to add across the former.

The possibility exists that lithium ion might be unique in its ability to coordinate with a phosphate prior to attack by a nucleophile. We have been unable to detect by spectroscopic means association between any of the esters employed in this study and lithium ion under a variety of conditions. For example, addition of lithium ion to solutions of the esters does

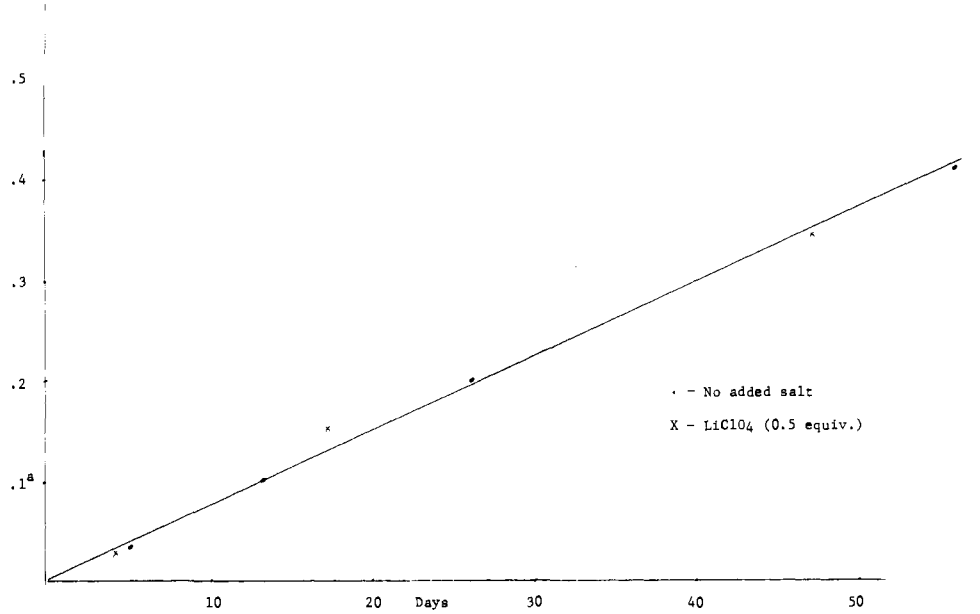


Figure 3. Treatment of **9** (0.2 M) with *p*-cresol (0.4 M) and triethylamine (0.4 M) with acetonitrile as solvent. Ratio of *p*-methyl hydrogen absorption to 5-methyl hydrogen absorption in isolated product mixtures; a ratio of 1.0 indicates complete substitution.

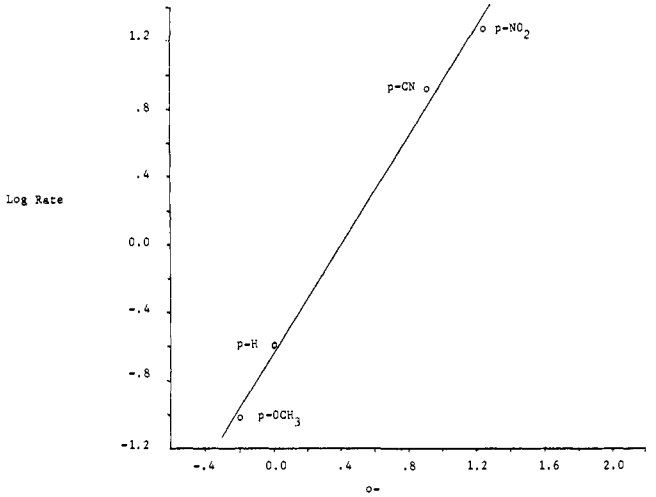
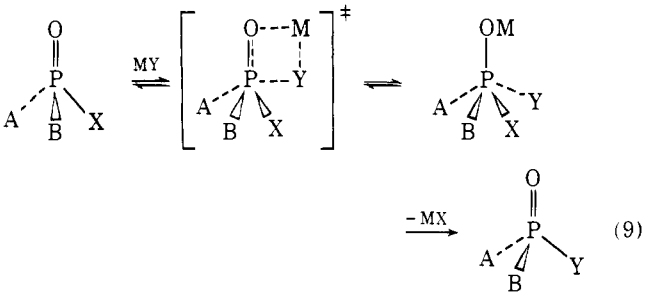


Figure 4. Hammett plot of substitution of para-substituted trans phenyl esters by *p*-methylphenoxide via retention, acetonitrile as solvent.

not cause a change in proton chemical shifts nor does it change P=O stretching frequencies or intensities.

Two possibilities for the retention mechanism exist. For the first, the ion pair might add across the phosphoryl group to form a trigonal bipyramidal intermediate similar to that depicted for the transition state of the inversion process. The intermediate must pseudorotate with the six-membered ring spanning axial and equatorial positions for groups must both enter and leave from apical positions.[14] One has difficulty rationalizing why pseudorotation would take place before departure of the leaving group, especially with chloride ion, an excellent leaving group, present initially in an apical position. One would expect inversion to always predominate and yet in the presence of lithium ion retention can be made essentially complete. Although it is conceivable that the six-membered ring can span equatorial and axial positions, such a move does present a barrier to pseudorotation.

The second alternative, the formation of a square pyramidal intermediate, is more appealing.[15] The ion pair enters from an edge position and since the only edge position which leads to inversion is blocked by the six-membered ring, retention only is possible (eq 9).



(9)

We believe the second step to be rate determining with the prior equilibrium far to the left. We have not been able to detect an intermediate and in those special cases where similar structures have been reported, structural modifications are employed to enhance their stability[16a-e]

To support our contention that the second step is the slow step, we find the process to follow a Hammett plot (Figure 4). To assure substitution by retention only, acetonitrile solutions of various trans para-substituted phenyl ethers were treated with *p*-cresol and triethylamine in the presence of lithium ion. To avoid complications due to isomerization of starting material and equilibrium, initial rates were obtained and plotted against σ^- values. A ρ value of 1.5 would indicate that breakage of the P-O bond occurs in the transition state of the slow step. Also, a change in the para substituent of the reacting phenol has little effect on the rate of substitution under these retention conditions. Thus, with 2 equiv each of lithium perchlorate, triethylamine, and *p*-cresol, 6 h was required for the substitution to be half complete whereas 7 h was required when *p*-methoxyphenol was used in place of the cresol. The slight difference, which is in a direction opposite to that expected if the first step were rate determining, may reflect merely a shift in the prior equilibrium. It would not be surprising if a tighter ion pair forms between lithium ion and *p*-methoxyphenoxide than between the same cation and *p*-methylphenoxide ion. We recognize that our data in no way exclude the possibility of a one-step mechanism proceeding through a square pyramidal transitional state and not an intermediate.

The thiophenoxide group is an excellent leaving group for retention but very poor for inversion.[8a,17] The *p*-methyl hydrogens in a *trans*-2-*p*-methylphenylthiophosphorinan are split into a doublet, J = 2.54 Hz, while those in the oxygen analogue, **6**, are unaffected by the phosphorus atom. Sulfur 3d orbitals may overlap more efficiently than oxygen 2p orbitals with phosphorus 3d orbitals, a condition which hinders the $S_N2(P)$ inversion process but evidently not the retention route. As stated earlier, methanolysis of thioesters is diverted to partial inversion if cations are added which are capable of coordinating with sulfur.

Whereas the phosphorochloridate, **1**, undergoes substitution by methoxide ion in a protic solvent, methanol, primarily by inversion, the *p*-nitrophenyl esters, **4** and **7**, under the same conditions, without added salt, substitute predominantly by retention. The change may reflect the difference in the basicities of the leaving groups. In the case of the *p*-nitrophenyl esters solvation by the protic solvent may stabilize the transition state leading to an ionic intermediate to such an extent that the retention pathway is of lower energy than the one-step inversion route. With chloride ion as a leaving group or with an aprotic solvent such would not be the case.

In the single acyclic phosphoryl system that we have looked at, ion association is important in regulation of the mechanism and rate of substitution. Diphenyl *p*-nitrophenylphosphate was selected and its rate of substitution with and without added lithium ion followed (Figure 5). The rate enhancement in the presence of lithium ion parallels that of the phosphorinans in a similar environment. Although a change in mechanism as measured by mode of substitution cannot be ascertained, from our data with the phosphorinan system we believe such an assumption to be valid. Other systems are under active investigation.

Experimental Section

NMR spectra were recorded on a Perkin-Elmer R-12B spectrophotometer and chemical shifts measured relative to a tetramethylsilane standard , $CDCl_3$ as solvent. The NMR spectra of both reactants and products have been recorded and will not be repeated.[18a-c] In general, the isomer ratios were obtained by integration of peaks due to 5-methyl hydrogens. Hydrogens of equatorial 5-methyl groups are unpfield by at least 0.3 ppm from those of axial 5-methyl groups.

Materials. The preparation and properties of the 2-substituted 5-chloromethyl-5-methyl-2-oxo(thio)-1,3,2-dioxaphosphorinans used in this work have been reported previously.[18a-c] The esters are prepared by a slightly modified procedure: addition of 2-chloro-5-chloromethyl-5-methyl-2-oxo(thio)-1,3,3-dioxaphosphorinan to a dimethylformamide solution of the sodium salt of the required phenol. All solvents were dried and distilled before use.

Substitution of 2-*p*-Nitrophenoxide ion by *p*-Methylphenoxide in DMF (2). In a typical run, Tables I and II, products were isolated by removing aliquots at regular intervals and adding them to a 20-fold excess of water. The water solutions were filtered and the product was dried under reduced pressure.

Thus, potassium *p*-methylphenoxide (0.37 g, 0.0025 mol) and anhydrous lithium perchlorate (0.53 g, 0.005 mol) were dissolved in 20 mL of dried and distilled DMF. The ester, *cis*-2-*p*-nitrophenyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan (**4**, 0.8 g, 0.0025 mol) was added and the solution immediately made up to 25 mL. Aliquots, 5 mL, were removed at 10-min intervals and added to 100 mL of water. The mixtures were allowed to stand for 1 h before workup.

Substitution of 2-*p*-Nitrophenoxide Ion by Methoxide Ion. Owing to the relatively low melting point of the methyl esters, substitutions conducted in methanol varied slightly from those in DMF. To 15 mL of methanol was added *trans*-2-*p*-nitrophenyl-5-chloromethyl-5-methyl-2-oxo-1,3,2-dioxaphosphorinan (**7**, 1.6 g, 0.005 mol) and triethylamine (0.51 g, 0.005 mol). The mixture after being diluted to 25 mL with methanol was allowed to stand for 1 h. Solvent was removed at reduced pressure (20 mm, 30 °C) and the residue extracted from water with two 20-mL portions of CH_2Cl_2. After combined extracts were dried over $CaCl_2$ and the solvent was removed, the residue was dissolved in $CDCl_3$ and its spectrum recorded.

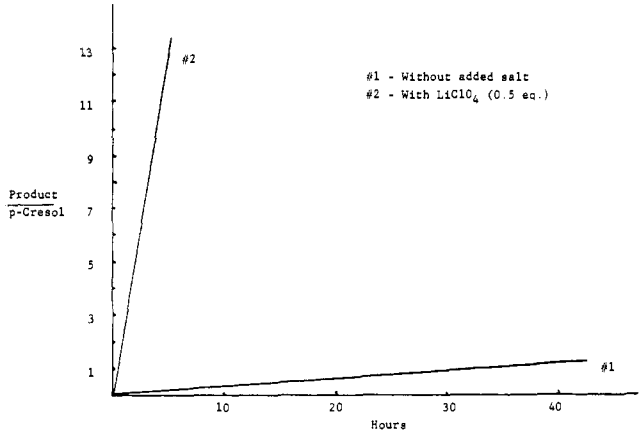


Figure 5. Treatment of diphenyl *p*-nitrophenylphosphate (0.1 M) with *p*-cresol (0.1 M) and triethylamine (0.1 M), acetonitrile as solvent.

An identical procedure was followed in those cases where the phosphorochloridate **1** was employed with the exception that the chloridate was added to the triethylamine-salt-methanol mixtures.

Isomerization of 2-*p*-Nitrophenylphosphorinans. An identical procedure was followed in all cases. The esters were dissolved in DMF, the required amount of sodium *p*-nitrophenoxide was added, and aliquots were periodically removed. Isomerization was quenched by adding the aliquots to water and the isomer ratios were obtained by filtering, drying the precipitate, and obtaining an NMR spectrum of the solid. Integration of peaks due to 5-methyl hydrogens afforded the isomer ratio.

***p*-Methylphenyl Ester (6) from trans-*p*-Nitrophenyl Ester (7), *p*-Cresol, and Triethylamine.** A procedure similar to that used for isomerization studies was employed. Aliquots of the acetonitrile solutions were added to an excess of water. After standing for a few hours, the solutions containing the insoluble crystalline product and reactant mixture were filterd, the precipitate was dried, and NMR spectra were obtained. The extent of reaction was determined by comparison of the peak area due to the *p*-methyl hydrogens of the product to the total absorption due to the 5-methylphosphorinan hydrogens of both product and reactant. A ratio of one corresponds to complete substitution.

Addition of the ester to an acetonitrile solution of triethylamine containing 1 equiv of lithium, sodium, or potassium perchlorate in the absence of *p*-cresol gives an almost immediate precipitate of the salt of the cyclic acid formed by C-O bond cleavage. In the case of the lithium cyclic phosphate, its identity was confirmed by comparison of its IR spectrum with that of an authentic sample. Similar results are obtained in the presence of *p*-cresol in the case of the sodium and potassium salts but precipitation is nearly negligible with lithium perchlorate.

Diphenyl *p*-Nitrophenylphosphate and *p*-Methylphenoxide. Diphenyl *p*-nitrophenylphosphate[18] (1.86 g, 0.005 mol), *p*-cresol (0.54 g, 0.005 mol), and anhydrous $LiClO_4$ (0.27 g, 0.0024 mol) were added to 25 mL of dried and distilled acetonitrile. Triethylamine (0.51 g, 0.005 mol) was added and the solution diluted immediately to 50 mL with acetonitrile. Aliquots (10 mL) were withdrawn and immediately added to 200 mL of water. The aqueous solutions were extracted with two 50-mL portions of methylene chloride, the combined extracts were dried over calcium chloride, and solvent was removed under reduced pressure. Spectra of the liquid residues dissolved in deuteriochloroform were taken and the peak areas due to *p*-methyl hydrogens of unreacted *p*-cresol, δ 2.20, were compared to those of the *p*-methyl hydrogens of the *p*-methylphosphate product, δ 2.28. No precipitation of lithium diphenylphosphate takes place during the course of the reaction.

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A Phosphorus Analogue of α-Pyrone and Evidence for Monomeric Mesitylmetaphosphonate

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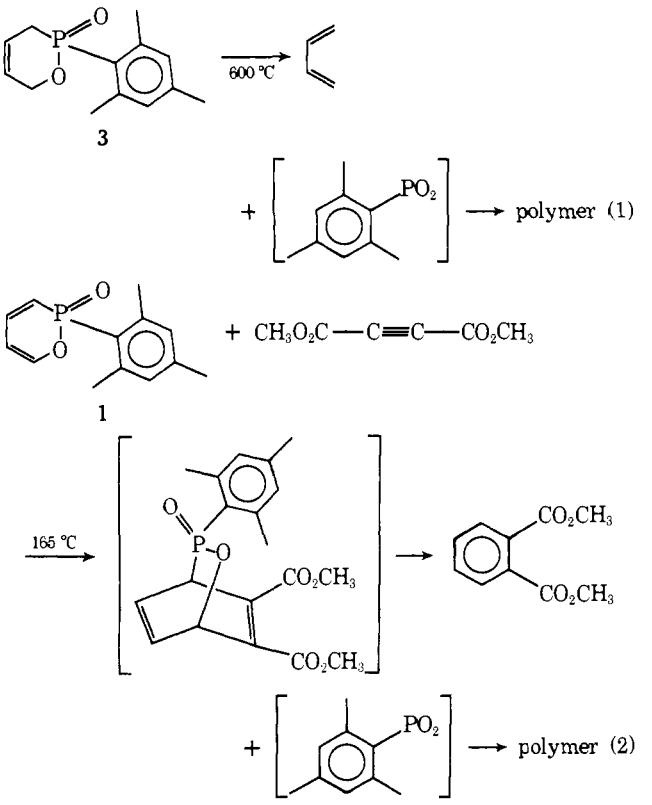
Abstract: A phosphorus analogue of α-pyrone, **1**, has been prepared by the addition of bromine to mesityl-2-butenylphostinate, followed by dehydrobromination. The compound undergoes Diels–Alder addition with maleic anhydride or dimethyl acetylenedicarboxylate, but only at temperatures above 140 °C; the postulated adducts apparently decompose at that temperature to yield the expected dihydroaromatic or aromatic compound, plus a polymer of mesitylmetaphosphonate. The latter has also been obtained by the pyrolysis of mesityl-2-butenylphostinate, **3**. These latter findings help illuminate the chemistry of monomeric metaphosphonates. Furthermore, both the polymerization and other data suggest that steric hindrance is not important for reactions at the phosphorus atom of mesitylphosphonate.

In pursuing investigations carried out in these laboratories,[2,3] on the chemistry of monomeric metaphosphates, we have attempted to prepare monomeric mesitylmetaphosphonate, $(CH_3)_3C_6H_2PO_2$. Evidence has been obtained that this compound can be produced by either of two methods: (1) pyrolysis of mesityl-2-butenylphostinate (**3**) according to eq 1, or (2) by the reaction of mesityl-2,4-butadienylphostinate[4] (**1**) with dienophiles. Presumably the Diels–Alder reaction with dimethyl acetylenedicarboxylate proceeds as shown in eq 2, and the reaction with maleic anhydride as shown in eq 3. In neither case, however, was either the initial adduct or the monomeric mesitylmetaphosphonate isolated; their formation has been inferred from the isolation of polymeric mesitylmetaphosphonate from both reactions, and from the isolation of dimethyl phthalate and of *cis*-bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic dianhydride, respectively, from the processes shown in eq 2 and 3. The stereochemistry of the Diels–Alder adducts is entirely conjectural, since neither was isolated.

Mesityl-2,4-butadienylphostinate (the phosphorus analogue of α-pyrone) was prepared as shown in eq 4. Evidence for these statements and the validity of these equations and a discussion of the polymerization of the postulated monomeric mesitylmetaphosphonate are presented below.



Experimental Section

Methods. ^1H NMR spectra were obtained with a Varian A-60, T-60, or CFT-80 spectrometer, and the data are quoted in parts per million downfield from Me_4Si. ^1H noise-decoupled ^{31}P NMR spectra

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