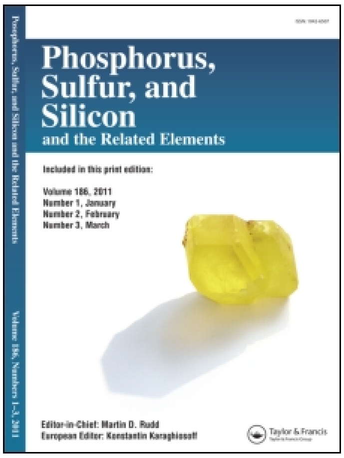

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SUBSTITUENT EFFECTS OF PHOSPHORUS CONTAINING GROUPS

Concerning the Meta-Nitration of the N- and O-Phosphorylated Aniline and Phenol

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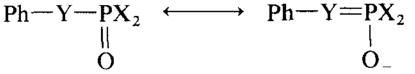
Polar effects of the acylated amino and hydroxy groups NH—X, O—X (X = $COCH_3$, PO_3Et_2) upon the adjacent benzene ring are compared. The specific mechanism for the *meta* nitration of the phosphoryl derivatives, involving the nucleophilic assistance of the PO group, is postulated.

In our studies on aromatic nitration we found[1] that the acylation of the amino and hydroxy functions of aniline and phenol by the acetyl or diethylphosphoryl groups results in a remarkably different orientation effects of these substituents. Acetanilide and phenyl acetate are exclusively *ortho/para* directing both in acidic and aprotic medium (% *meta*<2), whereas the corresponding N- and O-phosphorylated compounds yield *ortho*, *meta* and *para* products in comparable amounts (17–38 % of *meta* products). In the aprotic medium, where the participation of substrate's conjugate acid need not to be taken into account, the interpretation of the drastic decrease in the intramolecular selectivity observed for the Ph—Y—P(O)(OEt)$_2$ (Y = NH, O) system is difficult. The obvious implication is that the nitrogen (and oxygen) nonbonding electrons are involved in the $p_\pi - d_\pi$ back-donation to phosphorus to a greater extent than in the conjugation with carbonyl group. Such an involvement, illustrated by the resonance structure (**Ia**) would of course reduce significantly the highly selective *ortho/para* resonance donation of the nonbonding electrons of Y to the benzene ring.



$$\mathrm{Ph{-}\overset{\times\times}{Y}{-}\underset{\underset{O}{\|}}{P}X_2} \longleftrightarrow \mathrm{Ph{-}\overset{+}{Y}{=}\underset{\underset{O_-}{|}}{P}X_2} \qquad (1)$$

(**I**) (**Ia**)

According to this interpretation, phosphorylated derivatives should be also much less reactive in electrophilic substitution than their acetylated analogues; both because of the decrease of the -M effect of the substituent, and location of the positive charge in close proximity of the ring.

We have determined the relative reactivities of the N-phenyldiethylphosphoramidate and acetanilide as well as phenyldiethyl phosphate and phenyl acetate for nitration in acetic anhydride. Since both aniline derivatives give under these conditions almost identical proportions of the *p*-nitro product,[1] the relative total reactivities were determined by following spectrophotometrically the conversion of a substrate into the mixture of nitrocompounds. For phenol derivatives where different quantities of the *para* and *ortho* products are formed for the phosphoryl and acetyl compounds, the relative reactivities for the substitution at these two positions have been determined using the previously described[2] analytical technique. Relative reactivities are presented in Table I.

It is obvious that a difference in orientation cannot be a consequence of a difference in activation of the ring; both anilides have practically identical reactivity, and phenyl phosphate is only slightly less reactive than the acetyl compound.

Polar effects of the phosphoryl and carbonyl containing functions can also be examined by

TABLE I

Relative rates of nitration by acetyl nitrate in acetic anhydride, 25°C

Substrate	$k_{P(O)(OEt)_2}/k_{Ac}$		Number of determinations
Ph—NH—X	1.00 ± 0.20		25
	ortho	para	
Ph—O—X	0.35 ± 0.10	0.43 ± 0.12	4

another approach. Dual substituent parameter analysis[3] of the substituent-induced ^{13}C NMR chemical shift of the *meta* and *para* carbon atoms in compound PhX provides information about the inductive (σ_I) and resonance (σ_R°) contributions to the net electronic effects of substituent X. Such approach has been applied to the organophosphorus substituents[4] and the relevant values of substituent constants are listed in Table II.

Both phosphorylated groups are in fact *stronger* resonance donors than their acetyl analogues. Relative reactivities in nitration seem to follow the inductive parameters of the substituents. This is not surprising, since for electrophilic substitution resonance effects should rather be described using the σ_R^+ set of substituent constants.[5] The high demand for the resonance donation in the transition state of nitration would make all σ_R values much more negative than those evaluated from shielding effects, and the differences between individual constants would be most likely considerably decreased.

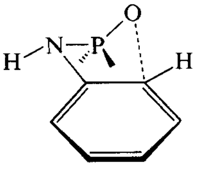
The striking difference in product distribution for the acetyl and phosphoryl derivatives of aniline and phenol cannot be therefore explained in terms of the conventional effects of substituents upon the reactivity of an aromatic ring.

We postulate that the observed effects result from the specific nucleophilic assistance of the phosphoryl group, selectively facilitating *meta*-substitution as a consequence of different geometry of the phosphoryl and acetyl derivatives. Acetanilide molecule is planar due to the extended conjugation involving 2p orbitals of the ring, nitrogen, and carbonyl group.[6] In the N-phenylphosphoramidate system, the conjugation of the nitrogen lone pair with phosphorus is negligible,[4] so the condition of coplanarity of the PhNPO system is removed. This should result in the essentially free rotation around the PN bond; conformational equilibrium (PN rotation) has been indeed demonstrated in the IR studies of the Ph—NH—P(O)Cl$_2$ molecule.[7] Assuming the free rotation around the PN bond, the examination of the molecular models shows that in the conformation A of the N-phosphorylated aniline the phosphoryl oxygen is located *above* the *ortho*-carbon atom at a distance not greater than 2 Å.

TABLE II

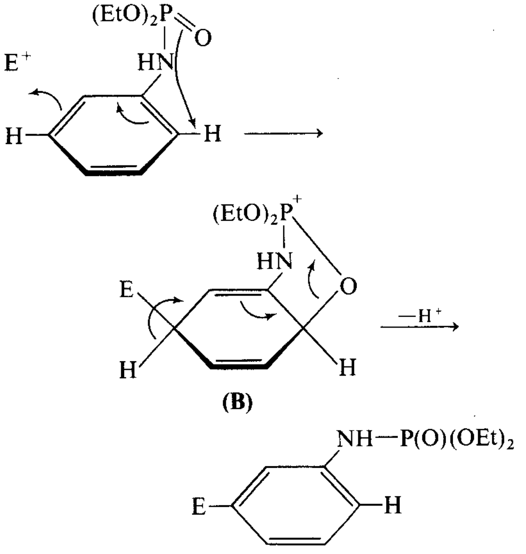
Estimated σ_I and σ_R^0 constants

X in PhX	σ_I	σ_R^0
NH—Ac	+0.16	−0.21
NH—P(O)(OEt)$_2$	+0.16	−0.40
O—Ac	+0.46	−0.22
O—P(O)(OEt)$_2$	+0.58	−0.29



(A)

If the attack of an electrophile takes place at the carbon *meta* to the nitrogen, one can envisage the reaction sequence involving the quasiphosphonium intermediate represented by the quinoidal resonance structure (**B**).†



(B)

(2)

Pathway (2) (or the analogous sequence for the derivative of phenol) should lower the activation

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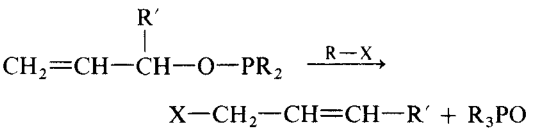
† Molecular models demonstrate that the structure (**B**) is virtually free of any angle or torsional strain.

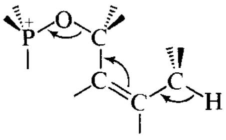
energy for *meta*-substitution relative to the "normal" attack at the *ortho* and *para* positions proceeding via the ammonium-like quinoidal intermediates.

The driving force for the collapse of the intermediate (B) is the rearomatization of a system and reestablishment of the phosphoryl group. Electrons reorganization involved in this process corresponds closely to that occuring in the collapse of the intermediate formed in Arbuzov reaction of the secondary allylic esters:[8]

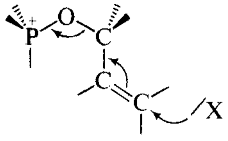


$$CH_2{=}CH{-}\overset{\overset{\textstyle R'}{|}}{C}H{-}O{-}PR_2 \xrightarrow{R-X} X{-}CH_2{-}CH{=}CH{-}R' + R_3PO \quad (3)$$

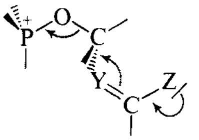
Decomposition of an adduct of diethyl phosphorisocyanatidite to α-oxophosphonic esters yielding mixtures of N- and O-ethylated 1,3,2-oxaphospholine derivatives[9] provides another example of similar collapse involving formation of the phosphoryl group, accompanying by the π bond migration and the shift of the σ bond or nonbonding electrons in an uni- or bimolecular process. The close analogy between these reactions can be easily demonstrated comparing the molecular frameworks and shifts of electrons actually involved in the product-determining steps:



Meta-nitration



Arbuzov reaction



Oxaphospholine formation (Y = O,N; Z = N,O)

EXPERIMENTAL

Products determination for nitration in acetic anhydride[1] and evaluation of reaction constants by ^{13}C NMR spectroscopy[10] have been described before.

Relative Rates

Solutions of identical concentrations of acetanilide and *N*-phenyldiethylphosphoramidate in acetic anhydride were treated with the solution of nitric acid in acetic anhydride at 25°C. Samples were taken simultaneously at intervals (corresponding to 10-60% of reaction) and the concentrations of nitroproducts were determined directly from the UV spectrum of the solutions at 320-330 nm. For phenyl acetate and phenyldiethyl phosphate samples of reaction mixtures were made alkaline in aqueous sodium hydroxide, refluxed until hydrolysis was complete, and the concentrations of the *ortho* and *para*-nitrophenol determined by the t.l.c. separation followed by the spectrophotometric estimations as described before.[2] Relative reactivities were calculated according to the Ingold equation.[11]

ACKNOWLEDGEMENT

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