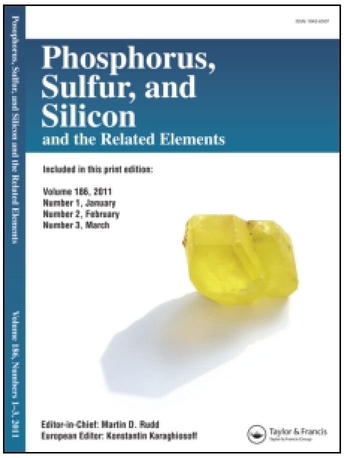

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REVIEW CHARACTERISTIC REACTIONS OF THE ALKOXY GROUPS OF THE ACID DIESTERS OF PHOSPHOROUS ACID

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REVIEW
CHARACTERISTIC REACTIONS OF THE ALKOXY GROUPS OF THE ACID DIESTERS OF PHOSPHOROUS ACID

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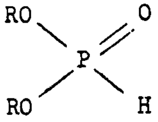
This review presents the characteristic reactions of the alkoxy group of the acid diesters of phosphorous acid $(RO)_2P(O)H$: transesterification—with the phosphorus atom as the reaction center; alkylation—with the α-carbon atom as the reaction center; dealkylation—with the α-carbon atom as the reaction center. The possibilities of these reactions in the synthesis of end products with various structures and compositions are demonstrated. The perspectives for the practical application of these esters of phosphorous acid are discussed.

INTRODUCTION

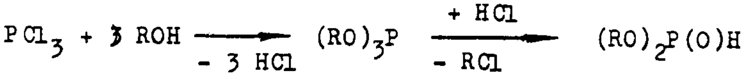
The chemistry of the organophosphorus compounds has nearly a centennial history. During the last several years, it has exhibited a dramatic development associated with the ever growing practical application of the organophosphorus compounds, i.e., as pesticides, plasticizers, stabilizers, extraction solvents, additives, medicines, catalysts, etc. All these developments are a result of progress in the chemistry of organophosphorus compounds. Until recently this progress was limited only to the methods of synthesis of new organophosphorus compounds, while in the last few years a clearly expressed tendency towards the theoretical investigation of their reactivity has been observed. This line of investigation revealed a more rational utilization of organophosphorus compounds as starting monomers in the synthesis of end products with various structures and compositions.

The acid diesters of phosphorus acids occupy an important position among the organophosphorus compounds. In the literature they are known as dialkyl phosphites:



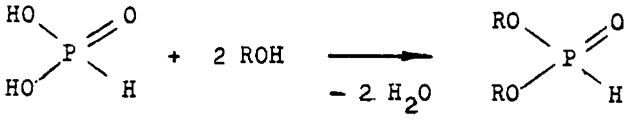
They are commercially available and their industrial synthesis is based on two starting monomers:

—phosphorus trichloride:[1]



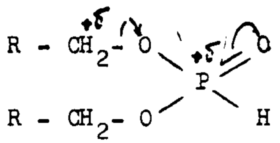
$$PCl_3 + 3\,ROH \xrightarrow[-\,3\,HCl]{} (RO)_3P \xrightarrow[-\,RCl]{+\,HCl} (RO)_2P(O)H$$

—phosphorous acid:[2]



CHARACTERISTIC REACTIONS OF THE ALKOXY GROUPS OF THE ACID DIESTERS OF PHOSPHOROUS ACID

The structure of the acid diesters of phosphorous acid makes it possible to predict their chemical properties:

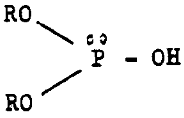


The presence of the phosphoryl group (P=O) in the molecule results in a reduction of the electron density at phosphorus and at the α-carbon atoms. Being electron-deficient centers, these atoms are vulnerable to the attack by nucleophiles, as a result of which the following reactions occur: transesterification with the phosphorus atom as the reaction center; alkylation and dealkylation with the α-carbon atom in the alkoxy group as the reaction center.

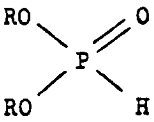
Transesterification Reaction

Despite the numerous investigations of the transesterification of the acid diesters of phosphorous acid with hydroxyl-containing compounds, the mechanism of this reaction is still uncertain. There is no agreement on the reaction forms with which esters take part in the reaction. On the basis of the available experimental data, two propositions have been advanced:

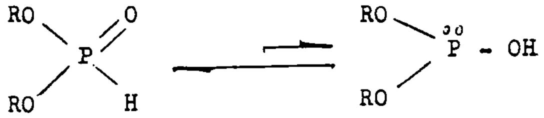
—the first reaction form is a 3-coordinate one:[3-5]



—the second reaction form is a 4-coordinate one:[6,7]

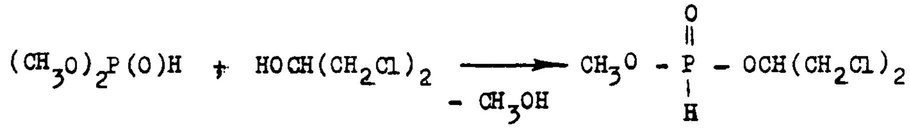


The basis for the first proposition is the observed tautomerism of dialkyl phosphites:[8,9]



The acceleration of the transesterification reaction by basic catalysts or, in cases when dioxane is used as a solvent,[4,10] associated with the tautomeric equilibrium.

Another reason for this assumption is the kinetic data, observed in some cases of transesterification. For example, the initial reaction rate of transesterification of dimethyl phosphite with 1,3-dichloro-2-propanol[11]



$$(CH_3O)_2P(O)H + HOCH(CH_2Cl)_2 \xrightarrow[-\ CH_3OH]{} CH_3O-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OCH(CH_2Cl)_2$$

depends only upon the concentration of dimethyl phosphite (Table I). The experimental data do not fit the kinetic equation for a second order bimolecular reaction. The authors describe the reaction as a monomolecular one, thus implying that the reaction form of the dialkyl phosphites during transesterification is the 3-coordinate one, inasmuch as the tautomeric conversion, being the first step of the reaction and the slowest one, will determine the rate of the transesterification.

This assumption is supported by the observed initial reaction rate in the presence of morpholine. The substantially higher rate can be attributed to the effect of morpholine on the rate of reaching the tautomeric equilibrium. It is agreed[12] that the concentration of the 3-coordinate form increases in the presence of basic compounds.

TABLE I

Kinetic data for the transesterification of dimethyl phosphite with 1,3-dichloro-2-propanol

C_{DMPh}	C_{DCP}	W_0	$k = \frac{W_0}{C_{DMPh} \cdot C_{DCP}}$	$k = \frac{W_0}{C_{DMPh}}$
mol/l	mol/l	mol/l · min	l/mol · min	min^{-1}
3.65	7.23	0.18	7.8×10^{-3}	0.049
7.17	3.65	0.33	12.6×10^{-3}	0.046
3.37*	7.04	0.57	24.0×10^{-3}	0.169

DMPh—dimethyl phosphite; DCP—1,3-dichloro-2-propanol.

*The experiment is carried out in the presence of morpholine as catalyst.

TABLE II

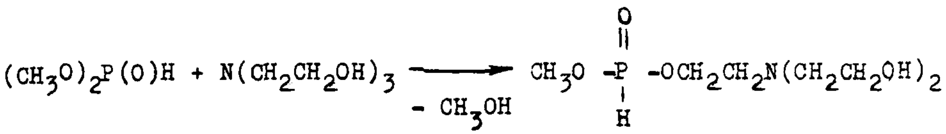
Kinetic data for the transesterification of dimethy phosphite with triethanolamine

C_{DMPh}	C_{TEA}	W_0	$k = \dfrac{W_0}{C_{DMPh} \times C_{TEA}}$
mol/l	mol/l	mol/l · min	l/mol · min
2.79	5.58	2.97	0.184
6.31	3.15	2.93	0.164

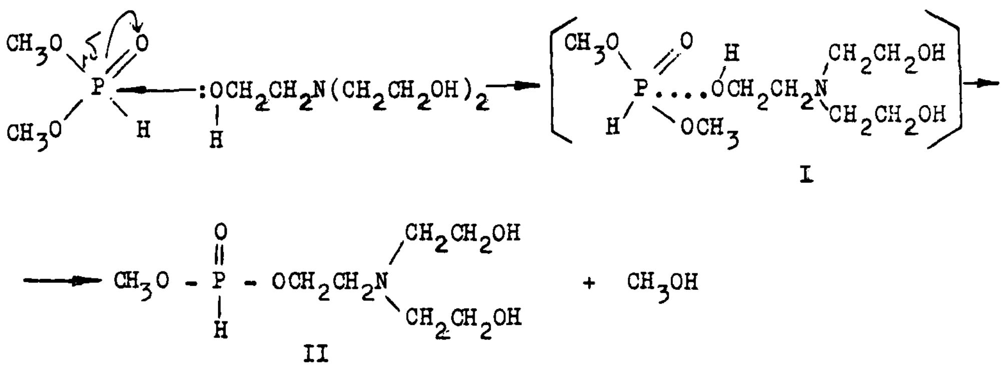
DMPh—dimethyl phosphite; TEA—triethanolamine.

The kinetic data suggest that the reaction form of the acid diesters of phosphorous acid during transesterification is the 4-coordinate one.

It is established,[13] that the transesterification of dimethyl phosphite with triethanolamine proceeds via a bimolecular nucleophilic substitution, the rate of which depends upon the concentration of both reagents:

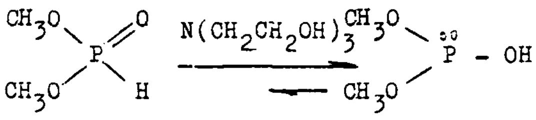


$$(CH_3O)_2P(O)H + N(CH_2CH_2OH)_3 \xrightarrow[- CH_3OH]{} CH_3O\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle H}{|}}{P}}-OCH_2CH_2N(CH_2CH_2OH)_2$$



The reaction was proposed to start with a nucleophilic attack of the oxygen atom on the phosphorus atom, as a result of which the transition state I formed which then decomposed with the evolution of alcohol and the formation of the monotransesterified product II.

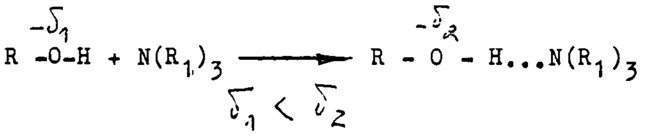
The same kinetic data also render probable a reaction scheme, according to which the reaction form is a 3-coordinate one. Why? In this case the basic compound is not present in catalytic amounts, but is commensurate with the concentration of dimethyl phosphite. This will bring about not only a faster establishment of the equilibrium, but also a change in the equilibrium constant. It can be therefore assumed that in the presence of a large amount of triethanolamine the dimethyl phosphite will be present exclusively in 3-coordinate form and that the tautomeric equilibrium will be not the rate determining step.



Since in this case the probability for the existence of the 3-coordinate form is the largest (higher basicity of the reaction medium), and investigation was carried out on the reaction mixture at various stages of completeness by means of ^{31}P-NMR spectroscopy. It was established that the spectrum reveals only the peaks of the 4-coordinate phosphorus atom at δ, ppm 9.8–12. This unequivocally indicates that the acid diesters of phosphorous acid take part in the transesterification reaction in their 4-coordinate form.

This conclusion entails a review of the explanation concerning the observed acceleration of the transesterification reaction by basic compounds, which has been related to the faster shift of the tautomeric equilibrium in the direction of 3-coordinate form.

The catalytic action of amines in the transesterification of dialkyl phosphites with hydroxyl-containing compounds could be interpreted in terms of the mechanism of basic catalysis.[14,15]



$$R-\overset{-\delta_1}{O}-H + N(R_1)_3 \longrightarrow R-\overset{-\delta_2}{O}-H\ldots N(R_1)_3$$
$$\delta_1 < \delta_2$$

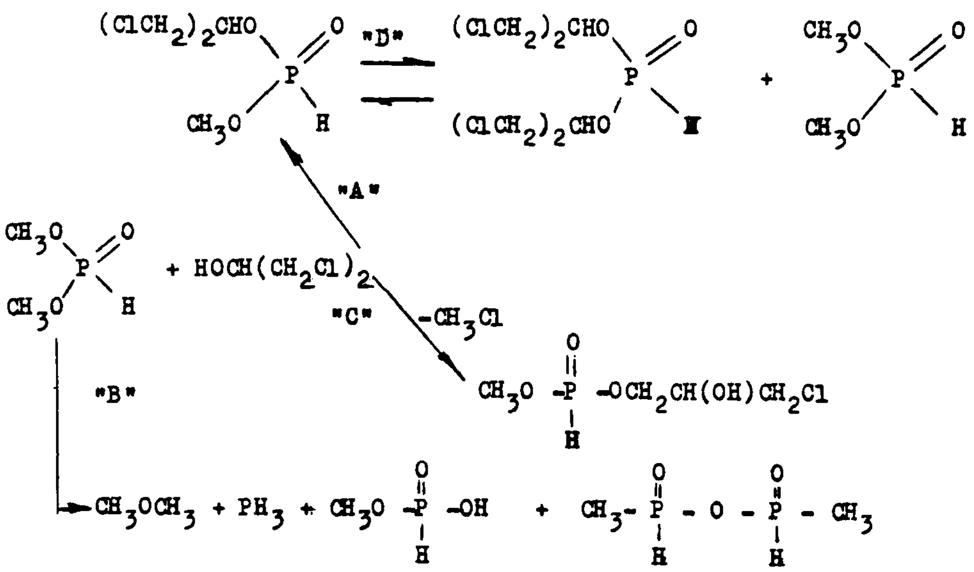
The protonation of the nitrogen atom will produce an increase in the electron density of the oxygen atom in the OH-group, which in turn will bring about a faster formation of the P—O bond in the transition state I (see p. 132).[16]

A detailed investigation of the transesterification of dimethyl phosphite with 1,3-dichloro-2-propanol reveals that it is accompanied by several side reactions: pyrolysis of dimethyl phosphite[17]—direction "B;" dealkylation[11]—direction "C;" disproportionation[18]—direction "D."

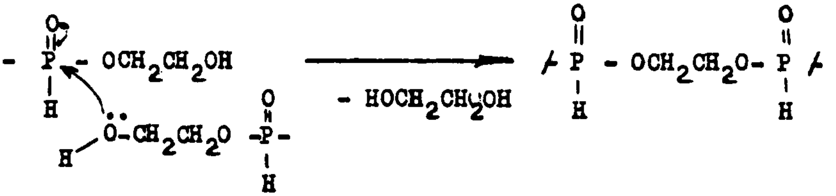
Obviously, the omission of these side reactions in the interpretation of the kinetic data is the reason for erroneous descriptions of the transesterification of dimethyl phosphite with 1,3-dichloro-2-propanol as a monomolecular reaction.

Depending on the molar ratios between the initial components and the reaction conditions, the following end products have been obtained in the transesterification of dialkyl phosphites with diols: monotransesterified product—linear I;[19,20] cyclic I-A;[21,22] bisphosphites—II;[23,24] bis(hydroxyl) phosphites—III;[25] oligomers—IV[26-47] (see the scheme on p. 134).

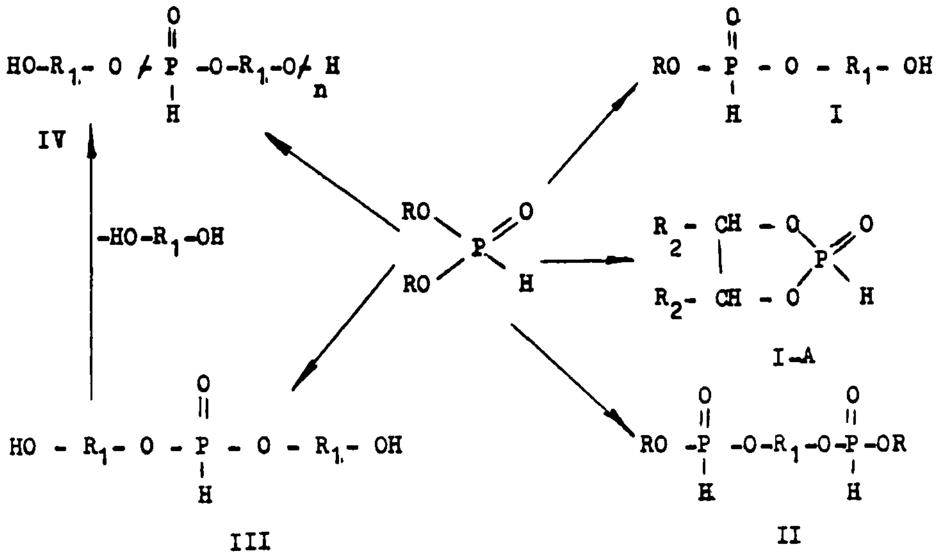
It was shown[16] that upon the elimination of the excess of diol from the reaction system, there proceeds a condensation of the bis(hydroxyalkyl) phosphites, similarly to the case of bis(2-hydroxyethyl) terephthalate, as a result of which oligomeric products are obtained. The condensation reaction of bis(hydroxyalkyl) phosphites is determined by the effect of the phosphoryl group (P=O) on the electronic density of the phosphorus atom and the reaction starts with a nucleophilic attack of the



oxygen atom on the phosphorus atom as a result of which ethylene glycol evolves and oligomeric product is obtained:



End products of the transesterification of dialkyl phosphites with diols



Alkylation Reaction

The interaction between phosphorous organic compounds and amines was reported by Baddiley and co-workers[48] in 1949:

$$(R)_3N + (PhCH_2O)_2P(O)Cl \longrightarrow \left[(R)_3NCH_2Ph\right]^{+}\left[O\text{-}P(O)(Cl)OCH_2Ph\right]^{-} \longrightarrow$$

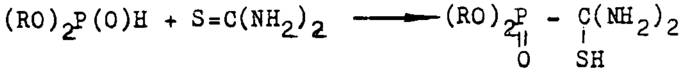
$$\longrightarrow \left[(R)_3\overset{+}{N}\text{-}CH_2Ph\right] Cl^{-} + PhCH_2OPO_2$$

This procedure was used as a method for the preparation of monoesters of the phosphoric and the phosphorous acids.

Later several patents[49–52] described the conditions for this procedure, showing that at high temperatures (200–250°C) aromatic amines can also be alkylated:

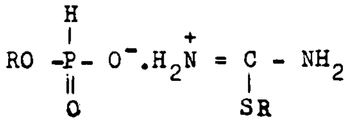
$$(RO)_2P(O)H + PhNH_2 \xrightarrow{200\text{–}230°C} PhNHR + PhNH_2 + PhNR_2 + (HO)_2P(O)H$$

Abramov[53] studied the reaction of dialkyl phosphites with thiourea, assuming that the end product has the following structure:



$$(RO)_2P(O)H + S{=}C(NH_2)_2 \longrightarrow (RO)_2\underset{\substack{\|\\ O}}{P} - \underset{\substack{|\\ SH}}{C}(NH_2)_2$$

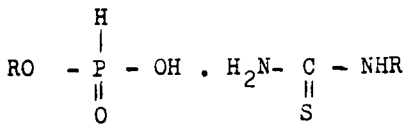
Miller and O'Leary[54] investigated the structure of the product of the same reaction by ^{1}H-NMR spectroscopy and proposed the following structure:



$$RO-\overset{\substack{H\\ |}}{\underset{\substack{\|\\ O}}{P}}-O^{-}.H_2\overset{+}{N}=\underset{\substack{|\\ SR}}{C}-NH_2$$

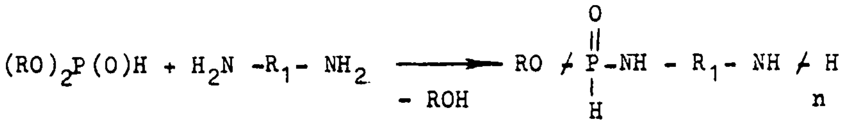
i.e., these authors assume an *S*-alkylation.

Parker and Smith[55] consider that the reaction between dialkyl phosphites and thiourea is accompanied by the alkylation of the amine as well as by the formation of a salt between the monoester of phosphorous acid and thiourea:



$$RO-\overset{\substack{H\\ |}}{\underset{\substack{\|\\ O}}{P}}-OH\ .\ H_2N-\underset{\substack{\|\\ S}}{C}-NHR$$

McConnell and co-workers[56] affirm that during the reaction between dialkyl phosphites and diamines a transesterification proceeds:

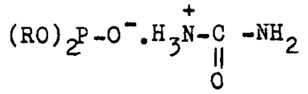


$$(RO)_2P(O)H + H_2N-R_1-NH_2 \xrightarrow[-\ ROH]{} RO\left[\overset{\substack{O\\ \|}}{\underset{\substack{|\\ H}}{P}}-NH-R_1-NH\right]_n H$$

On the other hand it is assumed[57–60] that as a result of the reaction of the acid diesters of phosphorous acid with amines a salt is formed between the 3-coordinate form and the amine:

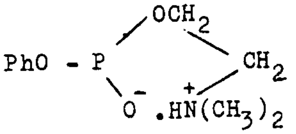
$$(RO)_2P{-}O^{-}.H\overset{+}{N}(R_1)_3$$

A similar structure is also proposed for the product of the reaction between dialkyl phosphites and urea:[61]

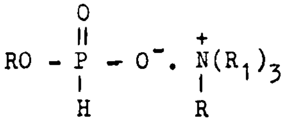


$$(RO)_2P{-}O^{-}.H_3\overset{+}{N}{-}\underset{\underset{O}{\|}}{C}{-}NH_2$$

In the transesterification of diphenyl phosphite with dimethylaminoethanol,[5] a product is obtained in which the diphenyl phosphite appears in its 3-coordinate form according to the authors:



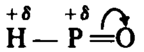
According to Thoung,[62] an alkylation of the amine proceeds also during the reaction between amines and dialkyl phosphites:



$$RO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O^{-}.\ \overset{+}{\underset{\underset{R}{|}}{N}}(R_1)_3$$

The structure of the end product was determined by means of ^{1}H-NMR and ^{31}P-NMR spectroscopy. Only the system dimethyl phosphite/dimethylamine was studied in this case and without separation of the end product.

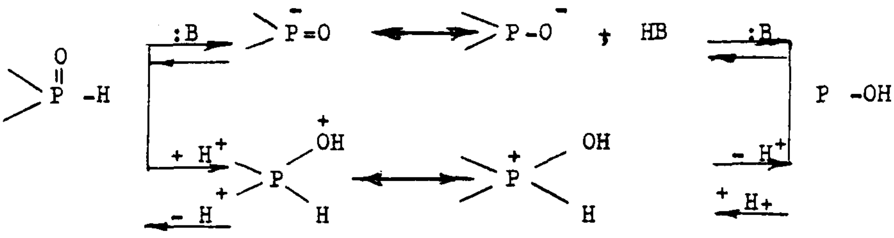
As shown by the above review, different assumptions have been presented regarding the mechanism and the structure of the end products of the reaction of dialkyl phosphites with amines. What is the reason for these differences? While in the case of full esters of phosphoric and phosphonic acids the alkylation reaction is the only possible one, in the case of the acid diesters of phosphorous acid the formation of a salt between the amine and the 3-coordinate form is also admitted. Why? In contrast with the esters of the phosphoric and the phosphonic acids, the diesters of the phosphorous acid has a mobile hydrogen atom



$$\overset{+\delta}{H}-\overset{+\delta}{P}{=}O$$

which according to Rasoumov and co-workers[63] determines the tautomerization, observed with the esters of phosphorous acid.[8,9]

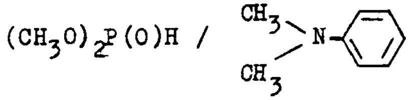
Tautomerization is a process accelerated by both acid and bases:[64]



The existing tautomerization has led many authors[57-60] to suppose that a reaction proceeds with salt formation between the 3-coordinate form and the amine and that no alkylation occurs.

The determination of the structure of the product of the reaction between dialkyl phosphites and amines will make it possible to prove the mechanism of transesterification of dialkyl phosphites with hydroxyl-containing compounds, the reaction between dialkyl phosphites and sulfur, as well as to explain the observed catalytic effect of amines on the transesterification reaction, as well as the addition of dialkyl phosphites to isocyanates and compounds with double and triple bonds.

We studied the system dimethyl phosphite/dimethylaniline*

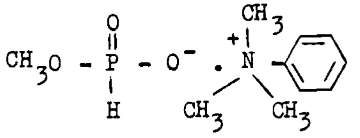


The ^{1}H-NMR spectrum of the mixture before heating (Figure 1a) revealed signals for the following protons δ, ppm: 0.83 (1 H, d, P—H, J_{Ph} = 703 Hz); 2.85 (6 H, s, CH_3—N); 3.66 (6 H, d, CH_3—O—P, J_{CH} = 12 Hz); 6.61–7.50 (5 H, m, ArH), characterizing the starting compounds. The spectrum of the same mixture after heating to 130°C indicates that a change has occurred (Figure 1b); there appear two types of P—H protons at δ, ppm 0.90 with J_{PH} = 703 Hz and 1.86 with J_{PH} = 604 Hz; two types of aromatic protons at δ, 6.61–7.47 and 7.72–8.21.

A product was isolated by crystallization in absolute ethanol. The ^{1}H-NMR spectrum disclosed the following protons: (Figure 1c), δ, ppm 1.83 (1 H, d, P—H, J_{PH} = 604 Hz); 3.51 (3 H, d, CH_3O—P, J_{CH} = 12 Hz); 3.91 (9 H, s, CH_3—N); 7.42–8.21 (5 H, m, ArH).

The total numbers of protons and their distribution (Table III) indicates that the compound obtained as a result of the reaction of dimethyl phosphite with dimethylaniline has 18 protons with an integral intensity at δ, ppm 3.91 for the CH_3—N protons corresponding to 9 H, and that at 3.51 for CH_3O—P to 3 H. The signal at 1.83 ppm can be assigned to the P—H proton with a coupling constant of 604 Hz. A signal at 10.57 ppm is observed in the ^{31}P-NMR spectrum, characteristic for the 4-coordinate phosphorus atom.[65]

The data from the ^{1}H, ^{31}P, and ^{13}C-NMR spectroscopic investigations indicate that the end product has the following structure:



i.e., it is the α-carbon atom of the alkyl group of the dialkyl phosphites which takes part in the reaction between dialkyl phosphites and amines and not the hydrogen atom of the P—H group as assumed so far by many investigators. In addition, the

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*This investigation was carried out jointly with Prof. Dr. S. Nakahama, Tokyo Institute of Technology, Department of Polymeres, in 1983.

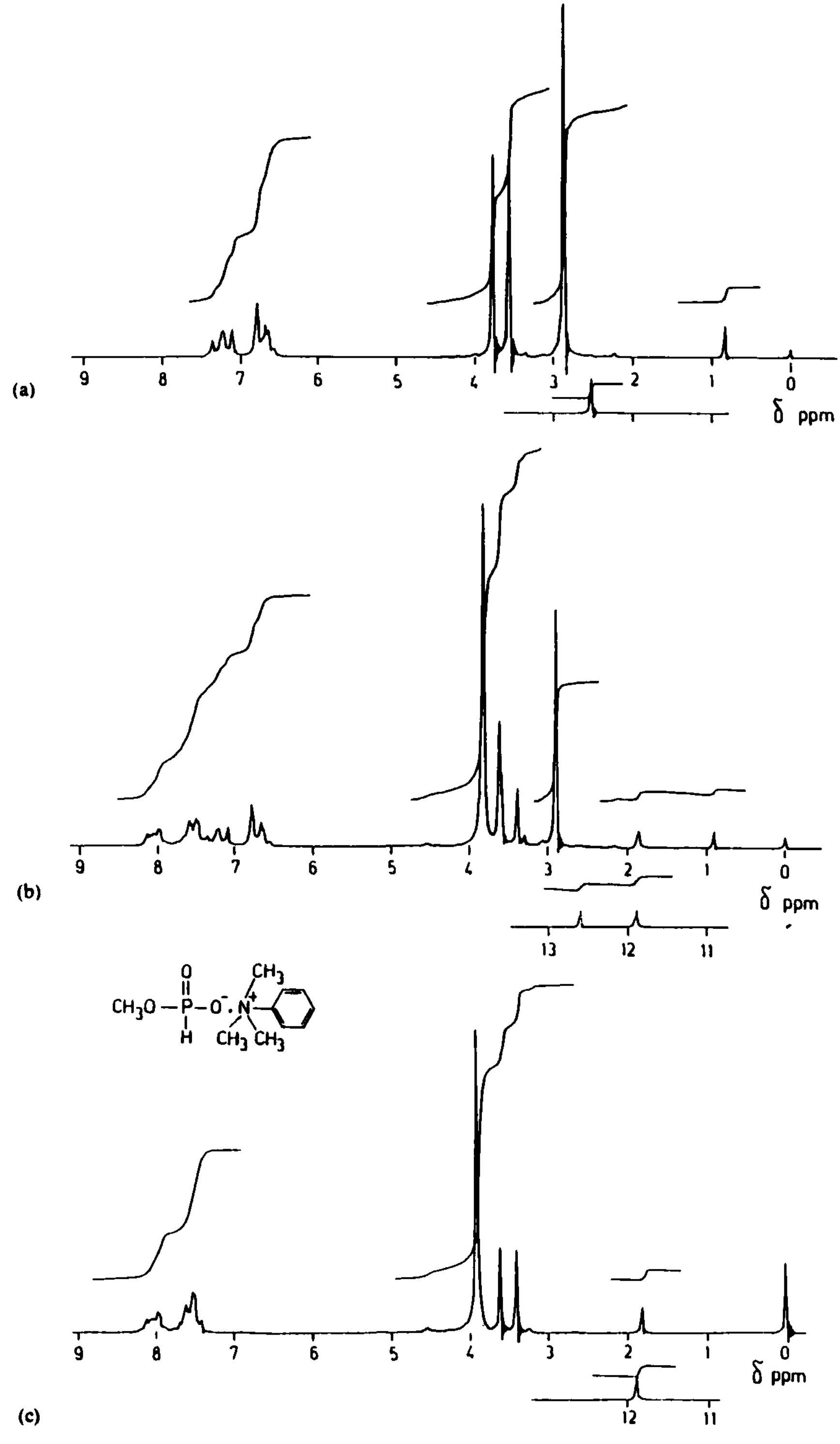


FIGURE 1 ^{1}H-NMR spectra of (a) reaction mixture of dimethyl phosphite and dimethylaniline before heating; (b) after heating at 130°C; (c) the end product.

TABLE III

Hydrogen distribution in the compound obtained by the reaction of dimethyl phosphite with dimethylaniline

Type of protons	Range ppm	Integral intensity, mm	Number of protons	
			Found	Calcd.
a	1.83	8.7	0.99	1.0
b	3.51	27.0	3.08	3.0
c	3.91	77.0	8.8	9.0
d	7.42–8.21	44.0	5.1	5.0
	Total:	157.5	17.97	18.0

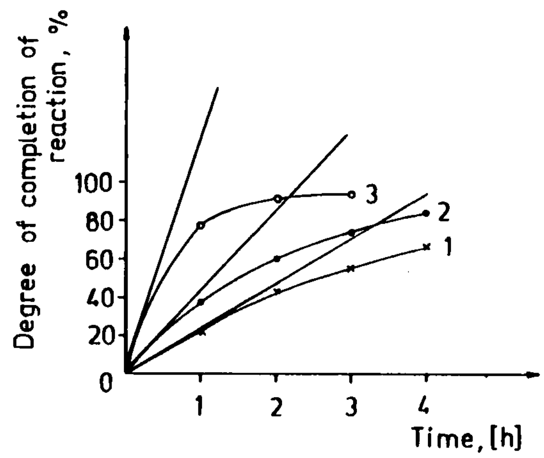
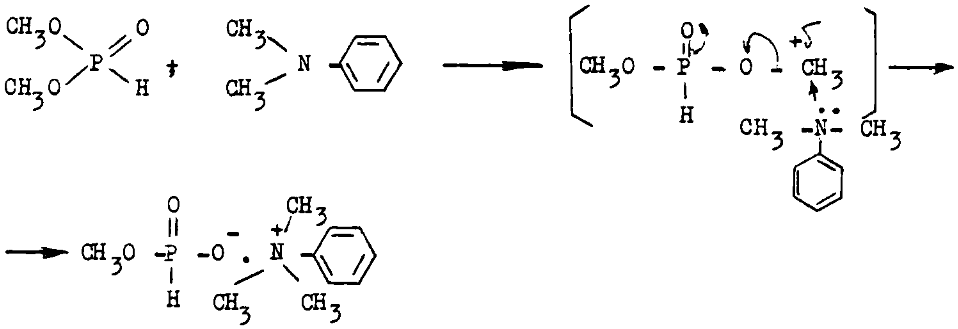


FIGURE 2 Degree of completion of the reaction between dimethyl phosphite and dimethylaniline at curve 1—90°C; curve 2—100°C; curve 3—120°C.

data clearly indicate that the acid diesters of phosphorous acid react in 4-coordinate form.

The alkylation reaction proceeds as a bimolecular interaction and its rate depends on the strength of the nucleophile as well as on the strength of the cationic center, i.e., on the value of the partial positive charge of the α-carbon atom. The initial rate of the reaction was determined and the activation energy estimated at 6.4 kcal/mol (Figure 2).



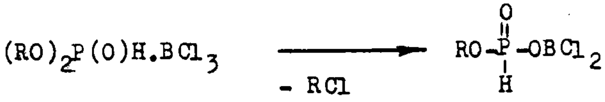
The experiments on the interaction between dialkyl phosphites and amines in excess of the amine revealed that only the monoalkylated product I is obtained. Evidently the positive charge of the α-carbon atom in this product is very low, on account of which the alkylation reaction is hampered.

By establishing the structure of the product of interaction between dialkyl phosphites and amines it was possible to confirm the proposed mechanism of the transesterification reaction, according to which the acid diesters of phosphorous acid react in their 4-coordinate form.

The reaction of alkylation can be used for the synthesis of phosphorus-containing monomers with ionogen groups in the molecule, the presence of which in the polymers confers to the latter a number of valuable properties.

Dealkylation Reaction

The process of dealkylation is characteristic for the α-carbon atom of the alkyl group in the acid diesters of phosphorous acid. Investigating the complex formation between dialkyl phosphites and boron trichloride, Bedell and co-workers[66] established for the first time that these complexes decompose by evolving alkyl halogenides:

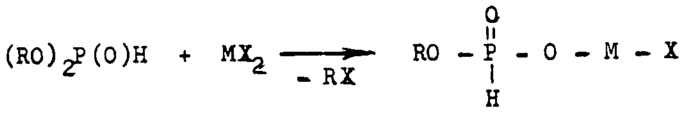


$$(RO)_2P(O)H.BCl_3 \xrightarrow[-\ RCl]{} RO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-OBCl_2$$

These authors showed that diphenyl phosphite does not form complexes with boron trichloride but reacts with the evolution of hydrogen chloride:

$$(PhO)_2P(O)H + BCl_3 \xrightarrow[-\ HCl]{} (PhO)_2P(O)BCl_2$$

Orlovski and co-workers[67] have also studied the reaction between dialkyl phosphites and ammonium and metal salts, demonstrating that the esters of phosphorous acid undergo dealkylation:



$$(RO)_2P(O)H + MX_2 \xrightarrow[-\ RX]{} RO-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O-M-X$$

The kinetic investigations[68] of the reaction between dialkyl phosphites and ammonium salts showed (Table IV) that it follows the kinetic equation for a bimolecular reaction of the second order:

$$W = k \cdot (C_a) \cdot (C_b)$$

The reaction rate is determined by the induction and steric effects of the substituents at the α-carbon atom, which is the center of the reaction. The stronger the substituents as electron donors and the larger the steric constants, the lower is the reaction rate.

Dimethyl phosphite reacts with diethylamine hydrochloride, whereas dibutyl and diisopropyl phosphites, under the same conditions, do not react. This is due to the

TABLE IV

Kinetic data of the reaction of dialkyl phosphites with ammonium salts

Starting compounds			C_A	C_B	W
A		*B*	mol/l	mol/l	mol/l · sec.
DEA · HCl	:	DMP	0.365	0.189	1.2×10^{-3}
DEA · HCl	:	DMP	0.367	0.368	2.03×10^{-3}
DEA · HCl	:	DMP	0.365	0.738	4.02×10^{-3}
DEA · HCl	:	DMP	0.183	0.367	1.18×10^{-3}
DEA · HCl	:	DMP	0.531	0.367	2.95×10^{-3}
DEA · HCl	:	DBP	0.367	0.368	no reaction
DEA · HCl	:	DIPP	0.367	0.368	no reaction
P · HCl	:	DMP	0.369	0.376	3.51×10^{-3}
P · HCl	:	DBP	0.368	0.367	2.04×10^{-4}
P · HCl	:	DIPP	0.370	0.371	no reaction

DEA HCl—diethylamine hydrochloride; P · HCl—pyridine hydrochloride; DMP—dimethyl phosphite; DBP—dibuthyl phosphite; DIPP—diisopropyl phosphite.

different values of the partial positive charge at the α-carbon atom, determined by the induction effects of the substituents and by their steric constants.

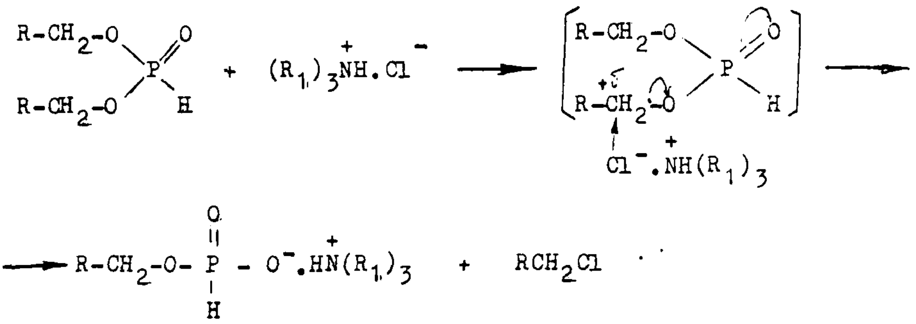
Orlovski and co-workers[67] assume that under the conditions of the reaction the ammonium salts dissociate, i.e., the first stage in the interaction is the dissociation and the chlorine ion will react as a nucleophile:

$$(R_1)_3\overset{+}{N} \cdot HCl^- \rightleftharpoons (R_1)_3\overset{+}{N}H + Cl^-$$

If this assumption is correct, then one has to accept that in the conditions of the reaction, the ammonium salts are completely dissociated and the dissociation step will not limit the rate of dealkylation, inasmuch as the kinetic data are describing it as a bimolecular process.

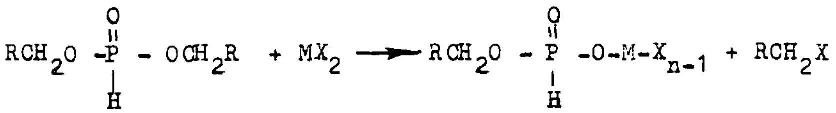
This assumption is plausible, but it cannot explain the finding that dibutyl phosphite reacts with pyridine hydrochloride but not with diethylamine hydrochloride. Consequently, if under the conditions of reaction the ammonium salts are completely dissociated and the chlorine ion acts as nucleophile, then irrespective of the type of the amine the nucleophile should behave in one and the same way.

The experimental results so far obtained imply that ammonium salts react as contact ion pairs and not as dissociated ions:



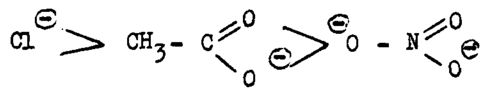
The observed differences in the rate of reaction between dimethyl phosphite and diethylamine hydrochloride and pyridine hydrochloride (Table IV) could be explained by the effect of the basicity of the amine on the strength of the nucleophile associated with it.

The effect of the strength of the nucleophile on the rate of dealkylation is most clearly expressed in the reaction between dialkyl phosphites and metal salts.[69]



$$RCH_2O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-OCH_2R + MX_2 \longrightarrow RCH_2O-\overset{\overset{O}{\|}}{\underset{\underset{H}{|}}{P}}-O-M-X_{n-1} + RCH_2X$$

Dialkyl phosphites react with calcium nitrate at 115°C (Figure 3, curve 4), with manganese acetate at 112°C (curve 5), and with calcium dichloride at 70°C (curve 3). The differences in the reaction temperatures are evidently caused by the difference in the strength of the nucleophiles participating in the reactions:



The electronegativity of the metal, on the other hand, also exerts an effect on the rate of the dealkylation reaction. Thus cobalt dichloride reacts with diethyl phosphite at 105°C, but calcium dichloride reacts at only 70°C. The strength of the nucleophile is reduced more significantly by cobalt, which is more electronegative than calcium.

It is probable that the interaction between dialkyl phosphites and metal salts includes a step during which complexes are formed. Evidence for this conclusion is

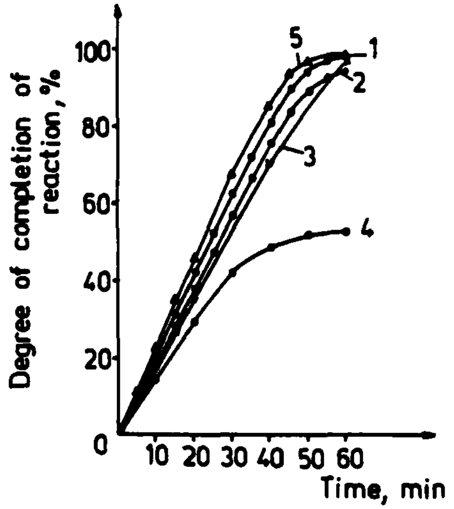
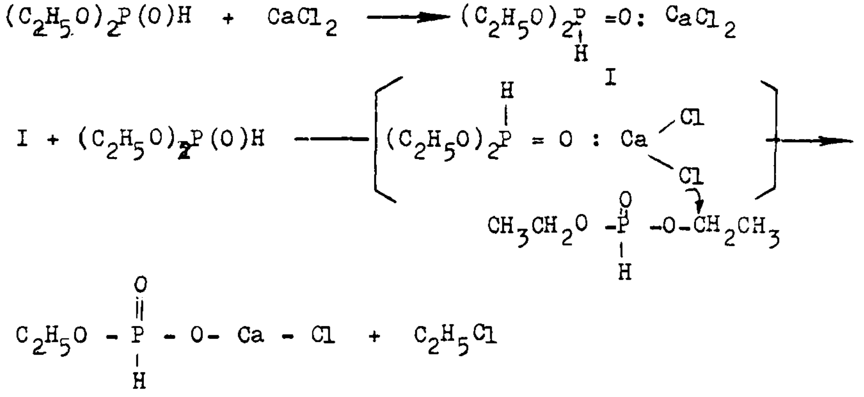


FIGURE 3 Degree of completion of the reaction between dialkyl phosphites and metal salts: curve 1—dibuthyl phosphite and $ZnCl_2$ at 125°C; curve 2—dibuthyl phosphite and $CaCl_2$ at 122°C; curve 3—diethyl phosphite and $CaCl_2$ at 70°C; curve 4—diethyl phosphite and $Ca(NO_3)_2$ at 115°C; curve 5—diethyl phosphite and $Mn(OOCCH_3)_2$ at 112°C.

the IR spectra[69] of mixtures of diethyl phosphite with metal salts. The absorption band for the group P=O for the mixture diethyl phosphite/calcium dichloride is shifted by 25 cm^{-1} with respect to that of the pure diethyl phosphite. It is probable that upon mixing of diethyl phosphite with calcium dichloride, a complex is initially formed, which subsequently decomposes with the evolution of alkyl halogenide:

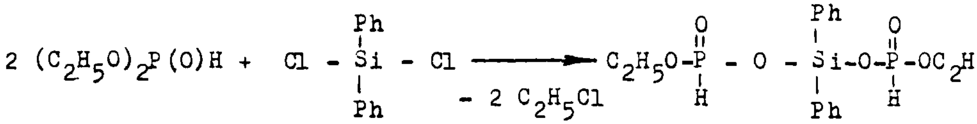


$$(C_2H_5O)_2P(O)H + CaCl_2 \longrightarrow \underset{I}{(C_2H_5O)_2\underset{H}{P}{=}O{:}\,CaCl_2}$$

$$I + (C_2H_5O)_2P(O)H \longrightarrow \left[\begin{matrix}(C_2H_5O)_2\overset{H}{P}=O : Ca\begin{matrix}Cl\\Cl\end{matrix}\\ CH_3CH_2O-\overset{O}{\underset{H}{P}}-O-CH_2CH_3\end{matrix}\right] \longrightarrow C_2H_5O-\overset{O}{\underset{H}{\overset{\|}{P}}}-O-Ca-Cl + C_2H_5Cl$$

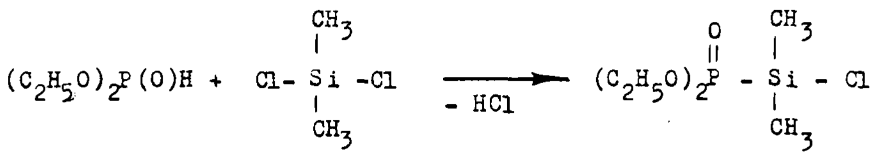
It is possible that the lower reaction temperature for the reaction of diethyl phosphite and calcium dichloride relates not only to the lower electronegativity of calcium but also to the formation of this complex.

It can be supposed that any donor of an electron pair, acting as nucleophile and capable of attacking an electron-deficient center will interact with dialkyl phosphites according to the proposed scheme. In effect dichlorodiphenylsilane reacts with diethyl phosphite according to this scheme:



$$2\,(C_2H_5O)_2P(O)H + Cl-\overset{Ph}{\underset{Ph}{Si}}-Cl \xrightarrow[-\,2\,C_2H_5Cl]{} C_2H_5O-\overset{O}{\underset{H}{\overset{\|}{P}}}-O-\overset{Ph}{\underset{Ph}{Si}}-O-\overset{O}{\underset{H}{\overset{\|}{P}}}-OC_2H_5$$

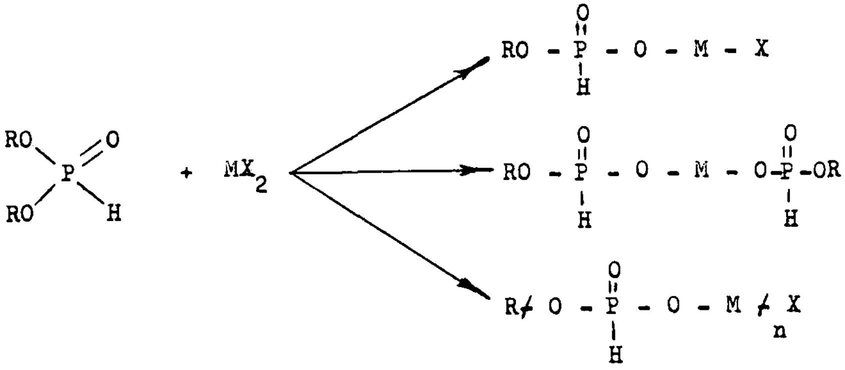
It appeared that the reaction between dichlorodimethylsilane and diethyl phosphite proceeds as an acid–base reaction:[69]



$$(C_2H_5O)_2P(O)H + Cl-\overset{CH_3}{\underset{CH_3}{Si}}-Cl \xrightarrow[-\,HCl]{} (C_2H_5O)_2\overset{O}{\overset{\|}{P}}-\overset{CH_3}{\underset{CH_3}{Si}}-Cl$$

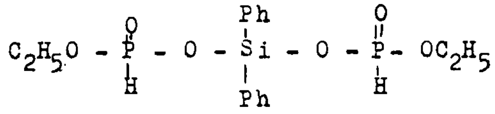
This difference in the behavior of the nucleophile, chloride ion, is most likely due to the type of the substituents attached to silicon. The phenyl nucleus has a clearly expressed negative induction effect, but the methyl group has a tendency to shift the electron density to the positive center. This in turn will affect the electron density of chlorine. These results make it possible to assume that when the nucleophile is a very strong base, as in the case of dichlorodimethylsilane, it will be attacked predominantly by a hydrogen atom.

The observed reactivity of chlorides and acetates (Figure 3) revealed that this reaction can be employed for the synthesis not only of monomers[69] but also of oligomers,[70] and polymers:



The investigation of the reactivity of the alkoxy group of the acid diesters of phosphorous acid demonstrated that it involves three characteristics reactions: transesterification, alkylation and dealkylation. This reactions open wide possibilities for the synthesis of products with a great variety of structures and compositions by using only one starting monomer.

The established kinetic relationships of these reactions allow the synthesis of a definite type of compound to be carried out by the most convenient reaction. For example, bisphosphite can be prepared by the transesterification reaction of dimethyl phosphite with silanediol at 150°C for 5 hours:



$$C_2H_5O-\overset{O}{\underset{H}{P}}-O-\overset{Ph}{\underset{Ph}{Si}}-O-\overset{O}{\underset{H}{P}}-OC_2H_5$$

The same product can be prepared by the dealkylation reaction of dimethyl phosphite with dichlorodiphenylsilane at 95°C for 1 hour.

A similar interchangeability exists also between the reactions of alkylation and dealkylation.

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