REARRANGEMENTS OF DIPHOSPHINE OXIDES AND ANHYDRIDES OF
PHOSPHORUS ACIDS. PHOSPHOROTROPIC TAUTOMERISM

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In honour of Academician A. N. Nesmeyanov on the occasion of
his 80th birthday.

Abstract. The effects of electronic and structural properties of
substituents on the relative thermodynamic stability of
diphosphine monoxides $R_2P(A)-PR'_2$ and isomeric compounds
$R_2P-P(A)R'_2$ or $R_2P-A-PR'_2$ (A=O,S,NX) have been demonstra-
ted. The irreversible and reversible (tautomeric) re-
arrangements have been found for these types of compounds.
First data on phosphorotropic and germanotropic tautome-
rism related with the change of phosphorus coordination
number are given. The relative stability of isomers con-
taining the three- or four-coordinate phosphorus was dis-
cussed.

In one of the best modern text-books "Basic principles of organic che-
mistry" by J. Roberts and M. Caserio, the section on organic derivatives of
phosphorus, it is pointed out that the energy of the formation of the phos-
phoryl group is a motive force in many reactions of the phosphorus compounds
/1/. Really, the energy of the phosphoryl group is rather high and, appa-
rently, because of this the most stable form of the acids of trivalent phos-
phorus is that with a four-coordinate phosphorus and the esters of triva-
lent phosphorus acids readily undergo the Arbuzov rearrangement.

However, in the laboratory of organophosphorus compounds of the Moscow
State University the facts have been discovered which allow an assumption to
be made as to the opening of the phosphoryl group of diphosphine monoxides
with a transition of phosphorus into a three-coordinate state /2/. This in-
duced us to study systematically different types of organophosphorus com-
pounds in order to find the factors affecting the stability of the compounds
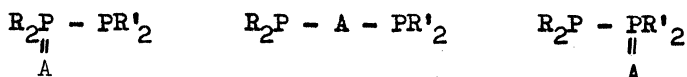containing a phosphoryl group.

One of the specific features of phosphorus is a possibility to change
the valency (coordination number) which gives rise to isomers of the follow-
ing type:

$$>P-A-E \quad \text{and} \quad >\underset{\underset{A}{\|}}{P}-E$$
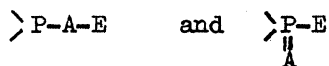
where E are various elements.

Diphosphine monoxides, their isomers and analogues (i.e. E=P, and
A=O,S, or NR) proved to be the suitable subjectes for studying the problem
of the relative stability of isomeric compounds containing three- and four-
coordinate phosphorus, since for these compounds the relative stability of
such forms can vary in a rather wide range. Below the types of the compounds

are given whose structure can be established with reliability by NMR $^{31}$P-spectroscopy /3/:
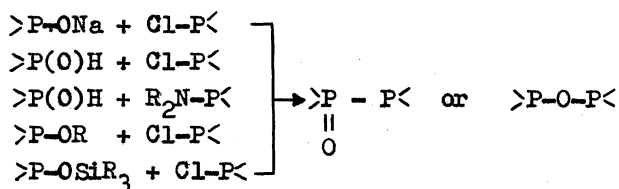
$$R_2P - PR'_2 \qquad R_2P - A - PR'_2 \qquad R_2P - PR'_2$$
$$\underset{A}{\overset{\|}{}} \qquad\qquad\qquad\qquad\qquad\qquad \underset{A}{\overset{\|}{}}$$

Type            I                    II                    III
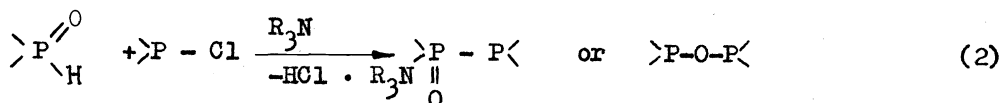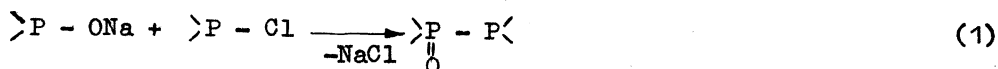
(R or R'=Alk, Ar, RO, NR$_2$; A=O,S, or NR).

When R = R' only two isomers are possible (monoxide I and anhydride II), when R $\neq$ R', three isomers can exist. Isomers I and III are conditionally named "monoxides" for any substituent "A" (a wide interpretation of this term is assumed); the notation III refers to thermodynamically more stable compounds. In order to understand which factors ensure the preferable stability of one or another form, we tried to synthesize all isomers for given R and A and we searched different rearrangements - irreversible, and, particularly, reversible ones, since namely in the case of tautomeric relations it is easier to evaluate which changes in the structure are responsible for the equilibrium shift in any direction.

To prepare diphosphine monoxides or isomeric anhydrides, use was made of a number of reactions the most part of which was either described (Issleib, Walter, Wieze, Fluck, Binder /4/) or have direct analogues in literature:

$$
\begin{array}{l}
>P{-}ONa + Cl{-}P< \\
>P(O)H + Cl{-}P< \\
>P(O)H + R_2N{-}P< \\
>P{-}OR\ \ + Cl{-}P< \\
>P{-}OSiR_3 + Cl{-}P<
\end{array}
\left.\rule{0pt}{2.5em}\right\} \rightarrow
\underset{O}{\overset{\|}{>P} - P<}\ \text{ or }\ >P{-}O{-}P<
$$

Kinetic and thermodynamic control of these reactions may give different results whereas to judge correctly about the direction of interaction between the reagents it must be quite clear which type of control takes place in every specific case.

In further discussion the main attention will be given to two processes:

$$>P - ONa + >P - Cl \xrightarrow{-NaCl} \underset{O}{\overset{\|}{>P} - P<} \tag{1}$$

$$>\!P\!\overset{\overset{O}{\diagup\!\diagup}}{\diagdown_H} + >P - Cl \xrightarrow[-HCl\cdot R_3N]{R_3N} \underset{O}{\overset{\|}{>P} - P<}\ \text{ or }\ >P{-}O{-}P< \tag{2}$$

It is a general opinion in literature that the products of interaction between the salts of trivalent phosphorus acid and phosphorus acid chlorides (i.e. reaction 1) may be both diphosphine monoxides and isomeric anhydrides (for instance, tetraethylpyrophosphite). The formation of any compound was related to the direction of an electrophilic attack on the phosphorus or oxygen atom of the ambidient anion $>\!\overset{..}{P}{-}\bar{O}$, i.e. it was considered a priori as the result of the kinetic control of the reaction. Since in the course of our study it became clear that isomeric compounds with structures I and II may be rearranged one into the other, a demand arose for a more thoroughly investigation of these reactions (1). To evaluate the effect of

various factors on the direction of the reaction, one must be sure of that
the reaction product obtained is primary. Only such a compound can be con-
sidered unequivocally as a primary reaction product which is not thermodyna-
mically stable and can be further rearranged into a more stable isomer. If
the reaction product is thermodynamically stable, the direction of the elec-
trophilic attack can be jugded only with the aid of similar cases when se-
ries of reactions and compounds are considered (from here follows the dif-
ficulty of discussing reactions 1 and 2 and erroneous opinions in literature
concerning these reactions).

   To study reaction (1), we interacted chlorides of different trivalent
phosphorus acids with salts of oxygen-containing acids, thioacids, and ami-
des of trivalent phosphorus acids. Many examples were found when kinetic and
thermodynamic control of the reaction (1) give different results and the
conditions of the kinetically controlled process could be maintained. It
became clear that, as a rule, electrophilic attack is selectively directed
on the phosphorus atom of the salt and the compounds with the P-P bond are,
thus, the primary products of the reaction:

$$>P - \bar{A}\overset{+}{N}a \;+\; >P - Cl \xrightarrow[-NaCl]{} \;>\!\!\underset{\underset{A}{\|}}{P} \;-\; P< \qquad\qquad A=O,S,NR$$
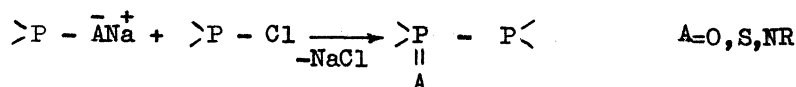
Two cases deserve special attention:
(1) tetraalkoxydiphosphine monoxides formed in reaction (1) isomerize irre-
versibly into pyrophosphite only after 1–3 hours /5/:

$$(RO)_2 \underset{\underset{O}{\|}}{P} - P(OR)_2 \xrightarrow{1-3h, \; 20^{\circ}} (RO)_2 P - O - P(OR)_2$$
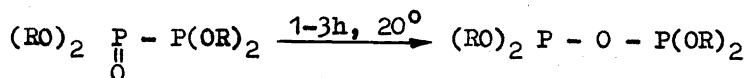
(2) diphosphine iminoxides are capable of being isomerized into diphosphino-
amines /6/:

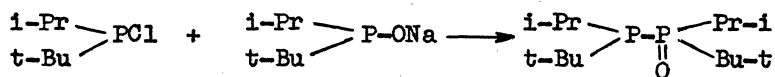$$R_2P - \underset{\underset{Ar-N}{\|}}{P}R_2 \longrightarrow R_2P - \underset{\underset{Ar}{|}}{N} - PR_2$$
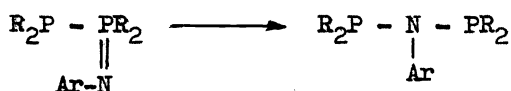
Thus, the explanations available in literature /7, 22/ according to which
the direction of the reaction between a chloride of trivalent phosphorus
acid and an anion of this acid is related for these two cases to the compe-
tition of hard and soft centres in the ambidient anion $>\!\overset{..}{P}\!-\!\bar{A}$, are not sub-
stantiated: the attack on P atom proceeds much faster than on A. We succeed-
ed to elucidate that if this competitive nucleophilic centre A is hard (for
instance, the oxygen atom), only very essential spatial hindrances may lead
to the formation of a compound with a bond system $>P-A-P<$ in the pro-
ducts of the kinetically controlled reaction. Thus, interaction of ditert-
butylchlorophosphine with a sodium salt of ditert-butylphosphinous acid
gives rise, in addition to monoxide, to anhydride whose part may account
for 20–30%.

$$R_2PCl + R_2PONa \longrightarrow R_2P\underset{\underset{O}{\|}}{-}PR_2 + R_2P-O-PR_2 \qquad (R=tert-Bu).$$
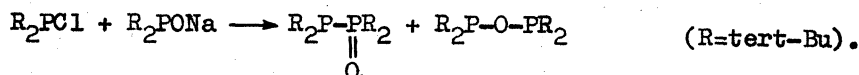
The formation of anhydride in this case is undoubtedly the result of the
kinetic control of the reaction, i.e. of the competiting attack on the oxy-

gen atom, since no rearrangement takes place under these conditions /8/.

The slightest decrease in the spatial hindrances (a substitution of an isopropyl group for a tert.-butyl one) results in that only the phosphorus atom is attacked and no anhydride is formed:

$$\underset{t\text{-}Bu}{\overset{i\text{-}Pr}{>}}PCl \ + \ \underset{t\text{-}Bu}{\overset{i\text{-}Pr}{>}}P\text{-}ONa \longrightarrow \underset{t\text{-}Bu}{\overset{i\text{-}Pr}{>}}\underset{\overset{\|}{O}}{P}\text{-}P\underset{Bu\text{-}t}{\overset{Pr\text{-}i}{<}}$$
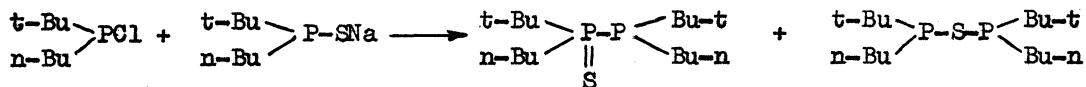
It means that in salts of oxygen-containing trivalent phosphorus acids the heteroatom is not a competitive nucleophilic centre and the electrophilic attack of phosphorus acid chlorides is directed on the phosphorus atom of the salt.

If the competitive nucleophilic centre A is soft (for instance, the sulphur atom) the affect of the volume of the radicals on the direction of the attack can be followed clearly enough. In the case of the compounds in which every phosphorus atom is bonded with two secondary radicals the rate of the attack on the phosphorus atom is still rather high and, therefore, at first monothiooxide is formed:
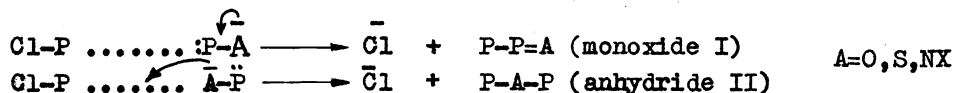
$$i\text{-}Pr_2PCl + i\text{-}Pr_2PSNa \longrightarrow i\text{-}Pr_2\underset{\overset{\|}{S}}{P}\text{-}PPr_2\text{-}i$$
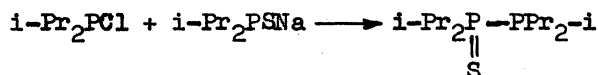
For one tertiary radical the reaction rates with respect to P and S become comparable and both isomers are formed:

$$\underset{n\text{-}Bu}{\overset{t\text{-}Bu}{>}}PCl \ + \ \underset{n\text{-}Bu}{\overset{t\text{-}Bu}{>}}P\text{-}SNa \longrightarrow \underset{n\text{-}Bu}{\overset{t\text{-}Bu}{>}}\underset{\overset{\|}{S}}{P}\text{-}P\underset{Bu\text{-}n}{\overset{Bu\text{-}t}{<}} \ + \ \underset{n\text{-}Bu}{\overset{t\text{-}Bu}{>}}P\text{-}S\text{-}P\underset{Bu\text{-}n}{\overset{Bu\text{-}t}{<}}$$

For the case of two tertiary radicals only sulphur atom is attacked:

$$t\text{-}Bu_2PCl + t\text{-}Bu_2P\text{-}SNa \longrightarrow t\text{-}Bu_2P\text{-}S\text{-}PBu_2\text{-}t$$
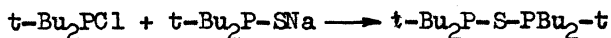
Thus, the bulky substituents only hinder the pronounced trend of chlorides of trivalent phosphorus acids to react with salts of these acids at the phosphorus atom. Since the reaction considered above is not charge-controlled, the main reason for a higher rate of the attack on the phosphorus atom of the salt is, in our opinion, the fact that in that case polarization of the whole system $\overset{..}{P}\text{-}\bar{A}$ takes place whereas the attack on the heteroatom A results in polarization of this atom only:

$$Cl\text{-}P \ldots\ldots\ldots :\overset{\frown}{\overset{..}{P}\text{-}\bar{A}} \longrightarrow \bar{C}l \ + \ P\text{-}P=A \text{ (monoxide I)}$$
$$Cl\text{-}P \ldots\ldots \overset{\nwarrow}{\overset{..}{A}\text{-}\overset{..}{P}} \longrightarrow \bar{C}l \ + \ P\text{-}A\text{-}P \text{ (anhydride II)} \qquad A=O,S,NX$$

In other words, as far as soft electrophiles are concerned (trivalent phosphorus acid chlorides), the polarizable system $>\overset{..}{P}\text{-}\bar{A}$ wins the competition with the atom A especially in those cases when this atom is a hard centre (O or N). A lower rate of the attack on the heteroatom A may also be partially due to its shielding with the cation of the salt.
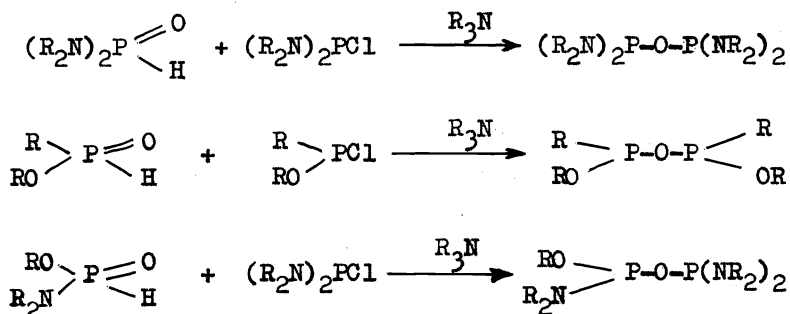
For synthesis of various anhydrides we have widely used a reaction of trivalent phosphorus acid with the acid chloride in the presence of tertiary amine (reaction 2). The interaction of these reagents can proceed in a more complicated way than the above-mentioned reaction of the acid chloride with the salt. A competition of two processes can be observed in the reac-

tion with the acid itself. First, an anhydride is formed due to the attack
of acid chloride on the only nucleophilic centre of the non-dissociated
acid, namely, oxygen atom:

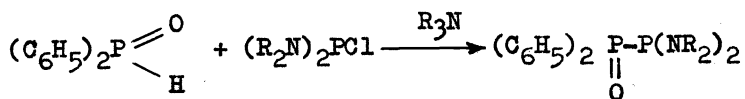$$>P\!\!\diagup_{H}^{\displaystyle O} \; + \; ClP< \; \xrightarrow[\;-HCl\;]{R_3N} \; >P-O-P< \qquad\qquad (2)$$
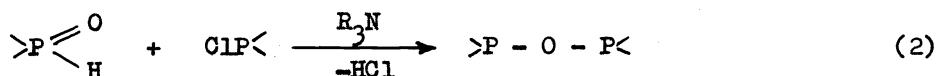
Secondly, the reaction may proceed with a three-coordinate form of the acid
(stabilized by a hydrogen bond with amine) or, as a limiting case, with the
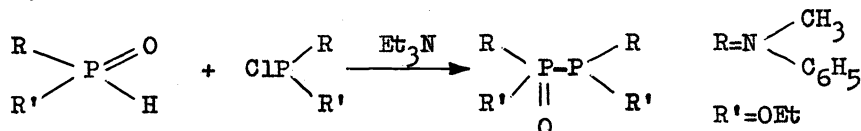ammonium salt of the acid which leads to the formation of monoxide (reaction
1).

   In many cases anhydrides can be isolated as a result of the reaction.
However, care should be taken in interpreting this fact as a consequence of
the kinetic control of the reaction with a non-dissociated acid since an
isomerizing effect of the acid chloride is possible (the reaction proceeds
rather slow, namely, tens of minutes). Apparently in the case of weaker
acids the attack on oxygen leading to the formation of anhydride does real-
ly dominate. Thus, diamidophosphite /9/ and even acid esters of phosphonous
/10/ and amidophosphorus acids react at the oxygen atom with the formation
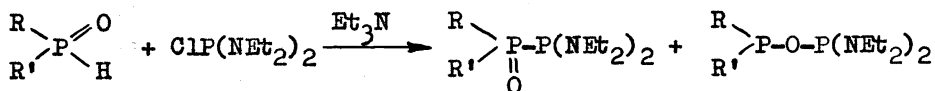of anhydrides:

$$(R_2N)_2P\!\!\diagup_{H}^{\displaystyle O} \; + \; (R_2N)_2PCl \; \xrightarrow{R_3N} \; (R_2N)_2P\text{-}O\text{-}P(NR_2)_2$$

$$\begin{array}{c} R \\ RO \end{array}\!\!>P\!\!\diagup_{H}^{\displaystyle O} \; + \; \begin{array}{c} R \\ RO \end{array}\!\!>PCl \; \xrightarrow{R_3N} \; \begin{array}{c} R \\ RO \end{array}\!\!-P\text{-}O\text{-}P\!\!<\!\!\begin{array}{c} R \\ OR \end{array}$$

$$\begin{array}{c} RO \\ R_2N \end{array}\!\!>P\!\!\diagup_{H}^{\displaystyle O} \; + \; (R_2N)_2PCl \; \xrightarrow{R_3N} \; \begin{array}{c} RO \\ R_2N \end{array}\!\!>P\text{-}O\text{-}P(NR_2)_2$$

At the same time only monoxides are formed from stronger acids under the
conditions of kinetic control of reaction (2) /11/:

$$(C_6H_5)_2P\!\!\diagup_{H}^{\displaystyle O} \; + \; (R_2N)_2PCl \; \xrightarrow{R_3N} \; (C_6H_5)_2\!\!\underset{\underset{O}{\|}}{P}\text{-}P(NR_2)_2$$

The data on the strength of three-coordinate phosphorus acids are given in
the paper of Tsvetkov, Kabachnik and Schatenstein with co-workers /12/. The
direction of condensation (2) strongly depends also on the electrophilic
agent. Thus, in the following reaction monoxide is formed:

$$\begin{array}{c} R \\ R' \end{array}\!\!>P\!\!\diagup_{H}^{\displaystyle O} \; + \; ClP\!\!<\!\!\begin{array}{c} R \\ R' \end{array} \; \xrightarrow{Et_3N} \; \begin{array}{c} R \\ R' \end{array}\!\!>\!\!\underset{\underset{O}{\|}}{P}\text{-}P\!\!<\!\!\begin{array}{c} R \\ R' \end{array} \qquad \begin{array}{l} R=N\!\!<\!\!\begin{array}{c} CH_3 \\ C_6H_5 \end{array} \\[4pt] R'=OEt \end{array}$$

But condensation with diamidochlorophosphite gives almost equal amounts of
monoxide and anhydride:

$$\begin{array}{c} R \\ R' \end{array}\!\!>P\!\!\diagup_{H}^{\displaystyle O} \; + \; ClP(NEt_2)_2 \; \xrightarrow{Et_3N} \; \begin{array}{c} R \\ R' \end{array}\!\!>\!\!\underset{\underset{O}{\|}}{P}\text{-}P(NEt_2)_2 \; + \; \begin{array}{c} R \\ R' \end{array}\!\!>P\text{-}O\text{-}P(NEt_2)_2$$

In the case of thioacids condensation with dialkylchlorophosphites yields monothiooxides:

$$i\text{-}Pr_2P(S)H + (EtO)_2PCl \xrightarrow{R_3N} i\text{-}Pr_2\underset{\underset{S}{\|}}{P}\text{-}P(OEt)_2$$
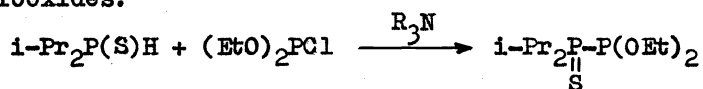
whereas that with dialkylchlorophosphines furnishes, predominantly, anhydride:

$$i\text{-}Pr_2P(S)H + i\text{-}Pr_2PCl \xrightarrow{R_3N} i\text{-}Pr_2P\text{-}S\text{-}PPr_2\text{-}i$$
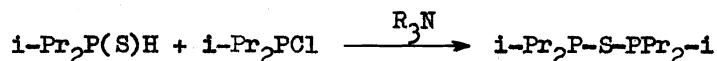
It should be noted that in all the above cases the formation of thermo-dynamically unstable compounds was given as an example and in other condi-tions these compounds do isomerize; this means that the reactions cited above were kinetically controlled. Although the values of $pK_a$ of the acids serve, to a certain extent, as a guiding line for determining the direction of the reaction (2), the scheme of the formation of the products in this reaction can be only conditionally considered as a competition of two pro-cesses. Evidently the mechanisms of interaction of the reagents are complex enough and with the above simplification one may predict the results proper-ly in the case of either very weak acids which give anhydrides by reaction (2) or relatively strong acids which yield monoxides. Reaction (2) must be conducted with an excess of tertiary amine /13/ in the reaction mixture to inhibit the functional groups exchange. Thus, interaction between phosphi-nous acid and chlorophosphite in the presence of amine furnishes anhydride:

$$R_2P{\Large\nwarrow^{O}_{H}} + ClP(OR)_2 \xrightarrow[-HCl]{R_3N} R_2P\text{-}O\text{-}P(OR)_2$$
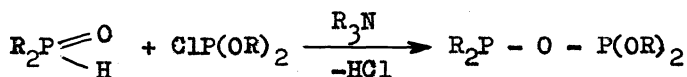
whereas without amine the irreversible exchange reaction takes place /14/:

$$R_2P{\Large\nwarrow^{O}_{H}} + ClP(OR)_2 \xrightarrow{\text{without amine}} R_2PCl + (RO)_2P{\Large\nwarrow^{O}_{H}} \qquad (3)$$
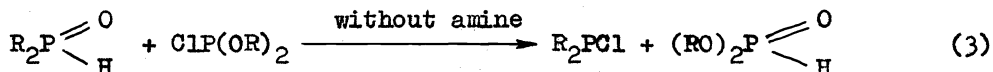
Anhydride cannot be separated upon condensation of the compounds formed in exchange reaction (3) because of its fast rearrangement into a more stable monoxide under the action of chlorophosphine /13/.

Thus, although the reaction of the salt with acid chloride, as a rule, gives monoxide and that of the acid itself gives anhydride, the retention of the products of kinetic control of these reactions can be attained only under certain conditions. The cause is that both monoxides and anhydrides can isomerize under the action of the number of electrophilic and nucleophi-lic catalysts and, first of all, under the action of the reagents, namely ambident anions of phosphorus acids and chlorides of these acids:
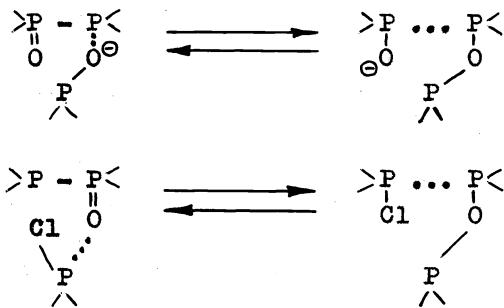
However, the use of acid chlorides and other highly effective electrophilic
catalysts for isomerization requires care since in this case a competitive
redox disproportionation of monoxide can take place. The initial act of such
disproportionation is an electrophilic attack not on the oxygen atom of the
phosphoryl group (which leads to isomerization) but on the three-coordinate
phosphorus atom. Such an attack leads to the formation of the bond between
two three-coordinate phosphorus atoms:

$$2 \underset{\overset{\|}{O}}{>\!P} - P\!< \longrightarrow \underset{\overset{\|}{O}}{>\!P} - P\!< + \begin{cases} \underset{O}{\overset{\|}{>\!P}} - \underset{O}{\overset{\|}{P}}\!< & \longrightarrow \\ \underset{\overset{\|}{O}}{>\!P} - O - P\!< & \end{cases} \quad (4)$$

$$\underset{\overset{\|}{O}}{>\!P} - O - \underset{\overset{\|}{O}}{P}\!< \quad + \quad \underset{\overset{\|}{O}}{>\!P} - P\!< \quad \xrightarrow{\text{redox}} \quad \cdots$$

and so on.
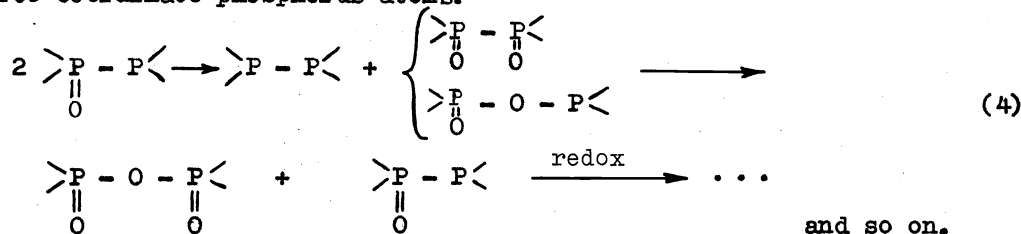
It turned out possible to show that the simultaneously formed compounds
containing two oxygen atoms transform further due to isomerization and dis-
proportionation in such a way that the final products of the whole process
are diphosphine and phosphinous acid anhydride. This redox disproportiona-
tion is often observed in the case of tetraalkyl(aryl)diphosphine oxides
and goes especially readily for the compounds containing primary radicals.

The great majority of phosphoryl-containing compounds and isomeric an-
hydrides (heteroatom A-oxygen) isomerize faster under the action of acid
chlorides. On the contrary, the compounds containing sulphur and nitrogen
as heteroatoms (A=S,NR) isomerize much faster under the action of correspond-
ing anions.

The study of the direction of rearrangements allows one to evaluate how
the relative stability of isomers changes depending on the nature of the
heteroatom and substituents bonded with phosphorus. The data on the relative
thermodynamic stability of isomers are listed in several Tables. The com-
pounds containing similar substituents at both phosphorus atoms are given
in Table 1. From the data of Table 1 it follows that the relative stability

Table 1

| X | $X_2\underset{O}{\overset{\|}{P}}$-PX$_2$ Type I | | $X_2$P-O-PX$_2$ Type II |
|---|---|---|---|
| OR | (RO)$_2\underset{\overset{\|}{O}}{P}$-P(OR)$_2$ | $\longrightarrow$ | (RO)$_2$P-O-P(OR)$_2$ |
| OR, NR$_2$ | $\underset{R_2N}{\overset{RO}{>}}\underset{\overset{\|}{O}}{P}\text{-}P\underset{NR_2}{\overset{OR}{<}}$ | $\underset{\longleftarrow}{\longrightarrow}$ | $\underset{R_2N}{\overset{RO}{>}}P\text{-}O\text{-}P\underset{NR_2}{\overset{OR}{<}}$ R=Et, 69%*) |
| NR$_2$ | (R$_2$N)$_2\underset{\overset{\|}{O}}{P}$-P(NR$_2$)$_2$ | $\underset{\longleftarrow}{\longrightarrow}$ | (R$_2$N)$_2$P-O-P(NR$_2$)$_2$ R=Et, 4%*) |
| R, OR' | $\underset{R'O}{\overset{R}{>}}\underset{O}{P}\text{-}P\underset{OR'}{\overset{R}{<}}$ | $\underset{\xleftarrow{R=n\text{-}Bu}}{\xrightarrow{R=t\text{-}Bu}}$ | $\underset{R'O}{\overset{R}{>}}P\text{-}O\text{-}P\underset{OR'}{\overset{R}{<}}$ R=i-Pr, 15%*) |
| Alk prim. or sec. | R$_2\underset{\overset{\|}{O}}{P}$-PR$_2$ | | —— |
| R=sec. R'=tert. | $\underset{R'}{\overset{R}{>}}\underset{\overset{\|}{O}}{P}\text{-}P\underset{R'}{\overset{R}{<}}$ | $\underset{\longleftarrow}{\longrightarrow}$ | $\underset{R'}{\overset{R}{>}}P\text{-}O\text{-}P\underset{R'}{\overset{R}{<}}$ 10%*) |
| Alk tert. | R$_2\underset{\overset{\|}{O}}{P}$-PR$_2$ | $\longrightarrow$ | R$_2$P-O-PR$_2$ |

*) at 20 °C

of anhydride is higher when the phosphorus atom is bonded with acceptor groups whereas the stability of monoxide is ensured by donor substituents. Thus, when passing in the substituent series from alkoxy groups to dialkyl-amino and further to alkyl groups, the stability of anhydride decreases and that of monoxide increases. However, great spatial hindrances can destabilize monoxide even in the case of alkyl substituents. Using different substituents and taking into consideration the above-cited regularities, we have succeeded to find first examples of non-protothropic tautomerism in the series of organophosphorus compounds related to disappearance of a phosphoryl group.
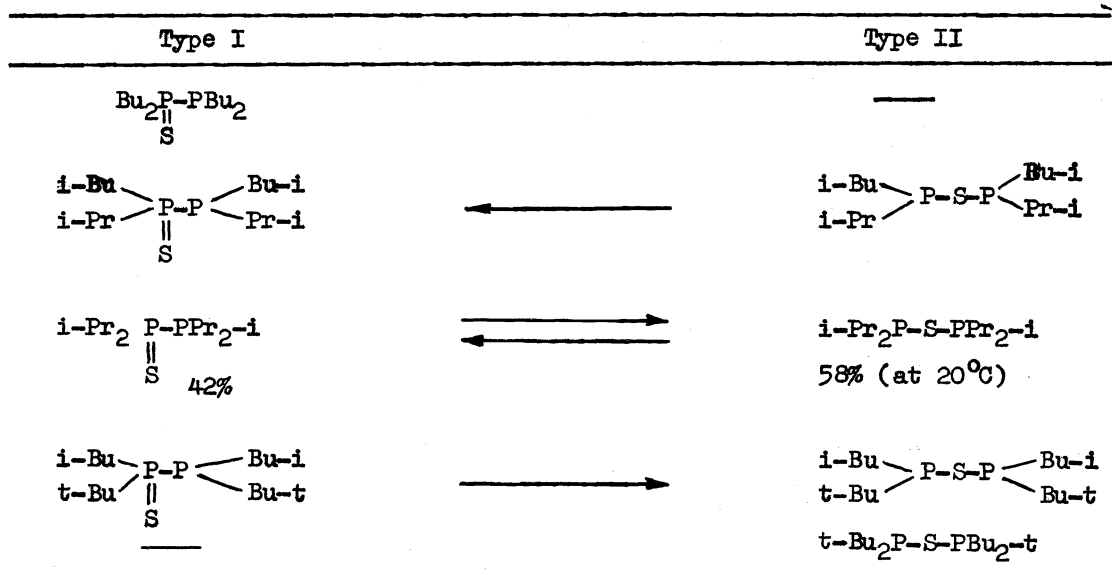
The tautomerism caused by the spatial factors /15,19/ is observed in a very narrow region. From Table 2 it is seen that in the case of diphosphine monoxides containing alkyl radicals tautomerism is observed spectroscopically for the compounds in which every phosphorus atom is bounded with secondary and tertiary radicals. Even a slight change in the structure (a change of the secondary, isopropyl, radical with a branched primary radical, for instance, isobutyl) results in that the anhydride signal disappears from the NMR spectrum.

Table 2

| Type I | Type II |
|---|---|
| $Bu_2P\underset{\underset{O}{\|\|}}{-}PBu_2$ | — |
| $\begin{array}{c} Bu \\ t\text{-}Bu \end{array} \!\!\!> \!\! \underset{\underset{O}{\|\|}}{P}\text{-}P \!\! <\!\!\! \begin{array}{c} Bu \\ Bu\text{-}t \end{array}$ | — |
| $\begin{array}{c} i\text{-}Bu \\ t\text{-}Bu \end{array} \!\!\!> \!\! \underset{\underset{O}{\|\|}}{P}\text{-}P \!\! <\!\!\! \begin{array}{c} Bu\text{-}i \\ Bu\text{-}t \end{array}$ | — |
| $\begin{array}{c} i\text{-}Pr \\ t\text{-}Bu \end{array} \!\!\!> \!\! \underset{\underset{O}{\|\|}}{P}\text{-}P \!\! <\!\!\! \begin{array}{c} Pr\text{-}i \\ Bu\text{-}t \end{array}$  ⇌ | $\begin{array}{c} i\text{-}Pr \\ t\text{-}Bu \end{array} \!\!\!> \!\! P\text{-}O\text{-}P \!\! <\!\!\! \begin{array}{c} Pr\text{-}i \\ Bu\text{-}t \end{array}$ |

$\Delta H^{o}(I\rightarrow II) = 5.0 \pm 0.5$ Kcal·M$^{-1}$
$\Delta S^{o}(I\rightarrow II) = 12.8 \pm 1.5$ cal·M$^{-1}$·grad$^{-1}$

| t°C | 20 | 80 | 110 | 155 |
|---|---|---|---|---|
| %II | 10 | 35 | 44.5 | 62 |

$t\text{-}Bu_2P\underset{\underset{O}{\|\|}}{-}PBu_2\text{-}t$  ⟶  $t\text{-}Bu_2P\text{-}O\text{-}PBu_2\text{-}t$

It is well known that the dissociation energy of a thiophosphoryl group is smaller than that of a phosphoryl one; probably due to this fact destabilization of monothiooxides takes place at smaller spatial hindrances and tautomerism is observed for the compounds with secondary radicals at phosphorus atom (Table 3). The data of the Table clearly illustrate that a gradual increase of the bulk of the substituents (i.e. growth of the spatial hindrances) leads to a higher relative thermodynamic stability of thioanhydrides. Tables 4 and 5 present tautomeric equilibria whose posi-

Table 3

| Type I | | Type II |
|---|---|---|
| $Bu_2\overset{\underset{\|}{S}}{P}\!-\!PBu_2$ | | — |
| $\underset{i\text{-}Pr}{\overset{i\text{-}Bu}{>}}P\overset{\|}{\underset{S}{-}}P\underset{Pr\text{-}i}{\overset{Bu\text{-}i}{<}}$ | $\longleftarrow$ | $\underset{i\text{-}Pr}{\overset{i\text{-}Bu}{>}}P\!-\!S\!-\!P\underset{Pr\text{-}i}{\overset{Bu\text{-}i}{<}}$ |
| $i\text{-}Pr_2\,\overset{\underset{\|}{S}}{P}\!-\!PPr_2\text{-}i$  42% | $\underset{\longrightarrow}{\overset{\longleftarrow}{\phantom{xxx}}}$ | $i\text{-}Pr_2P\!-\!S\!-\!PPr_2\text{-}i$  58% (at 20°C) |
| $\underset{t\text{-}Bu}{\overset{i\text{-}Bu}{>}}P\overset{\|}{\underset{S}{-}}P\underset{Bu\text{-}t}{\overset{Bu\text{-}i}{<}}$ | $\longrightarrow$ | $\underset{t\text{-}Bu}{\overset{i\text{-}Bu}{>}}P\!-\!S\!-\!P\underset{Bu\text{-}t}{\overset{Bu\text{-}i}{<}}$  $t\text{-}Bu_2P\!-\!S\!-\!PBu_2\text{-}t$ |
| — | | |

tions is mainly determined by the electron factors. It is seen from the
Tables that the equilibrium part of anhydrides is much higher in those cases
when the phosphorus atoms are bonded with alkoxygroups which have more pro-
nounced acceptor character than dialkylaminogroups.

Table 4

$$\underset{Et_2N}{\overset{RO}{>}}P\overset{\|}{\underset{O}{-}}P\underset{NEt_2}{\overset{OR}{<}} \;\rightleftharpoons\; \underset{Et_2N}{\overset{RO}{>}}P\!-\!O\!-\!P\underset{NEt_2}{\overset{OR}{<}}$$

Type I                          Type II
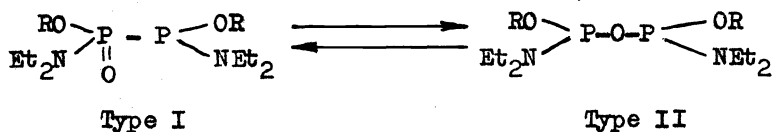
| R | The equilibria content of II in % (at t°C) | | | $\Delta H°(I \to II)$ [a] | $\Delta S°(I \to II)$ [b] |
|---|---|---|---|---|---|
| Et | 65.5(+2) | 69 (+20) | 80.7(+100) | 1.7±0.2 | 7.3±0.4 |
| i-Pr | 48.5(−2) | 57.4 (+25) | 76 (+100) | 2.4±0.2 | 8.7±0.5 |
| Bu | 70 (0 ) | 75.6 (+19) | 88.5(+100) | 2.4±0.2 | 10.6±0.7 |

[a] $Kcal \cdot M^{-1}$  [b] $cal \cdot M^{-1} \cdot grad^{-1}$
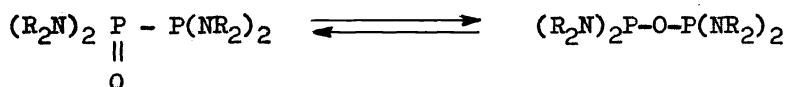
Table 5 shows one example of an irreversible rearrangement: whereas tetra-
amidodiphosphine oxides containing primary radicals (R=Me,Et,Pr) dominate in
a tautomeric equilibrium, introduction of a secondary iso-propyl radical to
the nitrogen atom results in a complete isomerization of monoxide into anhy-
dride. This example is another evidence for the fact that spatial hindrances
destabilize monoxide to a much greater extent than anhydride.

It should be noted that the equilibrium state in tautomeric systems
was approached in all cases from both sides. Equilibria for alkoxy and
dialkylamidosubstituted compounds not containing bulky radicals are estab-
lished rather fast. Mutual transformations of spatially hindered tetraalkyl-
diphosphine oxides and isomeric anhydrides proceed slow. For instance, at
180°C tetratret.-butyldiphosphine monoxide transforms into anhydride almost
completely but at room temperature both isomers can be stored for several
years without any change. Thus, spatial hindrances decrease very strongly

the rate of isomerisation.

Table 5

$$(R_2N)_2\ \underset{\underset{O}{\|}}{P} - P(NR_2)_2 \quad \rightleftharpoons \quad (R_2N)_2P-O-P(NR_2)_2$$

Type I                                    Type II

| R | The equilibria content of II in % (at t°C) | | | | $\Delta H^o(I \to II)$ [a] | $\Delta S^o(I \to II)$ [b] |
|---|---|---|---|---|---|---|
| Me | 6.5(+19) | 18.3(+81) | 22 (+98) | 27.6(+116) | $3.9^{\pm}0.4$ | $8.1^{\pm}1.0$ |
| Et | 4 (+18) | 17.6(+81) | 22.5(+98) | 30.6(+116) | $5.5^{\pm}0.3$ | $12.4^{\pm}0.8$ |
| Pr | | 45 (+107) | 55.8(+127) | 64 (+147) | $6.2^{\pm}0.4$ | $15.9^{\pm}1.1$ |
| i-Pr | The rearrangement I $\longrightarrow$ II is irreversible | | | | | |

[a] $Kcal \cdot M^{-1}$  [b] $cal \cdot M^{-1} \cdot grad^{-1}$

As is seen from Tables 2, 4, and 5 for tautomers having an oxygen atom as a heteroatom (A=O), a temperature rise increases noticeably the part of anhydride (a decrease in temperature returns the system to the initial state), which made it possible to determine $\Delta H^o$ and $\Delta S^o$. The transformation I $\longrightarrow$ II should be accompanied with the increase of entropy and even the first data obtained show how intensively $\Delta S^o$ grows (and the relative stability of anhydride also rises) with increasing spatial hindrances. The value of $\Delta H^o$ can, in first approximation, characterize the degree of the relative stabilization of monoxide I with donor substituents. Unfortunately, in the case of thiooxides the equilibrium position depends on temperature only slightly and redox reaction (4), yielding diphosphine, is rather pronounced even at temperatures about $120^oC$ which hampers the determination of $\Delta H^o$ and $\Delta S^o$. Because of side decomposition reactions, these values were not determined either for the tautomeric system alkylphosphonous acid anhydride with the corresponding monoxide /10/.

The data on the relative stability of isomers given in Tables 1-5 allow a conclusion to be made that a decrease of the phosphorus coordination number, i.e. opening of the P=O group with the formation of anhydride II, is favoured, firstly, by the acceptor nature, and secondly, by the bulk of substituents. By varying electronic and spatial factors, we succeeded in the series of monooxidated symmetrical diphosphines not only to attain the higher stability of a certain isomer but to observe phosphorotropic tautomerism.

Transformations in the series of monooxidated unsymmetrical diphosphines also proved to be very interesting. In general, these compounds may have three isomers: I, II, and III. However, if phosphorus atoms have only alkyl or aryl substituents, the corresponding anhydrides II are quite unstable and only two monoxides I and III exist.

It has been found that monoxides I containing alkyl and aryl radicals as substituents rearrange irreversibly in such a way that the phosphoryl group becomes bonded with alkyl radicals /16/:

$$(C_6H_5)_2\underset{\underset{O}{\|}}{P}\text{-}PR'_2 \xrightarrow[\substack{(1\text{-}3 \text{ hours depending} \\ \text{on the bulk of R})}]{MgX_2} (C_6H_5)_2P\underset{\underset{O}{\|}}{\text{-}}PR'_2$$
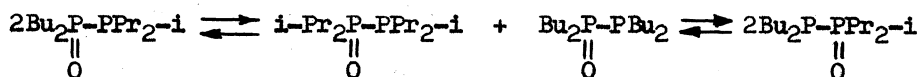
(I)                                             (III)
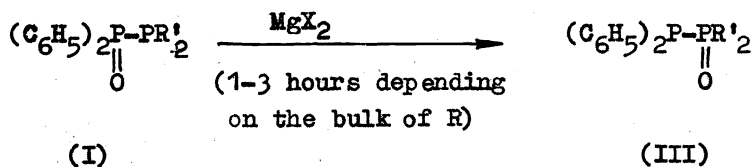
R=cyclo $-C_6H_{11}$, iso-Pr, tert.-Bu

The difference in the surrounding of the phosphorus atom caused by butyl and tert.-butyl groups is sufficient to cause the irreversible rearrangement:

$$Bu_2\underset{\underset{O}{\|}}{P}\text{-}PBu_2\text{-tert} \xrightarrow[3\text{-}4 \text{ hrs, } 180^\circ]{MgBr_2} Bu_2P\text{-}\underset{\underset{O}{\|}}{P}Bu_2\text{-tert}$$
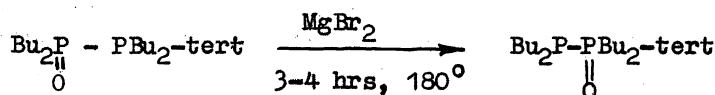
If one of the phosphorus atoms is bonded with primary radicals and another with secondary radicals, rearrangement becomes reversible:

$$2Bu_2\underset{\underset{O}{\|}}{P}\text{-}PPr_2\text{-}i \rightleftharpoons i\text{-}Pr_2\underset{\underset{O}{\|}}{P}\text{-}PPr_2\text{-}i + Bu_2\underset{\underset{O}{\|}}{P}\text{-}PBu_2 \rightleftharpoons 2Bu_2\underset{\underset{O}{\|}}{P}\text{-}PPr_2\text{-}i$$
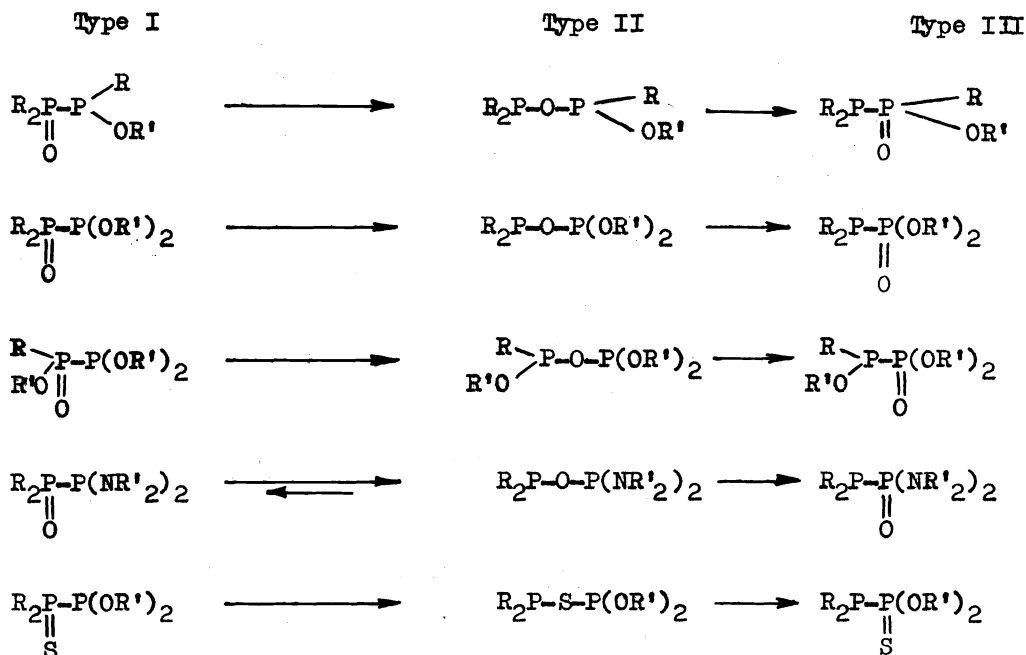
All the four compounds are in about equal amount (this fact means that all of them possess almost the same thermodynamic stability) and the equilibrium state can be approached by several ways. The data obtained may suggest both that stabilization of the P=O group is ensured by the donor character of the radicals bonded with this group and that the transition into a four-coordination state of the most shielded phosphorus atom decreases the spatial hindrances in the molecule as a whole. With a rise of the bulk of the radicals their electron-donor properties also increases; therefore, the observed direction of rearrangement cannot be related to only one of these two reasons. It is quite possible that the direction of these rearrangements is determined both by electron and steric factors. It should be noted that, if steric factors have played the main role in determining the direction of the rearrangement, the spatial hindrances in the compounds under study were, however, insufficient for anhydride to acquire the stability comparable with that of monoxide. Really, if two phosphorus atoms have different donor alkyl substituents, no anhydrides were observed whereas stable isomeric anhydrides are given in Table 2 for tetraalkyldiphosphine monoxides having the same substituents at both phosphorus. This difference may be due to the fact that in the first case /16/ the compounds were studied containing less bulky radicals than in the case of oxides of symmetrical diphosphines /19/. Therefore, oxide of unsymmetrical diphosphine $R_2\underset{\underset{O}{\|}}{P}\text{-}PR'_2$ could yet

decrease the spatial hindrances in the molecule as a whole isomerizing not into anhydride but into $R_2\underset{\underset{O}{\|}}{P}\text{-}PR'$ that is in such a way which permit the

phosphoryl group in the molecule, energetically favourable for donor (alkyl) substituents, to be retained.

If acceptor groups OR and $NR_2$ are among the substituents at the phosphorus atom, all three possible isomers including the anhydride II are observable unlike in the case of compounds containing only donor alkyl groups.

These three isomers are interconnected by an irreversible rearrangement (Table 6).

## Table 6

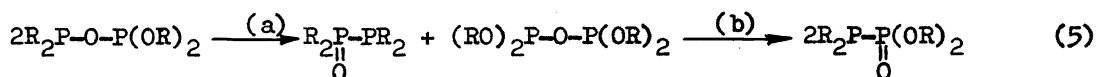| Type I | | Type II | Type III |
|---|---|---|---|
| $R_2P(O){-}P\!\!\begin{array}{l}R\\OR'\end{array}$ | $\longrightarrow$ | $R_2P{-}O{-}P\!\!\begin{array}{l}R\\OR'\end{array}$ $\longrightarrow$ | $R_2P(O){-}P\!\!\begin{array}{l}R\\OR'\end{array}$ |
| $R_2P(O){-}P(OR')_2$ | $\longrightarrow$ | $R_2P{-}O{-}P(OR')_2$ $\longrightarrow$ | $R_2P{-}P(O)(OR')_2$ |
| $\begin{array}{l}R\\R'O\end{array}\!\!P(O){-}P(OR')_2$ | $\longrightarrow$ | $\begin{array}{l}R\\R'O\end{array}\!\!P{-}O{-}P(OR')_2$ $\longrightarrow$ | $\begin{array}{l}R\\R'O\end{array}\!\!P{-}P(O)(OR')_2$ |
| $R_2P(O){-}P(NR'_2)_2$ | $\rightleftharpoons$ | $R_2P{-}O{-}P(NR'_2)_2$ $\longrightarrow$ | $R_2P{-}P(O)(NR'_2)_2$ |
| $R_2P(S){-}P(OR')_2$ | $\longrightarrow$ | $R_2P{-}S{-}P(OR')_2$ $\longrightarrow$ | $R_2P{-}P(S)(OR')_2$ |

The rate of these isomerizations depends on the type of the compounds and decreases sharply with a growth of the spatial hindrances. The least stable are all the compounds of the structure I, especially those containing OR groups. It was already mentioned that the acceptors bonded with a three-coordinate phosphorus destabilize monoxides i.e. a relative stabilization of isomeric anhydride takes place (see Tables 1, 4, 5). Rearrangement into II in this case proceeds readily at room temperature even when R=tert.butyl whereas $R_2P(O){-}P(NR'_2)_2$ can be retained unchanged for same time under these conditions even when R=primary alkyl.

Monothiooxides I isomerize much slower than oxygen analogues /17/. In-spite of the fact that thioanhydride of dialkylphosphorous acid is unstable and only monothiooxide isomeric to it exists /18/, the formation of mixed thioanhydride II was fixed upon rearrangement I $\longrightarrow$ III. Some data allow an assumption to be made that in the case of dialkylamide substituents re-arrangement of monoxide I into anhydride II is reversible /11/. It is re-markable that a complete transformation of monoxides of the type I contain-ing OR groups into the corresponding anhydrides of type II terminates ear-lier than the further transformations of the latters begin. Thus, the loss of the phosphoryl group taking place during rearrangement I $\longrightarrow$ II is ther-modynamically favourable. However, upon storage, heating, or, in particular, under the action of electrophilic catalysts all anhydrides of type II iso-merize irreversibly with the formation of phosphoryl-containing compounds, namely, monoxides III. In these thermodynamically most stable isomers the phosphoryl grouping P=O is bonded with alkoxy- or dialkylaminogroups, exhi-biting mesomeric donor properties at such position, and a three-coordinate

phosphorus atom has a less pronounced acceptor nature than in isomers I.
As far as the route of such transition is concerned, we can claim only that
there are several intermolecular ways of the reaction in which the essen-
tial is coordination of phosphorus atoms with different or similar surround-
ing:

$$
\begin{array}{ccc}
 & O & \\
R_2P & \curvearrowright & PX_2 \\
X_2P & & PR_2 \\
 & O & 
\end{array}
\qquad\qquad
\begin{array}{ccc}
 & O & \\
R_2P & \curvearrowright & PX_2 \\
R_2P & & PX_2 \\
 & O & 
\end{array}
$$

(the corresponding coordination with catalysts is performed even more
readily). Interaction according to the first scheme gives monoxides of
type III, and according to the second scheme proceeds with the intermediate
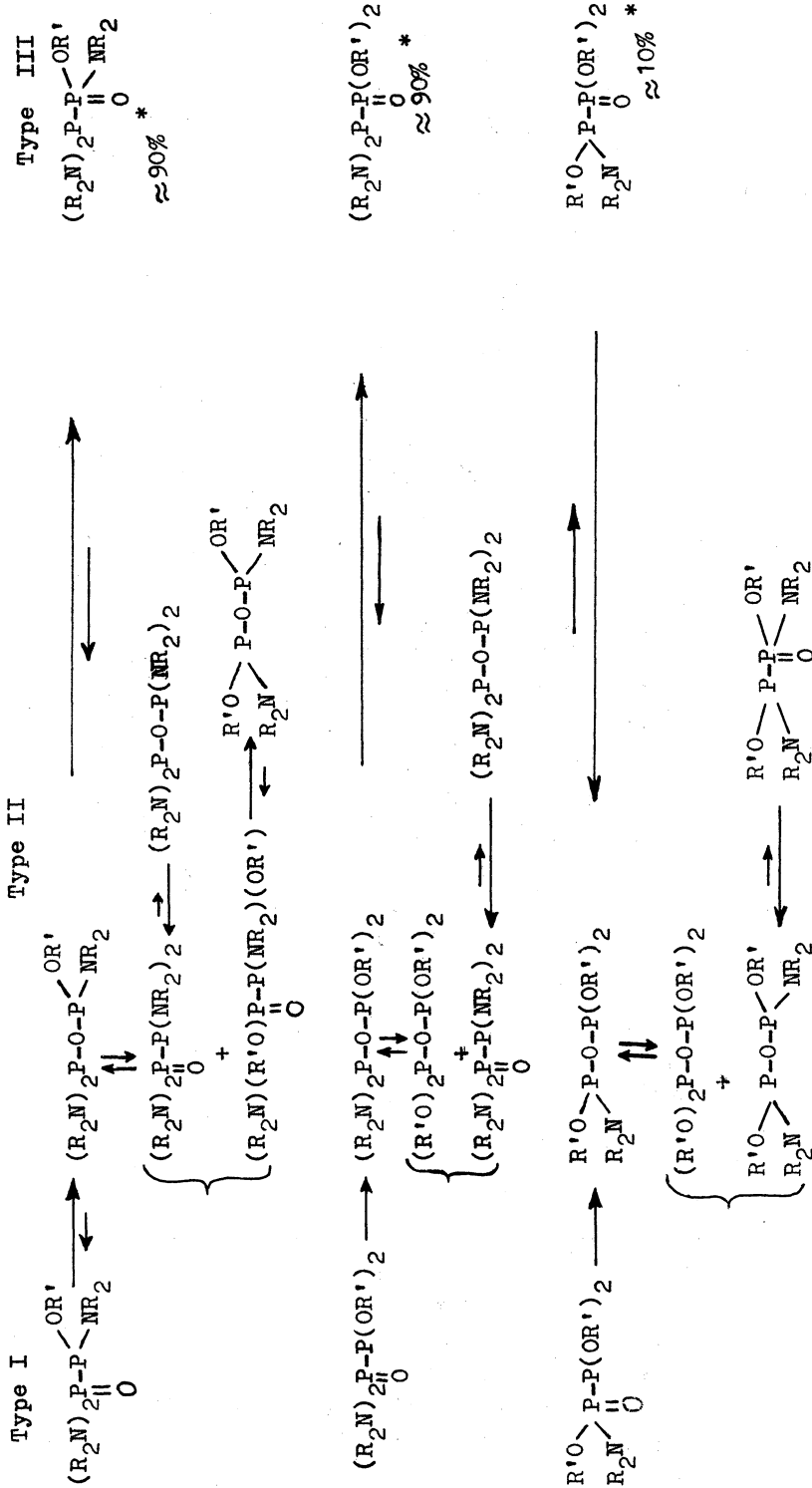formation of two molecules with similar radicals at the phosphorus atoms,
for instance:

$$2R_2P\text{-}O\text{-}P(OR)_2 \xrightarrow{\text{(a)}} R_2\overset{\|}{\underset{O}{P}}\text{-}PR_2 + (RO)_2P\text{-}O\text{-}P(OR)_2 \xrightarrow{\text{(b)}} 2R_2\overset{\|}{\underset{O}{P}}\text{-}P(OR)_2 \qquad (5)$$

The second way is clearly seen for numerous phosphorus compounds with dif-
ferent substituents. As special experiments have shown, the rate of the
reaction (b) of two symmetrical compounds can sometimes be higher than the
rate of isomerization II ⟶ III. The rate of interaction between two mono-
xides of symmetrical diphosphines containing alkyl and aryl radicals is
always much higher than the rate of isomerization of less stable monoxide
into a more stable one /3/. The trends observed can be explained in diffe-
rent ways but experimental data available up to now are insufficient for
a more detailed discussion of the isomerization routes.

The direction of rearrangement I ⟶ II ⟶ III (Table 6) is compar-
able with that of the functional exchange according to equation 3 and may
be caused by the different thermodynamic stability of the compounds of four-
coordination phosphorus due to different surrounding of the phosphoryl group.
As is known, the energy of dissociation of the phosphoryl group in compounds
of the $X_3P=O$ type decrases in the series $X=R_2N > OR > R > Ar$, evidently in
the sequence in which the donor properties of X decrease with respect to
strong acceptor, namely, the phosphorus atom in P=O.

As in the case of diphosphine monoxides considered above containing
sufficiently different substituents at the phosphorus atom, from two possible
isomers the more stable is the isomer of type III in which electrons of
the surrounding ligands are attracted by the positively charged phosphorus
atom stronger than in isomeric compounds of type I. In other words, in
isomer III destabilization of phosphoryl group by the acceptor substituents
present in the molecule (three-coordination phosphorus and groups bonded
to it) is less pronounced than in isomer I.

Using as an example the compounds containing only OR and $NR_2$ groups,
i.e. when the surrounding of both phosphorus atoms does not differ very
much, we succeeded to observe more complex relations between the isomers
than irreversible rearrangement I ⟶ II ⟶ III considered above. In par-
ticular, the data of Table 7 illustrate that accumulation of the acceptor

Table 7

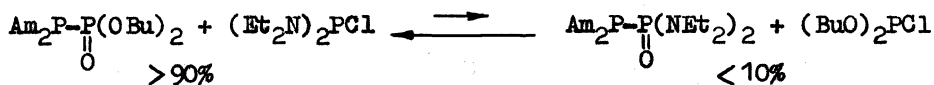| Type I | Type II | Type III |
|---|---|---|

**Type I**

$(R_2N)_2\overset{\text{OR'}}{\underset{\overset{\|}{O}}{P}}-P\diagdown_{NR_2} \;\rightleftarrows\; (R_2N)_2P-O-P\diagup^{OR'}_{\diagdown NR_2}$

**Type II**

$(R_2N)_2\overset{\|}{\underset{O}{P}}-P(NR_2)_2 \;\rightarrow\; (R_2N)_2P-O-P(NR_2)_2$

$+$

$(R_2N)(R'O)\overset{\|}{\underset{O}{P}}-P(NR_2)(OR') \;\rightleftarrows\; R'O\diagdown_{R_2N}P-O-P\diagup^{OR'}_{\diagdown NR_2}$

$(R_2N)_2\overset{\|}{\underset{O}{P}}-P(OR')_2 \;\rightarrow\; (R_2N)_2P-O-P(OR')_2$

$+$

$(R'O)_2\overset{\|}{\underset{O}{P}}-P(OR')_2$

$(R_2N)_2\overset{\|}{\underset{O}{P}}-P(NR_2)_2 \;\rightleftarrows\; (R_2N)_2P-O-P(NR_2)_2$

$R'O\diagdown_{R_2N}\overset{\|}{\underset{O}{P}}-P(OR')_2 \;\rightleftarrows\; R'O\diagdown_{R_2N}P-O-P(OR')_2$

$+$

$(R'O)_2\overset{\|}{\underset{}{P}}-P(OR')_2$

$R'O\diagdown_{R_2N}P-O-P\diagup^{OR'}_{\diagdown NR_2}$

**Type III**

$(R_2N)_2P-P\diagup^{OR'}_{\diagdown NR_2}$
$\qquad \overset{\|}{O}$
$\approx 90\%\;*$

$(R_2N)_2P-P(OR')_2$
$\qquad \overset{\|}{O}$
$\approx 90\%\;*$

$R'O\diagdown_{R_2N}P-P(OR')_2$
$\qquad \overset{\|}{O}$
$\approx 10\%\;*$
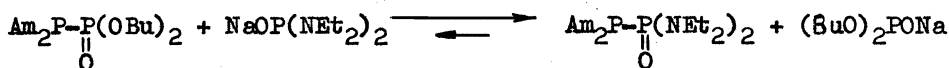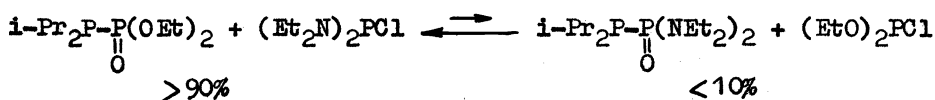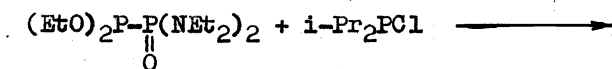
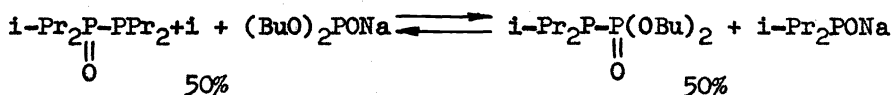*the equilibrium content at 20°C

R=R'=Et

groups at phosphorus atoms with different surrounding is responsible for
the fact that the anhydrides appear in equilibrium with the most stable
monoxide. Since mixed anhydrides can disproportionate reversibly, five or
six compounds participate in spectrally fixed equilibria. For the case of
three and even two $NR_2$ groups the part of monoxide III is still very high
(for $(R_2N)_2P-P(O)(OR)_2$ it is close to 90%), whereas the equilibrium part
of isomeric monoxide of symmetrical diphosphine $R_2N(RO)P-P(O)(OR)NR_2$ with
OR group at $P^{3+}$ is only 30% (see Table 4). This shows how strongly mono-
xide is destabilized by the acceptors bonded with $P^{3+}$. The same conclusion
is also illustrated by the much greater stability of the isomer of monoxide
not of type I but of type III (see Table 7), i.e. of the isomer not contain-
ing an alkoxy-group at a three-coordinate phosphorus atom. As is seen from
Table 7 destabilizing effect of acceptor groups (alkoxy-groups in this
case) bonded to three-coordinate phosphorus, is a more essential factor for
these monoxides than the difference in stabilizing effect of OR and $NR_2$ sub-
stituents bonded with the phosphoryl group and capable of stabilizing the
phosphoryl group due to their mesomeric donor properties. Although $NR_2$ are
stronger mesomeric donors than OR groups, the difference is not so great to
expect an especially high stability of monoxides $R_2P-P(O)(NR_2)_2$ as compared
with $R_2P-P(O)(OR)_2$. By the way it should be noted that all phosphoryl com-
pounds of type III do not possess a special chemical stability even if they
are formed irreversibly from their isomers. On the contrary, these compounds
are rather reactive and, when considering their formation as a result of any
reaction, the nature of the compounds obtained simultaneously must be taken
into account. In connection with this, it is interesting to discuss several
reactions in the course of which the reacting compounds may mutually ex-
change their phosphorus atoms bonded with all three types of substituents
considered above (R, OR, and $NR_2$):

$$Am_2P-P(OBu)_2 + NaOP(NEt_2)_2 \rightleftharpoons Am_2P-P(NEt_2)_2 + (BuO)_2PONa$$
$$\underset{O}{\|} \qquad\qquad\qquad\qquad\qquad \underset{O}{\|}$$

$$Am_2P-P(OBu)_2 + (Et_2N)_2PCl \rightleftharpoons Am_2P-P(NEt_2)_2 + (BuO)_2PCl$$
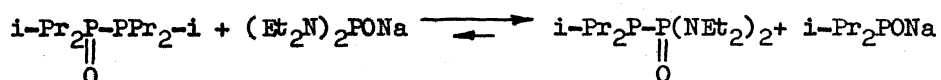$$\underset{O}{\|} \quad >90\% \qquad\qquad\qquad \underset{O}{\|} \quad <10\%$$

Almost complete shift of the first equilibrium to the right is related
to accumulation of a less nucleophilic anion, whereas a very strong shift of
the second equilibrium to the left is caused by the formation of a less
electrophilic acid chloride /11/. A similar strongly shifted equilibrium
between the compounds of the same type is established very fast upon inter-
action of other initial compounds although the formation of the products
requires a number of successive transformations of anhydrides and monoxides:

$$(EtO)_2P-P(NEt_2)_2 + i-Pr_2PCl \longrightarrow$$
$$\underset{O}{\|}$$

$$i-Pr_2P-P(OEt)_2 + (Et_2N)_2PCl \rightleftharpoons i-Pr_2P-P(NEt_2)_2 + (EtO)_2PCl$$
$$\underset{O}{\|} \quad >90\% \qquad\qquad\qquad \underset{O}{\|} \quad <10\%$$

Consequently, the phosphorus atoms containing groupings R, OR, and NR$_2$ are distributed in final compounds independently of the method of performing the reaction. Distribution proceeds in such a way that the pairs of least reactive compounds are formed. Although in the equilibrium given below monoxides are in almost equal concentration /11/

$$i\text{-Pr}_2\overset{\|}{\underset{O}{P}}\text{-PPr}_2\text{+i} + (\text{BuO})_2\text{PONa} \rightleftharpoons i\text{-Pr}_2\overset{\|}{\underset{O}{P}}\text{-P(OBu)}_2 + i\text{-Pr}_2\text{PONa}$$
$$\qquad\qquad 50\% \qquad\qquad\qquad\qquad\qquad\qquad\qquad 50\%$$

no conclusion should be made about similar stability of these monoxides. Equal amounts of these compounds in equilibrium may be due to a sharply different basicity of two anions (pK$_a$ of the corresponding acids according to Tsvetkov /12/ differ by 7 orders of magnitude). Only in the case when the basicity of anions is comparable, the position of equilibrium will be determined by the formation of the more stable (less reactive) phosphoryl-containing compound. Thus, the equilibrium of the reaction

$$i\text{-Pr}_2\overset{\|}{\underset{O}{P}}\text{-PPr}_2\text{-i} + (\text{Et}_2\text{N})_2\text{PONa} \rightleftharpoons i\text{-Pr}_2\overset{\|}{\underset{O}{P}}\text{-P(NEt}_2)_2\text{+} i\text{-Pr}_2\text{PONa}$$

is strongly shifted to the right.

From the above it follows, that only in some case the relative thermodynamic stability of non-isomeric diphosphine monoxides can be compared chemically (see also /13/). At the same time the relative stability of isomeric compounds of types I, II, and III is judged unambiguously by the direction of rearrangement. As far as only the relative stability of the isomers is concerned, the following statement is valid: if the influence of some general factors or, simply, the effect of substituents stabilizing or destabilizing one of the forms is clear, one may not concider the essence of such an influence on the other isomer. It is obvious that the same factors must exert an opposite effect on the relative stability of another form. The data presented for symmetrical and non-symmetrical compounds allow a conclusion to be made that the existence of diphosphine monoxides (i.e. the system with phosphoryl or thiophosphoryl groups) is favoured by a small bulk of the substituent and by a rise in donor (or a decrease in acceptor) properties of the substituents (namely because of this anhydride II is rearranged into monoxide III and not into monoxide I). The opposite changes in the molecule enhance the relative stability of the anhydride, that is an isomer with three-coordinate phosphorus atoms. The effect of substituents which determine what type of the structure is more stable (monoxide or anhydride) can be rather fine. This is evidenced, for example, by two irreversible isomerization processes when a change of two alkyl groups by alkoxyl causes the inversion of rearrangements

$$R_2\text{P-O-P(OR)}_2 \longrightarrow R_2\overset{\|}{\underset{O}{P}}\text{-P(OR)}_2 \qquad\qquad (\text{RO})_2\overset{\|}{\underset{O}{P}}\text{-P(OR)}_2 \longrightarrow (\text{RO})_2\text{P-O-P(OR)}_2$$

The similar inversion of the relative stability of anhydride and monoxide is clearly seen from Tables 1, 2, and 3 which include reversible isomerizations and, especially, from Table 6, where isomerization processes are irreversible. Really, the system of bonds P-O-P in anhydride II $R_2P-O-P(OR)_2$ is more stable than that of the bonds with the phosphoryl group $R_2P(O)-P(OR)_2$ in monoxide I what is supported by irreversibility of the rearrangement I $\longrightarrow$ II. At the same time the fact that transition II $\longrightarrow$ III is irreversible points to the higher stability of the bond system in monoxide III $R_2P-P(O)(OR)_2$ than in anhydride II $R_2P-O-P(OR)_2$.
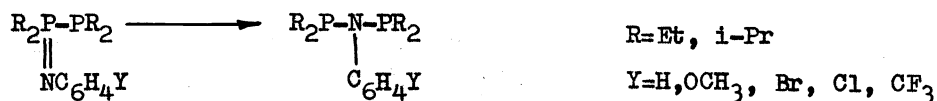
The given examples demonstrate that, although general trends determining the relations between isomers are clear, specific condlusions about the effect of electron factors on the stability of the bond system P-O-P and $\underset{O}{\overset{\|}{P}}$-P can be derived only for the studied substituents R, $NR_2$, and OR. If these substituents can be arranged in such a way that each of the phosphorus atoms of diphosphine monoxide becomes surrounded by the donors only, the formation of this isomer is irreversible (for instance, monoxides III, Table 6, which are also smoothly formed from two assymetric compounds, see route (b) of equation 5). If such an arrangement of the substituents is impossible and in any of the isomeric monoxides acceptors are retained at $P^{+3}$, the number of the acceptors in such position is less in a more stable isomer (see Table 7). The thermodynamic stability of such a monoxide will be commensurable with that of anhydrides whose part in the equilibrium state is the higher, the greater the number of acceptor substituents (see Table 1, 4, 5, 7).

The laws determing the structure of oxidized derivatives of organic diphosphines (A=O) are valid, in general, for thioanalogues (A=S), although thiophosphoryl group is destabilized by the acceptor substituents bonded with it apparently in a much lesser extent than the phosphoryl group /18/. When passing to iminooxides (A=NX), not only the nature of heteroatom (nitrogen) must be taken into account but the effect of the substituent X bonded with N.

In spite of the fact that both types of the compounds $R_2\underset{NX}{\overset{\|}{P}}-PR_2$ and $R'_2\underset{X}{\overset{|}{P}}-N-PR'_2$, which are of interest for us, are described in literature /20/, no isomers were observed among them and the possibility of rearrangement was not considered.

We have found that aryliminoxides of tetraalkyl diphosphines isomerize irreversibly into diphosphinoamines under the action of nucleophilic catalysts /7/:

$$R_2\underset{NC_6H_4Y}{\overset{\|}{P}}-PR_2 \longrightarrow R_2P-\underset{C_6H_4Y}{\overset{|}{N}}-PR_2 \qquad \begin{array}{l} R=Et, \text{ i-Pr} \\ Y=H, OCH_3, Br, Cl, CF_3 \end{array}$$

(without a catalyst decomposition of a novel type takes place with the formation of diphosphine and anilide /21/).

Quite unexpectedly it turned out that the rearrangement observed by us for X=Ar reverses its direction when X=$(CH_3)_3$Si:

$$Et_2P-N-PEt_2 \quad \longrightarrow \quad Et_2P-PEt_2$$
$$| \qquad\qquad\qquad\qquad\qquad || $$
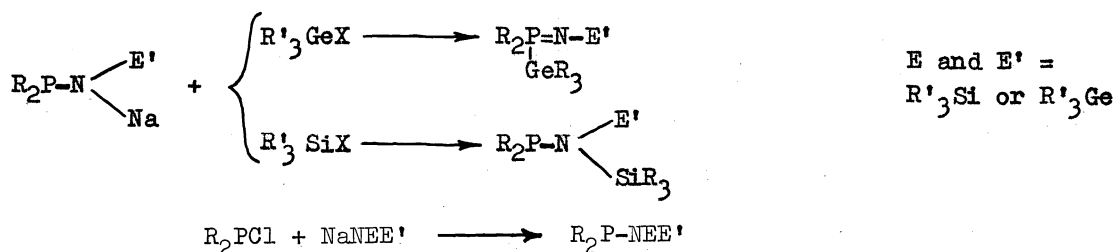$$SiMe_3 \qquad\qquad\qquad\qquad NSiMe_3$$
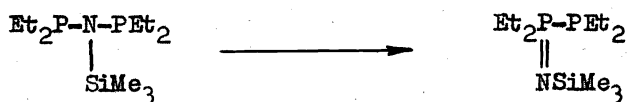
It seemed undoubtful that the acceptor substituents X bonded with the nitrogen atom must bring the polarity of the phosphazo-group nearer to that of phosphoryl group. Thus, they may increase the stability of iminoxides as compared with diphosphinoamines. It should be noted that in the papers of Schmidpeter a number of compounds was described in which the nitrogen atom was bonded with strong acceptors; all these compounds have the structure of iminoxides /22/.

In spite of the fact that Si has an undoubtfully acceptor character with respect to N, the inversion of thermodynamic stability of isomers cannot be associated with this factor only without additional investigations. Since the conformational requirements in the case of diphosphinoamines are rather strict /23/, an assumption has arisen that the observed transformation is also related to spatial hindrances caused by trimethylsilyl group. In order to study the effect of the bulk of the substituents on the interrelation between the stability of isomers containing three- and four-coordinate phosphorus atoms, we have chosen the most convenient compounds, namely, dielementosubstituted amides of phosphinous acids

$R_2P-N{<}^{E'}_{E}$ (IV) whose isomeric form contains four-coordinate phosphorus:

$R_2P=N-E'$ (V) (E and E' are elements of IV Group). Both types of the com-
$\quad|$
$\quad E$

pounds were obtained by the following reactions (in the first reaction germanium attacks the phosphorus atom and silicon - the nitrogen atom):

$$R_2P-N{<}^{E'}_{Na} \; + \; \begin{cases} R'_3GeX \longrightarrow R_2P=N-E' \\ \qquad\qquad\qquad\qquad GeR_3 \\ \\ R'_3SiX \longrightarrow R_2P-N{<}^{E'}_{SiR_3} \end{cases} \qquad\qquad \begin{array}{l} E \text{ and } E' = \\ R'_3Si \text{ or } R'_3Ge \end{array}$$

$$R_2PCl + NaNEE' \longrightarrow R_2P-NEE'$$

It was shown that the relative thermodynamic stability of the compounds of IV and V types depends both on the nature of E and E' and on spatial hindrances caused by radicals bonded with the phosphorus atom and an element of the IV group.

It turned out that all the obtained compounds containing two silicon atoms have three-coordinate phosphorus atom, $R_2P-N(SiR'_3)_2$ independently of the bulk of the radicals connected to phosphorus (Et, i-Pr, t-Bu). When E=$GeR_3$ and E'=$SiMe_3$ the structure of isomer is directly related to the bulk of the radicals: for R=Et the form is stable with three-coordinate phosphorus atom $Et_2P-N(GeMe_3)(SiMe_3)$; for R=t-Bu - with four-coordinate:

$t-Bu_2\underset{\underset{GeMe_3}{|}}{P} = NSiMe_3$. The latter isomer was described in a detailed paper by
Scherer and Schieder /24/. We succeeded to ascertain, however, that the
rearrangement observed by the authors, which they considered to be due to
mutual transposition of E and E' in compound of the type V, is really
caused by isomerization of the compound of type IV into that of type V,
i.e. by transition of phosphorus from three—coordinate state into four—
coordinate because of germanium migration:

$$t-Bu_2P-N \underset{GeMe_3}{\overset{SiMe_3}{<}} \longrightarrow t-Bu_2\underset{\underset{GeMe_3}{|}}{P}=N-SiMe_3$$

For R=i-Pr we have found a germanotropic equilibrium:

$$i-Pr_2P-N \underset{GeR_3}{\overset{SiMe_3}{<}} \rightleftharpoons i-Pr_2\underset{\underset{GeR_3}{|}}{P}=N-SiMe_3$$
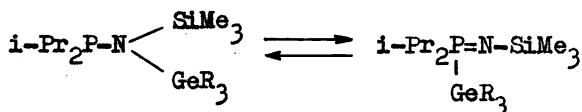
| R=Me | | R=Bu | |
|---|---|---|---|
| $t^\circ C$ | share of $P^V$ | $t^\circ C$ | share of $P^V$ |
| 20 | 1/15 | 20 | 1/3 |
| 200 | 1/4 | 160 | 2/3 |

Similar equilibrium has been observed also for the compounds containing
two germanium atoms. For the compounds containing isopropyl radicals at
the phosphorus atom the following rearrangement goes up practically to the
end:

$$i-Pr_2\underset{\underset{GeMe_3}{|}}{P}=N-GeMe_3 \longrightarrow i-Pr_2P-N \underset{GeMe_3}{\overset{GeMe_3}{<}}$$
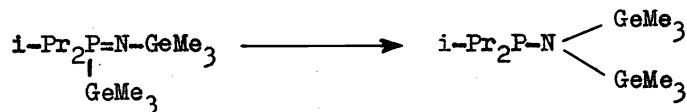
But an equilibrium is established for the compounds containing tert.-butyl
radicals:

$$t-Bu_2P-N \underset{GeMe_3}{\overset{GeMe_3}{<}} \rightleftharpoons t-Bu_2\underset{\underset{GeMe_3}{|}}{P}=N-GeMe_3$$
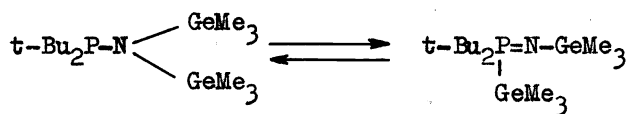
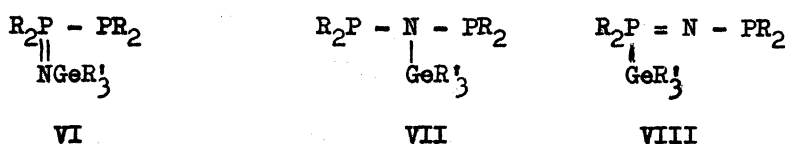| $t^\circ C$ | Share of $P^V$ |
|---|---|
| 20 | < 1/20 |
| 200 | > 20/1 |

For germanotropic equilibria, which proved to be very sensitive to tempera-
ture, the equilibrium in all cases is approached from both sides.

Thus, it turned out that in elementosubstituted amides of phosphorus
acids germanium can be bonded both with P and N, whereas silicon is always
bonded only with N. It has already been shown that thermodynamic stability
of isomer $R_2\underset{\underset{GeR_3}{|}}{P}=NX$, containing P-Ge bond, increases with a rise in spatial
hindrances. However, the acceptor nature of the substituent X bonded with
nitrogen also plays a role in stabilization. This conclusion may be made on
the basis of the fact that in $R_2P(GeR'_3)=NX$ the donor substituent X=t-Bu
contrary to X=SiMe₃ does not cause any noticeable stabilization of four—

coordinate phosphorus atom:

$$t\text{-Bu}_2\text{P-N} \begin{cases} \text{GeMe}_3 \\ \text{Bu-t} \end{cases}$$

100%

$$t\text{-Bu}_2\text{P=N-SiMe}_3 \\ | \\ \text{GeMe}_3$$

100%
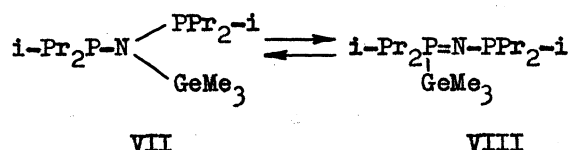
Since three-coordinate phosphorus, as well as silicon, is an acceptor with respect to nitrogen, we decided to study compounds in which X=$R_2$P, i.e. germanium derivatives of diphosphinoamine. Unlike Si-derivatives of diphosphino-amine considered above for which only two isomers have been obtained, for germanium derivatives all three possible isomers have been synthesized by independent methods:

$$\begin{matrix} R_2P - PR_2 \\ || \\ NGeR'_3 \end{matrix} \qquad \begin{matrix} R_2P - N - PR_2 \\ | \\ GeR'_3 \end{matrix} \qquad \begin{matrix} R_2P = N - PR_2 \\ | \\ GeR'_3 \end{matrix}$$

VI                        VII                       VIII

The compounds VI and VII can be interrelated by the migration of the phosphorus atom; VII and VIII by that of germanium atom. Only this latter migration which proceeds with the sufficient rate was observed. This iso-merization is reversible and, as in the case of the described above other germanotropic equilibria, the share of the isomer with the four-coordina-te phosphorus (compounds VIII) greatly increases with temperature.

$$i\text{-Pr}_2\text{P-N} \begin{cases} \text{PPr}_2\text{-i} \\ \text{GeMe}_3 \end{cases} \rightleftarrows i\text{-Pr}_2\text{P=N-PPr}_2\text{-i} \\ | \\ \text{GeMe}_3$$

VII                              VIII

| $t\,^\circ C$ | Share of $P^V$ |
|------|------|
| 20 | 1/4 |
| 165 | 2/3 |

The discovered increase in the relative thermodynamic stability of isomers containing the four-coordinate phosphorus atom with the increase of the bulk of the substituents may be due to greater spatial requirements of isomers with three-coordination phosphorus atom, in particular, confor-mational requirements including a certain orientation of unshared pairs. There are no contradictions in the opposite effect of the volume of the radicals on the relative stability of isomers for oxides and thiooxides on the one hand and iminoxides on the other. Bulky substituents linked by a short bond with nitrogen create great spatial hindrances to the molecules just with three-coordination atoms both of phosphorus and nitrogen. Upon phosphorus transition into a four-coordinate state, nitrogen becomes two-coordinate and spatial hindrances in the molecule as a whole decrease.

To evaluate the general laws determining the preferable stability of an isomer with three or four-coordinate phosphorus, it should be noted that there is no single reason for the stabilization. At least two main factors must be considered: the nature of the element A which forms a

double bond with phosphorus and the electronegativity of the element E. It
seems quite natural to expect a decrease in the stability of the isomer
$R_2\underset{\overset{\parallel}{A}}{P}$-E   as compared with $R_2$P-A-E in the series $A=O > S > NX > CX_2$; at the same
time a relative increase of the stability is observed with increasing accep-
tor character of $X^{a)}$. This gives rise to an idea that for the grouping P=A
some certain polarity is optimum. No less important factor stabilizing four-
coordinate phosphorus is high electronegativity of E, which, passing from A
to P, causes "internal oxidation" in the molecule. If electronegativity
values of P and E do not differ sufficiently and similar bond energies allow
the existence of both isomers, the structure of such compounds is determin-
ed by a number of factors. In addition to the above-mentioned factors, one
should note a very essential role of spatial hindrances. As was demonstrat-
ed above a rise in the bulk of the substituents may give opposite results
for A=O or N, although the reason for a change in coordination number of
phosphorus is always a trend to decrease steric hindrances in the molecule.
Electronic surrounding of phosphorus and element E is also important: ac-
ceptors increase the stability of three-coordinate form and donors at P
atom increase that of four-coordinate form. In those cases when the effect
of the above factors is opposite and approximately similar the tautomeric
interconversions have been observed. Further investigations allow for a bet-
ter understanding of the reasons for a predominant stability of the com-
pounds of trivalent phosphorus in three- or four-coordinate form.

TABLE 8. NMR Data for investigated compounds [b)]

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| Formula | $\delta^{31}P^{\underline{V}}$ ppm | $\delta^{31}P^{\underline{III}}$ ppm | $^1J_{PP}$ Hz |
| $R_2\underset{\overset{\parallel}{O}}{P}$-P$\underset{OR'}{\overset{R}{<}}$   ( Type I ) | | | |
| i-Pr$_2$P(O)-P(OPh)Bu-t | -64.4 | -135.2 | 290 |
| i-Pr$_2$P(O)-P(OBu)Bu-t | -63.1 | -139.0 | 332 |
| t-Bu$_2$P(O)-P(OBu)Bu | -70.0 | -135.0 | 288 |
| t-Bu$_2$P(O)-P(OBu)Pr-i | -61.5 | -134.0 | 324 |
| t-Bu$_2$P(O)-P(OBu)Bu-t | -71.0 | -155.0 | 326 |

a) For $A=CX_2$ see the data in paper /25/.
b) See also ref. /3/.

| 1 | 2 | 3 | | 4 |
|---|---|---|---|---|

$R_2P-O-P\langle\overset{A}{\phantom{}}\overset{B}{\phantom{}}\rangle$ 

| 1 | 2 | 3 | | 4 |
|---|---|---|---|---|
| $R_2\overset{A}{P}-O-\overset{B}{P}\langle^R_{OR'}$    (Type II) | | A | B | |
| $Bu_2P-O-P(OBu)Bu$ | | −128.0 | −183.0 | 95 [a)] |
| $Bu_2P-O-P(OBu)Bu-t$ | | −134.0 | −177.0 | 98 [a)] |
| $i-Pr_2P-O-P(OPh)Bu-t$ | | −144.3 | −184.3 | 76 [a)] |
| $i-Pr_2P-O-P(OBu)Bu-t$ | | −151.0 | −177.6 | 76 [a)] |
| $t-Bu_2P-O-P(OPh)Bu-t$ | | −156.6 | −181.8 | 82 [a)] |
| $t-Bu_2P-O-P(OBu)Bu-t$ | | −153.6 | −186.0 | 76 [a)] |
| $R_2P-\underset{O}{\overset{\|}{P}}\langle^R_{OR'}$    (Type III) | | | | |
| $Bu_2P-P(O)(OBu)Bu$ | −66.3 | +54.3 | | 224 |
| $Bu_2P-P(O)(OPh)Bu-t$ | −73.7 | +49.5 | | 310 |
| $i-Pr_2P-P(O)(OPh)Bu-t$ | −73.5 | + 7.4 | | 349 |
| $i-Pr_2P-P(O)(OBu)Bu-t$ | −62.6 | +10.0 | | 310 |
| $t-Bu_2P-P(O)(OBu)Bu-t$ | −72.7 | −23.8 | | 360 |
| $\overset{R}{\underset{R'O}{\diagdown\diagup}}\underset{O}{\overset{\|}{P}}-P\langle^R_{OR'}$   (Type I) [b)] | | | | |
| $Bu(BuO)P(O)-P(OBu)Bu$ | −63.1<br>−61.0 | −109.0<br>−116.0 | | 242<br>238 |
| $Ph(BuO)P(O)-P(OBu)Ph$ | −47.2<br>−44.6 | − 95.0<br>−101.0 | | 234<br>245 |
| $i-Pr(BuO)P(O)-P(OBu)Pr-i$ | −63.3<br>−60.8 | −124.3<br>−126.5 | | 254<br>277 |
| $t-Bu(BuO)P(O)-P(OBu)Bu-t$ | −62.9<br>−68.0 | −139.0<br>−144.0 | | 340<br>325 |
| $(R_2N)_2\underset{O}{\overset{\|}{P}}-P(NR_2)_2$   (Type I) | | | | |
| $(Me_2N)_2P(O)-P(NMe_2)_2$ | −34.0 | −78.7 | | 134 |
| $(Et_2N)_2P(O)-P(NEt_2)_2$ | −32.9 | −67.2 | | 124.5 |
| $(i-Pr_2N)_2P(O)-P(NPr_2-i)_2$ | −44.0 | −82.0 | | 290 |

a) The data refer to $^2J_{PAP}$ where A=O,S,NR. Of interest are the high values of this costant comparable with those of $^1J_{pp}$ .

b) The data refer to diastereomers.

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| $(R_2N)_2P-O-P(NR_2)_2$ (Type II) | | | |
| $(Me_2N)_2P-O-P(NMe_2)_2$ | | -129.0 | |
| $(Et_2N)_2P-O-P(NEt_2)_2$ | | -123.5 | |
| $(i-Pr_2N)_2P-O-P(NPr_2-i)_2$ | | -103.7 | |
| $\begin{matrix} R_2N \diagdown \quad \diagup NR_2 \\ \quad P-P \\ R'O \diagup \underset{O}{\overset{\|}{\quad}} \diagdown OR' \end{matrix}$ (Type I) [b] | | | |
| $EtO(Et_2N)P(O)-P(NEt_2)OEt$ | -29.6 | -124.2 | 158 |
| | -30.0 | -125.4 | 163 |
| $i-PrO(Et_2N)P(O)-P(NEt_2)OPr-i$ | -29.3 | -122.5 | 145 |
| | -29.6 | -122.5 | 146 |
| $BuO(Et_2N)P(O)-P(NEt_2)OBu$ | -30.0 | -125.7 | 160 |
| | -30.6 | -126.7 | 163 |
| $EtO(PhNMe)P(O)-P(PhNMe)OEt$ | -25.5 | -121.4 | 191.5 |
| | -26.7 | -122.0 | 198 |
| $EtO(Morph)P(O)-P(Morph)OEt$ | -27.0 | -122.6 | 161 |
| | -27.0 | -120.6 | 160 |
| $\begin{matrix} R'O \diagdown \quad \diagup OR' \\ \quad P-O-P \\ R_2N \diagup \quad \diagdown NR_2 \end{matrix}$ (Type II) | | | |
| $EtO(Et_2N)P-O-P(NEt_2)OEt$ [b] | | -136.8 | |
| | | -137.2 | |
| $i-PrO(Et_2N)P-O-P(NEt_2)OPr-i$ | | -137.0 | |
| $BuO(Et_2N)P-O-P(NEt_2)OBu$ [b] | | -137.8 | |
| | | -138.2 | |
| $EtO(Morph)P-O-P(Morph)OEt$ [b] | | -133.1 | |
| | | -133.0 | |
| $EtO(PhNMe)P-O-P(PhNMe)OEt$ | | -132.3 | |
| $(R_2N)_2\underset{O}{\overset{\|}{P}}-P(OR')_2$ (Type I) | | | |
| $(Et_2N)_2P(O)-P(OBu)_2$ | -32.8 | -169.5 | 200 |
| $(Et_2N)_2P(O)-P(OPr-i)_2$ | -33.2 | -165.5 | 190 |

b) The data refer to diastereomers.

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| $(R_2N)_2\overset{A}{P}\text{-O-}\overset{B}{P}(OR')_2$  (Type II) | | A          B | |
| $(Et_2N)_2P\text{-O-}P(OBu)_2$ | | −123.4  −130.0 | 110[a] |
| $(Et_2N)_2P\text{-O-}P(OPr\text{-}i)_2$ | | −122.3  −131.7 | 108[a] |
| $(R_2N)_2\underset{\overset{\|}{O}}{P}\text{-}P(OR')_2$   (Type III) | | | |
| $(Et_2N)_2P\text{-}P(O)(OBu)_2$ | −26.8 | −71.5 | 146 |
| $(Et_2N)_2P\text{-}P(O)(OPr\text{-}i)_2$ | −25.2 | −73.0 | 135 |
| $(R_2N)_2\underset{\overset{\|}{O}}{P}\text{-}P\overset{\nearrow NR_2}{\searrow OR'}$   (Type I) | | | |
| $(Et_2N)_2P(O)\text{-}P(NEt_2)OEt$ | −30.7 | −127.0 | 158 |
| $(Et_2N)_2P(O)\text{-}P(PhNMe)OEt$ | −32.5 | −119.0 | 190 |
| $(R_2N)_2\overset{A}{P}\text{-O-}\overset{B}{P}(NR_2)OR'$  (Type II) | | A          B | |
| $(Et_2N)_2P\text{-O-}P(NEt_2)OEt$ | | −124.3  −139.3 | 117.5[a] |
| $(Et_2N)_2P\text{-O-}P(PhNMe)OEt$ | | −126.9  −131.5 | 125 [a] |
| $(R_2N)_2\underset{\overset{\|}{O}}{P}\text{-}P\overset{\nearrow NR_2}{\searrow OR'}$   (Type III) | | | |
| $(Et_2N)_2P\text{-}P(O)NEt_2(OEt)$ | −32.4 | −70.4 | 117.5 |
| $(Et_2N)_2P\text{-}P(O)(PhNMe)OEt$ | −29.5 | −71.0 | 155 |
| $\underset{R_2N}{\overset{R'O}{\diagdown\diagup}}\underset{\overset{\|}{O}}{P}\text{-}P(OR')_2$  (Type I) | | | |
| $EtO(Et_2N)P(O)\text{-}P(OEt)_2$ | −28.4 | −158.5 | 227 |
| $\underset{R_2N}{\overset{R'O}{\diagdown\diagup}}P\text{-O-}P(OR')_2$  (Type II) | | A          B | |
| $EtO(Et_2N)P\text{-O-}P(OEt)_2$ | | −136.7  −128.2 | 66[a] |

a) The data refer to $^2J_{POP}$

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| $\begin{array}{c} RO \\ \diagdown \\ \quad\quad P-P(OR)_2 \quad \text{(Type III)} \\ \diagup \quad \underset{O}{\overset{\|}{}} \\ R_2N \end{array}$ | | | |
| $EtO(Et_2N)P-P(O)(OEt)_2$ | −24.7 | −126.2 | 191 |
| $\underset{S}{\overset{\|}{R_2P}}-PR_2$ | | | |
| $i\text{-}Bu(i\text{-}Pr)P(S)\text{-}P(i\text{-}Pr)Bu\text{-}i$ [b)] | −57.5 | +25.8 <br> +28.0 | 278 |
| $t\text{-}Bu(n\text{-}Bu)P(S)\text{-}P(Bu\text{-}n)Bu\text{-}t$ [b)] | −61.5 <br> −69.0 | +8.8 <br> +6.8 | 325 <br> 310 |
| $t\text{-}Bu(i\text{-}Bu)P(S)\text{-}P(Bu\text{-}i)Bu\text{-}t$ [b)] | −58.0 | +10.5 <br> + 6.7 | 320 |
| $Ph_2P(S)\text{-}PPh_2$ | −44.1 | +14.1 | 249 |
| $R_2P\text{-}S\text{-}PR_2$ | | | |
| $i\text{-}Bu(i\text{-}Pr)P\text{-}S\text{-}P(Pr\text{-}i)Bu\text{-}i$ | | −41.0 | |
| $Bu(t\text{-}Bu)P\text{-}S\text{-}P(Bu\text{-}t)Bu$ | | −60.0 | |
| $i\text{-}Bu(t\text{-}Bu)P\text{-}S\text{-}P(Bu\text{-}t)Bu\text{-}i$ | | −55.0 | |
| $\underset{S}{\overset{\|}{R_2P}}-PX_2 \quad \text{(Type III)}$ | | | |
| $Bu_2P\text{-}P(S)(OEt)_2$ | −117.0 | +33.0 | 255 |
| $i\text{-}Pr_2P\text{-}P(S)(OEt)_2$ | −109.0 | − 7.5 | 268 |
| $t\text{-}Bu_2P\text{-}P(S)(OEt)_2$ | −105.0 | −41.5 | 330 |
| $\underset{NER'_3}{\overset{\|}{R_2P}}-PR_2$ | | | |
| $Et_2P(=NGeMe_3)PEt_2$ | −21.4 | +38.8 | 216 |
| $i\text{-}Pr_2P(=NGeMe_3)PPr_2\text{-}i$ | −30.0 | +10.5 | 253 |
| $i\text{-}Pr_2P(=NSiMe_3)PPr_2\text{-}i$ | −25.3 | +11.7 | 252 |
| $\underset{ER'_3}{\overset{\|}{R_2P}}-N-PR_2$ | | | |
| $Et_2PN(SiMe_3)PEt_2$ | −52.5 | | |
| $Et_2PN(GeMe_3)PEt_2$ | −57.0 | | |
| $i\text{-}Pr_2PN(SiMe_3)PPr_2\text{-}i$ | −78.0 | | |
| $i\text{-}Pr_2PN(SnMe_3)PPr_2\text{-}i$ | −72.5 | | |
| $i\text{-}Pr_2PN(GeMe_3)PPr_2\text{-}i$ | −83.2 | | |

b) The data refer to diastereomers.

| 1 | 2 | 3 | 4 |
|---|---|---|---|
| $R_2P=N-PR_2$ <br>     $\overset{I}{ER'_3}$ | | | |
| $Et_2P(=NPEt_2)GeMe_3$ | −43.3 | −74.7 | 130 |
| $i-Pr_2P(=NPPr_2-i)GeMe_3$ | −32.7 | −74.9 | 101 |
| $i-Pr_2P(=NPPr_2-i)GeBu_3$ | −35.6 | −76.0 | 90 |
| $R_2\overset{II}{P}-ER'_3$ <br>     $NER''_3$ | | | |
| $Et_2P(=NSiMe_3)GeMe_3$ | −5.5 | | |
| $i-Pr_2P(=NSiMe_3)GeMe_3$ | −17.7 | | |
| $i-Pr_2P(=NSiMe_3)GeBu_3$ | −18.5 | | |
| $i-Pr_2P(=NGeMe_3)GeMe_3$ | −29.5 | | |
| $t-Bu_2P(=NSiMe_3)GeMe_3$ | −33.0 | | |
| $t-Bu_2P(=NGeMe_3)GeMe_3$ | −34.5 | | |
| $t-Bu_2P(=NGeBu_3)GeBu_3$ | −37.0 | | |
| $t-Bu_2P(=NSiMe_3)SnMe_3$ | −39.5 | | |
| $R_2P-N-ER'_3$ <br>      $E'R''_3$ | | | |
| $Et_2PN(SiMe_3)_2$ | | −57.0 | |
| $Et_2PN(SiMe_3)GeMe_3$ | | −62.0 | |
| $Et_2PN(GeMe_3)_2$ | | −65.0 | |
| $i-Pr_2PN(SiMe_3)_2$ | | −78.0 | |
| $i-Pr_2PN(GeMe_3)_2$ | | −88.0 | |
| $i-Pr_2PN(SiMe_3)GeMe_3$ | | −83.0 | |
| $i-Pr_2PN(SiMe_3)GeBu_3$ | | −83.0 | |
| $i-Pr_2PN(SiMe_3)SnMe_3$ | | −83.5 | |
| $i-Pr_2PN(Pr)GeMe_3$ | | −73.5 | |
| $i-Pr_2PN(Bu-t)GeMe_3$ | | −78.0 | |
| $t-Bu_2PN(SiMe_3)_2$ | | −93.0 | |
| $t-Bu_2PN(GeMe_3)_2$ | | −102.0 | |
| $t-Bu_2PN(SiMe_3)GeMe_3$ | | −98.0 | |
| $t-Bu_2PN(Bu-t)GeMe_3$ | | −92.0 | |

Chemical shifts of $P^V$ fragments of monoxides I and III are close to the values typical for the same fragments bonded with alkyl radicals; for $P^{III}$ fragments of these monoxides such a comparison is also rightful though the

scattering of the values is somewhat greater. For anhydrides II chemical shifts of both fragments containing $P^{III}$ agree well with values known for corresponding esters.

## REFERENCES

1.  J. D. Roberts, M. C. Caserio, Basic principles of organic chemistry, New-York (1964).
2.  I. F. Lutsenko, Phosphorus and Sulfur 1, 99 (1976); Yu. A. Veits, A. A. Borisenko, V. L. Foss, I. F. Lutsenko, Zhurn. Obshch. Khim. 43, 440 (1973); I. F. Lutsenko, M. V. Proskurnina, A. L. Chekhun, Phosphorus, 4, 57 (1974).
3.  I. F. Lutsenko, V. L. Foss, Vestnik Mosk. Univ-ta, ser. khim., 19, 379 (1978).
4.  K. Issleib, B. Walter, J. Organometal. Chem. 22, 375 (1970); B. Walter, M. Wiese, Chemistry and application of organophosphorus compounds; Proceedings of V conferece, Moscow, 161 (1974); E. Fluck, H. Binder, Inorg. Nucl. Chem. Lett. 3, 307 (1967).
5.  V. L. Foss, Yu. A. Veits, N. V. Lukashev, Yu. E. Tsvetkov, I. F. Lutsenko, Zhurn. Obshch. Khim. 47, 479 (1977).
6.  V. L. Foss, Yu. A. Veits, T. E. Tret'yakova, I. F. Lutsenko, Zhurn. Obshch. Khim. 47, 954 (1977).
7.  R. Pearson, J. Songstad, J. Am. Chem. Soc. 89, 1827 (1967).
8.  V. L. Foss, Yu. A. Veits, V. A. Solodenko, I. F. Lutsenko, Zhurn. Obshch. Khim. 46, 1651 (1976).
9.  V. L. Foss, Yu. A. Veits, N. V. Lukashev, I. F. Lutsenko, J. Organometal. Chem. 121, C27 (1976).
10. V. L. Foss, V. V. Kudinova, I. F. Lutsenko, Zhurn. Obshch. Knim. 49, 2428 (1979).
11. V. L. Foss, N. V. Lukashev, Yu. A. Veits, I. F. Lutsenko, Zhurn. Obshch. Khim. 49, 1712 (1979).
12. E. N. Tsvetkov, M. I. Terekhova, E. S. Petrov, R. A. Malevannaya, S. P. Mesyats, A. I. Schatenstein, M. I. Kabachnik, Izv. AN SSSR, ser. khim. 1978, 1981.
13. V. L. Foss, Yu. A. Veits, I. F. Lutsenko, Phosphorus and Sulphur 3, 299 (1977).
14. V. L. Foss, V. V. Kudinova, Yu. A. Veits, I. F. Lutsenko, Zhurn. Obshch. Khim. 44, 1209 (1974).
15. V. L. Foss, Yu. A. Veits, P. L. Kukhmisterov, V. A. Solodenko, I. F. Lutsenko, Zhurn. Obshch. Khim. 47, 477 (1977).
16. V. L. Foss, V. A. Solodenko, I. F. Lutsenko, Zhurn. Obshch. Khim. 46,

2382 (1976); ibid. <u>49</u>, 2418 (1979).

17. V. L. Foss, Yu. A. Veits, P. L. Kukhmisterov, I. F. Lutsenko,
    <u>Zhurn. Obshch. Khim.</u> <u>47</u>, 721 (1977).

18. V. L. Foss, Yu. A. Veits, P. L. Kukhmisterov, I. F. Lutsenko,
    <u>Zhurn. Obshch. Khim.</u> <u>47</u>, 478 (1977).

19. V. L. Foss, V. A. Solodenko, Yu. A. Veits, I. F. Lutsenko, <u>Zhurn.</u>
    <u>Obshch. Khim.</u> <u>49</u>, 1724 (1979).

20. O. J. Scherer, <u>Angew. Chem. Internat. Ed.</u> <u>8</u>, 861 (1969).

21. V. L. Foss, Yu. A. Veits, T. E. Chernikh, I. F. Lutsenko, <u>Zhurn.</u>
    <u>Obshch. Khim.</u> <u>49</u>, 713 (1979).

22. H. Rossknecht, W. P. Leman, A. Schmidpeter, <u>Phosphorus</u> <u>5</u>, 195 (1975);
    A. Schmidpeter, H. Rossknecht, <u>Z. Naturforsch.</u> <u>26 b</u>, 81 (1971).

23. I. J. Colquhoun, W. McFarlan, <u>J. Chem. Soc. Dalton,</u> <u>1977</u>, 1674;
    R. J. Cross, T. H. Green, R. Keat, <u>J. Chem. Soc. Dalton,</u> <u>1976</u>, 1424.

24. O. J. Scherer, G. Schieder, <u>Chem. Ber.</u> <u>101</u>, 4184 (1968).

25. O. I. Kolodyazhniy, <u>Zhurn. Obshch. Khim.</u> <u>49</u>, 104 (1979).