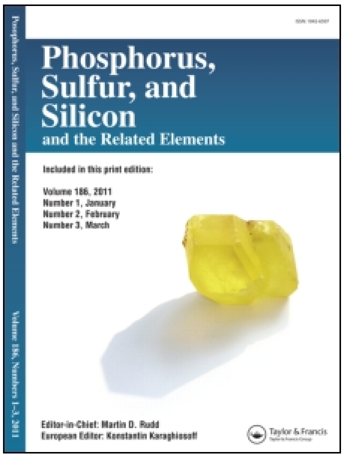

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V. L. Foss[a]; Yu. A. Veits[a]; I. F. Lutsenko[a]
[a] Chemistry Department, M. V. Lomonosov Moscow State University, Moscow, U.S.S.R.

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MIXED ANHYDRIDES OF DIALKYLPHOSPHINOUS ACIDS AND DIALKYL HYDROGEN PHOSPHITES, AND THE ISOMERIC MONOXIDES†

V. L. FOSS, Yu. A. VEITS and I. F. LUTSENKO

Chemistry Department, M. V. Lomonosov Moscow State University, 117234 Moscow V-234, U.S.S.R.

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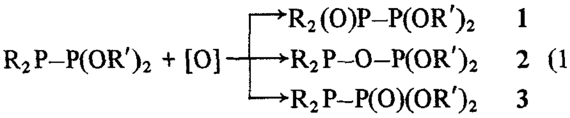
The three isomers possible for oxidized 1,1-dialkyl-2,2-dialkoxydiphosphines, $R_2(O)P{-}P(OR')_2$ **1**, $R_2P{-}O{-}P(OR')_2$ **2**, and $R_2P{-}P(O)(OR')_2$ **3**, have been synthesized. Irreversible transformations of **1** to **2** and **2** to **3** have been found and the rearrangement patterns, the role of electrophilic and nucleophilic catalysts are discussed. The fact that **3** is more stable than **1** is attributed to higher donor activity of the ligands attached to the four-coordinate phosphorus in **3**. Acid chlorides have been shown to attack the phosphorus atom of ambident anions of trivalent phosphorus acids (the products are **1** and **3**) whereas the acids proper react with the acid halides at the oxygen atom, to give **2**.

Oxidation of alkylalkoxydiphosphines[1] with the equivalent amount of an oxidant may be expected to result in three isomerical compounds.

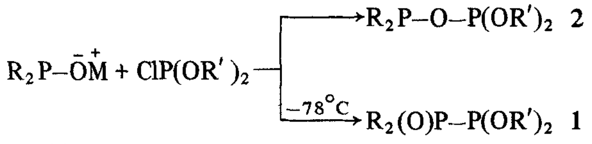


$$R_2P{-}P(OR')_2 + [O] \rightarrow \begin{cases} R_2(O)P{-}P(OR')_2 & 1 \\ R_2P{-}O{-}P(OR')_2 & 2 \\ R_2P{-}P(O)(OR')_2 & 3 \end{cases} \quad (1)$$

Preliminary experiments showed that the oxidation was complicated, involving rearrangement[2] of the reaction products. This led us to undertaking an independent synthesis of all the three isomers and studying their relative thermodynamical stability.

1 MONOXIDES $R_2P(O){-}P(OR')_2$, TYPE 1

These were obtained by reaction of sodium or potassium dialkylphosphinites with dialkyl phosphorochloridites. Both the isomers, **1** and **2**, might be expected from a dialkyl phosphorochloridite attacking the ambident anion $R_2P{\frown}O^-$. The reaction (2) was found to be quite selective however, the compounds **1** being the main products at −78°C.



$$R_2P{-}\overset{-}{O}\overset{+}{M} + ClP(OR')_2 \rightarrow \begin{cases} R_2P{-}O{-}P(OR')_2 & 2 \\ \xrightarrow{-78^\circ C} R_2(O)P{-}P(OR')_2 & 1 \end{cases}$$

$M = Na, K$ (2)
R = iso-C_3H_7, n-C_5H_{11}, cyclo-C_6H_{11}, tert-C_4H_9
$R' = n$-C_4H_9

The structure $R_2P(O){-}P(OR')_2$ **1** was verified by NMR ^{31}P methods. The spectra (Table I) contain two AX doublets and the coupling is about 250 Hz, indicating that a P–P bond is present. One of the doublets lies at −181 to −184 ppm regardless of R (except for R = tert-C_4H_9, $\delta(^{31}P^{III})$ −194 ppm). A low-field signal of this type is characteristic of a three-coordinate phosphorus having alkoxyls on and attached to another phosphorus ($\delta(^{31}P(OR)_2)$ is[1] at −195 to −216 ppm in 1,1-dialkyl-2,2-dialkoxydiphosphines, depending on the site R_2P while $\delta(^{31}P)$ is −184 ppm for tetrabutoxydiphosphine.[3] The other doublet lies at −50 to −60 ppm, chatacteristic of a four-coordinate phosphoryl phosphorus carrying alkyl groups.

The compounds **1** are very reactive. They hydrolyse and oxidize readily (fume in the air, are pyrophoric on cotton wool), are very unstable thermally, and can hardly be maintained for several hours at room temperature, let alone distilled. Their instability depends rather on impurities (dialkyl phosphorochloridite in the first place) than on the nature of R (although the monoxide **1b** is somewhat more stable). A control experiment has shown that the compounds **1** rearrange exothermally under the action of catalytical amounts of dibutyl phosphorochloridite, to give the anhydrides **2**. This may be explained by assuming that the electrophilic phosphorochloridite attacks the nucleophilic oxygen of the phosphoryl group and causes isomerization accompanied by regeneration of the catalyst.

$$R_2(O)P{-}P(OC_4H_9)_2 + (C_4H_9O)_2PCl \rightarrow$$
$$R_2P{-}O{-}P(OC_4H_9)_2 + (C_4H_9O)_2PCl \quad (3)$$

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† Translated by A. V. Grib, NMR Laboratory, Chemistry Department, Moscow University, 117234 Moscow V-234, U.S.S.R.

TABLE I

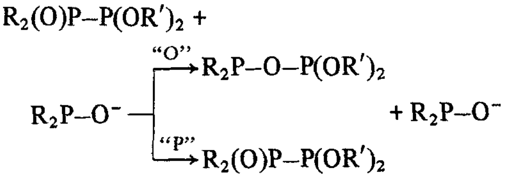
NMR ^{31}P-spectra of the monoxides $R_2P(O){-}P(OR')_2$, Type 1

Compound	$\delta(^{31}P^{V})^a$	$\delta(^{31}P^{III})^a$	$^1J(PP)^b$
1a $(iso\text{-}C_3H_7)_2(O)P{-}P(OC_4H_9)_2$	−55.5	−182.0	250
1b $(tert\text{-}C_4H_9)_2(O)P{-}P(OC_4H_9)_2$	−62.5	−194.5	290
1d $(cyclo\text{-}C_6H_{11})_2(O)P{-}P(OC_4H_9)_2$	−49.5	−183.5	250
1c $(n\text{-}C_5H_{11})_2(O)P{-}P(OC_4H_9)_2$	−50.5	−181.0	230

[a] NMR ^{31}P spectra were recorded on a C-60HL instrument against an 85% H_3PO_4 reference; the $\delta(^{31}P)$ values are accurate to ±0.5 ppm.

[b] The $^1J(PP)$ values are accurate to ±5 Hz.

To avoid the isomerization, an excess of the dialkylphosphinic acid salt should be employed in the synthesis of **1**. The **1** to **2** isomerization proceeds readily under the action of dialkylphosphinous chlorides since their attack on the oxygen of **1** leads to the tetraalkyldiphosphines monoxide $R_2P{-}\underset{\overset{\|}{O}}{P}R_2$ **4** and gives the isomerization catalyst, dialkylphosphorochloridite. A similar isomerization proceeds, somewhat more slowly in the presence of the anion $R_2P{-}O^-$. It may be caused by the attack of the oxygen on the electrophilic trivalent phosphorus of **1**.



$$R_2(O)P{-}P(OR')_2 + R_2P{-}O^- \begin{cases} \xrightarrow{\text{“O”}} R_2P{-}O{-}P(OR')_2 \\ \xrightarrow{\text{“P”}} R_2(O)P{-}P(OR')_2 \end{cases} + R_2P{-}O^- \qquad (4)$$

We have shown above that soft electrophiles, chlorides of trivalent phosphorus acids, attack preferentially the soft phosphorus atom of $R_2P{-}O^-$, and therefore the kinetically controlled reaction (2) allows one to obtain the compounds **1**. With the monoxide **1**, however, it is clear that a similar attack of the phosphorus atom on the three-coordinate phosphorus of **1** cannot yield a new compound, and in this situation another process is detected—an attack of the oxygen atom of the anion $R_2P{-}O^-$ leading to the isomerization of **1** to **2**. The attack may be facilitated by the fact that the three-coordinated phosphorus of **1**, a phosphorus attached to a phosphoryl group, should be a harder centre, and is more hindered spatially, than is the phosphorus of the phosphorochloridite.

Consequently, isomerization of the monoxide **1** to the mixed anhydride **2** may be caused by phosphorus-containing electrophiles (the process takes minutes above −20°C) as well as by nucleophiles (which are less effective catalysts in this case). Since the compound **1** contains both a nucleophilic (phosphoryl oxygen) and an electrophilic centre ($(R'O)_2P$ phosphorus), the monoxide **1** may isomerize to the anhydride **2** without any external catalyst. Indeed, **1** rearranges to **2** to a considerable degree at room temperature in 2–3 hr, although for the obvious reasons one cannot guarantee that the system contains no external catalyst whose concentration would be below the NMR sensitivity. The fact that the **1** to **2** rearrangement is irreversible points out that the mixed anhydride (a compound containing two three-coordinate phosphorus atoms) is thermodynamically more stable. A transformation of one of two adjacent four-coordinate phosphorus atoms to the three-coordinate atom was described for the hypophosphoric acid proper[4] and for its esters[5,6] (the latter rearrangement proceeded under very drastic conditions).

Let us come back to the conditions of the synthesis of **1**. When reaction (2) is carried out at −78°C, then, after filtration of the precipitate and removal of the solvents *in vacuo*, the purity of the compounds **1** is 80–90% for R being iso-C_3H_7, cyclo-C_6H_{11}, tert-C_4H_9, and 50–60% for R = n-C_5H_{11}, as measured by NMR in all cases. At −20 to 0°C, the reaction leads to considerable amounts of **2** and the products formally resulting from dismutation of **2**, viz., tetralkyl pyrophosphite and tetraalkyldiphosphine monoxide **4** (see Eq. 6). These arise from the **1** to **2** isomerization discussed above and followed by a reaction of **2** with the starting reagents: sodium dialkylphosphinite and dialkyl phosphorochloridite. Accordingly, addition of a phosphorochloridite to a salt of dialkylphosphinous acid at −10 to +10°C always causes not only a complete isomerization of **1** to **2** but also a reaction of **2** with the local excess of the salt resulting in the monoxide **4** and sodium dibutyl phosphite. The reaction course was verified by ^{31}P NMR techniques in a control experiment:

$$R_2P{-}O{-}P(OR')_2 + R_2P{-}O^- \rightarrow R_2(O)P{-}PR_2 + (R'O)_2P{-}O^- \qquad (5)$$

It should be noted that the formation of anhydride **2**, monoxide **4**, and tetraalkyl pyrophosphite as side products of reaction (2) is strongly dependent on the size of the groups R. With maximally hindered substituents such as R = tert-C_4H_9, reaction (2), carried out at −10°C, gave 90% **2b** (at the expense of **1b** isomerized by the anion) and only 5-10% of the pyrophosphite ($\delta(^{31}P)$ −127 ppm) and di-tert-butylphosphinous anhydride ($\delta(^{31}P)$ −164 ppm). With secondary-structured groups (**1a** and **1d**), the yield of **4a**, **4d** and, respectively, the pyrophosphite, are about 40-50% of that for the reaction at −20°C. For groups of the primary structure, the reaction at −20°C gives a mixture containing **4** and the pyrophosphite as the main products, and only 30% of **2**. Consequently, the side reaction decelerates with increasing spatial hindrance and is quite avoidable at −78°C for secondary and tertiary groups. (At this temperature, even the order in which the reactants are mixed is unimportant and the compounds **1** formed are practically pure). With primary groups almost the same amount of side products at −100°C as at −78°C. The reaction of dialkylphosphinous salts with dialkyl phosphorochloridites that leads, depending on the conditions, either to **1** or to a mixture of **1**, **2**, **4**, and tetraalkylpyrophosphite may be illustrated by the following scheme:

$$R_2P{-}O^- + ClP(OR')_2 \xrightarrow[-78^\circ]{} 1$$

$$1 \xrightarrow[> -70^\circ]{(1)(R'O)_2PCl \;\; (2)R_2P{-}O^-} \underset{2}{R_2P{-}O{-}P(OR')_2} \qquad (6)$$

$$\begin{tikzcd} 2 \arrow[r, "R_2P-O^-", "> -10^\circ C"'] & \underset{4}{R_2P-P(O)R_2} + (R'O)_2P-O^- \arrow[d, "(R'O)_2PCl"] \\ & (R'O)_2P-O-P(OR')_2 \end{tikzcd}$$

2 MIXED ANHYDRIDES $R_2P{-}O{-}P(OR')_2$, TYPE 2

These may be obtained by rearranging the monoxides **1** (Eqs. 3, 4). The synthesis is complicated (see above) only in the case of primary R, e.g., the isomerization of **1a**, **b**, **d** to **2**, gives neither pyrophosphite, monoxide **4**, nor compounds **3** (NMR follow-up). A catalyst, $(R'O)_2PCl$, accelerates the rearrangement strongly, without affecting the stability of the mixed anhydrides **2** formed.

Another method to synthesize **2** is condensation of phosphorochloridites with dialkylphosphine oxides

$$R_2P(O)H + ClP(OR')_2 + 4R''_3N \rightarrow R_2P{-}O{-}P(OR')_2 + R''_3N \cdot HCl \qquad (7)$$

R = iso-C_3H_7, n-C_4H_9, tert-C_4H_9, n-C_5H_{11}, C_6H_5, cyclo-C_6H_{11}

R′ = C_2H_5, n-C_4H_9, R″ = C_2H_5

The reaction, carried out at −5 to +5°C in an excess of a tertiary amine, is complete in 30-60 min; it is a reliable method to obtain the compounds **2** (Table II).

Structures of the anhydrides obtained were verified by NMR ^{31}P techniques. Assignment of the spectra was somewhat difficult since there are no analogies in the literature, and chemical shifts of the sites $R_2P{-}O$ and $(R'O)_2P{-}O$ should not be largely different. The spectra contain two AB doublets with a strikingly high P–O–P coupling of about 100 Hz (the reported ^2J(P–O–P) values[7] lie at 15 to 40 Hz). With the primary substituents, $\Delta\nu$ is by a factor of 2 to 2.5 greater than ^2J(P–O–P) whereas with the secondary groups (R is iso-C_3H_7 or cyclo-C_6H_{11}), the signals lie rather closer. For **2a** (R = iso-C_3H_7), the spectra recorded on C-60HL or 4H-100 instruments displayed just a broad singlet that could be resolved only on a Brucker HX-90 spectrometer. The inner signals are distanced by about

TABLE II
NMR ^{31}P-spectra of the mixed Anhydrides $R_2P{-}O{-}P(OR')_2$, Type **2**

Compound	$\delta(^{31}PR_2)$[a]	$\delta(^{31}P(OR')_2)$[a]	^2J(POP)	instrument
2a (iso-C_3H_7)$_2$P–O–P(OC_4H_9)$_2$	−135.55	−137.87	100.10	Bruker HX-90
2b (tert-C_4H_9)$_2$P–O–P(OC_4H_9)$_2$	−146.52	−137.62	111.10	Bruker HX-90
2c (n-C_5H_{11})$_2$P–O–P(OC_4H_9)$_2$	−121.58	−134.65	90.34	Bruker HX-90
2d (cyclo-C_6H_{11})$_2$P–O–P(OC_4H_9)$_2$	−132.8	−136.2	105	C-60HL
2e (n-C_4H_9)$_2$P–O–P(OC_4H_9)$_2$	−124.5	−134.0	85	C-60HL
2f (C_6H_5)$_2$P–O–P(OC_2H_5)$_2$	−96.5	−134.5	95	C-60HL

[a] The $\delta(^{31}P)$ values were calculated for **2a**, **b**, **d**, found from the doublet centre for **2c**, **e**, **f**.

5.5 Hz, the lateral lines of the doublets are almost invisible and lie at the distance of 100.1 Hz. Assignment of all signals was based on the fact that some chemical shifts did, whereas some did not, vary with R. The latter signals belong to the same $(R'O)_2P$–O sites (Table II). The assignment also agrees with the **2b** spectrum recorded on a C-6OHL machine (coupled phosphorus-methyl proton mode) in which the broad lines of the doubletst $\delta(^{31}P)$ of −146.5 are associated with the site $(tert\text{-}C_4H_9)_2P$–O.

The most realistic assumption is that dialkylphosphinous acids react (via 7) with the electrophilic phosphorochloridite by their sole nucleophilic centre the oxygen atom, and the anhydrides are primary products of the reaction. An alternative, formation of **1** via the reaction (2) followed by rearrangement to **2** under the action of the phosphorochloridite catalyst (Eq. 3), seems less probable since firstly, the acid anion concentration should be low in a medium of a relatively weak base such as tertiary amine while, secondly phosphorodiamidous anhydride, not the isomerical monoxide, is formed from phosphorodiamidous acid and its chloride under the similar conditions. Phosphorodiamidous anhydride is, undoubtedly, the primary product since it isomerizes to diamidodiphosphine monoxide (Ref. 15, 16). With stronger acids, however, the two-step mechanism is more probable and we have some data in favour of an assumption that the formation of **2f** under the conditions of reaction (7) is due to isomerization of **1f**.

When the starting compounds are pure and reaction (7) is carried out carefully the resulting anhydrides **2** are practically pure (NMR). The synthesis is the most facile with the spatially hindered, secondary and tertiary R's. If the optimal reaction mode is violated, mixtures of the pyrophosphite, and the monoxide R_2P–$P(O)(OR')_2$ **3** will result (especially when R is primary) the tetraalkyldiphosphine monoxide R_2P–$P(O)R_2$ **4** (the **4** $\delta(^{31}P)$ values obtained via Ref. 8 are listed in Table IV).

The mixture composition depends on several factors. The first one is the irreversible exchange.[9] It leads to compounds that react both with the starting

$$R_2P(O)H + (R'O)_2PCl \rightarrow R_2PCl + (R'O)_2P(O)H \qquad (8)$$

species and with one another, to give the side products mentioned above.† With R being tert-C_4H_9, the exchange (in the absence of base) is somewhat slower than is the condensation (7) in the other cases the rate ratio is the inverse of the above but the complica-

TABLE III
Some physical properties of the monoxides, Type 3

Compound	$\delta^{31}P^V$	$\delta^{31}P^{III}$	$^1J_{PP}$	B.p./mm	n_D^{20}	Found C	Found H	Found P	Cal. C	Cal. H	Cal. P	Comment
3j Et_2P–$P(O)(OEt)_2$[a]	−39.2	+45.4	220	97–98°/3	1.4707	–	–	–	–	–	–	(a)
3a i-Pr_2P–$P(O)(OBu)_2$	−37.56	+13.70	241.70	122-123°/2	1.4694	53.72	10.52	19.62	54.12	10.39	19.95	(b)
3e Bu_2P–$P(O)(OEt)_2$	−40.03	+54.31	212.41	124-126°/2	1.4640	50.84	10.12	21.64	51.05	10.00	21.94	(b)
3b $(tert\text{-}Bu)_2P$–$P(O)(OBu)_2$	−38.0	−13.5	288	122-124°/2	1.4738	56.22	10.64	18.08	56.72	10.78	18.30	(c)
3c Am_2P–$P(O)(OBu)_2$	−40.14	+54.41	214.84	168-169°/2	1.4662	58.72	11.08	16.44	58.98	11.00	16.90	(b)
3d $(cyclo\text{-}C_6H_{11})_2P$–$P(O)(OBu)_2$	−38.3	+23.1	245	181-183°/0.5	1.5052	61.52	10.44	15.52	61.55	10.25	15.88	(a)
3f Ph_2P–$P(O)(OBu)_2$	−31.96	+33.40	180.60	135-137°/8.10^{-2}	1.5440	63.22	7.46	15.88	63.48	7.63	16.37	(b)

[a] Reported earlier in [10]
(a) Recorded on 4H-100. (b) Recorded on Brucker HX-90. (c) Recorded on C-60HL.

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† The predominant formation of **3** rather than **2** in reaction (7) mentioned in,[2,9] may be explained by isomerization of **2** with R_2PCl via Eq. (13).

TABLE IV
NMR ^{31}P-spectra of the tetraalkyldiphosphine monoxides, Type 4

Compound	$\delta(^{31}P^V)$	$\delta(^{31}P^{III})$	$^1J(PP)$	Instrument
4a $(iso\text{-}C_3H_7)_2P{-}P(O)(iso\text{-}C_3H_7)_2$	−63.79	+13.64	275.88	Bruker HX-90
4b[a] $(tert\text{-}C_4H_9)_2P{-}P(O)(tert\text{-}C_4H_9)_2$	−88	−48	392	C-60HL
4c $(n\text{-}C_5H_{11})_2P{-}P(O)(nC_5H_{11})_2$	−49.90	+52.00	219.74	Bruker HX-90
4d $(cyclo\text{-}C_6H_{11})_2P{-}P(O)(cyclo\text{-}C_6H_{11})_2$	−59.3	+21.3	280	C-60HL
4e $(n\text{-}C_4H_9)_2P{-}P(O)(n\text{-}C_4H_9)_2$	−50.39	+52.00	219.73	Bruker HX-90

[a] Obtained by condensing di-tert-butylphosphinous chloride with sodium di-tert-butylphosphinite.

tions due to the exchange reaction are only significant when equivalent amounts of the tertiary amine are employed.[2] An excess of the base (200 to 300%) and a lower temperature helped to suppress the exchange reaction almost completely and the side products did not arise from the resulting mixture of 2 and the amine hydrochloride even after an hour at room temperature.

The second factor is interaction of the starting dialkylphosphine monoxide with the anhydride 2.

$$R_2P{-}O{-}P(OR')_2 + R_2P(O)H \rightarrow \underset{4}{R_2P{-}P(O)R_2} + (R'O)_2P(O)H \qquad (9)$$

The compounds 2 are cleaved (Eq. 9) by the weak nucleophile (acid) considerably more slowly than by the acid anion (Eq. 4) and the cleavage by acid is essential only with the primary substitutents. With R being $n\text{-}C_5H_{11}$, the cleavage is complete at room temperature in an hour. To suppress the side reaction (9), the condensation (7) was carried out by adding the acid slowly to a mixture of phosphorochloridite and amine dissolved in the ten-fold volume of ether. With the secondary or tertiary substituents, the anhydrides formed via (7) are not cleaved by acid during the condensation (with R = $tert\text{-}C_4H_9$, no cleavage was observed in 40 min at 110°C). It should be noted that tetrabutyl pyrophosphite quite readily reacts with $(iso\text{-}C_3H_7)_2P(O)H$ and equilibrium of the reaction lies well to the right (Eq. (10)).

$$(C_4H_9O)_2P{-}O{-}P(OC_4H_9)_2 + (iso\text{-}C_3H_7)_2P(O)H \rightarrow (iso\text{-}C_3H_7)_2P{-}O{-}P(OC_4H_9)_2 + (C_4H_9O)_2P(O)H \qquad (10)$$

The third factor responsible for the mixtures under discussion is dismutation of the anhydrides 2.

$$2R_2P{-}O{-}P(OR')_2 \rightarrow \underset{4}{R_2P - P(O)R_2} + (R'O)_2P - O{-}P(OR')_2 \qquad (11)$$

This reaction is considerably slower than are the condensation (7) or the side processes (8) and (9). Even if 2 contains primary substituents, there are practically no pyrophosphite and 4 signals in the anhydrides 2 for a period of time comparable with the time of reaction (7). The compound **2f** (R is C_6H_5) is strikingly different, it decomposes via Eq. (11) in 30 min after the solvent is removed; this may be attributed to an increased reactivity of the $(C_6H_5)_2P$ site.

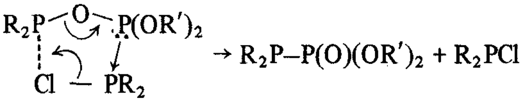
All the three-sided processes decelerate markedly with an increase in the spatial crowding, and 2 free of 4 and pyrophosphite can be obtained easily in the case of secondary and tertiary substituents. Note that reaction (7) carried out in an excess of amine never shows (NMR) any monoxide 3 ($R_2P{-}P(O)(OR')_2$) after the reaction is complete and the reaction mixture has been worked up (the work-up time is *ca.* 30 min, the overall synthesis time is 1 to 1.5 hr).

The mixed anhydrides 2 obtained were much more stable thermally compared with the monoxides **1**; they isomerize, however, irreversibly at room temperature to the monoxides 3 in several hours or several days, depending on R.

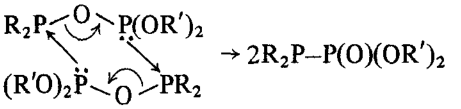
$$R_2P{-}O{-}P(OR')_2 \xrightarrow{12\text{–}72\ hr} R_2P{-}P(O)(OR')_2 \qquad (12)$$

With 2c (R = $n\text{-}C_5H_{11}$), e.g., the isomerization goes to the extent of more than 50% in 3 hr (that is, in 4 to 4.5 hr after reaction (7) starts) and is complete in 12 hr; with **2a, d** (R is $iso\text{-}C_3H_7$ or $cyclo\text{-}C_6H_{11}$) the similar transformation goes to the extent of *ca.* 70% in 20 hr and is complete in 2-3 days. Thirty minutes heating at 100°C is enough to isomerize the mixed anhydrides **2a** and **2d** completely, therefore the anhydrides 2 could not usually be isolated by distillation. Only the anhydride **2b** (R = $tert\text{-}C_4H_9$) is of higher thermal stability, being unchanged after nine months at 20°C and is not affected by distillation at 120°C (vapour temperature) *in vacuo.* To isomerize it to the monoxide **3b**, the anhydride should be heated at 120°C for 3 hr in the presence of several molar per cent $MgBr_2$. At higher temperatures (140–160°C), the isomerization is accompanied by some decomposition.

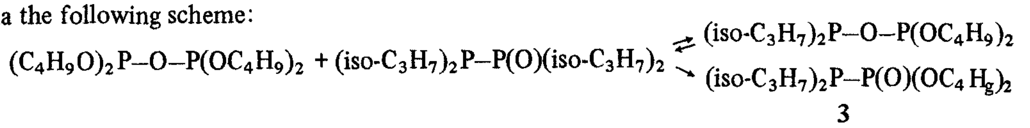
The mixed anhydrides **2** are very readily isomerized to the monoxides **3** by catalytical amounts of dialkylphosphinous chloride (not dialkyl phosphorochloridite), therefore a very plausible pattern of the **2**-to-**3**


$$\rightarrow R_2P{-}P(O)(OR')_2 + R_2PCl \quad (13)$$

isomerization in the absence of catalyst is coordination of two molecules of **2** at the different phosphorus atoms.


$$\rightarrow 2R_2P{-}P(O)(OR')_2 \quad (14)$$

In this coordination, the electrophilic centre of the anhydride is the R_2P site, which may be attributed both to its higher electrophilicity as compared with $(R'O)_2P$ and to the thermodynamical preference of the formation of the monoxide **3**, the most stable compound in the system. The fact is, however, that there is also one more intermolecular way from **2** to **3**, *via* **4** and the pyrophosphite. The spectra of **2c, e, f** subjected to thermolysis have demonstrated that the dismutation (11) is, at lower conversion depths, faster than is the formation of **3**. (The decomposition of **2f** results in the insoluble **4f**, so the scheme (15) cannot work and therefore the pyrophosphite and **4f** remain unaffected even at deeper conversions of **2f**.) The dismutation may indicate that in reaction (11) the faster coordination is due, not to a phosphorus atom but, to an oxygen (followed by fast isomerization of the resulting dialkylphosphinous anhydride to the tetraalkyldiphosphine monoxide **4**). The most striking fact is that equimolar amounts of the pyrophosphite and **4a** (R = iso-C_3H_7) react, as shown by a special experiment, without a solvent at room temperature to the extent of *ca.* 60% in 40 min, practically 100% in 2.5 hr, via the following scheme:


$$(C_4H_9O)_2P{-}O{-}P(OC_4H_9)_2 + (iso\text{-}C_3H_7)_2P{-}P(O)(iso\text{-}C_3H_7)_2 \rightleftarrows (iso\text{-}C_3H_7)_2P{-}O{-}P(OC_4H_9)_2 \;;\; \rightarrow \underset{\mathbf{3}}{(iso\text{-}C_3H_7)_2P{-}P(O)(OC_4H_9)_2} \quad (15)$$

that is, **3** is formed by this reaction much faster than it is formed from **2** (Eq. 12). The same scheme (15) may describe the reaction of di-tert-butylphosphinous anhydride with the pyrophosphite at a low temperature, whereas the isomerization of **2b** to **3b** (R is tert-C_4H_9) requires three hours' heating with $MgBr_2$ at 120°C. It is noteworthy that reaction (15) results both in **3** and the mixed anhydride **2**, in other words, after the pyrophosphite and the monoxide **4** are consumed the further accumulation of **3** is just slow with **3a** (R is iso-C_3H_7; the isomerization is complete in a week) and is practically none existent with **3b** (R = tert-C_4H_9). Reaction (15) can hardly be thought of as catalytical since the preparation and purification techniques applied to the reactants make quite improbable even minor dialkylphosphinous chloride impurities. Consequently, there may be a number of intermolecular pathways consistent with the **2** to **3** transformation; of course, an intramolecular pattern cannot be ruled out either and no mechanism can be given preference based on the present experiment. Probably, several mechanisms operate in parallel.

Dibutyl phosphorochloridite admixtures, unlike phosphinous chlorides, do not isomerize **2** to **3**. Higher (equimolar) amounts of phosphorochloridite readily convert the anhydride into the monoxide **3**. A reasonable assumption is that the anhydride **2** is decomposed to the pyrophosphite and the phosphinous chloride; the latter isomerizes the residual **2** via the scheme (13) or reacts with the pyrophosphite formed.

$$R_2P{-}O{-}P(OR')_2 \xrightarrow{(R'O)_2PCl} (R'O)_2P{-}O{-}P(OR')_2$$
$$+ R_2PCl \rightarrow R_2P{-}P(O)(OR')_2 + (R'O)_2PCl \quad (16)$$

A control experiment shows that pyrophosphite acted upon by dialkylphosphinous chloride reacts via (16) readily and quantitatively.

The anhydrides **2** isomerize readily to **3** even in the presence of catalytic amounts of R_2PCl, therefore it is quite clear why the reaction of dibutyl phosphite with dialkylphosphinous chlorides in the presence of an excess of R_3N (the reaction that would have led to **2**, owing to the attack on the nucleophilic oxygen of the phosphoryl group) leads instead to the monoxide **3**.

$$R_2PCl + (R'O)_2P(O)H + 5(C_2H_5)_3N \rightarrow R_2P{-}P(O)(OR')_2$$
$$R = iso\text{-}C_3H_7,\ cyclo\text{-}C_6H_{11};\ R' = n\text{-}C_4H_9 \quad (17)$$

No formation of **2** could be identified even when R_2PCl was added slowly at low temperature to an excess of the phosphite. We wanted to find whether **3** in reaction (17) forms from isomerization of **2** or results from a reaction of phosphinous chloride with dibutylphosphite anion *via* (19). The compound **2b** is not isomerized under these conditions, so we attempted to apply reaction (17) to di-tert-butylphosphinous chloride. Only the starting reactants were recovered, however, even after many hours refluxing the mixture. (A stronger nucleophile, sodium dibutyl phosphite, rapidly led, as expected, to the monoxide **3b**, see below, Eq. (19).) Thus, the problem of the monoxide **3** formation pathway in (17) is unclear.

Reaction of O-silylated dialkylphoshinous acids with dibutyl phosphorochloridite also resulted in the monoxides **3** and no compounds **2** were observed, despite the fact that the reaction was carried out *in vacuo* so as to remove the trimethylchlorosilane formed.

$$R_2P\text{–}OSi(CH_3)_3 + (C_4H_9O)_2PCl \xrightarrow[-(CH_3)_3SiCl]{} R_2P\text{–}P(O)(OC_4H_9)_2 \qquad (18)$$

To sum up the methods to synthesize, and the properties of, mixed anhydrides of dialkylphosphinous acids and dialkyl hydrogen phosphites, it should be noted that reaction (7) (adding $R_2P(O)H$ to dialkylphosphinous chloride in the presence of a high excess of triethylamine) is a convenient and reliable route to **2**; but with primary alkyl substituents, the reaction demands careful handling.

3 MONOXIDES $R_2P\text{–}P(O)(OR')_2$, TYPE 3

The preceding sections have demonstrated that the monoxides **3** are thermodynamically the most stable compounds among the three isomers under discussion and are formed as final products in various systems containing a 1 : 1 : 1 ratio of R_2P, $(R'O)_2P$ sites, and oxygen.

This bears a relation to the fact that the equilibrium

$$R_2P(O)H + ClP(OR')_2 \rightleftharpoons R_2PCl + (R'O)_2P(O)H$$

lies on the right almost totally.[9] Alongside the **1** and **2** rearrangement, quantitative formation of the monoxides **3** may be observed in the processes (15) to (21) i.e., even when the formation of **3** is carried out in the presence of only weak electrophiles or nucleophiles. The monoxides **3** (see Table III) are quite readily available; the most facile synthesis (yield 70 to 90%) is a direct reaction of dialkylphosphinous chloride with sodium dialkyl phosphite (see Table III).

$$R_2PCl + NaOP(OR')_2 \rightarrow R_2P\text{–}P(O)(OR')_2 \qquad (19)$$

R = iso-C_3H_7, *n*-C_5H_{11}, cyclo-C_6H_{11}, C_6H_5, tert-C_4H_9 or with dialkyl hydrogen phosphite by Eq. (17).

As in (2), the electrophile of reaction (19) attacks the phosphorus of the ambident anion and gives **3** in terms of not only thermodynamical but also kinetic control. The attack of acid chlorides on phosphorus, the softer centre in the ambident anion of three-valent phosphorus acids, must be a regular reaction feature; indeed, we have shown that even the reaction of dialkylphosphorochloridite with sodium dialkyl phosphite gives, at the first step, not tetraalkyl pyrophosphite but tetraalkoxydiphosphine monoxide (e.g., $(C_4H_9O)_2P\text{–}P(O)(OC_4H_9)_2$ $\delta(^{31}P^{III})$–156.5 ppm, $\delta(^{31}P^{V})$–22.23 ppm, $^1J(PP)$ 261.23 Hz) which isomerizes only after several hours to the pyrophosphite.[16]

The NMR ^{31}P spectra of the monoxides **3** obtained contain two AX doublets ($^1J(PP)$ of about 200 to 250 Hz) whose chemical shifts are typical of R_2P- and $(R'O)_2P(O)$- sites (Table III).

Similar spectral parameters were reported for some monoxides of type **3** which were obtained from trialkyl phosphite and dialkylphosphinous chloride.[11,13]

$$R_2PCl + P(OR')_3 \rightarrow R_2P\text{–}P(O)(OR')_2 + R'Cl \qquad (20)$$

The nucleophile of this and the similar[13] reactions is a phosphorus atom bonded with several alkoxyl groups, so the reaction naturally results in the most stable monoxide, of the type **3**. Our attempts to carry out the reaction in which the nucleophile has only one alkoxy group on and which, therefore, should not lead to the compounds **3** directly, have not given any new results; neither intermediates of the types **1** or **2** nor the exchange products could be identified by NMR in the course of reaction (21).

$$(\text{iso-}C_3H_7)_2POCH_3 + (C_4H_9O)_2PCl \rightarrow (\text{iso-}C_3H_7)_2P\text{–}P(O)(OC_4H_9)_2 + CH_3Cl \qquad (21)$$

At 20°C, the reaction is very slow (three days) and it is quite clear that it leads to nothing but **3**, the most stable compound in the system.

The data of 1958 (Ref. 10) indicate that diethylphosphinous chloride with sodium diethyl phosphite gave, after fractionation, the anhydride $(C_2H_5)_2P\text{–}O\text{–}P(OC_2H_5)_2$. We believe that this is not so, the electrophilic attack in reactions of the kind is on phosphorus, not oxygen. In fact, our monoxide $(C_2H_5)_2P\text{–}P(O)(OC_2H_5)$ has the constants close to those reported in[10] while the reaction with ethyl bromide in a sealed tube at 100° (the authors[10] thought it to be a proof of the anhydride structure) gives the products which have been proven by us to arise from the monoxide $(C_2H_5)P\text{–}P(O)(OC_2H_5)_2$.

The rearrangements and other reactions, readily leading to **3**, do not in the least imply that the compounds **3** are of any outstanding stability. In fact, they are quite reactive. The rearrangement leading to **3** is, *a fortiori*, not a proof of an increased stability of phosphoryl-containing compounds. On the contrary, the transformations described here demonstrate that small change in the phosphorus retinue, the change being due to different effects exerted by alkyls as opposed to alkoxyls, may make the >P–O–P< bond system more stable than >P(O)–P< (**2** more stable than **1**) or lead to the reverse stability order (**3** more stable than **2**). The higher stability of **3** as compared with **1** may be assigned to the fact that electrons are displaced to the positive phosphorus from the adjacent atoms in **3** to a greater extent that they are in **1**. On the other hand, a phosphoryl-containing compound may be destabilized by spatial effect of the substituents and the effect may be so high that, e.g., tetra(tert-butyl) diphosphine monoxide at 200°C rearranges to di-tert-butylphosphinous anhydride completely.[14]

$$(\text{tert-}C_4H_9)_2(O)P\text{–}P(\text{tert-}C_4H_9)_2 \xrightarrow{200^\circ} (\text{tert-}C_4H_9)_2P\text{–}O\text{–}P(\text{tert-}C_4H_9)_2 \qquad (22)$$

Isomers of the type under discussion may also have comparable stabilities (Ref. 15, 16, 17), as demonstrated by the tautomerism, for example, of phosphorotetraethyldiamidous anhydride and octaethyltetraaminodiphosphine monoxide.

$$[(C_2H_5)_2N]_2P\text{–}O\text{–}P[N(C_2H_5)_2]_2 \rightleftarrows [(C_2H_5)_2N]_2(O)P\text{–}P[N(C_2H_5)_2]_2 \qquad (23)$$

It is quite probable that, in general, the system >P–X–P< (X is O, S, NR) is in equilibrium with the system >P–P(X)<, the equilibrium being a function of, in the first place, the nature of X and the electronic and spatial effects of the substituents at phosphorus. Therefore, the irreversibility of the rearrangements $A_2(X)P\text{–}PB_2 \dashrightarrow A_2P\text{–}X\text{–}PB_2 \dashrightarrow A_2P\text{–}P(X)B_2$ can only be stated for the compounds (A = Alk, B = AlkO, X = O) studied in the present work, whereas when the difference between the retinues of the two phosphorus atoms is more moderate more complicated relations between the isomers may be expected.

EXPERIMENTAL

All operations were made in a dry argon atmosphere.

1,1-Dialkyl-1-oxo-2,2-dialkoxydiphosphines, Type 1

1,1-Diisopropyl-1-oxo-2,2-dibutoxydiphosphine **1a** (a) The reaction was carried out in a flask fitted with a magnetic stirrer, a dropping funnel and a reflux condenser. Diisopropylphosphinous acid (4.8 g, 0.036 mole) was added under stirring to potassium metal (1.56 g, 0.04 g-at.) in 8 ml dimethoxyethane for 10 min. After the spontaneous exothermal reaction was over the mixture was refluxed for 2 hr. Potassium was observed to pulverize, then white crystals of the salt precipitated. The mixture was cooled down to −78°C, the stirring was discontinued, ether (15 ml) was added, and the reflux condenser was replaced by a low-temperature thermometer. Dibutylphosphorochloridite (7.0 g, 0.0324 mole) in 20 ml ether was added under vigorous stirring for 30 min, the mixture was stirred at −70°C for 15 min, cooling was removed, and at 20°C 30 ml pentane were added, then the precipitate was isolated via a centrifuge. The solvents were removed at 1 Torr to give 1,1-diisopropyl-1-oxo-2,2-dibutoxydiphosphine, 9.0 g (90%).

The compounds **1b**, **1c**, **1d** were obtained in a similar way.

(b) The technique was similar to that described under Run (a). A solution of sodium hexamethyldisilylamide (0.028 mole) in 20 ml ether, was added to diisopropylphosphinous acid (3.6 g, 0.027 mole). The mixture was refluxed for an hour, cooled down to −78°C, and treated with dibutylphosphorochloridite (5.3 g, 0.025 mole) added for 20 min. After a work-up similar to that of Run (a) there was obtained **1a**, 7 g (90%). The compound **1b** was obtained in a similar way.

Mixed Anhydrides, Type 2

(a) *Anhydride* (**2b**) *of di-tert-butylphosphinous acid and dibutyl hydrogen phosphite* The reaction was carried out in a flask fitted with a magnetic stirrer, a dropping funnel, and a thermometer. Triethylamine (12.5 g, 0.124 mole) in 20 ml ether was added to di-tert-butylphosphinous acid (5.1 g, 0.031 mole) in 5 ml dimethoxyethane. To this mixture, dibutylphosphorochloridite (6.7 g, 0.03 mole) in 10 ml ether was added at 0°C for 30 min. Cooling was removed, the reaction mixture was stirred for 30 min at 20°C, the triethylamine hydrochloride was filtered off on a No. 3 glass filter and washed two times with ether. The solvents were removed, the residue was fractionated, to give the title anhydride, 7.8 g (77%), b.p. 128–130°C at 3 Torr, n_D^{20} 1.4634. Found: C, 56.19; H, 11.11; P, 18.16. $C_{16}H_{36}O_3P_2$ requires: C, 56.7; H, 10.78; P, 18.30%.

(b) *Anhydride* (**2a**) *of diisopropylphosphinous acid and dibutyl hydrogen phosphite* The reaction was made in a flask fitted with a magnetic stirrer, a dropping funnel, and a thermometer. To dibutylphosphorochloridite (4.48 g, 0.021 mole) in 10 ml ether was added triethylamine (8.9 g, 0.088 mole) under stirring; a white floccular precipitate was formed. Then, diisopropylphosphinous acid (3 g, 0.022 mole) was added at −10 to 0°C for 30 min, the mixture was stirred at +10 to +15°C for 40 min more, the precipitate was filtered off and washed twice with ether. The solvents were removed to give the title anhydride, 5.85 (90%), displaying no impurities in its NMR^{31}P spectrum. Found: C, 53.54; H, 10.22; P, 19.32. $C_{14}H_{32}O_3P_2$ requires: C, 54.12; H, 10.39; P 19.95%.

The compounds **2c**, **2d**, **2e**, **2f** were obtained in a similar way. The **2f** work-up time should not exceed 20 minutes.

1,1-Dialkyl-2,2-dialkoxy-2-oxodiphosphines, Type 3

(a) *1,1-Diisopropyl-2,2-dibutoxy-2-oxodiphosphine* **3a** The reaction was made in a flask fitted with a magnetic stirrer, a dropping funnel, and a reflux condenser. Diisopropylphosphinous chloride (8 g, 0.053 mole) was added under stirring to a mixture of a solution of dibutyl hydrogen phosphite (10.2 g, 0.053 mole) in 50 ml ether, and triethylamine (6 g, 0.06 mole). No spontaneous heating was observed. The mixture was refluxed for 30 min, the precipitate was filtered off and washed twice with ether. The ether was removed, the residue was fractionated, to give 1,1-diisopropyl-2,2-dibutoxy-2-oxodiphosphine, 13 g (80%). The compounds **3d**, **3f** were obtained analogously.

(b) *1,1-Di-tert-butyl-2,2-dibutoxy-2-oxodiphosphine* **3b** The reaction was made in a flask fitted with a stirrer, a reflux condenser, and a dropping funnel. Sodium metal (0.69 g, 0.03 g-at.) was added to a mixture of dibutyl hydrogen phosphite (5.1 g, 0.026 mole) and 25 ml ether. The reaction mixture was refluxed for two hours, cooled down to −10°C, and di-tert-butylphosphinous chloride (4.8 g, 0.026 mole) was added for 20 min. The mixture was stirred at room temperature for an hour, the precipitate was filtered off, washed twice with ether. The ether was removed under reduced pressure, and the residue was fractionated to give 1,1-di-tert-butyl-2,2-dibutoxy-2-oxodiphosphine, 6.6 g (75%). The compounds **3d**, **3f** were obtained in a similar way.

(c) *1,1-Diisopropyl-2,2-dibutoxy-2-oxodiphosphine* **3a** Diisopropylphosphinous chloride (0.2 g) was added to the anhydride **2a** (5.85 g). The mixture was fractionated in 10 min, to give the title compound, 4.8 g (82%).

The compound 3c was obtained analogously.

(d) *1,1-Diisopropyl-2,2-dibutoxy-2-oxodiphosphine* **3a** Tetraisopropyldiphosphine monoxide (0.338 g, 0.001 mole) and tetrabutyl pyrophosphite (0.37 g, 0.001 mole) were mixed in an NMR probe. After having heated the mixture at 80°C for an hour, only the NMR ^{31}P signals of the title compound were observable. Found: C, 53.9; H, 10.46; P, 19.65; $C_{14}H_{32}O_3P_2$ requires: C, 54.12; H, 10.39; P, 19.65%.

The compound 3e was obtained analogously.

Tetraalkyldiphosphine Monoxides, Type 4

Tetraamyldiphosphine Monoxide **4c** Diamylphosphinous chloride (6.25 g, 0.03 mole) in 80 ml ether was added to a mixture of a solution of diamylphosphinous acid (5.7 g, 0.03 mole) in 25 ml dimethoxyethane, and triethylamine (9.1 g, 0.09 mole). The reaciton mixture was stirred at room temperature for 2 hr, the precipitated salt was filtered off and washed twice with ether, the solvents were removed *in vacuo*, to give tetraamyldiphosphine monoxide, 8.7 g (80%). Found: C, 65.35; H, 11.71, P, 16.30. $C_{20}H_{44}OP_2$ requires: C, 66.26; H, 12.24; P, 17.09%.

Above 100°C, the decomposition of **4c** into tetraamyldiphosphine ($\delta(^{31}P)$ +43.8 ppm) and other products is very fast, therefore distillation is not a good method to isolate the monoxide.

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REFERENCES

1. V. L. Foss, Yu. A. Veits, V. V. Kudinova, A. A. Borisenko and I. F. Lutsenko, *Zhurn. Obshch. Khim.* **43**, 1000 (1973).
2. Yu. A. Veits, A. A. Borisenko, V. L. Foss and I. F. Lutsenko, *Zhurn. Obshch. Khim.* **43**, 440 (1973).
3. A. L. Chekhun, M. V. Proskurnina and I. F. Lutsenko, *Zhurn. Obshch. Khim.* **40**, 2116 (1970).
4. P. Nylen, *Z. anorg. allg. Chem.* **229**, 36 (1936); H. Remy and H. Falius, *Chem. Ber.* **92**, 2199 (1959).
5. J. Michalski, W. Stec and A. Zwierzak, *Chem. Ind.* **1965**, 347.
6. A. Zwierzak, *Khimiya i Primenenie FOS, Trudy III Konferentsii* (*Chemistry and Applications of Organophosphorus Compounds, Transactions of the 3rd Conference*), Moscow, 1972, p. 370.
7. J. R. Van Wazer, in *Determination of Organic Structures by Physical Methods*, edited by F. C. Nachod and J. J. Zuckerman, Vol. 4 (Academic Press, New York, 1971), pp. 323-358.
8. K. Issleib and B. Walther, *J. Organomet. Chem.* **22**, 375 (1970).
9. V. L. Foss, V. V. Kudinova, Yu. A. Veits, and I. F. Lutsenko, *Zhurn. Obshch. Khim.* **44**, 1209 (1974)
10. B. A. Arbuzov, N. I. Rizpolozhensky and I. A. Zvereva, *Izvest. Akad. Nauk SSSR* **1958**, 706.
11. E. Fluck and H. Binder, *Inorg. Nucl. Chem. Lett.* **3**, 307 (1967).
12. K. M. Abraham and J. R. Van Wazer, *Phosphorus* **6**, 23 (1975).
13. K. M. Abraham and J. R. Van Wazer, *Inorg. Chem.* **13**, 2346 (1974).
14. V. L. Foss. Yu. A. Veits, V. A. Solodenko and I. F. Lutsenko, *Zhurn. Obshch. Khim.* **46**, 1651 (1976).
15. V. L. Foss, Yu. A. Veits, N. V. Lukashev and I. F. Lutsenko, *J. Organomet. Chem.* **121**, C27 (1976).
16. V. L. Foss, Yu. A. Veits, N. V. Lukashev, Yu. E. Tzvetkov and I. F. Lutsenko, *Zhurn. Obshch. Khim.* **47**, 479 (1977)
17. V. L. Foss, Yu. A. Veits, P. L. Kukhmisterov, V. L. Solodenko and I. F. Lutsenko, *Zhurn. Obshch. Khim.* **47**, 477 (1977).