1,1-Bis(diphenylphosphinoyl)ethanol.
Synthesis and complexes with neodymium and copper nitrates

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A preparative method for the synthesis of 1,1-bis(diphenylphosphinoyl)ethanol (1) has
been elaborated. In CHCl₃ and MeCN solutions compound 1 is associated into H-bonded
dimers (ΔH ~ 12 kcal mol⁻¹). Complexes of compound 1 with Nd⁺³, Cu⁺², and Cu⁺
nitrates have been studied. The H-bonded dimers are retained upon complexing.

Key words: tetraphenylmethylene diphosphine dioxides; H-bonds; complexing.

Tetraphenylmethylene diphosphine dioxides, specifically
their well-known representative, Ph₂P(O)CH₂P(O)Ph₂,
are attracting the attention of scientists as efficient
extractants.¹,² However, they are not widely used due to
the lack of sufficiently simple methods for their synthe-
sis. Therefore, it was interesting to study 1,1-bis(diphenylphosphinoyl)ethanol (1), which is easier to syn-
thesize than the unsubstituted analog, as a potential
extractant.

The synthesis of compound 1 has been described in a
number of papers.³⁻⁷ However, in most cases this compound
was not isolated in the pure state, and the presence of compound 1 in the reaction mixture was only judged from NMR spectra. Pure 1,1-bis(diphenylphosphinoyl)ethanol has been isolated by two groups of authors.³⁻⁵ In both cases, the target product was obtained by treatment of Ph₂P(O)H with Ac₂O, but the reaction conditions differed greatly. In one instance,³ the synthesis was carried out for 6 h at 100 °C, whereas
the reaction performed by the other procedure⁴⁻⁵ was completed in 15 min at 40 °C. It should be noted that,
according to later data,⁶ heating the same mixture at
80 °C for 7 h results in complete phosphonate-phospho-
phosphate rearrangement of product 1. Thus, the second
method⁴⁻⁵ is likely to be the most promising and con-
venient and provides sufficiently pure compound 1 in
high yield.

Results and Discussion

We reproduced the above procedures for the synthe-
sis of compound 1, and also synthesized it from
O-methyldiphenylphosphinite by the Arbuzov reaction.⁵,⁸
It was found that the reproduction of these procedures
does not provide stable yields of the target product.

It is known that the synthesis of compound 1 from 2
and Ac₂O involves two steps and each of them is revers-
able.⁶

\[
\begin{align*}
\text{Ph}_2\text{P(O)}\text{H} + \text{Ac}_2\text{O} & \rightleftharpoons \text{AcP(O)Ph}_2 + \text{AcOH} \\
\text{AcP(O)Ph}_2 + \text{Ph}_2\text{P(O)}\text{H} & \rightleftharpoons \text{MeC(OH)[P(O)Ph}_2\text{]}_2
\end{align*}
\]

Compound 3, AcP(O)Ph₂, which is unstable at room
temperature and undergoes hydrolysis extremely readily,
is formed at the first step. The second step involves the addition of compound 2 to 3 resulting in the target
product 1.

We assumed that the difficulties in reproducing the synthesis of compound 1 arose from the fact that acids
and bases catalyze the decomposition of acetylphosphine
oxide 3. In fact, a series of experiments carried out in
a NMR tube demonstrated that the ³¹P NMR signal of
compound 1 (δ 32.9) disappears almost completely sev-
eral minutes after the addition of two or three drops of
Et₃N to a solution of compound 1 in dry CHCl₃ or after
passing dry HCl through the solution at room tempera-
ture. Instead, an intense signal of compound 2 appears
(δ 21.4, Jₚ,ₚ = 480 Hz). It could be assumed that
performing the reaction in a buffer system would hinder
the side processes, and precipitation of compound 1,
which is poorly soluble in ether, would shift the equilib-
rium in the desired direction.

In fact, when an ethereal solution of compound 2,
Ac₂O, and pyridine (or α-picoline) in the molar ratio
2 : 4 : 1 is kept at room temperature under argon,
compound 1 precipitates. This precipitate (yield ~66 %)
has m.p. 158—160 °C after thorough washing with dry ether without recrystallization. According to ³¹P NMR
spectral data, the product contains ~5% of compound 2. The content of the admixture does not decrease after recrystallization of the precipitate from benzene or ethanol, but the yield of the target product decreases sharply, probably due to the instability of compound 1 when boiled in the solvents used. When a solution of compound 1 in dry CHC13 is kept in a sealed tube at room temperature for several days, the content of compounds 1 and 2 does not change. However, if air moisture is present, the content of 1 decreases slowly (in several days) and the concentration of compound 2 increases. Furthermore, a weak signal of Ph2POOH appears in the 31P NMR spectrum (probably, due to the oxidation of compound 2).

**IR spectra and hydrogen bonds of 1,1-bis(diphenylphosphinoyl)ethanol.** A molecule of compound 1 contains three functional groups, namely, two P=O groups and one OH group, which can be involved in hydrogen bond formation.

![Diagram of compound 1](image)

A molecule of compound 1 contains an α-hydroxyphosphoryl moiety (marked with a dashed line), whose H-bonds have been studied in detail. It has been found that these compounds in solution are associated into dimers.

![Diagram of dimer A](image)

The IR spectra of these dimers are characterized by an intense band corresponding to OH group vibrations (3200–3300 cm⁻¹).

The OH group vibration region in the IR spectrum of solid compound 1 contains an intense broad band at ~3100 cm⁻¹ and a less intense band at ~2750 cm⁻¹ (an AB structure of the OH-band). Deformation OH vibrations are represented by an intense band at ~1370 cm⁻¹. The PO vibration region in the IR spectrum of compound 1 contains two bands at 1195 and 1180 cm⁻¹; the former band corresponds to the stretching vibrations of free P=O groups while the latter band is associated with the vibrations of P=O groups involved in intramolecular O–H ⋯ O=P H-bonds. These data imply association involving only one P=O group, while the other P=O group remains free.

![Diagram of intramolecular H-bond](image)

The band related to the intramolecular H-bond (ν(OH) 3100 cm⁻¹) in the IR spectrum of a solution of compound 1 in CHC13 disappears when the solution is diluted. Instead, a band at 3400 cm⁻¹ appears, which is typical of dimeric association. At the same time, the δ(OH) band is shifted towards lower frequencies (1350 cm⁻¹), which indicates the weakening of the H-bonds in the dimer. No bands of free OH group vibrations (~3580 cm⁻¹) were observed in the spectra of solutions of compound 1. Two bands remained in the region of PO vibrations (1190 and 1170 cm⁻¹). The band at 1190 cm⁻¹ corresponds to vibrations of free P=O groups, while the band at 1170 cm⁻¹ refers to the P=O groups involved in the H-bonds in the dimer. These spectroscopic data imply that compound 1 in solutions is associated into dimers (A), similarly to the association of α-hydroxyphosphoryl compounds.

![Diagram of complexes](image)

We have previously established a relationship between the shift of P=O vibration frequency and the enthalpy of the H-bonds in H-complexes of phosphoryl compounds. Here ν₁ and ν are the vibration frequencies of a free P=O group and that in an H-complex, respectively; the value ν = 987 cm⁻¹ has been accepted for a protonated phosphoryl group. Using this equation and the vibration frequencies for the P=O groups (ν₁ = 1190 cm⁻¹, ν = 1170 cm⁻¹), we estimated the enthalpy of one H-bond in the dimer A (~6 kcal mol⁻¹). The value of Δv(PO) in the spectrum of a solution of compound 1 equals to 20 cm⁻¹. The same value of Δv(PO) has been found for H-complexes of triphenylphosphine oxide with phenol. It thus follows that the acidity of the OH group in compound 1 is similar to pK of phenol.

**IR spectra and structure of complexes in solutions.** The following complexes of compound 1 (L) with neodymium and copper nitrates were obtained: L₂Nd(NO₃)₃ • 2H₂O (4), L · Cu(NO₃)₂ (5), L · Cu(NO₃)₂ • H₂O (6), and L₂ · Cu(NO₃)₂ (7). The IR spectra of these complexes in MeCN and CHCl₃ contain intense bands ν(OH) 3300 cm⁻¹, δ(OH) 1350 cm⁻¹, and ν(P=O) 1160–1170 cm⁻¹, which are similar to those in the spectrum of dimer A. Therefore, it is believed that the dimeric structure of the ligand is also retained in the solutions of the complexes. An analysis of molecular models allows us to suggest the general