# Reactivity of phosphine oxide $H_3PO$ in the reactions with ketones*

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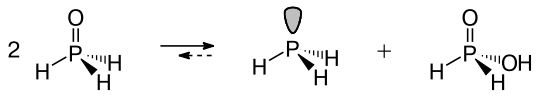
The reactivity of the electrochemically generated phosphine oxide $H_3PO$ towards ketones (acetone, ethyl methyl ketone, methyl *n*-propyl ketone, and *tert*-butyl methyl ketone) has been studied. It was found that this reaction led to the formation of mono- and bis(hydroxyalkyl)phosphine oxides of the formulas $RR'C(OH)P(O)H_2$ and $[RR'C(OH)]_2P(O)H$ (R = Me; R′ = Me, Et, Pr) and represents the first example of the P—C bond formation involving the intermediate $H_3PO$.

**Key words:** white phosphorus, phosphine oxide $H_3PO$, ketones, hydroxyalkylphosphine oxides, electrochemistry, NMR spectroscopy, ESI mass spectrometry, macroscale electrolysis.

One of the basic problems of modern phosphorus chemistry is the development of new highly efficient and environmentally friendly methods for obtaining organophosphorus compounds containing phosphorus—carbon bonds.[1—5] In this context, the use of highly active phosphorus intermediates is of undoubted interest. One of them is phosphine oxide $H_3PO$, which was long considered as unstable compound and could not be isolated in the pure form.[6] The use of electrochemical methods allowed us to selectively generate this intermediate in solution directly from white phosphorus ($P_4$) and stabilize it in the coordination sphere of water-soluble ruthenium complexes.[7] Note, however, that by the present moment there is no data on the reactivity of this intermediate in modern scientific literature. This is explained by its extremely low stability related to the disproportionation process, which leads to the formation of phosphine $PH_3$ and hypophosphorous acid $H_3PO_2$ (Scheme 1). This imposes strong restrictions on its selective involvement in the target processes of the formation of organophosphorus compounds.[7]

**Scheme 1**

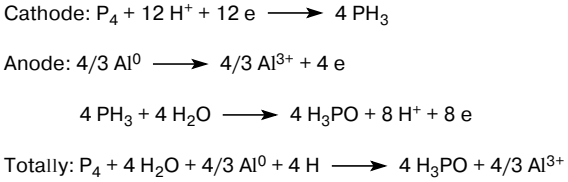


The purpose of the present studies is to investigate the reactivity of electrochemically generated phosphine oxide $H_3PO$ in the reactions with ketones: acetone (**1**), ethyl methyl ketone (**2**), methyl *n*-propyl ketone (**3**), and *tert*-butyl methyl ketone (**4**).

## Results and Discussion

Earlier,[7,8] we have found that phosphine oxide $H_3PO$ can be easily generated electrochemically in an undivided electrolyzer equipped with soluble anodes from aluminum, tin, or zinc. Optimization of the reaction conditions allowed us to selectively obtain phosphine oxide $H_3PO$ using an electrolyzer equipped with an aluminum anode.[8] Thus, in the studies of the reactivity of $H_3PO$ toward ketones **1**—**4**, it was generated in an electrolyzer equipped with an aluminum anode in aqueous organic solution (Scheme 2).[8]

**Scheme 2**




The use of an organic solvent is necessary to increase the solubility of the starting white phosphorus, which is a source of phosphorus atoms in the solution, and to in-

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crease the yield of the target product, that is phosphine oxide $H_3PO$. It was found experimentally that in the case of acetone (**1**), the process can be carried out in the absence of specially added alcohol due to the good mixibility of acetone with water. However, in the case of ketones **2**—**4** the reaction mixture in the absence of alcohol was a two-phase system (an emulsion of ketone in the aqueous phase), which somewhat hindered the electrochemical process.

The experiments showed that electrochemical generation of phosphine oxide $H_3PO$ in the presence of ketones **1**—**3** leads to the products with the P—C bonds, primary and secondary α-hydroxyalkylphosphine oxides **5**—**10** formed as a result of mono- and diaddition of ketones at the P—H bonds of phosphine oxide $H_3PO$. However, it was quite difficult to involve ketone **4** in this reaction: in the reaction mixture were formed only phosphorus oxyacids $H_3PO_2$ ($\delta_P$ 6.51, $^1J_{P,H}$ = 517.3 Hz) and $H_3PO_3$ ($\delta_P$ 3.12, $^1J_{P,H}$ = 669.1 Hz).[9] No any organophosphorus products were found in the reaction mixture in this case. The results of the experiments and the relative content of phosphorus-containing products obtained in their course are given in Table 1.

As it follows from the data in Table 1, the best results were obtained with ketones **1** and **2**. Thus, it was found that after completion of the reaction the $^{31}P$ NMR spectrum of the reaction mixture in the case of acetone exhibited one strong signal ($\delta_P$ 55.4, a doublet of multiplets) responsible for the formation of secondary bis(α-hydroxyalkyl)phosphine oxide **6** (Fig. 1). Note that in the initial steps of the reaction (after 3—4 h), the $^{31}P$ NMR spectra exhibit a signal for the intermediate primary phosphine oxide **5** at $\delta_P$ 27.0, which by the end of the reaction is completely transformed to the signal at $\delta_P$ 55.4 (more than 96% yield). This indicates a chemical reaction of the

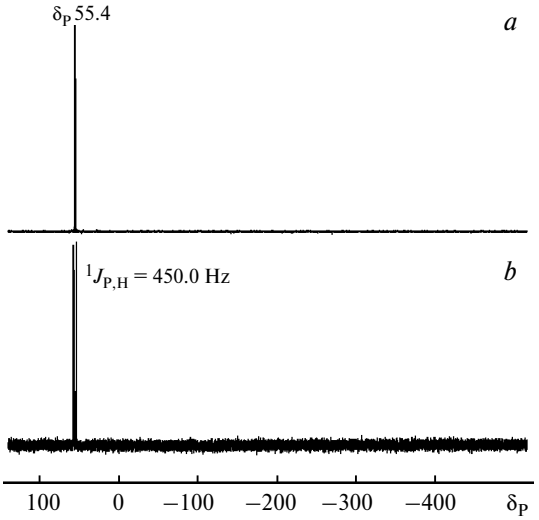
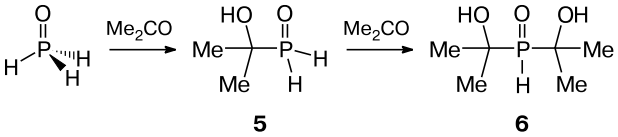



**Fig. 1.** The $^{31}P\{^1H\}$ (*a*) and $^{31}P$ NMR spectra (*b*) of the reaction mixture containing $H_3PO$ in the presence of acetone.

monoaddition product **5** with acetone to give bis(α-hydroxyalkyl)phosphine oxide **6** (Scheme 3), as it was shown earlier[10] for similar organophosphorus derivatives.

**Scheme 3**




The $^{31}P\{^1H\}$ and $^{31}P$ NMR spectra of the reaction mixture after carrying out electrochemical generation of

**Table 1.** Relative content of phosphorus-containing products in the reaction mixture obtained upon electrochemical generation of phosphine oxide $H_3PO$ in the presence of ketones **1**—**4** (Al anode, Pb cathode, 60 °C)

| Ketone | Conditions of generation | Products | Relative content* (%) |
|---|---|---|---|
| **1** | $H_2O/Me_2CO$ | $Me_2C(OH)P(O)H_2$ (**5**), | — |
| | | $[Me_2C(OH)]_2P(O)H$ (**6**) | 100 |
| **2** | $H_2O$/Me(Et)CO | Me(Et)C(OH)P(O)$H_2$ (**7**), | 15 |
| | | $[Me(Et)C(OH)]_2P(O)H$ (**8**), | 58 |
| | | $H_3PO_2$, | 9 |
| | | $H_3PO_3$ | 18 |
| **3** | $H_2O$/Me(Pr)CO | Me(Pr)C(OH)P(O)$H_2$ (**9**), | 6 |
| | | $[Me(Pr)C(OH)]_2P(O)H$ (**10**), | 45 |
| | | $H_3PO_2$, | 19 |
| | | $H_3PO_3$ | 30 |
| **4** | $H_2O/Me(Bu^t)CO$ | $H_3PO_2$, | 18 |
| | | $H_3PO_3$, | 58 |
| | | $H_3PO_4$ | 24 |

* Determined based on the integral intensities of signals in the $^{31}P$ NMR spectra immediately after completion of electrochemical process.

phosphine oxide $H_3PO$ in the presence of acetone are given in Fig. 1. In the reaction mixture, a full conversion of the elementary (white) phosphorus was observed, which was used as the starting reagent for the generation of phosphine oxide, as well as a complete absence of side phosphorus-containing products, including phosphine $PH_3$ electrochemically generated in the cathode process.

As it is seen from the experimental data, the reaction mixture contains only one phosphorus-containing product, that is secondary phosphine oxide **6**. The $^{31}P$ NMR spectrum of compound **6** exhibits a characteristic chemical shift at $\delta_P$ 55.4 (a doublet of multiplets) and a splitting the signal on the hydrogen atom directly bonded to the phosphorus atom ($^1J_{P,H}$ = 450.0 Hz), and the hydrogen atoms of the methyl groups ($^3J_{P,H}$ = 13.9 Hz) (Fig. 2).

Analysis of the $^1H$ NMR spectra obtained for compound **6** in acetonitrile-$d_3$ showed the presence of signals of two groups: twelve protons of the methyl groups (δ 1.48, a doublet, 6 H, $^3J_{P,H}$ = 13.9 Hz; δ 1.47, a doublet, 6 H, $^3J_{P,H}$ = 12.4 Hz) and one proton at the phosphorus atom (δ 6.17, a doublet, $^1J_{P,H}$ = 440.9 Hz). It is interesting that a small difference in the chemical shifts for the hydrogen atoms of the methyl group (6 H and 6 H) is explained by their magnetic nonequivalence because of the retarded rotation caused by the strong hydrogen bond between the hydroxy group and the phosphoryl oxygen (Fig. 3).

The formation of compound **6** in solution was also confirmed by electrospray ionization (ESI) mass spectrometry. Thus, the mass spectrum of phosphine oxide **6** exhibited a peak of the cationized molecule $[M + Na]^+$ with *m/z* 189.0.

To confirm the formation of products of primary addition of phosphine oxide at the carbonyl group of ketones under study, we used less active ethyl methyl ketone (**2**). This allowed us to detect in the reaction mixture the product of primary addition of ketone **2** at one P—H bond of the phosphine oxide molecule $H_3PO$, that was α-hydroxy-α-methylpropylphosphine oxide (**7**) (Fig. 4, Scheme 4).

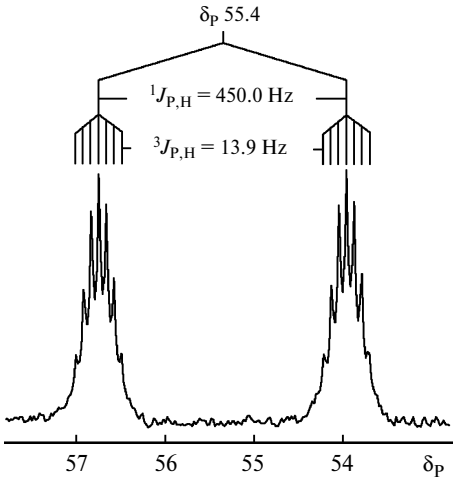



**Fig. 2.** A fragment of the $^{31}P$ NMR spectrum (water/acetone) of the addition product of acetone to phosphine oxide $H_3PO$, bis-(α-hydroxyisopropyl)phosphine oxide (**6**).

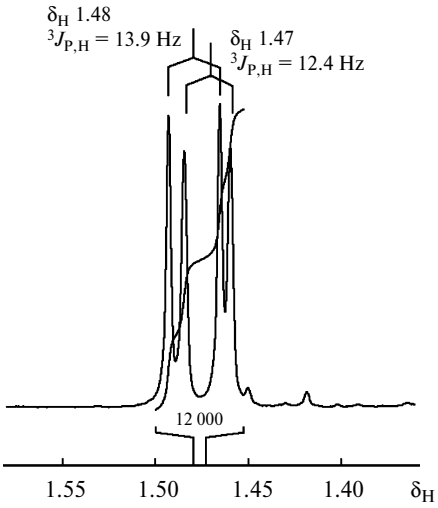
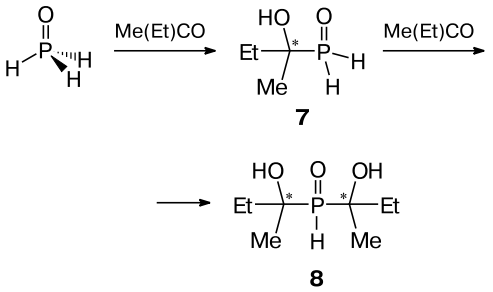



**Fig. 3.** A fragment of the $^1H$ NMR spectrum (acetonitrile-$d_3$) of the addition product of acetone to phosphine oxide $H_3PO$, bis-(α-hydroxyisopropyl)phosphine oxide (**6**).

**Scheme 4**




The formation of primary α-hydroxyalkylphosphine oxide **7** in solution was confirmed by NMR spectroscopy. Thus, the $^{31}P$ NMR spectrum of this compound exhibited a triplet of sextets at $\delta_P$ 26.3 ($^1J_{P,H}$ = 480.3 Hz, $^3J_{P,H}$ = = 15.0 Hz) attributed to the presence of two hydrogen

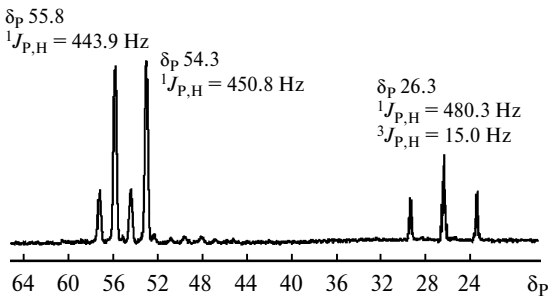



**Fig. 4.** $^{31}P$ NMR spectrum of the reaction mixture containing phosphine oxide $H_3PO$ in the presence of ketone **2**.

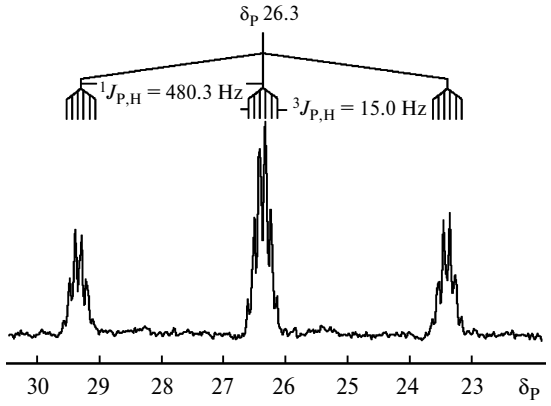



**Fig. 5.** A fragment of the $^{31}P$ NMR spectrum of the product of primary addition of phosphine oxide $H_3PO$ to ketone **2**, α-hydroxy-α-methylpropylphosphine oxide (**7**).

atoms at the phosphorus atom and five protons of α-methyl group ($CH_3$, 3 H) and β-methylene fragment ($CH_2$, 2 H) of the α-hydroxyalkyl substituent at the phosphorus atom (Fig. 5).

It should be noted that together with the signals of primary addition product **7**, the reaction mixture contained the signals for the secondary bis(α-hydroxy-α-methylpropyl)phosphine oxide (**8**). The presence in the $^{31}P$ NMR spectrum of several groups of signals (see Fig. 4) is explained by the formation of diastereomers and confirms the formation of secondary phosphine oxide **8** containing two chiral centers in the molecule (see Scheme 4). Such a behavior of primary phosphine oxide **7** is caused by the presence in its molecule of a chiral center, which influences the selectivity of the formation of diastereomers **8**. Thus, a chiral center at α-carbon atom of the alkyl substituent formed in first step of the reaction of phosphine oxide $H_3PO$ with ketone **2** can act as a chiral inductor of the process of subsequent addition of ketone **2** at the P—H bond of phosphine oxide **7**. This is confirmed experimentally by the presence of a diastereomeric excess of one of the forms of compound **8**.

Secondary phosphine oxide **8** was also studied by electrospray ionization mass spectrometry. The mass spectrum of compound **8** exhibited peaks of ions $[M + Na]^+$ (*m/z* 217.0) and $[2 M + Na]^+$ (*m/z* 411.2) (Fig. 6), the experimental isotope distribution of which is in good agreement with the theoretical. Note that the formation of adducts with sodium cations is frequently encountered[11] in the ESI mass spectrometry experiments.

It is necessary to emphasize that theoretically the formation of such organophosphorus products can be also suggested in the chemical reaction of acetone with phosphine $PH_3$, emerging as an intermediate in the course of electrochemical process. However, according to the available data[12—14] such a process is possible only under strongly acidic conditions (up to 12 *M* solutions of HCl), upon thermal activation (up to 100—120 °C), at increased pressure (up to 2.5—10 atm), or in superbasic medium.[15] Under other conditions, phosphine does not react with acetone.[14] Moreover, it was found that the reaction of $PH_3$ with acetone and some other ketones leads to the formation of only primary alkylphosphine oxides $R_2C(H)P(O)H_2$, *i.e.*, compounds which do not contain a hydroxy group at α-carbon atom of the alkyl substituent at the phosphorus atom (Scheme 5).

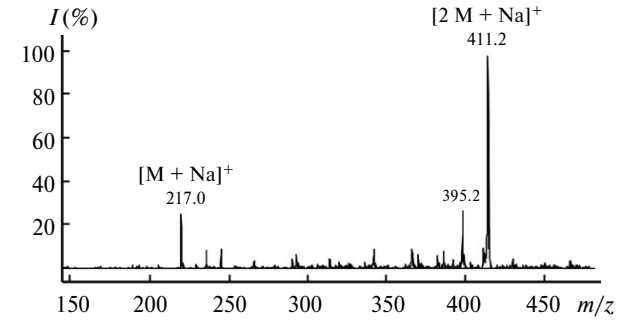
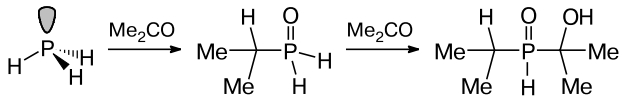



**Fig. 6.** Mass spectrum of the product of a double addition of ketone **2** to phosphine oxide $H_3PO$, bis(α-hydroxy-α-methylpropyl)phosphine oxide (**8**).

**Scheme 5**




The mechanism of the process postulated in the literature[12] indirectly suggests the formation of phosphine oxide $H_3PO$ in the first step *via* the transfer of the oxygen atom of the ketone carbonyl group on the phosphorus atom of the $PH_3$ molecule. In some cases, the formation of alkylphosphine oxide **11** is explained by the rearrangement of initially emerging α-hydroxyalkylphosphine $R_2C(OH)PH_2$ to **11**. However, no formation of phosphine oxide $H_3PO$ and α-hydroxyalkylphosphine oxides as the products of the earlier described processes involving phosphine $PH_3$ and ketones was detected. A primary alkylphosphine oxide **11** and a secondary alkyl-α-hydroxyalkylphosphine oxide **12** are the main products of these transformations involving unsubstituted ketones (see Scheme 5). An exception are some halogenated ketones such as 1,1,1-trifluoroacetone and hexafluoroacetone, which can react with phosphine $PH_3$ under mild conditions with the formation of the corresponding fluoro-substituted α-hydroxy(isopropyl)phosphines.[16,17] It is interesting that a possibility of the formation of tris(α-hydroxyalkyl)phosphine oxides under electrochemical conditions involving elementary phosphorus and phosphine has been shown earlier in the work,[18] where the authors successfully carried out the synthesis of tris(hydroxymethyl)phosphine oxide

and tris(α-hydroxyethyl)phosphine oxide in 60—70 and 40—45% yields, respectively.

As it follows from the experimental data, in all the cases phosphine oxide $H_3PO$ acts as an agent reacting with ketones **1—3**, since its reactivity considerably exceeds the reactivity of phosphine $PH_3$,[6] which is also confirmed by the target process taking place under relatively mild conditions at a high rate and with high selectivity. Moreover, on model reactions we experimentally confirmed that phosphine $PH_3$ does not react with ketones **1—4** under the conditions used.

In conclusion, the reaction of phosphine oxide $H_3PO$ with acetone, ethyl methyl ketone, and methyl *n*-propyl ketone, in contrast to phosphine $PH_3$, proceeds under mild conditions without use of strongly acidic medium, increased temperature and pressure. This indicates considerably more high reactivity of phosphine oxide $H_3PO$ as compared to phosphine $PH_3$ in the reactions of the formation of organophosphorus compounds, that opens wide prospects and new synthetic possibilities for selective preparation of organophosphorus compounds, including derivatives of tricoordinated phosphorus obtained by chemical reduction of phosphine oxides[19] and regarded as important and widely used reagents for modern catalytic chemistry and organophosphorus industry.

## Experimental

All the experiments were carried out under dry nitrogen using a standard Schlenk line. Solvents were purified by distillation immediately before use. White phosphorus used in the reactions was purified by a solution of potassium dichromate and concentrated sulfuric acid with subsequent recrystallization from the solution in DMF. The thus obtained phosphorus was rolled into balls in the molten state (50 °C) with stirring on a magnetic stirrer with subsequent cooling. Immediately before use, the white phosphorus was sequentially washed with ethanol, acetone, and diethyl ether. It is important to take precautions: the white phosphorus $P_4$ and phosphine $PH_3$ are very toxic, flammable, and dangerous compounds, which require special handling conditions in completely inert media in a well ventilated room.

Dichloromethane was purified by distillation immediately before use and stored in the dark in stoppered Schlenk flasks under nitrogen. Commercial acetone (99%, Aldrich), butanone (99%, Aldrich), pentan-2-one (98%, Aldrich), *tert*-butyl methyl ketone (98%, Aldrich), and hydrochloric acid (37%, Sigma—Aldrich) were used without additional purification.

Preparative electrolysis was carried out in a hermetically sealed undivided electrolyzer[20,21] equipped with an electrochemically soluble Al anode in galvanostatic regime ($I$ = 150 mA) using a B5-71/1U source of direct current.[8] The cathode (Pb) working surface was 32 $cm^2$. The working electrode (cathode) potential was detected by a Shch50-1 DC voltmeter relative to the reference electrode $Ag/AgNO_3$, 0.01 *M* solution in MeCN ($E°(Fc/Fc^+)$ = +0.20 V). In the course of electrolysis, the working electrode potential did not exceed –2.5 V.

$^1H$ and $^{31}P$ NMR spectra were recorded at room temperature (25 °C) on Bruker MSL-500 (500.1 MHz) and Bruker Avance III 400 (161.9 MHz) high resolution spectrometers, respectively. ESI mass spectra were obtained on a AmazonX mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany). Positive ions were detected in the range $m/z$ from 70 to 1000. Capillary voltage was –4500 V. Nitrogen was used as a drying gas at a temperature of 250 °C and at a rate of 8 L $min^{-1}$. The samples were injected using an Agilent 1260 chromatograph (USA). The data were processed using the DataAnalysis 4.0 program (Bruker Daltonik GmbH).

**Electrochemical generation of phosphine oxide $H_3PO$ in the presence of ketones 1—4 (general procedure).** A solution for the electrolysis was prepared by emulsification of white phosphorus (100 mg, 0.81 mmol) in a mixture of water/ketone (1 : 2 v/v, 30 mL) at 70 °C. A 2 *N* aqueous solution of HCl (0.5 mL) was added to the obtained finely dispersed emulsion (an opaque solution) and a direct voltage was applied with the current strength of 150 mA ($i$ = 46.9 A $m^{-2}$). Every 2 h after beginning of the electrolysis, an aqueous solution of HCl (0.5 mL) was added to the reaction mixture. A total volume of added hydrochloric acid was 2.0 mL. The electrolysis time was 8 h. A resulting mixture was extracted with dichloromethane and concentrated. The products were analyzed by $^{31}P$ and $^1H$ NMR spectroscopy and mass spectrometry with electrospray ionization. The conditions of electrochemical processes and relative content of phosphorus-containing products in the reaction mixture were evaluated based on the integral intensities of signals in the $^{31}P$ NMR spectra (see Table 1). Spectral characteristics of obtained organophosphorus compounds are given below. $^1H$ NMR spectra for compounds **5** and **7—10** are not reported because of the low stability of these derivatives, which decompose by the reaction of ketone elimination as described earlier[22] for α-hydroxyisopropyldiphenylphosphine oxide.

**1-Hydroxyisopropylphosphine oxide (5).** $^{31}P$ NMR ($H_2O$), δ: 27.0 (t.hept, $J$ = 484.4 Hz, $J$ = 18.2 Hz).

**Bis(1-hydroxyisopropyl)phosphine oxide (6).** $^1H$ NMR (MeCN-$d_3$), δ: 1.472 (d, 6 H, 2 $CH_3$, $J$ = 12.4 Hz); 1.479 (d, 6 H, 2 $CH_3$, $J$ = 13.9 Hz); 6.17 (d, 1 H, P—H, $J$ = 440.9 Hz). $^{31}P$ NMR ($H_2O$/acetone), δ: 55.4 (dm, $J$ = 450.0 Hz, $J$ = 13.9 Hz). MS (ESI), $m/z$ ($I_{rel}$ (%)): 189.0 $[M + Na]^+$ (21).

**1-Hydroxy-1-methylpropylphosphine oxide (7).** $^{31}P$ NMR ($H_2O$), δ: 26.3 (t.sext, $J$ = 480.3 Hz, $J$ = 15.0 Hz).

**Bis(1-hydroxy-1-methylpropyl)phosphine oxide (8).** $^{31}P$ NMR ($H_2O$), δ: 55.8 (dm, $J$ = 443.9 Hz); 54.3 (dm, $J$ = 450.8 Hz). MS (ESI), $m/z$ ($I_{rel}$ (%)): 217.0 $[M + Na]^+$ (28), 411.2 $[2 M + Na]^+$ (100).

**1-Hydroxy-1-methylbutylphosphine oxide (9).** $^{31}P$ NMR ($H_2O$), δ: 27.3 (t.sext, $J$ = 483.3 Hz, $J$ = 13.2 Hz).

**Bis(1-hydroxy-1-methylbutyl)phosphine oxide (10).** $^{31}P$ NMR ($H_2O$), δ: 53.2 (br.m).

**Hypophosphorous acid $H_3PO_2$.** $^{31}P$ NMR, δ: 6.51 (t, $J$ = = 517.3 Hz).

**Phosphorous acid $H_3PO_3$.** $^{31}P$ NMR, δ: 3.12 (d, $J$ = = 669.1 Hz).

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