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Selective synthesis and stabilization of peroxides via phosphine oxides†

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Reaction of bis(dicyclohexylphosphino)ethane dioxide with hydrogen peroxide leads to an extended crystalline network based on the formation of hydrogen bonds with the P=O groups of the diphosphine dioxide. The structural motif of the network is characterized by X-ray diffraction. A new selective synthesis for an industrially important MEKPO (methyl ethyl ketone peroxide) dimer is described. The dimer is created by reaction of dppe dioxide (bis(diphenylphosphino)ethane dioxide) with butanone and hydrogen peroxide. This peroxide is stabilized by forming strong hydrogen bonds to the phosphine oxide groups within an extended network, which has been characterized by single crystal X-ray diffraction. Reaction of acetylacetone with hydrogen peroxide, irrespective of the presence of phosphine oxide, leads to the stereoselective formation of two dioxolanes. Both cyclic peroxides have been obtained in crystalline forms suitable for single crystal X-ray diffractions.

Introduction

Phosphine oxides are compounds that have been described in inorganic chemistry textbooks for a long time. Recently, they came back into the spotlight in many different areas. They are, for example, unwanted byproducts of phosphine coordination chemistry, especially in the field of immobilized catalysts.^{1–4} Many linkers that are used to tether metal complexes to solid oxide supports contain phosphine groups. Once the latter are oxidized to phosphine oxides, the catalyst is no longer retained and leaches from the support.⁵ Furthermore, phosphine oxides are co-products of Wittig and Appel reactions. In another field, they are applied to probe surface acidities⁶ and recently became the focus of attention regarding the decomposition of warfare agents.⁷ In this context, phosphine oxides have been shown to be very mobile on surfaces, which leads to interesting line-narrowing effects in the ³¹P solid-state NMR spectra due to the averaging out of anisotropic interactions, most importantly the Chemical Shift Anisotropy (CSA).^{8,9} Finally, it should be noted that phosphine oxides are important synthetic targets and intermediates.^{10,11} For example, they are byproducts of the Mitsunobu reaction,^{11g} and recently became the focus of attention as redox-free Mitsunobu organocatalysts.^{11h}

One of the most important features of phosphine oxides is that they form hydrogen bonds with a variety of different donors. For example, phenols have been used in combination with

phosphine oxides to create extended hydrogen-bonded networks.^{12,13} Furthermore, hydrogen bonding with naphthol,¹⁴ sulfonic acids,¹⁵ and water has been reported.^{8,16–18} Even silanols, phenols, and chloroform crystallize as hydrogen-bonded assemblies.¹⁹ Besides single crystal X-ray diffraction, ³¹P solid-state NMR spectroscopy is a powerful method to analyze the hydrogen bonding characteristics of diverse P(V) species.^{8–10,17,20}

We discovered recently that phosphine oxides are also able to stabilize hydrogen peroxide and di(hydroperoxy)alkanes by forming hydrogen bonds.^{17,18,21–23} The Hilliard adducts can be generated by exposing phosphines or phosphine oxides to aqueous H₂O₂. They exhibit most commonly the structural motifs (R₃PO·H₂O₂)₂ or (R₃PO)₂·H₂O₂.^{21–23} Ahn adducts form assemblies of the type R₃PO·(HOO)₂CR'R'' (R, R', R'' = alkyl and aryl) when phosphines, their oxides, or Hilliard adducts are reacted with ketones in the presence of aqueous H₂O₂.^{21–23} Fig. 1 shows the most common structures of Hilliard^{17,18,21} and Ahn^{21–23} adducts synthesized and characterized so far. Importantly, all adducts are safe and robust with respect to mechanical and thermal impact. Even when bringing the powders directly into a flame, the oxygen escapes without a pronounced audible or

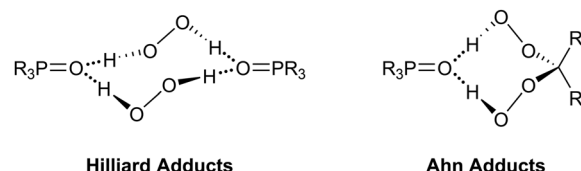


Fig. 1 Selected previously reported Hilliard adducts (R = Cy, ^tBu, Ph, *o*-Tol, *p*-Tol)^{17,18,21} and Ahn adducts (R, = Cy, Ph, Et; R', R'' = Me, Et, Pr, (CH₂)_{5–7}).^{21–23}

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visual effect. These stable, solid Hilliard and Ahn adducts are easy to synthesize, they crystallize readily, and are currently investigated regarding their potential as oxidizers.^{21–23}

Peroxides are ubiquitous and immensely important in daily life, medicine, academia, and industry.^{24–27} Recent applications in synthesis include the oxidation of amines²⁸ and sulfides,²⁹ alkane activation,³⁰ epoxidations,³¹ and Baeyer–Villiger oxidations.^{23,32}

Unfortunately, the most ubiquitous oxidizing agent, aqueous H_2O_2 , is far from ideal. The abundance of water it inevitably delivers to the reaction mixture can lead to unwanted secondary reactions. Additionally, most oxidations have to be performed in a biphasic system, slowing rates and requiring phase separations later. Commercial aqueous H_2O_2 also contains nitric acid as stabilizer. Aqueous H_2O_2 degrades at unpredictable rates,³³ especially in the presence of metal ion traces^{33c} and requires titration prior to critical applications.^{33a,b} Water-free formulations of H_2O_2 , like urea hydrogen peroxide (UHP)³⁴ and peroxocarbonates³⁵ do not have well-defined compositions and are insoluble in organic solvents. Encapsulated versions of H_2O_2 ,³⁶ and its adducts of metal complexes are known but not readily available commercially or synthetically.^{37,38} The peroxides $(\text{Me}_3\text{SiO})_2$ and $(\text{CH}_3)_2\text{C}(\text{OO})$ (DMDO) are applied, but their synthesis and storage are problematic.^{38,39}

In this contribution we describe the creation of a solid, crystalline network with well-defined composition that stabilizes H_2O_2 by hydrogen-bonding to the $\text{P}=\text{O}$ groups of dcpe dioxide (bis(dicyclohexylphosphino)ethane dioxide). Furthermore, we report a selective synthesis and the stabilization of a MEKPO (methyl ethyl ketone peroxide) dimer by hydrogen-bonding with dppe dioxide. Again, an extended network is obtained that has also been characterized by single crystal X-ray diffraction. Reaction of acetylacetone with aqueous H_2O_2 , in the presence or absence of a phosphine oxide resulted in the formation of two cyclic peroxides.

Results and discussion

Hilliard adducts^{17,18,21} (Fig. 1) have already proven to be safe, soluble, and solid incarnations of H_2O_2 with known and reproducible composition.

However, to render them more competitive with aqueous H_2O_2 , the weight of the carrier phosphine oxide needs to be reduced. One approach towards this goal is to offer a diphosphine dioxide, bis(dicyclophosphino)ethane dioxide, for stabilizing the H_2O_2 . The envisioned species included a monomeric adduct with two intramolecular $\text{P}=\text{O}$ groups, $(\text{CH}_2\text{Cy}_2\text{PO}\cdot\text{H}_2\text{O}_2)_2$, and a cyclic dimer containing four H_2O_2 molecules bridging four $\text{P}=\text{O}$ functions, $[(\text{CH}_2\text{Cy}_2\text{PO}\cdot\text{H}_2\text{O}_2)_2]_2$. The formation of cyclic structures seemed likely, especially with respect to Shenderovich's work on cyclic trimers of phosphinic acids.⁴⁰

However, when dcpe dioxide was reacted with aqueous H_2O_2 , an extended network with a zig-zag chain structure was formed (**1**, Fig. 2). The material **1** crystallized easily and could be investigated by single crystal X-ray diffraction (Fig. 3). The $\text{P}=\text{O}$ groups of each diphosphine dioxide molecule are oriented in

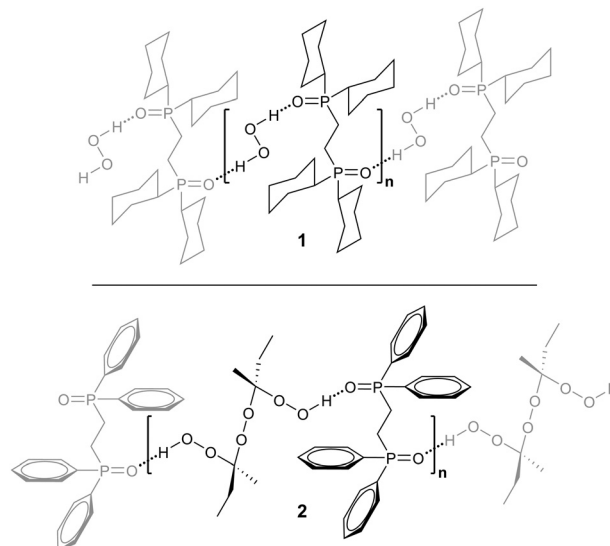


Fig. 2 The new materials **1** and **2**.

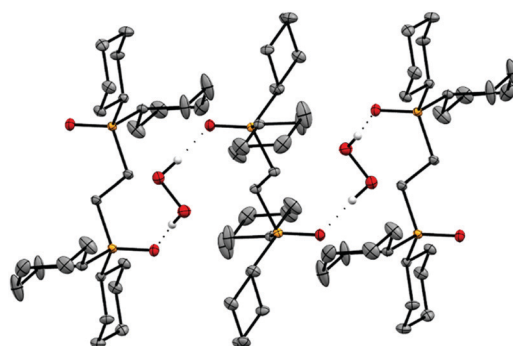


Fig. 3 Single crystal X-ray structure of the hydrogen peroxide adduct $[(\text{CH}_2\text{Cy}_2\text{PO})_2\cdot\text{H}_2\text{O}_2]_n$ (**1**).⁴¹

opposite directions, with a dihedral angle of 180° . This structural feature has been observed previously for Ahn adducts of dppe (bis(diphenylphosphino)ethane) dioxide.²² Every H_2O_2 molecule forms hydrogen bonds to two $\text{P}=\text{O}$ groups of neighboring dcpe dioxide molecules. The short distance of 1.755 Å between the $\text{P}=\text{O}$ oxygen and the H atoms corroborates the hydrogen bonding, as this distance is even slightly shorter than the values in the characteristic range that spans from 1.85 to 1.95 Å.⁴² Additionally, the hydrogen bonding manifests itself in the short distance between the two $\text{O}-\text{H}\cdots\text{O}$ oxygen atoms (2.704 Å), which also lies slightly below the typical range of values from 2.75 to 2.85 Å.⁴³ The $\text{P}=\text{O}$ groups are weakened and elongated (1.501 Å) due to the hydrogen bonding, consistent with comparable values of the Hilliard adducts described earlier.^{17,18,21}

The ^{31}P NMR resonance of adduct **1** also has a different chemical shift (53.78 ppm) than the signal of dcpe dioxide (54.27 ppm). The hydrogen bonding does, however, not manifest in a different IR wavenumber for $\nu(\text{P}=\text{O})$ in **1**, as the same value of 1134 cm^{-1} is measured for the neat compound dcpe dioxide. The smaller differences in the IR and NMR chemical shift values, as compared to previously described Hilliard adducts^{17,18,21} are

most probably due to the fact that in **1** only one hydrogen bond is formed between H_2O_2 and a $\text{P}=\text{O}$ group, while the majority of the Hilliard adducts have two. However, regarding the longterm stability of material **1**, it compares favorably with dimeric Hilliard adducts. For example, after about three years of storage in the laboratory atmosphere at room temperature (22°C), solid **1** retained 58% of its original oxidative power. Under the same conditions, after *ca.* three years, $(p\text{-Tol}_3\text{PO}\cdot\text{H}_2\text{O}_2)_2$ only retains 33% of its oxidative power.¹⁸

Based on the experience that phosphine oxides can efficiently stabilize bis(dihydroperoxy)alkanes *via* hydrogen bonding to form Ahn adducts,^{21–23} we sought to create an Ahn adduct with reduced weight of the phosphine oxide carrier. This should render Ahn adducts more competitive with respect to the commercially available aqueous H_2O_2 . We approached the new synthesis by using the dioxide of bis(diphenylphosphino)ethane (dppe dioxide) as carrier with lower weight and sought to produce the Ahn adduct $(\text{CH}_2\text{Ph}_2\text{PO}\cdot(\text{HOO})_2\text{CMeEt})_2$, in analogy to $(\text{CH}_2\text{Ph}_2\text{PO}\cdot(\text{HOO})_2\text{CtEt})_2$ that has been reported previously.²²

Interestingly, when butanone was reacted with aqueous H_2O_2 in the presence of dppe dioxide, the dimeric peroxide $(\text{HOOCMeEtO})_2$ was obtained. This peroxide dimer is stabilized by forming a hydrogen-bonded extended network with dppe dioxide, $[(\text{CH}_2\text{Ph}_2\text{PO})_2(\text{HOOCMeEtO})_2]_n$ (**2**) (Fig. 2). The material **2** is obtained in an unoptimized yield of 83%.

The selective formation of adduct **2** is remarkable regarding the properties and especially the reactivity of MEKPO (methyl ethyl ketone peroxides). MEKPO represents an indispensable class of reagents in the polymer industry, where it is used as a catalyst for acrylic resins or as curing agent for unsaturated polyester resins.^{44,45} However, despite its importance, it is regarded as a very hazardous material. Therefore, great efforts have been undertaken to produce MEKPO under controlled reaction conditions and on small scales, for example, by using a microreactor.⁴⁵ At present, MEKPO oligomers are synthesized by reacting butanone (MEK, methyl ethyl ketone) with H_2O_2 in a batchwise manner. The initial product is most probably $\text{EtC}(\text{OH})(\text{OOH})\text{Me}$ that undergoes secondary reactions to yield a mixture of linear and cyclic oligomers.⁴⁴ These oligomers are impossible to separate economically and therefore MEKPO is applied as a mixture based on the wt% of active oxygen.^{44,45} Industrial batches of MEKPO still contain residual MEK which increases its explosion hazard. Additionally, for industrial applications MEKPO is diluted with DMP (*o*-dimethylphthalate) to 40–60% solutions. Furthermore, it is a strong oxidizing agent and a corrosive. Acute and chronic toxicity can occur as an occupational hazard. Inhalation of MEKPO can lead to pneumonitis, acidosis, and liver and renal failure.⁴⁶ Finally, MEKPO is prone to runaway reactions when coming into contact with a variety of substances, for example, bases, or $\text{Fe}(\text{II/III})$ salts.⁴⁷

In contrast, material **2** is a much more benign version of MEKPO. It is solid, has a low vapor pressure, and besides the phosphine oxide carrier it is free of additives. Material **2** exhibits a well-defined composition and is less prone to uncontrolled decomposition. In fact, when mechanical stress like grinding or hammering are applied, no detonation occurs and bringing **2**

into a flame only leads to slow release of gas without pronounced visible or audible effects. Nevertheless, the active oxygen content of **2** amounts to 7.5 wt%, which is close to the range of commercially available MEKPO for academic use (32–35 wt% solutions with 8.7–9.0 wt% active oxygen).

In order to determine the longevity of peroxides that are stabilized by hydrogen-bonding in Hilliard^{17,18,21} or Ahn adducts,^{21–23} we have previously developed a method to quickly determine their oxidative power. The method is based on offering the peroxide a weighed amount of PPh_3 in excess and integrating the ^{31}P NMR signals of residual PPh_3 and produced OPPh_3 after the oxidation reaction.²¹ Accordingly, for material **2**, an oxidative power of 100% would correspond to three active oxygen atoms per adduct unit (Fig. 2). It turns out that the peroxide in **2** is stabilized very well by the dppe dioxide, and after 4.7 years of exposure to the atmosphere in a drawer in the lab at ambient temperature its remaining oxidative power still amounts to 24%.

Material **2** crystallizes readily and in large habits, and therefore the structure could also be characterized by single crystal X-ray diffraction (Fig. 4).

The two ketal carbon atoms in the dimeric peroxide component of the network display *R* and *S* configurations, therewith constituting the *meso* compound. The two hydroperoxy groups are hydrogen-bonded to the phosphine oxide groups. The two hydrogen-bonded $\text{P}=\text{O}$ groups of the dppe dioxide point in opposite directions with a dihedral angle of 180° , in analogy to the extended network of material **1**. The ideal packing with dppe dioxide (Fig. 4) may promote the formation of the dimeric peroxide as opposed to the di(hydroperoxy)butane moieties found in the adducts $\text{Ph}_3\text{PO}\cdot(\text{HOO})_2\text{CtEtMe}$ and $\text{C}_3\text{F}_7\text{PO}\cdot(\text{HOO})_2\text{CtEtMe}$.²² The crucial factor explaining the ease of crystallization of material **2** and favoring the structure of the network might be the similar lengths of the $\text{P}-\text{C}-\text{P}$ (4.412 Å) unit of the diphosphine dioxide and the $\text{C}-\text{O}-\text{C}$ (3.571 Å) moiety of the dimeric peroxide, which allow for their parallel and strainless stacking in the crystal. The slight difference in the lengths allows the hydrogen bonds to retain the favorable linear $\text{O}\cdots\text{H}-\text{O}$ arrangement.

Every MEKPO moiety forms hydrogen bonds to two $\text{P}=\text{O}$ groups of adjacent dppe dioxide molecules. The distance of 1.783 Å between the $\text{P}=\text{O}$ oxygen and the H atoms indicates the

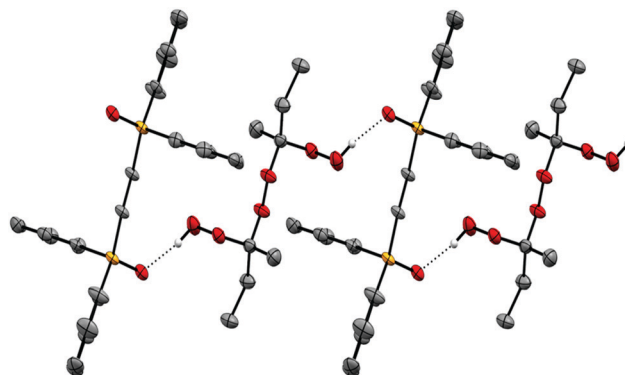


Fig. 4 Single crystal X-ray structure of adduct **2**.⁴¹

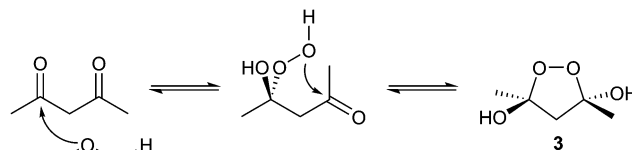
hydrogen bonding, being even slightly shorter than the values in the characteristic range from 1.85 to 1.95 Å.⁴² Furthermore, the hydrogen bonding leads to a short distance between the two O–H...O oxygen atoms (2.627 Å), which is slightly outside at the lower end of the typical range of values (2.75 to 2.85 Å).⁴³ The P=O groups are elongated (1.497 Å) due to the hydrogen bonding, consistent with comparable values of the Ahn adducts described earlier.^{21–23} Correspondingly, the ³¹P NMR resonance of **2** undergoes a downfield shift to 36.91 ppm with respect to 31.5 ppm reported for the adduct-free dppe dioxide.⁴⁸ The hydrogen bonding also manifests in the slight lowering of the IR wavenumber $\nu(\text{P}=\text{O})$ in **2** to 1173 cm^{−1} as compared to 1175 cm^{−1} for dppe dioxide.⁴⁸

Similarly to the Ahn adducts described previously,^{21–23} the solubility of **2** is highest in methylene chloride (66.9 mg mL^{−1}). It is relatively low in benzene (1.43 mg mL^{−1}), methanol (1.72 mg mL^{−1}), and dimethylformamide (2.24 mg mL^{−1}). Most probably, the nature of **2** with its extended hydrogen-bonded network leads to the comparatively low solubilities in the latter three solvents. Dichloromethane, due to its ability to strongly interact with P=O groups,¹⁹ might be able to split **2** into smaller, more soluble fragments of the network. It has been demonstrated earlier by DOSY experiments that in methylene chloride dimeric Hilliard adducts with triarylphosphine oxide carriers are dissociating into monomers.¹⁸ Nevertheless, it is noteworthy that even the lower solubilities are more than sufficient for potential applications of **2** as a polymerization starter.⁴⁹

Since dppe dioxide proved to be able to form multiple hydrogen bonds to di(hydroperoxy)alkanes, the next step in our synthesis endeavor involved expanding the scope of offered ketones to diketones. In this way, the weight of the adduct assemblies per active oxygen atom could be reduced. Furthermore, we sought to probe whether both carbonyl groups of a diketone could undergo nucleophilic attack by H₂O₂^{21,22} to each form the di(hydroperoxy)alkane moiety. The latter would be stabilized immediately by hydrogen-bonding to the offered phosphine oxide groups.

To test this idea, acetylacetone was selected as the 1,3-diketone because it is very versatile and, depending on the reaction conditions and additives, it can yield a variety of different products.^{50–52} Dppp dioxide (bis(diphenylphosphino)propane dioxide) was chosen as the phosphine oxide partner. The P=O groups are in close enough proximity to form strong hydrogen bonds, while the (CH₂)₃ tether between them should allow for sufficient flexibility to orient them towards the two di(hydroperoxy)alkane moieties potentially created from acetylacetone.

Interestingly, the presence of dppp dioxide does not prevent the cyclization of the diketone when being treated with aqueous H₂O₂. This result is in contrast to the cases of previously reported adducts, where the phosphine oxides formed hydrogen bonds with the di(hydroperoxy)alkane moieties and thereby prevented the condensation leading to cyclic acetone peroxide or butanone peroxide.^{21–23} The cyclic peroxide **3** is formed according to the pathway displayed in Scheme 1. Acetylacetone undergoes two consecutive nucleophilic attacks by aqueous



Scheme 1 Synthesis of the cyclic dioxolane derivative **3**.

H₂O₂ to form selectively the *trans*-cycloperoxides **3** (Scheme 1). The presence of nitric acid as stabilizer in the aqueous H₂O₂ most probably facilitates the nucleophilic attacks. However, it is remarkable that no I₂ was needed as a catalyst to create the dioxolane as reported for similar 1,3-diketone transformations to dioxolanes previously.⁵³ In contrast to earlier reports of *cis/trans* mixtures,⁵² only the *trans* isomer of **3** was obtained. Furthermore, in the sole presence of H₂O₂ and strong acids, bridged tetraoxanes have been reported.⁵¹

Depending on the amount of H₂O₂, either *trans*-3,5-dimethyl-1,2-dioxolane-3,5-diol (**3**) or *trans*-3,5-dihydroperoxy-3,5-dimethyl-1,2-dioxolane (**4**) is isolated as the sole product (Fig. 5). Curiously, the mixed dioxolane **5**,⁵² containing one OH and one OOH substituent (Fig. 5), was not observed.

It is remarkable that only the *trans* isomers are formed in both cases, while in the literature *cis/trans* isomer mixtures of **3** and **4** are obtained by different syntheses.^{52,54}

Since both **3** and **4** crystallize readily, the *trans* substitution is also proven by their single crystal X-ray structures.^{41,55} Fig. 6 displays the structure of **3**,⁴¹ the structure of **4** is in accord with the literature.^{41,54,55}

Both dioxolanes **3** and **4** form an intricate network of hydrogen bonds with neighboring molecules (Fig. 6), which may be the reason for their ease of crystallization. Furthermore, these intermolecular hydrogen bonds might compete with the adduct formation *via* the P=O groups of the phosphine oxides, in this way favoring the cyclic molecular products **3** and **4**.

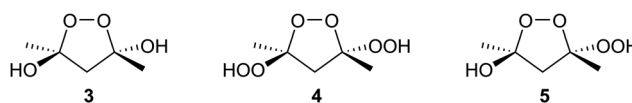


Fig. 5 Possible products of the reaction of acetylacetone with aqueous H₂O₂. Only **3** and **4**, but not **5** were observed experimentally.

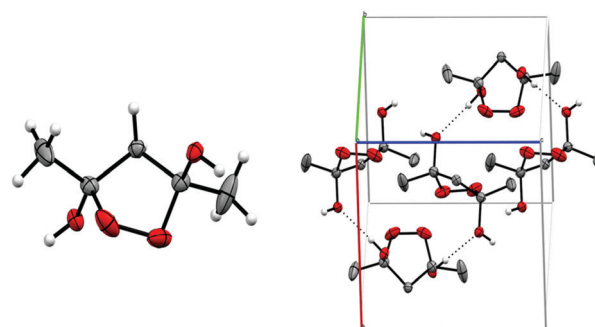


Fig. 6 Single crystal X-ray structure of **3** (left) and **3** in the unit cell (right).⁴¹

It is also noteworthy that compounds **3** and **4** could be obtained selectively and isolated in high yields of 71% and 68%, respectively. No elaborate purification operations like column chromatography, and no catalysts like I_2 and $SnCl_2 \cdot 2H_2O$ were needed.^{52,54} Furthermore, the aqueous H_2O_2 used was not as concentrated with 35 wt% (compared to 50 wt%) and no concentrated H_2SO_4 had to be added, in contrast to a previously described procedure.⁵⁴

Conclusion

For preparative chemistry, the ideal peroxide would be inexpensive, easily accessible, reproducible in its composition, and soluble in organic solvents. It should be safe and stable at ambient temperatures on the shelf. Finally, a solid oxidizing agent would be desirable that can easily be administered.

In this contribution we describe the easy synthesis, purification, and characterization of a H_2O_2 adduct of a diphosphine dioxide (**1**), and an adduct containing a MEKPO dimer (**2**). Furthermore, the selective syntheses of two dioxolane derivatives (**3** and **4**) are described.

The reaction of bis(dicyclohexylphosphino)ethane dioxide with hydrogen peroxide leads to an extended crystalline network based on the formation of hydrogen bonds with the $P=O$ groups of the diphosphine dioxide. The novel structural motif of the network is characterized by X-ray diffraction. Furthermore, a new selective synthesis for an industrially important MEKPO dimer and its stabilization by a diphosphine dioxide is described. The dimer is created by reaction of dppe dioxide with butanone and aqueous hydrogen peroxide. This dimeric peroxide is stabilized by strong hydrogen bonds to the phosphine oxide groups within an extended network, which has been characterized by single crystal X-ray diffraction. The dimeric peroxide material can easily be purified by crystallization. It is solid with a low vapor pressure and therefore poses less of a health hazard at the workplace than pure MEKPO. Phosphine oxide-supported MEKPO does not show tendencies to explode and is stable on the shelf at ambient temperatures over years. Furthermore, it is soluble in organic solvents, with the highest solubility in methylene chloride. In summary, material **2** might be an attractive alternative to MEKPO in the future.

The reaction of acetylacetone with aqueous H_2O_2 , irrespective of the presence of phosphine oxide, leads to the unprecedented stereoselective formation of two dioxolane derivatives in high isolated yields. Both cyclic peroxides have been obtained in crystalline forms suitable for single crystal X-ray diffractions and their stereochemistry has been determined.

Experimental

General considerations

All reactions were carried out using standard Schlenk line techniques and a purified N_2 atmosphere, if not stated otherwise. Reagents purchased from Sigma Aldrich or VWR were used without further purification. Aqueous H_2O_2 solution (35% w/w)

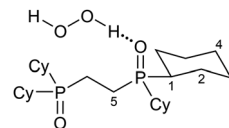
was obtained from Acros Organics and used as received. Solvents were dried by boiling them over sodium, then they were distilled and stored under purified nitrogen. Dichloromethane (Aldrich, ACS reagent grade) was dried over 3 Å molecular sieves (EMD Chemical Inc.) prior to use.

NMR Spectroscopy

The 1H , ^{13}C , and ^{31}P NMR spectra were recorded at 499.70, 125.66, and 202.28 MHz on a 500 MHz Varian spectrometer. The ^{13}C and ^{31}P NMR spectra were recorded with 1H decoupling. Neat Ph_2PCl ($\delta(^{31}P) = +81.92$ ppm) in a capillary centered in the 5 mm NMR tubes was used for referencing the ^{31}P chemical shifts. For referencing the 1H and ^{13}C chemical shifts the residual proton and the carbon signals of the solvents were used (C_6D_6 : $\delta(^1H) = 7.16$ ppm, $\delta(^{13}C) = 128.00$ ppm; $CDCl_3$: $\delta(^1H) = 7.26$ ppm, $\delta(^{13}C) = 77.00$ ppm). The signal assignments are based on 1H , 1H -COSY, 1H , ^{13}C -HSQC, and 1H , ^{13}C -HMBC NMR spectra. Virtual couplings are indicated and the frequency distances of the outer lines are reported.⁵⁶

Synthesis and characterization

Bis(dicyclohexylphosphino)ethane dioxide H_2O_2 adduct $[Cy_2POCH_2CH_2POCy_2 \cdot H_2O_2]_n$ (1**).**



Bis(dicyclohexylphosphino)ethane (169 mg, 0.4 mmol) is placed in a Schlenk flask under nitrogen atmosphere and dissolved in dichloromethane (1.4 mL). While stirring vigorously, aqueous hydrogen peroxide is added (0.6 mL, 35%, 7 mmol) and the biphasic mixture is stirred for 30 min. The phases are separated, and the organic phase is layered with 5 mL of pentane. After slow evaporation of the solvents, adduct **1** is obtained in the form of colorless needles (149 mg, 0.30 mmol, 76%). Melting range (decomp.) 135–145 °C.

NMR (δ , $CDCl_3$), $^{31}P\{^1H\}$ 53.78 (s); 1H 7.65 (br. s, 2H, OOH), 1.93 (s, 4H, H5), 1.91 (d, $^2J(^1H-^1H) = 16.4$ Hz, 8H, H2_{eq}), 1.85–1.72 (m, 12H, H1, H3_{eq}), 1.71–1.63 (m, 4H, H4_{eq}), 1.34 (q, $^3J(^1H-^1H) = 10.4$ Hz, 8H, H2_{ax}), 1.27–1.14 (m, 2H, H3_{ax}, H4_{ax}); $^{13}C\{^1H\}$ 36.26 (virtual triplet, 93.4 Hz, C1), 26.53 (virtual triplet, 12.1 Hz, C3), 25.87 (s, C4), 25.57 (virtual triplet, 28.8 Hz, C2), 15.10 (virtual triplet, 92.9 Hz, C5). IR: $\nu(O-H) = 3159$ cm^{-1} , $\nu(P=O) = 1134$ cm^{-1} .

Bis(diphenylphosphino)ethane dioxide (2,2'-peroxydi(butanone-2-peroxol)) adduct $[(CH_2Ph_2P(O))_2 \cdot (HOOCMeEtO)_2]_n$ (2**).** Bis(diphenylphosphino)ethane (dppe) dioxide (103 mg, 0.24 mmol) is dissolved in toluene (10 mL) in a round bottom flask. Butanone (10 mL, 112 mmol) and aqueous H_2O_2 (0.1 mL, 35%, 1.2 mmol) is added, and the reaction mixture is stirred overnight. The solution is concentrated to 5 mL in vacuum, then the mixture is left to stand exposed to the atmosphere, so that the product can crystallize. Adduct **2** is obtained in the form of large, colorless, rectangular crystals (126 mg, 0.20 mmol, 83% yield). M.p. (decomp.) > 176 °C.

NMR (δ , CDCl_3), $^{31}\text{P}\{^1\text{H}\}$ 36.91 (s); ^1H 11.27 (br. s, 2H, OOH), 7.76–7.71 (m, 8H, H_o), 7.56–7.51 (m, 4H, H_p), 7.49–7.45 (m, 8H, H_m), 2.59 (d, $^2J(^{31}\text{P}-^1\text{H}) = 2.7$ Hz, 4H, PCH_2), 1.81 (q, $^3J(^1\text{H}-^1\text{H}) = 7.6$ Hz, 4H, CH_2CH_3), 1.44 (s, 6H, CCH_3), 1.03 (t, $^3J(^1\text{H}-^1\text{H}) = 7.6$ Hz, 6H, CH_2CH_3); $^{13}\text{C}\{^1\text{H}\}$ 132.49 (s, C_p), 130.73 (virtual triplet, 102.8 Hz, C_i), 130.70 (virtual triplet, 9.4 Hz, C_o), 129.08 (virtual triplet, 12.2 Hz, C_m), 111.73 (s, CCH_3), 26.15 (s, CH_2CH_3), 21.31 (virtual triplet, 66.0 Hz, PCH_2), 17.49 (s, CCH_3), 8.39 (s, CH_2CH_3). IR: $\nu(\text{O}-\text{H}) = 3254$ cm^{-1} , $\nu(\text{P}=\text{O}) = 1173$ cm^{-1} .

trans-3,5-Dimethyl-3,5-diol-1,2-dioxolane (3). Dppp (bis(diphenylphosphino)propane) (1.001 g, 2.43 mmol) is dissolved in dichloromethane (60 mL). Aqueous H_2O_2 (5.0 mL, 35%, 58 mmol) is added, and the solution is stirred for 1 h. The organic layer is collected using a separation funnel, and the solvent is removed *in vacuo*. The resulting white residue is dissolved in acetylacetone (2.5 mL, 24.3 mmol), followed by the addition of excess aqueous H_2O_2 (0.1 mL, 35%, 1.2 mmol). The solution is stirred for 3 d, then the mixture is allowed to stand for crystallization. The product **3** is obtained in the form of white, crystalline needles (94 mg, 0.71 mmol, 71% yield with respect to amount of H_2O_2 added to the acetylacetone).

Alternative procedure. Acetylacetone (100 mg, 1 mmol) is weighed into a vial and aqueous H_2O_2 (0.15 mL, 35%, 1.7 mmol) is added. The solution is stirred overnight, and most of the water is removed *in vacuo*. Benzene (1.0 mL) is added to precipitate the product, which is filtered and dried *in vacuo* (83 mg, 0.62 mmol, 62% yield). M.p. (decomp.) 82 °C.

NMR (δ , CDCl_3), ^1H 2.74 (s, 2H, CH_2), 1.63 (s, 6H, CH_3); ^{13}C 105.50 (s, OC), 55.23 (CH_2), 22.59 (CH_3). ^1H and ^{13}C NMR data match literature values.⁵²

trans-3,5-Dihydroperoxy-3,5-dimethyl-1,2-dioxolane (4). Acetylacetone (100 mg, 1 mmol) is weighed into a vial and combined with 1.0 mL (10 mmol) of aqueous H_2O_2 . The solution is stirred overnight, and the excess of water is removed *in vacuo*. The product precipitates when benzene (1.0 mL) is added (113 mg, 0.68 mmol, 68% yield). M.p. (decomp.) 98 °C.

NMR (δ , CDCl_3), ^1H 8.54 (s, 2H, OH), 2.74 (s, 2H, CH_2), 1.63 (s, 6H, CH_3); ^{13}C 112.99 (s, OC), 51.11 (CH_2), 17.52 (CH_3). ^1H and ^{13}C NMR data match literature values.⁵²

Conflicts of interest

There are no conflicts of interest to declare.

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- 55 X-ray structure 4 (CCDC 1452863†) was deposited at CCDC on Feb. 10, 2016. On Sept. 5, 2016, an equivalent structure with the same crystal system (monoclinic) and space group ($P2_1/n$) (CCDC 1487205†, Refcode YAFDER), synthesized by using 50 wt% H_2O_2 and concentrated H_2SO_4 , I_2 , and $SnCl_2 \cdot 2H_2O$ as catalysts, and crystallized from a dichloromethane/ethyl acetate mixture, was published.⁵⁴ Unit cell parameters compare as follows (cited values) $a = 5.5661(6)$ Å ($5.5729(5)$ Å), $b = 15.4167(15)$ Å ($15.4498(12)$ Å), $c = 8.8545(9)$ Å ($8.7244(7)$ Å), $\beta = 92.306(3)^\circ$ ($90.055(4)^\circ$), volume = $759.20(13)$ Å³ ($751.17(11)$ Å³), $R_1 [I > 2\sigma(I)] = 5.07\%$ (6.18%), R_1 (all data) = 6.76% (8.03%).
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