

# Unexpected synthesis of (bis(diphenylphosphinoyl)ethane)·2(2,2-dihydroperoxypropane) 1 : 2 adduct: a new route to stable organic dihydroperoxides

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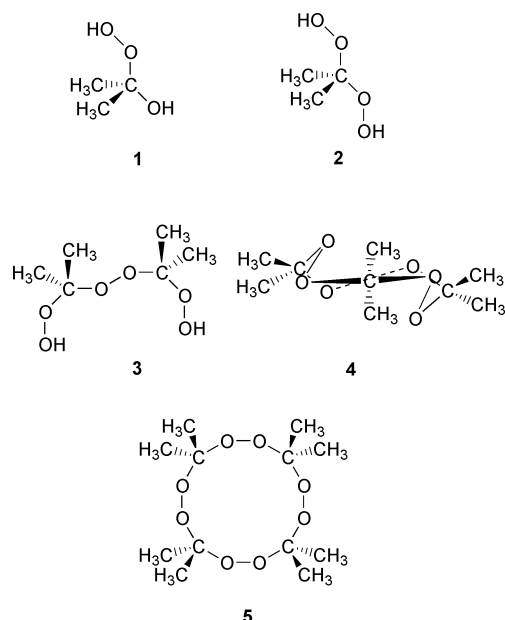
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By reaction of hydrogen peroxide and bis(diphenylphosphino)ethane in acetone, the 1 : 2 adduct (bis(diphenylphosphinoyl)ethane)·2(2,2-dihydroperoxypropane) (dppeO<sub>2</sub>)·2[Me<sub>2</sub>C(OOH)<sub>2</sub>], stabilized by H-bonding between Me<sub>2</sub>C(OOH)<sub>2</sub> and dppeO<sub>2</sub>, was rapidly obtained in high yields in the presence of R<sub>2</sub>SnCl<sub>2</sub> (R = Me or Bu<sup>n</sup>).

Organic peroxides derived from acetone and hydrogen peroxide have been extensively studied.<sup>1–5</sup> The products identified to date in aqueous acetone–hydrogen peroxide solutions are 2-hydroxy-2-hydroperoxy propane **1**,<sup>3</sup> 2,2-dihydroperoxypro-

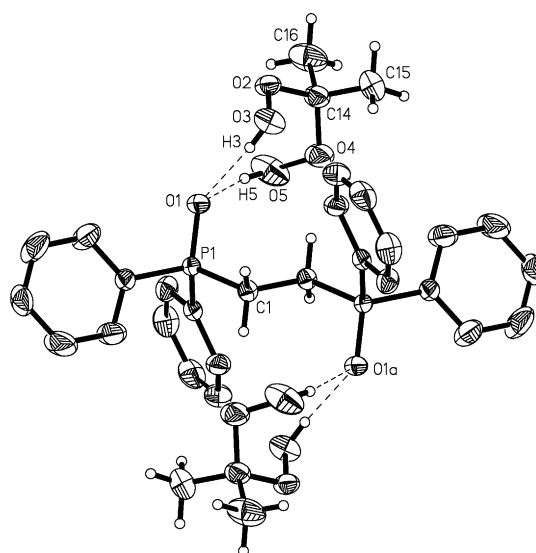


pane **2**,<sup>1,2</sup>  $\alpha,\alpha'$ -bis(hydroperoxy)diisopropyl peroxide **3**,<sup>1,2</sup> and 1,1,4,4,7,7-hexamethyl-1,4,7-cyclononatriperoxane **4**.<sup>1,2,5</sup>

Very recently a tetrameric species [1,1,4,4,7,7,9,9-octamethyl-1,4,7,9-tetraundecotetraperoxane] **5** has been isolated from an acetone–H<sub>2</sub>O<sub>2</sub> solution containing SnCl<sub>4</sub>·5H<sub>2</sub>O or SnCl<sub>2</sub>·2H<sub>2</sub>O. It has been hypothesized that tin(IV) salts catalyze the oxidation of acetone by hydrogen peroxide to tetrameric acetone peroxide at room temperature.<sup>6</sup> All the species **1–5** readily decompose. The structures of **1–3** and **5** have been hypothesized only on the basis of spectroscopic IR and NMR data, whereas the crystal structure of **4** was determined some years ago.<sup>5</sup> During our studies<sup>7</sup> on the interaction between tin(IV) acceptors and diphosphinoyl donors in acetone, using hydrogen peroxide as oxidizing agent for organic phosphines,

we observed the formation of the crystalline adduct (dppeO<sub>2</sub>)·2[Me<sub>2</sub>C(OOH)<sub>2</sub>] **6**.<sup>8</sup> Whereas the free 2,2-dihydroperoxypropane **2** decomposes rapidly due to its fast transformation into the more stable cyclic peroxy compounds **4** or **5**, **6** is very stable under the same conditions in both solid and solution states. The stabilization of dihydroperoxide **2** in the crystals of **6** can be explained by formation of H-bonds between the hydrogen atoms of Me<sub>2</sub>C(OOH)<sub>2</sub> and the oxygen atoms of dppeO<sub>2</sub>, which in this case acts as hydrogen acceptor. The energy of the hydrogen bond most likely prevents the oligomerization of the peroxide into the usual trimeric or tetrameric forms. The adduct **6** has a molecular structure<sup>9</sup> with two molecules of dihydroperoxide H-bonded to dppeO<sub>2</sub> (Fig. 1). The O–O distances in the peroxide (mean value 1.461 Å) are close to those in hydrogen peroxide (1.453 Å).<sup>10</sup> The bis(diphenylphosphinoyl)ethane molecule is stabilized in a staggered conformation. Each oxygen atom of dppeO<sub>2</sub> forms two H-bonds with a dihydroperoxide molecule (O(3)–H(3)···O(1) 2.758(2) Å,  $\angle$ O(3)–H(3)–O(1) 170(3)°; O(5)–H(5)···O(1) 2.824(3) Å,  $\angle$ O(5)–H(5)–O(1) 169(3)°).

When the reaction between dppe and H<sub>2</sub>O<sub>2</sub>–acetone was carried out in the absence of R<sub>2</sub>SnCl<sub>2</sub> (R = Me or Bu<sup>n</sup>) acceptors, compound **6** was obtained in only 40% yield after 10 days, whereas in the presence of tin acceptors the yield was much higher (90%) after only 24 h. This result is in accordance



**Fig. 1** Molecular structure of (dppeO<sub>2</sub>)·2[Me<sub>2</sub>C(OOH)<sub>2</sub>] **6**. Selected bond distances (Å) and angles: P(1)–O(1) 1.511(1), P(1)–C(1) 1.805(2), P(1)–C(2) 1.795(2), P(1)–C(8) 1.812(2), C(14)–O(2) 1.425(3), O(2)–O(3) 1.464(2), C(14)–O(4) 1.428(2), O(4)–O(5) 1.457(3);  $\angle$ O(2)–C(14)–O(4) 110.2(2)°.

with the recent work<sup>6</sup> on the oxidation of acetone by H<sub>2</sub>O<sub>2</sub> catalysed by tin(IV) and tin(II) compounds.

When the reaction between dppe and H<sub>2</sub>O<sub>2</sub>-acetone was carried out in the presence of Ph<sub>2</sub>SnCl<sub>2</sub>, the derivative Ph<sub>2</sub>SnCl<sub>2</sub>(dppeO<sub>2</sub>)<sup>11</sup> precipitated from the reaction mixture and no trace of **6** was detected after 48 h.

When **6** was reacted with Ph<sub>2</sub>SnCl<sub>2</sub>, the derivatives Ph<sub>2</sub>SnCl<sub>2</sub>(dppeO<sub>2</sub>),<sup>11</sup> **3** and **4** are afforded. In fact Ph<sub>2</sub>SnCl<sub>2</sub> is a stronger Lewis acid than dialkyltin(IV) dihalides and it is able to substitute the dihydroperoxide in **6**, yielding the well known stable adduct Ph<sub>2</sub>SnCl<sub>2</sub>(dppeO<sub>2</sub>).<sup>11</sup> On the other hand, when R<sub>2</sub>SnBr<sub>2</sub> (R = Me or Bu<sup>n</sup>) were employed, **6** was obtained in 90% yields after 6 h. The substitution of chloride groups with the less electronegative bromide in diorganotin(IV) seems to accelerate the formation of **6**, in accordance with the weaker acceptor power of the corresponding Lewis acid.

Finally, when dppm, dppp (1,3-bis(diphenylphosphino)propane) or triphenylphosphine were employed, no dihydroperoxide adducts such as **6** were obtained, thus indicating that the methylene chain between the -P(O)Ph<sub>2</sub> units can be an important steric factor.

In summary, oxidized diphosphine ligand dppeO<sub>2</sub> is able to stabilize 2,2-dihydroperoxide formed by interaction of acetone with H<sub>2</sub>O<sub>2</sub> and prevent cyclo-oligomerization. The formation of adduct **6** can be accelerated by R<sub>2</sub>SnCl<sub>2</sub> (R = Me or Bu<sup>n</sup>). Studies on the possibility of obtaining different dihydroperoxides by starting from different ketones, on the ability of other tin(IV) salts to catalyse the reaction between H<sub>2</sub>O<sub>2</sub> and acetone, and finally on the importance of the diphosphine chain for the obtainment of compounds as **6**, are actually in progress.

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## Notes and references

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- 8 [*Bis(diphenylphosphineoxo)ethane-2(2,2-dihydroperoxypropane)*] (**1**): Me<sub>2</sub>SnCl<sub>2</sub> (0.219 g, 1.0 mmol) and dppe (0.398 g, 1.0 mmol) were dissolved in 30 ml acetone. To the colorless solution, 5 ml 10% H<sub>2</sub>O<sub>2</sub> was added. The clear solution was stirred for 24 h, and then kept at 4 °C overnight. A colorless precipitate formed which has been identified as (dppeO<sub>2</sub>)<sub>2</sub>(2,2-dihydroperoxypropane). It was recrystallized from acetone. Yield 90%. Mp 146 °C dec. Found, %: C 59.70; H 6.30; calc. for C<sub>32</sub>H<sub>40</sub>O<sub>10</sub>P<sub>2</sub>: C 59.44; H 6.24. IR (nujol, cm<sup>-1</sup>): 3384br ν(O-H...O), 1704s δ(O-H...O), 1175sh, 1158s, 1148vs, 1120s ν(P=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.49s (12H, CH<sub>3</sub>), 2.61t (4H, PCH<sub>2</sub>CH<sub>2</sub>P), 7.5m (10H, P-C<sub>6</sub>H<sub>5</sub>), 7.8m (10H, P-C<sub>6</sub>H<sub>5</sub>), 10.7br (4H, OH).
- 9 *Crystal data* for **1**: C<sub>32</sub>H<sub>40</sub>O<sub>10</sub>P<sub>2</sub>, *M* = 646.58 g cm<sup>-3</sup>. IPDS(Stoe) Mo-Kα, *T* 180 K, orthorhombic, space group *Pbca*, *a* = 15.447(3), *b* = 10.989(2), *c* = 19.907(4) Å, *Z* = 4, *μ* = 12.07 cm<sup>-1</sup>, 3414 measured and 2081 independent reflections, no absorption corrections, hydrogen atoms of dppe were placed in the calculated positions, *R*<sub>1</sub> = 0.0362, *wR*<sub>2</sub> = 0.0861 with 2777 reflections and 210 parameters (SHELXL-93). CCDC reference number 182/1765. See <http://www.rsc.org/suppdata/b005221n/> for crystallographic files in .cif format.
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