

## Oxidation–Reduction of Bis(*o*-formylphenyl)phenylphosphine by Water

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Bis(*o*-formylphenyl)phenylphosphine (**1**) undergoes acid catalysed hydration yielding a phosphine oxide with concomitant reduction of one formyl group; mechanistic studies suggest the importance of phosphorane intermediates in this reaction.

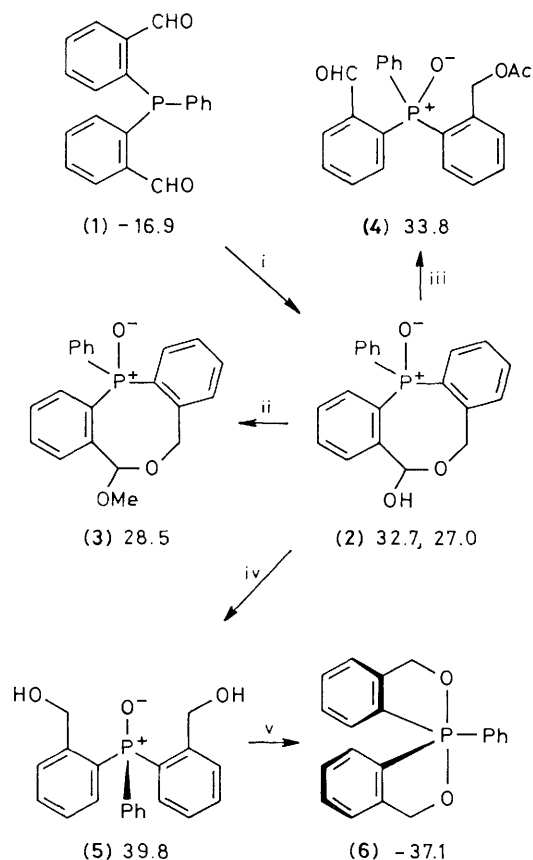
In the course of our studies on the chemistry of phosphine-substituted benzaldehydes,<sup>1</sup> we have discovered an unusual example of a tertiary phosphine which reacts with water.

Yellow bis(*o*-formylphenyl)phenylphosphine<sup>2</sup> (**1**) was found to react with water in acidic (0.01 M *p*-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H) aqueous tetrahydrofuran (THF) (1:1, v/v) to afford after 3 h the 'hydrate' (**2**),<sup>†</sup> as colourless crystals. The <sup>31</sup>P{<sup>1</sup>H} n.m.r.

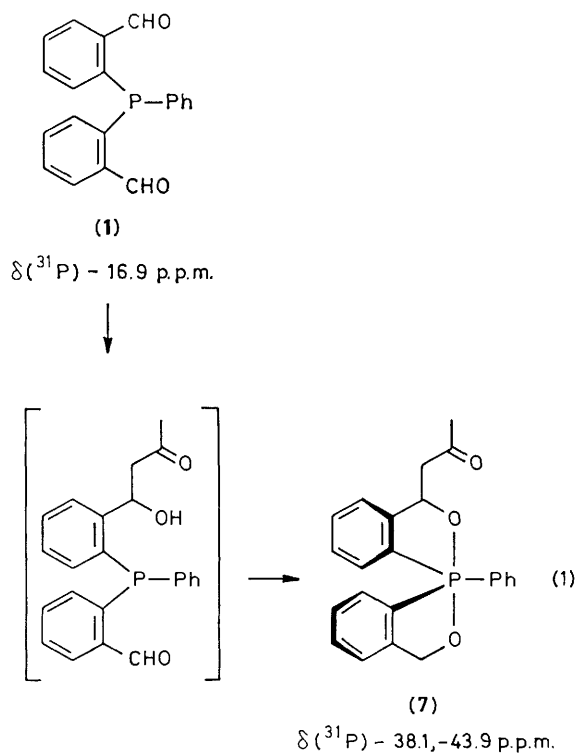
spectrum of (**2**) ([<sup>2</sup>H<sub>6</sub>]dimethyl sulphoxide, DMSO) shows resonances at 32.74 and 27.0 p.p.m. (ratio 11:1) downfield of 85% H<sub>3</sub>PO<sub>4</sub>. Its 360 MHz <sup>1</sup>H n.m.r. spectrum reveals two sets of AB quartets assignable to the benzylic protons of two diastereoisomers and no coupling between the methylene hydrogen atoms and phosphorus.<sup>‡</sup> These measurements together with the observation of a strong ν<sub>OH</sub> in its i.r.

<sup>†</sup> Compounds (**2**)–(**8**) were fully characterized by 360 (<sup>1</sup>H) and 40.5 MHz (<sup>31</sup>P{<sup>1</sup>H}) n.m.r. (CDCl<sub>3</sub> solution unless otherwise noted) and i.r. spectroscopy. Additionally, all new compounds gave mass spectra and elemental analyses fully consistent with their formulations.

<sup>‡</sup> 360 MHz <sup>1</sup>H n.m.r. spectrum of (**2**) (a mixture of diastereoisomers in [<sup>2</sup>H<sub>6</sub>]DMSO): δ 8.4 (2H, m), 7.0–7.4 (11H, m), 5.41 (0.7 H, d, *J* 6.7 Hz, CHOH), 5.16 (0.3 H, d, *J* 4.5 Hz, CHOH), 4.81 and 4.11 (1.4 H, AB quartet, *J* 14.9 Hz, CH<sub>2</sub>), and 4.49 and 4.32 (0.6 H, AB quartet, *J* 14.3 Hz, CH<sub>2</sub>). CHOH was not observed using this solvent.



**Scheme 1.** Reagents and conditions: i,  $\text{H}_2\text{O}$ ,  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$ , THF; ii,  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$ , MeOH,  $65^\circ\text{C}$ ; iii,  $\text{Ac}_2\text{O}$ ,  $138^\circ\text{C}$ ; iv,  $\text{NaBH}_4$  (excess), MeOH; v,  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$ , THF,  $65^\circ\text{C}$ .  $\delta(^{31}\text{P})$  values are quoted in p.p.m.



**Scheme 2**

spectrum and a molecular ion in its 70 eV e.i. mass spectrum indicate that (2) is the hemiacetal phosphine oxide depicted in Scheme 1. Acid catalysed methanolysis (0.01 M  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$ ,  $65^\circ\text{C}$ , 2 h) of (2) gave compound (3) (m.p.  $148\text{--}149^\circ\text{C}$ ) which analysed as (1)·MeOH and whose  $^1\text{H}$  and  $^{31}\text{P}$  n.m.r. parameters closely resemble those for (2). Acetylation (neat  $\text{Ac}_2\text{O}$ ,  $138^\circ\text{C}$ , 2 h) of (2) gave the monoacetyl derivative (4) whose i.r. spectrum exhibits strong absorptions at 1745 and  $1700\text{ cm}^{-1}$ .  $\text{NaBH}_4$  reduction converted (2) into the phosphine oxide (5) which undergoes acid catalysed dehydration to the known phosphorane (6).<sup>2</sup>

Reaction of (1) with 0.01 M  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{D}/\text{D}_2\text{O}$ -THF gave, after an  $\text{H}_2\text{O}$  wash, [ $^2\text{H}_1$ ]-2; by reference to the  $^1\text{H}$  n.m.r. spectrum for (2), it was ascertained that deuterium incorporation had occurred exclusively at the benzylic methylene group. Acetylation of [ $^2\text{H}_1$ ]-2 gave [ $^2\text{H}_1$ ]-4. Whereas the  $^1\text{H}$  n.m.r. absorptions assigned to the formyl (10.78), benzylic (5.52), and methyl (1.75 p.p.m.) protons in (4) appear as singlets with the intensities 1 : 2 : 3, the intensities for the corresponding absorptions in [ $^2\text{H}_1$ ]-4 occur in the ratio 1 : 1 (broadened) : 3.

When (1) was solvolysed in aqueous acetone (1 : 30, v/v, 0.1 M  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$ ,  $55 \rightarrow 80^\circ\text{C}$ , 2 h), we obtained in addition to (2), ca. 15% yield of the acetone adduct (7). Compound (7) exists as a mixture of two diastereoisomers which, unlike (2), (3), and (4), exhibit *high field*  $^{31}\text{P}$  n.m.r. resonances ( $-38.1$  and  $-43.9$  p.p.m.). The  $^1\text{H}$  n.m.r. spectrum of (7) has been completely analysed; this spectrum clearly shows phosphorus coupling (ca. 1–6 Hz) to one or two benzylic protons depending on the diastereoisomer. These and related measurements lead us to assign the structure indicated in Scheme 2, a structure which has been firmly established by a single crystal *X*-ray diffraction study.<sup>§</sup> The conversion of (1) into (7) is presumed to occur *via* the benzylic alcohol intermediate indicated in Scheme 2.<sup>3</sup> Furthermore, we suggest that a dioxaphosphorane intermediate analogous to (7) is involved in the formation of (2) from (1).<sup>4,5</sup>

In summary we have found a mechanistically intriguing reaction whereby a tertiary phosphine reacts with water. Tris(*o*-formylphenyl)phosphine behaves similarly while diphenyl- and dimethylphosphinobenzaldehyde are stable in aqueous acid. The conversion of (1) into (2) is closely related to the previously observed hydration of (2-phenylethynyl)phosphines.<sup>6</sup>

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§ Detailed discussion of this crystal structure will be presented in the full paper.