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## 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 phosphinesubstituted 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),† as colourless crystals. The <sup>31</sup>P {<sup>1</sup>H} n.m.r. spectrum of (2) ( $[{}^{2}H_{6}]$ 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  $v_{out}$  in its i.r.

 $<sup>\</sup>dagger$  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>a</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>‡ 360</sup> MHz <sup>1</sup>H n.m.r. spectrum of (2) (a mixture of diastereoisomers in [<sup>2</sup>H<sub>6</sub>]DMSO):  $\delta$  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, H<sub>2</sub>O, p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, THF; ii, p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, McOH, 65 °C; iii, Ac<sub>2</sub>O, 138 °C; iv, NaBH<sub>4</sub> (excess), MeOH; v, p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, THF, 65 °C.  $\delta$ <sup>(31</sup>P) values are quoted in p.p.m.



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-MeC<sub>6</sub>H<sub>4</sub>-SO<sub>3</sub>H, 65 °C, 2 h) of (2) gave compound (3) (m.p. 148—149 °C) which analysed as (1)·MeOH and whose <sup>1</sup>H and <sup>31</sup>P n.m.r. parameters closely resemble those for (2). Acetylation (neat Ac<sub>2</sub>O, 138 °C, 2 h) of (2) gave the monoacetyl derivative (4) whose i.r. spectrum exhibits strong absorptions at 1745 and 1700 cm<sup>-1</sup>. NaBH<sub>4</sub> 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-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>D/D<sub>2</sub>O-THF gave, after an H<sub>2</sub>O wash, [<sup>2</sup>H<sub>1</sub>]-(2); by reference to the <sup>1</sup>H n.m.r. spectrum for (2), it was ascertained that deuterium incorporation had occurred exclusively at the benzylic methylene group. Acetylation of [<sup>2</sup>H<sub>1</sub>]-(2) gave [<sup>2</sup>H<sub>1</sub>]-(4). Whereas the <sup>1</sup>H n.m.r. absorptions assigned to the formyl (10.78), benzyl (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 [<sup>2</sup>H<sub>1</sub>]-(4) occur in the ratio 1 : 1(broadened): 3.

When (1) was solvolysed in aqueous acetone (1:30, v/v, 0.1 M p-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H, 55  $\rightarrow$  80 °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 <sup>31</sup>P n.m.r. resonances (-38.1 and -43.9 p.p.m.). The 360 <sup>1</sup>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.§ The conversion of (1) into (7) is presumed to occur via the benzylic alcohol intermediate indicated in Scheme 2.3 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-phenyl)phosphines.<sup>6</sup>

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