Pergamon

Tetrahedron Letters 39 (1998) 3571–3574

TETRAHEDRON
LETTERS

First synthesis and structural characterisation of a tertiary phosphine containing an azo linkage.

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Received 5 February 1998; accepted 6 March 1998

Abstract: Tertiary phosphines containing an azo linkage have been synthesised for the first time and one has been characterised by a single crystal X-ray diffraction study of its oxide.

The reaction of triaryl- or trialkylphosphines with diazo compounds or azides (the Staudinger reaction) has been known since 1919.[1] Since then the reaction between arenediazonium salts and triarylphosphines has been investigated by Horner *et al.*[2-4] and their work showed that P-N coupling occurs followed by decomposition to either a phosphonium salt or a phosphine oxide with extrusion of nitrogen amongst a variety of other products depending upon the reaction conditions. The first example of a phosphorus(V) containing azo compound was reported in 1953;[5] since then several compounds containing phosphonic esters have been prepared.[6-8] Recently some coordination chemistry of these compounds was reported[9] showing complexation occurring through the azo link. To the best of our knowledge there are no examples of tertiary phosphines containing an azo moiety although there are several references to areneazophosphine oxides prepared by a Russian group in the 1970s.[10-12] There are several good reasons for this namely: the strongly oxidising nature of the conditions required to prepare a diazonium salt are likely to readily oxidise the phosphorus from oxidation state (III) to (V); the nucleophilicity of phosphorus (III) causes either decomposition of the diazonium salt or the formation of a P-coupled product. These technical difficulties can, however, be readily overcome in the following ways: isolation of the diazonium salts as the fluoroborate salt hence allieviating the oxidising conditions necessary for their preparation, carrying out the reaction in non-aqueous conditions and activating the tertiary phoshine to C-N coupling rather than P-N coupling. Herein we report, to the best of our knowledge, the first example of C-N coupling between an arenediazonium salt and a tertiary phosphine taking precedence over P-N coupling.

After treatment of **1** (scheme 1) with 1.5 mole equivalents of NaOH in ethanol a pale yellow solution was obtained which was cooled to 0 - 5°C. To this stirred solution 1 mole equivalent of an arenediazonium tetrafluoroborate salt dissolved in NCMe was added. After 1h the solvent was removed *in vacuo* affording a

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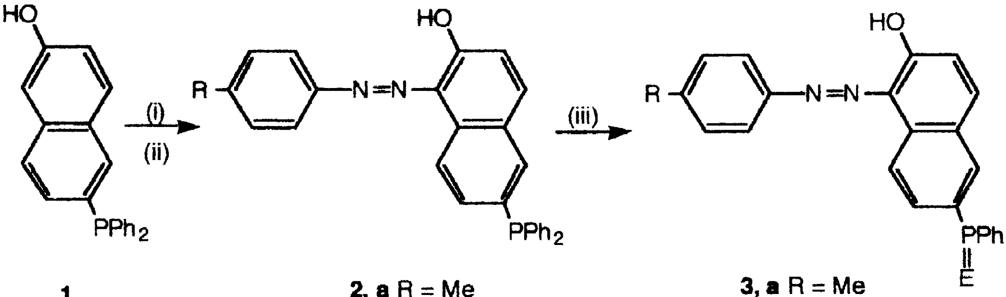
PII: S0040-4039(98)00551-6

deep red solid which was subsequently extracted into CH_2Cl_2 and filtered. After removal of solvent and recrystallisation from an alcohol the C-N coupled products **2a** and **2b** were obtained in *ca* 70% yield. An important point to note here is that it is essential to isolate the arenediazonium salts before addition to the anion of the tertiary phosphine to prevent undesirable reactions such as oxidation at phosphorus and decomposition of the diazonium salt by quaternisation. Compounds **2a** and **2b** have been characterised spectroscopically. [13] An indication that the coupling reaction had occurred was obtained from the ^{1}H NMR spectra of **2a** and **2b**. A resonance is observed at 16.16 ppm which is assigned to the formal O*H* proton: treatment of the NMR samples with D_2O leads to the disappearance of these signals. Additionally evidence for the coupling reaction was inferred from the integral ratio of the hydroxyl proton and the alkyl chain introduced with the diazonium salt. Furthermore, evidence that the tertiary phosphine had been introduced without oxidation to phosphorus(V) was obtained from the $^{31}P\{^{1}H\}$ NMR spectra of **2a** and **2b**; where δ = -5.21 ppm and -5.14 ppm respectively: these values are consistent with those observed for other tertiary arylphosphines. Compounds **2a** and **2b** are readily oxidised by either H_2O_2 or S_8 to give the corresponding phosphine oxides **3a** and **3b** or phosphine sulfides **4a** and **4b**. These compounds have also been spectroscopically characterised.[13] The most salient piece of information is obtained from the $^{31}P\{^{1}H\}$ NMR spectra which display resonances *ca* 30 ppm for the oxides and 40 ppm for the sulfides implying the phosphorus in **2a** and **2b** have been oxidised from phosphorus(III) to phosphorus(V). Conformation of the spectroscopic evidence was obtained by single crystal X-ray diffraction study on **3a**,[14] Figure 2 .



1

2, a R = Me
b R = Et

3, a R = Me
b R = Et
E = O
4, a R = Me
b R = Et
E = S

Scheme 1: (i) NaOH, EtOH, 10 min; (ii) $[4\text{-}RC_6H_4N_2][BF_4]$, NCMe, 0°C, 1h; (iii) H_2O_2, S_8.

The data obtained for **3a** was of reasonable quality and confirmed the oxidised nature of the phosphorus centre as implied by the spectroscopic evidence and suggests that compounds 2a and 2b are indeed tertiary phosphines that contain an azo link. The structural determination revealed that there was one methanol of crystallisation which was hydrogen bonded to the oxygen of the phosphine oxide [O3-H34 = 0.86 Å, H..O2 = 1.91 Å, O3..O2 = 2.77 Å, O3-H34..O2 = 171°]. On inspection of the bond lengths [C2-O1 = 1.277(5) Å, N1 - C1 = 1.356(6) Å, O1-H1 = 1.35 Å, N2-H1 = 1.24 Å, O1...N2 = 2.52 Å, O..H..N = 153°.] around the azo moiety it becomes apparent that there is a strong hydrogen bond interaction between O1, H1 and N2, and that the molecule tends towards, in the solid state at least, the keto- hydrazone tautomer, Figure 3. This is not an uncommon feature of azo pigments that contain the β-naphthol moiety.[15] Furthermore this strong hydrogen bond interaction appears, from the sharp signal in the ^{1}H NMR spectrum, to be retained in solution; all other bond lengths and angles are unexceptional and warrant no further comment.

In conclusion we have managed to directly introduce an azo linkage into a tertiary phosphine *via* diazonium coupling, avoiding the potential side reactions such as oxidation at phosphorus and P-N coupling followed by decomposition. We believe that this new class of functionalised tertiary phosphines will show a rich and varied coordination chemistry and are currently investigating this aspect of their chemistry.

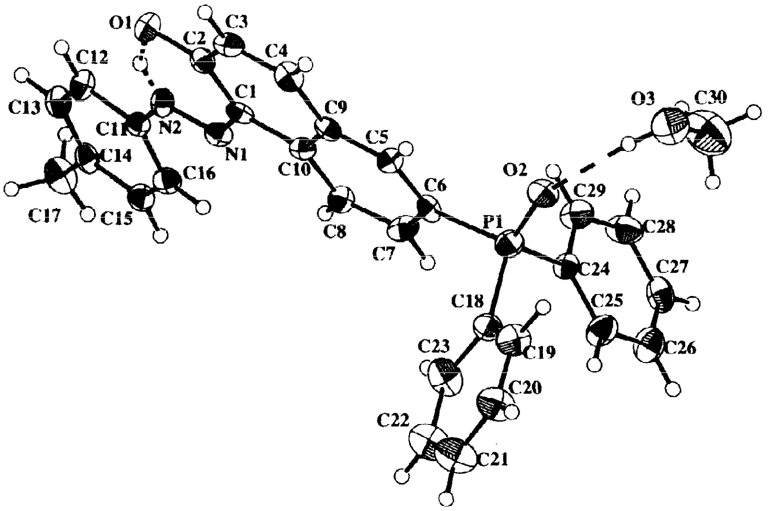


Figure 2 Molecular structure of **3 a** with one CH_3OH of crystallisation and atom labelling scheme. Selected bond lengths (Å) and angles (°): C(2) - O(1) 1.277 (5); C(2) -C(1) 1.432(7); C(1) - N(1) 1.365(6); N(1) - N(2) 1.306; N(2) - C(11) 1.419; N(1)- N(2) - C(11) 117.6(5); N(2) - N(1) - C(1) 116.3(5); N(1) - C(1) - C(2) 123.2(5); N(1) -C(1) - C(10) 115.6 (5).

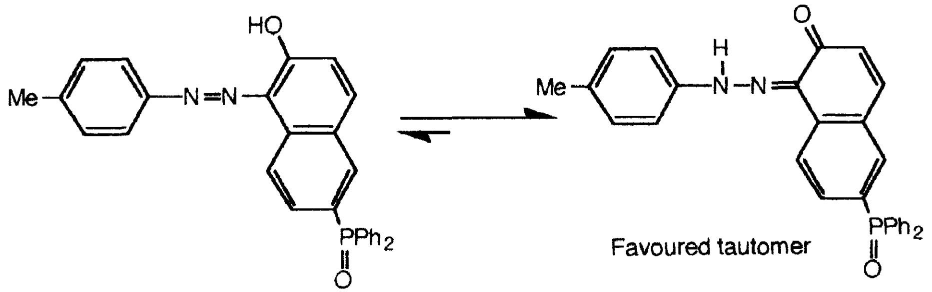


Figure. 3

We gratefully acknowledge financial support from the EPSRC (studentship for M.J.A). We also thank Professor M.B. Hursthouse and Mr D.E. Hibbs (EPSRC Crystallography Service, Cardiff) for collecting the X-ray data for **3a**.

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13. Selected spectral data for: **2a 2b 3a 3b 4a 4b**. Satisfactory elemental analysis were obtained for all new compounds. For **2a:** mp. 144 °C; FABMS: *m/z* 447 $[MH^+]$; δ_H (200 MHz, $CDCl_3$) 16.16 (s, 1 H, OH), 8.59 (d, 1 H, Ph-H), 7.69 - 7.30 (bm, 17 H, Ph-H), 6.90 (d, 1 H, Ph-H), 2.41 (s, 3H, CH_3); δ_P (81MHz, $CDCl_3$) -5.21; For **2b:** mp. 104 °C; FABMS: *m/z* 461 $[MH^+]$; δ_H (200 MHz, $CDCl_3$) 16.16 (s, 1 H, OH), 8.59 (d, 1 H, Ph-H), 7.69 - 7.28 (bm, 17 H, Ph-H), 6.91 (d, 1 H, Ph-H), 2.70 (q, 2H, CH_2), 1.28 (t, 3H, CH_3); δ_P (81MHz, $CDCl_3$) -5.14; For **3a:** mp. 214 °C; FABMS: *m/z* 463 $[MH^+]$; δ_H (200 MHz, $CDCl_3$) 16.18 (s, 1 H, OH), 8.71 (d, 1 H, Ph-H), 7.77 - 7.28 (bm, 17 H, Ph-H), 7.02 (d, 1 H, Ph-H), 2.40 (s, 3H, CH_3); δ_P (81MHz, $CDCl_3$) 29.80; For **3b:** mp. 118 °C; FABMS: *m/z* 477 $[MH^+]$; δ_H (200 MHz, $CDCl_3$) 16.22 (s, 1 H, OH), 8.70 (d, 1 H, Ph-H), 8.06 - 7.31 (bm, 17 H, Ph-H), 6.91 (d, 1 H, Ph-H), 2.71 (q, 2H, CH_2), 1.27 (t, 3H, CH_3); δ_P (81MHz, $CDCl_3$) 30.05; For **4a:** mp. 182 °C; FABMS: *m/z* 479 $[MH^+]$; δ_H (200 MHz, $CDCl_3$) 16.28 (s, 1 H, OH), 8.63 (d, 1 H, Ph-H), 8.08 - 7.28 (bm, 17 H, Ph-H), 7.02 (d, 1 H, Ph-H), 2.41 (s, 3H, CH_3); δ_P (81MHz, $CDCl_3$) 43.67; For **4b:** mp. 184 °C; FABMS: *m/z* 493 $[MH^+]$; δ_H (200 MHz, $CDCl_3$) 16.22 (s, 1 H, OH), 8.68 (d, 1 H, Ph-H), 8.16 - 7.29 (bm, 17 H, Ph-H), 7.01 (d, 1 H, Ph-H), 2.71 (q, 2H, CH_2), 1.27 (t, 3H, CH_3); δ_P (81MHz, $CDCl_3$) 43.67.

14. X-Ray crystal data for **3a:** $C_{30}H_{27}N_2O_3P$(includes CH_3OH solvate), M = 494.5, triclinic, P -1 (No. 2), a = 10.463(1), b = 10.5118(4), c = 13.800(4) Å, $\alpha = 71.92(4)°$, $\beta = 77.70(2)°$, $\gamma = 62.44(1)°$, Z = 2, U = 1274.9 Å^3, F(000) = 520, $D_c = 1.288$ mgm^{-3}, μ(Mo-Kα) = 0.1438 mm^{-1}, specimen 0.10 x 0.08 x 0.08, 5641 reflections collected for 2.2 < θ < 25°, 934 reflections with $I > 2\sigma(I)$, $R_1 = 0.042$, $wR_2 = 0.106$ (all data), T = 123 K, Enraf- Nonius FAST diffractometer, $\lambda = 0.71069$ Å. Full least- squares refinement with SHELXL-97, H atoms in riding mode and all non-hydrogen atoms anisotropic. Atomic coordinates, bond lengths and angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).

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