

A new reaction of arylphospholes: site-selective phosphorylation through reaction with phosphorus tribromide

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The reaction of arylphospholes **1a–c** with phosphorus tribromide followed by treatment with morpholine afforded the 2- or 3-substituted species **3a,b** or **7** (which after oxidation gave **4a,b** or **8**) in a selective manner.

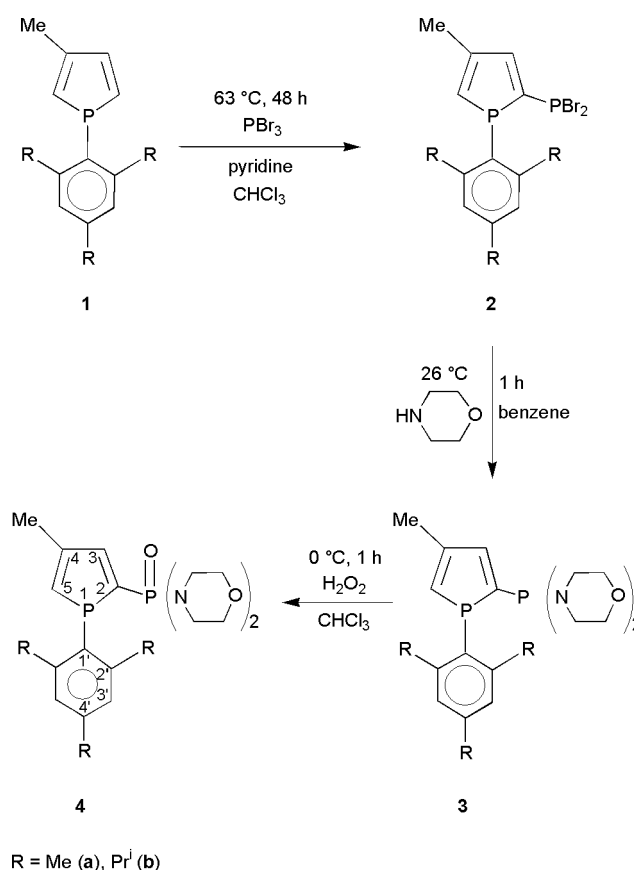
Phospholes are useful ligands in transient metal complexes and have attracted considerable attention recently.^{1–3} Not much is known, however, of the substitution reactions of this representative class of P-heterocycles. The modification of phospholes is of interest, as it may lead to P-ligands with new properties. For this reason, it was a challenge for us to study the substitution reactions of some arylphospholes available from our previous work.^{4–6}

In this paper, we disclose our results on the substitution of (trialkylphenyl)phospholes **1a–c** with phosphorus tribromide. Phosphorus halogenides are known to be useful in the phosphorylation of pyrroles.^{7,8} The reaction of (trimethylphenyl)phosphole **1a**⁴ and (triisopropylphenyl)phosphole **1b**⁵ with phosphorus tribromide in boiling chloroform in the presence of pyridine furnished 2-substituted products **3a** and **3b**, respectively, after treatment with morpholine (Scheme 1). To obtain stable derivatives, diphosphines **3a** and **3b** were oxidised to compounds **4a** and **4b**, respectively. It is noteworthy that the exocyclic P-moiety underwent selective oxidation, while the phosphorus heteroatom of the phosphole remained mostly unoxidised. According to ³¹P NMR, the conversion of phospholes **1** to products **4** was *ca.* 70%. The yield of phosphole derivatives **4a,b** was *ca.* 45% after purification by column chromatography. Intermediates **3**, as well as products **4** were characterised by ³¹P NMR; ²J_{PP} couplings of *ca.* 72 and 49 Hz, respectively, were detected.^{9–12} The ¹H NMR spectra of compounds **4a** and **4b** revealed that the protons of the hetero ring were not coupled to each other.^{11,12} The structure of product **4b** was also supported by ¹³C NMR.¹² Bis(phosphine oxides) **5a,b** were also formed in the above mentioned oxidation reactions in *ca.* 14% yields.^{13,14} Unlike other phosphole oxides,¹⁵ these species resisted undergoing dimerization and could be stored at room temperature for weeks.

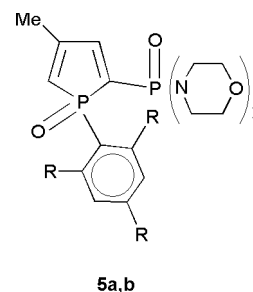
A similar transformation of (tri-*tert*-butylphenyl)phosphole, **1c**,¹⁶ resulted in the formation of product **8** via intermediates **6** and **7** (Scheme 2). Interestingly, the substitution took place at position 3 of the phosphole moiety. The different outcome is probably the consequence of the steric hindrance around the phosphorus heteroatom in **1c**. Species **7** and **8** were characterised as above. ³J_{PP} couplings of 50.4 and 21.8 Hz were obtained for **7** and **8**, respectively.^{16,17} The ¹³C and ¹H NMR spectral parameters of compound **8** were also consistent with the substitution in position 3.¹⁷

As can be seen, the phosphorylated phospholes are excellent models for the study of the ²J_{PP} and the ³J_{PP} couplings.

In the mechanism proposed, the π -electrons of the double bond in phosphole **1** attack the phosphorus atom of the reagent



Scheme 1

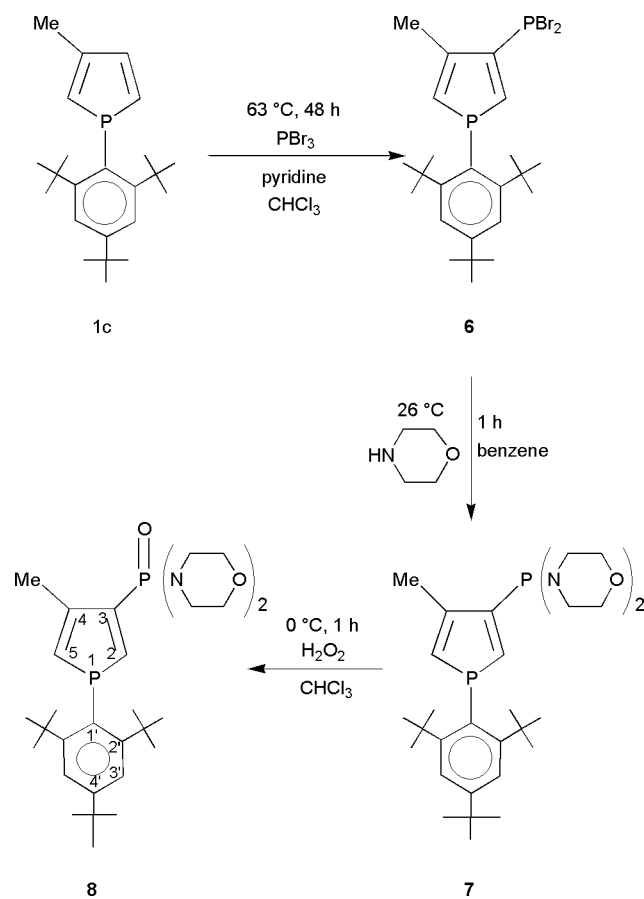


as a nucleophile to give intermediate **9** or **10** that may be stabilised by the loss of a proton, by pseudorotation and finally by the departure of a bromide anion.

In summary a new reaction of arylphospholes was explored; their interaction with phosphorus tribromide resulted in

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J. Chem. Soc., Perkin Trans. 1, 2000, 1495–1496 1495



2-substitution, or, in the case of the starting material with a bulky *P*-aryl group, the reaction led to 3-substitution.

Future work will be directed towards the utilisation of the above reaction in the preparation of a variety of phosphoric amides and esters and a study of their properties.

Experimental

General procedure for the phosphorylation of phospholes 1a–c

Phosphorus tribromide (0.12 cm³, 1.26 mmol) and pyridine (0.10 cm³, 1.24 mmol) were added to phosphole 1a, 1b or 1c (1.17 mmol) in dry CHCl₃ (50 cm³), and the solution was stirred at boiling point for 48 h under a nitrogen atmosphere. The volatile components were removed *in vacuo* to give 2a, 2b or 6, respectively.

The intermediate (2a, 2b or 6) (~1.17 mmol) was taken up in dry benzene (50 cm³) and treated with morpholine (0.41 cm³, 4.70 mmol) at 0 °C. After stirring at room temperature for 1 h, the mixture was filtered and the solvent of the filtrate evaporated to afford 3a, 3b or 7, respectively.

The bisphosphine (3a, 3b or 7) (~1.17 mmol) was dissolved in CHCl₃ (50 cm³) and oxidised by the addition of 30% hydrogen peroxide (0.68 cm³, ~6.0 mmol) at 0 °C. After stirring at room temperature for 1 h, the mixture was extracted with water (2 × 20 cm³). The organic phase was dried (Na₂SO₄), the solvent evaporated and the residue so obtained purified by repeated column chromatography (silica gel, 3% MeOH in CHCl₃) to furnish product 4a, 4b or 8, respectively.

Acknowledgements

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- 9 Selected data for 3a: δ_P (CDCl₃) 5.5 (P¹), 93.3 (C²-P), $^2J_{PP}$ = 72.6; M^+ found = 418.1920, C₂₂H₃₂N₂O₃P₂ requires 418.1939.
- 10 Selected data for 3b: δ_P (CDCl₃) 0.2 (P¹), 94.1 (C²-P), $^2J_{PP}$ = 70.6; M^+ found = 502.2870, C₂₈H₄₄N₂O₃P₂ requires 502.2878.
- 11 Selected data for 4a: δ_P (CDCl₃) 5.3 (P¹), 23.4 (C²-P), $^2J_{PP}$ = 48.3; δ_H 6.90 (dm, J_{PH} = 38.0, C⁵-H), 7.49 (ddd, J_{PH} = J_{PH} ≈ 13, J_{HH} = 1.4, C³-H); M^+ found = 434.1887, C₂₂H₃₂N₂O₃P₂ requires 434.1888.
- 12 Selected data for 4b: δ_P (CDCl₃) 0.9 (P¹), 24.1 (C²-P), $^2J_{PP}$ = 49.4; δ_C (CDCl₃) 18.4 (J_{PC} = 3.6, C⁴-CH₃), 23.1 (p -CH(CH₃)₂), 24.2 (o -CH(CH₃)₂), 32.1 (J_{PC} = 15.9, o -CHMe₂), 34.4 (p -CHMe₂), 44.5 (C²), 66.9 (J_{PC} = 6.9, C³), 119.8 (C¹), 122.2 (J_{PC} = 11.1, C³), 133.7 (J_{PC} = 19.9, J_{PC} = 151.4, C²), 137.7 (J_{PC} = J_{PC} = 5.4, C⁵), 142.4 (J_{PC} = 18.4, J_{PC} = 14.6, C⁴), 147.5 (J_{PC} = 17.3, J_{PC} = 6.1, C³), 152.8 (C⁴), 156.9 (J_{PC} = 14.7, C²); δ_H (CDCl₃) 7.04 (dm, J_{PH} = 38.2, C⁵-H), 7.42 (ddd, J_{PH} = J_{PH} ≈ 13, J_{HH} = 1.2, C³-H); M^+ found = 518.2832, C₂₈H₄₄N₂O₃P₂ requires 518.2827.
- 13 Selected data for 5a: δ_P (CDCl₃) 19.1 (P¹), 51.3 (C²-P), $^2J_{PP}$ = 34.7; M^+ found = 450.
- 14 Selected data for 5b: δ_P (CDCl₃) 19.5 (P¹), 52.2 (C²-P), $^2J_{PP}$ = 36.1; M^+ found = 534.
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- 16 Selected data for 7: δ_P (CDCl₃) 3.4 (P¹), 90.7 (C³-P), $^3J_{PP}$ = 33.6; M^+ found = 544.3323, C₃₁H₅₀N₂O₃P₂ requires 544.3348.
- 17 Selected data for 8: δ_P (CDCl₃) 7.1 (P¹), 23.4 (C³-P), $^3J_{PP}$ = 21.8; δ_C (CDCl₃) 19.2 (J_{PC} = 6.2, C⁴-CH₃), 31.3 (p -C(CH₃)₃), 33.3 (J_{PC} = 3.5, o -C(CH₃)₃), 35.4 (p -CMe₃), 38.9 (J_{PC} = 3.5, o -CMe₃), 44.9 (C²), 67.5 (J_{PC} = 5.8, C³), 118.6 (J_{PC} = 4.6, C¹), 123.1 (J_{PC} = 10.5, C³), 126.8 (J_{PC} = 13.2, J_{PC} = 21.0, C⁵), 128.2 (J_{PC} = 21.4, J_{PC} = 154.5, C³), 139.7 (J_{PC} = 15.8, C⁴), 139.9 (J_{PC} = 14.6, J_{PC} = 8.6, C²), 153.3 (J_{PC} = 2.4, C⁴), 158.8 (J_{PC} = 11.7, C²); δ_H (CDCl₃) 6.66 (dm, J_{PH} = 35.5, C⁵-H), 7.37 (ddd, J_{PH} = 28.1, J_{PH} = 12.1, J_{HH} = 2.5, C²-H); M^+ found = 560.3292, C₃₁H₅₀N₂O₃P₂ requires 560.3297.