

2,4,6-Trialkylphenyl-2*H*-phospholes from Slightly Aromatic 1*H*-Phospholes and Their Use in [4 + 2] Cycloaddition Reactions

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ABSTRACT: 1-(2,4,6-Trialkylphenyl)phospholes **1a,b** possess a moderate aromatic character. Despite of that they underwent a sigmatropic rearrangement at 150°C to afford 2*H*-phospholes **2a,b** which by trapping with toluene, or in reaction with another unit of **2** gave [4 + 2] cycloadducts **3a,b**, or in a reversible reaction, dimer **6**, respectively. Dedimerization of species **6** at 150°C in the presence of toluene, or at 0°C under oxidative circumstances, led to 1-phosphanorbornadiene **3a**, or phosphole oxide dimer **8**, respectively. © 2003 Wiley Periodicals, Inc. *Heteroatom Chem* 14:316–319, 2003; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.10151

INTRODUCTION

Phospholes, perhaps the most representative family of P-heterocycles are of considerable interest [1,2].

On the one hand, phospholes are widely used as ligands in transition-metal complexes, on the other hand, their chemistry offers many points of interest, such as the 1*H*-phosphole → 2*H*-phosphole sigmatropic rearrangement explored by Mathey [3]. For phenylphospholes, lacking aromaticity due to the pyramidal character of the phosphorus atom, the overlap between the π -dienic system and the σ -orbital of the exocyclic P–Ph bond promotes the migration of the Ph-group. The 2*H*-phospholes generated at 160°C were trapped by alkynes and alkenes or dimerized in [4 + 2] cycloadditions to yield 1-phosphanorbornene derivatives [3–7]. An important practical application of the reaction under discussion is the synthesis of 2,2'-bis-(1-phosphanorbornadienyl) (BIPNOR) which is an efficient biphosphine for asymmetric catalysis [8]. Proton [1,5] shifts in P-unsubstituted 1*H*-phospholes and subsequent dimerizations were also observed to take place [9].

RESULTS AND DISCUSSION

2,4,6-Trialkylphenylphospholes introduced recently [10–13] form a special class of phospholes, as they have some aromatic character due to the

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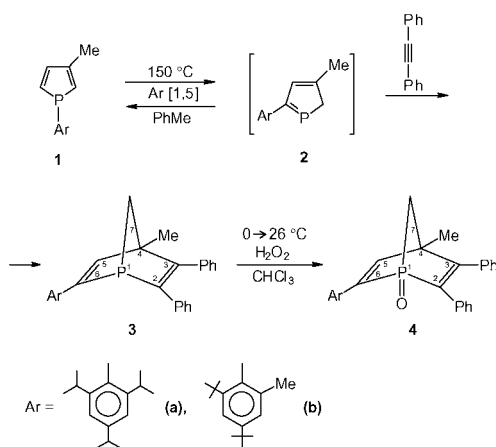
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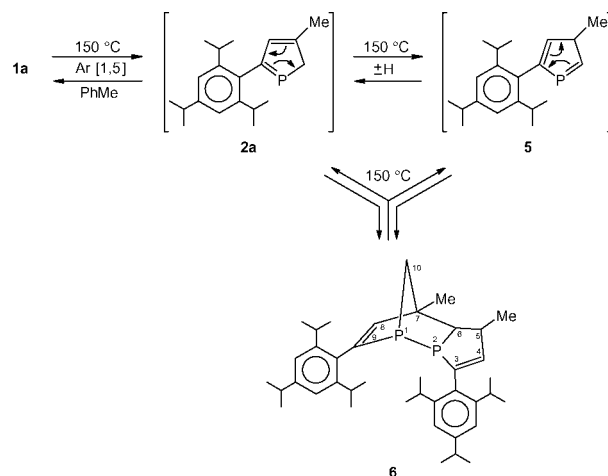
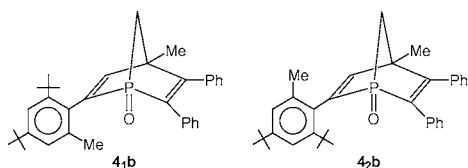
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planarization of the P-pyramid. For 1-(2,4,6-triisopropylphenyl)phosphole (**1a**), the Bird-index of aromaticity [14] was found to be 40.4, which entered, although not too efficiently, into an aromatic electrophilic substitution reaction [15]. At the same time, **1a**, as well as the 2,4-di-*tert*-butyl-6-methylphenyl phosphole (**1b**), could also be involved in Diels–Alder cycloadditions [16]. The dual reactivity of the arylphospholes **1a,b** is also reflected in our present finding that they undergo a sigma-tropic Ar[1,5] rearrangement on heating at 150°C in toluene, in a sealed tube. The intermediate 2*H*-phospholes **2a,b** were trapped by reaction with toluene to furnish 1-phosphanorbornadienes **3a,b**. To obtain stable products, the phosphines (**3a,b**) were oxidized to the corresponding phosphine oxides (**4a,b**) (Scheme 1). Product **4b** was isolated as a 52:48 mixture of two rotamers (**4_{1b}** and **4_{2b}**). The phosphanorbornadienes (**3a**, **4a**, and **4b**) were identified by ^{31}P , ^{13}C , and ^1H NMR, as well as HRMS data. ^{13}C NMR spectral parameters of compound **4a** closely resembled those of an analogue described earlier [5].

It was interesting to find that the 1-(2,4,6-tri-*tert*-butylphenyl)-3-methylphosphole exhibiting a Bird-index of 56.5, which is comparable with that of pyrrole (59), resisted the pericyclic reaction attempted. This is probably caused by the fact that the π -system of the phosphole moiety is not available due to the electron delocalization. Hence, it can be concluded that the extent of aromaticity controls the reactivity in the 1*H*- to 2*H*-phosphole rearrangement.



SCHEME 1

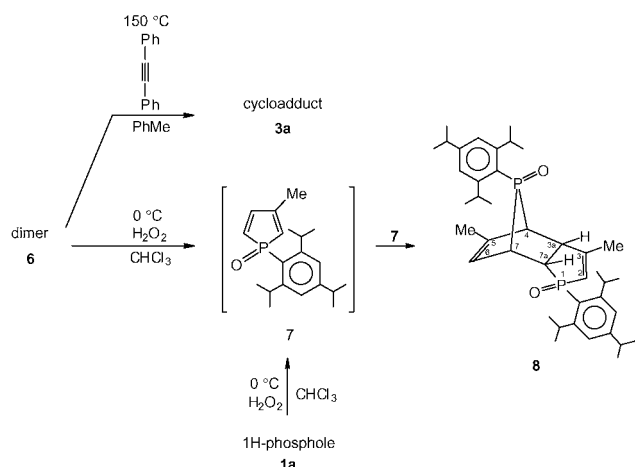


SCHEME 2

Thermal treatment of arylphosphole **1a** in the absence of toluene led to the formation of dimer **6** (Scheme 2). Formally, the dimer may be derived by the Diels–Alder reaction of 2*H*-phosphole **2a** with species **5** formed by another, this time a *H*[1,5] sigmatropic rearrangement. The structure of **6** was confirmed by ^{31}P , ^{13}C , and ^1H NMR spectral parameters, as well as HRMS. As regards the stereostructure of **6**, no direct proof is available at present. The ^{31}P NMR (δ_{P} 34.4 and -17.2 $^1J_{\text{PP}} = 216.6$ Hz) together with the ^{13}C NMR data obtained for **6** match those reported for the analogous *P*-phenyl derivative [7] that was believed to have the rings in the *exo*-fusion. At the same time, reversible formation of dimer **6** (see next paragraph) substantiated rather the *endo* form, such as an analogous species with relatively long and weak P–P and C–C bonds at the junction of the dimer [17]. Evaluation of the geometry of the highly sensitive cycloadduct will require *ab initio* quantum chemical calculations.

Reversibility for the formation of dimer **6** was proved first by its reaction with toluene, as it led to the formation of cycloadduct **3a** (Scheme 3). At 150°C, the dimer was decomposed to two units of 2*H*-phosphole (**2a** and **5**) (Scheme 2) entering into reaction with toluene. Mathey also described the reversible formation of a series of 2*H*-phosphole cycloadducts [6,9,18]. It is the novel and quite surprising observation of ours that precursor **6** was also dedimerized on treatment at 0°C with hydrogen peroxide to afford phosphole oxide intermediate **7** leading spontaneously to its dimer **8** (Scheme 3).

On the basis of its ^{31}P and ^{13}C NMR spectral parameters, the phosphole oxide dimer **8** obtained after purification by column chromatography was identical with an authentic sample described by us earlier [10]. It is noted, however, that the reaction under



SCHEME 3

discussion was accompanied by a series of side reactions. The complex composition of the mixture prevented the isolation and identification of the minor components.

To summarize our results, we found that 2,4,6-trialkylphenylphospholes with not too high extent of aromaticity (with a Bird-index around 40) underwent the 1*H*-phosphole → 2*H*-phosphole sigmatropic rearrangement. The latter species were trapped in Diels–Alder reaction with toluene, or in one case, the 2*H*-phosphole was dimerized in a [4 + 2] fashion. As the dimerization is reversible, the cycloadduct served as the precursor of 2*H*-phosphole in reaction with toluene, but on treatment with hydrogen peroxide, the dimer was the source of the corresponding 1*H*-phosphole.

EXPERIMENTAL

The ³¹P, ¹³C, and ¹H NMR spectra were taken on a Bruker DRX-500 spectrometer operating at 202.4, 125.7, and 500 MHz, respectively. Chemical shifts are downfield relative to 85% H₃PO₄ or TMS. The couplings are given in hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument.

Generation of 2a and Its Trapping with Toluene

A mixture of 0.6 g (2.0 mmol) of phosphole 1a and 0.37 g (2.1 mmol) of toluene in 15 ml of toluene was degassed by nitrogen and heated in a sealed tube at 150 °C for 4 days. The solvent was evaporated to give 0.96 g (~100%) of cycloadduct 3a. ³¹P NMR (CDCl₃) δ 5.9; ¹³C NMR δ 21.9 (C₄–Me), 23.5 (CHCH₃), 23.9 (CHCH₃), 25.0 (CH(CH₃)₂), 25.1 (CHCH₃), 26.0 (CHCH₃), 31.3 (*p*-CHMe₂), 35.1 (*o*-CHMe₂), 67.8 (C₄), 70.6 (*J* = 5.6, C₇), 138.5 (*J* =

19.5, C₂), 146.6 (*J* = 28.1, C₆), 148.2 (C_{2'}),* 148.3 (C_{4'}),* 149.4 (C_{6'}),* 152.8 (C₅), 161.2 (C₃), *tentative assignment; M + H = 479).

Phosphine 3a (0.96 g, ~2.0 mmol) in 40 ml of chloroform was treated with 0.70 ml (~6.2 mmol) of 30% hydrogen peroxide with intensive stirring at 0 °C. After addition was complete, the contents of the flask were allowed to warm to 25 °C and the stirring was continued for 1 h. The mixture was extracted with 2 × 15 ml of water and the organic phase was dried (Na₂SO₄). The crude product obtained after evaporating the solvent was purified by column chromatography (silica gel, 3% methanol in chloroform) to afford 0.60 g (61%) of phosphine oxide 4a. ³¹P NMR (CDCl₃) δ 52.0; ¹³C NMR δ 21.2 (*J* = 16.1, C₄–Me), 22.8 (CHCH₃), 23.8 (CHCH₃), 24.1 (CHCH₃), 24.2 (CHCH₃), 24.6 (CHCH₃), 25.3 (CHCH₃), 31.4 (*o*-CHMe₂), 31.5 (*o*-CHMe₂), 34.4 (*p*-CHMe₂), 46.9 (*J* = 29.0, C₄), 69.6 (*J* = 68.4, C₇), 139.3 (*J* = 76.3, C₂), 146.4 (*J* = 3.2, C_{2'}),* 147.1 (*J* = 3.5, C_{6'}),* 147.7 (*J* = 74.5, C₆), 148.7 (C_{4'}), 154.1 (*J* = 16.7, C₅), 162.0 (*J* = 15.9, C₃),* may be reversed; ¹H NMR δ 0.74 (d, *J* = 6.8, 3H, CHCH₃), 1.09 (d, *J* = 6.7, 3H, CHCH₃), 1.26 (d, *J* = 6.9, 6H, CH(CH₃)₂), 1.29 (d, *J* = 6.7, 3H, CHCH₃), 1.41 (d, *J* = 6.9, 3H, CHCH₃), 1.45 (s, 3H, C₄–CH₃), 2.68 (q, *J* = 6.8, 1H, CHMe₂), 2.86–2.97 (m, 3H, CHMe₂, CH₂), 3.25 (q, *J* = 6.7, 1H, CHMe₂), 7.14 (d, *J* ~ 39, CH=, overlapped by the aromatic signals); HRFAB (M + H)⁺_{found} = 495.2734, C₃₄H₄₀OP requires 495.2817.

The mixture of 4**1b** (δ_P 53.2, 52%) and 4**2b** (δ_P 52.0, for both species (M + H)⁺ = 495) was prepared in a similar way.

Preparation of Dimer 6

Same procedure was repeated with phosphole 1a, but without adding toluene. Evaporation of toluene gave a residue (~0.6 g) that was extracted with acetone to leave 0.20 g (33%) of 6 as a thick oil. All operations were performed under nitrogen. ³¹P NMR (CDCl₃) δ 34.4 (P₁) and –17.2 (P₂), ¹J_{PP} = 216.6; ¹³C NMR δ 24.2 (broad signal, CH(CH₃)₂), 25.2 (C₅–Me), a 25.8 (C₇–Me), a 34.4 (broad signal, CHMe₂), 43.4 (*J* = 20.2, C₁₀), 43.7 (*J* = 4.0, C₅), 55.6 (*J* = 26.0, C₆), 60.5 (*J*₁ = 3.6, *J*₂ = 6.1, C₇), 120.7 (C_γ), b 120.9 (C_{γ'}), b 121.0 (C_ε), b 121.2 (C_{ε'}), b 132.0 (*J* = 12.9, C_α), c 132.2 (*J* = 15.3, C_{α'}), c 141.0 (*J* = 32.1, C₃), 144.6 (*J*₁ = *J*₂ = 5.4, C₄), 146.1 (*J* = 33.7, C₉), 146.7 (C_β, C_{β'}), d 147.3 (C_ω, C_{ω'}), d 147.7 (C_δ, C_{δ'}), 151.5 (*J* = 8.2, C₈), a–d tentative assignment; ¹H NMR δ 1.06–1.33 (m, 39H, 6CH(CH₃)₂ + CH₃), 1.62 (s, 3H, CH₃), 5.82 (d, *J* = 10.0, 1H, CH=), 5.98 (dd, *J*₁ = 3.9, *J*₂ = 7.9, 1H, CH=); HRMS, M⁺_{found} = 600.3891, C₄₀H₅₈P₂ requires 600.4014.

Dedimerization of **6**

Dimer **6** (0.20 g, 0.33 mmol) in 10 ml of degassed toluene was heated with 0.12 g (0.67 mmol) of toluene at 150°C in a sealed tube for 4 days. Evaporation of the solvent left ~100% of **3a** with δ_p 5.8.

The reaction of **6** with hydrogen peroxide was performed as described above for the **3a** → **4a** transformation to give dioxide **8** in 21% yield. ^{31}P NMR (CDCl_3) δ 57.2 and 80.5, $^3J_{\text{PP}} = 38.0$ (δ_p lit. [10], 56.4 and 80.1, $^3J_{\text{PP}} = 38.1$); ^{13}C NMR (CDCl_3) δ 18.7 ($J = 16.8$, $\text{C}_3\text{--Me}$),* 19.1 ($\text{C}_5\text{--Me}$),* 43.3 ($J_1 = 74.6$, $J_2 = 12.8$, C_{7a}), 47.9 ($J = 60.0$, C_7), 51.8 ($J_1 = J_2 = 13.3$, C_{3a}), 52.4 ($J = 64.2$, C_4), C_6^* , 130.5 ($J = 97.9$, C_2), 135.5 ($J = 12.2$, C_5), 157.0 ($J_1 = 23.9$, $J_2 = 9.3$, C_3), *may be reversed, **overlapped in the range of = 119.8–124.6 (δ_c lit. [10], ^{13}C NMR (CDCl_3) δ 18.9 ($J = 16.7$, $\text{C}_3\text{--Me}$),* 19.3 ($\text{C}_5\text{--Me}$),* 43.5 ($J_1 = 74.8$, $J_2 = 12.8$, C_{7a}), 48.0 ($J = 60.0$, C_7), 51.9 ($J_1 = J_2 = 13.1$, C_{3a}), 52.6 ($J = 64.5$, C_4), C_6^* , 130.7 ($J = 97.9$, C_2), 135.8 ($J = 12.2$, C_5), 157.1 ($J_1 = 23.9$, $J_2 = 9.1$, C_3), *may be reversed, **overlapped in the range of = 119.9–124.5); ^1H NMR (CDCl_3) δ 1.61 (s, 3H, $\text{C}_5\text{--Me}$), 2.1 (s, 3H, $\text{C}_3\text{--Me}$), 6.18 (d, $J = 12.4$, 1H, $\text{C}_6\text{--H}$), 6.25 (d, $J = 23.8$, 1H, $\text{C}_2\text{--H}$) (δ_H lit. [10], ^1H NMR (CDCl_3) δ 1.61 (s, 3H, $\text{C}_5\text{--Me}$), 2.0 (s, 3H, $\text{C}_3\text{--Me}$), 6.17 (d, $J = 12.4$, 1H, $\text{C}_6\text{--H}$), 6.23 (d, $J = 23.9$, 1H, $\text{C}_2\text{--H}$)); MS, 632 (M^+).

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