Heteroatom Chemistry
Volume 14, Number 4, 2003

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

György Keglevich,[1] Renáta Farkas,[1] Tímea Imre,[2] Krisztina Ludányi,[2] Áron Szöllősy,[3] and László Tőke[4]

[1]*Department of Organic Chemical Technology, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

[2]*Chemical Research Center, Hungarian Academy of Sciences, 1525 Budapest, Hungary*

[3]*Department of General and Analytical Chemistry, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

[4]*Research Group of the Hungarian Academy of Sciences, Budapest University of Technology and Economics, 1521 Budapest, Hungary*

Received 13 November 2002; revised 2 December 2002

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 2H-phospholes* **2a,b** *which by trapping with tolane, 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 tolane, 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].

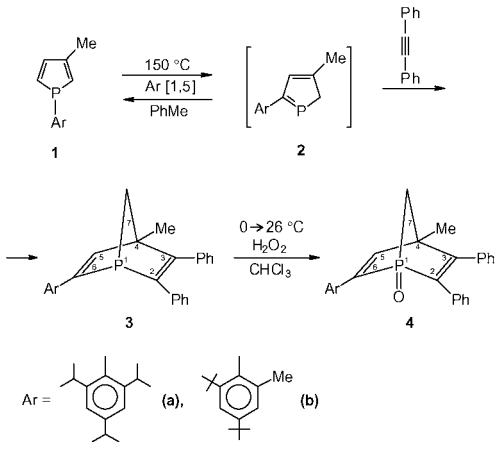
RESULTS AND DISCUSSION

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

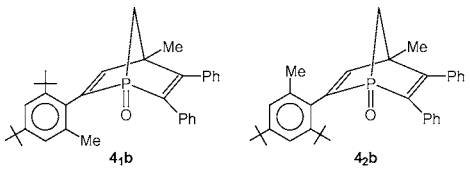
Correspondence to: György Keglevich; e-mail: keglevich@oct.bme.hu.
Contract grant sponsor: OTKA.
Contract grant number: T 042479.

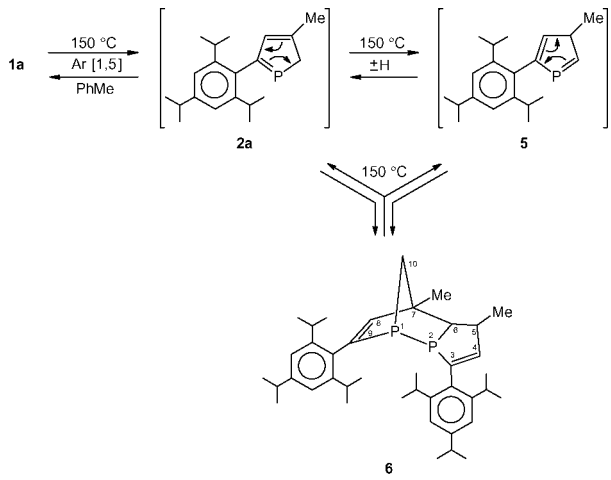
planarization of the P-pyramid. For 1-(2,4,6-triisopropylphenyl)phosphole (**1a**), the Bird-index of aromaticity [14] was found to be 40.4, which entered, although not too efficiently, into an aromatic electrophilic substitution reaction [15]. At the same time, **1a**, as well as the 2,4-di-*tert*-butyl-6-methylphenyl 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 sigmatropic 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 tolane 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$_1$b** and **4$_2$b**). The phosphanorbornadienes (**3a, 4a**, and **4b**) were identified by ^{31}P, ^{13}C, and ^{1}H 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



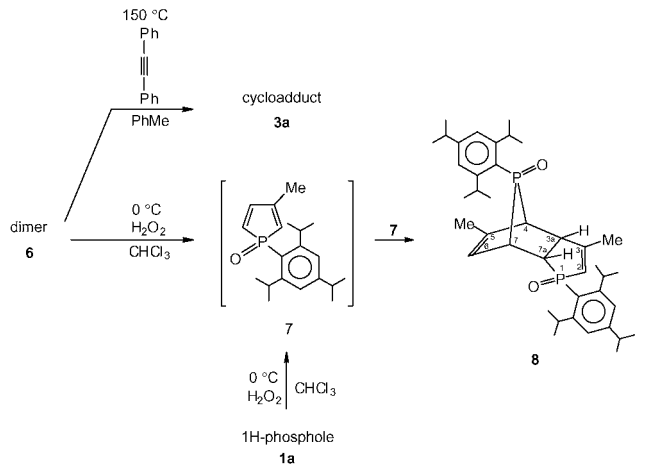


SCHEME 2

Thermal treatment of arylphosphole **1a** in the absence of tolane 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 ^{1}H 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 $^1J_{PP}$ = 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 tolane, 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 tolane. 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 tolane, 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 tolane, but on treatment with hydrogen peroxide, the dimer was the source of the corresponding 1*H*-phosphole.

EXPERIMENTAL

The ^{31}P, ^{13}C, and ^{1}H 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% H_3PO_4 or TMS. The couplings are given in hertz. Mass spectrometry was performed on a ZAB-2SEQ instrument.

Generation of **2a** *and Its Trapping with Tolane*

A mixture of 0.6 g (2.0 mmol) of phosphole **1a** and 0.37 g (2.1 mmol) of tolane 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**. ^{31}P NMR ($CDCl_3$) δ 5.9; ^{13}C NMR δ 21.9 (C_4—Me), 23.5 (CH*C*H_3), 23.9 (CH*C*H_3), 25.0 (CH(*C*H_3)$_2$), 25.1 (CH*C*H_3), 26.0 (CH*C*H_3), 31.3 (*p*-CHMe$_2$), 35.1 (*o*-CHMe$_2$), 67.8 (C_4), 70.6 (J = 5.6, C_7), 138. 5 (J = 19.5, C_2), 146.6 (J = 28.1, C_6), 148.2 ($C_{2'}$),* 148.3 ($C_{4'}$),* 149.4 ($C_{6'}$),* 152.8 (C_5), 161.2 (C_3), *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 (Na_2SO_4). 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**. ^{31}P NMR ($CDCl_3$) δ 52.0; ^{13}C NMR δ 21.2 (J = 16.1, C_4—Me), 22.8 (CH*C*H_3), 23.8 (CH*C*H_3), 24.1 (CH*C*H_3), 24.2 (CH*C*H_3), 24.6 (CH*C*H_3), 25.3 (CH*C*H_3), 31.4 (*o*-CHMe$_2$), 31.5 (*o*-CHMe$_2$), 34.4 (*p*-CHMe$_2$), 46.9 (J = 29.0, C_4), 69.6 (J = 68.4, C_7), 139.3 (J = 76.3, C_2), 146.4 (J = 3.2, $C_{2'}$),* 147.1 (J = 3.5, $C_{6'}$),* 147.7 (J = 74.5, C_6), 148.7 ($C_{4'}$), 154.1 (J = 16.7, C_5), 162.0 (J = 15.9, C_3),* may be reversed; ^{1}H NMR δ 0.74 (d, J = 6.8, 3H, CHC*H*$_3$), 1.09 (d, J = 6.7, 3H, CHC*H*$_3$), 1.26 (d, J = 6.9, 6H, CH(C*H*$_3$)$_2$), 1.29 (d, J = 6.7, 3H, CHC*H*$_3$), 1.41 (d, J = 6.9, 3H, CHC*H*$_3$), 1.45 (s, 3H, C_4—C*H*$_3$), 2.68 (q, J = 6.8, 1H, C*H*Me$_2$), 2.86–2.97 (m, 3H, C*H*Me$_2$, CH$_2$), 3.25 (q, J = 6.7, 1H, C*H*Me$_2$), 7.14 (d, J ∼ 39, CH=, overlapped by the aromatic signals); HRFAB $(M + H)^+_{found}$ = 495.2734, $C_{34}H_{40}OP$ requires 495.2817.

The mixture of **4$_1$b** (δ_P 53.2, 52%) and **4$_2$b** (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 tolane. 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. ^{31}P NMR ($CDCl_3$) δ 34.4 (P_1) and −17.2 (P_2), $^{1}J_{PP}$ = 216.6; ^{13}C NMR δ 24.2 (broad signal, CH(*C*H$_3$)$_2$), 25.2 (C_5—Me), a 25.8 (C_7—Me), a 34.4 (broad signal, CHMe$_2$), 43.4 (J = 20.2, C_{10}), 43.7 (J = 4.0, C_5), 55.6 (J = 26.0, C_6), 60.5 (J_1 = 3.6, J_2 = 6.1, C_7), 120.7 (C_γ), b 120,9 ($C_{\gamma'}$), b 121.0 (C_ε), b 121.2 ($C_{\varepsilon'}$), b 132.0 (J = 12.9, C_α), c 132.2 (J = 15.3, $C_{\alpha'}$), c 141.0 (J = 32.1, C_3), 144.6 ($J_1 = J_2$ = 5.4, C_4), 146.1 (J = 33.7, C_9), 146.7 (C_β, $C_{\beta'}$), d 147.3 (C_ω, $C_{\omega'}$), d 147.7 (C_δ, $C_{\delta'}$), 151.5 (J = 8.2, C_8), a–d tentative assignment; ^{1}H NMR δ 1.06–1.33 (m, 39H, 6CH(C*H*$_3$)$_2$ + CH$_3$), 1.62 (s, 3H, CH$_3$), 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, $C_{40}H_{58}P_2$ 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 tolane 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, $^3J_{PP} = 38.0$ (δ_P lit. [10], 56.4 and 80.1, $^3J_{PP} = 38.1$); ^{13}C NMR ($CDCl_3$) δ 18.7 ($J = 16.8$, C_3—Me),* 19.1 (C_5—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 ($J = 16.7$, C_3—Me),* 19.3 (C_5—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); ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3H, C_5—Me), 2.1 (s, 3H, C_3—Me), 6.18 (d, $J = 12.4$, 1H, C_6—H), 6.25 (d, $J = 23.8$, 1H, C_2—H) (δ_H lit. [10], ^{1}H NMR ($CDCl_3$) δ 1.61 (s, 3H, C_5—Me), 2.0 (s, 3H, C_3—Me), 6.17 (d, $J = 12.4$, 1H, C_6—H), 6.23 (d, $J = 23.9$, 1H, C_2—H)); MS, 632 (M^+).

REFERENCES

[1] Quin, L. D. In Comprehensive Heterocyclic Chemistry II, Katritzky, A. R.; Rees, C. V.; Scriven, E. F. V. (Eds.); Bird, C. W. (Vol. Ed.); Pergamon: Oxford, UK, 1996; Vol. 2, Ch. 15.

[2] Quin, L. D. In Phosphorus-Carbon Heterocyclic Chemistry: The Rise of a New Domain; Mathey, F. (Ed.); Pergamon: Amsterdam, 2001; Ch. 4.2.1–4.2.2.

[3] Mathey, F.; Mercier, F. C R Acad Sc Paris, Se II b, 1997, 324, 701.

[4] Mathey, F.; Mercier, F.; Charrier, C. J Am Chem Soc 1981, 103, 4595.

[5] Laporte, F.; Mercier, F.; Ricard, L.; Mathey, F. Bull Soc Chim Fr 1993, 130, 843.

[6] Goff, P.; Mathey, F.; Ricard, L. J Org Chem 1989, 54, 4754.

[7] Mercier, F., Mathey, F. J Organomet Chem 1984, 263, 55.

[8] Mathey, F.; Mercier, F.; Robin, F.; Ricard, L. J Organomet Chem 1998, 577, 117.

[9] Charrier, C.; Bonnard, H.; Lauzon, G.; Mathey, F. J Am Chem Soc 1983, 105, 6871.

[10] Keglevich, Gy.; Quin, L. D.; Böcskei, Zs.; Keserű, Gy. M.; Kalgutkar, R.; Lahti, P. M. J Organomet Chem 1997, 532, 109.

[11] Quin, L. D.; Keglevich, Gy.; Ionkin, A. S.; Kalgutkar, R.; Szalontai, G. J Org Chem 1996, 61, 7801.

[12] Keglevich, Gy.; Böcskei, Zs.; Keserű, Gy. M.; Újszászy, K.; Quin, L. D. J Am Chem Soc 1997, 119, 5095.

[13] Keglevich, Gy. In Targets in Heterocyclic Systems, Attanasi, O.; Spinelli, D. (Eds.); Italian Society of Chemistry (in press); 2002, Vol. 6.

[14] Bird, C. W. Tetrahedron 1990, 46, 5697.

[15] Keglevich, Gy.; Chuluunbaatar, T.; Dajka, B.; Dobó, A.; Szöllősy, Á.; Tőke, L. J Chem Soc, Perkin Trans 1, 2000, 2895.

[16] Keglevich, Gy.; Nyulászi, L.; Chuluunbaatar, T.; Bat-Amgalan, N.; Ludányi, K. Imre, T.; Tőke, L. Tetrahedron 2002, 58, 9801.

[17] Lauzon, G.; Charrier, C.; Bonnard, H.; Mathey, F.; Fischer, J.; Mitschler, A. J Chem Soc, Chem Commun 1982, 1272.

[18] Mercier, F.; Mathey, F. J Organomet Chem 1993, 462, 103.