Cyclic Phosphanes

Efficient One-Pot Synthesis of Secondary Cyclic Phosphanes with Easy Regeneration of the Phosphorus-Donor Reagent Used**

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New syntheses of cyclic phosphanes are of considerable current interest, principally because they play a central role in

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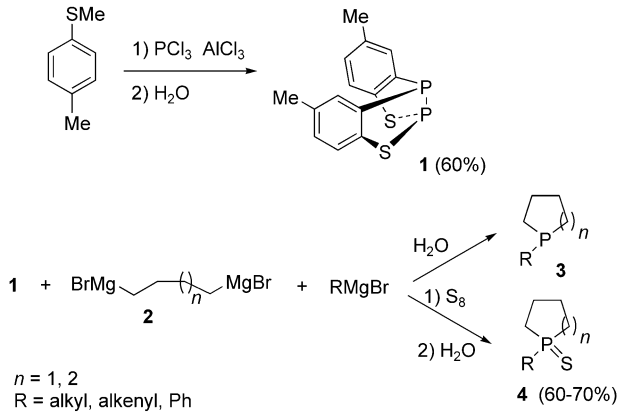
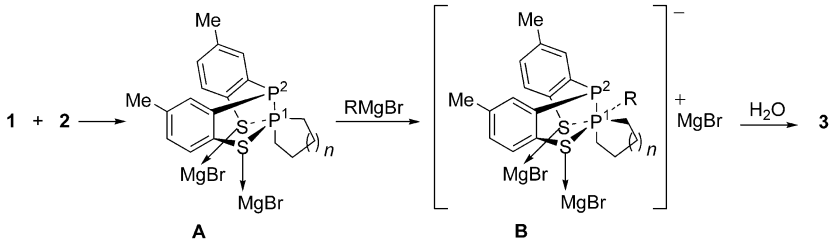
coordination chemistry and homogeneous catalysis,[1] but to date the most widely used procedures for obtaining secondary cyclic phosphanes give very low overall yields (3–5%).[2–5]

Secondary phosphanes are prepared by multistep procedures in which the final step is reduction of a phosphorus compound containing P–O, P–S, or P–Cl bonds with a wide variety of reagents and reaction conditions. However, whereas secondary acyclic phosphanes can be synthesized by several routes, only a few procedures for secondary five- (phospholanes) and six-membered cyclic phosphanes (phosphinanes) have been reported.[2] For example, phospholane **5a** (see Scheme 3) was prepared[3] by reaction of tetramethylenebis(magnesium bromide) $BrMgC_4H_8MgBr$ with dimethylphosphoramidous dichloride $(Me)_2NPCl_2$ at −78 °C to give the aminocyclophosphane $(Me)_2NPC_4H_8$ in 8% yield. This aminocyclophosphane was treated with B_2H_6 and then kept in a sealable tube at 220 °C. The tube was then sealed up and heated for 21 h at 210 °C, and subsequent distillation gave a fraction containing the desired C_4H_8PH (30%) and aminoborane impurities, which were separated by treatment with HCl. The overall yield of this multistep procedure was not higher than 3%. In another recent preparation, phospholane[4] was obtained in approximately 5% yield by flash vacuum pyrolysis of butyldichlorophosphane at 600 °C.



Scheme 1. Preparation of **1** and synthesis of cyclic tertiary phosphanes **3** and their sulfides **4**.



Scheme 2. Proposed reaction pathway for the formation of cyclic phosphanes **3**.

Phosphinane **5b** is obtained by similar multistep procedures[5] or by flash pyrolysis.[4] Other recent syntheses of these cyclic phosphanes use (trimethylsilyl)phosphane[6] or an organolanthanide-catalyzed hydrophosphination/cyclization reaction,[7] but the former reagent is very difficult and dangerous to prepare, and the latter procedure[7] often gives a mixture of phospholane and phosphinane.

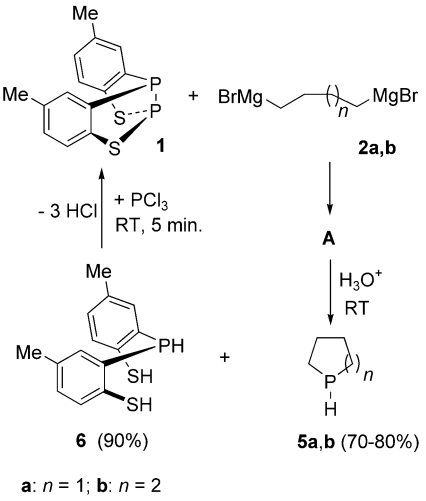
Herein we report a highly efficient and economical new method for one-pot preparation of **5a** and **5b** (70–80% yield) using an unusual phosphorus-donor reagent, namely, the benzothiadiphosphole **1** which, at the end of the process, can be easily regenerated by simple reaction of its end product **6** with PCl_3.

We have reported[8] that **1** is easily obtained by simple treatment of *p*-methylthioanisole with PCl_3 and $AlCl_3$, and that it can be isolated by crystallization from the reaction mixture. Compound **1** is an air-stable solid that can be stored for several years without particular precautions, and it is also easy to handle. Subsequently, we found[9] that **1** can be used as a phosphorus donor, and we recently reported[10] that simultaneous or sequential addition of an equimolar mixture of a bis(Grignard reagent) **2** ($n = 1, 2$; Scheme 1) and a Grignard reagent RMgBr (R = alkyl, phenyl, alkenyl) to an equimolar amount of **1** gave phosphanes **3** or, after addition of elemental sulfur, their sulfides **4** in good yield at room temperature.

The above results were explained by the intervention of hypervalent (penta- and hexacoordinate) phosphorus intermediates[11] such as **A** and **B** (scheme 2) in which the "dibenzo-butterfly" moiety of reagent **1**, as depicted in Scheme 2, might favor their formation. In pentacoordinate intermediate **A** coordination of the magnesium atom by a sulfur atom would activate P^1 toward further nucleophilic attack to give unstable hexacoordinate intermediate **B**. Treatment of **B** with water or sulfur gives phosphane **3** or its sulfide **4**, respectively.

To develop further applications of this reaction we then studied what happens when intermediate **A**, formed by reaction of **1** with one equivalent of **2**, is treated with water. Surprisingly, in this case we found that it is possible to obtain secondary cyclic phosphanes **5** in 70–80% yields (based on **2**). In addition, from the aqueous solution it is also possible to isolate, in very good yield (90% based on **1**), the new compound 4-methyl-2-[(5-methyl-2-sulfanylphenyl)phosphanyl]benzenethiol (**6**) which is the end product derived from **1** (Scheme 3).

As depicted in Scheme 3, we first prepared intermediate **A** by reaction of equimolar amounts of **1** and a bis(Grignard reagent) **2** in THF. Partial evaporation of the solvent, treatment of the reaction mixture with aqueous acid followed by extraction with organic solvent (CH_2Cl_2, diethyl ether) gave a mixture of secondary phosphanes **5** and residue **6**. These can be easily separated by treating the solution with aqueous NaOH; in this way the sodium salt of **6** dissolves in the aqueous solution, whereas the organic phase contains almost pure phosphanes **5** (70–80%), which can be purified by bulb-to-bulb distillation. Compounds **5a** and **5b** were characterized principally by ^1H, ^{31}P NMR, and IR spectroscopy and mass spectrometry, the data from which agree with the reported values.[4,6a,b] Compound **6** can be recovered from the basic aqueous layer by acidification and extraction, and purified by distillation. It was stored under argon and



Scheme 3. Synthesis of secondary cyclic phosphanes **5a,b** and regeneration of the starting reagent **1** from end product **6**.

characterized by ^{1}H and ^{31}P NMR spectroscopy and HR-MS.[12]

Simply treating a dry solution of **6** with an equimolar amount of PCl_3 regenerates **1** in sufficiently pure form that it can be reused without further purification (Scheme 3). Finally, we carried out the reaction shown in Scheme 1 to obtain tertiary phosphanes **3** using the same reaction conditions and separation procedure used to obtain compounds **5**, and we found that also in this case it was possible to isolate **6** (Scheme 4).

Scheme 4. Regeneration of **1** from **6**, obtained in the preparation of tertiary phosphanes **3**.

In conclusion, the syntheses of secondary and tertiary cyclic phosphanes reported herein can be carried out in a very simple, efficient, and low-cost procedure that gives higher yields than those previously reported. In addition, this synthesis is atom-economic[13] and environmentally friendly, because by-product **6** is easily transformed quantitatively into starting reagent **1**, which can be recycled.

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Keywords: hypervalent compounds · phosphanes · phosphorus heterocycles · synthetic methods

[1] a) R. Noyori, *Asymmetric Catalysis in Organic Synthesis*, Wiley, New York, **1994**; b) M. J. Burk, M. F. Gross, J. P. Martinez, *J. Am. Chem. Soc.* **1995**, *117*, 9375–9376; c) M. J. Burk, A. Pizzano, J. A. Martin, L. M. Liable-Sands, A. L. Rheingold, *Organometallics* **2000**, *19*, 250–260; d) Q. Jiang, D. Xiao, Z. Zhang, P. Cao, X. Zang, *Angew. Chem.* **1999**, *111*, 578–580; *Angew. Chem. Int. Ed.* **1999**, *38*, 516–518.

[2] a) K. Dimroth, Heterocyclic Rings Containing Phosphorus in *Comprehensive Heterocyclic Chemistry*, *Vol. I* (Eds.: A. R. Katritzky, C. W. Rees), Pergamon, New York, **1984**, pp. 500, 513; b) D. Quin, Phospholes in *Comprehensive Heterocyclic Chemistry II*, *Vol. 2* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven, C. W. Bird), Pergamon, New York, **1996**, pp. 826–831; c) D. G. Hewitt, Six-membered Rings with One Phosphorus Atom in *Comprehensive Heterocyclic Chemistry II*, *Vol. 5* (Eds.: A. R. Katritzky, C. W. Rees, E. F. V. Scriven, A. McKillop), Pergamon, New York, **1996**, p. 639–668.

[3] A. B. Burg, P. J. Slota, *J. Am. Chem. Soc.* **1960**, *82*, 2148–2151.

[4] R. A. Aitken, W. Masamba, N. J. Wilson, *Tetrahedron Lett.* **1997**, *38*, 8417–8420.

[5] J. B. Lambert, W. L. Oliver, *Tetrahedron* **1971**, *27*, 4245–4254.

[6] a) D. M. Schubert, A. D. Norman, *Inorg. Chem.* **1984**, *23*, 4130–4131; b) D. M. Schubert, P. F. Brandt, A. D. Norman, *Inorg. Chem.* **1996**, *35*, 6204–6209; c) P. F. Brandt, D. M. Schubert, A. D. Norman, *Inorg. Chem.* **1997**, *36*, 1728–1731.

[7] M. R. Douglass, T. J. Marks, *J. Am. Chem. Soc.* **2000**, *122*, 1824–1825.

[8] a) G. Baccolini, E. Mezzina, P. E. Todesco, E. Foresti, *J. Chem. Soc. Chem. Commun.* **1988**, 304–305; b) G. Baccolini, M. Beghelli, C. Boga, *Heteroat. Chem.* **1997**, *8*, 551–556; c) R. Gang Wu, E. Wasylishen, W. P. Power, G. Baccolini, *Can. J. Chem.* **1992**, *70*, 1229–1235.

[9] G. Baccolini, G. Orsolan, E. Mezzina, *Tetrahedron Lett.* **1995**, *36*, 447–450.

[10] G. Baccolini, C. Boga, U. Negri, *Synlett* **2000**, 1685–1687.

[11] For reviews on pentacoordinate and hexacoordinate phosphorus, see a) R. R. Holmes, *Pentacordinate Phosphorus Structure and Spectroscopy*, *Vols. I and II*, ACS Monograph 175, American Chemical Society, Washington, DC, **1980**; b) C. Y. Wong, D. K. Kennepohl, R. G. Cavell, *Chem. Rev.* **1996**, *96*, 1917–1951; c) R. R. Holmes, *Acc. Chem. Res.* **1998**, *31*, 535–542.

[12] 4-Methyl-2-[(5-methyl-2-sulfanylphenyl)phosphanyl]benzenethiol (**6**): 90%, colorless liquid, b.p. 110–115°C (0.5 mmHg); ^{1}H NMR (400 MHz, $CDCl_3$, TMS): $\delta = 2.23$ (s, 6H, CH_3), 4.30 (br s, 2H, exch. with D_2O, SH), 5.29 (d, 1H, $J_{PH} = 228$ Hz, PH), 6.99–7.07 (m, 2H), 7.07–7.12 (m, 2H), 7.63–7.72 ppm (m, 2H); ^{31}P NMR (161.89 MHz, $CDCl_3$, ext. 85% H_3PO_4): $\delta = -52.0$ ppm (br d, $J_{PH} = 228$ Hz). HR-MS (EI) calcd for $C_{14}H_{15}PS_2$: 278.0353, found: 278.0355.

[13] a) B. M. Trost, *Angew. Chem.* **1995**, *107*, 285–307; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 259–281; b) B. M. Trost, *Acc. Chem. Res.* **2002**, *35*, 695–705.

