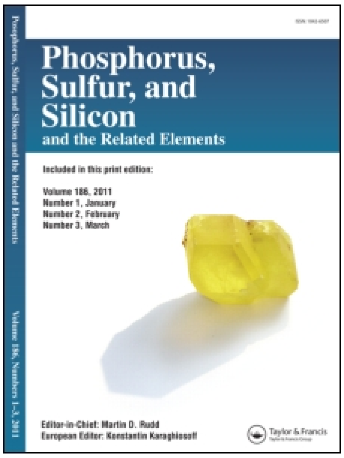


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

A SIMPLE ONE POT SYNTHESIS OF 1-CHLOROPHOSPHOLES

Herman T. Teunissen[a]; Carola B. Hansen[b]; Friedrich Bickelhaupt[a]
[a] Scheikundig Laboratorium, Vrije Universiteit, Amsterdam, The Netherlands [b] DSM Research,

To cite this Article Teunissen, Herman T. , Hansen, Carola B. and Bickelhaupt, Friedrich(1996) 'A SIMPLE ONE POT SYNTHESIS OF 1-CHLOROPHOSPHOLES', Phosphorus, Sulfur, and Silicon and the Related Elements, 118: 1, 309 — 312
To link to this Article: DOI: 10.1080/10426509608038822
URL: http://dx.doi.org/10.1080/10426509608038822

Phosphorus, Sulfur, and Silicon, 1996, Vol. 118, pp. 309–312
Reprints available directly from the publisher
Photocopying permitted by license only

Communication

A SIMPLE ONE POT SYNTHESIS OF 1-CHLOROPHOSPHOLES

HERMAN T. TEUNISSEN[a], CAROLA B. HANSEN[b] and
FRIEDRICH BICKELHAUPT[a,]*

[a]*Scheikundig Laboratorium, Vrije Universiteit, De Boelelaan 1083, NL-1081 HV Amsterdam The Netherlands;* [b]*DSM Research, P.O. Box 18, 6160 MD Geleen*

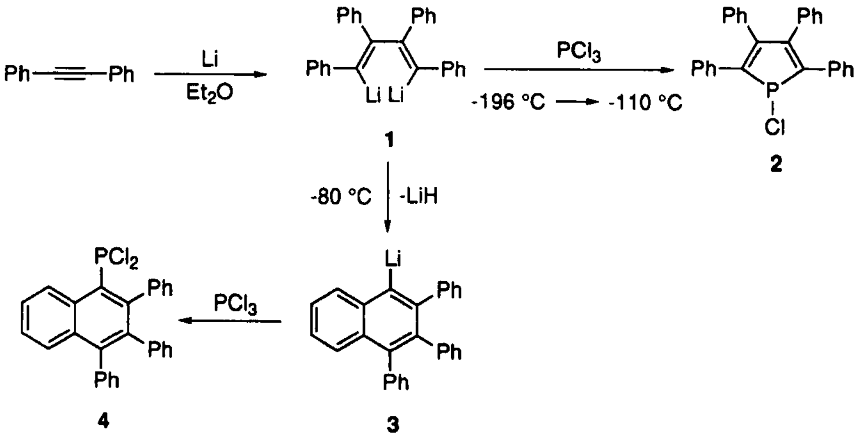
(Received 28 February 1996; In final form 10 July 1996)

The chemistry of phospholes has been extensively investigated and reviewed.[1,2] Among the numerous phosphole derivatives, however, the 1-halo functionalized systems are relatively scarce[3] and have not been systematically investigated. The synthesis of 1-halophospholes has been achieved from organozirconium intermediates,[3a,b] a 1,1′-biphosphole,[3c] a 1,4-dilithio compound,[3d] and a diazonium salt.[3e] As these syntheses involve rather complicated multistep procedures we decided to investigate a simple approach: the direct conversion of a dilithio compound with phosphorus chloride to furnish the 1-halophosphole system. Our first objective was the synthesis of 1-chloro-2,3,4,5-tetraphenylphosphole from 1,4-dilithio-1,2,3,4-tetraphenylbutadiene and phosphorus trichloride[3d] (Scheme 1).

As experimental details have not been described by Abel *et al.*[3d], we first tried the obvious synthetic strategy: dropwise addition of a solution of dilithio compound **1**[4] to a solution of phosphorus trichloride at −80°C. Unfortunately, the 1-chlorophosphole **2** was not formed. Instead, a product with $\delta(^{31}P) = 155$ ppm was obtained, to which on the basis of HRMS and ^{31}P NMR spectroscopy, the

---

*Corresponding author. Tel.: (31)-(0)20-4447479. Fax: (31)-(0)20-4447488. E-mail: bicklhpt@chem.vu.nl.

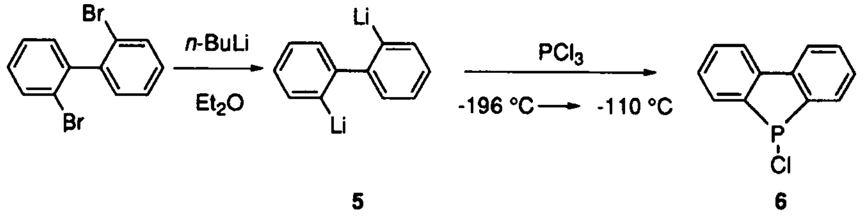


SCHEME 1

structure of **4** was tentatively assigned.[5] Compound **4** is the reaction product of phosphorus trichloride and **3**; the latter is known to be formed by rearrangement of **1**.[6]

Because of this rearrangement, we focussed on a second approach: distillation of phosphorus trichloride onto a suspension of **1** at low temperature (−196°C). After warming to −110°C and vigorous mixing, 1-chlorophosphole **2** was formed rather selectively in a preparatively satisfactory yield (57%). Analogously we prepared 5-chlorodibenzophosphole **6** from 2,2′-dilithiobiphenyl **5** and PCl_3 in high yield (77%) (Scheme 2); **6** had previously been obtained via the diazonium procedure in 6% yield.[3e]

In conclusion, we showed that the preparation of some 1-halophospholes via reaction of a 1,4-dilithio derivative with phosphorus trichloride at very low temperature is practically useful and furnishes the desired compounds in good yields.



SCHEME 2

EXPERIMENTAL

General Procedures

All oxygen and/or water sensitive reactions were carried out under dry nitrogen with oven dried glassware and oxygen free, dry solvents. THF was distilled first from NaH and finally from sodium/benzophenone. Pentane, diethyl ether and benzene were distilled from $LiAlH_4$.

NMR spectra were recorded at a Bruker AC 200 spectrometer at 200 MHz (^1H). For ^{31}P NMR spectroscopy, a Bruker WM 250 was used operating at 100.26 MHz.

The direct inlet mass spectra were measured with a Finnigan MAT 90 (Bremen, FRG), Source temperature 150°C (70 eV IP). In the mass spectra, the appropriate isotope pattern was observed.

Melting points (uncorrected) were determined with melting point equipment of Pleuger after Dr. Tottoli.

1-Chloro-2,3,4,5-tetraphenylphosphole (2)

A suspension of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene was prepared from diphenylacetylene (4.43 g, 24.9 mmol) and lithium (0.17 g, 25 mmol) in diethyl ether (25 mL).[4] The heterogeneous, dark reaction mixture was frozen by immersion into a Dewar containing liquid nitrogen (−196°C); the reaction mixture became dark green. Subsequently, phosphorus trichloride (3 mL, 34 mmol) was distilled onto the solid reaction mixture. Then, the mixture was warmed to −110°C. When it began to thaw, it was quickly homogenized with a vortex mixer. During mixing the color changed rapidly from dark green to yellow, and a voluminous yellow precipitate was formed. The reaction mixture was warmed to room temperature after which the volatile products were removed under reduced pressure. The yellow residue was washed with pentane (250 mL) and extracted with benzene (250 mL). The benzene extract was evaporated to give pure **2** (3.02 g, 7.15 mmol, yield: 57% relative to diphenylacetylene) as a yellow powder.

2: mp. 165°C (dec.); NMR (C_6D_6): $\delta(^1H)$ 6.80–7.07 (m, 16H), 7.44–7.49 (m, 4H); $\delta(^{31}P)$ 77.0; HRMS calcd for $C_{28}H_{20}{}^{35}ClP$ 422.0991, found 422.0993.

5-Chloro-dibenzo[b,d]phosphole (6)

To a cooled (0°C) solution of 2,2′-dibromobiphenyl[7] (4.27 g, 13.6 mmol) in Et_2O (80 mL), *n*-BuLi (1.6 M in hexanes, 17 mL, 27.2 mmol) was added dropwise. After complete addition the cooling bath was removed and the yellow solution was stirred at room temperature for 1 h. Then the solution was frozen with liquid nitrogen (−196°C). Subsequently, phosphorus trichloride (25 mL, 287 mmol) was distilled onto the solid reaction mixture which was then warmed to −110°C. When the reaction mixture began to thaw, it was quickly homogenized with a vortex mixer. The homogeneous solution was warmed to room temperature and a white precipitate formed. The reaction mixture was evaporated to dryness, and the residue was extracted with pentane (3 × 100 mL). The extract was evaporated to 35 mL and cooled to −20°C to give pure **6** as colorless crystals (2.29 g, 10.5 mmol, yield: 77% relative to 2,2′-dibromobiphenyl).

6: mp. 72°C (dec.);[8] NMR (C_6D_6)[9]: $\delta(^1H)$ 6.92 (dt, 2H, $^3J(HH) = 7.3$ Hz, $^4J(PH) = 3.0$ Hz, H-3,7), 7.04 (t, 2H, $^3J(HH) = 7.5$ Hz, H-2,8), 7.30 (d, 1H, $^3J(HH) = 7.6$ Hz, H-1,9) 7.53 (dd, $^3J(HH) = 7.4$ Hz, $^3J(PH) = 3.9$ Hz, H-4,6); $\delta(^{31}P)$ 69.0.

References

[1] F. Mathey, *Chem. Rev.*, **88**, 429 (1988).

[2] A.N. Hughes, in *Handbook of Organophosphorus Chemistry*, R. Engel (Ed) (M. Dekker Inc., New York 1992), Chap. 10, pp. 483–558.

[3] (a) F. Nief and L. Ricard, *J. Organomet. Chem.*, **464**, 149 (1994). (b) T. Douglas and K.H. Theopold, *Angew. Chem.*, **101**, 1394 (1988). (c) C. Charrier, H. Bonnard, F. Mathey and D. Neibecker, *J. Organomet. Chem.*, **231**, 361 (1982). (d) E.W. Abel and C. Towers, *J. Chem. Soc. Dalton Trans.*, 814 (1979). (e) G.O. Doak, L.D. Freedman and J.B. Levy, *J. Org. Chem.* **29**, 2382 (1964).

[4] A. Sekiguchi, S.S. Zigler, K.J. Haller and R. West, *Recl. Trav. Chim. Pays-Bas* **107**, 197 (1988).

[5] **4**: $\delta(^{31}P)$ 155 ppm; HRMS calcd for $C_{28}H_{19}{}^{35}Cl_2P$ 456.0601, found 456.0598.

[6] (a) J.J. Eisch, *Organometallic Synthesis* (Academic Press, New York, 1981), Vol. 2, pp. 99–100. (b) W. Schlenk and E. Bergmann, *Justus Liebigs Ann. Chem.*, **463**, 1 (1928). (c) E. Bergmann and O. Zwecker, *Justus Liebigs Ann. Chem.*, **487**, 155 (1931).

[7] H. Gilman and B.J. Gaj, *J. Org. Chem.*, **22**, 447 (1957).

[8] In the literature,[3e] **6** is described as yellow crystals of mp. 53–56°C; apparently this sample was not quite pure.

[9] The assignment is tentative and in part based on the analogy of the ^1H NMR spectrum of 5-phenyldibenzophosphole: J.H. Nelson, S. Affandi, G.A. Gray and E.C. Alyea, *Magn. Res. Chem.*, **25**, 774 (1987).