New General One-Pot Synthesis of 1-Alkoxy Cyclic Phosphine Derivatives

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Abstract: Treatment, at room temperature, of benzothiadiphosphole 1 with bis-Grignard 2, sodium alcololate and finally with S₈ afforded 1-alkoxy cyclic phosphine sulfides in good yields. In a similar manner, reactions with sodium phenylthiolate gave the corresponding 1-phenylsulfanyl cyclic phosphine derivatives.

Key words: phosphorus, heterocycles, Grignard reactions, cyclizations, 1-alkoxy cyclic phosphine sulfides

In the past years, we have reported that fused benzothiadiphosphole 1 can be easily obtained by an unexpected simple one-pot reaction by treating p-methylthioanisole with PCl₃ and AlCl₃ and separated by simple crystallization from the reaction mixture (Scheme 1). Compound 1 is an air insensitive solid; it can be stored for several years without particular precaution and then it is easy to handle. Subsequently, we found that 1 can be used as phosphorus donating reagent.

These results were explained by the presumed intervention of hypervalent phosphorus intermediates (penta- and hexacoordinate) such as A’ and A (Scheme 3) in which the ‘dibenzo-butterfly’ moiety of reagent 1, as depicted in Scheme 1, might favour their formation. In particular, we think that unstable hexacoordinate A is formed by a nucleophilic attack of RMgX on A’. Very likely such an attack is favoured by the Mg salt coordination to the sulfur atoms. In other words, in pentacoordinate intermediate A’ the coordination of Mg atom to sulfur activates the P₁ atom to undergo a nucleophilic attack. If this is true, a similar attack might occur with other nucleophilic reagents such as alcoholates to give the corresponding 1-alkoxy cyclic phosphine derivatives. It should be noted that the residue 4 of reagent 1 was inferred by GC/MS, but never isolated in the final reaction mixture. Thus, presumably it is unstable and is lost by final quenching with water.
It should be noted that compounds 5a,b,d are known but their unique reported preparation involved five different types of reaction with isolation of intermediates, which gave an overall yield of about 25%. In addition, the starting donating phosphorus reagent was 1-phenyl-3,4-dimethyl-phosphole, which has a low oxidative stability, as recently reported.6 In contrast, our one-pot synthesis exploits a very stable reagent, which is easy to prepare and easy to handle because it is air insensitive and the reaction is always carried out at room temperature with good final yields.

In conclusion, we have reported the development of a facile, mild and efficient synthesis that appears to be a general route to 5- and 6-membered cyclic sulphide s for hydrazines bearing an OR group on the phosphorus atom. At present, there is no general and facile procedure for obtaining heterocycles such as 5. Preliminary results show that this reaction, when carried out on phenyl thiocyanates, leads to the corresponding phenylsulfonyl cyclic phosphate derivatives 6a,b, which are new compounds (Scheme 5).

All manipulations involving Grignard reagents were carried out under Ar using anhydrous solvents. The solutions of Grignard reagents, when not commercially available, were prepared in THF by reacting Mg turnings with the appropriate alkyl bromide and titrated prior to use by reported methods.7 NMR spectra were recorded in CDCl3 on a Varian Gemini 300 spectrometer (at 300 MHz, 75.56 MHz and 121.47 MHz for 1H, 13C and 31P, respectively). TMS (1H), CDCl3 (77.0 ppm for 13C), or external 85% H3 PO4 (31P) were used as reference standards. IR spectra were recorded on a Perkin–Elmer 1600 FTIR spectrophotometer. Mass spectra were recorded on a VG 7070 spectrometer at an ionization voltage of 70 eV. Mps were determined with a Büchi apparatus and are uncorrected.

1-Alkoxy Cyclic Phosphines. 1-Ethoxy-1,5-phosphinane-1-thione (5c): Typical Procedure
A solution of bis-Grignard reagent 2 (n = 2, 1 mmol) in THF was added dropwise to a solution of 1 (1 mmol) in THF (30 mL), at r.t. The mixture was allowed to react for 30 min until the phosphinane ring formation was complete (or 15 min in the case of phospholane ring formation); then excess sodium ethoxide (2 mmol) was added. The reaction mixture was stirred for 4–7 h, treated with elemental sulfur (1.5 mmol) for 40 min, quenched with H2O and extracted with CH2Cl2. The residue of 1 was eliminated during the work-up. The organic layer was dried (Na2SO4) and concentrated. Flash chromatography on silica gel of the residue gave 0.146 g (82%) of 1-ethoxy-1,5-phosphinone-1-thione 5e, as an oil. The spectral data for new compounds 5e, 5f, 6a and 6b are reported.

1-Phenoxy-1,5-phospholane-1-thione (5e)
Yield: 77%; greasy solid.
Rf = 0.64 (CH2Cl2).
IR (neat): 728 (PS), 1022 (POC), 1100 (PC) cm–1.
1H NMR (CDCl3): δ = 4.14–4.00 (m, 2 H, OCH2), 2.40–1.70 (m, 10 H, CH2), 1.32 (t, 3 H, J = 6.7 Hz, CH3).
13C NMR (CDCl3): δ = 60.2 (d, J = 6 Hz, 34.2 (d, J = 6 Hz), 26.1 (d, J = 7 Hz), 23.2 (d, J = 6 Hz), 16.5 (d, J = 7 Hz).
31P NMR (CDCl3): δ = 92.3.
MS (EI): m/z (%) = 212 (M+ , 100), 119 (48).
Anal. Calcd for C7H15OPS: C, 47.17; H, 8.48. Found: C, 47.10; H, 8.40.

1-Phenoxy-1,5-phosphino-1-thione (5f)
Yield: 85%; greasy solid.
Rf = 0.6 (CH2Cl2–light petroleum, 1:1).
IR (neat): 623, 770, 1024, 1110, 1203, 1488, 1590 cm–1.
1H NMR (CDCl3): δ = 7.40–7.30 (m, 2 H), 7.24–7.13 (m, 3 H), 2.50–2.30 (m, 2 H), 2.15–1.95 (m, 6 H).
13C NMR (CDCl3): δ = 129.6, 124.8, 121.2 (d, J = 5 Hz), 34.7 (d, J = 7 Hz), 34.3 (d, J = 6 Hz).
31P NMR (CDCl3): δ = 122.1.
MS (EI): m/z (%) = 212 (M+, 100), 119 (48).
HRMS: m/z calcld for C7H15OPS: 212.0423. Found: 212.0425.

1-Phenoxy-1,5-phosphino-1-thione (5f)
Yield: 85%; greasy solid.
Rf = 0.6 (CH2Cl2–light petroleum, 1:1).
IR (neat): 621, 690, 738, 1031, 1191, 1205, 1488, 1591 cm–1.
1H NMR (CDCl3): δ = 7.38–7.29 (m, 2 H), 7.25–7.13 (m, 3 H), 2.60–2.30 (m, 2 H), 2.20–2.10 (m, 8 H).
13C NMR (CDCl3): δ = 150.6 (d, J = 10 Hz), 129.5, 124.9, 121.5 (d, J = 5 Hz), 34.3 (d, J = 6 Hz), 25.9 (d, J = 8 Hz), 23.3 (d, J = 7 Hz).
$^{31}$P NMR (CDCl$_3$): $\delta = 94.6$.

MS (EI): $m/z$ (%) = 226 (M$^+$, 100), 133 (20).

HRMS: $m/z$ calcd for C$_{11}$H$_{15}$OPS: 226.0581. Found: 226.0583.


$^1$-(Phenylsulfanyl)-1$^5$-phospholane-1-thione (6a)
Yield: 55%; greasy solid.

IR (neat): 600, 694, 750, 844, 1022, 1050, 1100, 1433, 1467 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta =$ 7.67–7.57 (m, 2 H), 7.48–7.36 (m, 3 H), 2.50–2.30 (m, 2 H), 2.30–1.70 (m, 6 H).

$^{13}$C NMR (CDCl$_3$)(selected data): $\delta =$ 135.9 (d, $J = 4$ Hz), 129.8 (d, $J = 3$ Hz), 129.3 (d, $J = 2$ Hz), 37.3 (d, $J = 52$ Hz), 25.5 (d, $J = 8$ Hz).

$^{31}$P NMR (CDCl$_3$): $\delta = 88.0$.

MS (EI): $m/z$ (%) = 228 (M$^+$, 80), 119 (100).

HRMS: $m/z$ calcd for C$_{10}$H$_{13}$PS$_2$: 228.0196. Found: 228.0191.

Anal. Calcd for C$_{10}$H$_{13}$PS$_2$: C, 52.61; H, 5.74. Found: C, 52.68; H, 5.78.

$^1$-(Phenylsulfanyl)-1$^2$-phosphinane-1-thione (6b)
Yield: 65%; greasy solid.

IR (neat): 689, 720, 745, 1071, 1122, 1271, 1456, 1539 cm$^{-1}$.

$^1$H NMR (CDCl$_3$): $\delta =$ 7.75–7.37 (m, 5 H), 2.40–1.80 (m, 4 H), 1.80–1.20 (m, 6 H).

$^{13}$C NMR (CDCl$_3$)(selected data): $\delta =$ 136.5 (d, $J = 3$ Hz), 129.8 (d, $J = 3$ Hz), 129.3 (d, $J = 2$ Hz), 34.1 (d, $J = 46$ Hz), 26.0 (d, $J = 7$ Hz), 23.1 (d, $J = 7$ Hz).

$^3$P NMR (CDCl$_3$): $\delta = 66.5$.

MS (EI): $m/z$ (%) = 242 (M$^+$, 100), 133 (93), 99 (42).


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