One-Pot Synthesis of 1-Alkenyl Derivatives of Phospholane and Phosphinane – New Classes of Compounds

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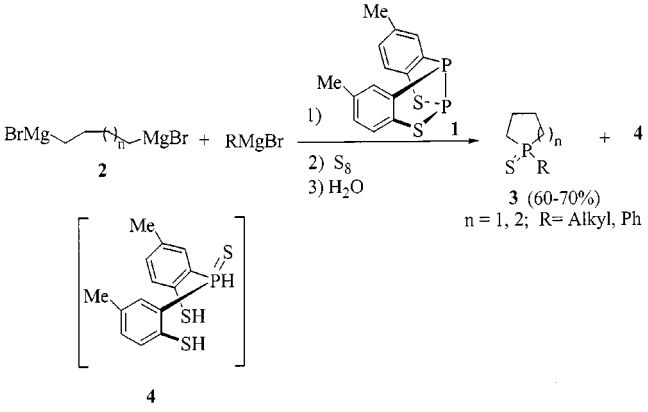
The synthesis of the title compounds at room temperature in a one-pot reaction involves the transfer of a phosphorus atom from a benzothiadiphosphole to incoming nucleophilic bis- and mono-Grignard reagents.

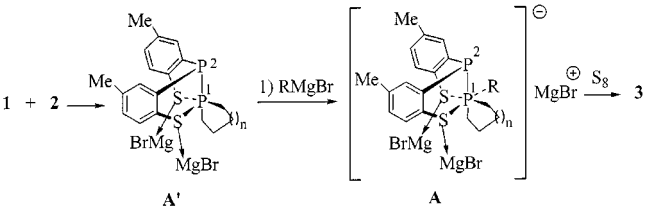
New syntheses of cyclic phosphane derivatives are of considerable current interest principally because these compounds play a central role in coordination chemistry and in homogeneous catalysis.[1] Generally, the reported syntheses of 1-substituted cyclic phosphanes are related to the interaction of several reagents with halophosphanes[2,3]or with primary and secondary phosphanes.[4–6] However, we have noted with surprise that 1-alkenyl derivatives of tri-coordinate phospholane and phosphinane are still unknown. To the best of our knowledge, the only reported 1-alkenyl derivatives of cyclophosphanes are phosphole complexes[7] and 1-vinylphosphiranes,[8] obtained by the thermolysis of phosphoranylidene phosphane complexes. Primary or secondary phosphanes (RPH_2 or R_2PH) cannot be used to obtain 1-alkenyl derivatives of cyclic phosphanes with alkenyl derivatives because of the possible reactivity of the PH group with the double bond.[6] Furthermore, the use of halophosphanes as starting products means the production of HX during the reaction, and this might react with the starting or final alkenyl derivatives. In addition, the stability of 1-alkenyl cyclophosphanes is probably very low. In other words, it is either not possible or very difficult to obtain 1-alkenyl cyclophosphane derivatives with the hitherto known procedures.

We have previously reported[9] that benzothiadiphosphole **1** is easily obtained by an unexpected domino reaction upon treating *p*-methylthioanisole with PCl_3 and $AlCl_3$, and that it can be separated by simple crystallization from the reaction mixture.[9b] Subsequently, we found that **1** can be used as a phosphorus donor.[10] Compound **1** is an air-stable solid that can be stored for several years without special precautions and is easy to handle. Recently, we reported[11] that the simultaneous addition of an equimolar mixture of a bis-Grignard **2** (n = 1, 2) and a mono-Grignard RMgBr (R = alkyl, phenyl) to an equimolar amount of **1** and treatment of the final reaction mixture with elemental sulfur, at room temperature, gave the phosphane sulfides **3** after quenching with water, (Scheme 1). We also expected the formation of compound **4**, observed by GC-MS but never isolated. This was probably missed during the final quenching with water because of its hydrolysis or solubility.



Scheme 1

These results were explained by the presumed intervention of hypervalent phosphorus intermediates (penta- and hexacoordinate)[12] such as **A′** and **A** (Scheme 2), in which the "dibenzo-butterfly" moiety of reagent **1** might favour their formation.



Scheme 2

If the above pentacoordinate intermediate **A′** were stable we assume that the reaction could also be carried out in two steps with a better control of the final products. Consequently, we realised that in the second step we could use a large variety of Grignard reagents and obtain various 1-substituted cyclophosphane derivatives. Thus, we decided to try to obtain 1-alkenyl derivatives of phospholanes and

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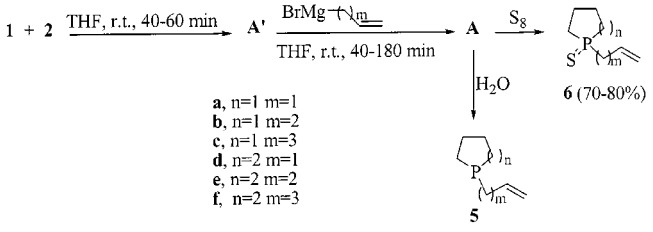
phosphinanes using Grignard reagents containing an alkenyl group in the second step in the hope that the double bond does not react with any intermediates or by-products of the reaction.

The first target of our study was to obtain information about the stability of the hypothetical intermediate **A′**. We therefore carried out a reaction in a one-pot, three-step procedure between **2** (n = 2) and **1** (as reported in Scheme 2), monitoring the progress of the reaction by ^{31}P NMR spectroscopy. A few minutes after mixing the reagents we noted the disappearance of the two doublets of **1** [δ = 88.3 (d, P_1), 65.4 (dt, P_2, $^3J_{PH}$ = 7.8 Hz), $^1J_{PP}$ = 211.5 Hz] and the concomitant appearance of two new doublets of an AB system [δ = −43.3 (dm, P_1, J_{PP} = 188 Hz); δ = −47.0 (dt, P_2 J_{PH} = 7 Hz), J_{PP} = 188 Hz)], tentatively due to the intermediate **A′**. The large P−P coupling constant indicates that intermediate **A′** again has a P−P bond; the doublet of triplets (dt) observed for P_2 indicates that this P atom is bonded to two phenyl groups, while the doublet of multiplets suggests that P_1 is bonded to alkyl groups. This intermediate **A′** is very stable. In fact, its signals remain even after several hours. Only after addition of pentylmagnesium bromide did we observe the disappearance of these signals and the appearance of new signals, which we tentatively assigned to intermediate **A** or its isomers. After the addition of S_8 we noted the disappearance of the latter signals and the appearance of a signal at δ = 38.1 corresponding to the phosphane sulfide **3** (n = 2, R = pentyl).[11]

We then tried to synthesize some 1-alkenylphospholanes and 1-alkenylphosphinanes using our phosphorus-donating reagent **1** by the addition of the two different Grignard reagents. In this manner we obtained the 1-alkenylphospholane sulfides **6a**,**b**,**c** and 1-alkenylphosphinane sulfides **6d**,**e**,**f** (70−80% yield) by addition, in the first step, of equimolar amounts of a bis-Grignard **2** (n = 1 or 2) and **1**, and, in the second step, addition of a mono-Grignard RMgBr (R = alkenyl group) followed by final treatment with S_8, always at room temperature (Scheme 3).



Scheme 3

If the reaction mixture was treated with water instead of S_8, the corresponding cyclic phosphanes **5**, which are very air-sensitive compounds, were obtained. These phosphanes **5** have a low stability in solution even under argon and thus they were analyzed only by ^{31}P NMR and by mass spectrometry. In fact, when a solution of **5** in $CDCl_3$ or THF was allowed to stand under argon for about 30 min., we noted the gradual disappearance of the ^{31}P NMR signals of **5** and the appearance of several other signals.

In conclusion, we have described a facile, one-pot preparation of 1-alkenyl cyclic phosphanes which represent the first examples of a new class of phosphorus heterocycles that are very difficult or impossible to synthesise by previously reported methods. These new compounds could be interesting ligands in asymmetric catalysis.[1]

Experimental Section

General Remarks: All manipulations involving Grignard reagents were carried out under argon using dried solvents. The solutions of Grignard reagents, when not commercially available, were prepared in THF by reacting magnesium turnings with the appropriate alkyl bromide and titrated prior to use by reported methods.[13] NMR spectra were recorded in $CDCl_3$ solutions, if not otherwise specified, on a Varian Gemini 300 spectrometer (at 300, 75.56 and 121.47 MHz for ^1H, ^{13}C and ^{31}P, respectively) using $SiMe_4$ (^1H), $CDCl_3$ (δ = 77.0 for ^{13}C) or external 85% H_3PO_4 (^{31}P) as 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. Melting points were determined with a Büchi apparatus and are uncorrected. The phosphanes **5** have a low stability in solution and thus they were analysed only by ^{31}P NMR spectroscopy and by GC-MS spectrometry. All compounds **6a**−**f** showed characteristic IR signals at 700−732 cm^{-1} (P=S) and 1634−1642 cm^{-1} (C=C) and gave either correct elemental analysis or were analyzed by high resolution mass spectrometry in the EI mode. The yields of compounds **6** are calculated on the basis of starting mono-Grignard reagent. Reagent **1** was prepared by an improved procedure based on a previously reported method.[9b]

Synthesis of [1,2,3]-Benzothiadiphosphole-[2,3b]-[1,2,3]-Benzothiadiphosphole (1): A mixture of *p*-methylthioanisole (6.73 mL, 0.05 mol) and sublimed $AlCl_3$ (3.33 g, 0.025 mol) was stirred for about 15 min. under dry nitrogen. Subsequently, PCl_3 (27.68 mL, 0.30 mol) was added to the mixture and the reaction was heated at 60−70 °C for 5−6 h with vigorous stirring. After removal of the unreacted PCl_3 by distillation the reaction mixture was quenched with a water/ice mixture then extracted with CH_2Cl_2. After evaporation of the organic solvent, crystallization of the crude product gave pure **1** (4.59 g, 60%) as white crystals (m.p.159 °C), ref.:[9a] 157−159 °C.

General Procedure for the Synthesis of Compounds 5a−f and 6a−f: A solution of bis-Grignard reagent (1 mmol) in THF was added dropwise to a solution of **1** (1 mmol) in THF (15−25 mL), at room temperature. The mixture was stirred for 15 min. to complete the phospholane ring formation, or for 90 min. in the case of phosphinane formation. A solution of mono-Grignard reagent (1 mmol) in THF was then slowly added dropwise. The reaction mixture was stirred for 4 h at room temperature and then treated with a large excess of elemental sulfur for 40 min., quenched with water and extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate and concentrated in vacuo. The phosphane sulfides **6** were purified by flash chromatography on a silica gel column.

Treatment of the above reaction mixture with water only gave the corresponding phosphanes **5**.

1-Allylphospholane (5a): ^{31}P NMR (120.75 MHz, THF): δ = −26.4. − GC-MS (70 eV, EI): *m/z* (%) = 128 (47) [M^+], 100 (97), 85 (64), 71 (34), 57 (100), 41 (72).

1-Allyl-1λ⁵-phospholane-1-thione (6a): Greasy solid, 70% yield; R_f = 0.50 (dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.40−2.30 (m, 8 H, cyclic CH_2), 2.76−2.92 (m, 2 H, CH_2CH=), 5.15−5.40 (m, 2 H, CH_2=), 5.80−6.05 (m, 1 H, CH=). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 26.1 (d, *J* = 6.0 Hz), 32.2 (d, *J* = 52.0 Hz), 40.2 (d, *J* = 44.0 Hz), 120.6 (d, *J* = 12.0 Hz), 128.4 (d, *J* = 9.0 Hz). − ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = 62.5. − MS (70 eV, EI): *m*/*z* (%) = 160 (67) [M^+], 119 (86), 85 (32), 63 (100), 57 (19), 41 (32). − HRMS calcd. for $C_7H_{13}PS$: 160.0476; found 160.0471. − $C_7H_{13}PS$: calcd. C 52.48, H 8.18; found C 52.53, H 8.19.

1-(3-Butenyl)phospholane (5b): ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = −25.5. − GC-MS (70 eV, EI): *m*/*z* (%) = 142 (42) [M^+], 141 (100), 114 (96), 101 (39), 86 (40), 73 (38), 57 (33).

1-(3-Butenyl)-1λ⁵-phospholane-1-thione (6b): Greasy solid, 72% yield; R_F = 0.48 (dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70−2.30 (m, 10 H, aliphatic and cyclic CH_2), 2.35−2.60 (m, 2 H, CH_2CH=), 5.00−5.22 (m, 2 H, CH_2=), 5.78−6.00 (m, 1 H, CH=). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 25.9 (d, *J* = 6.0 Hz), 27.0 (d, *J* = 3.0 Hz), 33.3 (d, *J* = 52.0 Hz), 33.7 (d, *J* = 46.0 Hz), 115.8 (s), 136.8 (d, *J* = 15.0 Hz). − ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = 64.6. − MS (70 eV, EI): *m*/*z* (%) = 174 (66) [M^+], 120 (100), 92 (13), 86 (36), 63 (26)]. − HRMS calcd. for $C_8H_{15}PS$: 174.0632; found 174.0630. − $C_8H_{15}PS$: calcd. C 55.15, H 8.68; found C 55.20, H 8.71.

1-(4-Pentenyl)phospholane (5c): ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = −26.0. − GC-MS (70 eV, EI): *m*/*z* (%) = 156 (18) [M^+], 155 (32), 141 (23), 128 (51), 114 (10), 100 (100), 87 (31), 74 (46), 59 (27).

1-(4-Pentenyl)-1λ⁵-phospholane-1-thione (6c): Greasy solid, 71% yield; R_f = 0.41 (dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$) δ = 1.50−2.60 (m, 14 H, aliphatic and cyclic CH_2), 4.90−5.25 (m, 2 H, CH_2C=), 5.65−5.90 (m, 1 H, CH=). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 22.2 (d, *J* = 3.0 Hz), 25.9 (d, *J* = 6.0 Hz), 32.8 (d, *J* = 47.0 Hz), 33.1 (d, *J* = 51.0 Hz), 34.2 (d, *J* = 15.0 Hz), 115.8 (s), 137.0 (s). − ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = 64.5. − MS (70 eV, EI): *m*/*z* (%) =188 (41) [M^+], 120 (100), 106 (23), 86 (24), 63 (55), 41 (39)]. − HRMS calcd. for $C_9H_{17}PS$: 188.0789; found 188.0781. − $C_9H_{17}PS$: calcd. C 57.42, H 9.10; found C 57.50, H 9.12.

1-Allylphosphinane (5d): ^{31}P NMR (120.75 MHz, THF): δ = −42.5. − GC-MS (70 eV, EI): *m*/*z* (%) = 142 (40) [M^+], 114 (100), 99 (36), 88 (43), 73 (88), 57 (55), 41 (71).

1-Allyl-1λ⁵-phosphinane-1-thione (6d): White solid m.p. 65−66 °C (from diethyl ether), 70% yield; R_f = 0.48 (dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.50−2.30 (m, 10 H, cyclic CH_2), 2.75−2.90 (m, 2 H, CH_2−CH=), 5.20−5.40 (m, 2 H, CH_2=), 5.85−6.10 (m, 1 H, CH=). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.8 (d, *J* = 6.0 Hz), 26.2 (d, *J* = 6.0 Hz), 30.1 (d, *J* = 49.0 Hz), 37.2 (d, *J* = 49.0 Hz), 120.5 (d, *J* = 12.0 Hz), 127.6 (d, *J* = 9.0 Hz). − ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = 36.2. − MS (70 eV, EI): *m*/*z* (%) = 174 (93) [M^+], 133 (86), 99 (81), 63 (100), 41 (78). − HRMS calcd. for $C_8H_{15}PS$: 174.0632; found 174.0629. − $C_8H_{15}PS$: calcd. C 55.15, H 8.68; found C 55.21, H 8.70.

1-(3-Butenyl)phosphinane (5e): ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = −41.5. − GC-MS (70 eV, EI): *m*/*z* (%) = 156 (49) [M^+], 155 (100), 141 (16), 128 (61), 115 (35), 100 (90), 87 (22), 73 (27).

1-(3-Butenyl)-1λ⁵-phosphinane-1-thione (6e): White solid m.p.65−66 °C (from diethyl ether), 80% yield; R_f = 0.35 (dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.70−2.50 (m, 12 H, aliphatic and cyclic CH_2), 2.60−2.82 (m, 2 H, CH_2CH=), 5.23−5.45 (m, 2 H, CH_2=), 6.05−6.25 (m 1 H, CH=). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.9 (d, *J* = 6.0 Hz), 25.8 (d, *J* = 2.0 Hz), 26.4 (d, *J* = 6.0 Hz), 29.9 (d, *J* = 50.0 Hz), 31.0 (d, *J* = 48.0 Hz), 115.7 (s), 137.2 (d, *J* = 15.0 Hz). − ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = 38.8. − MS (70 eV, EI): *m*/*z* (%) = 188 (80) [M^+], 155 (3), 134 (100), 100 (15). − HRMS calcd. for $C_9H_{17}PS$: 188.0789; found 188.0780. − $C_9H_{17}PS$: calcd. C 57.42, H 9.10; found C 57.51, H 9.13.

1-(4-Pentenyl)phosphinane (5f): ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = −31.0. − GC-MS (70 eV, EI): *m*/*z* (%) = 170 (32) [M^+], 169 (44), 155 (43), 142 (40), 128 (27), 114 (100), 100 (42), 88 (60), 73 (35), 62 (30).

1-(4-Pentenyl)-1λ⁵-phosphinane-1-thione (6f): White solid m.p. 43−44 °C (from diethyl ether), 78% yield; R_f = 0.26 (dichloromethane). − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20−2.35 (m, 16 H, aliphatic and cyclic CH_2), 4.90−5.20 (m, 2 H, CH_2=), 5.65−5.90 (m, 1 H, CH=). − ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 20.9 (d, *J* = 3.0 Hz), 21.9 (d, *J* = 6.0 Hz), 26.4 (d, *J* = 6.0 Hz), 30.1 (d, *J* = 51.0 Hz), 30.9 (d, *J* = 48.0 Hz), 34.5 (d, *J* = 16.0 Hz), 115.9 (s), 137.3 (s). − ^{31}P NMR (120.75 MHz, $CDCl_3$): δ = 38.5. − MS (70 eV, EI): *m*/*z* (%) = 202, [M^+], 134, 106, 73, 63, 41. − HRMS calcd. for $C_{10}H_{19}PS$: 202.0945; found 202.0942. − $C_{10}H_{19}PS$: calcd. C 59.37, H 9.47; found C 59.46, H 9.50.

Acknowledgments

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