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Addition of secondary phosphines to a vinyl ether of diacetone-D-glucose: a new approach to optically active phosphines and their derivatives

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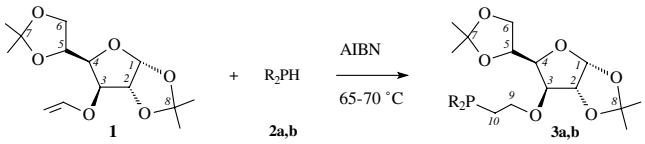
Abstract—Secondary phosphines react readily with a vinyl ether of diacetone-D-glucose under radical initiation conditions to give, in high yield, anti-Markovnikov adducts, diorganyl{2-[3-*O*-(1,2:5,6-di-*O*-isopropylidene)-D-glucofuranosyloxy]ethyl}phosphines, which oxidize almost quantitatively upon reacting with air oxygen or elemental sulfur to form the corresponding optically active phosphine oxides or sulfides.

Optically active phosphines and their phosphoryl and thiophosphoryl derivatives are widely applied in asymmetric synthesis as efficient chiral ligands for transition metal catalysts.[1] Recently, interest has been shown in chiral phosphine ligands with carbon-based chirality, which are easier to prepare, whereas their transition metal complexes are more efficient in asymmetric catalysis.[2] Therefore, the search for new convenient routes to the synthesis of such prospective phosphorus-containing chiral ligands remains an important synthetic task. One approach to this task involves the use of optically active starting materials, which can be easily derived from enantiomerically pure natural compounds.[3] The addition of secondary phosphines to alkenes[4] (including functional alkenes, such as alkyl vinyl ethers,[5] alkyl vinyl chalcogenides,[6] vinyl pyrroles,[7] vinyl pyridines,[8] etc.) represents a straightforward atom-economic ('green') approach to C–P bond formation.

Herein we describe the synthesis of novel optically active polyfunctional tertiary phosphines and their phosphoryl and thiophosphoryl derivatives, based on the hydrophosphination of chiral vinyl ether **1** (readily prepared from diacetone-D-glucose and acetylene under elevated[9] or atmospheric[10] pressure as well as by transvinylation of diacetone-D-glucose with an excess of isobutyl vinyl ether[11]) with readily available secondary phosphines **2a**,**b**.[12] These phosphines add to the vinyl ether **1** regiospecifically in the presence of azobisisobutyronitrile (AIBN) at 65–70 °C to form the corresponding optically active tertiary diorganyl{2-[3-*O*-(1,2:5,6-di-*O*-isopropylidene)-D-glucofuranosyloxy]ethyl}phosphines **3a**,**b** in high yield (Scheme 1, Table 1).[13]

Upon reacting with air, oxygen or elemental sulfur, the phosphines **3a**,**b** were quantitatively oxidized to the



1 **2a,b** **3a,b**

Scheme 1.

Keywords: Secondary phosphines; Vinyl ether of diacetone-D-glucose; Addition; Radical initiation; Optically active tertiary phosphines; Phosphine oxides and sulfides.
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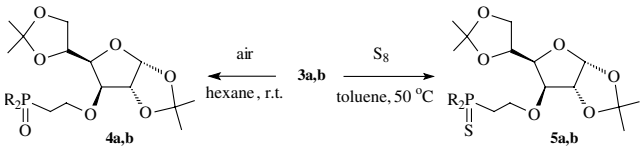
Table 1. Synthesis of phosphines **3**[a]

Entry	Reactants (mmol)	Time (h)	Product yield[b] (%)
1	**1**, 1.90	**2a** (R = *n*-Bu), 1.90	80	**3a**, 74
2	**1**, 2.86	**2b** (R = $PhCH_2CH_2$), 2.86	90	**3b**, 90

[a] All experiments were carried out under argon.
[b] Isolated yields.



Scheme 2.

Table 2. Synthesis of phosphine oxides **4** and phosphine sulfides **5**

Entry	Reactants (mmol)	Temperature (°C)	Time (h)	Solvent (mL)	Product yield[a] (%)
1	**3a**, 0.35	Air O_2, excess	20–22	15	Hexane, 2	**4a**, 98
2	**3a**, 6.00	S_8, 9.0	50	3	Toluene, 4	**5a**, 98
3	**3b**, 0.55	Air O_2, excess	20–22	20	Hexane, 2	**4b**, 98
4	**3b**, 0.97	S_8, 1.39	50	3	Toluene, 5	**5b**, 85

[a] Isolated yields.

optically active phosphine oxides **4a**,**b**[14] or phosphine sulfides **5a**,**b**,[15] respectively (Scheme 2, Table 2).

In summary, the atom-economic addition of secondary phosphines to the optically active vinyl ether **1**, which is readily available from glucose, represents a convenient approach to the synthesis of optically active sugar-based tertiary phosphines and their derivatives. The polydent phosphines, phosphine oxides, and phosphine sulfides thus obtained, containing protected hydroxy functionalized tetrahydrofuran and dioxolane moieties, are promising chelating ligands for metal complex catalysts for asymmetric synthesis.

Acknowledgements

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10. Vinyl ether **1** was prepared by vinylation of diacetone-D-glucose with acetylene in KOH/DMSO system under atmospheric pressure (flow system, 105–115 °C). Selected analytical data for **1**: bp 127–130 °C (3 mmHg), n_D^{20} 1.4628, optical rotation $[\alpha]_D^{22}$ −26.7 (*c* 2.0, CCl_4); lit.[9]: bp 115–116 °C (1.5 mmHg), n_D^{20} 1.468; lit.[11]: bp 68 °C (0.008 mmHg), n_D^{20} 1.4593, $[\alpha]_D^{20}$ −30.5 (*c* 1.0, $CHCl_3$). IR (film, cm^{-1}): 507, 531, 632, 694, 790 (shld), 837, 887, 936, 953 (δ, CH=, CH_2=), 1008, 1032 (shld), 1060, 1105 (shld), 1150, 1177, 1203 (ν, COC, COCOC), 1245, 1283, 1315, 1323, 1351 (shld), 1366, 1380, 1441, 1477 (δ, CH=, CH_2, CH), 1610, 1631, (ν, C=C), 2887, 2927, 2980 (ν, Me, CH_2), 3060, 3110 (ν, CH=, CH_2=). ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.30 (s, 3H, Me), 1.33 (s, 3H, Me), 1.42 (s, 3H, Me), 1.50 (s, 3H, Me), 4.01 (dd, 1H, ^2J = 8.6 Hz, $^3J_{5,6}$ = 5.5 Hz, H-6), 4.08 (dd, 1H, ^2J = 8.6 Hz, $^3J_{5,6}$ = 6.1 Hz, H-6), 4.14 (dd, 1H, $^3J_{cis}$ = 6.7 Hz, ^2J = 2.2 Hz, =CH_{cis}), 4.18 (dd, 1H, $^3J_{4,5}$ = 7.7 Hz, $^3J_{3,4}$ = 3.0 Hz, H-4), 4.30 (dt, 1H, $^3J_{4,5}$ = 7.7 Hz, $^3J_{5,6}$ = 5.7 Hz, H-5), 4.34 (*d* 1H, $^3J_{3,4}$ = 3.0 Hz, H-3), 4.38 (dd, 1H, $^3J_{trans}$ = 14.3 Hz, ^2J = 2.2 Hz, =CH_{trans}), 4.58 (d, 1H, $^3J_{1,2}$ = 3.7 Hz, H-2), 5.87 (d, 1H, $^3J_{1,2}$ = 3.7 Hz, H-1), 6.38 (dd, 1H, $^3J_{trans}$ = 14.3 Hz, $^3J_{cis}$ = 6.7 Hz, =CHO). ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.17, 26.10, 26.61, 26.71 (4Me), 66.93 (C-6), 72.03 (C-5), 80.28 (C-3,4), 82.01 (C-2), 89.31 (=CH_2), 105.02 (C-1), 108.98 and 111.76 (C-7,8), 149.94 (=CHO).
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13. General procedure for the preparation of **3**: An equimolar mixture of secondary phosphine and vinyl ether of diacetone-D-glucose was heated at 65–70 °C in the presence of AIBN (0.5–1.5 wt% of the reactants' mass) in a sealed ampoule. The crude product, a viscous undistillable liquid, was purified by column chromatography on Al_2O_3 (diethyl ether) to give the phosphine **3** (Table 1).

Compound **3a**: colorless oil, $[\alpha]_D^{26}$ −15.6 (*c* 1.5, EtOH). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.90 (t, 6H, ^3J = 6.4 Hz, Me, 1.30 (s, 3H, Me), 1.35 (s, 3H, Me), 1.38 (m, 10H, $CH_2CH_2CH_2P$), 1.43 (s, 3H, Me), 1.48 (m, 5H, C-10, Me), 1.66–1.70 (*m*, 2H, CH_2P), 3.68–3.72 (m, 2H, H-9), 3.86 (d, 1H, $^3J_{3,4}$ = 3.0 Hz, H-3), 3.96 (dd, 1H, ^2J = 8.3 Hz, $^3J_{5,6}$ = 5.5 Hz, H-6), 4.06 (dd, 1H, ^2J = 8.3 Hz, $^3J_{5,6}$ = 5.8 Hz, H-6), 4.09 (dd, 1H, $^3J_{4,5}$ = 6.8 Hz, $^3J_{3,4}$ = 3.0 Hz, H-4), 4.12–4.16 (m, 1H, H-5), 4.51 (d, 1H, $^3J_{1,2}$ = 3.1 Hz, H-2), 5.92 (d, 1H, H-1). ^{13}C NMR (100.69 MHz): δ 13.85 (Me), 24.50 (d, $^3J_{P,C}$ = 10.7 Hz, CH_2Me), 25.23, 25.50, 26.24 (3Me), 26.56 (d, $^1J_{P,C}$ = 12.0 Hz, C-10), 26.90 (Me), 27.10 (d, $^2J_{P,C}$ = 11.1 Hz, CH_2CH_2P), 27.17 (d, $^2J_{P,C}$ = 11.5 Hz, CH_2CH_2P), 27.98 (d, $^1J_{P,C}$ = 14.4 Hz, CH_2P), 28.02 (d, $^1J_{P,C}$ = 14.6 Hz, CH_2P), 67.62 (C-6), 68.91 (d, $^2J_{P,C}$ = 21.0 Hz, C-9), 72.57 (C-5), 81.21 (C-3), 82.27 (C-4), 85.19 (C-2), 105.34 (C-1), 109.54 and 111.80 (C-7,8). ^{31}P NMR (161.98 MHz): δ −33.94. Elemental analysis: Calcd for $C_{22}H_{41}O_6P$ (432.53): C, 61.09; H, 9.55; P, 7.16%. Found: C, 61.05; H, 9.67; P, 7.39%.

Compound **3b**: colorless oil, $[\alpha]_D^{26}$ −7.1 (*c* 1.0, EtOH); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.31 (s, 6H, Me), 1.43 (s, 3H, Me), 1.53 (s, 3H, Me), 1.73–1.81(m, 6H, H-10, CH_2P), 2.71–2.86 (m, 4H, CH_2Ph), 3.64–3.77 (m, 2H, H-9), 3.84 (d, 1H, $^3J_{3,4}$ = 2.7 Hz, H-3), 3.99 (dd, 1H, ^2J = 8.8 Hz, $^3J_{5,6}$ = 5.9 Hz, H-6), 4.06 (dd, 1H, ^2J = 8.8 Hz, $^3J_{5,6}$ = 5.9 Hz, H-6), 4.09 (dd, 1H, $^3J_{4,5}$ = 7.7 Hz, $^3J_{3,4}$ = 2.7 Hz, H-4), 4.34 (dd, 1H, $^3J_{4,5}$ = 7.7 Hz, $^3J_{5,6}$ = 5.9 Hz, H-5), 4.53 (d, 1H, $^3J_{1,2}$ = 3.7 Hz, H-2), 5.83 (d, 1H, H-1), 7.17–7.30 (m, 10H, Ph). ^{13}C NMR (100.69 MHz): δ 23.44, 25.17, 25.23, 25.48 (4Me), 27.67 (d, $^1J_{P,C}$ = 14.9 Hz, C-10), 29.38 (d, $^1J_{P,C}$ = 13.2, CH_2P) 29.47 (d, $^1J_{P,C}$ = 13.6 Hz, CH_2P), 32.23 (d, $^2J_{P,C}$ = 14.2 Hz, CH_2Ph), 67.55 (C-6), 68.66 (d, $^2J_{P,C}$ = 19.7 Hz, C-9), 72.47 (C-5), 81.18 (C-4), 82.18 (C-3), 82.75 (C-2), 105.26 (C-1), 109.02 and 111.80 (C-7,8), 126.08 (C-*p*), 128.13 (C-*o*), 128.52 (C-*m*), 142.69 (d, $^3J_{P,C}$ = 10.4 Hz, C-*i*), 142.73 (d, $^3J_{P,C}$ = 10.3 Hz, C-*i*). ^{31}P NMR (161.98 MHz): δ −31.18. Elemental analysis: Calcd for $C_{30}H_{41}O_6P$ (528.62): C, 68.17; H, 7.82; P, 5.86%. Found: C, 68.39; H, 7.73; P, 5.65%.

14. General procedure for the preparation of **4**: A solution of phosphine **3** in hexane was stirred at rt under air or O_2 atmosphere. After reaction completion, as indicated by TLC, the solvent was removed under reduced pressure to afford phosphine oxide **4** (Table 2).

Compound **4a**: colorless oil, $[\alpha]_D^{26}$ −12.2 (*c* 0.5, CCl_4); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.89 (t, 6H, ^3J = 7.2 Hz, Me, 1.21–1.31 (m, 4H, CH_2Me), 1.28 (s, 3H, Me), 1.32–1.39 (m, 2H, CH_2CH_2P), 1.33 (s, 3H, Me), 1.41 (s, 3H, Me), 1.46 (s, 3H, Me), 1.47–1.58 (m, 3H, CH_2CH_2P), 1.63–1.71 (m, 2H, CH_2P), 1.94–2.00 (m, 1H, CH_2P), 2.22–2.28 (m, 2H, H-10), 3.79–3.85 (m, 2H, H-9), 3.95 (dd, 1H, ^2J = 8.6 Hz, $^3J_{5,6}$ = 5.3 Hz, H-6), 4.03 (m, 1H, H-3), 4.12 (dd, 1H, ^2J = 8.6 Hz, $^3J_{5,6}$ = 6.3 Hz, H-6), 4.28–4.33 (m, 2H, H-4,5), 4.49 (d, 1H, $^3J_{1,2}$ = 3.6 Hz, H-2), 5.90 (d, 1H, H-1). ^{13}C NMR (100.69 MHz): δ 13.54 (Me), 23.56 (d, $^3J_{P,C}$ = 3.8 Hz, CH_2Me), 23.78 (d, $^3J_{P,C}$ = 3.8 Hz, CH_2Me), 24.15 (d, $^2J_{P,C}$ = 13.9 Hz, CH_2CH_2P), 24.17 (d, $^2J_{P,C}$ = 14.8 Hz, CH_2CH_2P), 25.07, 26.10, 26.68, 26.77 (4Me), 28.28 (d, $^1J_{P,C}$ = 66.1 Hz, C-10), 28.34 (d, $^1J_{P,C}$ = 63.9 Hz, CH_2P), 28.80 (d, $^1J_{P,C}$ = 65.4 Hz, CH_2P), 63.78 (d, $^2J_{P,C}$ = 3.2 Hz, C-9), 67.53 (C-6), 73.35 (C-5), 75.02 (C-4), 81.06 (C-3), 85.02 (C-2), 105.19 (C-1), 109.52 and 111.72 (C-7,8). ^{31}P NMR (161.98 MHz): δ 48.39. Elemental analysis: Calcd for $C_{22}H_{41}O_7P$ (448.53): C, 58.91; H, 9.21; P, 6.91%. Found: C, 58.76; H, 9.43; P, 6.78%.

Compound **4b**: colorless oil, $[\alpha]_D^{26}$ −1.9 (*c* 4.0, CCl_4); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.25 (s, 3H, Me), 1.29 (s, 3H, Me), 1.38 (s, 3H, Me), 1.48 (s, 3H, Me), 2.0–2.12 (m, 6H, H-10, CH_2P), 2.80–2.98 (*m*, 4H, CH_2Ph), 3.80–3.85 (m, 2H, H-9), 3.96–4.15 (m, 4H, H-3,4,6), 4.17–4.21 (m, 1H, H-5), 4.61 (d, 1H, $^3J_{1,2}$ = 3.2 Hz, H-2), 5.78 (d, 1H, H-1), 7.16–7.28 (m, 10H, Ph). ^{13}C NMR (100.69 MHz): δ 25.44, 26.23, 26.83, 26.98 (4Me), 27.81 (d, $^2J_{P,C}$ = 18.4 Hz, CH_2Ph), 27.83 (d, $^2J_{P,C}$ = 17.7 Hz, CH_2Ph), 28.89 (d, $^1J_{P,C}$ = 63.0 Hz, C-10), 30.82 (d, $^1J_{P,C}$ = 62.5 Hz, CH_2P), 31.35 (d, $^1J_{P,C}$ = 62.5 Hz, CH_2P), 63.92 (d, $^2J_{P,C}$ = 2.8 Hz, C-9), 67.55 (C-6), 72.35 (C-5), 81.02 (C-4), 82.22 (C-3), 82.52 (C-2), 105.26 (C-1), 109.29 and 111.92 (C-7,8), 126.08 (C-*p*), 128.06 and 128.12 (C-*o*), 128.83 (C-*m*), 140.91 (d, $^3J_{P,C}$ = 13.7 Hz, C-*i*). ^{31}P NMR (161.98 MHz): δ 46.18. Elemental analysis: Calcd for $C_{30}H_{41}O_7P$ (544.62): C, 66.16; H, 7.59; P, 5.69%. Found: C, 66.22; H, 7.32; P, 5.85%.

15. General procedure for the preparation of **5**: A mixture of phosphine **3** and elemental sulfur in toluene was heated at 50 °C upon stirring under argon for 3 h. The crude product, a viscous undistillable liquid, was purified by column chromatography on Al_2O_3 (hexane) to give the phosphine sulfide **5** (Table 2).

Compound **5a**: yellow solid, mp 98–99 °C (hexane), $[\alpha]_D^{26}$ −7.1 (*c* 1.0, EtOH); ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 0.90–0.95 (m, 6H, Me), 1.25 (s, 3H, Me), 1.31 (s, 3H, Me), 1.34 (s, 3H, Me), 1.41 (m, 4H, CH_2Me), 1.48 (s, 3H, Me), 1.54–1.58 (m, 4H, CH_2CH_2P), 1.81–1.86 (m, 6H, H-10, CH_2P), 3.80–3.91 (m, 2H, H-9), 3.98 (dd, 1H, ^2J = 8.5 Hz, $^3J_{5,6}$ = 5.5 Hz, H-6), 4.03–4.07 (m, 2H, H-3,6), 4.08–4.14 (m, 1H, H-4), 4.18–4.25 (m, 1H, H-5), 4.72 (d, 1H, $^3J_{1,2}$ = 3.3 Hz, H-2), 5.82 (d, 1H, H-1). ^{13}C NMR (100.69 MHz): δ = 13.58 (Me), 23.78 (CH_2Me), 24.03 (CH_2Me), 24.50 (d, $^2J_{P,C}$ = 16.2 Hz, CH_2CH_2P), 24.57 (d, $^2J_{P,C}$ = 16.2 Hz, CH_2CH_2P), 25.42, 26.14, 26.72, 26.83 (4Me), 30.48 (d, $^1J_{P,C}$ = 49.9 Hz, C-10), 31.30 (d, $^1J_{P,C}$ = 51.4 Hz, CH_2P), 32.38 (d, $^1J_{P,C}$ = 50.4 Hz, CH_2P), 64.26 (d, $^2J_{P,C}$ = 2.9 Hz, C-9), 67.35 (C-6), 72.26 (C-5), 80.79 (C-4), 81.90 (C-3), 82.09 (C-2), 105.17 (C-1), 109.06 and 111.74 (C-7,8). ^{31}P NMR (161.98 MHz): δ 46.73. Elemental analysis: Calcd for $C_{22}H_{41}O_6PS$ (464.60): C, 56.88; H, 8.89; P, 6.67; S, 6.90%. Found: C, 56.98; H, 8.69; P, 6.51; S, 6.72%.

Compound **5b**: yellow solid, mp 87–88 °C (hexane), $[\alpha]_D^{26}$ −25.7 (*c* 1.0, CCl_4). ^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.26 (s, 3H, Me), 1.29 (s, 3H, Me), 1.38 (s, 3H, Me), 1.47 (s, 3H, Me), 1.96–2.17 (m, 6H, H-10, CH_2P), 2.89–2.94 (m, 4H, CH_2Ph), 3.82–3.90 (m, 2H, H-9), 3.94–4.02 (m, 3H, H-3,6), 4.05–4.12 (m, 1H, H-4), 4.14–4.20 (m, 1H, H-5), 4.73 (d, 1H, $^3J_{1,2}$ = 3.3 Hz, H-2), 5.78 (d, 1H, H-1), 7.16–7.28 (m, 10H, Ph).^{13}C NMR (100.69 MHz): δ 25.11, 26.14, 26.71, 26.86 (4Me), 28.60 (d, $^2J_{P,C}$ = 27.0 Hz, CH_2Ph), 30.90 (d, $^1J_{P,C}$ = 49.7 Hz, C-10), 33.31 (d, $^1J_{P,C}$ = 48.4 Hz, CH_2P), 34.19 (d, $^1J_{P,C}$ = 47.5 Hz, CH_2P), 64.23 (d, $^2J_{P,C}$ = 3.6 Hz, C-9), 67.41 (C-6), 72.18 (C-5), 80.88 (C-4), 81.93 (C-3), 82.20 (C-2), 105.14 (C-1), 109.15 and 111.80 (C-7,8), 126.51 and 126.54 (C-*p*), 128.06 and 128.18 (C-*o*), 128.68 (C-*m*), 140.52 (d, $^3J_{P,C}$ = 14.6 Hz, C-*i*). ^{31}P NMR (161.98 MHz): δ 48.03. Elemental analysis: Calcd for $C_{30}H_{41}O_6PS$ (560.69): C, 64.27; H, 7.37; P, 5.52; S, 5.72%. Found: C, 64.45; H, 7.55; P, 5.35; S, 5.58%.