Efficient method for the synthesis of 1,2,3,8-tetrahydroindeno[2,1-*b*]phospholes and their derivatives

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An efficient method for the synthesis of 1,2,3,8-tetrahydroindeno[2,1-*b*]phospholes was developed. The method is based on the direct reduction of the corresponding quasiphosphonium salts with $LiAlH_4$.

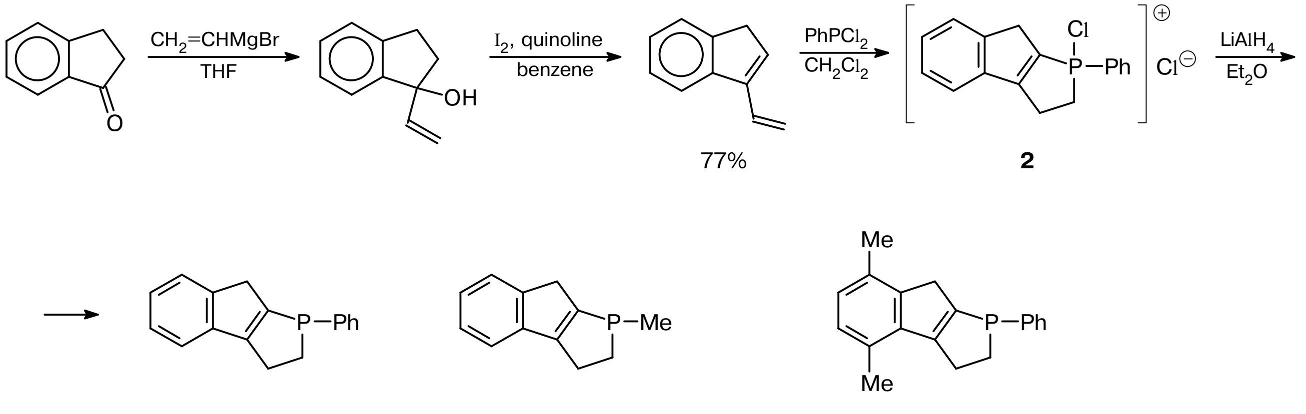
Key words: 1,2,3,8-tetrahydroindeno[2,1-*b*]phospholes, quasiphosphonium salts, 1,2,3,8-tetrahydro-1λ^5-indeno[2,1-*b*]phosphol-1-ones, 1,2,3,8-tetrahydro-1λ^5-indeno[2,1-*b*]phosphole-1-thiones.

Cyclopentadienyl- and indenylphosphines can be used as promising cyclopentadienyl ligands for the preparation of transition metal complexes. Cyclopentadienyl- and 1-indenylphosphines have been obtained and extensively studied,[1,2] which is not the case of 2-indenylphosphines. The only known compound, which may be considered as 2-indenylphosphine, is 1-phenyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phosphole (**1**).

However, the published method[3] for the synthesis of compound **1** is very complicated and ineffective; its seven steps afford the final product only in 8.7% yield.

We developed a simpler procedure for the preparation of indenophosphole **1** from 3-vinylindene, which had been previously used as the starting material in the synthesis of the target compound.[3] 3-Vinylindene was obtained according to the known procedure.[4] The yield of the product was significantly increased by purifying it with the use of column chromatography instead of the molecular distillation proposed earlier.[4] Then 3-vinylindene was made to react with $PhPCl_2$. The resulting quasiphosphonium salt **2** is unstable in air and poorly soluble in available deuterated solvents; because of this, the salt cannot be characterized by NMR spectroscopy. Because this product already has the same skeleton as that of the target compound, except for the environment of the P atom, the adduct should be reduced, *e.g.*, with lithium aluminum hydride. 1-Methyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phosphole (**3**) and 4,7-dimethyl-1-phenyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phosphole (**4**) were synthesized in a similar manner (Scheme 1).

Scheme 1



1 (61%)

3 (43%)
(from 3-vinylindene)

4 (28%)
(from 4,7-dimethyl-3-vinylindene)

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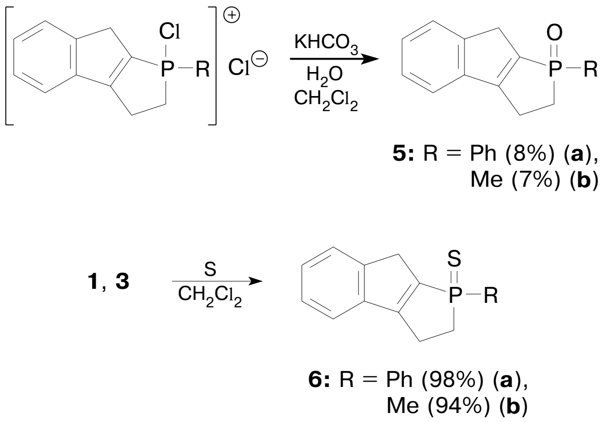
The target compound **1** was obtained in high overall yield (61% from 3-vinylindene). Thus, the use of this method under laboratory conditions allows one to synthesize compound **1** in tens grams (it should be emphasized that the substance is temperature-resistant and virtually not oxidized when isolated in air).

Although the method for the preparation of compounds **3** and **4** is also very simple, their overall yields are lower than the yield of compound **1**. Unlike crystalline compound **1**, phospholes **3** and **4** are yellow and pale rose oils, respectively. Compound **3** is difficult to isolate because of being easily oxidized by atmospheric oxygen, as distinct from products **1** and **4**.

The target products were additionally characterized when their derivatives with phosphoryl and thiophosphoryl groups were synthesized. Thus, the hydrolysis of intermediate quasiphosphonium salts gave crystalline 2,3-dihydro-8*H*,λ^5-indeno[2,1-*b*]phosphol-1-ones (**5a**) and (**5b**) in low yield. 2,3-Dihydro-8*H*,1λ^5-indeno[2,1-*b*]-phosphol-1-thiones (**6a**) and (**6b**) were synthesized by treating compounds **1** and **3** with finely dispersed sulfur in CH_2Cl_2 (Scheme 2).

Scheme 2



The thiones are thick oils which are spectrally pure according to ^{1}H and ^{31}P NMR data.

Hence, the simple and efficient method for the preparation of 2,3-dihydroindeno[2,1-*b*]phospholes and their derivatives was elaborated.

Experimental

All experiments were carried out in an atmosphere of argon. The solvents were purified as described in Ref. 5. Ethereal solvents were kept and distilled over KOH and then over sodium benzophenone ketyl; CH_2Cl_2 was washed successively with water, conc. H_2SO_4, and water to a neutral reaction, dried over $CaCl_2$, and distilled over P_2O_5; and hexane was distilled over an Na/K eutectic. Lancaster, Merck, and Fluka reagents were used. ^{1}H and ^{13}C NMR spectra were recorded on Varian VXR-400 and Varian VXR-300 instruments. J_{C-P} values were measured for the ^{13}C NMR spectra. The elemental composition of all compounds was determined on a Carlo Erba automated C,H,N,O analyzer at the Montell research center (Ferrara, Italy). The content of sulfur was determined on an Anton Paar Sulfuranalyser S analyzer (Austria).

3-Vinylindene. 1-Indanone (42.24 g, 0.32 mol) was added at 0 °C to a solution of CH_2=CHMgBr (obtained from Mg (14.4 g, 0.6 mol) and CH_2=CHBr (43 mL, 0.6 mol) according to the known procedure^{6}) in THF (330 mL). After stirring for 12 h, water (10 mL) and 10% NH_4Cl (200 mL) were added to the reaction mixture cooled to 0 °C. The products were extracted with Et_2O (3×100 mL). The combined organic fractions were washed with water and dried over $MgSO_4$, and the solvents were removed at a reduced pressure. Quinoline (1.44 mL), I_2 (20 mg), and benzene (380 mL) were added, and the resulting mixture was refluxed in a flask equipped with a Dean—Stark adapter for 1.5 h, washed with water, and dried over $MgSO_4$. The solvent was removed at a reduced pressure. The resulting reddish brown oil was purified by column chromatography on silica gel 60 with hexane : CH_2Cl_2 (4 : 1) as an eluent. The solvent was removed at a reduced pressure to give a reddish brown oil (35.1 g, 77%). The chromatographically pure product was used at the next stage without additional purification.

4,7-Dimethyl-3-vinylindene (7). The compound was synthesized as described for 3-vinylindene from Mg (6.72 g, 0.28 mol), vinyl bromide (20 mL, 0.28 mol), THF (157 mL), 4,7-dimethylindan-1-one (24 g, 0.15 mol) prepared according to the known procedure,^{7} quinoline (0.85 mL), a crystal of iodine, and benzene (226 mL). Compound **5** is a yellowish red oil, yield 14.65 g (57.3%). ^{1}H NMR ($CDCl_3$), δ: 2.4, 2.7 (both s, each 3 H, C(4)Me, C(7)Me); 3.3 (br.s, 2 H, CH_2); 5.35, 5.7 (both dd, 2 H, =CH_2); 6.33 (m, 1 H, CH=); 6.6 (br.s, 1 H, CH= Cp rings); 6.9—7.2 (m, 2 H, Ar). Found (%): C, 91.68; H, 8.32. $C_{13}H_{14}$. Calculated (%): C, 91.71; H, 8.29.

1-Chloro-1-phenyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phospholium chloride (2). $PhPCl_2$ (14.4 mL, 0.106 mol) was added with stirring to a solution of 3-vinylindene (15 g, 0.106 mol) in CH_2Cl_2 (30 mL). The reaction mixture was heated for 1 h and left without stirring for 10 days. The precipitate that formed was filtered off in an atmosphere of argon, washed with hexane, and dried at 0.01 Torr to give adduct **2** (23.44 g, 69%) as a finely crystalline light brown powder. The product was used at the next stage without additional purification.

1-Chloro-1-methyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phospholium chloride (8). The compound was synthesized as described for compound **2** (except that the reaction mixture was heated for 4 h) from $MePCl_2$ (8.25 mL, 0.092 mol), and 3-vinylindene (13 g, 0.092 mol). The product is a finely crystalline light yellow powder, yield 12.67 g (53%).

1-Chloro-4,7-dimethyl-1-phenyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phospholium chloride (9). $PhPCl_2$ (2.98 mL, 0.022 mol) was added with stirring to a solution of compound **7** (3.7 g, 0.022 mol) in CH_2Cl_2 (50 mL). The reaction mixture was heated for 8 h. The resulting suspension was left at ~20 °C for 10 days. The precipitate that formed was filtered off in an atmosphere of argon, washed with hexane, and dried in a high vacuum to give finely crystalline beige salt **9** (3.21 g, 42.24%).

1-Phenyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phosphole (1). Salt **2** (18.85 g, 0.059 mol) was added at −40 °C to a suspension of $LiAlH_4$ (2.24 g, 0.059 mol) in Et_2O (100 mL). Then the cooling was removed, and stirring was continued for 1 day. Water (100 mL) was added in small portions to the reaction mixture. After gas evolution ceased, an additional portion of water (100 mL) was added. The organic phase was separated, and the products were extracted with Et_2O (3×100 mL). The combined organic extracts were washed with water and dried over $MgSO_4$. The solvent was removed at a reduced pressure, and the residue was dried at 0.01 Torr to give compound **1** (13.06 g, 89%) as pale yellow crystals, m.p. 63—64 °C (*cf.* Ref. 3: m.p. 80 °C). ^{1}H NMR (C_6D_6), δ: 2.1—2.18, 2.4—2.6, 2.68—2.78 (all m, 4 H, CH_2 of P ring); 3.2 (AB, 2 H, CH_2 of Cp ring, ^2J = 40 Hz); 6.9—7.4 (m, 9 H, Ar). ^{31}P NMR (C_6D_6), δ: −13.1 (s). ^{13}C NMR ($CDCl_3$), δ: 26.79 (d, CH_2, ^2J = 5.0 Hz); 31.16 (br.s, CH_2); 36.67 (d, CH_2P, $^1J_{PC}$ = 15.7 Hz); 119.88, 124.17, 125.15, 127.78 (C(4)—C(7)); 128.37 (d, C_m, $C_{m'}$, $^3J_{PC}$ = 7.0 Hz); 128.97 (br.s, C_p); 132.12 (d, C_o, $C_{o'}$, $^2J_{PC}$ = 18.7 Hz); 133.86 (d, J_{PC} = 10.9 Hz); 139.8 (d, J_{PC} = 17 Hz); 141.33, 150.0 (d, J_{PC} = 8 Hz); 150.1 (d, J_{PC} = 4.2 Hz), C_i, C(3a), C(3b), C(7a), C(8a). Found (%): C, 81.54; H, 6.06. $C_{17}H_{15}P$. Calculated (%): C, 81.58; H, 6.04.

1-Methyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phosphole (3). Compound **3** was synthesized as described for compound **1** (except that stirring was continued for 3 days) from salt **8** (10.38 g, 0.04 mol) and $LiAlH_4$ (1.52 g, 0.04 mol) in Et_2O (50 mL). The product was a yellow oil, yield 6.05 g (80.4%). ^{1}H NMR ($CDCl_3$), δ: 1.23 (d, 3 H, Me, J = 2.2 Hz); 2.16—2.24, 2.58—2.72, 2.82—2.94, 3.03—3.18 (all m, 4 H, CH_2 of P ring); 3.43 (AB, 2 H, CH_2 of Cp ring, ^2J = 3.4 Hz); 7.24 (td, 1 H); 7.29—7.37 (m, 2 H); 7.5 (d, 1 H) (ABCD, Ar). ^{31}P NMR ($CDCl_3$), δ: −32.74 (s). ^{13}C NMR ($CDCl_3$), δ: 13.8 (d, CH_3, $^1J_{PC}$ = 20.7 Hz); 26.36 (d, CH_2, $^2J_{PC}$ = 5.9 Hz); 29.86 (d, CH_2, $^2J_{PC}$ = 8.8 Hz); 36.11 (d, CH_2P, $^1J_{PC}$ = 16.0 Hz); 119.3, 123.8, 124.3, 126.1 (C(4)—C(7)); 141.64 (d, J_{PC} = 3.8 Hz); 149.4 (d, J_{PC} = 14.7 Hz); 149.64 (d, J_{PC} = 3.8 Hz); 155.9 (d, J_{PC} = 6.0 Hz), (C(3a), C(3b), C(7a), C(8a). Found (%): C, 76.61; H, 6.94. $C_{12}H_{13}P$. Calculated (%): C, 76.58; H, 6.96.

4,7-Dimethyl-1-phenyl-2,3-dihydro-8*H*-indeno[2,1-*b*]phosphole (4). Compound **4** was synthesized as described for compound **1** from salt **9** (3.21 g, 9.2 mmol) and $LiAlH_4$ (0.35 g, 9.2 mmol) in Et_2O (50 mL). Compound **4** is a rose oil, yield 1.67 g (65.23%). ^{1}H NMR (C_6D_6), δ: 2.04, 2.32 (both s, each 3 H, C(4)Me, C(7)Me); 2.4—2.8 (m, 4 H, CH_2 of P ring); 3.04 (AB, 2 H, CH_2 of Cp ring, ^2J = 8 Hz); 6.86, 6.96 (both d, 2 H, Ar, J = 8 Hz); 7.07—7.1, 7.12—7.16, 7.43—7.48 (all m, 5 H, Ph). ^{31}P NMR (C_6D_6), δ: −18.76 (s). Found (%): C, 81.94; H, 6.91. $C_{19}H_{19}P$. Calculated (%): C, 81.99; H, 6.88.

1-Phenyl-2,3-dihydro-8*H*,1λ^5-indeno[2,1-*b*]phosphol-1-one (5a). A 10% aqueous solution of $KHCO_3$ (20 mL) was added to a solution of compound **2** (0.77 g, 0.0024 mol) in CH_2Cl_2 (30 mL). The reaction mixture was stirred for 1 h. The products were extracted with CH_2Cl_2 (3×20 mL), and the combined organic phases were washed with water and dried over $MgSO_4$. The solvent was removed at a reduced pressure, and the residue was recrystallized from heptane to give compound **5a** (0.05 g, 7.8%) as yellow crystals, m.p. 162 °C. ^{1}H NMR ($CDCl_3$), δ: 2.6—2.76, 2.96—3.08, 3.18—3.28 (all m, 4 H, CH_2 of P ring); 3.5 (AB, 2 H, CH_2 of Cp ring, ^2J = 22.8 Hz); 7.3—7.7 (m, 9 H, Ar). ^{31}P NMR ($CDCl_3$), δ: 44.84 (s). ^{13}C NMR ($CDCl_3$), δ: 23.24 (d, CH_2, $^2J_{PC}$ = 2.7 Hz); 31.75 (d, CH_2P, $^1J_{PC}$ = 74.1 Hz); 34.43 (d, CH_2, ^2J = 10.6 Hz); 120.9, 124.92 (d, $^4J_{PC}$ = 1.5 Hz); 126.75 (d, $^4J_{PC}$ = 1.5 Hz); 127.66 (C(4)—C(7)); 128.58 (d, C_o, $C_{o'}$, $^2J_{PC}$ = 12.2 Hz); 130.45 (d, C_m, $C_{m'}$, $^3J_{PC}$ = 10.6 Hz); 131.59 (d, C_P, $^4J_{PC}$ = 2.9 Hz); 133.76 (d, J = 101.1 Hz); 138.39, 140.02, 149.99 (d, J_{PC} = 8 Hz); 166.95 (d, J_{PC} = 35.6 Hz), C_i, C(3a), C(3b), C(7a), C(8a). Found (%): C, 76.71; H, 5.67; O, 6.02. $C_{17}H_{15}OP$. Calculated (%): C, 76.68; H, 5.68; O, 6.01.

1-Methyl-2,3-dihydro-8*H*,1λ^5-indeno[2,1-*b*]phosphol-1-one (5b). Compound **5b** was synthesized as described for compound **5a** from salt **8** (12.78 g, 0.049 mol) in CH_2Cl_2 (60 mL). Compound **5b** is a pale yellow crystalline substance, yield 0.72 g (7.2%), m.p. 114 °C. ^{1}H NMR ($CDCl_3$), δ: 1.7 (d, 3 H, Me, J = 13.2 Hz); 2.46—2.54, 2.8—2.92, 3.04—3.16 (all m, 4 H, CH_2 of P ring); 3.49 (AB, 2 H, CH_2 of Cp ring, ^2J = 22.85 Hz); 7.31—7.53 (m, 4 H, Ar). ^{31}P NMR ($CDCl_3$), δ: 48.07 (s). ^{13}C NMR ($CDCl_3$), δ: 17.62 (d, CH_3, $^1J_{PC}$ = 71 Hz); 22.85 (CH_2); 30.44 (d, CH_2P, $^1J_{PC}$ = 72.5 Hz); 34.37 (d, CH_2, $^2J_{PC}$ = 10.85 Hz); 120.76, 124.82, 126.71, 127.47 (C(4)—C(7)); 139.2, 140.2, 149.4 (d, J_{PC} = 7.5 Hz); 164.4 (d, J_{PC} = 35.1 Hz), C(3a), C(3b), C(7a), C(8a). Found (%): C, 70.56; H, 6.43; O, 7.82. $C_{12}H_{13}OP$. Calculated (%): C, 70.58; H, 6.42; O, 7.83.

1-Phenyl-2,3-dihydro-8*H*,1λ^5-indeno[2,1-*b*]phosphole-1-thione (6a). Sulfur (0.79 g, 0.024 mol) was added to a solution of compound **1** (5 g, 0.02 mol) in CH_2Cl_2 (100 mL). the reaction mixture was stirred for 2 h and then filtered. The filtrate was concentrated at a reduced pressure to give compound **6a** (5.5 g, 97.5%) as a thick oil. ^{1}H NMR (C_6D_6), δ: 3.9—4.2 (m, 4 H, CH_2 of P ring); 4.68 (AB, 2 H, CH_2 of Cp ring, ^2J = 22.7 Hz); 8.57—9.45 (m, 9 H, Ar). ^{31}P NMR (C_6D_6), δ: 46.88 (s). ^{13}C NMR (C_6D_6), δ: 24.43 (CH_2); 33.72 (d, CH_2, $^2J_{PC}$ = 11.3 Hz); 39.29 (d, CH_2P, $^1J_{PC}$ = 59.2 Hz); 120.97, 125.13, 126.79, 127.31 (C(4)—C(7)); 128.6 (d, C_o, $C_{o'}$, $^2J_{PC}$ = 12.3 Hz); 131.14 (C_p); 131.23 (d, C_m, $C_{m'}$, $^3J_{PC}$ = 4.1 Hz); 135.19 (d, J_{PC} = 77.4 Hz); 140.35, 141.24, 150.14 (d, $^2J_{PC}$ = 7.9 Hz); 163.64 (d, J_{PC} = 31.9 Hz) C_i, C(3a), C(3b), C(7a), C(8a). Found (%): C, 72.30; H, 5.36; S, 11.38. $C_{17}H_{15}PS$. Calculated (%): C, 72.32; H, 5.35; S, 11.36.

1-Methyl-1,2,3,8-tetrahydro-1λ^5-indeno[2,1-*b*]phosphole-1-thione (6b). The compound was synthesized as described for compound **6a** from phosphole **3** (2 g, 0.011 mol) in CH_2Cl_2 (100 mL) and sulfur (0.42 g, 0.013 mol). The product is a thick oil. Yield 2.2 g (94%). ^{1}H NMR ($CDCl_3$), δ: 2.05 (d, 3 H, Me, J = 13.2 Hz); 2.71—2.83, 2.87—2.96, 2.97—3.08, 3.14—3.24 (all m, 4 H, CH_2 of P ring); 3.61 (AB, 2 H, CH_2 of Cp ring, ^2J = 22.8 Hz); 7.35—7.56 (m, 4 H, Ar). ^{31}P NMR ($CDCl_3$), δ: 45.88 (s). ^{13}C NMR ($CDCl_3$), δ: 23.48 (d, CH_3, $^1J_{PC}$ = 54.2 Hz); 24.25 (CH_2); 33.75 (d, CH_2, $^2J_{PC}$ = 11.6 Hz); 36.89 (d, CH_2P, $^1J_{PC}$ = 58.1 Hz); 120.78, 124.81, 126.76, 127.28 (C(4)—C(7)); 139.68, 140.53, 149.3 (d, J = 7.7 Hz); 161.92 (d, J_{PC} = 32.2 Hz), C(3a), C(3b), C(7a), C(8a). Found (%): C, 65.45; H, 5.94; S, 14.53. $C_{12}H_{13}PS$. Calculated (%): C, 65.43; H, 5.95; S, 14.55.

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