Phosphorylation of diphenylacetylene with phosphorus pentachloride

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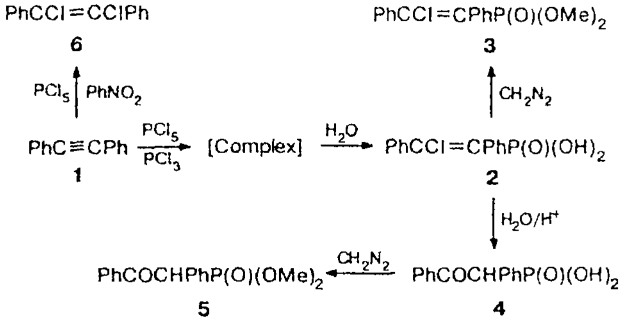
Earlier,[1] it has been reported that symmetrically substituted diarylacetylenes cannot be phosphorylated with phosphorus pentachloride. We found that tolan (**1**) reacts with PCl_5 in the presence of PCl_3 as a solvent. After quenching of the reaction mixture with water, 1,2-diphenyl-2-chloroethenylphosphonic acid (**2**) is formed, which is transformed into dimethyl phosphonate **3** under the action of CH_2N_2. Compound **2** was converted into 1-benzoyl-1-phenylmethylphosphonic acid (**4**) by acid hydrolysis and characterized as dimethyl ester (**5**). The reaction of PCl_5 with compound **1** in nitrobenzene leads to (*E*)-1,2-dichlorostilbene (**6**) in a small yield (13%).



^1H NMR spectra were recorded on a Bruker WH-250 spectrometer ($CDCl_3$) with Me_4Si as the internal standard. IR spectra were obtained on a Specord 75-IR instrument (solutions in CCl_4). Mass spectra (EI, 75 eV) were measured on an LKB 9000S instrument (direct inlet). Melting points were determined on a Boetius stage.

1,2-Diphenyl-2-chloroethenylphosphonic acid (2). A mixture of diphenylacetylene (**1**) (1.5 g, 8.4 mmol), PCl_5 (1.75 g, 8.4 mmol), and PCl_3 (5 mL, 23.1 mmol) was heated at 110—120 °C for 10 h and then kept at -20 °C for 12 h. The crystals of compound **2** that formed were separated and washed with hexane. Yield 20%, m.p. 169—171 °C (EtOH). Found (%): C, 56.64; H, 4.59; P, 11.0. $C_{14}H_{12}ClO_3P$. Calculated (%): C, 57.06; H, 4.10; P, 10.51. IR, ν/cm^{-1}: 2700—1800, 1600, 1000 (P—O—H); 1605, 1590, 1566 (Ph, C=C).

***O,O*-Dimethyl 2-chloro-1,2-diphenylethenylphosphonate (3).** A solution of CH_2N_2 in Et_2O obtained according to the known procedure[2] was added to acid **2** (1.5 g, 5.1 mmol) until nitrogen ceased to evolve. The ether was evaporated to give compound **3**. Yield 1.53 g (93%), m.p. 80 °C. Found (%): C, 58.75; H, 5.08; P, 9.98. $C_{16}H_{16}ClO_3P$. Calculated (%): C, 59.55; H, 5.00; P, 9.60. ^1H NMR, δ: 3.33, 3.72 (both d, 6 H, P—OCH_3, *J* = 11.0 Hz). MS, *m/z*: 322, 324 [M$^+$] (intensity ratio 3 : 1).

1-Benzoyl-1-phenylmethylphosphonic acid (4). A mixture of acid **2** (7.4 g, 25.1 mmol) and conc. H_2SO_4 (24.5 g) was stirred at 30 °C for 4 h (until HCl ceased to evolve). The reaction mixture was poured into ice, and the precipitate of compound **4** was separated off and washed with water. Yield 4.2 g (60%), m.p. 186—188 °C (EtOH). Found (%): C, 59.91; H, 4.38; P, 11.11. $C_{14}H_{13}O_4P$. Calculated (%): C, 60.88; H, 4.74; P, 11.21. IR, ν/cm^{-1}: 2700—2300 (P—O—H); 1670 (C=O); 1595 (Ph).

***O,O*-Dimethyl 1-benzoyl-1-phenylmethylphosphonate (5)** was obtained by analogy with compound **3** from acid **4** (3.0 g, 10.9 mmol). Yield 2.9 g (88%), m.p. 100 °C (ether). Found (%): C, 61.89; H, 5.06; P, 10.06. $C_{16}H_{17}O_4P$. Calculated (%): C, 63.16; H, 5.63; P, 10.18. IR, ν/cm^{-1}: 1680 (C=O); 1595 (Ph); 1240 (P=O); 1033 (P—O—C). ^1H NMR, δ: 3.70 and 3.78 (both d, 6 H, P—OCH_3, *J* = 11.0 Hz); 5.35 (d, 1 H, *J* = 22.0 Hz); 7.25—8.00 (m, 10 H, H arom.). MS, *m/z*: 304 [M$^+$].

(*E*)-1,2-Dichlorostilbene (6). A mixture of diphenylacetylene (**1**) (1.08 g, 6.1 mmol), PCl_5 (2.49 g, 12.0 mmol), and nitrobenzene (5 mL) was refluxed at 145 °C for 12 h. On cooling, hexane (10 mL) and water (10 mL) were added. The organic layer was separated and concentrated to give dichlorostilbene **6** (0.2 g, 13%), m.p. 152—153 °C (hexane). Literature data[3]: m.p. 147—148 °C. MS, *m/z* (I_{rel} (%)): 248 (100), 250 (63), 252 [M$^+$] (11).

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