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**LETTERS
TO THE EDITOR**

Photochemical Chlorophosphination of Phenylacetylene

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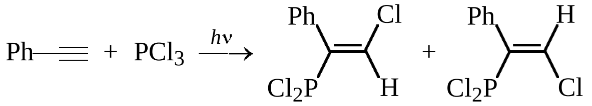
It is known that under UV irradiation phosphorus tribromide adds across multiple bonds to form the corresponding P(III) adducts [1–3]. However, PCl_3 does not add under these conditions. Although study by chemically induced dynamic nuclear polarization did reveal formation of products upon irradiation of a mixture of phenylacetylene with PCl_3, the reaction products were not isolated [2]. Addition products were isolated only when the reaction was induced by γ-irradiation [4] or sensitized with PBr_3 [3]. Addition of PCl_3 to alkylthiochloroacetylene under UV irradiation was reported in [5].

We found that under irradiation with an immersion mercury lamp PCl_3 regiospecifically and with a high regioselectivity adds to phenylacetylene to form 1-phenyl-2-chlorovinyldichlorophosphine (isomer ratio *E* : *Z* 97 : 3).



I **II**

The reaction does not occur without UV irradiation. Compound **I** was isolated and oxidized to the corresponding phosphonyl dichloride; the physicochemical parameters of the latter agree with published data [6].

The structure of the products was proved by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy.

1-Phenyl-2-chlorovinyldichlorophosphine (I, II). Phenylacetylene (40 g) was added dropwise with stirring over a period of 1 h at 20–40°C to 345.4 g of PCl_3 irradiated with an immersion mercury UV lamp. After adding the whole amount of phenylacetylene, the mixture was irradiated for an additional 1 h. Then unchanged PCl_3 and phenylacetylene were distilled off, and the residue was distilled in a vacuum. A fraction (40.7 g) boiling at 100–105°C (1 mm Hg) was obtained; it contained, according to the ^{31}P NMR spectrum, 97% *E* isomer **I** and 3% *Z* isomer **II**. *E* Isomer **I** was isolated with a yield of 37.7 g (39% based on phenylacetylene); bp 103°C (1 mm Hg), mp 26°C.

***E*-1-Phenyl-2-chlorovinyldichlorophosphine (I).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.5 m (5H), 7.32 d (1H, $^3J_{PH}$ 10.81 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 145.65 d (C^1, $^1J_{CP}$ 65.02 Hz), 131.61 d (C^2, $^2J_{CP}$ 89.48 Hz), 131.15 d (C^4, $^2J_{CP}$ 4.58 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 152.48 d ($^3J_{PH}$ 10.81 Hz).

***Z*-1-Phenyl-2-chlorovinyldichlorophosphine (II).** ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 7.5 m (5H), 6.86 d (1H, $^3J_{PH}$ 14.61 Hz). ^{31}P NMR spectrum ($CDCl_3$), δ_P, ppm: 148.23 d ($^3J_{PH}$ 14.61 Hz).

The ^{1}H, ^{13}C, and ^{31}P NMR spectra were taken with a Bruker C-200 spectrometer, working frequencies 200.132, 50.327, and 81.026 MHz, respectively. The chemical shifts are given relative to internal TMS (^{1}H, ^{13}C) and external 85% H_3PO_4 (^{31}P).

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