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A NOVEL SYNTHESIS OF TETRAPHENYLDIPHOSPHINE

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Calcium carbide has been found to undergo smooth reaction with diphenylchlorophosphine forming tetraphenyldiphosphine, calcium chloride and very surprisingly elemental carbon.

$$CaC_2 + 2(C_6H_5)_2PCl \rightarrow 2C + (C_6H_5)_2PP(C_6H_5)_2 + CaCl_2$$

As an example of this method, diphenylchlorophosphine, $(C_6H_5)_2PCl$, is vacuum distilled and the fraction boiling at 134-136°, 2-2.5mm, $n_d^{21.5}$ 1.6364 used in the reaction. Under an atmosphere of argon 3.3g 15mmole of this material are added to 0.32g 5.0mmole of calcium carbide of 99.9% purity (Research Inorganics/Organics Co., Inc., Sun Valley, California, USA). The reaction is carried out in a 25ml bulb sealed to approximately 10mm glass tubing. This apparatus in turn is connected to a conventional high vacuum system. The reaction is heated to 150° under autogeneous pressure, with stirring. Almost immediately the mixture is observed to darken, through formation of elemental carbon. After approximately 20 hours no further change is observed. Unreacted diphenylchlorophosphine is distilled out of the reaction bulb. Tetraphenyldiphosphine can then be sublimed into the upper portion of the glass apparatus as a white solid. The material is further purified by first washing with dry ether and then recrystallizing from toluene solution after filtering to remove carbon. All operations were carried out under an argon atmosphere.

The compound was verified by melting point 118°, lit. 120.5 (1) and the infrared spectrum which agreed with the reported spectrum. (1,2) The observed low melting point is attributed to the presence of trace amounts of oxygenated material, tetraphenyldiphosphine mono and/or dioxide. The presence of the compound was further substantiated by dissolving it in toluene and subsequent reaction with oxygen to form tetraphenyldiphosphine dioxide or with sulfur to form tetraphenyldiphosphine disulfide. The infrared spectra of these compounds agreed exactly with the reported spectra. (1) The dioxide was observed to melt at 168-169° (1) and the disulfide melted at 170-171°, lit. 168.5°. (1) Elemental analyses for these compounds were in excellent agreement with the formulas. The mass spectra of these materials exhibited a parent ion and fragmentation pattern consistent with the observed compounds. Yield of dioxide and disulfide were both approximately 50% based on calcium carbide introduced and assuming the above equation.

The available evidence suggests that calcium carbide functions as a reducing agent under unusually mild conditions apparently forming a free radical intermediate which leads to the observed product.

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