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THE REACTION OF DIPHENYLPHOSPHINE OXIDE WITH ACETIC ANHYDRIDE IN THE PRESENCE OF PYRIDINE

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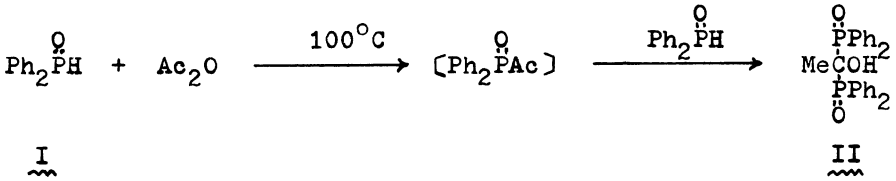
A new method for the formation of the phosphorus-phosphorus bond was discovered, that is, the reaction of diphenylphosphine oxide and acetic anhydride in the presence of pyridine afforded tetraphenyldiphosphine monoxide in a good yield.

It was stated[1] that the reaction of diphenylphosphine oxide (I) with acetic anhydride at 100°C led to 1,2-bis(diphenylphosphinyl)ethanol (II).



This paper will describe that the product obtained in the presence of pyridine at room temperature was mainly tetraphenyldiphosphine monoxide (III).

A solution of 5.0 g (0.0025 mol) of I and 10 g (0.01 mol) of acetic anhydride in 25 ml of pyridine was left to stand for 3 days at room temperature under nitrogen to give crystalline precipitates (3.1 g, 65% yield) of III and the successive crops (0.9 g, 19% yield) were obtained from the filtrate of the reaction mixture. The product was identified as III by elemental analysis, the IR spectrum, and properties in agreement with those reported.[2] Repetition of recrystallization of III from toluene gave needles of tetraphenyldiphosphine dioxide (IV) by air-oxidation. The structure was identified as IV by elemental analysis and the IR spectrum in agreement with that reported.[3]

The PMR spectrum of the reaction mixture changed with the reaction time; at the beginning of the reaction, the absorption of P-H proton and Ac_2O protons appeared as a doublet (τ 5.75, $J_{P,H}$ 439 Hz) and a singlet (τ 7.86), respectively, and after 24 hours, the absorption of P-H proton disappeared and the absorption of Ac_2O protons decreased, while the absorption of methyl protons of pyridine-acetic acid salt (V) appeared as a singlet (τ 7.93). The PMR spectrum of solution of diphenylphosphinous chloride and sodium acetate in pyridine showed the absorption of methyl protons of acetoxydiphenylphosphine (VI)[4] (τ 7.96, $J_{P,H}$ 1.2 Hz, doublet) and the small absorption of sodium acetate (τ 7.59, singlet). On the addition of I in the solution,

the absorption of methyl protons of VI disappeared immediately and the absorption of methyl protons V appeared.

The reaction may proceed by the initial formation of VI which then reacts further with I to yield III as follows.

$$\underset{\text{I}}{Ph_2\overset{O}{\overset{\|}{P}}H} + Ac_2O \xrightarrow[\text{slow}]{\text{pyridine}} \underset{\text{VI}}{[Ph_2POAc]} + \text{pyridine}\cdot\text{AcOH}$$

$$[Ph_2POAc] + \underset{}{Ph_2\overset{O}{\overset{\|}{P}}H} \xrightarrow[\text{fast}]{\text{pyridine}} \underset{\text{III}}{Ph_2P\text{-}\overset{O}{\overset{\|}{P}}Ph_2} + \text{pyridine}\cdot\text{AcOH}$$

Further experimental works are in progress and the results will be described in the forthcoming paper.

References

1) R.S. Davidson, R.A. Sheldon, and S. Trippett, J. Chem. Soc.(C), 1968, 1700.
2) J. McKechnie, D.S. Payne, and W. Sim, J. Chem. Soc., 1965, 3500.
3) W. Kuchen and H. Buchwal, Chem. Ber., 91, 2871 (1958).
4) The reverse one of the reaction has been reported:[5]

$$(RO)_2POAc + AcOH \longrightarrow (RO)_2\overset{O}{\overset{\|}{P}}H + Ac_2O$$

5) E.E. Nifantév and I.V. Fursenko, Zh. Obshch. Khim., 38, 1295 (1968). Chem. Abstr. 69, 58786 (1969).

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