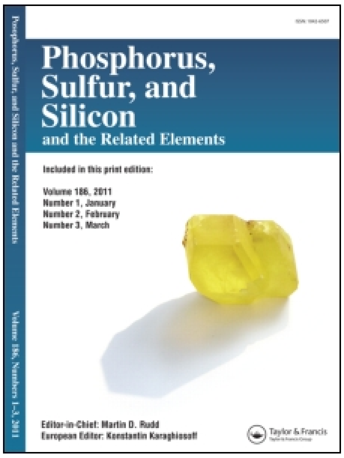

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THE REACTION OF DIPHENYLPHOSPHINE OXIDE WITH DIPHENYLPHOSPHINOUS CHLORIDE IN THE ABSENCE OF BASE

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Diphenylphosphinous chloride (**1**) and diphenylphosphine oxide (**2**) (2 mol. equivalent) react to form diphenylphosphinic acid (**4**), together with tetraphenyldiphosphine (**5**) (at 80°C), or its hydrochloride (**6**) (at 20°C), as the only products.

INTRODUCTION

In a recent study of the reaction of diphenylphosphinous chloride (**1**) with acetic acid,[1] a key step was suggested to be the reaction of (**1**) with diphenylphosphine oxide (**2**). This reaction has been reported to yield tetraphenyldiphosphine oxide (**3**), when carried out in the presence of base.[2] In order to confirm that (**3**) was formed in our reaction conditions, we looked at the uncatalysed reaction of diphenylphosphinous chloride (**1**) with diphenylphosphine oxide (**2**), but were surprised to find that the ^{31}P n.m.r. of the product showed only singlet absorptions (^1H decoupled). We report here our results on this system.

$$\underset{(\mathbf{1})}{Ph_2PCl} + \underset{(\mathbf{2})}{Ph_2P(O)H} \xrightarrow{\text{base}} \underset{(\mathbf{3})}{Ph_2P(O)PPh_2}$$

RESULTS AND DISCUSSION

When diphenylphosphinous chloride (**1**) and diphenylphosphine oxide (**2**) are stirred, either with or without solvent, with rigorous exclusion of both oxygen and moisture, a copious precipitate of diphenylphosphinic acid (**4**) is formed after several hours. The chloroform soluble material in the product shows one strong ^{31}P n.m.r. absorption, although small amounts of (**4**) are usually present, and accompanied by either (**1**) or (**2**), depending on the initial ratio of the reactants. When two mol. equivalents of (**2**) are used at the start, then both the initial reactants are fully consumed.

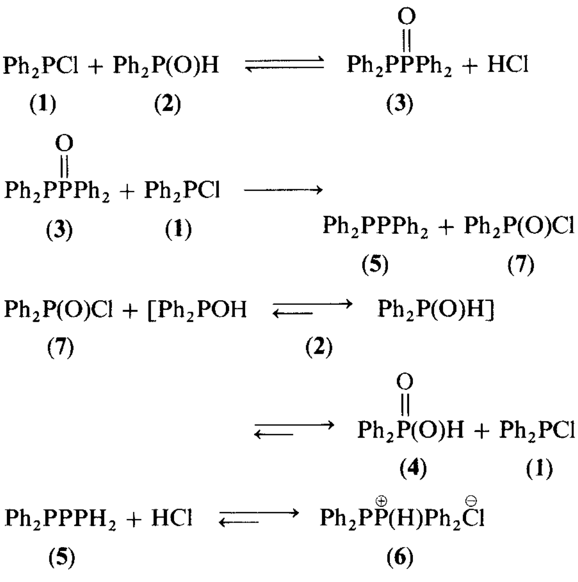
$$\underset{(\mathbf{1})}{Ph_2PCl} + \underset{(\mathbf{2})}{2Ph_2P(O)H} \longrightarrow \underset{(\mathbf{6})}{Ph_2PPPh_2 \cdot HCl} + \underset{(\mathbf{4})}{Ph_2P(O)OH}$$

Stoichiometry suggested that the other product would be tetraphenyldiphosphine, and indeed this is the case when the reaction of (**1**) with (**2**) is carried out at 80°C. However, when the reaction is performed at 20°C, the ^{31}P shift of the product is about 34 ppm [which is much lower than tetraphenyldiphosphine (**5**)] and this was identified as being due to the hydrochloride (**6**). Thermal loss of hydrogen chloride from the hydrochloride of tetraphenyldiphosphine (**6**) has been observed previously,[3] and is presumably a reflection of the low basicity of (**5**).[4,5]

The course of the reaction was then followed at 20°C, using ^{31}P n.m.r. This clearly revealed the initial formation of tetraphenyldiphosphine monoxide (**3**), which showed a double-doublet with J_{PP}224 Hz. Thereafter the slow formation of (**6**) and diphenylphosphinic acid (**4**) at 20°C, or of (**5**) and diphenylphosphinic acid (**4**) at 80°C is observed. We suggest that cleavage of the P—P bond in (**3**) is the result of phosphinylation of the phosphorus(III) centre in (**3**) by diphenylphosphinous chloride, in a manner which is well established with alkylating, acylating or halogenating agents on a range of P(III)-P(III) and P(III)-P(IV) compounds.[2,6]

This process also produces diphenylphosphinic chloride (**7**) which we have shown to undergo rapid halogen exchange with diphenylphosphine oxide (**2**), to produce (**1**). These reactions are summarised in the scheme.

The crucial difference between the present experimental conditions and those previously described,[2] lies in the role of the base. Presumably it converts the starting oxide (**2**) into its anion, and this consumes the chlorophosphine (**1**) rapidly, relative to its sluggish reaction with the diphosphine



$$\underset{(1)}{Ph_2PCl} + \underset{(2)}{Ph_2P(O)H} \rightleftharpoons \underset{(3)}{Ph_2\overset{\overset{O}{\|}}{P}PPh_2} + HCl$$

$$\underset{(3)}{Ph_2\overset{\overset{O}{\|}}{P}PPh_2} + \underset{(1)}{Ph_2PCl} \longrightarrow \underset{(5)}{Ph_2PPPh_2} + \underset{(7)}{Ph_2P(O)Cl}$$

$$\underset{(7)}{Ph_2P(O)Cl} + \underset{(2)}{[Ph_2POH} \rightleftarrows Ph_2P(O)H]$$

$$\rightleftarrows \underset{(4)}{Ph_2\overset{\overset{O}{\|}}{P}(O)H} + \underset{(1)}{Ph_2PCl}$$

$$\underset{(5)}{Ph_2PPPH_2} + HCl \rightleftarrows \underset{(6)}{Ph_2\overset{\oplus}{P}P(H)Ph_2\overset{\ominus}{Cl}}$$

SCHEME

monooxide (**3**). Thus our observations are quite compatible with the work of McKechnie and Payne.[2] Some analogy for our work is shown by the reactions of chlorodimethylphosphine with the corresponding oxide.[7]

EXPERIMENTAL

All experiments were conducted in a thoroughly dry atmosphere under dry nitrogen. Diphenylphosphinous chloride and diphenylphosphine oxide were commercial samples, redistilled and recrystallized, respectively. ^1H n.m.r. were obtained at 90 MHz in $CDCl_3$, using tetramethylsilane as an internal standard. ^{31}P n.m.r. were obtained at 24.3 MHz, and shifts are relative to 85% H_3PO_4. Positive shifts are downfield from the reference in both cases.

Reaction of Diphenylphosphinous Chloride (**1**) *with Diphenylphosphine Oxide* (**2**)

a) At room temperature Diphenylphosphinous chloride (**1**) (0.22 g, 0.001 mol) was added to a solution of diphenylphosphine oxide (**2**) (0.40 g, 0.002 mol) in chloroform (1.5 ml, dry), and the mixture stirred in a sealed flask. A precipitate began to appear after 45 min, and this became thicker over the next 14 h. After filtration, the precipitate (0.209 g) was identified as diphenylphosphinic acid (**4**) m.p. 194–196°C (lit.[8] 195–196°C); ν_{max}^{nujol} 2700–2500 (broad), 1750–1600 (broad), 1180, 1125, 960 (broad, s), 750, 720, and 690 cm^{-1}; δ ^{31}P 25.9 ppm. The filtrate showed δ_P 34.2 ppm, and this signal was wholly coincident with that of tetraphenyldiphosphine hydrochloride, made independently, and carefully added to the above filtrate.

The chloroform solution was washed with aqueous sodium bicarbonate, and then with water, and dried. Evaporation of the solvent yielded an oil, which was largely diphenylphosphine oxide (i.r. and ^{31}P n.m.r. spectra).

b) At 80°C A mixture of diphenylphosphinous chloride (0.44 g, 0.002 mol) and diphenylphosphine oxide (0.80 g, 0.004 mol) in dry chloroform (4 ml) was refluxed for 8 h in an open flask heated by an oil bath (80°C). After 0.5 h, the major absorptions were due to tetraphenyldiphosphine monooxide (**3**), δ_P-21.8 and 35.4 (J 226 Hz) (lit.[10] δ_P-21.6 and 36.9 ppm, J 224 Hz). After 2 h these absorptions were considerably diminished, relative to those of the final products, diphenylphosphinic acid (δ_P 25.6 ppm) and tetraphenyldiphosphine (δ_P-15.4 ppm). These were the only products after 8 h. The acid (0.393 g, 90%) was precipitated by slow addition of dry ether (15 ml) to the mixture, collected by filtration, and identified by i.r. and by m.p. (193–196°C).

Tetraphenyldiphosphine Hydrochloride (**6**) A mixture of diphenylphosphinous chloride (1.10 g, 0.005 mol) and diphenylphosphine (0.93 g, 0.005 mol) in pentane (10 ml, dry) under nitrogen was refluxed for 2 h on a steam bath. The white precipitate thus produced was removed by filtration and washed with a little pentane. It was identified as tetraphenyldiphosphine (**5**) (0.5 g, 35%), m.p. 120–122°C (lit.[9] 121–122°C); δ_P-15.2 ppm. When a gentle flow of dry gaseous hydrogen chloride was passed through the diphosphine in chloroform, the signal at δ_P-15.2 ppm disappeared, to be replaced by a single absorption at δ_P 33.6 ppm. This shift was somewhat variable, depending upon solvent and concentration. Slow evaporation of the chloroform from this sample yielded a slush, which, by ^{31}P n.m.r., was a mixture of tetraphenyldiphosphine, its hydrochloride, and small amounts of hydrolysis products.

Reaction of Diphenylphosphine Oxide (**2**) *with Diphenylphosphinic chloride* (**7**)

Diphenylphosphine oxide (**2**) (0.308 g, 0.0015 mol) was dissolved in diphenylphosphinic chloride (**7**) (0.362 g, 0.0015 mol), under nitrogen. The mixture warmed up noticeably and a ^{31}P n.m.r. showed that diphenylphosphinous chloride (**1**) (δ_P 80.5 ppm) was the major component of a mixture which also contained diphenylphosphinic acid (**4**), but no diphenylphosphinic chloride. The composition of the mixture did not alter the initial mixing.

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