

Reactions of Carbonyl Compounds with Tervalent Phosphorus Reagents. Part 8.¹ Acetyldiphenylphosphine Oxide

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Detailed spectra are described for acetyldiphenylphosphine oxide (1), prepared as a crystalline solid from acetyl chloride and methyl diphenylphosphinite. The oxide (1) is a potent acylating agent and readily undergoes carbonyl addition reactions. Acetoxydiphenylphosphine and (1) interconvert spontaneously, and then slowly form a dimer.

ACETYLDIPHENYLPHOSPHINE OXIDE (1) is a most reactive substance, which has given rise to a number of confusing observations. Thus claims of its preparation from methyl diphenylphosphinite (2)² and by oxidation of acetyldiphenylphosphine³ suggested that it was a stable, crystalline, yellow substance, with m.p. ca. 160 °C. However, subsequent work⁴ showed that these earlier efforts had led to the isolation of the dioxide (3), formed by addition to the carbonyl group of (1). More recently, Pudovik and Sudakova⁵ have isolated the acylphosphine oxide (1) from the reaction of diphenylphosphine oxide (4) with acetyl chloride. They found it to be a distillable liquid, but their yield was low and the structural assignment was not supported by micro-analytical data, nor by spectral information.⁵

Meanwhile, our own attempts to repeat the preparation of acetyldiphenylphosphine oxide (1) from the ester (2) yielded only a complex mixture of compounds formed by further addition to (1).⁶ Not satisfied with the outcome of these efforts, we reinvestigated this reaction, and now find that (1) may be prepared quanti-

tatively at -10 °C from methyl diphenylphosphinite (2) (Scheme 1), provided that both the ester and the acetyl chloride have been rigorously purified. The co-product is chloromethane, and once this has been removed the oxide (1) is left as a white, crystalline, low-melting solid. It is stable enough, in the absence of moisture, to permit a full spectroscopic characterisation, and for some of its reactions to be studied.

The ¹H n.m.r. spectrum shows a doublet at δ 2.6 (²J_{PH} 3.8 Hz); its ³¹P n.m.r. spectrum shows a signal at -16.4 p.p.m., downfield from 85% H₃PO₄. The ¹³C n.m.r. shows two non-benzenoid absorptions, at δ 30.35 (²J_{PC} 45.6 Hz) and 216.4 (¹J_{PC} 75.1 Hz), respectively, for the methyl and carbonyl carbon atoms. The i.r. spectrum reveals the expected strong bands for C=O (1695) and P=O (1175 cm⁻¹). The mass spectrum exhibited a parent ion at *m/e* 244, and a base peak at *m/e* 201.

Acetyldiphenylphosphine oxide (1) is also formed, albeit in low yield, in other acylation reactions of

⁴ R. S. Davidson, R. A. Sheldon, and S. Trippett, *J. Chem. Soc. (C)*, 1968, 1700.

⁵ A. N. Pudovik and T. M. Sudakova, *Proc. Acad. Sci. U.S.S.R.*, 1970, **190**, 144.

⁶ N. J. De'ath, S. T. McNeilly, and J. A. Miller, *J.C.S. Perkin I*, 1976, 741.

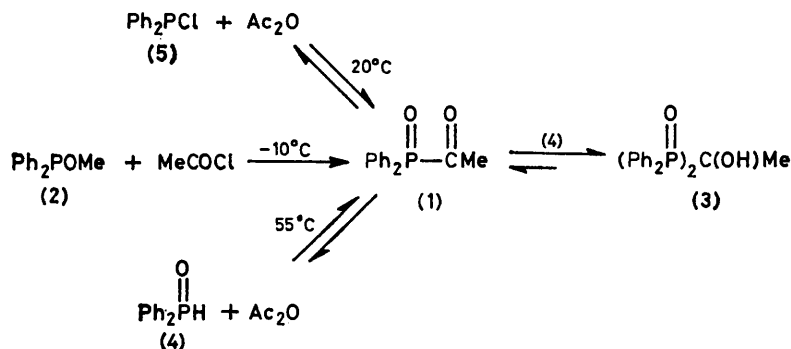
¹ Part 7, J. A. Miller and D. Stewart, *J.C.S. Perkin I*, 1977, 1340.

² A. E. Arbusov and K. V. Nikonorov, *Zhur. obshchei Khim.*, 1948, **18**, 2008 (*Chem. Abs.*, 1949, **43**, 3802).

³ K. Issleib and E. Priebe, *Chem. Ber.*, 1959, **92**, 3183.

diphenylphosphino-derivatives (see Scheme 1). Thus chlorodiphenylphosphine (5) reacts slowly but steadily with acetic anhydride at room temperature, to produce

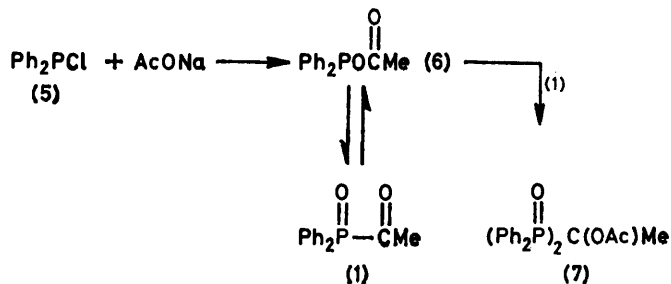
When a sample of acetyldiphenylphosphine oxide (1) is kept at temperatures up to 45 °C, a slow isomerisation to acetoxydiphenylphosphine (6) takes place, followed by



SCHEME 1 Routes to the oxides (1) and (3)

an equilibrium mixture with acetyl chloride and the oxide (1). Diphenylphosphine oxide (4) reacts with acetic anhydride at 55 °C to give a mixture of the oxide

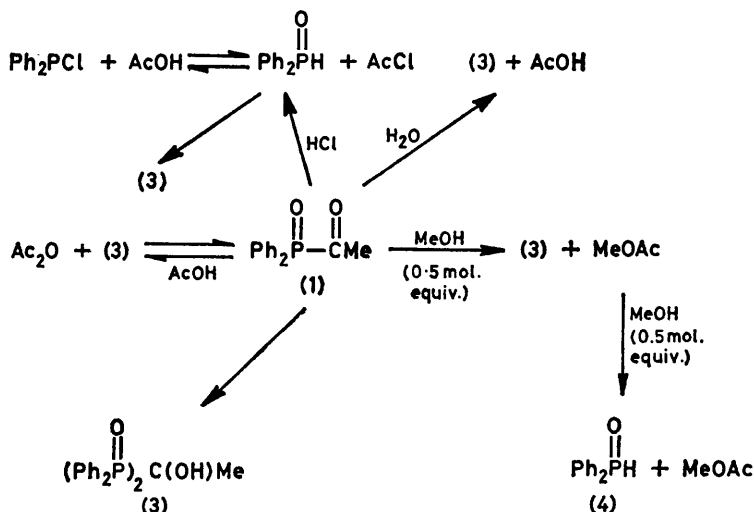
partial dimerisation to give 1,1-bis(diphenylphosphinoyl)ethyl acetate (7), the acetate ester of (3). The acetate structure (7) has been tentatively assigned⁶ to a product formed in the acetyl chloride–methyl diphenylphosphinite (2) reaction. A pure sample of this acetate (7) was obtained from acetoxydiphenylphosphine (6) which had been kept stored at –10 °C for several months. The structure of the dimer follows from microanalytical data and its i.r. (1763 cm⁻¹) and ¹H n.m.r. spectra [δ_{Me} 2.17 (s) and 2.1 (t, ²J_{PH} 15.3 Hz)]. This dimerisation is quite different from the behaviour of acetoxydiphenylphosphine (6) at higher temperatures.⁴ Although no detailed evidence has been sought on the pathway to (7), it seems possible that acetyldiphenylphosphine oxide is an intermediate (Scheme 2).



SCHEME 2 Dimerisation of acetoxydiphenylphosphine (6)

(1) and 1,1-bis(diphenylphosphinoyl)ethanol (3). This reaction has been described previously,⁴ but the formation of (1) was not reported. In agreement with the previous study,⁴ we find that the use of higher temperatures affords 1-diphenylphosphinoyl-1-diphenylphosphinoxyethane, which has been described on several other occasions.⁴⁻⁶

Otherwise the reactions of the oxide (1) are fairly standard acylations (Scheme 3) in which the dioxide (3) is also formed. For example, addition of water to the oxide (1) in solution yields acetic acid and (3), presumably formed by addition of diphenylphosphine oxide (4) to (1). Although this addition reaction was found to be fast in a separate experiment, we have



SCHEME 3 Acylation reactions of acetyldiphenylphosphine oxide (1)

nevertheless observed on several occasions that compounds (1) and (4) could both be present in significant concentrations in equilibrium with the dioxide (3). This suggests that acetyldiphenylphosphine oxide (1), under certain conditions, may not be as reactive as the literature implies.

One further point which has emerged concerns the reversibility of the addition of diphenylphosphine oxide (4) to the oxide (1). When dry methanol (0.5 mol. equiv.) is added to the oxide (1), methyl acetate and the dioxide (3) are formed instantly. Further addition of methanol (0.5 mol. equiv.) slowly produces more methyl acetate, together with diphenylphosphine oxide (4), presumably the result of reversal of the addition of (4) to (1). The literature contains many instances of the conversion of >P(O)-C(OH)< structures into isomeric >P(O)-O-CH< systems, and there is often some doubt about the mode of such rearrangements. The present result demonstrates the facility with which addition at a carbonyl carbon atom can be reversed, and underlines that a dissociation-recombination pathway should at least be considered for this type of rearrangement.*

EXPERIMENTAL

I.r. spectra were recorded on a Perkin-Elmer 137 spectrometer, and n.m.r. spectra on a Perkin-Elmer R10 (^1H), a Bruker Spectrospin HX90 (^{31}P), or a Varian CFT 20 spectrometer (^{13}C). Solvents were dried and redistilled before use, and all reactions were carried out under dry nitrogen. Chlorodiphenylphosphine and methyl diphenylphosphinite were redistilled and stored at -10°C under nitrogen. Acetyl chloride, acetic anhydride, acetic acid, and methanol were all distilled immediately before use. Diphenylphosphine oxide was purchased from Maybridge Chemical Company.

Acetyldiphenylphosphine Oxide (1).—Methyl diphenylphosphinite (1.16 g, 5.37×10^{-3} mol) under nitrogen was cooled to -30°C in a flask sealed with a septum. Acetyl chloride (0.42 g, 5.3×10^{-3} mol) was added *via* the septum, by syringe. On allowing the mixture to warm to -10°C , bubbles were noticed at the solid(ester)-liquid interface, and the ester was observed to dissolve slowly. The resultant thick syrup was colourless, and found to dissolve readily in dry deuteriochloroform (0.5 ml). A ^1H n.m.r. spectrum of this solution showed δ 1.8–2.6 (10 H, m), 3.00 (variable integral 2–3 H, s), and 2.65 (3 H, d, J 3.8 Hz). When a stream of dry nitrogen was passed through the sample, the δ 3.00 absorption (due to chloromethane) rapidly disappeared. The residual solution showed a ^{31}P n.m.r. absorption at -16.4 p.p.m., downfield from H_3PO_4 (85%), and $^{13}\text{C}\{^1\text{H}\}$ n.m.r. signals at δ 30.35 (2J – 45.6 Hz), 126–133, and 216.4 (1J – 75.1 Hz).

In further experiments, the chloromethane was evaporated off in a current of dry nitrogen before the deuteriochloroform was added. It was found that the oily residue gradually crystallised, and that the white solid had $m.p.$ 23–28 $^\circ\text{C}$. The mass spectrum of this solid showed m/e

244 (M^+) and 201 (100%) (m^* 165.6). Dissolution of the solid in deuteriochloroform showed it to be acetyldiphenylphosphine oxide (1), with the same ^1H n.m.r. spectrum as reported above. The same solution showed ν_{max} 1 695, 1 175, and 1 108 cm^{-1} . It was not possible to analyse the sample in view of its sensitivity to water and to heat.

When a solution of acetyldiphenylphosphine oxide (1) and chloromethane in deuteriochloroform, prepared as above, was kept sealed in an n.m.r. tube, the acetyl signal (δ 2.65) decreased and a signal at δ 2.17 (s) accumulated over a period of 3 days at room temperature. After further storage at 45°C for 3 days, the high-field portion of the spectrum showed absorptions at δ 2.2 (s) and 2.12 (t), and the integral showed that 30% of the acetyldiphenylphosphine oxide (1) remained unchanged. These high field signals were assigned to 1,1-bis(diphenylphosphinoyl)ethyl acetate (7) (see below).

Reactions of Acetyldiphenylphosphine Oxide (1).—Acetyldiphenylphosphine oxide (10^{-2} mol) was made as above, and the sample was flushed with dry nitrogen for a few minutes to remove chloromethane. The oxide was then dissolved in dry CDCl_3 (2.5 ml) and samples (0.5 ml) of this solution were removed and subjected to the following reactions.

(a) *Hydrolysis.* To one sample (2×10^{-3} mol), water (0.036 g, 2×10^{-3} mol) was added with stirring. Analysis by ^1H n.m.r. showed that none of the oxide (1) remained, and that equimolar amounts of acetic acid and 1,1-bis(diphenylphosphinoyl)ethanol (3), δ 1.58 (t, J 15.4 Hz), had been produced. The identification of the products was confirmed by n.m.r. signal augmentation, and the solution had a strong smell of acetic acid.

(b) *Methanolysis.* To a sample (2×10^{-3} mol) was added dry methanol (0.030 g, 1×10^{-3} mol). Analysis by ^1H n.m.r. showed that methyl acetate and 1,1-bis(diphenylphosphinoyl)ethanol (3), δ 1.58 (t, J 15.4 Hz), were formed very rapidly, and were the only products. Addition of a further portion of dry methanol (0.030 g, 1×10^{-3} mol) resulted in slow formation of more methyl acetate, and of diphenylphosphine oxide (4), δ 8.23 (d). The triplet due to (3) had almost disappeared after 30 min. Each assignment was checked by signal augmentation, and the solution had a smell of methyl acetate.

(c) *Acetolysis.* To a sample (2×10^{-3} mol) was added dry acetic acid (0.120 g, 2×10^{-3} mol). After 19 h at room temperature, a ^1H n.m.r. spectrum of the mixture showed signals for acetyldiphenylphosphine oxide (1), acetic acid [δ 2.08 (s)], acetic anhydride [δ 2.18 (s)], and 1,1-bis(diphenylphosphinoyl)ethanol (3) [δ 1.60 (d, J 15.4 Hz)]. Integration showed these to be present in roughly equimolar amounts, and this ratio did not change over several days.

(d) *With diphenylphosphine oxide (4).*—To a sample (2×10^{-3} mol) at 20°C was added diphenylphosphine oxide (0.40 g, 2×10^{-3} mol). A ^1H n.m.r. spectrum taken immediately showed that none of (1) remained, and that 1,1-bis(diphenylphosphinoyl)ethanol (3), δ 1.64 (t, J 15 Hz), was essentially the only product [a very small absorption at δ 2.06 (s) had the same shift as acetic acid].

(e) *With hydrogen chloride.* To a sample (2×10^{-3} mol) at -10°C was added an excess of dry hydrogen chloride. The ^1H n.m.r. spectrum showed new signals at δ 2.52 (s) and 2.05 (s), both of which appeared immediately. These were assigned to acetyl chloride and acetic acid, respectively, after signal augmentation by genuine samples, and their proportion was 1 : 3. A relatively small absorption for

* For example, recent discussion of the mechanism of the reaction between trifluoroacetic acid and chlorodiphenylphosphine has largely ignored this point (see P. Sartori, R. H. Hochleitner, and G. Hägele, *Z. Naturforsch.*, 1976, **31b**, 76).

1,1-bis(diphenylphosphinoyl)ethanol (3), δ 1.60 (t, J 15.2 Hz), was observed after several hours at room temperature.

1,1-Bis(diphenylphosphinoyl)ethyl Acetate (7).—Acetoxydiphenylphosphine (6) was prepared from chlorodiphenylphosphine by a standard procedure.^{1,4} When a sample was stored under nitrogen at -10°C , crystals began to form after several weeks, and after 4 months the sample had completely solidified. The solid was recrystallised from benzene, and identified as 1,1-bis(diphenylphosphinoyl)ethyl acetate (7), m.p. 177—179 $^\circ\text{C}$, ν_{max} (Nujol) 1 763, 1 220, 1 197, 1 107, 782, 720, 700, and 690 cm^{-1} , δ (CDCl_3) 8.2—7.1 (20 H, m), 2.18 (3 H, s), and 2.10 (3 H, t, J 14.7 Hz) (Found: C, 68.75; H, 5.45; P, 12.5. $\text{C}_{28}\text{H}_{26}\text{O}_4\text{P}_2$ requires C, 68.85; H, 5.35; P, 12.7%). This acetate was identical with that produced from acetyldiphenylphosphine oxide (1).

Reaction of Chlorodiphenylphosphine with Acetic Anhydride.—Chlorodiphenylphosphine (0.22 g, 10^{-3} mol) and acetic anhydride (0.102 g, 10^{-3} mol) were mixed under nitrogen at room temperature, and the mixture was dissolved in deuteriochloroform (1 ml). Analysis by ^1H n.m.r. showed the formation of acetyl chloride, δ 1.55 (s), after a few minutes, and then of acetyldiphenylphosphine oxide (1), δ 2.64 (d, J 3.8 Hz), after 80 min. Thereafter, the composition of the sample changed slowly, and after 8 days the absorptions at δ 1.55 (s) and δ 2.12 (s) were of approximately equal intensity, while that at δ 2.64 (d) was very weak.

Reaction of Diphenylphosphine Oxide (4) with Acetic Anhydride.—(a) At 55°C . Diphenylphosphine oxide (4) (2.02 g, 10^{-2} mol) and acetic anhydride (0.51 g, 5×10^{-3}

mol) were dissolved in dry chloroform (5 ml) under nitrogen. The mixture was observed (n.m.r.) to react slowly to form acetic acid and 1,1-bis(diphenylphosphinoyl)ethanol (3) (about 25% after 4 h). After 7 days a small amount of acetyldiphenylphosphine oxide (1) was formed and the oxide (4) had been consumed. Addition of light petroleum (b.p. $40\text{--}60^\circ\text{C}$) yielded a mixture of the oxides (3) (major component) and (1).

(b) In refluxing benzene. When the above reagents were dissolved in dry benzene and the solution was refluxed for 7 h and then left overnight, the ^1H n.m.r. spectrum indicated complete consumption of diphenylphosphine oxide (4). Evaporation yielded an oil (2.5 g), which did not crystallise,^{4,6} and was identified as 1-diphenylphosphinoyl-1-diphenylphosphinoyloxyethane, ν_{max} (film) 1 186, 1 175, 1 123, 953, 728, and 694 cm^{-1} ; m/e 446 (M^+), 402, 325, 262, 245, 217, and 201 (100%); δ (CDCl_3) 8.3—7.3 (20 H, m), 5.6 (1 H, m), 1.56 (3 H, dd, J_{HH} 7, J_{PH} 14 Hz); δ (^{31}P) 32.6 and 29.8 p.p.m. upfield from 85% H_3PO_4 . Distillation of the oil (b.p. $250\text{--}260^\circ\text{C}$ at 0.1 mmHg) gave material which solidified in the condenser. The solid was shown to be the foregoing phosphinite, but attempts at recrystallisation from various solvents yielded white crystals which were always sticky, and exhibited a wide m.p. range (e.g. $173\text{--}185^\circ\text{C}$).

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