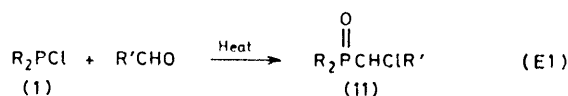


## Reactions of Carbonyl Compounds with Tervalent Phosphorus Reagents. Part 10.<sup>1</sup> Monochlorophosphines and Aldehydes

By Norman J. De'ath, J. Allen Miller,\* M. John Nunn, and Denis Stewart, Chemistry Department, The University, Dundee DD1 4HN, Scotland

The reaction of chlorophosphines (1) with aldehydes to give  $\alpha$ -chloroalkylphosphine oxides (11) has been shown to involve two stable organophosphorus intermediates. Detailed study of the reaction of chlorodiphenylphosphine (1a) with benzaldehyde has revealed that the intermediates are  $\alpha$ -chlorobenzyl  $\alpha$ -(diphenylphosphinoyl)benzyl ether (8a) and bis- $[\alpha$ -(diphenylphosphinoyl)benzyl] ether (12a), and that each is formed as one diastereoisomer only. 2-Chloro-2,2,3,5-tetraphenyl-1,4,2 $\lambda^5$ -dioxaphospholan (4a) is suggested as the precursor of these phosphine oxides, and experimental evidence for the overall pathway to  $\alpha$ -chlorobenzyl diphenylphosphine oxide (11a) is presented. Previous rationalisations of these complex reactions are shown to need reappraisal.

HALOGENOPHOSPHINES and aldehydes undergo a general reaction at elevated temperatures to produce I-halogenoalkylphosphine oxides [equation (E1)].<sup>2</sup> However, relatively little is known about the mechanism of this



- |  |   |
|--|---|
| a; R = Ph  | a; R = R' = Ph  |
| b; R <sub>2</sub> = —CMe <sub>2</sub> CH <sub>2</sub> CMe <sub>2</sub> — | b; R' = Ph; R <sub>2</sub> = —CMe <sub>2</sub> CH <sub>2</sub> CMe <sub>2</sub> — |
| c; R = Cl  | c; R' = Ph; R = Cl  |
| d; R <sub>2</sub> = Cl, Ph   | d; R' = Ph; R <sub>2</sub> = Cl, Ph   |
| e; R <sub>2</sub> = —CMe <sub>2</sub> CHMeCMe <sub>2</sub> —             | e; R' = Ph; R <sub>2</sub> = —CMe <sub>2</sub> CHMeCMe <sub>2</sub> —             |
| f; R = Me  | f; R' = Ph; R = Me  |
| g; R = Et  | g; R' = Ph; R = Et  |
| h; R = Bu <sup>t</sup>   | h; R' = Ph; R = Bu <sup>t</sup>   |
|  | i; R = Ph; R' = <i>p</i> -MeOC <sub>6</sub> H <sub>4</sub>                        |

reaction,<sup>3</sup> although recent work has shed some light on the reactions of aldehydes with phosphorus trichloride.<sup>4</sup> In this paper, we describe the results of study of reactions of alkyl and aryl derivatives of phosphorus trichloride with a range of aldehydes.

### RESULTS AND DISCUSSION

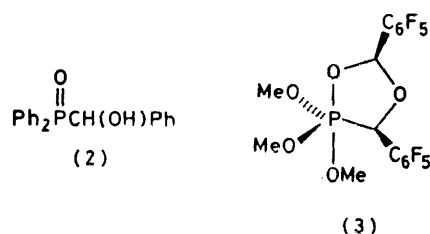
Preliminary studies of the reaction of benzaldehyde with monochlorophosphines led to the recognition that two organophosphorus intermediates accumulate prior to the formation of the final  $\alpha$ -chlorobenzylphosphine oxide product. These intermediates were tentatively assigned structures,<sup>5</sup> but further evidence was deemed to be desirable, and a discussion of this comprises much of this paper. On the grounds of reagent availability, and of convenient kinetics, we chose to study the reaction of benzaldehyde with chlorodiphenylphosphine (1a) in greatest detail. This turned out to be a fortuitous choice, since many other combinations either do not produce an  $\alpha$ -chloroalkylphosphine oxide so efficiently, or do not lend themselves to facile accumulation of intermediates.

*Structure of the First Intermediate.*—When two molar equivalents of benzaldehyde are stirred with chlorodiphenylphosphine (1a), at room temperature under nitrogen, the aldehyde is consumed fairly rapidly until the mixture begins to solidify. The product at this stage

is very nearly homogeneous (by n.m.r.), and is a white crystalline solid which can be stored for many weeks in the absence of water. Contact with atmospheric moisture results in formation of hydrogen chloride, and regeneration of benzaldehyde.

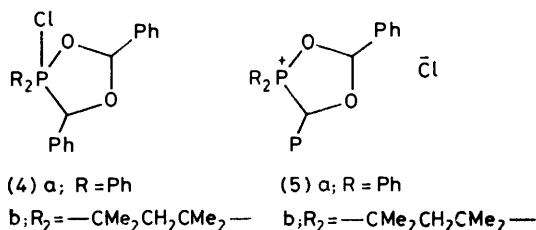
The stoichiometry of the reaction leading to the first intermediate suggests that it is a 2 : 1 adduct, and this was confirmed by hydrolysis of the adduct, to yield equimolar quantities of benzaldehyde and  $\alpha$ -hydroxybenzyl diphenylphosphine oxide (2). Incorporation of two aldehyde units into the 2 : 1 adduct was also indicated by the <sup>1</sup>H n.m.r. spectrum, which showed absorptions for non-aromatic protons at  $\delta$  6.6 (1 H, singlet) and 6.1 (1 H, doublet, *J* 8.5 Hz), as well as absorptions due to the hydrogens of four phenyl groups.

This <sup>1</sup>H n.m.r. spectrum bears considerable resemblance to those of the phosphoranes isolated by other groups from reactions of aromatic aldehydes with various phosphorus(III) esters. For example, the cyclic



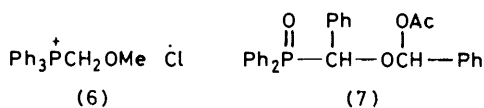
*cis*-phosphorane (3) shows <sup>6</sup>H<sup>5</sup> at  $\delta$  6.48 (doublet, *J* 2 Hz) and H<sup>3</sup> at  $\delta$  5.27 (doublet, *J* 17 Hz), while in the corresponding *trans*-isomer the *J*<sub>PH</sub> values are each of intermediate magnitude. A 1,4,2 $\lambda^5$ -dioxaphospholan structure, (4a), for the chlorodiphenylphosphine 2 : 1 adduct also appeared to be compatible with its proton-decoupled <sup>13</sup>C n.m.r. spectrum, which displayed two doublets for benzylic carbon atoms, each coupled to phosphorus, but with very different coupling constants (*J*<sub>PC</sub> 87.4 and 12.0 Hz). However the <sup>31</sup>P n.m.r. spectrum of the 2 : 1 adduct revealed a shift of +28.5 p.p.m. (downfield from H<sub>3</sub>PO<sub>4</sub>). In recent years, it has become accepted<sup>7-9</sup> that a phosphorane structure is associated with a downfield <sup>31</sup>P shift. There are a few exceptions to this generalisation, and indeed some of the factors<sup>9</sup> which can lower <sup>31</sup>P n.m.r. shifts would apply

to the 2 : 1 adduct (4a). However, we could find no good analogy for a shift of +28.5 p.p.m. being associated with a structure such as (4a).



Alternatively, a phosphonium salt structure (5a) would be in reasonable accord with all the data discussed above, and indeed this was the structure previously suggested.<sup>5</sup> On the other hand it seems unlikely<sup>10</sup> that a 1,4,2λ<sup>5</sup>-dioxaphospholanium salt, with a phosphonium centre placed in a five-membered ring, would be structurally preferred to a 1,4,2λ<sup>5</sup>-phospholan. Furthermore, we have been unable to obtain any evidence that the <sup>1</sup>H n.m.r. spectrum of the 2 : 1 adduct is noticeably dependent upon solvent, or on temperature, as might have been expected,<sup>8</sup> if a phospholan–phospholanium equilibrium were available to the 2 : 1 adduct. It has also been found that when benzaldehyde reacts with 1-chloro-2,2,4,4-tetramethylphosphetan (1b), the resultant 2 : 1 adduct shows all the features noted in the case of the adduct from (1a). Incorporation of a phosphorus atom into a spirocyclic structure would be expected<sup>11</sup> to favour even more [relative to (4a), (5a)] the phospholan (4b) over the phospholanium salt (5b). The 2 : 1 adduct from (1b) shows a <sup>31</sup>P shift of +56.5 p.p.m., a value not influenced by solvent or temperature changes, and hence structure (5b) looks an unlikely candidate for this adduct.

In principle, conductivity measurements with the 2 : 1 adduct from chlorodiphenylphosphine and benzaldehyde should allow a distinction between the possible structures (4a) and (5a),<sup>12</sup> but, in practice, the interpretation of such measurements was complicated by the presence of traces of hydrogen chloride, produced by contact of the 2 : 1 adduct with adventitious water. The conductivity of the 2 : 1 adduct was compared, in two different sol-



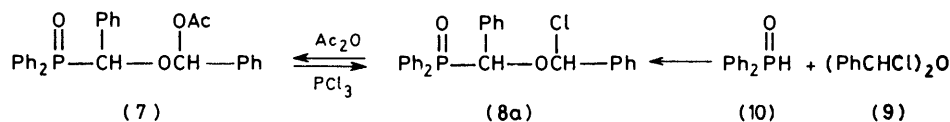
vents, with the conductivities of the phosphonium salt (6) and the phosphine oxide (7),<sup>1</sup> and found to be much closer to the latter. Deliberate addition of water (1 mol equiv.) to a solution of the 2 : 1 adduct produced a

dramatic increase in conductivity, due presumably to the generation of hydrogen chloride. On the other hand, addition of water to the phosphonium salt solution resulted only in a small (6%) increase in conductivity. The increase in conductivity of the solution of the 2 : 1 adduct was quite regular as the mol fraction of added water was increased, and it seems that the relatively small conductivity of the original solution of the adduct can be ascribed to traces of hydrogen chloride. Indeed the conductivity of solutions of the 2 : 1 adduct increases slowly on standing, no doubt due to a slow hydrolysis reaction.

These conductivity studies thus suggest that the 2 : 1 adduct is not a phospholanium salt, and is more likely to be a neutral, covalent substance. At this stage we began to consider that the adduct might be a phosphine oxide, such as the α-chloroether (8a), although it had previously been suggested<sup>5</sup> that the second detectable intermediate in the reaction had this structure. Structure (8a) has the merit of being quite compatible with all the n.m.r. evidence for the 2 : 1 adduct. In particular, it has now become accepted<sup>13</sup> that <sup>2</sup>J<sub>PC</sub> and <sup>3</sup>J<sub>PC</sub> values can be extremely difficult to distinguish. Hence the observed *J* value (12.0 Hz) for the 2 : 1 adduct is just as likely to be in keeping with the expected value for <sup>3</sup>J<sub>PC</sub> in the chloroether (8a), as with <sup>2</sup>J<sub>PC</sub> in the 1,4,2λ<sup>5</sup>-dioxaphospholan (4a). Moreover, the lack of <sup>1</sup>H–<sup>31</sup>P coupling for one of the benzylic hydrogens of the 2 : 1 adduct is accounted for by structure (8a).

Another feature of the <sup>1</sup>H n.m.r. spectrum of the 2 : 1 adduct from (1a) is its similarity to that of the acyl analogue (7), recently isolated from other reactions of benzaldehyde.<sup>1</sup> The implication that structure (8a) was reasonable for the 2 : 1 adduct was confirmed by conversion of this into (7) using acetic anhydride. Conversely, when (7) was treated with phosphorus trichloride,<sup>14</sup> the 2 : 1 adduct (8a) was formed.<sup>1</sup> A further synthesis of the 2 : 1 adduct (8a) was achieved by treatment of bis-(α-chlorobenzyl) ether (9)<sup>4</sup> with 1 mol equiv. of diphenylphosphine oxide (10) (see Scheme 1). It seems unlikely that a 1,4,2λ<sup>5</sup>-dioxaphospholan structure could adequately account for all of the reactions in Scheme 1, and we believe that the α-chloroether structure (8a) is the best one for the 2 : 1 adduct.

The reactions in which benzaldehyde is involved are highly stereoselective, in that the ether (8a) appears to be only one diastereoisomer, as do the related phosphetan derivatives (8b) and (8e). This was particularly evident in the phosphetan series, because both aldehyde-derived benzylic hydrogen absorptions are sharp singlets. As far as we are aware, a value of zero for <sup>2</sup>J<sub>PCH</sub> in phosphetans has not been observed previously. This stereoselectivity is not repeated, however, with the

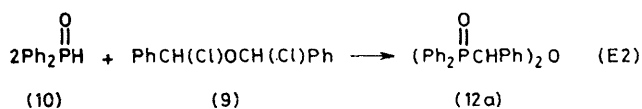


SCHEME 1

reactions of chlorodiphenylphosphine (1a) with other aromatic aldehydes. Although none of these  $\alpha$ -chloroether analogues of (8a) was actually isolated, evidence from n.m.r. studies suggests that both diastereoisomers were formed from either *p*-nitrobenzaldehyde or *p*-cyanobenzaldehyde. Moreover, these diastereoisomers appeared to be thermally much more stable than is (8a). When *p*-methoxybenzaldehyde was reacted with chlorodiphenylphosphine (1a), no  $\alpha$ -chloroether was observed, and this presumably reflects the enhanced reactivity of an  $\alpha$ -chloro-*p*-methoxybenzyl ether structure. A similar trend in stability of aldehyde-derived bis-( $\alpha$ -chlorobenzyl) ethers has been observed previously.<sup>4</sup>

**Structure of the Second Intermediate.**—When the 2 : 1 adduct (8a) is heated in solution, or a 2 : 1 mixture of benzaldehyde and chlorodiphenylphosphine (1a) is warmed, analysis by <sup>1</sup>H n.m.r. shows the slow, but steady, formation of a second organophosphorus intermediate, with a <sup>1</sup>H n.m.r. absorption at  $\delta$  5.05 (d, *J* 8.8 Hz). Simultaneously, benzal chloride is also formed, and some benzaldehyde is regenerated. Before all the chloroether (8a) has been converted, absorptions begin to appear at  $\delta$  5.62 (d, *J* 3.4 Hz), and these are due to the final pyrolysis product,  $\alpha$ -chlorobenzyl diphenylphosphine oxide (11a). The relative rates of formation of the products from (8a) are critically dependent upon the conditions (especially temperature), and it was not possible to isolate the second organophosphorus intermediate cleanly from our original conditions.

It was ultimately found that this second intermediate is bis-( $\alpha$ -diphenylphosphinoyl)benzyl ether (12a), which was recently isolated<sup>15</sup> from the reaction of chlorodiphenylphosphine (1a) with benzaldehyde in the pre-

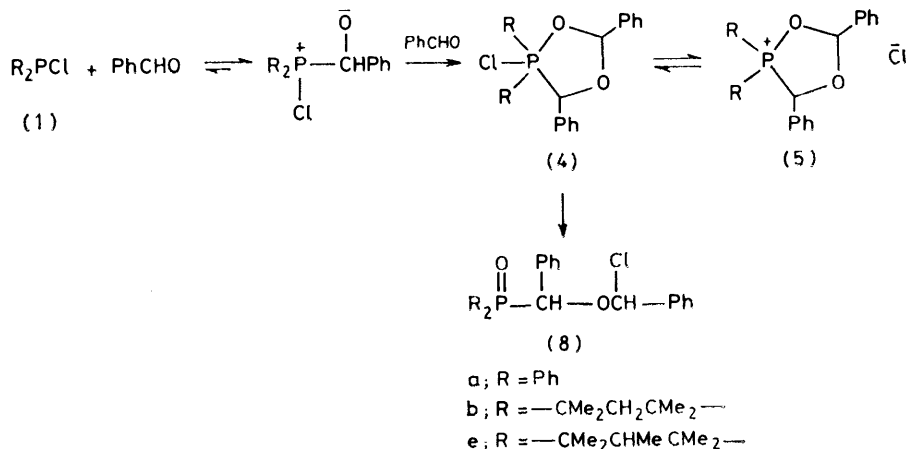


sence of acetic acid (Conant's reaction). The structure of the ether (12a) was confirmed<sup>15</sup> by synthesis from diphenylphosphine oxide (10) (2 mol equiv.) and bis-( $\alpha$ -chlorobenzyl) ether (9)<sup>4</sup> [equation (E2)].

**Mechanism of the Chlorophosphine-Aldehyde Reactions.**—The sequence of reactions leading from chlorodiphenylphosphine (1a) via the chloroether (8a) and the ether (12a) to  $\alpha$ -chlorobenzyl diphenylphosphine oxide (11a) is clearly very complex. The kinetically significant role of the chlorophosphine (1a) is suggested by the rates of reaction of benzaldehyde with substituted chlorophosphines. Thus phosphorus trichloride (1c) and chlorodiphenylphosphine (1a) are both much more reactive than dichloro(phenyl)phosphine (1d), a trend which indicates that a change in mechanism occurs across the series. It is now believed that phosphorus trichloride behaves as an electrophile towards aldehydes,<sup>4</sup> and the effect of replacing two of the chlorines by phenyl groups seems to be most conveniently explained by suggesting an altered role for the phosphorus atom. Such changes in behaviour are not common, although a clear example<sup>16</sup> has emerged from a recent study of the reaction of acetals with various chlorophosphines.

A corresponding demonstration of the changed role of the aldehyde component of these reactions was sought by comparing the relative rates of reaction of (1a) with *p*-cyanobenzaldehyde. However, no significant substituent effect was observed, possibly indicating that the aldehyde has different roles to play in and before the rate-determining step.

Perhaps the most notable feature of the reaction sequence leading to the chloroether (8a) is its stereoselectivity. In the related reactions leading to the acylal (7), stereoselectivity was ascribed to factors, probably steric, operating in a pentacovalent 1,4,2-dioxaphospholan intermediate.<sup>1</sup> Stereoselectivity in the formation of cyclic phosphoranes has also been reported by others.<sup>6,17</sup> In the present case, however, the stereoselectivity may well result from thermodynamic factors in (8a), since reaction of either diastereoisomer of (7) with phosphorus trichloride leads to the same diastereoisomer of (8a); the preparation of (8a) from bis-( $\alpha$ -chlorobenzyl) ether (9) also leads to this stereoisomer. Although the cyclic phosphorane (4a) is therefore not an obligatory intermediate on stereochemical grounds, it

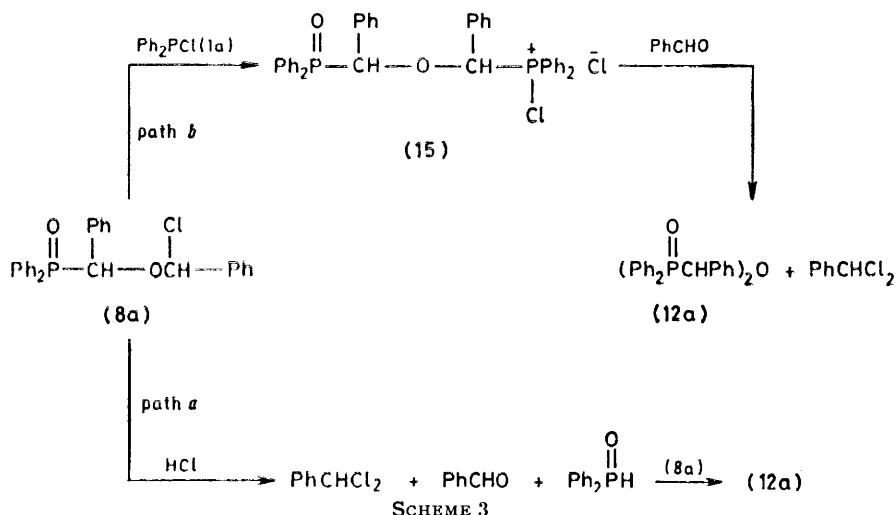


SCHEME 2

seems nevertheless to be an attractive precursor of (8a), since it would be expected to be very reactive, and its ring-opening could explain the stoichiometry of the overall reaction, *i.e.* the fact that the aldehyde oligomerisation stops at the 'dimer' level (see Scheme 2).

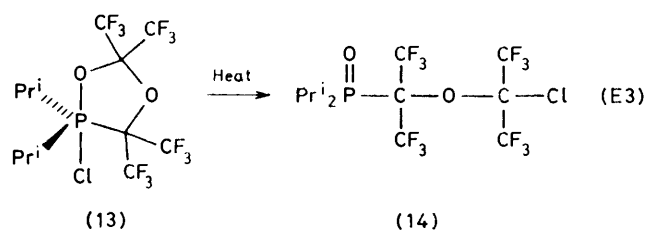
oxide (10), which we have previously shown to react with (8a) to produce the ether (12a).<sup>15</sup> Attempts to model this process, by treatment of (8a) with hydrogen chloride, were not successful.

Another possibility is that the chloroether (8a) may



Moreover the *p*-substituent effect, discussed above, can also be conveniently rationalised by a two-step sequence leading to (4a), *via* a presumed 1 : 1 adduct, as in Scheme 2.

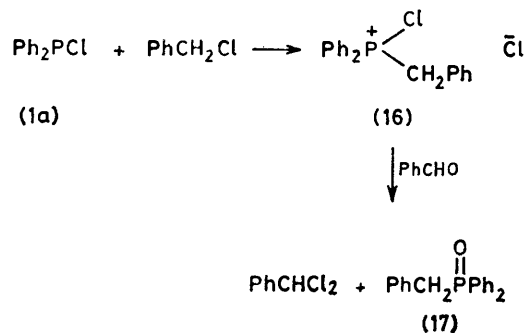
Since this work was completed, others<sup>18</sup> have reported the isolation of related chlorophosphoranes, in each case derived from hexafluoroacetone. The presence of *gem*-trifluoromethyl groups clearly stabilises these phosphoranes towards dealkylation (*i.e.* ring-opening), although the work of Knunyants *et al.*<sup>18a</sup> shows that it can be achieved at high temperatures, as in conversion of the cyclic phosphorane (13) into the  $\alpha$ -chloroether (14) [equation (E3)].



Subsequent conversion of the chloroether (8a) into the ether (12a) also appears to be stereospecific, in that (12a) shows no signs<sup>15</sup> of consisting of more than one diastereoisomer. However, a number of plausible routes (see Scheme 3) exist whereby (8a) may be suggested to produce (12a), together with an equimolar amount of benzal chloride. For example, reaction of (8a) with hydrogen chloride could give benzal chloride and benzaldehyde directly, as in Scheme 3, path *a*. This fragmentation is akin to that observed previously<sup>4</sup> with bis-( $\alpha$ -chlorobenzyl) ether (9) except that, in the present case, the third product would be diphenylphosphine

react with (1a) to give a chlorophosphonium chloride (15) (or the equivalent phosphorane), which, in the presence of benzaldehyde, would be expected<sup>19</sup> to give the ether (12a) and benzal chloride (Scheme 3, path *b*). A good analogy for these reactions was obtained by converting chlorodiphenylphosphine (1a) into the salt (16) with benzyl chloride<sup>20</sup> and showing that (16) reacts with benzaldehyde at room temperature, to produce benzal chloride and benzyldiphenylphosphine oxide (17) (Scheme 4). Unfortunately, whilst this suggestion is chemically sound, it is unlikely to represent a major pathway to (12a), because in systems which have been allowed to react at room temperature [thereby producing (8a) in >90% yield], there is not enough (1a) available to convert all the (8a) into (12a). This argument assumes that (8a) cannot revert to (1a) under the reaction conditions, and there seems no reason to doubt this assumption.

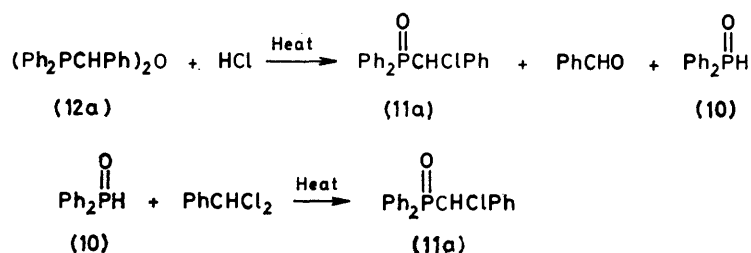
The final stages of the reaction of benzaldehyde with (1a) involve conversion of the ether (12a) into  $\alpha$ -chlorobenzyl diphenylphosphine oxide (11a). Attempts to



model this stage in the sequence have shown that mixtures of benzal chloride and the ether (12a) are stable to heat, but that addition of hydrogen chloride causes a slow generation of  $\alpha$ -chlorobenzyl-diphenylphosphine oxide (11a) and benzaldehyde at 180 °C. The initial cleavage of the ether (12a) seems likely to produce (11a), together with benzaldehyde and diphenylphosphine oxide (10). We have found that, at this temperature, diphenylphosphine oxide (10) is alkylated by benzal chloride. Thus both the phosphine oxide moieties in (12a) are transformed into the final oxide (11a), albeit by different routes, as outlined in Scheme 5. The key to this sequence lies in the catalytic effect of hydrogen chloride, traces of which are almost certainly produced

likely to account for anything like complete conversion to (11a). We therefore conclude that complete loss of (8a) is mainly dependent on the slow conversion of the ether (12a) into (11a) and diphenylphosphine oxide (10), as in Scheme 5. Given the choice of reaction with either benzyl chloride or the  $\alpha$ -chloroether (8a), diphenylphosphine oxide (10) would, on our evidence, react much faster with the latter. This links Scheme 5 with the fate of (8a), and generates a kind of diphenylphosphine oxide (10) 'cycle', which ends when benzyl chloride remains as the only available reactant for (10).

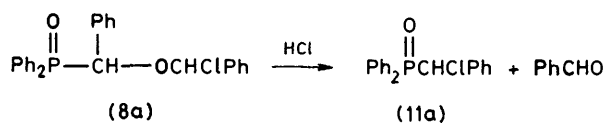
*Reaction of Other Phosphines and Aldehydes.*—Our studies of systems with chlorophosphines other than (1a), or with aldehydes other than benzaldehyde, have



SCHEME 5

in the system by the reaction of traces of either moisture or benzoic acid with the chlorophosphine.

The possibility was also considered that the sequence from chlorodiphenylphosphine (1a) to the final oxide (11a) need not necessarily pass through both (8a) and (12a). Thus the chloroether (8a) may possibly be converted directly into the oxide (11a) by attack of chloride ion at the benzylic carbon to which the phosphorus atom is attached, as in Scheme 6. Evidence in



SCHEME 6

favour of this view comes from experiments in which chlorodiphenylphosphine (1a) and benzaldehyde were heated at 110 °C, at which temperature the ether (12a) and benzal chloride are stable to hydrogen chloride. Under these relatively mild conditions, some  $\alpha$ -chlorobenzylphosphine oxide (11a) is formed, together with the ether (12a) and benzal chloride. Maintenance of this system at 110 °C for 36 h did not alter the initial proportions of (11a) and (12a) present. The observation that some benzaldehyde is regenerated from the chloroether (8a), at the same time as the ether (12a) and benzal chloride are formed, is also explicable by the direct conversion of (8a) into the oxide (11a).

It is therefore reasonably clear that conversion of the oxide (8a) into the final product (11a) may involve more than one route, *viz.* path *b* in Scheme 3 and that in Scheme 6. On the other hand, our evidence suggests that, even taken in combination, these routes are not

shown than the analogy with the chlorodiphenylphosphine-benzaldehyde system is rarely complete, and sometimes rather feeble.

For example, with benzaldehyde the phosphetan derivatives (1b) and (1e) show the same general pathway, although the formation of the initial adduct seems to stick below 70% conversion. Moreover, the tetramethylphosphetan (1b) is many times more reactive than (1e), for reasons which are not clear to us. Of the simple chlorodialkylphosphines, only the diethyl compound (1g) yielded a clean final product, (11g). The dimethyl compound (1f) was extremely reactive, but the course of its reaction was clearly very complex, a full account of which must await more detailed work. By contrast, chloridi-*t*-butylphosphine (1h) was totally unreactive, even at 180 °C. The inhibiting effect of two *t*-butyl groups attached to phosphorus has been noted previously,<sup>21</sup> although this effect was not observed in the reactions of (1h) with alkyl benzoates.<sup>22</sup> There are clearly mechanistic implications in these observations.

We also studied several systems in which (1a) was reacted with aldehydes other than benzaldehyde, and some of this work has been discussed above, in the context of substituent effects. When acetaldehyde was chosen as partner for (1a), a complex set of competing reactions was observed. Some of these may be related to the main schemes discussed for benzaldehyde, but this will only become apparent after further investigation.

In conclusion, the present phosphorus(III) chloride-aldehyde reactions have been shown to bear a close resemblance to the carbonyl addition reactions described by other groups in recent years.<sup>23</sup> The crucial difference

in our systems arises from the high reactivity of the presumed pentacovalent intermediates. This can be ascribed to the combination of a potent nucleophile, chloride ion, and the presence of secondary carbon centres, usually benzylic, which can readily undergo substitution reactions. It is also clear from this work that those reactions to which acetic acid was added<sup>15</sup> (Conant's conditions<sup>24</sup>) have a fundamentally different pathway from the purely thermal processes described here. Interpretations based on 1:1 stoichiometry, notably those involving oxaphosphirans,<sup>2</sup> must now be highly questionable. Finally, the present work, taken in conjunction with that on phosphorus trichloride (1c),<sup>4</sup> shows that there are some fundamental differences in pathway between the reactions of electrophilic chlorophosphines, such as (1c), and more nucleophilic chlorophosphines, such as (1a). This point was certainly not recognised in early work on the latter.<sup>24</sup>

#### EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 137 spectrometer. <sup>1</sup>H N.m.r. spectra were recorded with a Perkin-Elmer R-10 spectrometer operating at 60 MHz, using solutions in deuteriochloroform with tetramethylsilane as internal standard.

All aldehydes were redistilled, or recrystallized and dried before use. Dichloro(phenyl)phosphine and chlorodiphenylphosphine were purchased (Aldrich Chem. Co.), and redistilled samples were stored under nitrogen at -10 °C. The following chlorophosphines were prepared by standard methods: Me<sub>2</sub>PCl,<sup>25</sup> Et<sub>2</sub>PCl,<sup>26</sup> Bu<sub>2</sub>PCl,<sup>27</sup> and 1-chloro-2,2,3,4,4-pentamethylphosphetan.<sup>28</sup> These were distilled under a dry nitrogen atmosphere and used immediately. All experiments with chlorophosphines were carried out in an atmosphere of nitrogen, using dry apparatus.

*Reactions of Chlorodiphenylphosphine (1a) with Benzaldehyde.*—(a) *Equimolar at 180 °C.* A mixture of benzaldehyde (1.06 g, 10<sup>-2</sup> mol) and chlorodiphenylphosphine (2.40 g, 1.09 × 10<sup>-2</sup> mol) was heated at 180 °C for 10 h, by which time the i.r. spectrum of the mixture showed no carbonyl absorption. On cooling the mixture solidified, and recrystallization from benzene-chloroform yielded α-chlorobenzyl(diphenyl)phosphine oxide (11a), (2.75 g, 85%) as white needles, m.p. 197–199 °C (lit.,<sup>29</sup> 198 °C).

(b) *Two-fold molar excess of benzaldehyde at 20 °C.* When a mixture of benzaldehyde (2.12 g, 2 × 10<sup>-2</sup> mol) and chlorodiphenylphosphine (2.20 g, 10<sup>-2</sup> mol) was stirred at room temperature for 5 h, the mixture solidified. The <sup>1</sup>H n.m.r. spectrum of this solid revealed that the aldehyde had been fully consumed. The solid was identified as one diastereoisomer of α-chlorobenzyl α-(diphenylphosphinoyl)benzyl ether (8a); δ<sub>H</sub> 8.0–6.8 (20 H, m, Ph), 3.4 (1 H, s, PhCHClO), and 3.9 [1 H, d, *J* 8.5 Hz, Ph<sub>2</sub>P(O)CH(Ph)O]; δ<sub>C</sub> 78.8 [d, <sup>1</sup>*J*<sub>CP</sub> 87.4 Hz, (O)P-CH] and 94.2 [d, <sup>2</sup>*J*<sub>CP</sub> 12.0 Hz, (O)P-CH-O-CH] (in addition to aromatic carbons); δ<sub>P</sub> + 28.5. The adduct was extremely sensitive to moisture, and most i.r. spectra of (8a) showed small absorptions due to benzaldehyde.

When a further mixture of the same reactants was heated at temperatures in the range 50–100 °C, the formation of (8a) was more rapid, and was accompanied by the successive formation of benzal chloride, bis-[(α-diphenylphosphinoyl)-

benzyl] ether (12a), and α-chlorobenzyl(diphenyl)phosphine oxide (11a). Prolonged heat at 110 °C did not greatly alter the proportions of these (over 36 h), but gradual elevation of the temperature to 190 °C resulted in slow conversion of (12a) into (8a). The ether (12a) was isolated by quenching with water a mixture of benzaldehyde and (1a) which had been kept at 80 °C for 20 h. The resulting solid was partially dissolved in chloroform (20 ml), and the filtered solution washed with aqueous NaHCO<sub>3</sub>, then water. Evaporation of chloroform from the dried solution yielded a sticky solid, which was washed with ether. Fractional crystallization from light petroleum (b.p. 40–60 °C)-benzene yielded (12a), m.p. 237–238 °C (lit.,<sup>15</sup> 237–238 °C); δ<sub>H</sub> 8.0–6.9 (30 H, m, Ph) and 5.05 [2 H, d, *J* 8.8 Hz, Ph<sub>2</sub>P(O)CH(Ph)O].

When a further mixture of benzaldehyde and (1a) was heated directly to 160 °C, the formation of α-chlorobenzyl(diphenyl)phosphine oxide (11a) was more rapid. Observation of the <sup>1</sup>H n.m.r. of the heated sample revealed that benzaldehyde was present throughout the reaction, and that it was present in equimolar amounts relative to (11a) after 6 h.

The experiments using 2 mol equiv. of benzaldehyde were also performed in sealed n.m.r. tubes, using deuteriochloroform as solvent (10 ml for each 0.01 mol of chlorodiphenylphosphine). The course of these reactions was exactly as described above, although the relative rates of the formation and loss of (8a) and (12a) were different under homogeneous conditions.

*Reactions of Chlorodiphenylphosphine (1a) with Substituted Benzaldehydes.*—Solutions were made up in chloroform (10 ml), and contained chlorodiphenylphosphine (2.2 g, 10<sup>-2</sup> mol) and aldehyde (2 × 10<sup>-2</sup> mol). These solutions were kept at 20 °C under nitrogen for 48 h and their <sup>1</sup>H n.m.r. spectra were run periodically.

(a) *p-Nitrobenzaldehyde.* This reaction was found to produce absorptions at δ 6.4 (s, ArCHCl) and 6.13 [d, *J* 8.0 Hz, ArCHP(O)], of equal integrated intensity, along with weaker signals of equal intensity at δ 6.48 (s, ArCHCl) and 5.89 [d, *J* 11 Hz, ArCHP(O)]. The integral of these sets of absorptions suggested that the ratio of diastereoisomers was 7:3. Heating the solution to 150 °C caused the slow growth of a signal at δ 5.2 [d, *J* 8.0 Hz, ArCHP(O)], presumed to be due to the analogue of (12a). Heating at 150 °C did not cause any further changes in the reaction mixture.

(b) *p-Cyanobenzaldehyde.* This was found to react at 20 °C to produce new <sup>1</sup>H n.m.r. absorptions at δ 6.35(s) and 6.10 (d, *J* 8 Hz), and at δ 6.43(s) and 5.89 (d, *J* 10 Hz), which were assigned to the diastereoisomeric analogues of (8a), and at δ 5.25 (d, *J* 8.2 Hz). The proportion of the δ 5.25 absorption increased as the temperature of the mixture was raised, and this signal was assigned to an analogue of (12a). When an equimolar mixture of benzaldehyde and *p*-cyanobenzaldehyde was heated with chlorodiphenylphosphine (4 mol equiv.) in deuteriochloroform at 32 °C, both aldehydes were consumed steadily, at rates indistinguishable by measurement of integrals.

(c) *p-Methoxybenzaldehyde.* This was not typical in its reactions, in that it reacted at 20 °C to give one new absorption in the <sup>1</sup>H n.m.r. spectrum, at δ 5.5 [d, *J* 2 Hz, ArCHP(O)]. The reaction was completed by warming to 60 °C for 12 h, and then quenched by pouring into a toluene-light petroleum (b.p. 40–60 °C) mixture. The product was recrystallized from the same solvent mixture, to give (α-chloro-*p*-methoxybenzyl)diphenylphosphine oxide (11i), m.p. 179–181 °C (lit.,<sup>30</sup> 181–182 °C).

*Hydrolysis of  $\alpha$ -Chlorobenzyl  $\alpha$ -(Diphenylphosphinoyl)benzyl Ether (12a).*—The ether (12a) was made *in situ* from benzaldehyde and chlorodiphenylphosphine ( $10^{-2}$  mol) in chloroform (10 ml), and shown to be free of benzaldehyde (by n.m.r.). To this solution was added wet tetrahydrofuran (10 ml) and the mixture stirred for 5 min. Benzene (30 ml) was then added and the mixture filtered. The residue was  $\alpha$ -hydroxybenzylidiphenylphosphine oxide (2), m.p. 176–178 °C (lit.<sup>31</sup> 178–179.5 °C), identified by comparison of its i.r. spectrum with that of an authentic sample, yield 2.1 g (96%). The solvent was carefully evaporated from the filtrate, and the oily residue (2.22 g) was shown by its i.r. spectrum to be almost pure benzaldehyde.

*Reaction of Bis-( $\alpha$ -chlorobenzyl) Ether (9) with Diphenylphosphine Oxide (10).*—A mixture of benzaldehyde (0.212 g,  $2 \times 10^{-3}$  mol) and thionyl chloride (0.119 g,  $10^{-3}$  mol) in deuteriochloroform (1 ml) was allowed to stand at room temperature under nitrogen for two weeks, until the singlet for bis-( $\alpha$ -chlorobenzyl) ether (9)<sup>4</sup> at  $\delta_{\text{H}}$  7.2 had ceased to increase in intensity, relative to the CHO signal for benzaldehyde ( $\delta_{\text{H}}$  10.1). To this mixture was added a solution of diphenylphosphine oxide (0.100 g,  $5 \times 10^{-4}$  mol) in deuteriochloroform (0.5 ml). After several hours at room temperature, the ether (9) had been converted to  $\alpha$ -chlorobenzyl  $\alpha$ -(diphenylphosphinoyl)benzyl ether (8a);  $\delta$  8.0–7.1 (m, Ph), 6.50 (s, PhCHCl), and 6.29 [d,  $J$  8.4 Hz, Ph<sub>2</sub>P(O)CHPh]. A sample of (8a) in deuteriochloroform, which was saturated with hydrogen chloride, showed an identical set of absorptions, and there was no sign of absorptions due to the second diastereoisomer of (8a).

*Conductivity Measurements.*—These were obtained using a simple platinum wire electrode cell and a Wayne–Kerr Universal Bridge. The cell constant was found to be 2.89 cm<sup>-1</sup>, from measurements at 25 °C on a 0.02M solution of KCl.<sup>32</sup> *o*-Dichlorobenzene was purified by double passage through alumina,<sup>33</sup> and found to have a conductance of 0.0009  $\mu$ S at 23 °C. Acetonitrile was purified by refluxing over, then distillation from, CaH<sub>2</sub> and was found to have a conductance of 2.70  $\mu$ S at 23 °C.

(a) *Methoxymethyltriphenylphosphonium chloride* (6). For a 0.05M solution of (6) in acetonitrile,  $K$  was found to be 950  $\mu$ S at 23 °C. This value did not change after 2 h at 23 °C. Addition of water to the solution resulted in relatively small changes in  $K$ . After the addition of 1 mol equiv. of water  $K$  had increased to 1 015  $\mu$ S. The salt (6) was not very soluble in *o*-dichlorobenzene, but a saturated solution (*ca.* 0.02M) had a value for  $K$  of 5.2  $\mu$ S.

(b)  *$\alpha$ -Acetoxybenzyl  $\alpha$ -(diphenylphosphinoyl)benzyl ether* (7). A 0.05M solution of (7) in acetonitrile had a  $K$  of 2.53  $\mu$ S at 23 °C. Dilution of this to 0.01M resulted in no change in this value.

(c)  *$\alpha$ -Chlorobenzyl  $\alpha$ -(diphenylphosphinoyl)benzyl ether* (8a). This was prepared as required from benzaldehyde (2 mol equiv.) and chlorodiphenylphosphine, and its purity checked by n.m.r. to be at least 95% before use in conductivity studies. A 0.04M solution of (8a) in acetonitrile at 23 °C had a  $K$  of 137.5  $\mu$ S. This increased slowly on standing for 2 h, to a value of 159.6  $\mu$ S. Addition of small aliquots of moist acetonitrile resulted in a rapid increase in conductance, up to 440  $\mu$ S after the addition of 1 mol equiv. of water. A 0.2M solution of (8a) in *o*-dichlorobenzene at 23 °C, had  $K$  2.9  $\mu$ S.

*Reaction of Chlorodiphenylphosphine (1a) with Acetaldehyde.*—Chlorodiphenylphosphine (2.20 g, 0.01 mol) and

acetaldehyde (0.88 g, 0.02 mol) were mixed in chloroform (5 ml) and stood at 20 °C. After 20 min the aldehyde had reacted completely and <sup>1</sup>H n.m.r. revealed a mixture of products. There were four clear quartets, at  $\delta_{\text{H}}$  4.65 ( $J$  5 Hz), 4.88 ( $J$  8 Hz), 5.37 ( $J$  6 Hz), 5.92 ( $J$  5.5 Hz), and many lines in the range 1.3–1.8. When this mixture was warmed, initially to 50 °C (4 h), and then 110 °C (4 h), no changes in spectrum were observed. Heating to a higher temperature caused severe decomposition of the mixture, and consequent blackening of the sample.

*Reactions of Bis-[ $\alpha$ -(diphenylphosphinoyl)benzyl] Ether (12a).*—A solution of the ether (12a) (0.12 g,  $2 \times 10^{-4}$  mol) in deuteriochloroform was heated in a sealed n.m.r. tube at 190 °C for 16 h, but no change in <sup>1</sup>H n.m.r. could be detected. After addition of benzal chloride (0.032 g,  $2 \times 10^{-4}$  mol), the mixture was heated for 2 h at 190 °C, but again no reaction was detected by <sup>1</sup>H n.m.r. When the solution was made acidic with gaseous hydrogen chloride (*ca.* 1 mol equiv.), and then re-sealed, further heating for 15 h at 190 °C resulted in complete reaction of (12a). The major products were  $\alpha$ -chlorobenzyl(diphenyl)phosphine oxide (11a) and benzaldehyde in the molar ratio of 2 : 1, while small absorptions were detected for unreacted benzal chloride and for benzylidiphenylphosphine oxide (both *ca.* 8 mol %). Each product absorption was carefully checked by <sup>1</sup>H n.m.r. signal augmentation using authentic samples.

*Reaction of Benzaldehyde with the Benzyl(chloro)diphenylphosphonium Chloride (16).*—From chlorodiphenylphosphine (2.2 g,  $10^{-2}$  mol) and benzyl chloride (1.26 g,  $10^{-2}$  mol) in deuteriochloroform, a sample of benzyl(chloro)diphenylphosphonium chloride (16) was prepared as previously described.<sup>30</sup> To this solution was added benzaldehyde (1.06 g,  $10^{-2}$  mol) and the mixture stirred at 20 °C for 5 min. The <sup>1</sup>H n.m.r. of the mixture showed that all the aldehyde had been consumed, and that benzal chloride ( $\delta_{\text{H}}$  6.8, s) and benzylidiphenylphosphine oxide (17) ( $\delta_{\text{H}}$  3.9, d,  $J$  13 Hz) were the only products formed.

*Reaction of Benzal Chloride with Diphenylphosphine Oxide (10).*—Diphenylphosphine oxide (1.0 g,  $5 \times 10^{-3}$  mol) was added to a solution of benzal chloride (0.64 g,  $4 \times 10^{-2}$  mol) in deuteriochloroform. The <sup>1</sup>H n.m.r. spectrum of the mixture was observed as it was heated gradually up to 140 °C. The first new peak to appear was due to  $\alpha$ -chlorobenzyl(diphenyl)phosphine oxide (11a) ( $\delta$  5.68, d,  $J$  3.5 Hz). By the time all the benzal chloride had been consumed, the major product was benzylidiphenylphosphine oxide (17) ( $\delta_{\text{H}}$  3.9, d,  $J$  13 Hz), although some (11a) remained. Further addition of diphenylphosphine oxide (0.50 g,  $2.5 \times 10^{-3}$  mol) resulted in complete conversion of (11a) into (17).

*Reaction of Benzaldehyde with Chloro(dialkyl)phosphines.*—In each case benzaldehyde (0.106 g,  $10^{-3}$  mol) and the chlorophosphine ( $5 \times 10^{-4}$  mol) were mixed cautiously with cooling at <20 °C in deuteriochloroform (0.5 ml), and the mixture analysed periodically by <sup>1</sup>H n.m.r.

(a) *Chloro(di-*t*-butyl)phosphine* (1h). No reaction was detected after 14 days at 20 °C, or after a further 5 h at 180 °C. When another reaction mixture was heated directly at 180 °C, the same result was observed.

(b) *Chloro(diethyl)phosphine* (1g). A mild exothermic reaction was observed on mixing the reactants. After 2 h *ca.* 25% of the aldehyde had reacted, and after 24 h at 20 °C *ca.* 60% had reacted. New absorptions appeared at  $\delta_{\text{H}}$  6.8(s), due to benzal chloride, and at  $\delta_{\text{H}}$  5.15 (d,  $J$  6 Hz).

This reaction was then scaled up (2.12 g benzaldehyde).

After stirring at 20 °C for 48 h, the solvent (chloroform) was removed to give an oil. This was chromatographed on alumina, and a white crystalline solid eluted with ether-methanol (20:1). This was recrystallized from light petroleum (b.p. 60–80 °C) to give white needles of  $\alpha$ -chlorobenzyl(diethyl)phosphine oxide (11g) (0.42 g, 18%), m.p. 92–94 °C (Found: C, 57.2; H, 6.7; P, 13.4.  $C_{11}H_{16}ClOP$  requires C, 57.00; H, 6.96; P, 13.36%);  $\delta_H$  0.8–2.2 (10 H, m,  $MeCH_2-P(O)$ ), 5.05 (1 H, d,  $J$  6 Hz), and 7.3–7.8 (5 H, m, Ph);  $\nu_{max}$ . (Nujol) 1 175s, 1 035, 755, 735, and 703  $cm^{-1}$ .

(c) *Chloro(dimethyl)phosphine* (1f). This reaction was instantaneous and very violent on mixing the reactants, and this was therefore done gradually. The aldehyde was not completely changed after 1 h at 20 °C, by which time the  $^1H$  n.m.r. of the mixture showed absorptions at 1.4–1.8 (several doublets), 2.0 [d,  $J$  13 Hz,  $MeP(O)$ ], 5.1 (d,  $J$  8 Hz), 5.45 (d,  $J$  10 Hz), 6.40(5), 6.75(5), and 7.4 (br s). This complex mixture of products was not investigated further.

*Reaction of Dichloro(phenyl)phosphine (1d) with Benzaldehyde*.—A mixture of dichloro(phenyl)phosphine (1.79 g,  $10^{-2}$  mol) and benzaldehyde (1.06 g,  $10^{-2}$  mol) was stirred under nitrogen at room temperature for 5 h, but no reaction was observed ( $^1H$  n.m.r.). The temperature was raised to 150 °C, over 4 h, then to 200 °C over 2 h, and the aldehyde absorptions in the  $^1H$  n.m.r. of the mixture were found to decrease slowly. At this stage, the major non-aromatic absorptions were due to a mixture of the diastereoisomers of chloro( $\alpha$ -chlorobenzyl)phenylphosphine oxide (11d);  $\delta_H$  5.53 (d,  $J_{PH}$  6 Hz) and 5.59 (d,  $J_{PH}$  6 Hz). It was not possible to obtain a pure sample from this reaction product.

*Reaction of  $\alpha$ -Chlorobenzyl  $\alpha$ -(Diphenylphosphinoyl)benzyl Ether (8a) with Hydrogen Chloride*.—The adduct (8a) (0.326 g,  $10^{-3}$  mol) was dissolved in deuteriochloroform (1 ml) which had previously been made (*ca.* 1M) with dry hydrogen chloride. The mixture was sealed under nitrogen in an n.m.r. tube, and stood at room temperature for four days. The mixture was then warmed cautiously at 50 °C for 10 h, but there was no change in the  $^1H$  n.m.r. spectrum of the mixture.

*Preparation of 1-Chloro-2,2,4,4-tetramethylphosphetan (1b)*.—2,4-Dimethylpent-2-ene (16.8 g, 0.175 mol) in dry dichloromethane (25 ml) was added dropwise over 20 min at 0–5 °C to a preformed complex of aluminium chloride (23.5 g, 0.175 mol) with phosphorus trichloride (24.0 g, 0.175 mol) in dichloromethane (150 ml). The mixture was then allowed to come to 20 °C, and it was stirred overnight, before being added dropwise to vigorously stirred ice-water. The organic phase was separated, washed with dilute sodium hydrogencarbonate solution (2  $\times$  50 ml), and then dried. Evaporation yielded a pale brown oil (25 g), which was fractionally distilled to give 1-chloro-2,2,4,4-tetramethylphosphetan 1-oxide (12.3 g), b.p. 60–66 °C at 0.5 mmHg.

The oxide (12.3 g) was then deoxygenated using silicone oil (MS 1 107) (12.5 ml) at 160 °C for 2 h. Distillation of volatile material gave a main fraction (4.5–6.2 g), b.p. 48–56 °C at 5 mmHg. Redistillation gave pure 1-chloro-2,2,4,4-tetramethylphosphetan (1b) (2.8–3.2 g, 10–12%), b.p. 72–74 °C at 20 mmHg (Found:  $M^+$ , 164.051 9.  $C_7H_{14}ClP$  requires  $M^+$ , 164.051 9);  $\delta_H$  1.25 (6 H, d,  $J$  6 Hz), 1.38 (6 H, d,  $J$  20 Hz), and 2.2–2.5 (2 H, m).

*Reaction of 1-Chloro-2,2,4,4-tetramethylphosphetan (1b) with Aromatic Aldehydes*.—(a) *Benzaldehyde* at 20 °C. The chlorophosphetan (1b) ( $1.65$  g,  $10^{-2}$  mol) and benzaldehyde

(2.12 g,  $2 \times 10^{-2}$  mol) were stirred together in deuteriochloroform (3 ml) under nitrogen for 200 h. During this period, analysis by  $^1H$  n.m.r. revealed that the aldehyde was consumed fairly rapidly at first, and then more slowly up to 60%. When the solvent was removed, the resultant brown oil solidified. After trituration under dry petroleum (b.p. 40–60 °C), a white solid was obtained, but was found to be too moisture-sensitive to give an acceptable microanalysis. On the basis of spectroscopic evidence the solid was identified as 1-[ $\alpha$ -( $\alpha$ -chlorobenzyl)oxy]benzyl]-2,2,4,4-tetramethylphosphetan 1-oxide (8b) (0.85 g, 22%), m.p. (sealed capillary) 114–120 °C;  $\delta_H$  1.29 (3 H, d,  $J_{P-Me}$  18 Hz), 1.35 (3 H, d,  $J_{P-Me}$  16 Hz), 1.50 (3 H, d,  $J_{P-Me}$  18 Hz), 1.59 (3 H, d,  $J_{P-Me}$  18 Hz), 1.9–2.15 (m), 5.7 (1 H, s), 6.35 (1 H, s,  $CH-ClPh$ ), and 7.2–7.8 (10 H, m, Ph);  $^{13}C$ - $\{^1H\}$   $\delta_C$  131–129.5 (aromatic), 93.7 (d,  $J_{PC}$  10.4 Hz), 76.4 (d,  $J_{PC}$  36.9 Hz,  $P-CHPh$ ), 45.9 (d,  $J_{PC}$  12 Hz,  $CH_2$ ), 44.7 (d,  $J_{PC}$  58.8 Hz,  $CMe_2$ ), 43.3 (d,  $J_{PC}$  54.1 Hz,  $CMe_2$ ), and 26.0–24.37 (m,  $Me_2C$ );  $\delta_P$  56.4.

(b) *Benzaldehyde* at 140 °C. The chlorophosphetan (1b) (1.65 g,  $10^{-2}$  mol) was treated with benzaldehyde (1.06 g,  $10^{-2}$  mol) at 140 °C for 10 h. Analysis by  $^1H$  n.m.r. showed the rapid formation and slow loss of absorptions due to the phosphetan 1-oxide (8b). More slowly, a new absorption ( $\delta$  4.87, d,  $J$  3.5 Hz) accumulated, to be followed by another ( $\delta$  5.55, d,  $J$  5 Hz) which appeared to come from the final product of the reaction. When the mixture was heated to 200 °C for 2 h, the absorption at  $\delta$  4.87 slowly diminished. Sublimation (140 °C at 0.5 mmHg) of the crude product yielded 1-( $\alpha$ -chlorobenzyl)-2,2,4,4-tetramethylphosphetan 1-oxide (11b) (0.55 g, 21%), m.p. 182–184 °C (after recrystallization from benzene-light petroleum) (Found: C, 62.2; H, 7.3; P, 11.2.  $C_{14}H_{20}ClOP$  requires C, 62.25; H, 7.45; P, 11.43%);  $m/e$  270 ( $M^+$ ), 235 ( $M^+ - Cl$ ), 179, 164, 145, and 125;  $\nu_{max}$ . (Nujol) 1 380, 1 200s, 1 180s, 1 155s, 725, and 700  $cm^{-1}$ ;  $\delta_H$  0.98 (3 H, d,  $J$  17.5 Hz), 1.14 (3 H, d,  $J$  16 Hz), 1.47 (3 H, d,  $J$  16.5 Hz), 1.53 (3 H, d,  $J$  18 Hz), 5.55 (1 H, d,  $J$  3.5 Hz), and 7.1–7.9 (5 H, m, Ph).

(c) *p-Methoxybenzaldehyde*. A mixture of the chlorophosphetan (1b) (0.164 g,  $10^{-3}$  mol) and *p*-methoxybenzaldehyde (0.136 g,  $10^{-3}$  mol) was dissolved in deuteriochloroform (0.4 ml) and the solution sealed in an n.m.r. tube. After 24 h at 20 °C a new absorption at  $\delta$  5.3, (d,  $J$  5 Hz) was observed in the  $^1H$  n.m.r. spectrum of the mixture. This signal amounted to 40% of the mixture after 1 week. Heating at 100 °C for 12 h had no effect on the spectrum of the mixture, and heating at 180 °C resulted in diminishing intensity of the methoxy-signal at  $\delta$  3.8, and generation of chloromethane.

(d) *p-Nitrobenzaldehyde*. A mixture of the chlorophosphetan (1b) (0.164 g,  $10^{-3}$  mol) and *p*-nitrobenzaldehyde (0.151 g,  $10^{-3}$  mol) was dissolved in deuteriochloroform, as in (c) above. After 3 days at 20 °C, *ca.* 50% loss of the aldehyde had occurred ( $^1H$  n.m.r.), and the only new absorptions outside the methyl and aryl regions were at  $\delta$  5.88(s) and 6.35(s), each of the same intensity. Heating to 100 °C for 12 h did not alter the spectrum. Heating to 180 °C for 5 h caused complete loss of the singlets at  $\delta$  5.88 and 6.35, and regeneration of some of the aldehyde CHO absorption ( $\delta$  10.2 s). There was no sign of absorptions between  $\delta$  2.5 and 8.0.

*Reaction of 1-Chloro-2,2,3,4,4-pentamethylphosphetan (1e) with Benzaldehyde*.—The phosphetan  $^{28}$  (0.178 g, 0.001 mol) and benzaldehyde (0.106 g, 0.001 mol) were dissolved in deuteriochloroform (0.25 ml) at 20 °C. Analysis by  $^1H$



n.m.r. revealed that no reaction had taken place after 48 h. The mixture was then heated at 75 °C for 18 h, and some loss of aldehyde (ca. 30%) resulted. Weak absorptions now appeared at  $\delta_{\text{H}}$  3.7 (d,  $J$  11 Hz), 5.65 (d,  $J$  6 Hz), 5.68 (s), and 6.32 (s), each of comparable intensity. When the solution was heated at 160 °C for 3 days, the singlet absorptions disappeared, and considerable darkening of the solution was observed.

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