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REACTION OF CHLORODIPHENYLPHOSPHINE WITH ACETIC ACID

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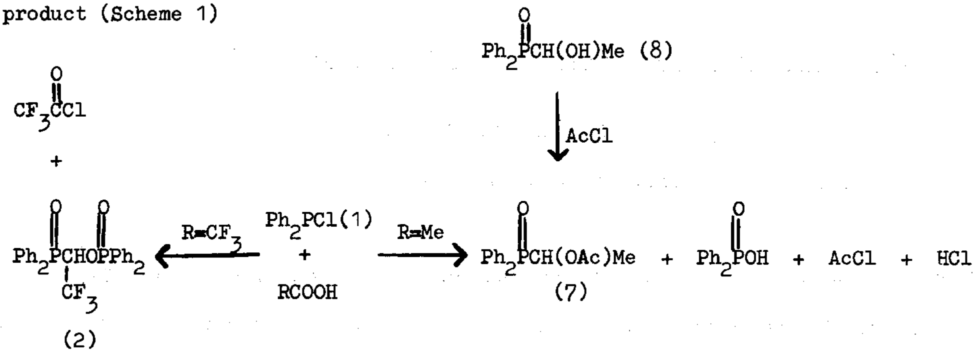
TRIFLUOROACETYLPHOSPHINE derivatives have been described a number of times in recent years,[1,2] and the reaction between chlorodiphenylphosphine (1) and trifluoroacetic acid, in particular, has been examined in some detail,[2] and is now known[2b,c] to result in the ester (2). In view of the fact that simple carboxylic acids, such as acetic acid, have been used to influence the reactions of halogenophosphines with carbonyl compounds,[3] it seemed that a closer study should be made of the reaction of chlorodiphenylphosphine with a carboxylic acid more typical than trifluoroacetic acid.

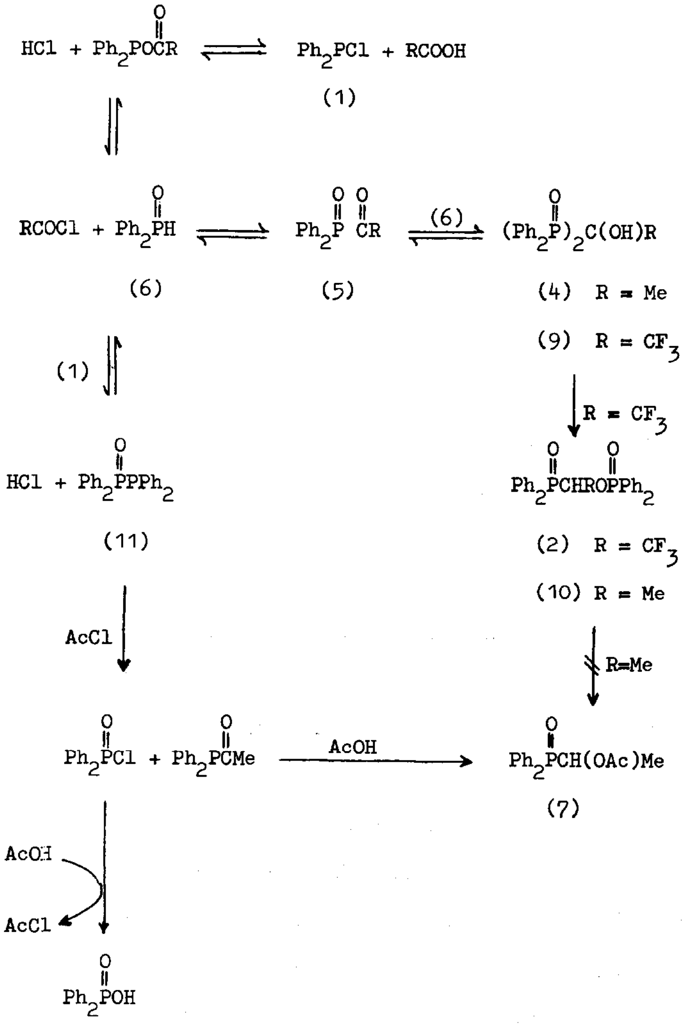
We have therefore followed the reaction at room temperature of acetic acid with equimolar amounts of chlorodiphenylphosphine, using ^1H and ^{31}P n.m.r. It has been found that acetyl chloride is formed slowly and steadily, followed by acetyldiphenylphosphine (3) and 1,1-bis (diphenylphosphinoyl)ethanol (4), the known[4] adduct of acetyldiphenylphosphine oxide (5,R=Me) and diphenylphosphine oxide (6). Over a period of several days at room temperature, the signals due to (3) and (4) diminish, to be replaced by new, strong absorptions in the methyl region. Distillation of the product gives a good yield of 1-(diphenylphosphinoyl)ethyl acetate (7), readily identified by its ^1H n.m.r. spectrum, which shows aromatic absorptions (δ 8.2-7.3, 10H), a double quartet (δ 5.97, J 3 and 8, 1H), a singlet (δ 1.9, 3H), and a double doublet (δ 1.45, J 8 and 16, 3H). This structure is in accord with other analytical and spectral data, and was confirmed by an independent synthesis from 1-(diphenylphosphinoyl)ethanol (8). At the end of the acetic acid-Ph_2PCl reaction, an n.m.r. of the reaction mixture shows equimolar amounts of acetyl chloride and (7), and work-up yields diphenylphosphinic acid as a further product (Scheme 1)



Scheme 1: Products isolated from Ph_2PCl + RCOOH reactions.

Despite the obvious structural relationship between (2) and (7), we have no evidence that the acetate (7) is formed via (10), the analogue of (2), since (10) is unaffected by the conditions leading to (7). Thus the pathway from (9) to (10) suggested[2b,c] to hold for the trifluoroacetic acid - chlorodiphenylphosphine (1) system, and recently confirmed by other workers,[5] does not apply to the reaction of acetic acid with (1). The formation of (4) in the present case would seem to be reversible, and we suggest that this is achieved *via* acetyldiphenylphosphine oxide (5, R=Me) as shown in scheme 2, since it is known[6] that the original starting materials readily equilibrate with acetyl chloride and diphenylphosphine oxide (6).

Acetyldiphenylphosphine (3) has been confirmed as the other intermediate by synthesis and we have been able to show, in separate experiments, that it may be converted into the acetate (7) by treatment with hydrogen chloride in acetic acid. This conversion is very efficient, but proceeds slowly, at a rate compatible with the rate of formation of (7) from acetic acid and (1). The addition of acetic acid to (3) is thus the key step in the



Scheme 2: Intermediates and Pathways in Ph_2PCl + RCOOH reactions.

sequence leading to (7), and distinguishes the present system from that using trifluoroacetic acid.

As regards the remaining steps in Scheme 2, the formation of tetraphenyldiphosphine monoxide (11) has good analogy,[7] and, moreover, explains our failure to observe diphenylphosphine oxide (6) as an intermediate. We have shown independently that (11) is readily acetylated by acetyl chloride. Finally, we have also shown that acetic acid and diphenylphosphinoyl chloride react rapidly to form acetyl chloride and diphenylphosphinic acid, thus accounting for the other products of the reaction.

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