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REACTION OF HALOPHOSPHINES WITH ALDEHYDES

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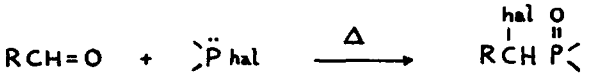
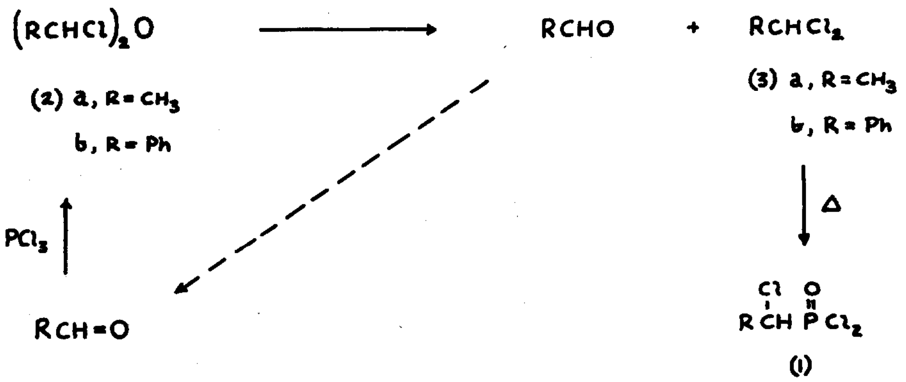
The thermal reaction of aldehydes with halophosphines is a general route[1] to α-haloalkylphosphoryl compounds (equation a) that has been known for almost a century.[2] Synthetically it is a useful reaction because it results in the bonding of a conveniently functionalised alkyl group to phosphorus. However a number of studies of this and other related reactions have not resulted in the conclusive identification of the intermediates between the starting aldehyde and the final oxides (1).[3] In consequence, any rationalisation[4] of these reactions has been rather speculative, and it has not been firmly established whether the phosphine acts as an electrophile or a nucleophile, and, if the latter, whether towards the carbonyl carbon or oxygen atoms. We wish to report evidence regarding the intermediates in reactions of type (a), and to present a rationale which allows these reactions to be classified along with other established reactions of aldehydes with electrophilic halogen compounds.



$$\mathrm{RCH{=}O} + {>}\ddot{\mathrm{P}}\,\mathrm{hal} \xrightarrow{\Delta} \mathrm{R}\overset{\mathrm{hal}}{\underset{}{\mathrm{C}}}\mathrm{H}\,\overset{\mathrm{O}}{\overset{\|}{\mathrm{P}}}{<} \qquad \text{(a)}$$

(1)

We find that the reactions of both aliphatic and aromatic aldehydes with equimolar amounts of phosphorus trichloride at room temperature yield bis-α-chloroalkyl ethers (2).[*] In the case of acetaldehyde, the ether (2a) is the stable reaction product. However in the case of aromatic aldehydes the ethers, e.g. (2b), are unstable and rearrange to give equal amounts of a benzal chloride (3) and the starting aldehyde, which, using benzaldehyde as an example, then reacts further in a similar fashion until benzal chloride (3b) is the only aldehyde-derived product. If the temperature in these reactions is then increased to 150°C (i.e. conditions of earlier pyrolyses[3]) the intermediates are rapidly and irreversibly converted to the oxides (1) (see scheme 1).



Scheme 1

The formation of (2) and (3) from aldehydes is thus akin to the known reactions of other electrophilic halides with aldehydes. For example, gaseous hydrogen chloride[5] or thionyl chloride[6] convert acetaldehyde into (2a), and, more strikingly, boron trichloride reacts with acetaldehyde to form (2a)[7], and with benzaldehyde to form (3b)[7]. Furthermore, the essential features of these aldehyde reactions are retained when phosphorus tribromide or triiodide is used in place of phosphorus trichloride.

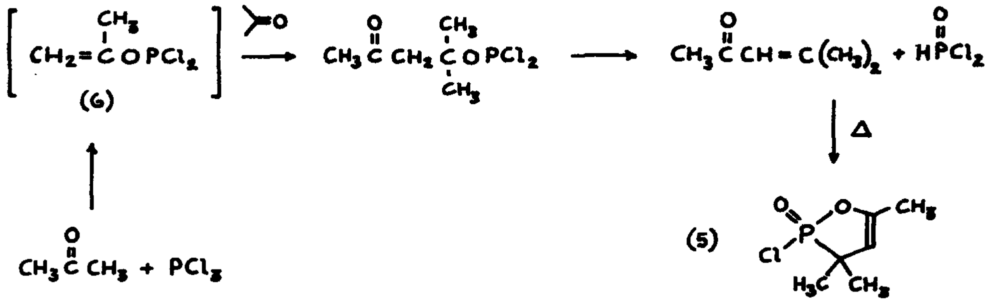
The implication behind these analogies is that the phosphorus trihalides act as electrophiles towards the aldehydes, and this is confirmed by the fact that p-anisaldehyde is much more reactive, and p-nitrobenzaldehyde much less reactive, than benzaldehyde itself. Further indication of this is the observation that the reactivity of the phosphorus trihalides with benzaldehyde lies in the order $PI_3 > PBr_3 > PCl_3$. This view of the role of the phosphorus trihalides in the initial stages of these reactions is contrary to the opinions of Conant et al.[4a], but in agreement with those of Kabachnik,[4b] and of Atherton et al.[4c] The opinion of the latter authors was largely based on the isolation of benzal chloride from a prolonged reaction (followed by distillation at ~150°C) of benzaldehyde and phosphorus trichloride in the presence of sulphuryl chloride. They interpreted the isolation of (3b) in terms of the reaction of sulphuryl chloride with an intermediate α-chlorobenzyl phosphite (4), although it is clear from our studies that (3b) would have been formed in the absence of sulphuryl chloride. Our results do not rule out (4) as an intermediate, but it is evident, that, if formed, it must react extremely rapidly with further benzaldehyde to give (2b), and that it does not yield the oxide (1, R = Ph) directly.[4c]

$\mathrm{Ph}\overset{\mathrm{Cl}}{\mathrm{C}}\mathrm{HOPCl_2}$

(4)

The final stage of the sequence, leading from (3), to the oxides (1), appears to be an Arbusov-type reaction,[8] and it is this nucleophilic behaviour of phosphorus which distinguishes the present reactions from those of other halides.[5,6,7] The exact nature of the phosphorus reagent involved is open to question, since our ^{31}P-n.m.r. studies have shown that the benzaldehyde reactions with phosphorus trichloride or tribromide are not describable in terms of simple stoichiometry at either of the initial stages, when the aldehyde has been completely converted to either (2b), or (3b), since relatively large amounts of the trihalides are still present at both stages. This is perhaps not surprising in view of the recent demonstration of the complexities of the exchange reactions in a related system between tervalent phosphorus species containing halogen and oxygen ligands.[9]

These aldehyde reactions provide a notable contrast to those of ketones with phosphorus trichloride and related phosphines,[10] which generally produce 1,2-oxaphospholene-1-oxides (5), by the pathway outlined for acetone in scheme 2[9,11]. It seems that the difference between the two series of reactions is that, for aldehydes, an intermediate, such as (4), readily reacts with further aldehyde to give (2), whereas, for ketones, the loss of a proton occurs (where possible) to give (6), which then reacts with further ketone by an Aldol-type process.



Scheme 2

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