The Preparation of Aromatic Aldehydes from Acid Chlorides

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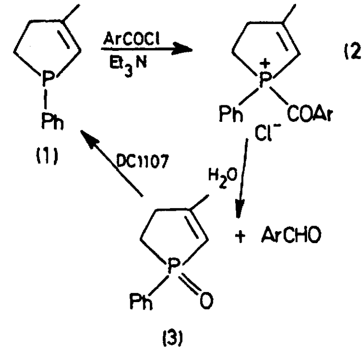
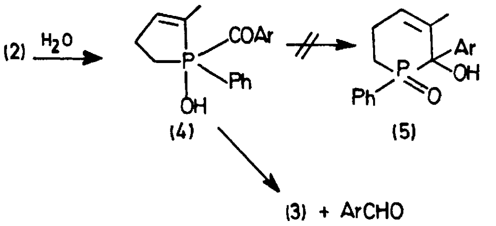
Summary The reaction of phospholenes with aromatic acid chlorides gives acylphospholenium salts which on treatment with water give the corresponding aldehydes and phospholene oxides.

The reaction[1] of 3-methyl-1-phenyl-2-phospholene (**1**) with benzoyl chloride in the presence of triethylamine gave an acylphospholenium salt (**2**)† which on hydrolysis did not give the expected ring-expanded product (**5**), but instead gave the corresponding phospholene oxide (**3**) and benzaldehyde.





We have investigated this reaction as a possible aldehyde synthesis. The acid chlorides used are listed in the Table. The phospholene is treated with an aromatic acid chloride in the presence of triethylamine in an inert solvent, the mixture refluxed for 1—2 h and water added. The aldehydes formed may be separated by distillation, column chromatography, or *via* bisulphite adducts. The yields have not been optimised. Nitro- and hydroxy-acid chlorides appear to form complexes with (**1**) which are not decomposed by water to give aldehydes. The corresponding reaction with aliphatic acid chlorides gives the acid and free (**1**).

Isslieb has shown[2] that the hydrolysis of acyclic acyl phosphonium salts proceeds *via* nucleophilic attack at the carbonyl carbon. When the phosphorus is in a strained ring [as in (**2**)] the rate of nucleophilic attack at phosphorus is increased so the initial attack of water is at the phosphorus atom. This gives a five-co-ordinate intermediate (**4**) containing a highly apicophilic acyl group[3] which then forms (**3**) and the aldehyde. In the hydrolysis of acylphospholium[1] or acylphosphetanium[4] salts, containing rings more highly strained than (**2**), some strain is still present in the intermediate which collapses by ring-expansion. Trippett[5] has shown that in the alkaline hydrolysis of phosphonium salts the leaving anions are protonated as formed. It is therefore unlikely that free acyl anions are produced in the decomposition of (**2**).

Table

Conversion of acid chlorides into aldehydes using 3-methyl-1-phenyl-2-phospholene (**1**)

Ar group in ArCOCl	Aldehyde %
Ph	80
p-$Me_2NC_6H_4$	65
p-$MeOC_6H_4$	89
o-MeC_6H_4	87
p-ClC_6H_4	70
p-BrC_6H_4	72
3,4,5-$Me_3C_6H_2$	77
2-furyl	82

This is a useful alternative method for converting aromatic acid chlorides into aldehydes, since the Rosemund reduction is difficult[6] and other methods such as low-temperature complex metal hydride reductions are costly, difficult to handle and impractical on a large scale.

The phospholene (**1**) used is obtained from isoprene and dichlorophenylphosphine,[7] although all other phospholenes tried have also been successful. (**3**) can be reduced to (**1**) using a polymethylhydrogen siloxane,[8]‡ so that the (**3**) recovered from the reaction can be recycled.

We thank the S.R.C. and Allen and Hanburys Ltd., for a C.A.S.E. Research Studentship.

(*Received*, 10*th April* 1975; *Com.* 417.)

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† These salts can be, but are not usually, isolated in this reaction sequence.

‡ DC 1107 fluid manufactured by Dow-Corning Ltd., supplied by Hopkin and Williams Ltd.

[1] F. Mathey, *Tetrahedron*, 1973, **29**, 707.
[2] K. Issleib and E. Priebe, *Chem. Ber.*, 1959, **92**, 3183.
[3] S. Trippett and P. J. Whittle, *J.C.S. Perkin I*, in the press.
[4] H. Ali, D. J. H. Smith, and S. Trippett, unpublished observations.
[5] J. R. Corfield and S. Trippett, *Chem. Comm.*, 1970, 1267.
[6] R. C. Fuson, in 'The Chemistry of the Carbonyl Group,' ed. S. Patai, Interscience, 1966.
[7] W. B. McCormack, *Org. Synth.*, 1963, **43**, 73.
[8] H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, 1965, **98**, 1681; see also J. R. Corfield, R. K. Oram, D. J. H. Smith, and S. Trippett, *J.C.S. Perkin 1*, 1972, 713.

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