Reactions of Secondary Phosphines with Hexafluoroacetone

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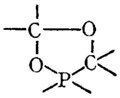
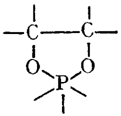
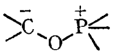
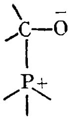
CERTAIN monocarbonyl compounds react with trivalent phosphorus derivatives like trialkylphosphites to give either 1,3,2- or 1,4,2-dioxaphospholans. For example, simple aliphatic monoaldehydes give rise to 1,4,2-dioxaphospholans (I),[1] while *p*-nitrobenzaldehyde or hexafluoroacetone give the 1,3,2-dioxaphospholan structure (II).[2] In the latter case the phosphorus atom tends to attack the oxygen atom of the carbonyl group, whenever it is surrounded by groups which are capable of stabilizing a negative charge at the carbonyl-carbon.[2,3] With the 1,4,2-system the attack appears to be at the carbonyl-carbon atom.


(I)


(II)


(III)


(IV)

In all cases a 2 : 1 adduct is isolated, with a 1 : 1 adduct (III or IV) postulated as an intermediate. A few 1 : 1 adducts have recently been isolated; however, these involved α-diketone compounds.[4]

Proof of a 1 : 1 adduct involving monocarbonyl derivatives would yield greater insight in establishing the actual mechanism. With electron-withdrawing carbonyl compounds it is possible that the initial attack is at the carbonyl-carbon rather than the carbonyl-oxygen. If this is true, then the initial intermediate must be of the type (IV) followed by rearrangement to (III) before reacting with another carbonyl molecule to give the 1,3,2-dioxophospholan product.

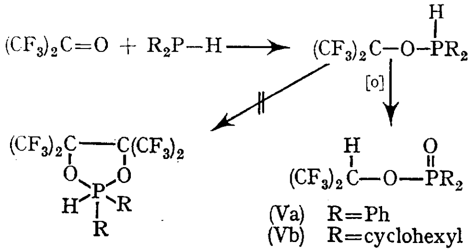
Information regarding the mode of attack by the phosphorus atom on the carbonyl moiety was obtained by using secondary phosphines. In this system an intramolecular or intermolecular proton transfer of the initial 1 : 1 adduct should compete favourably with the reaction of the initial 1 : 1 adduct with another carbonyl molecule.[4] One can anticipate this on the basis of electronegativities (C = 2·50; P = 2·06), bond energies (C–H = 98·8 kcal.; P–H = 76·4 kcal.), and acid–base equilibria considerations.[5]

In the reactions of diphenyl- and dicyclohexylphosphines with an excess of hexafluoroacetone, the expected tertiary phosphine was formed, followed by aerial oxidation to the phosphinate ester.

The isolation of this type of product is convincing evidence that the initial attack by the nucleophilic phosphorus compound on hexafluoroacetone is at the carbonyl-oxygen.

Analysis and i.r. spectra were satisfactory for the proposed structures. Further evidence for (Va), diphenyl-2,2,2-trifluoro-1-(trifluoromethyl)-ethyl phosphinate (m.p. 60—60·5°, yield 68%) was;

^{1}H n.m.r. (C_6D_6; Me_4Si) shows typical aromatic absorption and a septet at δ 6·25 due to the methine hydrogen; ^{19}F n.m.r. [dimethylformamide (DMF); $CFCl_3$] shows a doublet at ϕ 73·0; ^{31}P n.m.r. (DMF; Et_3PO_4) shows a peak at −34·3 p.p.m. The H:F ratio ($CH_2{=}CH{-}CH_2O_2C{\cdot}CF_3$) ϕ-H:CH:F is 10:1:6. For (Vb) dicyclohexyl-2,2,2-trifluoro-1-(trifluoromethyl)ethyl phosphinate (m.p. 89—90°, 84%); ^{1}H n.m.r. (C_6D_6; Me_4Si) shows a septet at δ 5·95 and aliphatic absorption between 2·3 and 1·1; ^{19}F n.m.r. (DMF; $CFCl_3$) shows a doublet ϕ at 74·3; ^{31}P n.m.r. (DMF; Et_3PO_4), −65·5 p.p.m. The H:F ratio (ϕCF_3), alicyclic H:CH:F, is 22:1:6.



(Va) R=Ph
(Vb) R=cyclohexyl

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[1] F. Ramirez, A. V. Patwardham, and S. R. Heller, *J. Amer. Chem. Soc.*, **1964, 86, 514.**

[2] F. Ramirez, S. B. Bhatia, and G. P. Smith, *Tetrahedron*, 1967, **23**, 2067.

[3] R. F. Stockel, *Tetrahedron Letters*, 1966, 2833.

[4] M. Eigen, *Angew. Chem. Internat. Edn.*, 1964, **3**, 1.

[5] L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, New Jersey, 1963, p. 48 and 179.