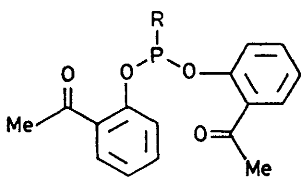
Reaction of *o*-Hydroxyacetophenone with Dichlorophenylphosphine. *X*-Ray Crystal and Molecular Structure of an Unusual Tricyclic Tetraoxaphospha-undecane

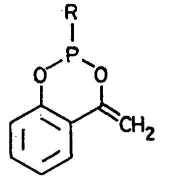
By Gordon M. L. Cragg,* Bette Davidowitz, G. Victor Fazakerley, and Luigi R. Nassimbeni
(*School of Chemical Sciences, University of Cape Town, Private Bag, Rondebosch* 7700, *Republic of South Africa*)
and Raymond J. Haines*
(*Department of Chemistry, University of Natal, P.O. Box* 375, *Pietermaritzburg, Republic of South Africa*)

Summary Treatment of $\mathrm{PhPCl_2}$ with o-$\mathrm{HOC_6H_4COMe}$ in the presence of $\mathrm{NEt_3}$ affords $\mathrm{PhPOC_6H_4C(Me)OCO(Me)C_6H_4O}$, the structure of which has been determined by means of ^{13}C n.m.r. spectroscopy and *X*-ray crystallography.

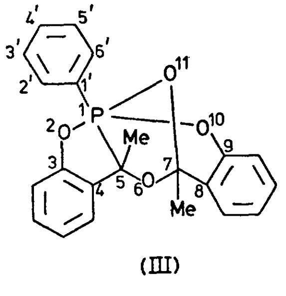
As reported previously the attempted synthesis of the tertiary phosphite (I; R = o-$\mathrm{OC_6H_4COMe}$) by reaction of $\mathrm{PCl_3}$ with 3 equiv. of o-$\mathrm{HOC_6H_4COMe}$ in the presence of 1 equiv. of $\mathrm{NEt_3}$ led instead to the formation of the 1,3,2-dioxaphosphorinan (II; R = o-$\mathrm{OC_6H_4COMe}$).[1] A more detailed investigation of this reaction revealed that (II; R = Cl) is an intermediate in the formation of (II; R = o-$\mathrm{OC_6H_4COMe}$), and that reaction of this species with various alcohols and phenol gives rise to a variety of 1,3,2-dioxaphosphorinans (II; R = OMe, $\mathrm{OPr^i}$, $\mathrm{OBu^t}$, $\mathrm{OCH_2Ph}$, and OPh). With the aim of synthesising (II; R = Ph), $\mathrm{PhPCl_2}$ in benzene was treated with an equimolar amount of o-$\mathrm{HOC_6H_4COMe}$, together with $\mathrm{NEt_3}$, but in this case a white crystalline compound (III) of stoicheiometry $\mathrm{PhP(OC_6H_4COMe)_2}$, as determined by elemental and mass spectrometric (m/e = 378) analyses, was obtained. The absence of C=O stretching peaks in the i.r. spectrum of this compound, and the presence of two methyl resonances, one split into a doublet (J = 20 Hz), in its ^{1}H n.m.r. spectrum indicated that it was not (I; R = Ph).



(I)



(II)



(III)

Repetition of the reaction using 2 equiv. of o-$\mathrm{HOC_6H_4COMe}$ and $\mathrm{NEt_3}$ gave the tricyclic tetraoxaphospha-undecane (III) as a white crystalline product, m.p. 179—180 °C, δ 1·65 (d, J 20 Hz, 5-Me), 2·0 (s, 7-Me), 6·7—7·7 (11H) and 8·0—8·4 (2H). The structure (III) has been assigned on the basis of ^{13}C n.m.r. and *X*-ray crystallographic data.

The ^{13}C n.m.r. spectrum of (III) contains 21 resonances or multiplets, one of which is of an intensity corresponding to two carbon nuclei. There are two methyl carbon resonances; one at δ 25·3 is unsplit and is assigned to the C(7)-*Me*, and the other at δ 26·0 is a doublet and is assigned to C(5)-*Me* ($^2J_{\mathrm{P-C}}$ = 10·0 Hz). A large doublet centred at δ 74·7 ($J_{\mathrm{P-C}}$ = 129 Hz) must arise from a one-bond coupling and must thus be C(5). A doublet at δ 101·3 ($J_{\mathrm{P-C}}$ = 3·0 Hz) is assigned to the remaining bridging carbon C(7). The resonances of the directly bonded phenyl group show no coincidence and the ring cannot be free to rotate about the phosphorus–carbon bond. Two pairs of doublets of similar coupling to phosphorus are found. The resonances at δ 118·5 ($J_{\mathrm{P-C}}$ = 12·0 Hz) and δ 125 ($J_{\mathrm{P-C}}$ = 13·8 Hz) arise from C(2′) and C(6′) and those at δ 113·7 ($J_{\mathrm{P-C}}$ = 4·6 Hz) and δ 133·2 ($J_{\mathrm{P-C}}$ = 4·0 Hz) from C(3′) and C(5′). The quaternary carbons C(3), C(4), C(8), and C(9), with coupling to phosphorus of 4—6 Hz, cannot be individually assigned. Only one-half of the expected doublet for C(1′) (found at δ 134·6) is readily assigned.

The compound was crystallised from benzene. *Crystal data*: $\mathrm{C_{22}H_{19}O_4P}$; monoclinic, a = 13·874(7), b = 7·924(4), c = 16·572(8) Å, β = 94·53(5)°, U = 1816·2 Å^3; $F(000)$ = 792; space group $P2_1/c$; Z = 4; D_{c} = 1·38, D_{m} = 1·36 g

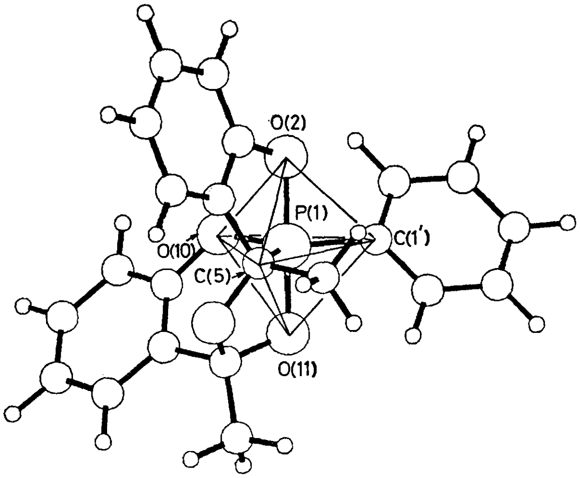


Figure. Perspective view of compound (III).

cm^{-3}; μ(Mo-K_α) = 1·33 cm^{-1}. The intensities of 3257 independent reflections in the range $3° < \theta < 24°$ were measured on a Philips PW1100 four-circle diffractometer using Mo-K_α radiation. With the criterion $I_{\mathrm{rel}} > 3\sigma(I_{\mathrm{rel}})$ for an observed reflection and omitting systematic absences, 2305 unique reflections remained which were employed in the structural analysis. The structure was solved by application of the automatic centrosymmetric direct-methods routine in the SHELX[2] system, in which an E-map yielded the positions of all the non-hydrogen atoms. The final full-matrix least-squares refinement converged to an R value of 0·070 (phosphorus and oxygen atoms anisotropic, carbon atoms isotropic, constrained refinement on hydrogen atoms). The co-ordination about the phosphorus is distorted trigonal bipyramidal with the phenyl group co-ordinated at one of the equatorial positions. The diapical axis is slightly bent, ∠O(2)–P(1)–O(11) = 175·0°, and the diequatorial bond angles range from 112·5 to 129·9°. The structure of (III) is shown in the Figure.† Although more detailed studies are required before a definite proposal for the mechanism of formation of (III) can be made, it is accepted, on the basis that reaction of $PhPCl_2$ with PhOH in the presence of a base readily affords $PhP(OPh)_2$, that (I; R = Ph) is an intermediate in the reaction. The reason why this should rearrange to give (III) is, however, not apparent.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] G. M. L. Cragg, B. Davidowitz, R. G. F. Giles, and R. J. Haines, *J.C.S. Chem. Comm.*, 1977, 569.

[2] G. M. Sheldrick, The SHELX System for Crystallographic Calculations, University of Cambridge, 1976.