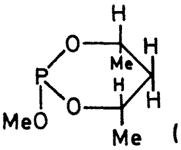
The Crystal Structure of *cis*-4,6-Dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinan

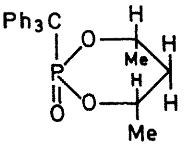
By M. G. B. DREW and J. RODGERS*
(*Department of Chemistry, The University, Whiteknights Park, Reading, Berks.* RG6 2AD)
and D. W. WHITE and J. G. VERKADE
(*Department of Chemistry, Iowa State University, Ames, Iowa* 50010)

Summary The crystal structure of *cis*-4,6-dimethyl-2-oxo-2-triphenylmethyl-1,3,2-dioxaphosphorinan shows the 1,3,2-dioxaphosphorinan ring to be much more distorted than in related structures, and to have the 'half-chair' conformation.

THE reaction of the phosphite (**I**) with triphenylmethyl chloride in methyl cyanide at 80 °C gives (**II**). We have determined the three-dimensional *X*-ray structure of (**II**) in order to study the conformation of the six-membered ring and the solution chemistry of (**I**), the precursor of (**II**).

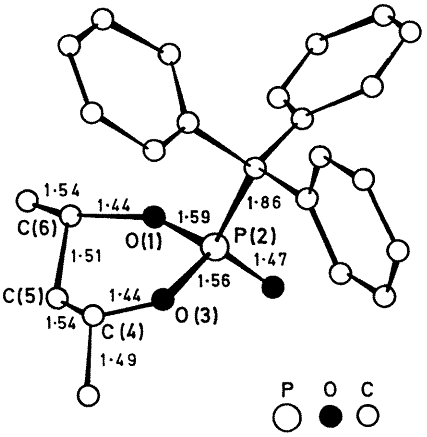


(I)



(II)

Colourless parallelepipeds of $C_{24}H_{25}PO_3$ (M 392·4) are monoclinic, space group Cc with $a = 16·21(2)$, $b = 8·40(1)$, $c = 16·61(2)$ Å, $\beta = 118·0(1)°$, $U = 1998$ Å^3, $D_m = 1·31(2)$, $D_c = 1·29$ g cm^{-3}, $Z = 4$, $F(000) = 832$. The intensities of 1783 independent reflections ($2\theta < 50°$) were recorded using Zr-filtered Mo-K_α radiation on a GE XRD-5 manual diffractometer by the stationary-crystal–stationary-counter method. The structure was solved by statistical methods. Least-squares refinement (P, O, non-phenyl C anisotropic, and phenyl C isotropic) on the 1312 reflections with $I > \sigma(I)$ has reached a conventional R factor of 0·085. The Figure shows the conformation of the ring (standard deviations are P–O 0·02, C–O, and C–C 0·03 Å). Least-squares planes calculations show that atoms O(1), O(3), C(4), C(6), and P(2) are almost planar (deviations −0·08, 0·06, −0·08, 0·07, and 0·02 Å, respectively). Atom C(5) is −0·75 Å from this plane. The ring can thus be described as having the 'half-chair' conformation. The dihedral angle between the planes containing the atoms O(1), C(6), C(4), O(3) and the atoms O(1), P(2), O(3) is 3·7° compared to values of 33·5, 36·7, 36·5, and 40·4° found for other 2-oxo-1,3,2-dioxaphosphorinans with Me,[1] Br,[2] OPh,[3] and OH,[4] replacing CPh_3 in the 2 position. (These four compounds contain non-substituted, 5-monosubstituted, or 5,5-disubstituted rings). The P–O–C angles in the present structure average to 127·5°, about 8° larger than those found in the other compounds.[1–4] The dihedral angles between the planes containing atoms O(1), C(6), C(4), O(3) and atoms C(4), C(5), C(6) are similar in all five structures, all being within 2° of 54°. There are no intermolecular contacts short enough to affect the conformation of the ring. The conformation adopted does, however, lessen intramolecular contacts between the axial hydrogens on C(4), C(6), and the phenyl rings.



FIGURE

The oxo-group in the present structure is *cis* to the 4,6-methyl groups; from this we can deduce, first, that the methoxy-group in the phosphite (**I**) is *cis* to the 4,6-methyl groups if the generally accepted stereochemical course for the Michaelis–Arbuzov reaction[5] is followed and secondly, as discussed elsewhere,[6] that values of vicinal POCH and HCCH nuclear spin–spin coupling constants for (**I**) indicate a chair-like conformation with equatorially disposed 4,6-methyl groups. Thus, the methoxy-group in the phosphite (**I**) occupies an equatorial position. This conclusion is of importance since considerable evidence has been presented which indicates a greatly preferred axial methoxy-disposition in several substituted 2-methoxy-1,3,2-dioxaphosphorinans.[6,7]

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