1-Isopropyl-4,6-dimethyl-6-phospha(v)bicyclo[3.1.1]hept-3-ene 6-Oxide: a Distorted Phosphetan Synthesized from α-Pinene and the Methylphosphonous Dichloride–Aluminium Chloride Complex; *X*-Ray Crystal and Molecular Structure

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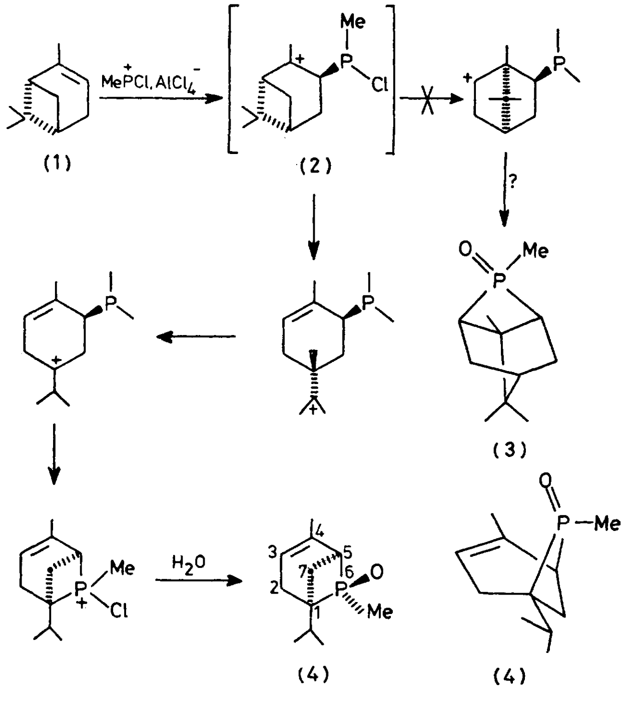
Summary Reaction of α-pinene with $MePCl_2$–$AlCl_3$ gives the title compound (**4**), a bridged bicyclic phosphetan, whose structure has been unequivocally assigned on the basis of chemical, spectral, and *X*-ray analysis.

SUBSTITUTED phosphetans are easily made from a branched olefin and $RPCl_2$–$AlCl_3$ in a reaction which involves a 1,2-Me shift[1] (*cf.* also ref. 2). Since such alkyl migrations are common in terpene and especially pinene chemistry,[3] tricyclic phosphetan (**3**)† would be expected to be formed from the reaction of (−)-α-pinene (**1**) and $MePCl_2$–$AlCl_3$ in dichloromethane at 0 °C; it would arise from the intermediate ion (**2**) by enlargement of the cyclobutane ring (Scheme).



SCHEME

However, the product isolated in 20—30% yield after quenching with water, usual work-up,[1] and high-vacuum distillation {m.p. 124—125 °C (Et_2O), $[\alpha]_D^{25}$ −76° (*c* 2, $CHCl_3$), $C_{11}H_{19}OP$, pure on t.l.c.} was found to have the bridged bicyclic structure (**4**) as shown by the following data: i.r.: ν_{max} ($CHCl_3$) 1625, 1290 (P–Me), and 1160 (P=O) cm^{-1}; mass spectra: *m/e* (70 eV) 198 (M^+, 69%), 183 (15), 155 (9), 135 (77), 134 (76), and 93 (100). The compound consumes 1 mol of bromine in $CHCl_3$ [mass spectral peaks for the product at *m/e* 277 and 279 (M^+ − Br)]. ^{1}H n.m.r.: δ ($CDCl_3$, Me_4Si, 250 MHz) 0·87 and 1·03 (2 × 3H, d, *J* 7 Hz, *Me*-CH-*Me*), 1·40 (2H, m, CH_2-CH-P), 1·63 (3H, d, *J* 12 Hz, *Me*-P), 1·80 (3H, q, *J* 2 Hz, *Me*-C=C), 1·98 (1H, q, *J* 7 Hz, C*H*Me$_2$), 2·43—2·52 (2H, m, CH_2-C=C), 2·74 (1H, t of d, *J* 7 Hz, C*H*-P), and 5·51 [1H, m, C*H*=C; disappears after catalytic hydrogenation (uptake of 1 mol. equiv. of hydrogen)]. ^{13}C n.m.r.: δ (p.p.m., $CDCl_3$, Me_4Si, 62·86

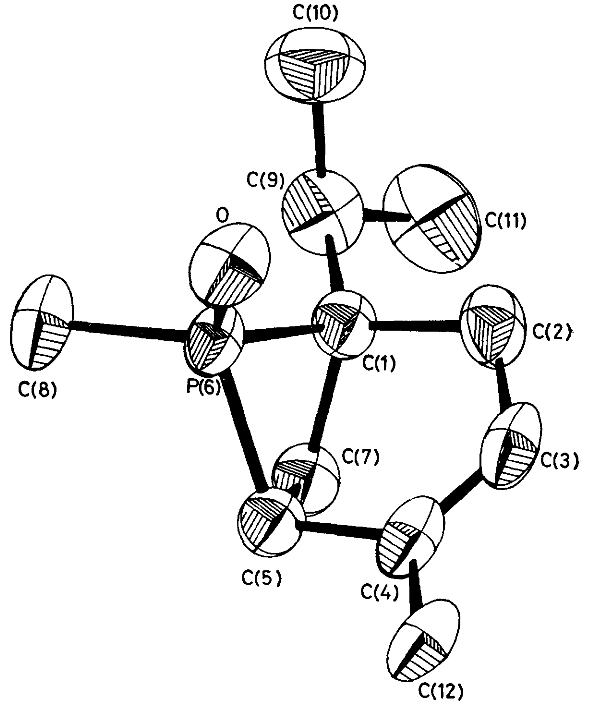


FIGURE. ORTEP drawing of the molecular structure of (**4**). Principal bond lengths and angles: (σ = ± 0·005 Å); P–O 1·478, P–C(1) 1·844, P–C(5) 1·829, P–C(8) 1·789; (σ = ± 0·008 Å); C(5)–C(7) 1·543, C(1)–C(7) 1·558 Å; (σ = 0·2°): ∠C(1)–P–C(5) 76·9, P–C(1)–C(7) 86·3, P–C(5)–C(7) 87·1, C(1)–C(7)–C(5) 94·9, O–P–C(1) 123·2, O–P–C(5) 123·2, O–P–C(8) 112·9, C(8)–P–C(5) 107·6, C(8)–P–C(1) 107·7°.

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† A structurally related tetracyclic phosphetan has been prepared by the homoconjugate cycloaddition of $MePCl_2$ to bicyclo[2.2.1]-heptadiene (M. Green, *J. Chem. Soc.*, 1965, 541; S. E. Cremer, F. R. Farr, P. W. Cremer, Hai-ok-Hwang, G. A. Gray, and M. G. Newton, *J.C.S. Chem. Comm.*, 1975, 374).

MHz) 8·3 (d, J 48 Hz, CH_3–P); the chemical shift and coupling constant of the methyl attached to phosphorus are consistent with an *exo* configuration, *i.e.*, axial with respect to the phosphetan ring.[4] ^{31}P n.m.r.: δ (p.p.m., $CDCl_3$, P_4O_6 external, 40·5 MHz) +76·7.

This structure has been confirmed by X-ray crystallography. Repeated crystallization from ether provided crystals of suitable quality for the X-ray diffraction study. Diffraction data for a single crystal, sealed in a capillary, were collected by an automatic diffractometer, with Cu-K_α radiation. 1068 intensities were considered above background $[I \geqslant 2\sigma(I)]$. *Crystal data:* monoclinic, space-group $P2_1$, $a = 8{\cdot}990(2)$, $b = 5{\cdot}882(4)$, $c = 10{\cdot}871(3)$ Å, $\beta = 92{\cdot}2(1)°$, $Z = 2$. The structure was solved by the Patterson method; all the H atoms were localised, and refinement led to an R factor of 5·7%.‡

The molecular structure is shown in the Figure. The phosphetan ring is puckered with an angle of 41°, well outside the range of 19—26° usually noted in other phosphetan structures.[5] This is almost certainly due to the bridging coplanar (within 0·01 Å) atoms, C(1), C(2), C(3), C(4), and C(5). Consequently C(8) is in an axial position with respect to the four-membered ring [dihedral angle C(8)–P–C(1)–C(2) is 175°]. The valency angles around the phosphorus atom are considerably distorted from their tetrahedral value, owing to the particularly small angle of the phosphetan ring [$\angle$C(1)–P–C(5) 76·9°]. The isopropyl conformation, with a torsional angle C(2)–C(1)–C(9)–C(11) of 55°, ensures the least steric hindrance as shown by molecular models and presumably this conformation also prevails in solution, accounting for the large (0·16 p.p.m.) difference in the ^1H n.m.r. chemical shifts of the magnetically non-equivalent methyls C(10) and C(11).

The formation of (**4**) can be rationalized by the opening of the cyclobutane ring in the primary adduct (**2**) followed by a 1,2-H migration and phosphetan ring closure (Scheme).

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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. The structure factor table may be obtained as a Supplementary publication (No. 22261, 9 pp.) from the British Library. For details of obtaining this material, see Notice to Authors No. 7. Index Issues of *J.C.S. Perkin I or II*.

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[3] *Cf.* for instance P. de Mayo, 'Mono- and Sesqui-terpenoids,' Interscience, New York, 1959.

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