Stereochemistry and Reactions of 4-Methyl-4-phosphatetracyclo-[3,3,0,$0^{2,8}$,$0^{3,6}$]octane 4-Oxide

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Summary The isolation and assignment of the *exo* and *endo* isomers of the title compound has been made; reaction of this compound and its derivatives with nucleophiles is rapid and leads to exclusive ring opening.

WE describe the isolation and identification of the *exo* (**3**) and *endo* (**4**) isomers of the title compound and several of its reactions. Previously only one isomer had been synthesised whose stereochemistry was unspecified.[1]

The precursor of (**3**) and (**4**), namely the salt (**1**), was prepared (60—70%) by heating an excess of bicyclo[2,2,1]-heptadiene with $MePCl_2$ for 1—2 weeks at 60—80 °C; contrary to the earlier described preparation, reaction at room temperature is slow (20% after 11 days).† The ^1H n.m.r. spectrum of (**1**) at 25—30 °C shows rapid isomer interconversion (time averaged spectrum); at −20 °C both isomers are observed individually (two P-Me doublets). Treatment of (**1**) in CH_2Cl_2 with dry $AlCl_3$ stops intercon-

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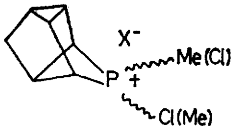
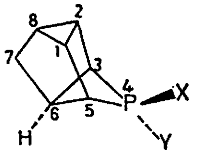
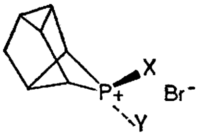
† A 72% yield was reported after 24 h at room temperature.



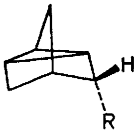
(1), X = Cl
(2), X = AlCl$_4$



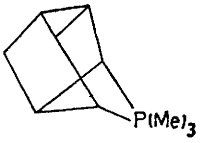
(3); X = O, Y = Me (*exo*)
(4); X = Me, Y = O (*endo*)
(5); X = Me, Y = electron-pair
(6); X = S, Y = Me
(7); X = Me, Y = S



(9), X = Y = Me
(10); X = Me, Y = Bz



(8), R = MePO$_2$H
(11), R = PO(Me)$_2$
(12); R = POMeBz
(13); P$^+$(Me)$_3$ Br$^-$



(14)

version and gives a 2 : 1 isomer ratio. The AlCl$_3$ combines with the chloride ion and prevents formation of pentaco-ordinate phosphorus intermediates which provide a route for equilibration.[2a] The pure *exo* isomer (3), m.p. 156—157 °C, was obtained by dropwise addition of water to (1) in CH$_2$Cl$_2$. Slow addition of (2) (3 : 1 isomer mixture‡ in CH$_2$Cl$_2$) to ice–water gave a mixture of (3) and (4), 4 : 1 respectively.[2] Fractional recrystallisation (benzene–cyclohexane) gave (4), m.p. 71—74 °C (95% isomer purity), which is the more soluble component.

The proton at C-6 in (4) is in close proximity to P=O and appears at δ 3·3 (CDCl$_3$; ref. Me$_4$Si) but at δ 1·90 in (3).[3] Eu(fod)$_3$ addition[4] to (3) and (4) led to a more pronounced downfield shift of this proton in (4). ^{13}C-N.m.r. spectra (CDCl$_3$) revealed shifts and couplings consistent[5] with this stereochemistry: δ (from Me$_4$Si in p.p.m.) 31·03 (J_{CCP} 7·1 Hz, C-6) for (3) and δ 39·49 (J_{CCP} 20·1 Hz, C-6) in (4). A preliminary *X*-ray[6] examination on (3) confirms the isomer disposition.

Reduction of (3) as a dilute solution in benzene with Cl$_3$SiH gave (5) with overall inversion of configuration about phosphorus; epimerization by HCl[7] to give the more stable isomer apparently took place. To confirm the stereochemistry of the reduction step, the phosphine (5) was converted into the sulphide (7), m.p. 111—113·5 °C, by sulphur (a retention step[8]); reduction of (3) with Cl$_3$SiH–Et$_3$N followed by sulphur treatment gave the epimeric sulphide (6), m.p. 129—133 °C. The expected configurations of (6) and (7) were verified by their ^{13}C n.m.r. spectra which showed the usual stereospecific couplings.[5]

Treatment of (3) with 5N NaOH gave the phosphinic acid (8) (90% complete in 75 min at room temperature). The salts (9) and (10) rapidly ring open in 0·001N NaOH to give the oxides (11) and (12), respectively; $< 1\%$ of toluene was detected in the latter reaction. Usually the benzyl anion is the better leaving group.[9] Reaction of (10) with <1 equiv. of NaOH revealed epimerization of the unchanged salt, presumably *via* 'pseudorotation' of pentaco-ordinate phosphorus intermediates.[10] Reaction of (9) with MeLi led to 57% of the bromide salt (13) and about 10% each of (Me)$_3$P and norbornadiene; these products imply the formation of the thermally labile P$^{\mathrm{V}}$ intermediate (14).[11]

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‡ Enrichment in either isomeric salt was achieved through fractionation.

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[3] The anisotropy of the P=O (and S=O) shifts neighbouring protons downfield: (a) Y. Kashman and O. Awerbouch, *Tetrahedron*, 1970, **26**, 4213; (b) C. R. Johnson and W. O. Siegl, *Tetrahedron Letters*, 1969, 1879; (c) F. Lautenschlaeger, *J. Org. Chem.*, 1969, **34**, 3998.

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[9] S. E. Cremer, B. C. Trivedi, and F. L. Weitl, *J. Org. Chem.*, 1971, **36**, 3226.

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