

## Stereochemistry and Reactions of 4-Methyl-4-phosphatetracyclo- [3,3,0,0<sup>2,8</sup>,0<sup>3,6</sup>]octane 4-Oxide

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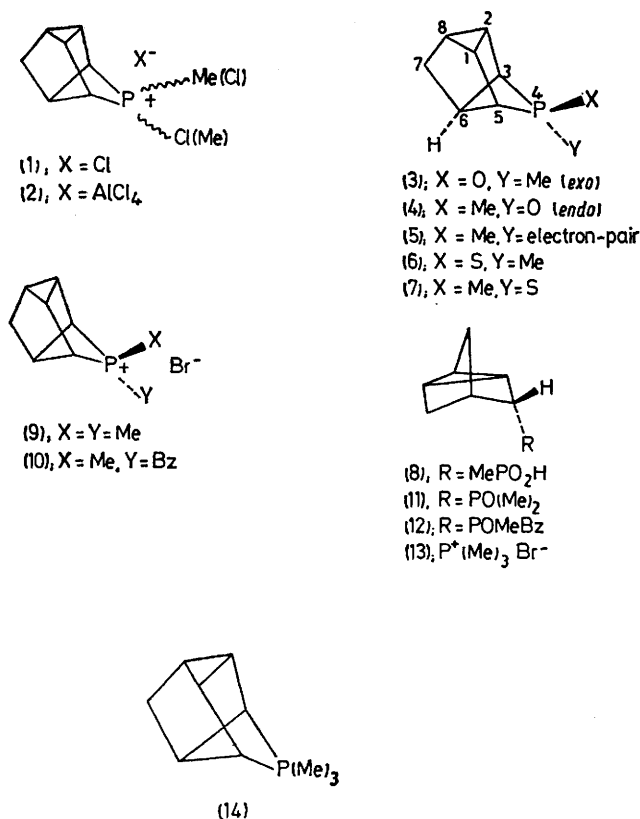
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**Summary** The isolation and assignment of the *exo* and *endo* isomers of the title compound has been made; reaction of this compound and its derivatives with nucleophiles is rapid and leads to exclusive ring opening.

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.<sup>1</sup>

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<sub>2</sub> 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 <sup>1</sup>H 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<sub>2</sub>Cl<sub>2</sub> with dry AlCl<sub>3</sub> stops intercon-

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



version and gives a 2:1 isomer ratio. The AlCl<sub>3</sub> combines with the chloride ion and prevents formation of pentacoordinate phosphorus intermediates which provide a route for equilibration.<sup>2a</sup> The pure *exo* isomer (3), m.p. 156–157 °C, was obtained by dropwise addition of water to (1) in CH<sub>2</sub>Cl<sub>2</sub>. Slow addition of (2) (3:1 isomer mixture)† in CH<sub>2</sub>Cl<sub>2</sub> to ice-water gave a mixture of (3) and (4), 4:1

† Enrichment in either isomeric salt was achieved through fractionation.

<sup>1</sup> M. Green, *J. Chem. Soc.*, 1965, 541.

<sup>2</sup> (a) S. E. Cremer, F. L. Weigl, F. R. Farr, P. W. Kremer, G. A. Gray, and H. Hwang, *J. Org. Chem.*, 1973, **38**, 3199; (b) The influence of the mode of quenching by water on the isomer distribution was discussed in related systems (ref. 2a).

<sup>3</sup> 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.

<sup>4</sup> Lanthanide shift reagents have been used in similar cases: B. D. Cuddy, K. Treon, and B. J. Walker, *Tetrahedron Letters*, 1971, 4433.

<sup>5</sup> G. A. Gray and S. E. Cremer, *J. Org. Chem.*, 1972, **37**, 3458.

<sup>6</sup> M. G. Newton, unpublished results, The University of Georgia.

<sup>7</sup> T. J. Katz, C. R. Nicholson, and C. A. Reilly, *J. Amer. Chem. Soc.*, 1966, **88**, 3832.

<sup>8</sup> L. Horner and H. Winkler, *Tetrahedron Letters*, 1964, 175; D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johnson, and C. A. VanderWerf, *ibid.*, p. 359.

<sup>9</sup> S. E. Cremer, B. C. Trivedi, and F. L. Weigl, *J. Org. Chem.*, 1971, **36**, 3226.

<sup>10</sup> S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Comm.*, 1969, 769.

<sup>11</sup> E. W. Turnblom and T. J. Katz, *J. Amer. Chem. Soc.*, 1973, **95**, 4292.

respectively.<sup>3</sup> 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  $\delta$  3.3 (CDCl<sub>3</sub>; ref. Me<sub>4</sub>Si) but at  $\delta$  1.90 in (3).<sup>3</sup> Eu(fod)<sub>3</sub> addition<sup>4</sup> to (3) and (4) led to a more pronounced downfield shift of this proton in (4). <sup>13</sup>C-N.m.r. spectra (CDCl<sub>3</sub>) revealed shifts and couplings consistent<sup>5</sup> with this stereochemistry:  $\delta$  (from Me<sub>4</sub>Si in p.p.m.) 31.03 (*J*<sub>CCP</sub> 7.1 Hz, C-6) for (3) and  $\delta$  39.49 (*J*<sub>CCP</sub> 20.1 Hz, C-6) in (4). A preliminary X-ray<sup>6</sup> examination on (3) confirms the isomer disposition.

Reduction of (3) as a dilute solution in benzene with Cl<sub>3</sub>SiH gave (5) with overall inversion of configuration about phosphorus; epimerization by HCl<sup>7</sup> 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<sup>8</sup>); reduction of (3) with Cl<sub>3</sub>SiH-Et<sub>3</sub>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 <sup>13</sup>C n.m.r. spectra which showed the usual stereospecific couplings.<sup>5</sup>

Treatment of (3) with 5*N* NaOH gave the phosphinic acid (8) (90% complete in 75 min at room temperature). The salts (9) and (10) rapidly ring open in 0.001*N* 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.<sup>9</sup> Reaction of (10) with <1 equiv. of NaOH revealed epimerization of the unchanged salt, presumably *via* 'pseudorotation' of pentacoordinate phosphorus intermediates.<sup>10</sup> Reaction of (9) with MeLi led to 57% of the bromide salt (13) and about 10% each of (Me)<sub>3</sub>P and norbornadiene; these products imply the formation of the thermally labile P<sup>V</sup> intermediate (14).<sup>11</sup>

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