# Steric Hindrance in the Alkaline Hydrolysis of Phosphinate Esters

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BERGESEN[1] has studied the alkaline hydrolysis of the four-membered phosphinate ester (I; $R=Et$) and found that the rate of hydrolysis is approximately equal to that of triethyl phosphate. We too have studied this hydrolysis, with the same result, although the relief of steric strain in the intermediate trigonal bipyramid (II), in which the four-membered ring will occupy an apical–equatorial position,[2] would be expected to lead to rapid hydrolysis.[3] Speculation that the 'normal' rate of hydrolysis is the result of acceleration due to this relief of steric strain, and retardation due to steric hindrance to attack of hydroxyl anion on phosphorus from the α-methyl groups, led us to investigate the possibility of a "neo-pentyl" effect in organophosphorus chemistry analogous to that observed in substitution at sulphur.[4]

Our results on the alkaline hydrolysis of the esters $RP(:O)(OEt)_2$ (Table) agree with these of Hudson and Keay.[5] One t-butyl group attached to phosphorus produces little steric hindrance to attack of $OH^-$ on phosphorus. However in the series of esters $R_2P(:O)\cdot OEt$ there is a sharp fall in the rate of hydrolysis between $R=Pr^i$ and

R=Bu$^{t}$. This retardation is also observed in other substitutions: while dialkylphosphinyl chlorides normally react exothermically with ethanolic sodium ethoxide at room temperature, di-t-butylphosphinyl chloride is essentially unchanged after refluxing for 24 hr. with this reagent.

With two t-butyl groups attached to phosphorus, one must occupy an equatorial position in the first intermediate trigonal bipyramid (III). In the transition state (IV) leading to this intermediate the angle $\theta$ is less than 90° and, despite a P–C bond length of ~1·87 Å, substantial hindrance from the "equatorial" t-butyl group to attack of the nucleophile is apparent at this point. With only one t-butyl group on phosphorus, there is little hindrance to attack of the nucleophile, as the t-butyl group can occupy an apical position in the first intermediate trigonal bipyramid (V). Pseudorotation to the trigonal bipyramid (VI) then occurs before expulsion of the group Y from an apical position.

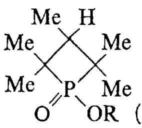
Confirmation that the normal rate of alkaline hydrolysis of the ester (I; R=Et) is due to competing steric acceleration and retardation comes from the extremely rapid hydrolysis of the ester (VII), a mixture of geometrical isomers, in which the relief of strain in going to the intermediate (VIII) is not balanced by a "neopentyl" effect.

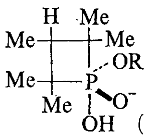
*Alkaline hydrolysis of phosphonate and phosphinate esters second order rate constants* (l.mole$^{-1}$sec.$^{-1}$ × $10^{6}$)

| $RP(:O)(OEt)_2$ | R | Et | Pr$^{i}$ | Bu$^{t}$ |
|---|---|---|---|---|
| | *k* | 300/70°<br>1200/90° | 440/120° | 60/120° |
| $R_2P(:O)OEt$ | R | Et | N-Pr$^{i}$ | 2N-Bu$^{t}$ |
| | *k* | 260/70° | 10/100°<br>41/120° | 0·08/120° |
| | | (I; R=Et) | (I; R=Me) | (VI) |
| | *k* | 300/70° | 840/70° | 390,000†/45° |

Hydrolyses were carried out under pseudo-first order conditions in 0·1N-NaOH except where stated. Ethanol was estimated by g.l.c. with propanol as internal standard.

† Automatic titration at pH 10·0.


(I)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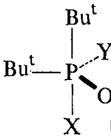
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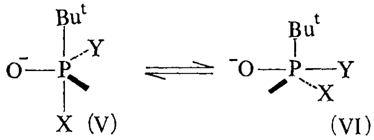
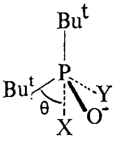

(V) (VI)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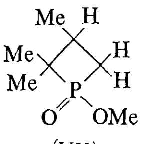
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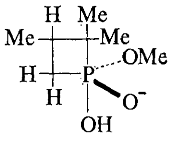
(VIII)

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[1] K. Bergesen, *Acta Chem. Scand.*, 1967, **21**, 1587. Bergesen claimed to isolate *cis*- and *trans*-forms of this ester, whose rates of hydrolysis were in the ratio 7:1. Separation was achieved by partial alkaline hydrolysis of the mixture, the preferentially formed *cis*-acid being then re-esterified *via* the acid chloride. Alkaline hydrolysis of the isomeric esters gave isomeric acids. Since the "isomeric acids" have a common anion the status of this work is uncertain. Our rate constants for the ester (I; R=Et), which from its n.m.r. spectrum appears to be homogeneous, agree with those of Bergesen for his *trans*-ester.

[2] S. E. Fishwick, J. Flint, W. Hawes, and S. Trippett, *Chem. Comm.*, 1967, 1113.

[3] R. Kluger, F. Kerst, D. G. Lee, E. A. Dennis, and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1967, **89**, 3918.

[4] A. Fava and A. Iliceto, *J. Amer. Chem. Soc.*, 1958, **80**, 3478.

[5] R. F. Hudson and L. Keay, *J. Chem. Soc.*, 1956, 2463.