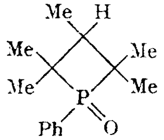
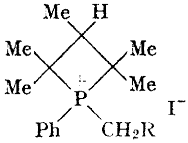
Ring Expansion in the Alkaline Hydrolysis of Phosphetanium Salts

By S. E. Fishwick and J. Flint
(Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, P.O. Box 11, The Heath, Runcorn, Cheshire)
and W. Hawes and S. Trippett*
(Department of Chemistry, University of Leicester)

The alkaline hydrolyses of phosphonium salts have three outstanding characteristics, (*a*) the rate $\propto [OH^-]^2$, (*b*) inversion occurs at the phosphorus atom, and (*c*) that group is lost which is most stable as the anion.[1] These facts are usually accommodated in a mechanism which involves an intermediate trigonal bipyramidal phosphorane (I) which loses that group most stable as the anion from an *apical* position. If the phosphorus atom is part of a small strained ring the difference in bond angles between apical and equatorial (90°) and diequatorial (120°) positions could lead to constraints on the conformation of the intermediate (I) and to unusual behaviour. This has been observed in the alkaline hydrolyses of phosphetanium salts.


(I)


(II)

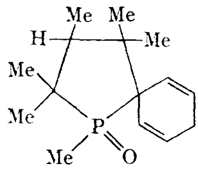

(III)

The phosphine oxide (II) was obtained by the action of dichlorophenylphosphine and aluminium chloride on 2,4,4-trimethylpent-2-ene.[2] Reduction with lithium aluminium hydride and quaternisation with methyl iodide gave the phosphetanium salt (III; R = H). Alkaline hydrolysis of this gave a phosphine oxide (88%), $C_{15}H_{25}OP$, m.p. 155°, ν_{max} 1630, 1150 cm.$^{-1}$, which we formulate as (IVa). The infrared spectrum of the oxide lacks the features expected of phenyl attached to phosphorus (1430 cm.$^{-1}$) and of monosubstituted phenyl while the ultraviolet spectrum shows no aromatic or cyclohexa-1,3-dienyl absorption. The n.m.r. spectrum (100 Mc./sec.) shows no aromatic protons, a complex centred on τ 4·3 (4H), a broad doublet at τ 7·12 and 7·4 (2H), a quartet at τ 8·17 (1H; J_{HH} = 7·2 c./sec.), a doublet at τ 8·61 (3H; J_{PH} = 12 c./sec.), and the remaining five methyls as indicated on (IVb). Besides the molecular ion at *m/e* 252, the mass spectrum shows the major cracking pattern outlined in (IVb). The oxide absorbs two moles of hydrogen (Pt) to give a saturated oxide, m.p. 133—135°, molecular ion *m/e* 256.

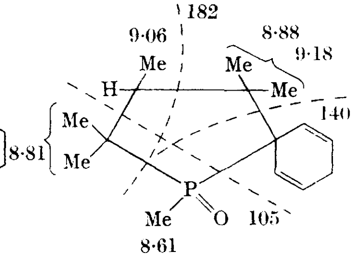
Quaternisation of the phosphetan with methylene iodide gave the salt (III; R = I). Alkaline hydrolysis of this gave a phosphine oxide (30%), $C_{15}H_{23}OP$, m.p. 141°, ν_{max} 1590, 1430 (P–phenyl), 1165, 760, 695 cm.$^{-1}$, which we formulate as (V).

The n.m.r. spectrum (60 Mc./sec.) shows a multiplet from τ 2—2·7 (5H) and a multiplet from τ 7·68—7·85 (2H; the methylene in ethyldiphenylphosphine oxide is centred on τ 7·76). Besides the molecular ion at *m/e* 250 the mass spectrum shows the major cracking pattern outlined in (V).

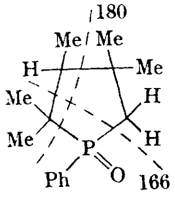
Presumably in the intermediates (VI) and (VII) in the hydrolyses of the salts (III), the four-membered rings are constrained to occupy apical–equatorial positions thus blocking the expected migration[3] (in VI) or loss (from VII) of phenyl which must occur from an apical position. Migration of the apical CMe$_2$ therefore occurs either to the methylene with expulsion of iodide ion (VI) or to phenyl (VII) giving a cyclohexadienyl anion which protonates as expected to give the non-conjugated isomer.



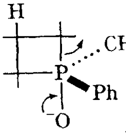
(IVa)



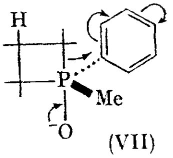
(IVb)



(V)



(VI)



(VII)

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[1] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, New York, 1965.

[2] For the analogous reaction with phosphorus trichloride, see J. J. McBride, E. Jungermann, J. V. Killhefer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833.

[3] H. Hellmann and J. Bader, *Tetrahedron Letters*, 1961, 724; M. Schlosser, *Angew. Chem.*, 1965, **74**, 291.