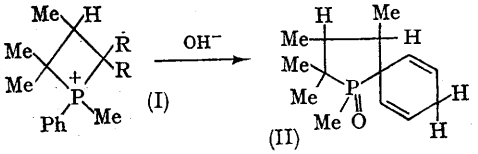
Alkaline Hydrolysis of Trimethylphosphetanium Iodide

By S. E. FISHWICK and J. A. FLINT*

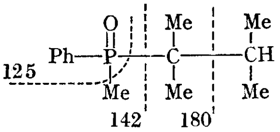
(*Imperial Chemical Industries Limited, Petrochemical and Polymer Laboratory, P.O. Box* 11, *The Heath, Runcorn, Cheshire*)

IN a Communication[1] we have described the unusual rearrangement of 1-methyl-1-phenyl-2,2,3,4,4-pentamethylphosphetanium iodide (I; R = Me) into the five-membered phosphorus heterocycle bearing a spiro-cyclohexadiene group (II). This reaction occurred smoothly and in high yield when the iodide was treated with aqueous sodium hydroxide. We have now examined the alkaline hydrolysis of 1-methyl-1-phenyl-2,2,3-trimethylphosphetanium iodide (I; R = H).



(I) (II)

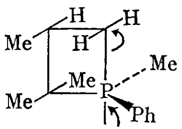
Neohexene (3,3-dimethylbut-1-ene) was treated with dichlorophenylphosphine and aluminium chloride to give 1-phenyl-2,2,3-phosphetane 1-oxide.[2] The phosphine oxide was reduced with trichlorosilane[3] to the phosphine which was quaternised with methyl iodide to yield 1-methyl-1-phenyl-2,2,3-trimethylphosphetanium iodide (I; R = H). On alkaline hydrolysis this phosphonium iodide yielded a phosphine oxide (63%), m.p. 74—76°, $C_{13}H_{21}OP$. The n.m.r. spectra (60, 100, and 220 Mc./sec.) show clearly that this compound was methylphenyl-(1,1,2-trimethylpropyl)phosphine oxide (III) [aromatic proton complexes at 2·25–2·39 τ (2H) and 2·52—2·71 τ (3H), doublet at 8·28 τ (3H; J_{PH} 12c./sec.), multiplet at 8·00–8·27 (1H), and doublets centred at 8·92 τ (3H; J_{PH} 15 c./sec.), 9·02 τ (3H; J_{PH} 16 c./sec.), 9·02 τ (3H; J_{HH} 7 c./sec.), and 9·06 τ (3H; J_{HH} 7 c./sec.)]. This was confirmed by the i.r. spectrum with bands at ν = 700 cm.$^{-1}$ and 750 cm.$^{-1}$ monosubstituted phenyl; 1210 cm.$^{-1}$, P–Ph, 1160 cm.$^{-1}$, P=O; 1290 cm.$^{-1}$, 875 cm.$^{-1}$, and 890 cm.$^{-1}$, P–Me, and 1365 cm.$^{-1}$ and 1385 cm.$^{-1}$, CMe_2. The mass spectrum showed a molecular ion at 224 and a major cracking pattern as indicated in (III).



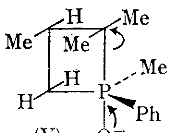
(III)

The formation of this phosphine oxide (III) indicates that the four-membered ring has opened by breaking the P–CH_2 bond in the trigonal bipyramidal phosphorane intermediate (IV) (followed by protonation) rather than by breaking the P–CMe_2 bond shown in (V). In contrast to the alkaline hydrolysis of the pentamethylphosphetanium iodide no products of the migration of the apical CH_2 or CMe_2 in the intermediates (IV and V) to the phenyl group were observed.

At present we account for the reaction product from the hydrolysis of trimethylphosphetanium iodide on electronic grounds, because the CH_2 carbanion from (IV), which is more stable than the CMe_2 carbanion from (V), can separate and add a proton. The less stable CMe_2 carbanion, which is formed in the hydrolysis of the pentamethylphosphetanium salt, does not separate and add a proton, but attacks the phenyl group to give the rearranged product (II).



(IV)



(V)

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

[2] For analogous reaction with 2,4,4-trimethylpent-2-ene and phosphorus trichloride, see J. J. McBride, E. Jungerman, J. V. Killheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, 27, 1833.

[3] H. Fritzsche, U. Hasserodt, and F. Korte, *Chem. Ber.*, 1965, 98, 171.

[4] R. F. Hudson, "Structure and Mechanism in Organophosphorus Chemistry", Academic Press, New York, 1965, p. 204.