Alkaline Hydrolysis of a Phosphonium Salt with Retention of Configuration at Phosphorus

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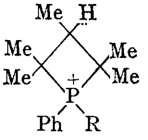
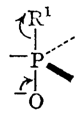
WE have previously shown[1] that the restraints imposed by a four-membered ring on the conformations of the trigonal bipyramidal intermediates in the alkaline hydrolysis of the phosphetanium salts (I; R=Me, CH_2I) lead to ring expansion instead of the expected loss (R=Me) or migration (R=CH_2I) of phenyl. The results were consistent with a mechanism for the alkaline hydrolysis of phosphonium salts in which the apical group R^1, opposed to the O^- in the intermediate (II), is expelled as the anion, leading to the observed[2] inversion of configuration at phosphorus. We now report that alkaline hydrolysis of the salt (I; R=CH_2Ph) proceeds with retention of configuration at phosphorus.

The phosphine oxide (III) exists as two geometrical isomers, m.p. 118° and 127°, separable by chromatography. Their isomeric nature is shown by their similar i.r., n.m.r., and mass spectra. Reduction of the mixture with lithium aluminium hydride and quaternisation with benzyl bromide gives a homogeneous crystalline benzylphosphetanium bromide (I; R=CH_2Ph), m.p. 202—203°. Both alkaline hydrolysis of this salt and a Wittig olefin synthesis with benzaldehyde and ethanolic sodium ethoxide give in high yield the same isomeric phosphine oxide (III), m.p. 127°. The Wittig olefin synthesis proceeds with retention of configuration at phosphorus[2] and the presence of two four-membered rings spanning equatorial–apical positions in the intermediate (IV) should not affect this. The alkaline hydrolysis of the benzyl salt must therefore have involved retention of configuration at phosphorus.

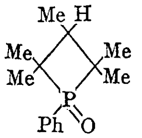
This result is consistent with our previous view that the four-membered ring in the intermediate (V) in the hydrolysis of phosphetanium salts occupies an equatorial–apical position. This blocks the loss of benzyl anion from an apical position opposite to O^- with inversion at phosphorus. Loss of benzyl anion from an equatorial position of (V), or conversion of (V) to the new trigonal bipyramid (VI) followed by loss of benzyl anion from an apical position, leads to retention of configuration at phosphorus. The direction of the reaction, as opposed to the rearrangement observed with the methyl salt, is dictated by the relative stability of the benzyl anion.



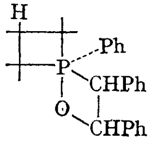
(I)



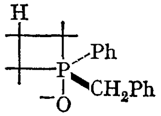
(II)



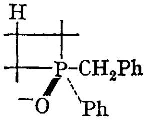
(III)



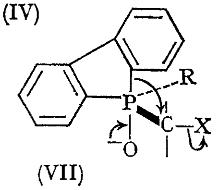
(IV)



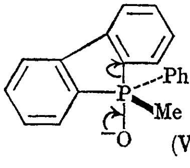
(V)



(VI)



(VII)



(VIII)

The isomeric phosphine oxides (III) are not interconverted on heating under reflux either in 2N-sodium hydroxide or in concentrated hydrochloric acid. Under the latter conditions, optically active phosphine oxides racemise rapidly,[3] presumably by nucleophilic attack of water or chloride ion on the protonated phosphine oxide with inversion of configuration. The stability of the isomers (III) in concentrated acid is a further consequence of the strain involved in placing the four-membered ring diequatorial in a trigonal bipyramid.

The general thesis that the presence of a small ring, which prefers the equatorial–apical 90° bond angle to the diequatorial 120° angle in a trigonal bipyramidal intermediate, can direct the course of subsequent reaction is nicely illustrated by recent results, involving ring expansion[4,5] and ring fission[6] of 9-phosphafluorenes. The 2,2′-biphenylylene system is known[7] to prefer the equatorial–apical position. Consequently in the intermediates (VII) ring expansion occurs with migration of the apical group irrespective of the nature of the group R. Similarly in the intermediate (VIII) only ring fission is observed.

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