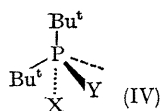
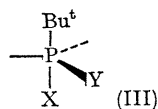
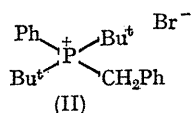
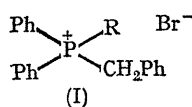


## t-Butylphosphonium Salts: the Alkaline Hydrolysis of an Acyclic Phosphonium Salt with Retention of Configuration at Phosphorus

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WE previously showed<sup>1</sup> that, in the alkaline hydrolysis of phosphorus esters, one t-butyl group attached to phosphorous has little effect on the rate of hydrolysis but two t-butyl groups have a great effect. A similar situation is



found in the alkaline hydrolysis of t-butylphosphonium salts. Thus the salt (I; R = Bu<sup>t</sup>) is hydrolysed about 50 times

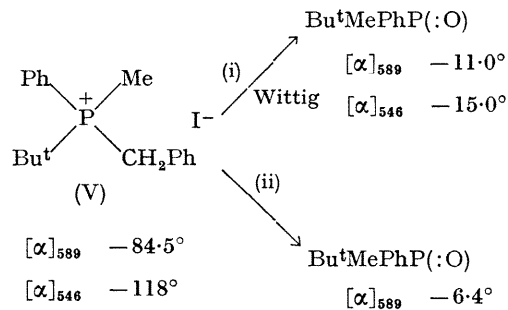
more slowly than the salt (I; R = Me) to give the expected products, toluene and t-butyldiphenylphosphine oxide, while the di-t-butylphosphonium salt (II) is extremely resistant to alkaline hydrolysis. After 11 days in 90% ethanolic n-NaOH at 100°, 21% of this salt is unchanged and the major phosphorus-containing product is benzyl-t-butylphenylphosphine, isolated as the methiodide (16%). No toluene is produced.

Possible explanations for the differing effects of one and two t-butyl groups are (a) the general steric crowding theory that two t-butyl groups are difficult to accommodate in a pentacovalent intermediate, and (b) that the reagent (X) can attack with little difficulty opposite to one t-butyl group to give the intermediate (III) while with two t-butyl groups one of necessity occupies an equatorial position in the intermediate trigonal bipyramid, and in the transition state (IV) leading to this intermediate hinders attack of the nucleophile. These explanations have different stereochemical consequences for nucleophilic substitutions at a tetrahedral phosphorus bearing *one* t-butyl group. In particular, if the reagent prefers to attack opposite the t-butyl, expulsion of Y

from the intermediate (III) will lead to retention of configuration at the phosphorus instead of the usually observed inversion. We find that (–)-benzyl-*t*-butylmethylphenylphosphonium iodide (V) undergoes alkaline hydrolysis with predominant *retention* of configuration (see Scheme 2). The optically active phosphine oxide is not racemised under the conditions of the hydrolysis and phosphonium salt recovered from an interrupted hydrolysis has unchanged rotation. The results are consistent with the hydrolysis proceeding to at least 79% by attack of hydroxide ion opposite the *t*-butyl followed by expulsion of benzyl anion either from an equatorial position, or, after pseudorotation,<sup>3</sup> from a new apical position. This is a minimum figure: the rotation of the phosphine oxide from the alkaline hydrolysis was determined after purification by crystallisation, a process which concentrates the racemic oxide.

Previous hydrolyses of phosphonium salts with retention of configuration at phosphorus<sup>4,5</sup> have involved cyclic

systems in which the rings are constrained to occupy apical-equatorial positions in the intermediate trigonal bipyramids.



Reagents: (i) PhCHO–EtOH–EtONa; (ii) 75% Ethanolic *n*-NaOH under reflux. Rotations were measured in methanol at 20°.

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<sup>1</sup> W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 577.

<sup>2</sup> A. Bladé-Font, C. A. VanderWerf, and W. E. McEwen, *J. Amer. Chem. Soc.*, 1960, **82**, 2396, showed that alkaline hydrolysis of benzylethylmethylphenylphosphonium iodide involves complete inversion of configuration at phosphorus.

<sup>3</sup> F. H. Westheimer, *Accounts Chem. Res.*, 1968, **1**, 70.

<sup>4</sup> W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 295.

<sup>5</sup> K. L. Marsi, *Chem. Comm.*, 1968, 846.