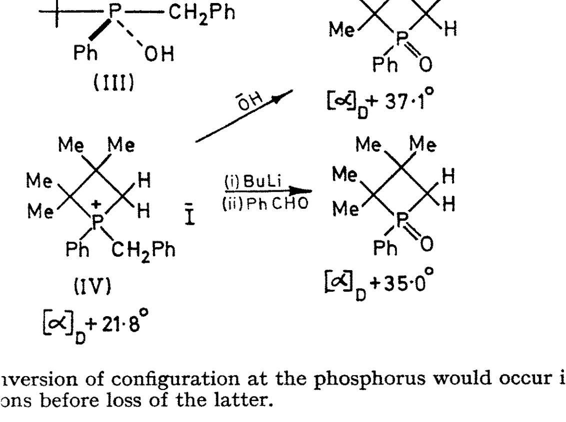
The Stereochemistry of the Alkaline Hydrolysis of Phosphetanium Salts. Change in Configuration at Phosphorus on Ylide Formation

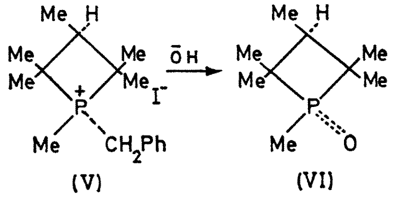
By J. R. Corfield, J. R. Shutt, and S. Trippett*
(*Department of Chemistry, The University, Leicester* LE1 7RH)

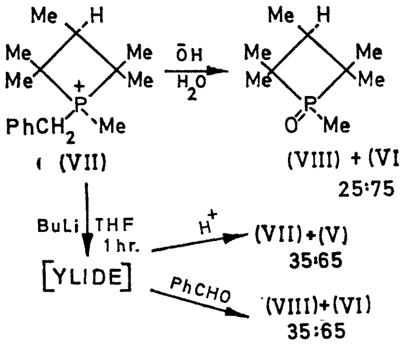
Summary Partial inversions of configuration at phosphorus occur both on ylide formation from, and alkaline hydrolysis of, the benzylphosphetanium salts (VII) and (IX).

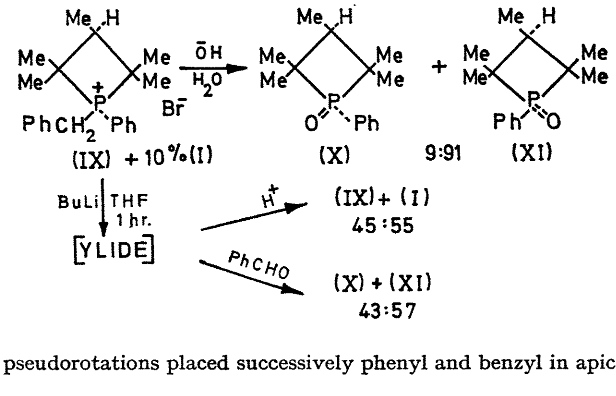
We previously showed[1] that alkaline hydrolysis of the benzylphosphetanium salt (I) proceeds with retention of configuration at phosphorus and ascribed this to the preference of the four-membered ring for an apical-equatorial position in the initially formed trigonal-bipyramid (II), the benzyl anion departing either from an equatorial position of (II) or, after one pseudorotation,† from an apical position of (III). We now report that similar retention of configuration accompanied hydrolysis of the optically active 2,2,3,3-tetramethylphosphetanium salt (IV).



However while hydrolysis of, and olefin synthesis with the 1-benzyl-1,2,2,3,4,4-hexamethylphosphetanium salt (V)







---

† Inversion of configuration at the phosphorus would occur if two pseudorotations placed successively phenyl and benzyl in apical positions before loss of the latter.

gave entirely the oxide (VI), alkaline hydrolysis of, and *olefin synthesis with*, the isomeric salt (VII) gave mixtures of the isomeric oxides (VI) and (VIII). These oxides were not interconverted in alkaline solution. Cross-over in the olefin synthesis with (VII) occurred at the ylide stage: regeneration of salt from an ylide solution prepared from the pure isomer (VII) and butyl-lithium in tetrahydrofuran gave a mixture of salts (V) and (VII) corresponding to the mixture of oxides (VI) and (VIII) produced when this ylide solution was used in the olefin synthesis. The relative amounts of (V) and (VI) produced from the ylide solution increased with time. Similar results were observed with the benzylphosphetanium salt (IX) isomeric with (I), although in this case the salt (IX) was not obtained free of its isomer, and also with mixtures of the 1-benzyl-2,2,3-trimethyl-1-phenylphosphetanium bromides, neither of which was obtained pure. Hydrolysis of (IX) in deuterium oxide led to no incorporation of deuterium at the 3-position of the resulting oxides.

The partial inversions observed on alkaline hydrolysis of the salts (VII) and (IX) probably involve partial conversion, *via* ylides, into their isomers prior to hydrolysis. The overall rates of hydrolysis of the salts (V) and (VII) in 75% ethanol are not significantly different: when the pure isomer (VII) was partially hydrolysed, to the extent of 50%, under these conditions [which give the oxides (VIII) and (VI) in the ratio 40 : 60] the recovered salt contained 60% of the isomer (V). Ylide interconversion may involve a square planar sp^2d-hybridised phosphorus; the driving force must be associated with steric interference from the 3-methyl group in these highly strained and hindered systems.

(*Received, May 14th*, 1969; *Com.* 681.)

---

[1] W. Hawes and S. Trippett, *Chem. Comm.*, 1968, 295; *J. Chem. Soc.* (*C*), in the press.