Stereochemistry of Alkaline Cleavage of *cis*- and *trans*-1-Benzyl-1,3-dimethylphospholanium Bromide

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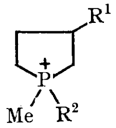
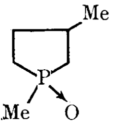
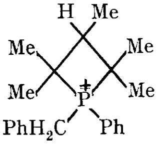
IN connection with the behaviour of the phosphorus atom in phosphorus-containing heterocycles, especially five-membered ring systems,[1] we report that cleavage of the *cis*- and *trans*-isomers of 1-benzyl-1,3-dimethylphospholanium bromide (I) by hydroxide ion in aqueous solution results in the formation of the corresponding oxides (II) with complete retention of configuration at phosphorus. Two significant facts emerge from these results: (1) inversion of configuration of the phosphorus atom by alkaline cleavage of phosphonium salts is not as general as has been believed,[2] and (2) there is no common intermediate between the *cis*- and *trans*-isomers and the oxides resulting from their base decomposition.



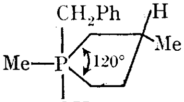
(Ia,b) R^1=Me R^2=CH_2Ph
(VI) R^1=H, R^2=Ph



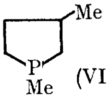
(IIa,b)



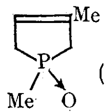
(III)



(IV)

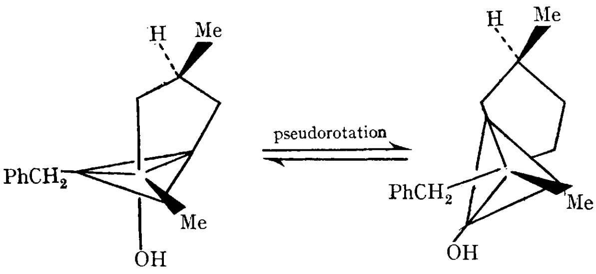


(VIIa,b)



(VIII)

A recent example of retention of configuration of phosphorus has resulted from the alkaline cleavage of a phosphetanium salt (III).[3] In basic medium such highly strained rings are known to undergo ring cleavage,[4,5] and novel ring expansions[5,6] of a kind not observed in larger non-fused ring systems. Our results show that the stereochemical behaviour of (III) is not just another unique feature of the four-membered ring. Evidently, the unfavourable intermediate (IV), displaying a C–P–C ring angle approaching 120°, precludes inversion of configuration by apical attack and apical departure in the manner proposed for acyclic phosphonium salts.[2] Apical departure of the benzyl group, if it occurs at all, would necessitate pseudorotation of (V), assuming that the hydroxide ion occupies an apical position in the initially formed pentacovalent intermediate.[7]



(V)

Although such a pseudorotation would lead to the observed stereochemistry, further pseudorotations would produce intermediates common to (Ia) and (Ib) and result in loss of stereospecificity.

Lack of a common intermediate between (Ia) and (Ib) characterizes a system behaving differently from both hydrogen ethylene phosphate, where rapid ^{18}O exchange with water is indicative of rapid pseudorotation,[8] and from the *cis*- and *trans*-isomers of methyl 1,2-dimethylethylene phosphate which have been observed to equilibrate readily in the presence of water.[9]

The results reported here also appear consistent with apical introduction of hydroxide ion and equatorial departure of the benzyl anion *via* the conjugate base of (V). Third-order kinetics has been demonstrated for the alkaline cleavage of (VI),[10] and it would seem reasonable that the decomposition of (I) is also third order.

The phosphines (VII) were prepared by reduction of a mixture of phosphine oxides (II) with trichlorosilane.[11] The mixture was carefully fractionated through a spinning band column to yield pure (VIIa), b.p. 141° [60 MHz. n.m.r. spectrum (neat): τ 7·74—8·87 (m, 7H), 8·97 (d, 3H; J_{HH} 6) and 9·08 (d, 3H; J_{PH} 3 c./sec.)] and several cuts within a boiling range of 138·5—141° having additional doublets at τ 8·88 (J_{HH} 6) and 9·07 (J_{PH} 3 c./sec.). The configurational stability of (VII) was shown by heating a mixture of (VIIa) and (VIIb) at various temperatures up to 150° for a three day period without any noticeable change occurring in the n.m.r. spectrum when it was recorded again at room temperature. Compound (VIIa), when treated with benzyl bromide, gave (Ia), m.p. 168·5—169·5° [60 MHz. n.m.r. spectrum in D_2O (with reference to the exchanging H_2O peak): singlet at 2·79 p.p.m. downfield (5H); upfield doublets at 0·85 p.p.m. (2H; J_{PH} 16), 2·73 p.p.m. (3H; J_{PH} 14), 3·68 p.p.m. (3H; J_{HH} 5 c./sec.); multiplet at 1·93—3·53 p.p.m. upfield (7H). The first fraction of mixed phosphines was similarly quaternized and the resulting mixture of salts fractionally recrystallized to yield (Ib), m.p. 180—181°, whose n.m.r. absorptions were nearly identical to those of (Ia). (Ia) and (Ib) were separately decomposed in refluxing 1·00N-sodium hydroxide to the respective hydroscopic oxides (IIa), m.p. 22° [60 MHz. n.m.r. spectrum in benzene: multiplet at τ 7·98—9·03 and doublet at 8·65 (J_{PH} 12·5) (10H); unresolved doublet at τ 9·10 (3H; J_{HH} 4 c./sec.)] and (IIb), m.p. 70—71° multiplet at τ 7·85—9·63 and doublet at τ 8·88 (J_{PH} 12·5) (10H); doublet of doublets at τ 9·29 (3H; J_{HH} 6, J_{PCCH} 0·9 c./sec.)]. Toluene and (II) were the only products detected by gas chromatographic analysis of the reaction mixtures.

The melting point and n.m.r. spectrum of (IIa) are identical to those of the oxide formed by oxidation of (VIIa) with t-butyl hydroperoxide, which is known to oxidize phosphines stereospecifically with retention of configuration at phosphorus.[12] Similarly, (IIb) was found to be identical with the phosphine oxide obtained by fractional crystallization of a mixture of (IIa) and (IIb) prepared by catalytic hydrogenation of (VIII).[13]

All new compounds gave satisfactory carbon and hydrogen analyses.

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