Stereochemistry of the Base Decomposition of Phosphetanium Bromides

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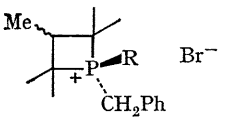
Summary The *cis*- and *trans*-isomers of several substituted phosphetanium bromides are rapidly equilibrated on treatment with hydroxide ion and give rise to a predominance of one isomeric phosphetan 1-oxide in each case.

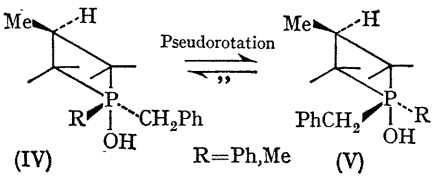
THE stereochemistry of the alkaline hydrolysis of phosphonium salts generally proceeds by an inversion mechanism.[1] Recently several noteworthy exceptions to this have appeared.[2] These results prompt us to report† the outcome of hydroxide decomposition of the *cis*- and *trans*-phosphetanium salts (I) and related compounds (II), (III).



R
(I) Ph
(II) Me
(III) $PhCH_2$

When various mixtures (9 : 1, 1 : 1, 1 : 4) of the *cis*- and *trans*-isomers of (I) were treated with aqueous base, a predominance (about 9 : 1) of one isomeric product, 2,2,3,4,4-pentamethyl-1-phenylphosphetan-1-oxide (VI), m.p. 124—126°, was obtained. Likewise, either isomer of (II) gave mainly one oxide and the dibenzyl salt (III) led to a predominance of one isomeric oxide. Under the reaction conditions the isomeric oxides do not interconvert; however, with 2N-NaOH–95%-EtOH (reflux), changes in the isomer ratio of (VI) have been observed,‡ and phosphinic acids are slowly formed during this period.

Hence, salts (I) or (II) unlike the 1-benzyl-1,3-dimethylphospholanium bromides[2a] (in which *trans* salt → *trans* oxide and *cis* salt → *cis* oxide) decompose with isomer crossover. Apparently, the initially formed intermediate (IV) (or V) undergoes pseudorotation (minimum of three steps are required to convert (IV) into (V) or the reverse process) prior to decomposition to product. Support for pseudorotation was obtained experimentally: a drop of 1N-NaOH added to a 20—30% solution ($CDCl_3$) of the *cis*- or *trans*-salts (I) or (II) produced immediatee quilibration of the individual isomers (observed by n.m.r. techniques).§



The base decomposition of (I) in aqueous ethanol was consistent with the mechanism (third-order overall) suggested by McEwen;[1b,3] the observed rate constant (in 1 : 1 EtOH–H_2O at 25°) was $1{\cdot}8 \times 10^2$ l.^{2} mole^{-2} sec.$^{-1}$ which is considerably faster than that of methylethylphenylbenzylphosphonium chloride[1b] ($k_3 = 2{\cdot}2 \times 10^{-3}$ l.^{2} mole^{-2} sec.$^{-1}$ in aqueous solution at 99·4°).

The detailed pseudorotational processes, stereochemical assignments, syntheses,[4] and extended rate studies will be discussed in a full publication.

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† Dr. Trippett has also reported (ref. 2b) on the base decomposition of (I), that work involving a "homogeneous crystalline" bromide The finding that *both* the *cis*- and *trans*-salts give the same isomeric oxide and that the salts equilibrate in base are emphasized in this communication.

‡ A 1 : 1 mixture of isomers changes into a 2·2 : 1 ratio (124—126° isomer in greater abundance) after about 90 hr. under these conditions.

§ An alternate route for equilibration of the salts through an ylide intermediate may be considered. Indeed, we have noted that deuterium exchange occurs in the presence of NaOD–D_2O. However, if the concept of epimerization about phosphorus by an "ylide mechanism" is generally applied to acyclic (ref. 1) or cyclic systems (ref. 2a), the observed stereochemistry (inversion and retention, respectively) would be inconsistent with salt equilibration. Moreover, McEwen (ref. 1b) has actually prepared the ylide of optically active methylethylphenylbenzylphosphonium iodide; this was quenched with water to give back the salt which showed no change in rotation.

[1] (a) A. Bladé-Font, C. A. VanderWerf, and W. E. McEwen, *J. Amer. Chem. Soc.*, 1960, **82**, 2396; (b) W. E. McEwen, K. F. Kumli, A. Bladé-Font, M. Zanger, and C. A. VanderWerf, *ibid.*, 1964, **86**, 2378.

[2] (a) K. L. Marsi, *Chem. Comm.*, 1968, 846; (b) W. Hawes and S. Trippett, *Chem. Comm.*, 1968, **295**; (c) N. J. De'ath and S. Trippett, *Chem. Comm.*, 1969, 172.

[3] W. E. McEwen, G. Axelrad, M. Zanger, and C. A. VanderWerf, *J. Amer. Chem. Soc.*, 1965, **87**, 3948; see also H. Hoffmann, *Ann. Chem.*, 1960, **634**, 1.

[4] The synthesis of each isomer of (I) and a predominance of one isomer of (II) has been reported, S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066. The preparation of (III) and the other isomer of (II) was achieved by treatment of the appropriate phosphinic acid chloride, J. J. McBride, jun., E. Jungermann, J. V. Kilheffer, and R. J. Clutter, *J. Org. Chem.*, 1962, **27**, 1833 with benzylmagnesium bromide to give the 1-benzylphosphetan 1-oxide; reduction of the oxide to the phosphetan was followed by quaternization with methyl or benzyl bromide to give (II) and (III), respectively (see S. E. Cremer, *Chem. Comm.*, 1968, 1132 for a similar sequence using phenylmagnesium bromide as the Grignard reagent).