Rates of Deuterium Exchange in Phosphetanium Salts

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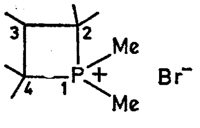
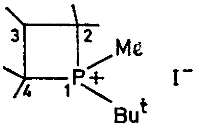
Summary The rate of exchange (hydrogen by deuterium, in basic solution) of methylphosphetanium salts is fast relative to those of acyclic methylphosphonium salts; in addition, selective exchange has been observed in 1,1-dimethylphosphetanium salts and in isomeric compounds.

IN a previous study[1] we reported on the rate of exchange for a series of substituted phosphonium salts $Ph_{(4-n)}P^{+}$-$(Me)_{n}X^{-}$ (n = 1—4) in $NaOD$–D_2O; a linear increase in rate as a function of the number of phenyl groups on phosphorus was found. The extension of this work to phosphetanium salts proved difficult because of the ready decomposition of these systems in base to give ring expansion[2] and opening,[3] or expulsion of a group external to the ring.[4] We now record the rates of exchange[5] in salts (I) and (II).[6] Under the mild reaction conditions† both compounds are stable; however, (I) leads to (III) (70%) with 2N-NaOH (reflux, 2 hr.) and (II) *very* slowly gives (IV) in 1N-NaOH–methyl Cellosolve under reflux.‡



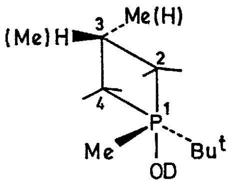
(I)



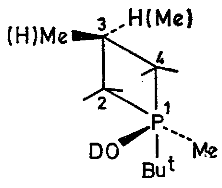
(IIa) 3-Me,Bu^t *cis*
(IIb) 3-Me,Bu^t *trans*

$Me_2CH{\cdot}CHMe{\cdot}CMe_2{\cdot}P(:O)RMe$
(III) R = Me; (IV) R = Bu^t

The individual methyl groups of (I) exchanged at different rates; $k_2(24{\cdot}8°) = 7{\cdot}2 \times 10^{-3}$ and $7{\cdot}1 \times 10^{-4}$ l.mole^{-1} sec.$^{-1}$. The ten-fold difference is similar to that for the exchange of the methylene protons α to a sulphinyl group in which the rate differential was dependent on the *trans* or *gauche* relation of the hydrogen to the S=O and sulphur lone pair.[7] However, in (I) no comparable effect exists, and explanations based on steric hindrance to the approach of OD^- or the possibility that d_π–p_π-bonding[8] is not entirely independent of the geometrical disposition of the methyl groups undergoing exchange, should be considered.



(VI)



(VII)

The observed rates for (I) are about 3800 and 375 times faster than for a single methyl group in $Me_4P^{+}I^{-}$; moreover, the former rate is only 0·4 that for $Ph_3MeP^{+}Br^{-}$ (V). The enhanced acidity in (I) is consistent with the short P^{+}–Me bond length in 1,2,2,3,4,4-hexamethyl-1-phenylphosphetanium bromide.[9] In (IIa) $k_2(24{\cdot}7°) = 2{\cdot}0 \times 10^{-4}$ l.mole^{-1} sec.$^{-1}$ and that of (IIb) is approximately 10—15 times slower.§ By extrapolation, it appears that the P^{+}–Me in (I) which is *trans* to the 3-Me exchanges more rapidly than that *cis* to the 3-Me group. Decreasing the number of methyl groups on the ring (adjacent to phosphorus) in (I) should increase the rate and thus render an aliphatic salt of comparable acidity to (V).

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† The rates for (I) and (IIa) were followed in 0·0675 N-NaOD and (IIb) in 0·3374 N-NaOD at about 25°.
‡ Treatment of (IIa) with powdered NaOH at 170—180° for 3 hr. gave (IV) (85%).
§ The measurement was performed on an 11 : 9 mixture of (IIb : IIa) after (IIa) had undergone complete deuterium exchange.

Neither (IIa) nor (IIb) interconverts after complete deuterium incorporation has occurred; under more vigorous conditions [partial conversion to (IV)] no isomer cross-over took place. Apical attack of OD^- on (IIa) or (IIb) produces the trigonal bipyramid (VI) which would have to pass through a high energy[10] intermediate (VII) by pseudorotation in order for isomerization to occur. In contrast, isomeric benzylphosphetanium salts interconvert on treatment with base.[4a] The transformation of (II)—(IV) most likely proceeds by an apical-in (OD^-)–apical-out (P–C ring bond) inversion mechanism without prior pseudorotation.[11]

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[1] S. E. Cremer and R. J. Chorvat, *Tetrahedron Letters*, **1966**, 419.

[2] S. E. Cremer, *Chem. Comm.*, 1968, 1132; W. Hawes and S. Trippett, *J. Chem. Soc.* (*C*), 1969, 1455; S. Trippett, W. Hawes, S. E. Fishwick, and J. Flint, *Chem. Comm.*, 1967, 1113.

[3] S. E. Fishwick and J. A. Flint, *Chem. Comm.*, 1968, 182.

[4] (a) S. E. Cremer, R. J. Chorvat, and B. C. Trivedi, *Chem. Comm.*, 1969, 769; (b) J. R. Corfield, J. R. Shutt, and S. Trippett, *ibid.*, 1969, 789.

[5] The kinetics were carried out according to a modified procedure[1] of W. von E. Doering and A. K. Hoffmann, *J. Amer. Chem. Soc.*, 1955, **77**, 521. Although linear first-order (pseudo) plots were obtained, the error in k_2 is at least ±15% due to overlapping n.m.r. signals which broaden with deuterium exchange.

[6] For the preparation of (I) see S. E. Cremer and R. J. Chorvat, *J. Org. Chem.*, 1967, **32**, 4066. The synthesis of (IIa) and a mixture of (IIa) and (IIb) was achieved by quaternization of the phosphetane precursors; see S. E. Cremer, R. J. Chorvat, C. H. Chang, and D. W. Davis, *Tetrahedron Letters*, 1968, 5799. As stated in the above references, the stereochemical assignments are *tentative*.

[7] B. J. Hutchison, K. K. Andersen, and A. R. Katritzky, *J. Amer. Chem. Soc.*, 1969, **91**, 3839.

[8] For a discussion of d_π–p_π-bonding, see D. P. Craig and N. L. Paddock, *J. Chem. Soc.*, 1962, 4118. Katritzky[7] has also suggested that differences in proton acidity in his compounds "may involve preferential interactions of the electron pair linking the acidic hydrogen atoms with the $(d\text{–}p)_\pi$-orbital of the SO double bond."

[9] C. Moret and L. M. Trefonas, *J. Amer. Chem. Soc.*, 1969, **91**, 2255.

[10] An increase in energy is needed to place an aklyl group (*e.g.*, Bu^t) in an apical position; also the OD(OH) substituent "favours" an apical position. See R. Kluger and F. H. Westheimer, *J. Amer. Chem. Soc.*, 1969, **91**, 4143, and references therein.

[11] K. Mislow, R. A. Lewis, K. Naumann, and K. E. DeBruin, *Chem. Comm.*, 1969, 1010.