An Intermediate in the Bromination of the Trialkyl Phosphite $P(OCH_2)_3CMe$

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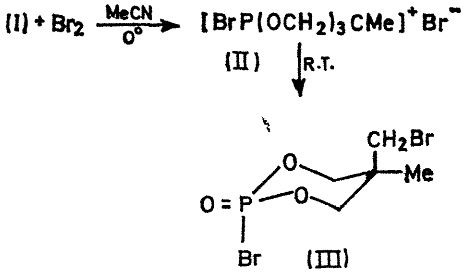
Summary N.m.r. and conductivity studies show that the intermediate in the Michaelis–Arbuzov reaction of bromine with $P(OCH_2)_3CMe$ is the salt $[BrP(OCH_2)_3CMe]^+Br^-$.

INTERMEDIATES formed in the Michaelis–Arbuzov reaction of a phosphorus ester with an alkyl halide or halogen are elusive and difficult to characterize owing to their instability or their tendency to exist in equilibrium with other species.[1] Previous characterizations involving alkyl halides and triphenyl phosphite as a substrate consisted of the observation that precipitation of AgI from the "quasi-phosphonium" intermediate $(PhO)_3PMeI$ was slow compared to $[Ph_3PMe]I$. In the case of trialkyl phosphite substrates, dipole moment and conductivity studies showed only that the intermediate possessed partial ionic character except in one case where conductimetric evidence in acetonitrile indicated the presence of a 1:1 electrolyte of the type $[(RO)_3PR]^+X^-$. The halogenation of phosphorus esters is even less definitive; only triphenyl phosphite has been investigated because it undergoes the dealkylation step much less readily than alkyl phosphites. Salts isolated have various compositions in the series $[(PhO)_nPX_{4-n}][(PhO)_nPX_{6-n}]$ the reaction being a complex one involving extensive disproportionation.



The greater stability of $P(OCH_2)_3CMe$ (I) towards dealkylation has made it possible to characterize an intermediate in the bromination of this trialkyl phosphite and we now report evidence for its formulation as the ionic species (II). The conformation of the Michaelis–Arbuzov product (III) as shown was verified recently from *X*-ray diffraction experiments.[2] The ambient temperature ^1H n.m.r. spectrum of an equimolar mixture of (I) and bromine prepared in CD_3CN at 0° reveals a doublet (δ 5·19,† J 7·2 Hz) and a singlet (δ 1·08 p.p.m.) in a 2:1 ratio. Peaks attributable to a very small amount of $OP(OCH_2)_3CMe$[3] are also visible and arise from trace amounts of water as shown by addition of water. Also present are peaks associated with (III)[4] which increase with time at the expense of the new peaks. The yellow-orange solid precipitated from an ice-cooled benzene solution of (I) by adding an equimolar amount of bromine is unstable to moisture [forming $OP(OCH_2)_3CMe$], readily decomposes into (III) and has never been obtained free of these contaminants. In CD_3CN, however, it affords the same ^1H spectrum as the solution prepared in this solvent.

The molar conductance of 193 mhos l cm^{-1} mol^{-1} measured for an equimolar mixture of (I) and bromine in acetonitrile at 0° is comparable to 158 mhos l cm^{-1} mol^{-1} for $(Bu^n{}_4N)NO_3$ in the same solvent and indicates that (II) is a 1:1 electrolyte. The formulation of (II) as shown is supported by the ^{31}P chemical shift of $-36·5$ p.p.m. (obtained by INDOR experiments) which is reasonable for a phosphonium salt of (I) such as $[MeP(OCH_2)_3CMe]BF_4$ for which δ ^{31}P is $-60·15$ p.p.m.[5] The ionicity of (II) is confirmed by the largest downfield methylene proton shift and the highest ^3J (POCH) value measured for any derivative of (I). The linear correlation of these parameters which increase in the series[6] $AP(OCH_2)_3CMe$ (A is an electron lone pair) $<BMe_3<BH_3<Et^+<Ph_3C^+$, is further verified by the inclusion of A = Br^+ (correlation coefficient = 0·98). The extended linear correlation not only demonstrates the stronger electronegativity of the bromonium compared to a carbonium ion in $AP(OCH_2)_3CMe$ as rationalized on isovalent hybridization arguments,[6] but it also emphasizes the lack of π back donation from Br to P compared to derivatives of (I) in which A is oxygen, sulphur or a metal carbonyl moiety.[6,7]

Further studies in these and analogous systems will be presented later. We thank the National Science Foundation for support of this work.

Note added in proof. A low-temperature intermediate in the reaction of $(Bu^tO)_2PCHMe_2$ and MeI was recently isolated, which on warming gave the expected Michaelis–Arbuzov product. The ^1H and ^{31}P n.m.r. parameters were interpreted to indicate an ionic P–I interaction (A. I. Razumov, B. G. Liorbev, T. V. Zhykova, and I. Ya. Bambushek, *Zhur. obshchei Khim.*, 1970, **40**, 2009).

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† ^1H and ^{31}P chemical shifts were measured in CD_3CN with respect to internal Me_4Si and external 85% H_3PO_4, respectively.

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