Michaelis–Arbuzov Intermediates: *X*-Ray Crystal Structures of the Methyl Bromide Adducts of Neopentyl Diphenylphosphinite and Dineopentyl Phenylphosphonite

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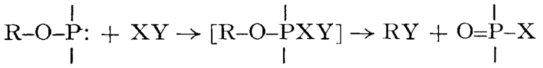
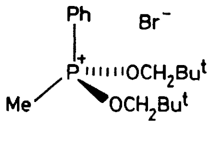
Summary Single crystal *X*-ray structure determinations of the Michaelis–Arbuzov intermediates $Ph_2Me(Bu^tCH_2O)P^+Br^-$ and $PhMe(Bu^tCH_2O)_2P^+Br^-$ clearly demonstrate that these species are four-co-ordinate phosphonium salts.

Intermediates of the Michaelis–Arbuzov reaction (Scheme) have either a tetraco-ordinate (phosphonium) or pentaco-ordinate (phosphorane) structure in solution, depending on the nature of XY and the reaction conditions.[1–4] For reactions in which XY is an alkyl halide, only the phosphonium species has been detected by ^{31}P n.m.r. spectroscopy,[1,3,4] although it was previously suggested that the pentacovalent form might exist in the solid state or in non-polar media.[5] Stereochemical evidence for the initial formation of a pentaco-ordinate intermediate in the reaction of a cyclic phosphite with methyl iodide[6] has been questioned.[7]

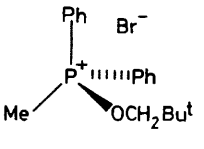


$$\mathrm{R{-}O{-}\overset{|}{\underset{|}{P}}\!: + XY \rightarrow [R{-}O{-}\overset{|}{\underset{|}{P}}XY] \rightarrow RY + O{=}\overset{|}{\underset{|}{P}}{-}X}$$

Scheme



(1)



(2)

The absence of crystallographic data for Michaelis–Arbuzov intermediates is due in part to the difficulties associated with the handling of these moisture-sensitive and thermally unstable compounds. We have found that the attachment of phenyl groups to phosphorus considerably enhances their stability,[8] both to hydrolysis and to thermal decomposition [relative *k* ($CDCl_3$; 33 °C; R = neopentyl: $(RO)_3PMeBr$ 1·00, $(RO)_2PPhMeBr$ 0·21, $(RO)PPh_2MeBr$ 0·0023]. Compounds (**1**) and (**2**) were prepared by the reaction of bromomethane with the corresponding phosphorus esters in sealed tubes at room temperature. The crystals which separated were washed with anhydrous ether and dried *in vacuo* and could be handled in the open laboratory without difficulty.

The *X*-ray structures of (**1**) and (**2**) clearly show that these compounds are phosphonium salts composed of tetrahedral cations with minimum $P^+ \ldots Br^-$ distances of 4·43 and 4·61 Å for (**1**) and (**2**) respectively (see Figures 1 and 2 respectively).

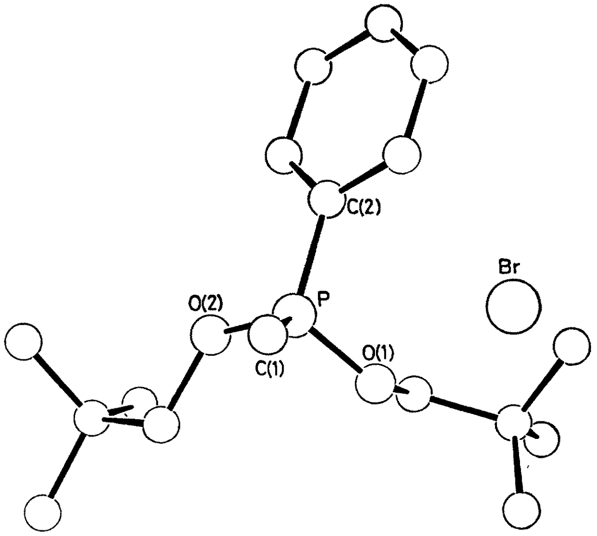


Figure 1. The structure of the dialkoxyphosphonium bromide (**1**). Bond lengths to the P atom (Å) are C(1) 1·756(7), C(2) 1·771(8), O(1) 1·545(5), O(2) 1·553(5). Bond angles at the P atom (°) are, O(1)–P–O(2) 111·4(3); O(1)–P–C(1) 103·4(4); O(1)–P–C(2) 111·0(3); O(2)–P–C(1) 113·5(4); O(2)–P–C(2) 103·8(4); C(1)–P–C(2) 114·0(4); mean 109·5(1).

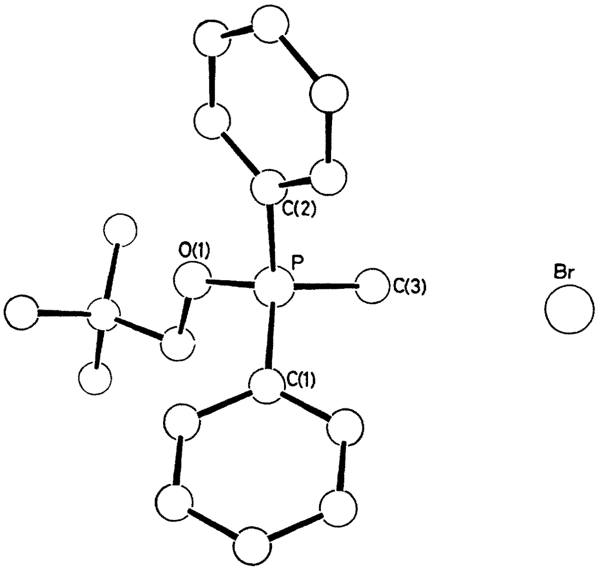


FIGURE 2. The structure of the diphenylphosphonium bromide (**2**). Bond lengths to the P atom (Å) are C(1) 1·785(6), C(2) 1·790(6), C(3) 1·779(7), O(1) 1·568(4). Bond angles at the P atom (°) are, C(1)–P–C(2) 111·9(3); C(1)–P–C(2) 110·4(3); C(1)–P–O(1) 109·7(3); C(2)–P–C(3) 108·7(3); C(2)–P–O(1) 104·2(3); C(3)–P–O(1) 111·9(3); mean = 109·4(1).

It has been stated that phosphorus acts as an electron-acceptor with respect to an attached aryl substituent and that the effect is partly mesomeric.[9] Whilst such an effect could account for the stabilising influence of phenyl groups in the intermediates (**1**) and (**2**), the observed bond lengths do not support this view. The P–Me and P–Ph bond lengths are similar in both compounds, with the P–Ph being marginally longer in each case. These results accord with previous data on P–methyl and P–phenyl bond lengths in the same compound[10] and indicate that the P–phenyl bond possesses very low double bond character. On this basis, the stability of quasiphosphonium intermediates would be expected to increase, as phenyl groups are replaced by alkoxy, if p_π–d_π interaction between oxygen and the P atom is the controlling influence.[3] The reverse order of stability is observed and suggests that it is the inductive effect of the attached groups which is the more important factor.

Crystal data: (**1**) $C_{17}H_{30}BrPO_2$, monoclinic, space group $P2_1/n$, $a = 13{\cdot}621(5)$, $b = 12{\cdot}002(4)$, $c = 12{\cdot}502(2)$ Å, $\beta = 102{\cdot}27(2)°$, $Z = 4$, $M = 377{\cdot}1$, $D_c = 1{\cdot}25$ g cm^{-3}, $U = 1997{\cdot}1$ Å^3, μ(Mo-K_α) = 20·7 cm^{-1}, $I/\sigma(I) > 3{\cdot}0$, θ-range 3—25°, $R = 0{\cdot}052$ for 1300 data. (**2**) $C_{18}H_{24}BrPO$, monoclinic, space group $P2_1/c$, $a = 9{\cdot}148(2)$, $b = 10{\cdot}451(3)$, $c = 19{\cdot}250(1)$ Å, $\beta = 92{\cdot}02(3)°$, $Z = 4$, $M = 367{\cdot}2$, $D_c = 1{\cdot}32$ g cm^{-3}, $U = 1839{\cdot}3$ Å^3, μ(Mo-K_α) = 22·5 cm^{-1}, $I/\sigma(I) > 3{\cdot}0$, θ-range 3·25°, $R = 0{\cdot}046$ for 1628 data. Both data sets were collected on a Philips PW1100 diffractometer with Mo-K_α radiation.† Important bond lengths and angles are shown with Figure 1 and Figure 2.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] H. R. Hudson, R. G. Rees, and J. E. Weekes, *Chem. Comm.*, 1971, 1279; *J.C.S. Perkin I*, 1974, 982.

[2] H. R. Hudson and J. C. Roberts, *J.C.S. Perkin II*, 1974, 1575; G. K. McEwen, and J. G. Verkade, *Chem. Comm.*, 1971, 668; A. Skowronska, J. Mikolajczak, and J. Michalski, *ibid.*, 1975, 986; D. B. Denney, D. Z. Denney, and G. DiMiele, *Phosphorus and Sulfur*, 1978, **4**, 125.

[3] L. V. Nesterov, A. Ya. Kessel, Yu. Yu. Samitov, and A. A. Musina, *Doklady Akad. Nauk S.S.S.R.*, 1978, **180**, 116; *Zhur. obshchei Khim.*, 1969, **39**, 1179.

[4] A. I. Razumov, B. G. Liorber, T. V. Zykova, and I. Yu. Bambushek, *Zhur. obshchei Khim.*, 1970, **40**, 2009.

[5] A. I. Ruzumov and N. N. Bankovskaya, *Zhur. obshchei Khim.*, 1964, **34**, 1859.

[6] C. L. Bodkin and P. Simpson, *Chem. Comm.*, 1970, 1579; *J.C.S. Perkin II*, 1972, 2049.

[7] R. D. Adamcik, L. L. Chang, and D. B. Denney, *J.C.S. Chem. Comm.*, 1974, 986.

[8] L. V. Nesterov and R. I. Mutalapova, *Zhur. obshchei Khim.*, 1967, **37**, 1843.

[9] G. P. Schiemenz, *Angew. Chem. Internat. Edn.*, 1974, **13**, 351.

[10] R. Böhme, H. Burzlaff, R. Luckenbach, M. Gomm, and H.-J. Bestmann, *Chem. Ber.*, 1975, **108**, 3525; F. Giordano and A. Ripamonti, *Acta Cryst.*, 1967, **22**, 678; D. Fenske, R. Mattes, J. Löns, and K.-F. Tebbe, *Chem. Ber.*, 1973, **106**, 1139.