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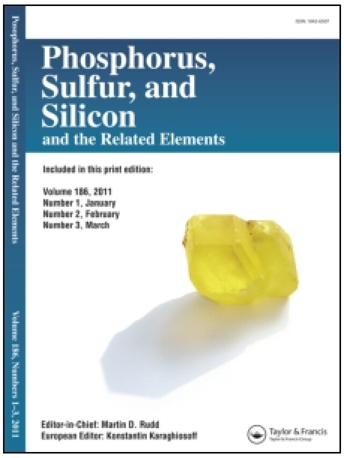

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FURTHER STUDIES IN THE CHEMISTRY OF 10-PHENYLPHENOXAPHOSPHINE Rate of Quaternization, and an X-ray Structural Study of a Related Phosphonium Salt, 10(-4-Bromobenzyl)-10-Phenylphenoxaphosphonium Bromide

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FURTHER STUDIES IN THE CHEMISTRY OF 10-PHENYLPHENOXAPHOSPHINE

Rate of Quaternization, and an X-ray Structural Study of a Related Phosphonium Salt, 10(-4-Bromobenzyl)-10-Phenylphenoxaphosphonium Bromide

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10-Phenylphenoxaphosphine (2) undergoes quaternization with phenacyl bromide in nitromethane five times more slowly than triphenylphosphine and almost twenty times more slowly than *o*-methoxyphenyldiphenylphosphine. It is argued that stabilization of the developing phosphonium centre by interaction with the ortho-oxygen atom, previously suggested as being involved in the quaternization of the latter (McEwen *et al.*[1]), is not significant for the quaternization of the phenoxaphosphine (2), and that the predominant role of the ether oxygen is electron-withdrawal from phosphorus. This conclusion is supported by an X-ray structural study of the title compound (3). Crystals of (3) are orthorhombic, $a = 18.954\,(11)$, $b = 25.715\,(14)$, $c = 9.322\,(5)$ Å, $Z = 8$, in space group $Pbca$ (D_{2h}^{15}, No. 61). The structure was determined by Patterson and electrondensity methods, and refined by least squares techniques to $R = 0.045$ for 1505 independent reflections. The fused ring system of the phenoxaphosphonium cation is not planar, the central ring having a boat-like conformation with the phosphorus and oxygen atoms displaced from the four effectively coplanar carbon atoms by 0.14 and 0.07 Å respectively. The average exocyclic angles at phosphorus are 110.7°; the endocyclic angle is 103.1°. The transannular $P^+ \ldots O$ distance is 3.11 Å, indicating little interaction.

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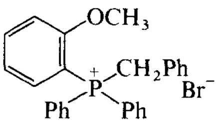
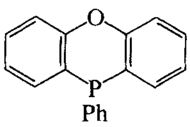
It has been shown that the presence of an *o*-methoxy substituent in an aryl phosphine causes a significant acceleration of the rate of quaternization with alkyl halides. Thus e.g. *o*-methoxyphenyldiphenylphosphine undergoes quaternization with benzyl chloride some four times faster than the corresponding *para*-isomer, and seven times faster than triphenylphosphine. It has been suggested that these effects are due to the overlap of a pair of 2p electrons of the *o*-methoxy group with a 3*d* (or hybrid orbital) of phosphorus in the transition state of the reaction, such that the developing phosphonium centre is stabilised. Evidence in support of this type of interaction has been adduced from spectroscopic studies of the parent phosphines and related phosphonium salts,[1,2] and also from the results of an X-ray diffraction study of the salt (1) in which the observed $P^+ \ldots O$ distance of 2.88 Å suggests a weak bonding interaction,[3] the sum of the accepted Van der Waals radii being 3.30 Å.[4] In related studies, the reduction in the rate of alkaline hydrolysis of salts of type (1) compared to the corresponding *para*-isomers has also been attributed to the stabilisation of the phosphonium cation by such an interaction.[5]



(1)



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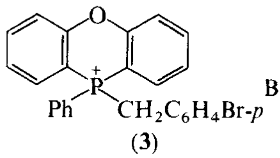

(3)

In extension of our earlier studies on the chemistry of phenoxaphosphines e.g. (2) and related phosphonium salts,[6,7] we wished to investigate whether a similar $P^+ \ldots O$ interaction was significant between the *o*-ether oxygen and phosphorus in a heterocyclic system in which the oxygen was perhaps not as free to move towards phosphorus as in the above example (1). Accordingly, we now report rate data for the quaternization of 10-phenylphenoxaphosphine (2), together with

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comparable data for triphenylphosphine and *o*-methoxyphenyldiphenylphosphine, and also the results of an X-ray structural study of the salt (**3**).

QUATERNIZATION STUDIES

Rate and activation data for the quaternization of 10-phenylphenoxaphosphine (**2**) and related acyclic phosphines with phenacyl bromide are presented in Table I. It is seen that the phenoxaphosphine (**2**) undergoes quaternization some five times more slowly than triphenylphosphine. In contrast *o*-methoxyphenyldiphenylphosphine quaternizes almost four times faster than triphenylphosphine, in keeping with earlier studies with other alkyl halides.[1,2] There is thus almost a twentyfold difference in the rate of quaternization of the phenoxaphosphine (**2**) and *o*-methoxyphenyldiphenylphosphine, which is due to the significantly lower activation energy for quaternization of the latter, in keeping with the earlier suggestion of the stabilisation of the forming phosphonium centre in the transition state of the reaction by oxygen (**2p**)-phosphorus (**3d**) interaction.[1,2] Clearly, this is not significant for the phenoxaphosphine system, and the predominant effect of the oxygen atom here would seem to be an electron withdrawal from phosphorus, thereby causing a reduction in the rate of quaternization. It is of interest that while the enthalpy of activation for the quaternization of the *o*-methoxyphenyldiphenylphosphine with phenacyl bromide is the lowest of the series, the entropy of activation for this reaction is the most negative of the series, perhaps supporting the suggestion of a specific orientation of oxygen and phosphorus in the transition state of the reaction. In contrast, in the systems studied by McEwen *et al.*,[1,2] the entropy of activation rather than E_a has been the dominant term, being much less negative for *o*-methoxyphenyldiphenylphosphine than e.g. for the *p*-methoxy analogue, suggesting solvation effects to be of importance.

The Structure of 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium Bromide (**3**)

Crystal data $[C_{25}H_{19}OPBr]^+ Br^-$, $M = 526.2$. Orthorhombic, $a = 18.954$ (11), $b = 25.715$ (14), $c = 9.322$ (5) Å, $U = 4{,}543.38$ Å^3, $D_m = 1.55$, $Z = 8$, $D_c = 1.54$g cm^{-3}, $F(000) = 2{,}104$. Mo $- K_\alpha$ radiation, $\lambda = 0.710\ 69$ Å; μ (Mo $- K_\alpha$) $= 35.5$ cm^{-1}. Space group *Pbca* (D_{2h}^{15}, No. 61) from systematic absences.

Intensity data were measured on a Stöe-Stadi 2 diffractometer; the crystal was mounted with the *c*-axis coincident with the rotation (ω) axis. The background—ω scan—background technique was used to collect 4,171 reflections of which 1,505 had $I \geqslant 2.5\ \sigma\ (I)$ and were classed as observed. Lorentz and polarization factors were applied but no absorption correction was made.

Structure solution and refinement The positions of the bromines were determined from a Patterson synthesis, and the remaining atoms (including hydrogens) located from successive electron-density difference syntheses. The structure was refined by full-matrix least-squares methods with all non-hydrogen atoms given anisotropic thermal parameters for the final stages of refinement. Once located from difference maps, hydrogen atoms were included in positions calculated from the geometry of the molecule (C—H bond length 1.08 Å) and a common isotropic temperature factor applied. Scattering factors were calculated using an analytical approximation[9] and the weighting scheme $w = 0.523\ 9/[\sigma^2(F) + 0.0025\ F^2]$ used. Refinement converged at $R = 0.045$ and the final difference map showed no peaks greater than 0.47 e. Å^{-3}. Final observed and calculated structure factors, thermal parameters and least-square planes equations are available on request from the authors (IWN). Positional parameters are given in Table II, bond lengths and valency angles in Table III.

TABLE I

Second order rate data and activation parameters for quaternization of phosphines with phenacyl bromide in nitromethane

Phosphine	k(1 mol^{-1} sec^{-1}) 30°C	40°C	Relative rate at 30°C	E_a (kJmol^{-1})	$\Delta S\dagger$(JK^{-1} mol^{-1})
10-phenylphenoxaphosphine (**2**)	0.012	0.023	0.18	48.0	−131.4
triphenylphosphine[8]	0.064	0.115	1.00	45.2	−126.7
o-methoxyphenyldiphenylphosphine	0.228	0.370	3.56	38.1	−139.8

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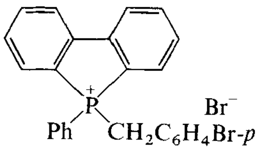
TABLE II

Final positional parameters with standard deviations in parentheses

	x	*y*	*z*
Br^-	0.352 6(1)	0.543 0(1)	0.604 0(1)
Br	0.079 6(1)	0.181 0(1)	−0.130 5(2)
P	0.341 7(1)	0.107 9(1)	0.371 4(3)
O	0.393 5(4)	0.219 8(3)	0.300 5(9)
C(1)	0.387 5(5)	0.072 2(4)	0.509 1(12)
C(2)	0.349 2(6)	0.044 4(5)	0.611 0(14)
C(3)	0.384 5(7)	0.020 5(5)	0.723 8(16)
C(4)	0.455 4(7)	0.024 1(5)	0.731 4(18)
C(5)	0.493 5(6)	0.050 7(6)	0.630 3(16)
C(6)	0.460 3(6)	0.074 6(5)	0.517 2(15)
C(7)	0.270 3(5)	0.067 9(4)	0.305 6(12)
C(8)	0.224 6(5)	0.095 4(4)	0.198 6(12)
C(9)	0.166 4(5)	0.123 4(4)	0.244 8(14)
C(10)	0.122 3(6)	0.148 9(5)	0.146 8(14)
C(11)	0.137 1(6)	0.143 3(4)	0.001 3(15)
C(12)	0.192 9(6)	0.114 8(5)	−0.050 3(15)
C(13)	0.235 6(6)	0.091 0(5)	0.051 3(13)
C(14)	0.310 6(5)	0.167 7(4)	0.442 6(12)
C(15)	0.340 1(6)	0.215 1(4)	0.397 7(14)
C(16)	0.315 8(8)	0.261 2(5)	0.457 6(17)
C(17)	0.265 6(8)	0.261 2(6)	0.558 0(17)
C(18)	0.234 5(7)	0.215 1(5)	0.603 4(16)
C(19)	0.257 7(6)	0.168 2(5)	0.543 8(13)
C(20)	0.401 0(5)	0.128 1(4)	0.233 2(13)
C(21)	0.431 9(6)	0.089 9(5)	0.146 7(14)
C(22)	0.481 9(7)	0.106 3(7)	0.046 3(16)
C(23)	0.500 1(7)	0.157 9(7)	0.032 8(17)
C(24)	0.467 5(6)	0.194 5(5)	0.119 7(16)
C(25)	0.419 3(5)	0.179 8(4)	0.220 1(12)
H(2)	0.292 5	0.041 4	0.602 5
H(3)	0.355 1	−0.000 4	0.804 7
H(4)	0.482 7	0.005 2	0.818 8
H(5)	0.550 2	0.053 0	0.639 4
H(6)	0.490 7	0.095 0	0.436 9
H(71)	0.238 2	0.055 8	0.394 8
H(72)	0.292 7	0.034 0	0.253 8
H(9)	0.154 7	0.125 4	0.358 0
H(10)	0.078 6	0.172 4	0.183 0
H(12)	0.202 9	0.111 1	−0.163 9
H(13)	0.279 6	0.067 9	0.014 5
H(16)	0.338 0	0.297 6	0.422 1
H(17)	0.249 2	0.297 8	0.604 5
H(18)	0.193 1	0.215 4	0.683 1
H(19)	0.234 2	0.131 9	0.577 1
H(21)	0.417 8	0.049 3	0.157 5
H(22)	0.506 4	0.077 9	−0.022 9
H(23)	0.539 4	0.169 6	−0.044 6
H(24)	0.480 7	0.235 1	0.108 1

DISCUSSION

As with the parent phosphine[10] (**2**), the fused ring system of the phosphonium cation is not planar (Figure). In particular, the central ring has a boat-like conformation with the phosphorus and oxygen atoms displaced from the four effectively co-planar carbon atoms by 0.14 and 0.07 Å respectively. These displacements are less than those found in 10-phenylphenoxaphosphine (**2**) (0.22 and 0.17 Å for phosphorus and oxygen) and the overall displacement from planarity is less for the phosphonium cation with the dihedral angle between the outer rings being considerably smaller (4.1° compared to 15° in (**2**)). Quaternization produces significant changes in the bond angles about phosphorus, with the endocyclic and average exocyclic C–P–C angles increasing from 98.0 and 101.0° in (**2**) to 103.1 and 110.7° in (**3**). Accompanying quaternization, there is also a change from 87 to 76.7° in the dihedral angle between the C(**1**)–(**6**) phenyl ring (plane B) and the plane containing C(**14**), C(**15**), C(**20**) and C(**25**) (plane A). The plane associated with the C(**8**)–(**13**) of the p-bromobenzyl phenyl ring makes angles of 69.7 and 49.2° with planes A and B respectively, which are similar to the values of 73.0 and 44.4° found in the dibenzophospholium salt (**4**).[11]



(**4**)

While the P . . . O distances in both (**2**) and (**3**), (3.20 and 3.11 Å respectively) lie within the sum of the Van der Waals radii (3.30 Å), they are very significantly larger than the value of 2.88 Å found in (**1**). It thus seems unlikely that the weak phosphorus - oxygen interactions suggested for the acyclic salt (**1**) are significant in either (**2**) or (**3**).

The endocyclic C–P–C angles in (**2**) and (**3**), 98.0 and 103.1° respectively are equally distorted from the ideal strain-free values of *ca* 90 and 109.5° for the phosphine and phosphonium salt respectively. However, the endocyclic angle at phosphorus in the phosphonium salt (**3**) is very close to the smallest angle at phosphorus (105°) in the cation $Ph_3\overset{+}{P}Me$[12] (which may be considered as an acyclic analogue of (**3**)), implying that there is little significant deformation of bond angle at phosphorus in (**3**), and that the reduction in rate of quaternization of the phenoxaphosphine (**2**) cannot be attributed to an increase in angle strain at phosphorus. The structural data therefore lends support to the above suggestion that in the phenoxaphosphonium system the predominant

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TABLE III

Bond distances (Å) and angles (°), with standard deviations in parentheses

(a) *Distances*			
P—C(1)	1.80 (1)	C(11)—C(12)	1.37 (2)
P—C(7)	1.81 (1)	C(12)—C(13)	1.39 (2)
P—C(14)	1.78 (1)	C(14)—C(15)	1.40 (2)
P—C(20)	1.79 (1)	C(14)—C(19)	1.38 (2)
C(1)—C(2)	1.39 (2)	C(15)—O	1.36 (2)
C(1)—C(6)	1.38 (2)	C(15)—C(16)	1.39 (2)
C(2)—C(3)	1.39 (2)	C(16)—C(17)	1.33 (2)
C(3)—C(4)	1.35 (2)	C(17)—C(18)	1.39 (2)
C(4)—C(5)	1.37 (2)	C(18)—C(19)	1.40 (2)
C(5)—C(6)	1.37 (2)	C(20)—C(21)	1.40 (2)
C(7)—C(8)	1.50 (1)	C(20)—C(25)	1.38 (1)
C(8)—C(9)	1.39 (1)	C(21)—C(22)	1.40 (2)
C(8)—C(13)	1.39 (2)	C(22)—C(23)	1.38 (3)
C(9)—C(10)	1.40 (2)	C(23)—C(24)	1.39 (2)
C(10)—C(11)	1.39 (2)	C(24)—C(25)	1.36 (2)
C(11)—Br	1.91 (1)	C(25)—O	1.37 (1)
(b) *Angles*			
C(1)—P—C(7)	108.3 (5)	C(11)—C(12)—C(13)	116 (1)
C(1)—P—C(14)	109.6 (5)	C(8)—C(13)—C(12)	123 (1)
C(1)—P—C(20)	111.0 (5)	P—C(14)—C(15)	121 (1)
C(7)—P—C(14)	111.8 (5)	P—C(14)—C(19)	120 (1)
C(7)—P—C(20)	113.0 (5)	C(15)—C(14)—C(19)	119 (1)
C(14)—P—C(20)	103.1 (5)	O—C(15)—C(14)	125 (1)
P—C(1)—C(2)	120 (1)	O—C(15)—C(16)	116 (1)
P—C(1)—C(6)	120 (1)	C(14)—C(15)—C(16)	119 (1)
C(2)—C(1)—C(16)	120 (1)	C(15)—C(16)—C(17)	121 (1)
C(1)—C(2)—C(3)	120 (1)	C(16)—C(17)—C(18)	121 (1)
C(2)—C(3)—C(4)	119 (1)	C(17)—C(18)—C(19)	119 (1)
C(3)—C(4)—C(5)	122 (1)	C(14)—C(19)—C(18)	121 (1)
C(4)—C(5)—C(6)	121 (1)	P—C(20)—C(21)	118 (1)
C(1)—C(16)—C(5)	119 (1)	P—C(20)—C(25)	120 (1)
P—C(7)—C(8)	113 (1)	C(21)—C(20)—C(25)	121 (1)
C(7)—C(8)—C(9)	120 (1)	C(20)—C(21)—C(22)	117 (1)
C(7)—C(8)—C(13)	122 (1)	C(21)—C(22)—C(23)	122 (1)
C(9)—C(8)—C(13)	118 (1)	C(22)—C(23)—C(24)	119 (1)
C(8)—C(9)—C(10)	121 (1)	C(23)—C(24)—C(25)	121 (1)
C(9)—C(10)—C(11)	118 (1)	O—C(25)—C(20)	126 (1)
Br—C(11)—C(10)	117 (1)	O—C(25)—C(24)	114 (1)
Br—C(11)—C(12)	120 (1)	C(20)—C(25)—C(24)	120 (1)
C(10)—C(11)—C(12)	123 (1)	C(15)—O—C(25)	124 (1)

effect of the oxygen atom is electron-withdrawal from phosphorus. This effect is without doubt also responsible for the greatly increased rate of alkaline hydrolysis of phenoxaphosphonium salts compared to related acyclic salts.[7,15]

EXPERIMENTAL

^{1}H nmr spectra were recorded at 60 MHz on a JEOL spectrometer, using tetramethylsilane as internal standard. Operations involving tertiary phosphines were conducted under nitrogen.

10 - Phenylphenoxaphosphine[13] and o - methoxyphenyldiphenylphosphine[1] were prepared as described previously.

KINETIC STUDIES

The rates of quaternization of the above phosphines with α-bromoacetophenone in nitromethane solution were determined using the conductance procedure described by Borowitz *et al.*[14] A Wayne-Kerr conductance bridge was employed. The quaternization reactions followed a second order rate law. Rate constants and activation parameters were calculated as described by Borowitz *et al.*[14] and are presented in Table I. Evaporation of the solution obtained at the conclusion of each kinetic run gave the appropriate phenacylphosphonium salt, whose structure was confirmed by microanalysis and ^{1}H nmr spectroscopy. The following salts were characterised:

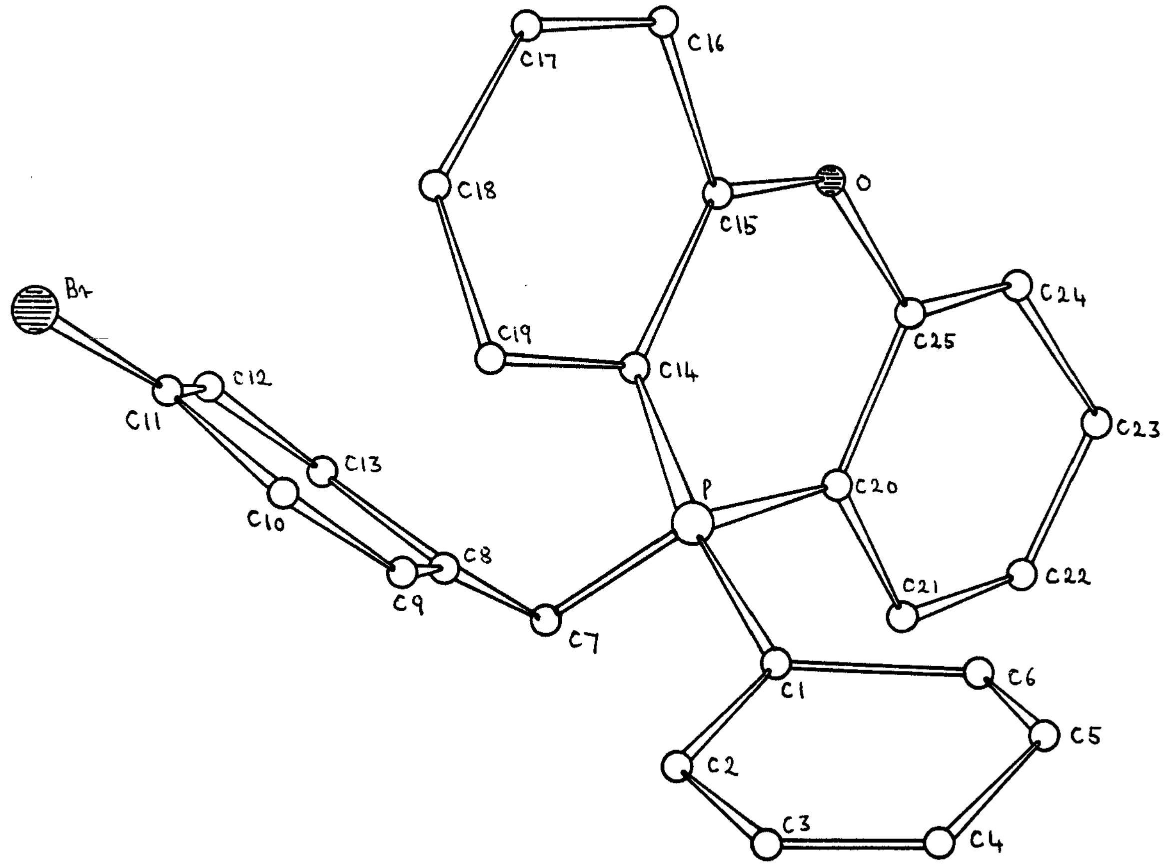

FIGURE 1 The structure of the 10-(4-bromobenzyl)-10-phenylphenoxaphosphonium cation.

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o - Methoxyphenyl(phenacyl)diphenylphosphonium Bromide, m.p. 195–196° (ex EtOAc-EtOH). Found: C, 65.95; H, 5.05. $C_{27}H_{24}BrO_2P$ requires C, 65.95; H, 4.95%). $\delta(CDCl_3)$: 8.6–7.0 (m, 19 ArH); 6.09 (d, $^2J_{PCH}$ 13.5 Hz, $\overset{+}{P}CH_2$) and 3.58 (s, 3H, OCH_3) ppm.

10 - Phenacyl - 10 - phenylphenoxaphosphonium Bromide (as the mono hydrate), m.p. 220° (ex EtOAc-EtOH). (Found: C, 63.7; H, 4.65; $C_{26}H_{20}BrO_2P.H_2O$ requires C, 63.3; H, 4.5%). $\delta(CDCl_3)$: 8.7–7.1 (m, 18 ArH) and 6.4 (d, $^2J_{PCH}$ 12.75 Hz, $\overset{+}{P}CH_2$).

Preparation of 10 - (4 - bromobenzyl) - 10 - phenylphenoxaphosphonium Bromide(**3**)-10-Phenylphenoxaphosphine (0.138 g, 0.5 mmol), and 4-bromobenzyl bromide (0.15 g, excess) were heated together under reflux in toluene (3 cm^3) for 2 hr. After filtration and washing with ether, the salt was recrystallised from ethyl acetate-ethanol to give *crystals*, m.p. > 250° d. (Found: C, 56.5; H, 4.05; $C_{25}H_{19}BrO_2P$ requires C, 57.0; H, 3.65%).

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