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Quasiphosphonium intermediates

VI *. Crystal structure of neopentyloxy(phenacyl)diphenylphosphonium bromide: a stable Michaelis–Arbuzov intermediate formed in the reaction of neopentyl diphenylphosphinite with phenacyl bromide **

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Abstract

Single crystal X-ray diffraction measurements on the adduct obtained from neopentyl diphenylphosphinite and phenacyl bromide show this Michaelis–Arbuzov intermediate to be a phosphonium compound, with a tetrahedral arrangement of bonds around phosphorus and a $P^+ \cdots Br^-$ interatomic distance of 4.229 Å. The phenyl–phosphorus bonds are of normal length for single P–C bonds. Although the phosphorus–oxygen bond length (1.573 Å) indicates significant double bond character, the reactivity of intermediates of this type is thought to be controlled mainly by inductive effects. Rearrangement of this intermediate to the isomeric vinyloxyphosphonium bromide (Perkow intermediate) does not occur.

Introduction

Intermediates (I) in the Michaelis–Arbuzov reaction (Scheme 1) are, generally, undetectable and short-lived species, although a number of stable examples have been isolated in cases in which the final dealkylation is slow because of steric hindrance [2]. Stability is also increased by the presence of electron-releasing substituents which reduce the positive charge on phosphorus. Crystal structures

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* For part V see ref. 1.

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phosphorus–oxygen bond formation [6,7], or (in the presence of protic solvents) α -hydroxyphosphonates (VII) and dehalogenated ketones (VIII) [5,8]. The intermediates formed in each of these reactions are of interest in connection with the reaction mechanisms involved. The possible involvement of a common first intermediate has been discussed [9,10].

Results and discussion

The ketophosphonium bromide (Arbuzov intermediate) (IV) that was formed by the interaction of neopentyl diphenylphosphinite with phenacyl bromide in acetone was sufficiently stable and resistant to hydrolysis to allow a single crystal X-ray diffraction study to be carried out in the open laboratory without the need for special precautions to exclude atmospheric moisture. Principal bond lengths are shown in Table 1 and bond angles in Table 2. The compound is clearly seen to be a phosphonium salt (Fig. 1) rather than a pentacoordinate species, with bond angles at phosphorus approximating to a tetrahedral arrangement and a $P^+ \cdots Br^-$ interatomic distance of 4.229 Å. There is no significant difference between the length of the bond from phosphorus to the aromatic carbon atoms (mean 1.789 Å) and that to the saturated CH_2 group of the phenacyl substituent (1.798 Å). Closely similar phosphorus–carbon bond lengths were previously found [3] for the P–aromatic and P–methyl bonds in methyl(neopentyloxy)diphenylphosphonium bromide (II) (P–C_{Ar} mean, 1.788; P–Me, 1.779 Å) and in methyl(dineopentyloxy)phenylphosphonium bromide (III) (P–C_{Ar}, 1.771; P–Me, 1.756) in accordance with the view that the P–phenyl bonds possess little if any double bond character. Mesomeric electron release from phenyl to phosphorus does not therefore appear to be a significant factor in the stabilisation of quasiphosphonium salts of these types. The possibility of weak inductive electron release to positive phosphorus by phenyl is indicated by the internal bond angles of the benzene ring at C _{α} (Fig. 2). A linear correlation has previously been established [11] between the internal bond angle of a benzene ring at C _{α} for a range of substituted benzene derivatives and

Table 1

Principal bond lengths (Å) in neopentyloxy(phenacyl)diphenylphosphonium bromide (IV)

P–C(1)	1.798(11)	C(4)–C(6)	1.476(20)
P–C(21)	1.792(11)	C(4)–C(7)	1.548(20)
P–C(31)	1.786(12)	C(21)–C(22)	1.426(16)
P–O(1)	1.573(8)	C(22)–C(23)	1.376(17)
C(1)–C(2)	1.500(15)	C(23)–C(24)	1.364(19)
C(2)–C(11)	1.510(18)	C(24)–C(25)	1.390(18)
C(2)–O(2)	1.217(13)	C(25)–C(26)	1.388(17)
C(11)–C(12)	1.376(17)	C(21)–C(26)	1.377(15)
C(12)–C(13)	1.400(20)	C(31)–C(32)	1.372(16)
C(14)–C(13)	1.345(22)	C(31)–C(36)	1.385(17)
C(14)–C(15)	1.411(22)	C(32)–C(33)	1.393(18)
C(15)–C(16)	1.346(19)	C(33)–C(34)	1.369(18)
C(16)–C(11)	1.393(17)	C(34)–C(35)	1.358(19)
O(1)–C(3)	1.458(13)	C(35)–C(36)	1.392(18)
C(4)–C(3)	1.490(17)	C(31)–C(36)	1.385(17)
C(4)–C(5)	1.573(22)		

Table 2

Principal bond angles (deg) in neopentyloxy(phenacyl)diphenylphosphonium bromide (IV)

C(21)–P–C(31)	111.8(6)	C(6)–C(4)–C(5)	110.1(1.6)
C(31)–P–O(1)	109.5(5)	C(7)–C(4)–C(3)	106.3(1.2)
C(31)–P–C(1)	112.3(6)	C(7)–C(4)–C(5)	107.0(1.5)
C(21)–P–C(1)	113.0(5)	C(7)–C(4)–C(6)	111.0(1.4)
C(1)–P–O(1)	107.8(5)	C(26)–C(21)–C(22)	121.0(1.1)
C(21)–P–O(1)	102.0(5)	P–C(21)–C(22)	118.9(9)
P–C(1)–C(2)	113.0(8)	P–C(21)–C(26)	119.2(9)
C(1)–C(2)–C(11)	117.5(1.2)	C(23)–C(22)–C(21)	119.8(1.2)
C(1)–C(2)–O(2)	120.3(1.2)	C(24)–C(23)–C(22)	119.2(1.4)
C(11)–C(2)–O(2)	122.1(1.2)	C(25)–C(24)–C(23)	121.0(1.3)
C(11)–C(12)–C(13)	119.7(1.5)	C(26)–C(25)–C(24)	121.5(1.3)
C(12)–C(13)–C(14)	119.3(1.7)	C(21)–C(26)–C(25)	117.5(1.3)
C(15)–C(14)–C(13)	120.4(1.7)	P–C(31)–C(32)	122.1(1.0)
C(14)–C(15)–C(16)	121.2(1.7)	C(36)–C(31)–P	116.6(1.0)
C(11)–C(16)–C(15)	118.4(1.4)	C(36)–C(31)–C(32)	121.2(1.2)
C(12)–C(11)–C(16)	121.0(1.4)	C(31)–C(32)–C(33)	119.5(1.4)
C(2)–C(11)–C(12)	117.7(1.3)	C(34)–C(33)–C(32)	119.2(1.4)
C(2)–C(11)–C(16)	121.2(1.3)	C(33)–C(34)–C(35)	121.5(1.4)
C(4)–C(3)–O(1)	109.6(1.1)	C(34)–C(35)–C(36)	120.3(1.4)
C(5)–C(4)–C(3)	107.8(1.3)	C(31)–C(36)–C(35)	118.4(1.4)
C(6)–C(4)–C(3)	114.2(1.4)		

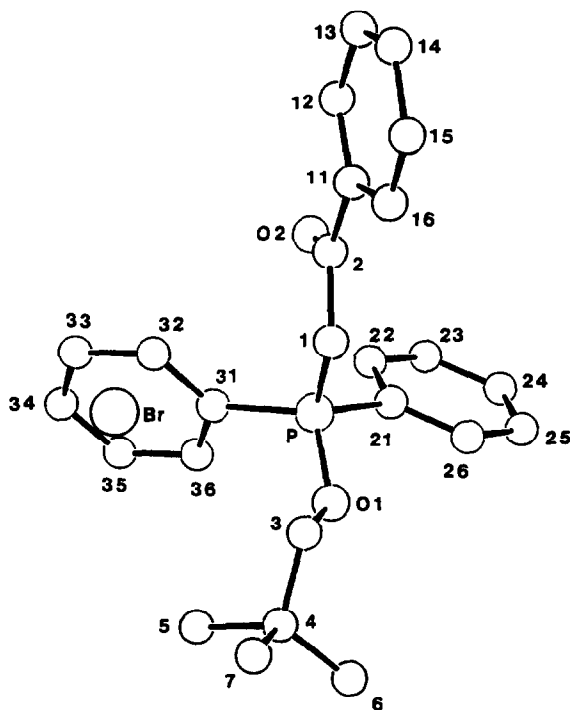


Fig. 1. Structure of neopentyloxy(phenacyl)diphenylphosphonium bromide (IV).

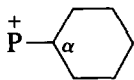


Fig. 2. Possible weak inductive electron release to positive phosphorus.

the Pauling electronegativity [12] of the substituent group. For thirteen selected phosphines containing one or more phenyl–phosphorus bonds, or their coordination complexes, the mean bond angle at C_α ($118.5(1)^\circ$) was taken to correspond to an electronegativity for phosphorus on the Pauling scale of 2.1. On the basis of this correlation, the larger average bond angle at C_α for seven typical phenylphosphonium compounds ($119.8(1)^\circ$) indicated an electronegativity for the positively charged phosphorus in these compounds of 2.5 [11], which is similar to that for carbon [12]. It is of interest that the corresponding bond angles in the ketophosphonium bromide (IV) (121.0° , 121.2°) and in the previously reported [3] quasiphosphonium salts (II) (120.6° , 120.6°) and (III) (120.7°) are all considerably larger, being in the region of 121° . Although the differences from the mean value of $119.8(1)^\circ$ observed for typical phenylphosphonium compounds [11] are of low significance in the context of the estimated standard deviations that are involved, it should be noted that the variations are all systematically in the same direction. Such an increase above 120° would be expected as a result of increased electronegativity of phosphorus in the quasiphosphonium salts (II, III, IV) because of the presence of electron-attracting alkoxy and/or β -keto substituents. From the average of the five C_α bond angles in these compounds (120.8°), the Pauling electronegativity for phosphorus is estimated [11] as 2.8, which is higher than that for carbon.

The phosphorus–oxygen bond length in the ketophosphonium bromide (IV) ($1.573(8) \text{ \AA}$), as in other examples of alkoxyphosphonium salts [13], is significantly shorter than the calculated length for a single P–O bond (*ca.* 1.75 \AA), indicating appreciable double bond character and delocalisation of electron density from oxygen to the *d*-orbitals of the positively charged phosphorus atom. However, the increase in reactivity of quasiphosphonium salts which accompanies an increase in the number of oxygen ligands [2], suggests that reactivity is more dependent on the inductive effects of the attached alkoxy groups than on mesomeric interaction of oxygen with phosphorus.

The possible rearrangement of β -ketophosphonium (Michaelis-Arbuzov) intermediates to vinyloxyphosphonium (Perkow) intermediates via a four-membered cyclic intermediate (IX) (Scheme 3) has been suggested [14] but we have found no evidence to support such a process in the systems that we have studied [4,13]. The estimated minimum interatomic distance (2.88 \AA) between the carbonyl oxygen atom and the phosphorus atom in the β -ketophosphonium bromide (IV), assuming coplanarity of the relevant groups, shows that rearrangement as proposed [14] would involve considerable strain within the species. Although a similar cyclic intermediate is thought to be involved in the course of the Wittig reaction [15], the latter process may be assisted by the formal negative charge on oxygen in the initially formed betaine. The Arbuzov intermediate also has an alternative and more favourable reaction route via dealkylation to give the ketophosphonate (Arbuzov product).

Experimental

Neopentyloxy(phenacyl)diphenylphosphonium bromide (**4**) was prepared as previously described [4] by treatment of a solution of α -bromoacetophenone in dry acetone with neopentyl diphenylphosphinite at 0°C. The crystals were washed with anhydrous ether and dried in a desiccator.

X-ray crystallographic measurements were carried out with a Philips PW1100 4-circle diffractometer with Mo- K_{α} radiation. The bromine atom was located from a Patterson synthesis and the remaining atoms from subsequent difference-Fourier syntheses. In the full matrix least squares refinements of the atomic parameters, 1529 unique reflections [$I > 3\sigma(I)$] were used and the hydrogen atoms were included in calculated positions riding on the appropriate carbon atoms. In the final stages, anisotropic thermal parameters were assigned to all non-hydrogen atoms and refinements converged at R 0.0601 (R_w 0.0608).

Crystal data: (**3**) $C_{25}H_{28}BrO_2P$, monoclinic, space group $P2_1/n$, $a = 17.806(4)$, $b = 11.349(3)$, $c = 12.023(3)$ Å, $\beta = 90.46(2)^\circ$, $V = 2429.53$ Å³, $Z = 4$, $F(000) = 976$, $\mu = 17.11$ cm⁻¹. Principal bond lengths and bond angles are shown in Tables

Table 3

Fractional atomic coordinates for non-hydrogen atoms in neopentyloxy(phenacyl)diphenylphosphonium bromide (**IV**)

Atom	x	y	z
Br	0.2355(1)	0.2651(1)	0.3747(1)
P	0.2038(2)	0.1107(3)	0.0287(3)
C(1)	0.2911(6)	0.0844(10)	0.1007(9)
C(2)	0.3575(7)	0.1354(10)	0.0417(11)
O(2)	0.3485(5)	0.1980(8)	-0.0395(8)
C(11)	0.4385(8)	0.1089(12)	0.0890(11)
C(12)	0.4945(9)	0.1704(13)	0.0468(12)
C(13)	0.5670(9)	0.1477(17)	0.0871(17)
C(14)	0.5769(10)	0.0658(21)	0.1667(17)
C(15)	0.5148(11)	0.0039(15)	0.2097(13)
C(16)	0.4450(8)	0.0218(13)	0.1693(12)
O(1)	0.1412(4)	0.0367(7)	0.0884(6)
C(3)	0.1385(7)	0.0234(11)	0.2089(9)
C(21)	0.2018(6)	0.0499(10)	-0.1089(9)
C(22)	0.2094(7)	0.1258(12)	-0.2026(11)
C(23)	0.2059(7)	0.0796(14)	-0.3084(12)
C(24)	0.1954(8)	-0.0387(15)	-0.3216(12)
C(25)	0.1866(7)	-0.1123(13)	-0.2302(13)
C(26)	0.1904(7)	-0.0692(11)	-0.1222(10)
C(4)	0.0588(9)	0.0153(15)	0.2450(12)
C(5)	0.0207(9)	0.1382(20)	0.2227(18)
C(6)	0.0154(10)	-0.0792(20)	0.1898(15)
C(7)	0.0609(9)	-0.0025(17)	0.3726(13)
C(31)	0.1782(7)	0.2629(11)	0.0290(9)
C(32)	0.2207(8)	0.3467(12)	0.0824(10)
C(33)	0.1972(9)	0.4637(12)	0.0814(11)
C(34)	0.1308(11)	0.4922(13)	0.0297(12)
C(35)	0.0885(9)	0.4093(16)	-0.0229(12)
C(36)	0.1116(9)	0.2922(13)	-0.0244(12)

1 and 2. Fractional atomic coordinates for all non-hydrogen atoms are given in Table 3.

Atomic coordinates, a complete list of bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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