Ligand coupling and neighbouring-group effects in the alkaline hydrolysis of arylphosphonium salts: new stable tetraarylphosphonium benzimidazolate betaines

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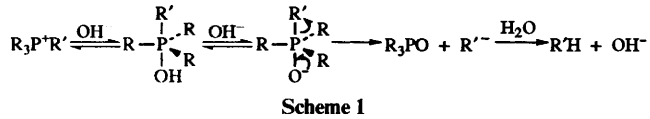
The reactions with aqueous alkali of a series of 2-(*o*- and *p*-triphenylphosphoniophenyl)-benzimidazoles and -benzothiazoles have been investigated. Evidence of a neighbouring-group hypervalent interaction between the pyridine-like nitrogen of the benzazole and the 2-(*o*-triphenylphosphoniophenyl) substituent is presented from the results of a study of the course of alkaline hydrolysis of the salts and a comparison with that of the related 2-(*p*-triphenylphosphoniophenyl) systems in which such hypervalent interactions are not possible. Hydrolysis of the latter proceeds abnormally, in some cases, with the formation of biaryl coupling products in addition to the expected hydrolysis products. Similar results have been obtained from a comparison of the products of hydrolysis of *o*- and *p*-(benzoylphenyl)triphenylphosphonium salts, hydrolysis of the latter also giving rise to a biaryl coupling product, 4-benzoylbiphenyl. Traces of 4-cyanobiphenyl were also detected in the products of hydrolysis of *p*-cyanophenyl(triphenyl)phosphonium bromide. The kinetics of hydrolysis of the above range of salts has also been investigated in an ethanol–water solvent system (80:20, v/v). Whereas the benzoylphenylphosphonium salts undergo hydrolysis according to the usual third-order rate law, both series of salts derived from 1-methyl-2-phenylbenzimidazole and 2-phenylbenzothiazole are hydrolysed according to a second-order rate law, perhaps attributable to the interaction of the azole nitrogen with the solvent. Treatment of both 2-(*o*- and *p*-triphenylphosphoniophenyl)benzimidazoles with 1 equivalent of aqueous alkali results in the formation of the related tetraarylphosphonium benzimidazolate betaines. The *ortho*-isomer exhibits a marked shielding of the ^{31}P nucleus (δ_P −14.7) compared with the *para*-isomer (δ_P 22.6), consistent with a hypervalent interaction of the phosphonium centre with the benzimidazolate moiety.

Introduction

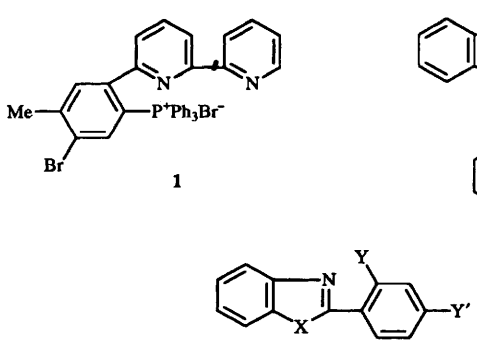
The mechanism of alkaline cleavage of phosphonium salts has attracted considerable attention, and the main features are well-known.[1] The reaction proceeds *via* the initial formation of a trigonal bipyramidal hydroxyphosphorane (in which the hydroxo and the most apicophilic group originally bound to phosphorus occupy apical positions[2]) which subsequently undergoes deprotonation to form the related phosphorane oxide anion without undergoing a Berry pseudorotation.[3] Rate-determining collapse of the latter then occurs with expulsion of the apical group as a forming carbanion[4] (which is subsequently protonated to give a hydrocarbon), and the formation of a phosphine oxide (Scheme 1). Consistent with this mechanism, a third-order rate law is usually observed.[5–8]



Scheme 1

In the course of studies of the operation of a kinetic template effect in the metal ion-catalysed formation of arylphosphonium salts,[9–13] we isolated a range of phosphonium salts in which a donor group is present in the *ortho* position of one of the aryl groups attached to phosphorus, *e.g.*, **1** and **2**.

X-Ray studies of such salts[11,12] revealed that there is a significant interaction between the sp^2-hybridised nitrogen of the nearby heterocyclic ring and the phosphonium centre, resulting in a considerable distortion of the tetrahedral geometry at phosphorus, and also in a phosphorus–nitrogen bond length which is well within the sum of the Van der Waal's



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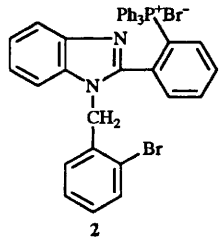
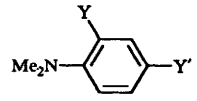


2

3 Y = $R^1_2R^2P^+Br^-$, Y′ = H
4 Y = H, Y′ = $R^1_2R^2P^+Br^-$

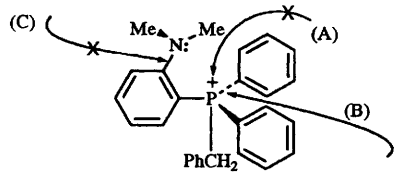
radii. We were interested in exploring the chemical consequences of such a neighbouring group interaction, and now report a study of the alkaline hydrolysis of a series of arylphosphonium salts **3** in which these effects might be apparent, and, for comparison, the related reactions of the electronically similar salts **4** in which such intramolecular interactions are not possible.

Neighbouring group effects in organophosphorus chemistry have been briefly noted in a wide range of compound types, including phosphorus esters,[14–18] phosphatranes,[19] fluorophosphoranes,[20] phosphines,[21] halogenophosphines[22] and phosphonium salts.[23,24] In the last-mentioned area, the work of McEwen *et al.*[23,24] on the course of the alkaline hydrolysis of *o*- and *p*-dimethylaminophenylphosphonium salts is especially pertinent to the present discussion. Whereas hydrolysis of the salt **5** proceeds with the expected loss of the benzyl group, that



5 Y = H, Y′ = $PhCH_2(Ph)_2P^+Br^-$
6 Y = $PhCH_2(Ph)_2P^+Br^-$, Y′ = H

of the isomeric salt **6** proceeds with cleavage of the *o*-dimethylaminophenyl group with the predominant formation of *N*,*N*-dimethylaniline and benzyldiphenylphosphine oxide. McEwen *et al.* have argued that a neighbouring group interaction of the sp^3-hybridised nitrogen lone pair with the phosphonium centre imposes constraints on the approach of the hydroxide ion, such that only the reaction coordinate (B) (Scheme 2), involving attack opposite the *o*-dimethylamino-



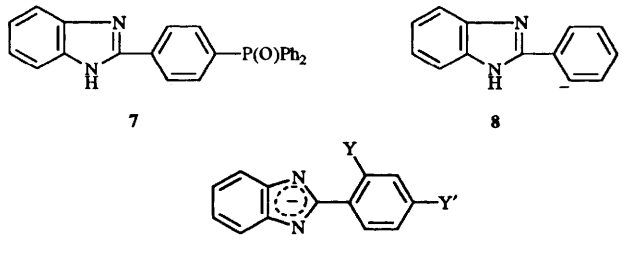
Scheme 2

phenyl group, is likely to be successful. Attack opposite the benzyl group (A), or opposite *either* of the phenyl groups (C), is likely to be inhibited as a result of the N→P^+ interaction.

The phosphonium salts under discussion here offer a similar potential interaction to those described by McEwen *et al.*, except that the nitrogen lone pair is now of the sp^2-type associated with the heterocyclic nitrogen atom.

Results and discussion

Comparison of the products of alkaline hydrolysis of the salts **3** and **4** (X = NH, R^1 = Ph, R^2 = $PhCH_2$) lends support to the suggestion of a chemically significant neighbouring group effect between nitrogen and the phosphonium centre. Whereas hydrolysis of salt **4** (X = NH, R^1 = Ph, R^2 = $PhCH_2$) in the presence of an excess of aqueous alkali in ethanol proceeded with the expected loss of the benzyl group to form toluene and the phosphine oxide **7**, that of the related salt **3** (X = NH, R^1 = Ph, R^2 = $PhCH_2$) resulted predominantly in the formation of 2-phenylbenzimidazole and benzyl(diphenyl)-phosphine oxide. In a similar manner, hydrolysis of the related salt **4** (X = NH, R^1 = R^2 = Ph) also gave the phosphine oxide **7** together with benzene, as the predominant products, whereas that of the salt **3** (X = NH, R^1 = R^2 = Ph) gave triphenylphosphine oxide and 2-phenylbenzimidazole. The major differences observed in the course of hydrolysis of the above series of salts can be accounted for, as argued by McEwen *et al.*, in terms of inhibition of approach of the hydroxide nucleophile opposite the anticipated leaving group as a result of the presumed hypervalent interaction between the pyridine-like nitrogen and the phosphonium centre; an alternative pathway is, therefore, followed. However, the predominant formation of 2-phenylbenzimidazole in the hydrolysis of the salts **3** (X = NH) might also be attributable to some exceptional stabilisation of the related forming carbanion **8**. Nevertheless, in the specific instance of the above reactions, we do not believe that the latter is significant, for the following reason. In a preliminary study of the kinetics of hydrolysis of the above salts **3** and **4** (X = NH, R^1 = R^2 = Ph) (see later) using conductivity techniques, we found that treatment of these salts with 1 equiv. of hydroxide ion resulted in an immediate and significant reduction in the conductivity

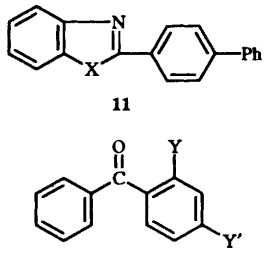


7 8

9 Y = Ph_3P^+, Y′ = H
10 Y = H, Y′ = Ph_3P^+

of the system with the formation of the stable betaines **9** and **10**, which were subsequently isolated on a preparative scale and fully characterised. On treatment with an excess of alkali, under reflux conditions, these betaines underwent gradual decomposition to form the phosphine oxide and related hydrocarbon products observed earlier from the parent phosphonium salts. The presence of the negatively charged benzimidazolate moiety would be expected to disfavour anionic cleavage of the phenyl group bearing this substituent, yet this is the favoured course for the salts **3** (X = NH). The formation of the phosphine oxide **7** from the salt **4** (X = NH, R^1 = R^2 = Ph) is also consistent with this argument.

The products of hydrolysis of the salts **3** and **4** (X = NMe or S, R^1 = R^2 = Ph) also lend support to the neighbouring group effect concept, although as will become apparent, the results are not as clear cut as the above. Hydrolysis of the salts **3** (X = NMe or S; R^1 = R^2 = Ph) proceeded, as expected, to give the appropriate 2-phenylbenzazole and triphenylphosphine oxide. However, the course of hydrolysis of the related salts **4** (X = S or NMe, R^1 = R^2 = Ph) proved unexpectedly complex. The principal products in each case were again the 2-phenylbenzazole and triphenylphosphine oxide, together with varying amounts of the biaryl-coupling products **11** (X = S or NMe),



11

12 Y = H, Y′ = $Ph_3P^+Br^-$
13 Y = $Ph_3P^+Br^-$, Y′ = H

and various largely unidentified phosphorus-containing products. In the case of the *N*-methylbenzimidazole system, only a trace of the biaryl coupling product was formed (< 5%), whereas with the benzothiazole system, the biaryl was isolated in *ca.* 30% yield. The contrast between the course of hydrolysis of the salts **4** (X = NH, R^1 = R^2 = Ph) and **4** (X = NMe or S, R^1 = R^2 = Ph), and the formation of the biaryl coupling products, are worthy of comment. Clearly, in the case of the salts **4** (X = NMe or S, R^1 = R^2 = Ph), betaine intermediates are not possible, and it would seem that the course of hydrolysis is governed by the electronic properties of the 2-benzazole substituent on the benzene ring that is cleaved from phosphorus in giving rise to the appropriate 2-phenylbenzazole and triphenylphosphine oxide. In recent years, efforts have been made to quantify the electronic effects of heterocyclic groups as substituents in other systems.[25–27] A view has emerged which indicates that the 2-benzazole systems are significantly electron-withdrawing in situations in which they are not involved in

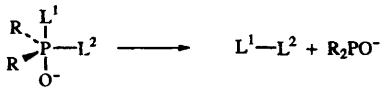
direct resonance interactions with the reaction site, having σ_I values comparable to that of the acetyl group.[25]

To explore further this indication that a crucial factor in the formation of biaryl coupling products is the presence of an electron-withdrawing group in the *para*-position of the benzene ring attached to phosphorus, we studied the course of hydrolysis of the salt **12** bearing a *p*-benzoyl substituent, and, for comparison, that of the related *ortho*-isomer **13**.

In the hydrolysis of **12**, the biaryl coupling product, 4-phenylbenzophenone, was formed in significant quantities (*ca.* 30%), together with benzophenone and triphenylphosphine oxide, and other minor, as yet unidentified, products. In contrast, the hydrolysis of the salt **13** gave rise solely to benzophenone and triphenylphosphine oxide, again possibly indicating the involvement of a hypervalent interaction between the carbonyl oxygen and the phosphonium centre.

A ^{31}P NMR study of the hydrolysis of the salts **4** (X = S, $R^1 = R^2$ = Ph) and **12** revealed the apparent complexity of these reactions, each system displaying the formation of a range of phosphorus species, including diphenylphosphine oxide which appeared as a broad signal at δ 26 in aqueous MeOH–MeOD/OH^-. In contrast, a similar study of the hydrolysis of **13** showed a very simple spectrum, with triphenylphosphine oxide being the only species observable.

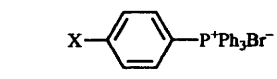
Although unprecedented in the aqueous alkaline hydrolysis of simple arylphosphonium salts, ligand coupling has been observed to a very limited extent in other reactions of phosphonium salts and phosphine oxides. Thus, for example, 2,2′-bipyridyls have been isolated from the aqueous acid-promoted decomposition of benzyltris(2-pyridyl)phosphonium salts and related aryl bis(2-pyridyl)phosphine oxides.[28] Similar coupling reactions to form 2,2′-bipyridyls occur on treatment of tris(2-pyridyl)phosphine oxide with Grignard reagents[29] or sodium ethoxide.[30] These reactions have all been assumed to involve intramolecular decomposition of an oxyphosphorane intermediate, in which apical-equatorial ligand coupling occurs, with the concomitant formation of a 'trivalent' phosphorus species (Scheme 3). Ligand coupling has also been observed in the decomposition of pentaorganophosphoranes.[31,32]



Scheme 3

Our observation of the formation of diphenylphosphine oxide in the ^{31}P NMR study is consistent with the above scheme. However, in order to explore the possibility of the involvement of a free-radical pathway leading to the biaryl coupling products, the hydrolysis of the salt **4** (X = S, R^1 = R^2 = Ph) was conducted in the presence of an equimolar amount of the free radical trap TEMPO. The overall course of the reaction, and the yield of the biaryl coupling product **11** (X = S) were unchanged, again consistent with the above intramolecular scheme.

In the reactions reported in the present study, it is clear that the nature of the remote substituent in the aryl ring attached to phosphorus is of considerable significance in influencing the course of decomposition of oxyphosphorane intermediates. In order to extend the study of substituent effects, we have sought evidence of biaryl formation in the hydrolysis of other tetraarylphosphonium salts **14** bearing a *para*-substituent in one of the rings. For a series of such salts, in which the *para*-substituent was cyano, trifluoromethyl or phenyl, hydrolysis occurred with predominant formation of triphenylphosphine oxide and the related substituted arene; only in the case of the salt **14** (X = CN) was a trace of a biaryl coupling product



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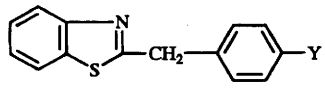


15 Y = $Ph_3P^+Br^-$
16 Y = $P(O)Ph_2$

(4-cyanobiphenyl), detected by GC-MS techniques. In the salt **15**, the electronic effect of the benzothiazolyl group is insulated from the phosphonium centre, and hydrolysis did not lead to the formation of biaryl coupling product, giving instead a mixture of triphenylphosphine oxide, 2-benzylbenzothiazole and the phosphine oxide **16**. A GC-MS study of this reaction mixture also revealed the presence of benzothiazole as a significant product, the origin of which is uncertain.

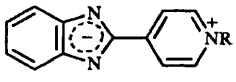
We have also carried out a preliminary study of the kinetics of hydrolysis of some of the above systems. The rates of hydrolysis of the salts **3** and **4** (X = NH, NMe or S, $R^1 = R^2$ = Ph) and **12** and **13** have been followed by a conductimetric technique at 40 °C in aqueous ethanol (20:80, v/v) as solvent, and the data compared with that for the hydrolysis of tetraphenylphosphonium bromide under the same conditions. Both salts **12** and **13** underwent hydrolysis *ca.* 10^4 times faster than tetraphenylphosphonium bromide [Table 1(a)], the expected third order rate law being observed, suggesting the rate-determining collapse of a phosphorane oxide intermediate. The *para*-isomer **12** was hydrolysed almost twice as fast as the *ortho*-isomer **13**, in which the possibility of a neighbouring group interaction has been raised. The much greater rate of hydrolysis of salts **12** and **13** compared to tetraphenylphosphonium bromide doubtless reflects the inductive effect of the benzoyl substituent which will exert its influence in each stage of the multistep mechanism. However, the rate data for hydrolysis of the salts **3** and **4** were rather surprising [Table 1(b)]. As previously indicated, treatment of the salts **3** and **4** (X = NH, $R^1 = R^2$ = Ph) with equimolar quantities of hydroxide ion led to the rapid formation of the stable betaines **9** and **10** which did not react further under these conditions. Hydrolysis of the related salts, **3** and **4** (X = NMe or S, $R^1 = R^2$ = Ph) proceeded quite rapidly (by comparison of half-life data) compared to tetraphenylphosphonium bromide, but consistently exhibited a *second order* rate law, which was also confirmed by a titrimetric approach. Attempts to evaluate the data in terms of the usual third-order rate law failed: Second-order kinetics have been observed only rarely in phosphonium salt hydrolysis, usually when a very stable leaving group is present, *e.g.* *p*-nitrobenzyl[33,34] or an anionic leaving group arising from the opening of a cyclic phosphonium salt in which considerable ring-strain is present.[35] It is of interest that McEwen *et al.*[23,24] have reported that the salts **5** and **6**, which also possess basic functionalities, undergo hydrolysis in accordance with the usual third-order law. The origin of the observed second-order rate law in the case of the salts **3** and **4** is not apparent although it may possibly be a consequence of an interaction between the azole nitrogen and the solvent producing a small equilibrium concentration of OH^-. Nor is it possible to rationalise easily the relative rate data for the respective *ortho* and *para* isomers of the salts **3** and **4**. In the case of the benzothiazolyl systems, the *ortho*-isomer undergoes hydrolysis at about half the rate of the corresponding *para*-isomer, this ratio being comparable to that observed for salts **12** and **13**. However, for the *N*-methylbenzimidazolyl system, the *ortho*-isomer undergoes hydrolysis some seven times faster than the related *para*-isomer. This may reflect a steric effect by the *N*-methyl group in influencing one or more of the

Table 1 Rate data for alkaline hydrolysis of arylphosphonium salts, in ethanol–water (80:20, v/v) at 40 °C.

Salt Ar $\overset{+}{P}Ph_3$ Br^-	Rate constant	Relative rate
(a)	k_{obs}/dm^4 mol^{-2} min^{-1}	
Ar = Ph	3.9	1
Ar = *o*-PhCOC$_6$H$_4$	2.7 × 10^4	7 × 10^3
Ar = *p*-PhCOC$_6$H$_4$	4.8 × 10^4	12 × 10^3
(b)	k_{obs}/dm^3 mol^{-1} min^{-1}	
Ar = *o*-benzothiazol-2-ylC$_6$H$_4$	6.6	1
Ar = *p*-benzothiazol-2-ylC$_6$H$_4$	14.1	2.1
Ar = *o*-(1-methylbenzimidazol-2-yl)C$_6$H$_4$	41.0	6.2
Ar = *p*-(1-methylbenzimidazol-2-yl)C$_6$H$_4$	5.7	0.9

steps in the mechanism of the hydrolysis of the *ortho*-isomer **3** (X = NMe, R^1 = R^2 = Ph). It is of interest that in the case of the salts **5** and **6** the *ortho*-isomer **6** was hydrolysed *ca.* 10^3 times faster than the *para*-isomer **5**.[23,24]

As mentioned above, treatment of the salts **3** and **4** (X = NH, R^1 = R^2 = Ph with an equimolar proportion of aqueous sodium hydroxide in ethanol gave the stable phosphonium betaines **9** and **10**. The former, **9**, was precipitated from the ethanolic solution of the parent phosphonium salt as a pale yellow solid on addition of the alkali, whereas **10** was precipitated as a yellow solid on further dilution of the reaction mixture with water. Both compounds gave a negative halide test on treatment with aqueous silver nitrate in aqueous ethanol acidified with dilute nitric acid, conditions under which the parent phosphonium salts readily gave a precipitate of silver bromide. Microanalytical data were consistent with the betaine formulation although both strongly retained molecules of polar solvents, *e.g.* acetonitrile or water on recrystallisation. This phenomenon has also been noted in a range of related pyridinium benzimidazolate betaines *e.g.* **17**, described by



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Alcalde *et al.*[36] These compounds are also readily formed on deprotonation of the related benzimidazolylpyridinium salts under aqueous conditions. Thus, the triphenylphosphoniophenyl and methylpyridinium moieties seem equally able to increase the acidity of the NH bond of the benzimidazole system and to stabilise the related 'onium-benzimidazolate betaine structure. Deprotonation of conventional benzimidazoles usually requires a much stronger base, *e.g.* sodium hydride in DMF.

The ^{31}P NMR chemical shift of the *ortho*-phosphoniobetaine **9** (δ −14.7) in $CDCl_3$ is markedly different to that of its parent salt **3** (X = NH, R^1 = R^2 = Ph) (δ 25.3); treatment of the betaine with trifluoroacetic acid resulted in protonation, the ^{31}P signal moving to δ 22.8, identical with the signal observed on adding trifluoroacetic acid to a solution of the parent phosphonium salt in deuteriochloroform. The marked shift on forming the *ortho*-phosphonio betaine **9** was not observed in the case of the related *para*-betaine **10**, the ^{31}P chemical shift of which (δ 22.6) in $CDCl_3$ being little different to that of the parent salt **4** (X = NH, R^1 = R^2 = Ph) (δ 23.0). The markedly high-field shift of the ^{31}P signal for the *ortho*-betaine **9** indicates an interaction between the benzimidazolate system and the phosphonium centre, tending towards a phosphorane-like species, again a significant hypervalent neighbouring-group phenomenon. This is clearly impossible in the related *para*-betaine **10**. Treatment of both betaines with iodomethane in acetonitrile resulted in conversion into the related *N*-methylbenzimidazolylphenyl-phosphonium cations, as present in the salts **3** and **4** (X = NMe, R^1 = R^2 = Ph). The chemistry of the above phosphonio-benzimidazolate betaines is currently receiving further study.

Experimental

^{31}P, ^{13}C and ^{1}H NMR studies were carried out using a Brüker AC 250 FTNMR spectrometer; *J* values are in Hz. Mass spectra were recorded on a VG Micromass 7070F instrument. Accurate mass determinations were carried out using perfluorokerosene as the internal standard, with a resolution of 5000. GC-MS studies were conducted using a Trio-1 instrument equipped with SE30 or SE54 columns.

Arylphosphonium salts were prepared by the established general procedure[37] from the related bromoarene and tertiary phosphine in the presence of nickel(II) bromide in the molten state at 150–200 °C or, alternatively, using benzonitrile as the solvent. The following new salts were isolated, and characterised.

***o*-(Benzimidazol-2-yl)phenyl(triphenyl)phosphonium bromide 3 (X = NH, R^1 = R^2 = Ph).** Characterised as the corresponding *perchlorate*, mp > 300 °C (Found: C, 67.0; H, 4.3; N, 5.0. $C_{31}H_{24}N_2P{\cdot}ClO_4$ requires C, 67.1; H, 4.35; N, 5.05%). *Bromide* salt: $\delta_P(CDCl_3)$ 25.3; $\delta_H(CDCl_3)$ 13.8 (br s, NH, exchanges with D_2O), 9.3 (m, 1 ArH), 8.1 (t, 1 ArH), 7.8–7.1 (m, 18 ArH), 7.05 (t, 1 ArH), 6.9 (t, 1 ArH) and 6.75 (d, 1 ArH).

***p*-(Benzimidazol-2-yl)phenyl(triphenyl)phosphonium bromide 4 (X = NH, R^1 = R^2 = Ph).** Characterised as the corresponding *perchlorate*, mp > 300 °C (Found: C, 66.7; H, 4.35; N, 5.05. $C_{31}H_{24}N_2P{\cdot}ClO_4$ requires C, 67.1; H, 4.35; N, 5.05%). *Bromide* salt: $\delta_P(CDCl_3)$ 23.0; $\delta_H(CDCl_3)$ 9.0 (m, 2 ArH) and 7.9–7.1 (m, 23 ArH + NH; evidence of exchange with D_2O).

***o*-(Benzimidazol-2-yl)phenyl(benzyl)diphenylphosphonium bromide 3 (X = NH, R^1 = Ph, R^2 = PhCH$_2$).** Characterised as the corresponding *tetraphenylborate*, mp > 200 °C (decomp.) (ex. aq. EtOH) (Found: C, 84.55; H, 5.8; N 3.5. $C_{56}H_{46}BN_2P$ requires C, 85.25; H, 5.90; N, 3.55%). *Bromide* salt: $\delta_H(CDCl_3)$ 13.7 (br s, NH), 8.3–6.9 (m, 23 ArH), 5.15 (d, 2 H, J_{PCH} 15.1); $\delta_P(CDCl_3)$ 24.7.

***p*-(Benzimidazol-2-yl)phenyl(benzyl)diphenylphosphonium bromide 4 (X = NH, R^1 = Ph, R^2 = PhCH$_2$).** Characterised as the corresponding *perchlorate*, mp > 150 °C (decomp.) (Found: C, 67.15; H, 4.7; N, 5.3. $C_{32}H_{26}N_2P{\cdot}ClO_4$ requires C, 67.55; H, 4.60; N, 4.90%). *Bromide* salt: $\delta_H(CDCl_3)$ 9.0–6.6 (m, 23 ArH) and 4.8 (d, 2 H, J_{PCH} 14.3); $\delta_P(CDCl_3)$ 22.3.

***o*-(1-Methylbenzimidazol-2-yl)phenyl(triphenyl)phosphonium bromide 3 (X = NMe, R^1 = R^2 = Ph).** Characterised as the corresponding *perchlorate*, mp > 300 °C (decomp.) (Found: C: 67.8; H, 4.7; N, 4.9. $C_{32}H_{26}N_2P{\cdot}ClO_4$ requires C, 67.55; H, 4.60; N, 4.90%). *Bromide* salt: $\delta_H(CDCl_3)$ 8.3–6.7 (m, 23 ArH) and 3.7 (s, 3 H); $\delta_P(CDCl_3)$ 24.5.

***p*-(1-Methylbenzimidazol-2-yl)phenyl(triphenyl)phosphonium bromide 4 (X = NMe, R^1 = R^2 = Ph).** Characterised as the corresponding *perchlorate*, mp > 300 °C (decomp.) (Found: C, 67.65; H, 4.55; N, 4.9. $C_{32}H_{26}N_2P{\cdot}ClO_4$ requires C, 67.55; H, 4.60; N, 4.90%). *Bromide* salt: $\delta_H(CDCl_3)$ 8.6–6.9 (m, 23 ArH) and 4.1 (s, 3 H); $\delta_P(CDCl_3)$ 23.1.

***o*-(Benzothiazol-2-yl)phenyl(triphenyl)phosphonium bromide 3 (X = S, R¹ = R² = Ph).** Characterised as the corresponding *hexafluorophosphate*, mp 270 °C (decomp.) (from water) (Found: C, 60.15; H, 3.75; N, 2.3. $C_{31}H_{23}NSP{\cdot}PF_6$ requires C, 60.30; H, 3.75; N, 2.25%). *Bromide* salt: $\delta_P(CDCl_3)$ 27.6; $\delta_H(CDCl_3)$ 8.35 (m, 2 ArH), 8.20 (m, 2 ArH), 8.0–7.5 (m, 15 ArH), 7.4 (m, 2 ArH) and 7.25 (m, 2 ArH).

***p*-(Benzothiazol-2-yl)phenyl(triphenyl)phosphonium bromide 4 (X = S, R¹ = R² = Ph).** Characterised as the related *hexafluorophosphate*, mp >260 °C (decomp.) (from water) (Found: C, 60.15; H, 3.75; N, 2.3. $C_{31}H_{23}NSP{\cdot}PF_6$ requires C, 60.30; H, 3.75; N, 2.25%). *Bromide* salt: $\delta_P(CDCl_3)$ 23.0; $\delta_H(CDCl_3)$ 8.45 (m, 2 ArH) and 8.2–7.3 (m, 21 ArH).

***p*-(Benzothiazol-2-ylmethyl)phenyl(triphenyl)phosphonium bromide 15.** Characterised as the corresponding *perchlorate*, mp 226–228 °C (Found: C, 65.6; H, 4.3; N, 2.4. $C_{32}H_{25}NSP{\cdot}ClO_4$ requires C, 65.65; H, 4.30; N, 2.40%). *Bromide* salt: $\delta_H(CDCl_3)$ 8.2–7.2 (m, 23 ArH) and 4.6 (s, CH_2); $\delta_P(CDCl_3)$ 22.4.

***o*-(Benzoyl)phenyl(triphenyl)phosphonium bromide 13.** Characterised as the related *hexafluorophosphate*, mp >250 °C (decomp.) (Found: C 62.95; H, 4.05. $C_{31}H_{24}OP{\cdot}PF_6$ requires C, 63.25; H, 4.10%). *Bromide* salt: ν_{max}/cm^{-1} 1630 (CO); $\delta_P(CDCl_3)$ 26.5; $\delta_H(CDCl_3)$ 8.2–7.5 (m, 21 ArH) and 7.4 (m, 2 ArH); $\delta_C(CDCl_3)$ 196 (CO).

***p*-(Benzoyl)phenyl(triphenyl)phosphonium bromide 12.** Characterised as the corresponding *perchlorate*, mp 184–185 °C (from water) (Found: C, 68.55; H, 4.45. $C_{31}H_{24}OP{\cdot}ClO_4$ requires C, 68.60; H, 4.45%). *Bromide* salt: ν_{max}/cm^{-1} 1642 (CO); $\delta_P(CDCl_3)$ 22.8; $\delta_H(CDCl_3)$ 8.2–7.4 (m, ArH); $\delta_C(CDCl_3)$ 197 (CO).

Alkaline hydrolyses

These were carried out under reflux on the phosphonium salt (10^{-3} mol) in ethanol–water (70:30; 5 cm^3) in the presence of aqueous sodium hydroxide (5 × 10^{-3} mol). Reaction mixtures were analysed initially by GC-MS, prior to isolation of the products, by pouring the reaction mixture into water, extracting the products (CH_2Cl_2) and subjecting them to preparative TLC separation (Kieselgel). The principal products of the various reactions were as follows.

From the bromide 3 (X = NH, R¹ = Ph, R² = PhCH₂). This gave 2-phenylbenzimidazole and benzyldiphenylphosphine oxide, identical with authentic materials.

From the bromide 4 (X = NH, R¹ = Ph, R² = PhCH₂). This gave toluene and 2-(4-*diphenylphosphinoylphenyl*)-1H-*benzimidazole* **7**, mp 278 °C (ex benzene–petroleum) (Found: C, 76.05; H, 4.85; N; 6.9. $C_{25}H_{19}N_2OP$ requires C, 76.10; H, 4.85; N, 7.10%); *m/z* 394 (M^+, 100%); $\delta_H(CDCl_3)$ 13.3 (br s, NH; exchanges with D_2O); 8.3 (m, 2 ArH), 8.0–7.4 (m, 14 ArH) and 7.25 (m, 2 ArH); $\delta_P(CDCl_3)$ 30.4.

From the bromide 3 (X = NH, R¹ = R² = Ph). This gave 2-phenylbenzimidazole and triphenylphosphine oxide, identical with authentic materials. Treatment of the above salt (10^{-3} mol) dissolved in ethanol with aqueous sodium hydroxide (1 mol dm^{-3}; 1 cm^3) gave 2-(*o*-triphenylphosphoniophenyl)benzimidazolate **9** as pale yellow crystals, mp 230–232 °C (from MeCN) (Found: C, 81.0; H 5.15; N 8.7. $C_{31}H_{23}N_2P{\cdot}CH_3CN$ requires C, 80.00; H, 5.30; N, 8.50%); $\delta_P(CDCl_3)$ −14.7 ppm; $\delta_H(CDCl_3)$ 8.7 (m, 1 ArH), 7.9–7.2 (m, 18 ArH), 7.05 (m, 2 ArH) and 6.8 (m, 2 ArH).

From the bromide 4 (X = NH, R¹ = R² = Ph). This gave benzene and 2-(4-diphenylphosphinoylphenyl-1*H*-benzimidazole **7**, mp 278 °C (ex benzene–petroleum), identical with the substance isolated from the hydrolysis of the salt **4** (X = NH, R^1 = Ph, R^2 = $PhCH_2$) described above.

Treatment of the salt **4** (X = NH, R^1 = R^2 = Ph) (10^{-3} mol) in ethanol with aqueous sodium hydroxide (1 mol dm^{-3}; 1 cm^3), followed by addition of water, gave 2-(*p*-triphenylphosphoniophenyl)benzimidazolate **10** as yellow crystals, mp 145–147 °C (from CH_2Cl_2–diethyl ether) (Found: C, 77.35; H, 5.25; N, 5.85. $C_{31}H_{23}N_2P{\cdot}H_2O$ requires C, 78.8; H, 5.35; N, 5.95%); $\delta_P(CDCl_3)$ 23.0; $\delta_H(CDCl_3)$ 8.9 (m, 2 ArH), 8.0–7.4 (m, 19 ArH) and 7.1 (m, 2 ArH).

From the bromide 3 (X = NMe, R¹ = R² = Ph). This gave 1-methyl-2-phenylbenzimidazole and triphenylphosphine oxide, identical with authentic materials.

From the bromide 4 (X = NMe, R¹ = R² = Ph). This gave principally 1-methyl-2-phenylbenzimidazole and triphenylphosphine oxide, together with a small amount (< 5%) of 1-methyl-2-(1,1′-biphenyl-4-yl)benzimidazole **11** (X = NMe).[38]

From the bromide 3 (X = S, R¹ = R² = Ph). This gave 2-phenylbenzothiazole and triphenylphosphine oxide, identical with authentic materials.

From the bromide 4 (X = S, R¹ = R² = Ph). This gave 2-(1,1′-biphenyl-4-yl)benzothiazole **11** (X = S)[39] (30%), 2-phenylbenzothiazole (54%), and triphenylphosphine oxide (60%). The same products were formed when the reaction was conducted in the presence of the free-radical trap TEMPO.

From the bromide 13. This gave benzophenone and triphenylphosphine oxide as the sole product.

From the bromide 12. This gave benzophenone (24%), 4-benzoylbiphenyl (28%) and triphenylphosphine oxide (26%).

From the bromide 15. This gave triphenylphosphine oxide (25%), 2-benzylthiazole (31%) and 2-(4-*diphenylphosphinoylbenzyl*)*benzothiazole* **16** (23%); $\delta_H(CDCl_3)$ 8.7–7.0 (m, 18 ArH) and 4.5 (s, 2 H) [Found: *m/z* 425.10 084 (M^+, 80%). $C_{26}H_{20}NOPS$ requires 425.10 031 (M^+)]. GC-MS analysis of the reaction mixture also indicated the presence of benzothiazole.

Kinetic studies

The hydrolyses were carried out at 40 °C in ethanol–water (80:20 v/v) at equal initial concentrations of phosphonium salt and sodium hydroxide in the range 0.25 × 10^{-2} to 1.0 × 10^{-2} mol dm^{-3}. The progress of the rcactions was followed by the conductimetric procedure described previously.[40] Rate data were evaluated by the method of integration, and the kinetic order confirmed by the 'half-life' method.

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