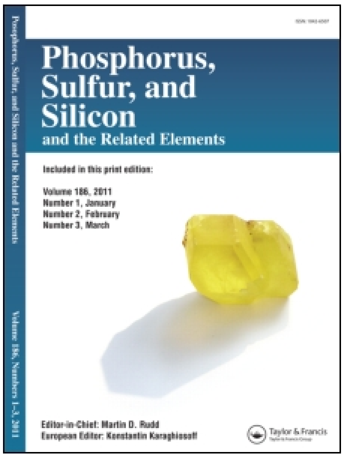

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LIGAND-COUPLING IN THE ALKALINE HYDROLYSIS OF ARYLPHOSPHONIUM SALTS

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Communication

LIGAND-COUPLING IN THE ALKALINE HYDROLYSIS OF ARYLPHOSPHONIUM SALTS

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Biaryls are formed via a ligand-coupling process in the alkaline hydrolysis of a series of tetraarylphosphonium salts which bear electron-withdrawing substituents in the *para* position of one of the aryl rings.

Key words: Biaryls; tetraarylphosphonium salt hydrolysis; hypervalent intermediates.

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 phosphoranoxide 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] the rate showing a second order dependence on the concentration of OH^-.

During the course of studies of the chemistry of a range of tetraarylphosphonium salts bearing heteroaryl groups as substituents in one of the aryl rings, we investigated the course of alkaline hydrolysis of the salts (1).

Whereas the hydrolysis of the salt (1, X = NH), on treatment with an excess of aqueous alkali in ethanol under reflux conditions, proceeded with loss of a phenyl group to form the phosphine oxide (2), that of the related N-methyl derivative (1, X = NMe) resulted in the predominant formation of triphenylphosphine oxide and 1-methyl-2-phenylbenzimidazole, together with a small amount (~5%) of the ligand-coupling product (3, X = NMe), in which coupling of a phenyl group and the heteroaryl-substituted phenyl group had occurred. In the case of the *p*-benzothiazolyl-substituted phosphonium salt (1, X = S), the biaryl coupling product (3, X = S) was formed in *ca* 30% yield, crystallizing from the solution as the reaction proceeded. In addition, triphenylphosphine oxide (60%) and 2-phenylbenzothiazole were also isolated from this reaction. The biaryl coupling product (3, X = 0) was also formed to a similar extent in the hydrolysis of the related *p*-

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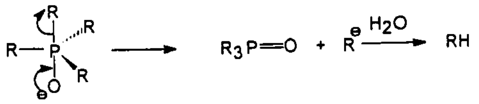
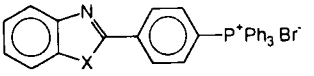
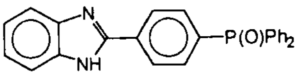
†Author to whom correspondence should be addressed.



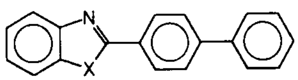
SCHEME 1



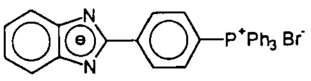
(1) (X = NH, NMe,O, or S)



(2)



(3)



(4)

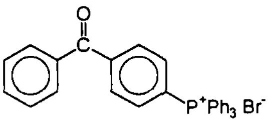
benzoxazolyl-phenylphosphonium salt (1, X = O), together with triphenylphosphine oxide and 2-phenylbenzoxazole.

In recent years, efforts have been made to quantify the electronic effects of heterocyclic systems as substituents in other systems.[9-11] 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.[9]

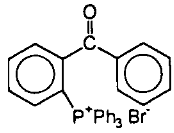
For comparison, we investigated the course of hydrolysis of *p*-dimethylaminophenyl (triphenyl)phosphonium bromide under identical conditions, observing the expected, selective cleavage of a phenyl group with the formation of *p*-dimethylaminophenyl (diphenyl)phosphine oxide, and no other significant products.

Of the above salts (1), only the *p*-(2-benzimidazolyl)phenyl phosphonium salt (1, X = NH) does not give rise to any ligand-coupling product on hydrolysis, and the contrast with the course of hydrolysis of the related 1-methylbenzimidazolyl system requires as explanation. In a preliminary study of the kinetics of the above reactions[12] using conductivity techniques, we found that treatment of the salt (1, X = NH) with one equivalent of hydroxide ion resulted in an immediate significant reduction in the conductivity of the system with the formation of the stable betaine (4), which was subsequently isolated on a preparative scale and fully characterized. On treatment with excess alkali, under reflux conditions, the betaine underwent gradual decomposition to form the phosphine oxide (2) isolated from the hydrolysis of the original salt. Clearly, the course of the reaction is influenced by the negatively charged benzimidazolate moiety, which would be expected to disfavor anionic cleavage of the phenyl group bearing this substituent.

To explore further the indication that a crucial factor in the formation of the above biaryl coupling products (3) is the presence of an electron-withdrawing group in the *p*-position of the benzene ring, we studied the course of hydrolysis of the salt (5) in which a *p*-benzoyl substituent is present. The biaryl coupling product, 4-phenylbenzophenone, was formed in significant quantities (*ca* 30%), together with triphenylphosphine oxide and benzophenone, and other minor, unidentified, products.



(5)



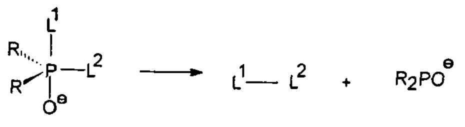
(6)

A ^{31}P nmr study of the hydrolysis of the salts (1, X = S), and (5) revealed the apparent complexity of these reactions, each system displaying the formation of a range of phosphorus species, including diphenylphosphine oxide, appearing as a broad signal at $\delta = 26.0$ ppm in aqueous MeOH-MeOD/OH$^-$. In contrast, a similar study of the hydrolysis of the salt (6), (which gave rise solely to triphenylphosphine oxide, and benzophenone), showed a very simple spectrum, with triphenylphosphine oxide being the only species observable.

The marked difference in the course of hydrolysis of salts (5) and (6) may be due to the operation of a coordinative interaction between the carbonyl oxygen and the phosphonium center which influences the approach of the hydroxide ion and the stability of the ensuing hypervalent intermediate. In a similar manner, the *o*-phosphoniophenyl analogues of the salts (1, X = NMe or S) also undergo a clean hydrolysis with formation of triphenylphosphine oxide and the respective 2-phenylbenzazole. These aspects are currently receiving further study.

Although unprecedented in the aqueous alkaline hydrolysis of phosphonium salts, ligand coupling has been observed to a very limited extent in other reactions of phosphonium salts and phosphine oxides. Thus, e.g., 2,2'-bipyridyls have been isolated from the aqueous acid-promoted decompositions of benzyltris(2-pyridyl)phosphonium salts and related bis(2-pyridyl)arylphosphine oxides.[13] Similar coupling reactions to form 2,2'-bipyridyls occur on treatment of tris(2-pyridyl)phosphine oxide with Grignard reagents[14] or sodium ethoxide.[15] 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 2). Ligand coupling has also been observed in the decomposition of pentaorganophosphoranes.[16,17]

In the reactions reported in the present study, it is clear that the nature of the remote substituent in the aryl rings is of considerable significance in influencing the course of decomposition of such oxyphosphorance intermediates.



SCHEME 2

EXPERIMENTAL

Arylphosphonium salts were prepared by the established general procedure[18] from the related bromoarene and triphenylphosphine in the presence of nickel(II) bromide. Alkaline hydrolysis reactions were carried out on a 10^{-3} mole scale in aqueous ethanol (1:2, 5 cm^3), in the presence of aqueous sodium hydroxide (5×10^{-3} mole). Products were separated by preparative TLC on silica, and characterized by ^1H and ^{31}P nmr and by microanalysis, or by comparison with authentic substances. ^{31}P nmr studies were carried out using a Brüker AC 250 FTNMR spectrometer.

Key compounds isolated were as follows: 2-(1,1'-biphenyl-4-yl)benzoxazole (3, X = O),[19] 2-(1,1'-biphenyl-4-yl)benzthiazole (3, X = S),[20] 1-methyl-2-(1,1'-biphenyl-4-yl)benzimidazole (3, X = NMe),[21] and *2-(4-diphenylphosphinylphenyl)-1H-benzimidazole* (2), mp 278° (ex benzene-petrol). Anal. calcd. for $C_{25}H_{19}N_2OP$: C, 76.11; H, 4.86; N, 7.10%. Found: C, 76.07; H, 4.83; N, 6.92%. MS (m/e): 394 (M^+).

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