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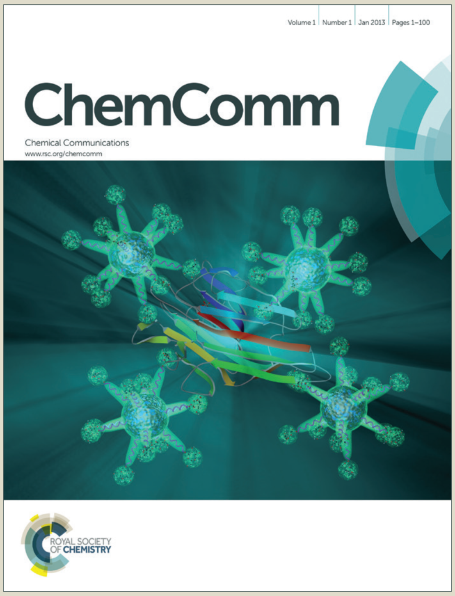

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ARTICLE TYPE

First Ever Observation of the Intermediate of Phosphonium Salt & Ylide Hydrolysis: *P*-Hydroxytetraorganophosphorane

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***P*-hydroxytetraorganophosphorane, the long-postulated intermediate in phosphonium salt & ylide hydrolysis, has been observed and characterised by low temperature NMR, finally definitively establishing its involvement in these reactions. The results require modification of the previously accepted mechanism for ylide hydrolysis: *P*-hydroxytetraorganophosphorane is generated directly by 4-centre reaction of ylide with water.**

The alkaline hydrolysis of phosphonium salts has been afforded extensive attention in the chemical literature, and has been put to good use in the synthesis of tertiary phosphine oxides.[1,2] Phosphonium ylide hydrolysis too has been employed in diverse synthetic applications.[3] Recently, several examples of tandem or domino reactions have been reported[4,5,6] in which the reactivity of an ylide is utilised (e.g. for the synthesis of dihydrobenzofurans,4 or peptidyl ketones5) followed by hydrolytic extrusion of phosphine oxide from the resulting adduct (which may be a phosphonium ylide, betaine, or salt). Furthermore, as a result of recent developments in phosphine oxide reduction methodology (and indeed the reduction of the P=O bond in related species),[7] phosphonium salt hydrolysis followed by phosphine oxide reduction has now become an attractive route to phosphines (and derivatives). This is of particular importance for chiral phosphonium salts, which are hydrolysed stereospecifically[8] and thus give the possibility of obtaining enantiopure or enantio-enriched chiral phosphines.

The hydrolysis of a phosphonium ylide (by addition of water to an anhydrous solution of the ylide)2[,9,10] and that of the parent phosphonium salt under alkaline conditions afford the same products – phosphine oxide and the alkane or arene that results from scission of the P-C bond to the group that gives the most stable carbanion (i.e. the order of ease of P-C bond clavage is *p*-nitrobenzyl > benzyl > phenyl > alkyl).[8,11,12,13,14,15,16,17,18,19,20,21] Hydrolysis of phosphonium salts has been shown to be 3rd order (1st order in phosphonium salt, 2nd order in hydroxide) for benzyltriphenylphosphonium,[11,12,14] benzyltrialkylphosphonium,[14] mixed benzyl/alkyl/phenyl phosphonium, mixed alkyl/phenyl phosphonium,[14] tetraphenylphosphonium,[12,14] and tetrabenzylphosphonium salts.[13] 3rd order hydrolysis has also been observed for cyclic phosphonium salts.[22] The hydrolysis reactions of *para*-nitrobenzyltriphenylphosphonium bromide (**1**, Chart 1),[12,23] of methyltris(pentafluorophenyl)phosphonium triflate,[23] and of phospholium iodides,[20] respectively, are exceptional in that they exhibit 1st order dependence on hydroxide concentration.

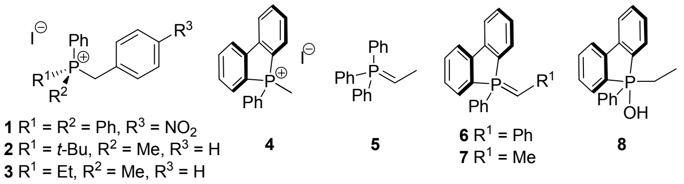
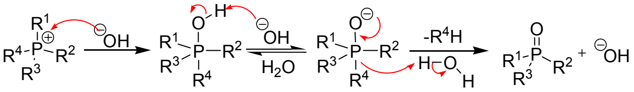


Chart 1. Phosphonium salts, ylides, & *P*-hydroxytetraorganohydroxyphosphorane **8**.

The mechanism that has been proposed for alkaline hydrolysis of phosphonium salts is shown in Scheme 1.[11,12,13,14,16,17,24] Nucleophilic attack of hydroxide at phosphorus gives a hydroxyphosphorane (with apical oxygen[8,25,26]). This is deprotonated by hydroxide to give an oxyanionic phosphorane, which expels a carbanion (probably protonated in the process of its expulsion) to give phosphine oxide and alkane or arene.[27] Largely on the basis that ylide hydrolysis gives the same products as phosphonium salt hydrolysis,[15] it has generally been concluded that ylide hydrolysis proceeds by the same mechanism with one extra (initial) step - protonation of the ylide by water to give phosphonium hydroxide.[10,28,29]



Scheme 1. The mechanism of alkaline hydrolysis of a phosphonium salt.

The existence of an intermediate in these reactions is a necessity in view of the kinetic order of the reaction (& in particular that it is 2nd order in hydroxide). Based on analogy with many other instances in which phosphoranes are involved,[25,30,31,32,33,34,35] including the relatively stable *P*-alkoxytetraorganophosphoranes that have been observed spectroscopically,[35] it is reasonable to conclude that the intermediate in question is a trigonal bipyramidal (TBP) *P*-hydroxytetraorganophosphorane, as shown in Scheme 1. Consistent with this interpretation are the results of hydrolysis reactions of phosphonium salts in which the phosphorus atom is in a cycle of five or fewer members (see the ESI for additional discussion on this topic).† Certain chiral small ring phosphonium salts (and also compound **2**; see Chart 1)[24,36] have been shown to undergo hydrolysis with retention of

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configuration at phosphorus,[37] while other cyclic phosphonium salts undergo ring opening in the course of hydrolysis,[20,22,38] including dibenzophospholium salts such as **4** (Chart 1).[18,39] In TBP phosphoranes, the leaving group is obliged to depart from an apical site.[25,40] However, in a cyclic hydroxyphosphorane, the apical sites are expected to be occupied by hydroxide and one ring P-C bond.[25,26,30,35,41] Thus, for decomposition of the intermediate to occur, the reaction must proceed either with ring cleavage or with stereomutation by pseudorotation to place the leaving group in an apical site in the transition state.[42] If starting from a chiral phosphonium salt, the ligand permutation that occurs during pseudorotation can reveal itself in the product phosphine oxide. Racemisation or retention of configuration (the latter is observed in the examples cited above) at phosphorus in the product indicates the intervention of stereomutation in the intermediate. That both ring cleavage and phosphorus ligand permutation (resulting in retention of configuration at phosphorus) are known to occur during phosphonium salt hydrolysis gives strong support to the existence of a TBP intermediate. The hydrolysis of **3**, (in which the phosphorus is not constrained in a ring) proceeds stereospecifically with *inversion* of configuration at P.8.[43]

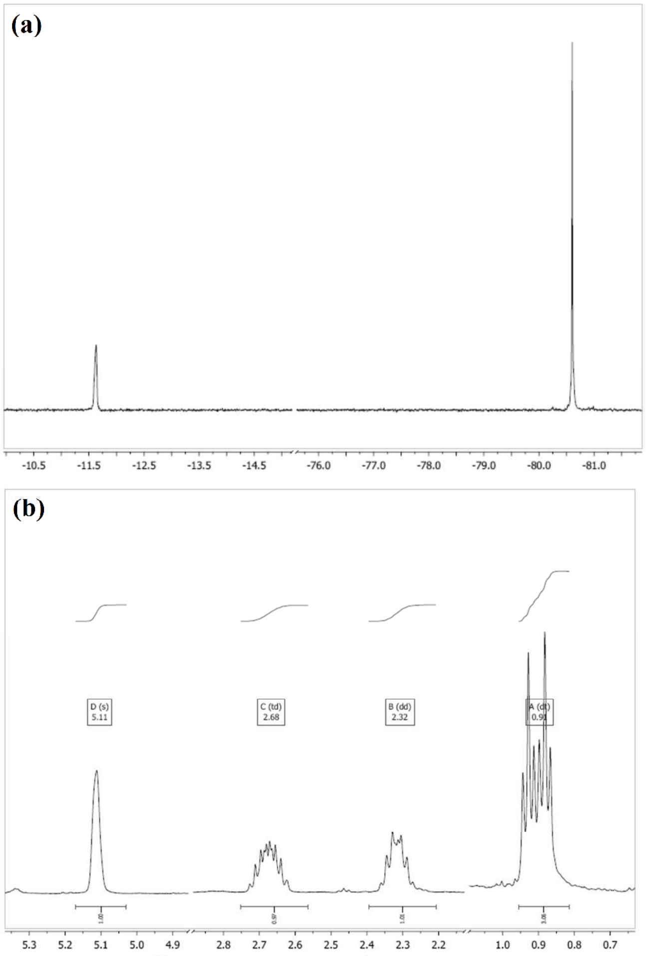

Fig. 1. (a) Partial ^{31}P NMR and (b) partial ^{1}H NMR showing signals for *P*-hydroxyphosphorane **8**.

Despite the strong evidence implicating *P*-hydroxytetraorganophosphoranes formation in phosphonium salt & ylide hydrolysis, this putative intermediate has never been observed or characterised spectroscopically.[44,45,46,47,48] Since low temperature NMR analysis of oxaphosphetanes (OPAs)[32,33,34] and of alkoxyphosphoranes[35] was known to be possible, and had proven to be so useful in the analysis of the reactions in which these species are involved, we undertook to determine if spectroscopic observation of *P*-hydroxytetraorganophosphorane(s) could be realised. We also considered that these experiments might allow us to clarify what seemed to us to be an inconsistency in the accepted mechanism of ylide hydrolysis.[10,15,28] The supposition that the first step of ylide hydrolysis involves formation of phosphonium hydroxide is inconsistent with the relative pK$_a$s of H_2O (31 in DMSO)[49] and phosphonium ylides (e.g. pK_a = 22 in DMSO for deprotonation of $MePh_3P^+$),[50] in organic media. Since stepwise protonation and subsequent hydroxide addition seems therefore to be an impossible process in organic media, we hoped to establish if there exists any evidence for the formation (or otherwise) of phosphonium hydroxide in these reactions.

Ylide hydrolysis reactions are extremely rapid at ambient temperature (20 °C), and all such reactions investigated by us resulted only in the observation of phosphine oxide (by ^{31}P NMR). Indeed, even at -70 °C, rapid conversion of ylide to phosphine oxide was observed by ^{31}P NMR for ylides **5** and **6** (Chart 1), with no appearance of any high field signals that could be attributed to an intermediate.

However, the addition of water to a solution of constrained (cyclic) ylide **7** (Chart 1) at -80 °C resulted in the formation of a compound with a chemical shift of -80.6 ppm in the ^{31}P NMR (see Fig. 1(a); obtained at -70 °C).† The high field chemical shift is indicative of a phosphorane structure (electron-rich at phosphorus).[51] This compound was also characterised by ^{1}H, ^{13}C, gCOSY, gHSQC, ^{1}H-^{13}C gHMBC and ^{1}H-^{31}P HMBC. The ^{1}H NMR (Fig. 1(b)) contains a double triplet for the methyl group at δ_H 0.90, two multiplets arising from the diastereotopic CH_2 protons (δ_H 2.32 & 2.68, each of which couples to methyl group by COSY), and a distinctive broadened singlet at δ_H 5.11 for the *P*-hydroxyl proton. The hydroxyl proton is shown to be coupled to phosphorus by ^{1}H-^{31}P HMBC, and to the methylene carbon by ^{1}H-^{13}C HMBC, indicating beyond doubt that this species is indeed *P*-hydroxyphosphorane (**8**, shown in Chart 1). In the ^{13}C NMR of **8**, a value of $^{1}J_{PC}$ of 119 Hz is observed for the methylene carbon.† The magnitude of the value of $^{1}J_{PC}$ observed for the methylene group of **8** is consistent with its occupation of an equatorial position in a pentavalent phosphorane.[30,31,33,34,35]

This is the first time that a *P*-hydroxytetraorganophosphorane – the proposed intermediate in phosphonium salt and ylide hydrolysis – has been observed spectroscopically. Significantly, a small amount of residual ylide could also be observed in the ^{31}P NMR (δ_P -11.6). Since water (present in excess), ylide and *P*-hydroxyphosphorane can be seen from the ^{31}P and ^{1}H NMR to co-exist in solution, it is apparent that an equilibrium involving these three species is in operation (*cf.* reactions of ylides and alcohols to give alkoxyphosphoranes[35]). Furthermore, since the pK_a of the ylide is too low in organic media to effect deprotonation of water, we conclude that that phosphonium hydroxide (which is

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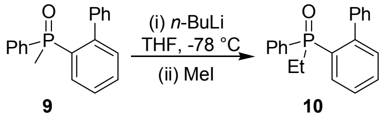
not detected) plays no role in the process of interconversion between ylide and *P*-hydroxytetraorganophosphorane. We propose instead that the phosphorane is formed directly from ylide + H_2O by (reversible) concerted addition of an O-H bond cross the P=C bond. Indeed, it is even possible that the hydrolysis of *p*-nitrobenzyl phosphonium salt **1** (Chart 1), which is 1st order in each of phosphonium salt & hydroxide, may proceed by initial formation of ylide, and hence occurs by a different mechanism to that shown in Scheme 1. The sample of *P*-hydroxyphosphorane **8** was stored at -19 °C, and was observed by ^1H & ^{31}P NMR (run at 25 °C) to have survived for 5 days at -19 °C. Warming of the sample to 25 °C resulted in the formation of ring-opened phosphine oxide **10** (Scheme 2) almost to the exclusion of the other two possible phosphine oxide products (*cf.* other cyclic phosphonium salts, especially **4**, *vide supra*). The identity of **10** was confirmed unambiguously by comparison with the NMR data of an authentic sample prepared by independent means – α-methylation of phosphine oxide **9** via a phosphinoxy carbanion (see Scheme 2).



Scheme 2. Synthesis of phosphine oxide **10**.

In conclusion, we have succeeded in carrying out the first ever spectroscopic observation of a *P*-hydroxytetraorganophosphorane, the intermediate of phosphonium salt and ylide hydrolysis. The ^{31}P NMR chemical shift and associated spectral data reported above establish that the intermediate is a TBP phosphorane, and validates the operation of the proposed mechanism shown in Scheme 1 for phosphonium salt hydrolysis. The establishment of the structure of this intermediate provides a basis for a unifying explanation of the outcomes (ring opening, ring expansion, retention of stereochemistry at phosphorus) of the hydrolysis reactions of the various cyclic phosphonium salts.[28] It seems likely that spectroscopic observation of the *P*-hydroxyphosphoranes arising from hydrolysis of other cyclic phosphonium salts (e.g. **4**) should be possible, at least in some cases. Given the relative stability of **8** (it survived under inert atmosphere for several days at -19 °C), it may be possible to pursue novel synthetic avenues by testing the reactivity of **8** and analogues. Finally, we have provided evidence that the first step of ylide hydrolysis is not protonation of the ylide, but rather is concerted addition of an O-H bond across the P=C bond.

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Notes and references

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