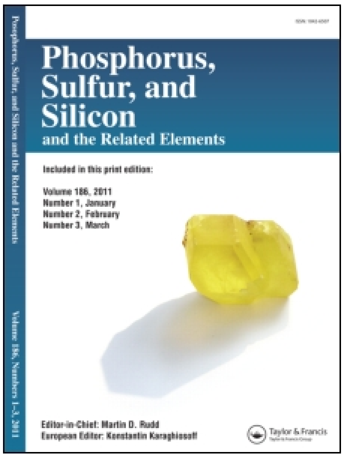

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MONO- AND DIHYDROPHOSPHORANES AND DIHYDROPHOSPHORANATES AS INTERMEDIATES IN THE REACTION OF PHOSPHONIUM SALTS WITH $LiAiH_4$[*]

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Reduction of tetraphenylphosphonium bromide with $LiAlH(D)_4$ at room temperature affords first the monohydrophosphorane Ph_4PH, then the dihydrophosphoranate anion $[Ph_4PH_2]^-$ which decomposes to the dihydrophosphorane Ph_3PH_2, all of which are identified by ^{31}PNMR. Reductions of other phosphonium salts appear to follow a similar path. At elevated temperatures none of these intermediates is observed and attempted isolation leads to extensive decomposition.

Keywords: Hydrophosphoranes; hydrophosphoranates; metal hydride reduction; phosphonium salts.

The chemistry of phosphoranes, species with five ligands covalently bound to phosphorus, is extensive and has attracted great interest since the initial preparation by Wittig of pentaphenylphosphorane in 1948[1]. Structure, stereochemistry, and bonding have been discussed in detail as has their involvement as reaction intermediates in biological pathways and in the Wittig olefination[2]. The parent compound, PH_5, is unknown and acyclic compounds of the type HPR_4 and H_2PR_3 are rare and found only when the non-hydrogen ligands are strongly electron withdrawing (F, Cl, or CF_3)[3]. Many mono- and bicyclic R_4PH, e.g. **1**, are known[4] where at least two of the attached groups are O, N or S. A solitary example of a bicyclic dihydrophosphorane, **2**, has been described[5]. The bis-2,2-biphenylylphosphoranes, **3**, prepared by Hellwinkel[6] in his elegant studies of the stereochemistry of C5 phosphoranes[2d], are the only C_4H species so far reported and earlier attempts to prepare Ph_4PH were unsuccessful[7]. Nevertheless, the racemic nature of the phosphines obtained by $LiAlH_4$ reduction of chiral phos-

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[*] Dedicated to Professor Robert Wolf, a founding father of phosphorous chemistry, on the occasion of his 70th birthday

phonium salts[8-11] suggests that configurationally mobile phosphoranes are involved.

Acyclic P(VI) compounds are known but invariably carry strongly electronegative substituents, Cl, F, CN etc. As with P(V) numerous cyclic P(VI) species are known, including a small number of compounds with a P-H bond[3b] but no examples with two PH bonds have been reported to our knowledge. As part of a study of the pathway of phosphonium salt cleavages with metal hydrides we examined the reduction of $Ph_4P^+Br^-$ with $LiAlH_4$ by ^{31}P nmr. If this reaction is carried out at reflux in tetrahydrofuran the only observed phosphorus containing product is Ph_3P but at room temperature four species, **4** - **7**, are clearly visible by ^{31}P nmr. (Eq. 1).

$$Ph_4P^+ \xrightarrow{LiAlH_4} \underset{\mathbf{4}}{Ph_4PH} + \underset{\mathbf{5}}{Ph_3PH_2} + \underset{\mathbf{6}}{[Ph_4PH_2]^-} + \underset{\mathbf{7}}{Ph_3P} \quad \dots\dots\dots (1)$$

Structures are assigned to **4** - **6** on the basis of their large upfield ^{31}P chemical shift values and characteristic $^1J_{PH}$ splittings (Table). The latter are rather broad in the ^{31}P nmr spectra due to coupling to the aromatic protons but sharper signals can be obtained by using $LiAlD_4$ which gives the corresponding deuterated species, with appropriately different splitting patterns, and allows the ^{31}P spectra to be observed with proton decoupling. Running sequential spectra on the reaction mixture, beginning as soon as possible after mixing, shows that **4** is formed first followed rapidly by **6** and only then do **5** and **7** make their appearance. Thereafter **4** and **6** decline and **5** and **7** increase until eventually only **5** and **7** remain. These reactions are relatively slow and do not appear to be affected by exposure to light though **3** are sensitive to photochemical homolysis of the PH bond in solution[6]. When the final solution, containing only **5** and **7**, is left to stand no further changes were observed in the ^{31}P nmr spectrum after 24 hours at room temperature. However, addition of more of the salt results in the reappearance of **4**, a reduction in the dihydrophosphorane **5**, and an apparent increase in **7** suggesting hydride transfer from **4** to the salt. Analogous results were obtained with $Ph_3P^+CH_3I^-$ and $Ph_2P^+(CH_3)_2I^-$ though reaction was much slower, possibly as a consequence of lower electrophilicity at phosphorus, and more complex mixtures resulted because of loss of either Ph or CH_3 from phosphorus (Eq. 2, 3)

$$Ph_3\overset{+}{P}CH_3 + LiAlH_4 \longrightarrow \underset{\mathbf{8}}{Ph_3P(H)CH_3} + \underset{\mathbf{5}}{Ph_3PH_2} + \underset{\mathbf{9}}{Ph_2P(H)_2CH_3}$$

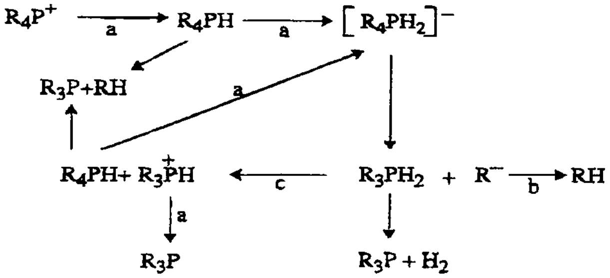
$$+ \underset{\mathbf{10}}{Ph_2PCH_3} + \underset{\mathbf{7}}{Ph_3P} \quad \dots\dots\dots\dots\dots (2)$$

$$Ph_2\overset{+}{P}(CH_3)_2 + LiAlH_4 \longrightarrow \underset{\mathbf{11}}{Ph_2P(H)(CH_3)_2} + \underset{\mathbf{9}}{Ph_2P(H_2)CH_3} + \underset{\mathbf{12}}{PhP(H_2)(CH_3)_2}$$

$$+ \underset{\mathbf{10}}{Ph_2PCH_3} + \underset{\mathbf{13}}{PhP(CH_3)_2} \qquad \ldots\ldots\ldots\ldots\ldots(3)$$

However, we only observe an anionic P(VI) species for the tetraphenyl salt reduction. Benzyl salts $(PhCH_2)_{4-n}$, P^+Ph_n ; n=0-3) are reduced rapidly and for n=0, 1 or 2 no intermediates at all are observed but when n=3, **5** and **7** are the final products.

We interpret these results as shown in the Scheme



Reagents: a, $LiAlH_4$; b, THF; c, R_4P^+

SCHEME

Support for this behaviour comes from the known[2d] instability of acyclic P(VI) anionic species due, presumably, to steric crowding[2c] and the theoretically predicted[12] and observed[2d] decomposition of phosphorane, $R_5P \rightarrow R_3P + R_2$. The latter reaction is calculated to have a considerable E_A and this may account for the relative stability of R_3PH_2 in the reaction mixtures. It is not obvious, however, why loss of H_2 is the only path followed. Attempted workup of these reaction mixtures by standard procedures invariably destroys the great bulk of the phosphoranes **4** and **5** and the phosphoranate, **6.** This may be due either to heat involved in the quenching process or to exposure to protic solvents as the hydrogens of the P-H bonds are expected to exhibit anionic character[12]. Attempted chromatographic isolation over acidic, neutral or basic column packing was also unsuccessful. We are currently extending our study to a greater range of salts and reducing agents and exploring experimental modifications in order to isolate at least some of these very novel species whose spectroscopy and chemistry should be of great interest. The stability of the R_4PH and R_3PH_2 observed here suggests that other R_nPH_{5-n} and even PH_5 and PH_6^- may be reasonable synthetic targets.

TABLE ^{31}P NMR Data for reduction products of R_4P^+ with $LiAlH(D)_4$

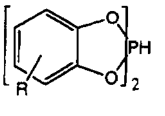
		$\delta^{31}P$	^1JPH *(Hz)*	^1JPD *(Hz)*
Ph_4PH	**(4)**	-87.3 (D)	324[a]	48.5[b]
		-86.6 (H)		
Ph_3PH_2	**(5)**	-70.0 (D)	336[b]	50.9[c]
		-68.4 (H)		
$[Ph_4PH_2]^-$	**(6)**	-186.9 (H)	446[b]	68.7[c]
		-187.2(D)		
Ph_3P	**(7)**	-4.5	-	-
$Ph_2P(CH_3)_2H$	**(11)**	-102.75 (H)	343[a]	53.5[b]
		103.6 (D)		
$Ph_2P(H_2)CH_3$	**(9)**	-106.4 (D)	389[b]	48.3[c]
		-104.7 (H)		
Ph_2PCH_3	**(10)**	-26.2	-	-
$Ph_3P(H)CH_3$	**(8)**	-116.2 (H)	374[a]	55.9[b]
		-116.9 (D)		
$PhP(CH_3)_2H_2$	**(12)**	-143.7 (D)		41.85[c]
		-142.3 (H)		
$PhP(CH_3)_2$	**(13)**	-45.3	-	-

a. doublet; b. triplet; c. quintet

EXPERIMENTAL

All experiments were carried out under dry argon in tetrahydrofuran purified by distillation from sodium-benzophenone ketyl. $LiAlH_4$, $LiAlD_4$ and $Ph_4P^+Br^-$ were commercial samples and were used as received. Other phosphonium salts were prepared by simple quaternisation reactions and their identity confirmed by comparison of their ^1H NMR, ^{31}P NMR, and m.pts. with literature values. ^{31}P NMR were measured on a Bruker ACP 300P instrument at room temperature (300°K) with a sweep width of 30 000Herz(-200 to 50 ppm[$\delta H_3PO_4 = 0$]; 32 K data points zero filled to 64K were collected.). The absence of peaks outside this range was routinely checked.

Attempts to isolate the intermediates have not, as yet, afforded pure materials.



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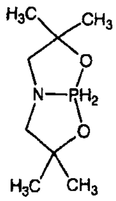

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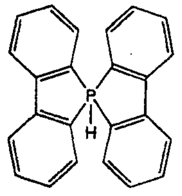

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Acknowledgements

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