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MONO- AND DIHYDROPHOSPHORANES AND DIHYDROPHOSPHORANATES AS INTERMEDIATES IN THE REACTION OF PHOSPHONIUM SALTS WITH LIAIH₄*

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Reduction of tetraphenylphosphonium bromide with LiAlH(D)₄ at room temperature affords first the monohydrophosphorane Ph₄PH, then the dihydrophosphoranate anion [Ph₄PH₂] which decomposes to the dihydrophosphorane Ph₃PH₂, all of which are identified by ³¹PNMR. 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 1948¹. Structure, stereochemistry, and bonding have been discussed in detail as has their involvement as reaction intermediates in biological pathways and in the Wittig olefination². The parent compound, PH₅, is unknown and acyclic compounds of the type HPR₄ and H₂PR₃ are rare and found only when the non-hydrogen ligands are strongly electron withdrawing (F, Cl, or CF₃)³. Many mono- and bicyclic R₄PH, e.g. 1, are known⁴ where at least two of the attached groups are O, N or S. A solitary example of a bicyclic dihydrophosphorane, **2**, has been described⁵. The bis-2,2-biphenylylphosphoranes, **3**, prepared by Hellwinkel⁶ in his elegant studies of the stereochemistry of C5 phosphoranes^{2d}, are the only C₄H species so far reported and earlier attempts to prepare Ph₄PH were unsuccessful⁷. Nevertheless, the racemic nature of the phosphines obtained by LiAlH₄ reduction of chiral phos-

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

phonium salts⁸⁻¹¹ 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 LiAlH₄ by ³¹P 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 ³¹P nmr. (Eq. 1).

$$\frac{Ph_4P^+}{4} \xrightarrow{LlAH4} Ph_4PH + Ph_3PH_2 + [Ph_4PH_2]^- + Ph_3P \qquad \dots \dots (1)$$

Structures are assigned to 4 - 6 on the basis of their large upfield ³¹P chemical shift values and characteristic ¹J_{PH} splittings (Table). The latter are rather broad in the ³¹P nmr spectra due to coupling to the aromatic protons but sharper signals can be obtained by using LiAlD₄ which gives the corresponding deuterated species, with appropriately different splitting patterns, and allows the ³¹P 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 solution⁶. When the final solution, containing only 5 and 7, is left to stand no further changes were observed in the ³¹P 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 $Ph_3P^+CH_3l^-$ and $Ph_2P^+(CH_3)_2l^-$ 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 CH₃ from phosphorus (Eq. 2, 3)

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+

$$Ph_{2}\overset{+}{P}(CH_{3})_{2} + LiAlH_{4} \longrightarrow Ph_{2}P(H)(CH_{3})_{2} + Ph_{2}P(H_{2})CH_{3} + PhP(H_{2})(CH_{3})_{2}$$

$$11 \qquad 9 \qquad 12$$

$$+ Ph_{2}PCH_{3} + PhP(CH_{3})_{2} \qquad \dots \dots \dots \dots \dots (3)$$

$$10 \qquad 13$$

However, we only observe an anionic P(VI) species for the tetraphenyl salt reduction. Benzyl salts (PhCH₂)_{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, LiAlH₄; b, THF; c, R₄P+ 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 predicted¹² and observed^{2d} decomposition of phosphorane, $R_5P \rightarrow R_3P + R_2$. The latter reaction is calculated to have a considerable EA and this may account for the relative stability of R₃PH₂ in the reaction mixtures. It is not obvious, however, why loss of H₂ 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 character¹². 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 R₄PH and R₃PH₂ observed here suggests that other R_nPH_{5-n} and even PH₅ and PH₆⁻ may be reasonable synthetic targets.

		$\delta^{31}P$	¹ JPH (Hz)	¹ JPD (Hz)
Ph ₄ PH	(4)	-87.3 (D)	324 ^a	48.5 ^b
		-86.6 (H)		
Ph ₃ PH ₂	(5)	-70.0 (D)	336 ^b	50.9 ^c
		-68.4 (H)		
[Ph ₄ PH ₂] ⁻	(6)	-186.9 (H)	446 ^b	68.7 ^c
		-187.2(D)		
Ph ₃ P	(7)	-4.5	-	-
Ph ₂ P(CH ₃) ₂ H	(11)	-102.75 (H)	343 ^a	53.5 ^b
		103.6 (D)		
Ph ₂ P(H ₂)CH ₃	(9)	-106.4 (D)	389 ^b	48.3 ^c
		-104.7 (H)		
Ph ₂ PCH ₃	(10)	-26.2	-	
Ph ₃ P(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	-	-

TABLE ³¹P NMR Data for reduction products of R_4P^+ with LiAlH(D)₄

a. doublet; b. triplet; c. quintet

EXPERIMENTAL

All experiments were carried out under dry argon in tetrahydrofuran purified by distillation from sodium-benzophenone ketyl. LiAlH₄, LiAlD₄ and Ph₄P⁺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, ³¹P NMR, and m.pts. with literature values. ³¹P 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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