Pentacovalent Phosphorus Compounds *via* Iminophosphoranes

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Summary The reaction of phenyl azide with a $P^{III} \rightleftharpoons P^{V}$ tautomeric equilibrium mixture leads to new spirophosphoranes derivatives (**3a**—**d**) bearing an exocyclic —NH·Ph group.

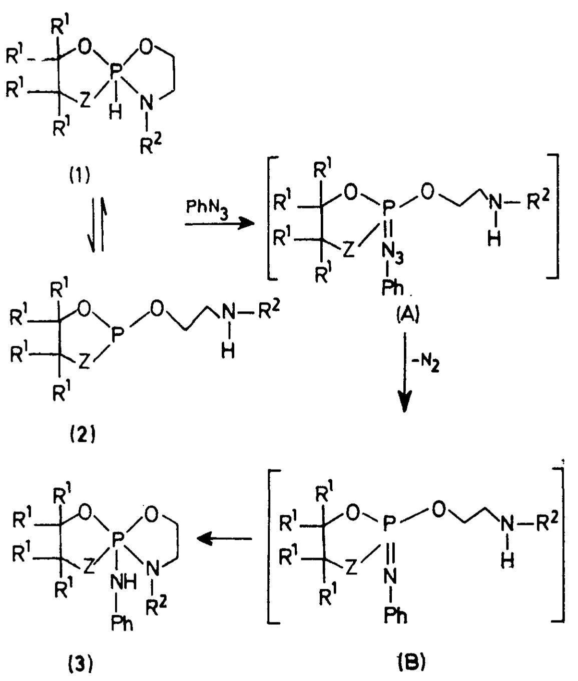
THE most stable hybridization scheme in phosphorus chemistry is the one in which the phosphorus atom, using its five valence electrons, is directly bonded to four atoms: $\geqslant P{=}X$. It has been shown[1] that the addition of a Y–H

TABLE

Compound	δ (^{31}P)[a]	*H*–N< δ (^{1}H)[b]	*H*–N< ^{2}J (H–P)[c]	*Me*–N< δ (^{1}H)	*Me*–N< ^{3}J (H–P)[c]
(**3a**)[d]	45·9	4·64	7·9	2·87	9·3
(**3b**)[d]	52·6	4·66	8·2	2·96	9·2
(**3c**)[e]	59·5	4·55	7·1	2·81	9·7
(**3d**)[d]	47·5	4·83	8·7	—	—

[a] In CH_2Cl_2, p.p.m. to high field of H_3PO_4 (85%). [b] In CH_2Cl_2, Me_4Si reference. [c] In Hz. [d] ν(N–H) 3420 cm^{-1}. [e] ν(N–H) 3425 cm^{-1}.

group to the P=X bond can lead to a five co-ordinated species $\geqslant PY{\cdot}XH$ ($X = CH_2$, $Y = OMe$).

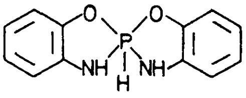


	R¹	R²	X	% (1)	⇌% (2)
a;	H	Me	O	15	85
b;	Me	Me	O	25	75
c;	H	Me	NMe	10	90
d;	H	Ph	O	0	100

We have attempted the intramolecular addition of an N–H group (Y–H) to the P=N bond (P=X) of a cyclic imino phosphorane. By the Staudinger procedure[2] PhN_3 was added in ether at room temperature to a mixture of a spirophosphorane (**1**) and phosphite (**2**) in equilibrium.[3] We have isolated and characterized the four spirophosphoranes (**3a**—**d**) having an exocyclic –NH·Ph group.

The structures of compounds (**3a**—**d**) were assigned on the basis of ^1H and ^{31}P n.m.r. and i.r. data (Table); compounds (**3a**) and (**3b**) also gave satisfactory analytical data.

Preliminary attempts to detect the intermediates (A) and (B) in the reaction were unsuccessful, although the ^{31}P n.m.r. spectra of mixtures of compounds (**3b**) and (**3d**) indicated the presence of the P^{IV} species $\delta^{31}P$ -12 and -14 p.p.m. for (**3b**), and $-3{\cdot}4$ p.p.m. for (**3d**)]; these resonances are absent from the spectra of the recrystallized products.



(4)

The existence of compound (**3d**), which has been obtained starting exclusively from the phosphite form (**2d**), shows that the presence of the five-co-ordinated structure in the $P^V \rightleftharpoons P^{III}$ equilibrium is not a condition for the reaction to proceed. Moreover, the *o*-aminophenol spirophosphorane derivative (**4**) which exists only in the P^V form, even at 150 °C,[4] did not react under the same conditions as above.[5]

The system studied is closely related to the Stegmann reaction[6] of an iminophosphorane bearing an OH group, and also is connected with our previous attempts to characterize a hydroxy spirophosphorane.[7]

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