

## Pentacovalent Phosphorus Compounds *via* Iminophosphoranes

By MICHEL SANCHEZ, JEAN-FRANÇOIS BRAZIER, DOURAID HOULLA, AURELIO MUNOZ, and ROBERT WOLF\*

(*E.R. 82, Chimie Physique II, Université Paul Sabatier, Toulouse Cedex 31077, France*)

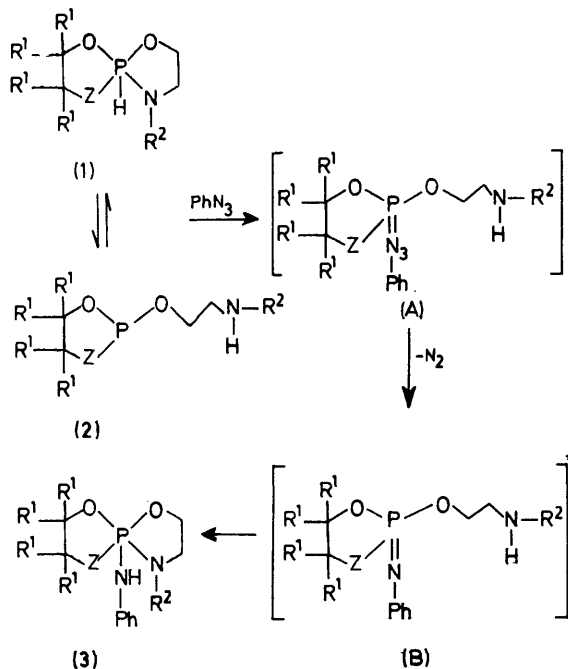
**Summary** The reaction of phenyl azide with a  $P^{III} \rightleftharpoons P^V$  tautomeric equilibrium mixture leads to new spiro-phosphoranes derivatives (**3a—d**) bearing an exocyclic —NH·Ph group.

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:  $\geq P=X$ . It has been shown<sup>1</sup> that the addition of a Y-H

Compound	$\delta$ ( <sup>31</sup> P) <sup>a</sup>	TABLE H-N <		Me-N <	
		$\delta$ ( <sup>1</sup> H) <sup>b</sup>	<sup>2</sup> J (H-P) <sup>c</sup>	$\delta$ ( <sup>1</sup> H)	<sup>3</sup> J (H-P) <sup>c</sup>
( <b>3a</b> ) <sup>d</sup>	45.9	4.64	7.9	2.87	9.3
( <b>3b</b> ) <sup>d</sup>	52.6	4.66	8.2	2.96	9.2
( <b>3c</b> ) <sup>e</sup>	59.5	4.55	7.1	2.81	9.7
( <b>3d</b> ) <sup>d</sup>	47.5	4.83	8.7	—	—

<sup>a</sup> In CH<sub>2</sub>Cl<sub>2</sub>, p.p.m. to high field of H<sub>3</sub>PO<sub>4</sub> (85%). <sup>b</sup> In CH<sub>2</sub>Cl<sub>2</sub>, Me<sub>4</sub>Si reference. <sup>c</sup> In Hz. <sup>d</sup>  $\nu$ (N-H) 3420 cm<sup>-1</sup>. <sup>e</sup>  $\nu$ (N-H) 3425 cm<sup>-1</sup>.

group to the P=X bond can lead to a five co-ordinated species  $\geq\text{PY}\cdot\text{XH}$  (X = CH<sub>2</sub>, Y = OMe).



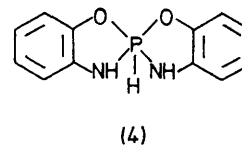
	R <sup>1</sup>	R <sup>2</sup>	X	% (1) ⇌ % (2)
a;	H	Me	O	15 85
b;	Me	Me	O	25 75
c;	H	Me	NMe	10 90
d;	H	Ph	O	0 100

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<sup>2</sup> PhN<sub>3</sub> was added in ether at room temperature to a mixture of a spirophosphorane (1) and phosphite (2) in equilibrium.<sup>3</sup> 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 <sup>1</sup>H and <sup>31</sup>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 <sup>31</sup>P n.m.r. spectra of mixtures of compounds (3b) and (3d) indicated the presence of the P<sup>IV</sup> species  $\delta^{31}\text{P} -12$  and  $-14$  p.p.m. for (3b), and  $-3.4$  p.p.m. for (3d); these resonances are absent from the spectra of the recrystallized products.



The existence of compound (3d), which has been obtained starting exclusively from the phosphite form (2d), shows that the presence of the five-coordinated structure in the P<sup>V</sup> ⇌ P<sup>III</sup> equilibrium is not a condition for the reaction to proceed. Moreover, the *o*-aminophenol spirophosphorane derivative (4) which exists only in the P<sup>V</sup> form, even at 150 °C,<sup>4</sup> did not react under the same conditions as above.<sup>5</sup>

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

(Received, 3rd June 1976; Com. 632.)

<sup>1</sup> H. Schmidbaur and H. Stühler, *Angew. Chem. Internat. Edn.*, 1972, **11**, 145; H. Schmidbaur, W. Buchner, and F. H. Köhler, *J. Amer. Chem. Soc.*, 1974, **96**, 6208.

<sup>2</sup> H. Staudinger and J. Meyer, *Helv. chim. Acta*, 1919, **2**, 635; M. I. Kabachnik and V. A. Gilyrov, *Izvest. Akad. Nauk. S.S.S.R.*, 1956, 790 (*Chem. Abs.*, 1957, **51**, 1823b); H. Goldwhite, P. Gysegem, S. Schow, and C. Swyke, *J.C.S. Dalton*, 1975, 16.

<sup>3</sup> M. Sanchez, J. F. Brazier, D. Houalla, and R. Wolf, *Bull. Soc. chim., France*, 1967, 3930; M. Sanchez, R. Wolf, R. Burgada, and F. Mathis, *ibid.*, 1968, 773.

<sup>4</sup> R. Burgada and C. Laureço, *J. Organometallic Chem.*, 1974, **66**, 255.

<sup>5</sup> Unpublished results.

<sup>6</sup> H. B. Stegmann, G. Bauer, E. Breitmaier, E. Herrmann, and K. Scheffer, *Phosphorus*, 1975, **5**, 207.

<sup>7</sup> A. Munoz, M. Gallagher, A. Kläbe, and R. Wolf, *Tetrahedron Letters*, 1976, (9), 673.