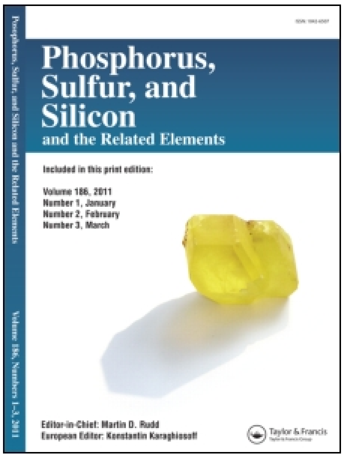

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EXTENSION OF THE STAUDINGER REACTION TO THE PHOSPHENIUM CATION [—P—]: SYNTHESIS OF A NEW CLASS OF TETRAVALENT TRICOORDINATED PHOSPHORUS CATIONS

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EXTENSION OF THE STAUDINGER REACTION TO THE PHOSPHENIUM CATION [—P—]$^+$: SYNTHESIS OF A NEW CLASS OF TETRAVALENT TRICOORDINATED PHOSPHORUS CATIONS

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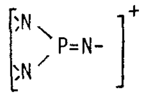
Three types of P=N phosphazene bonds are known: R—P=N—R, $R{-}N{=}\overset{R}{\overset{|}{P}}{=}N{-}R$ and $R_3P{=}N{-}R$, here classified according to the coordination numbers: 2,3,4 and valences 3,5,5, respectively. In this communication we describe a new phosphazene bond in a cation having a coordination number three and valence four:



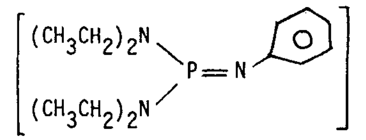
Among the methods available to form the P=N bond, the Staudinger reaction[1] has been widely applied:

$$R_3P \quad + \quad N_3R' \longrightarrow \left[R_3P{=}N_3R'\right] \xrightarrow{-N_2} R_3P{=}NR'$$

A recent Tetrahedron Report[2] shows the very large development that this pioneering reaction has undergone.

On the other hand, it has been known for ten years now[3] that a heterolytic cleavage of the P-halogen bond in halo-aminophosphanes $X{-}P(NR_2)_2$ induced by halide ion acceptors, results in the formation of a dicoordinated phosphenium cation: $[R_2N{-}\ddot{P}{-}NR_2]^+$. Since in this cation, the phosphorus still possesses a lone pair of electrons, we might imagine that it would be capable of reacting with organyl azide in the same way as a phosphane R_3P. The results presented in this preliminary note prove that is indeed so.

Treatment of **1a** with stoichiometric amount of $AlCl_3$ in dichloromethane[4] at room temperature, gives rise to the phosphenium cation **1b**.[5] The mole-to-mole addition to this solution of phenyl azide at −20°C causes a quantitative evolution of nitrogen as the temperature approaches the ambient temperature. The reaction results in three phosphorus derivatives detected by ^{31}P NMR (F.T., ^1H decoupled): $\delta_1 = 48.7$ (20%, broad signal), $\delta_2 = +37.0$ (70%) $\delta_3 = +19.0$ (10%). After purification, a solution containing only the main product has been obtained and a solid was isolated. Spectroscopic evidence demonstrates that this phosphorus species possesses all the features of cation **1**



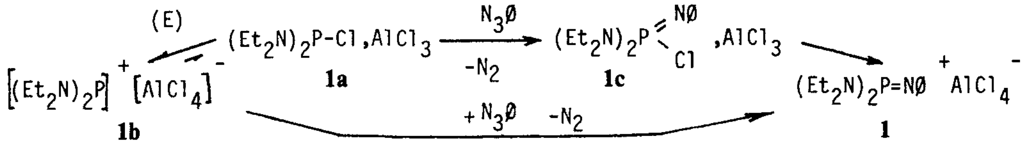
1

(i) In ^{31}P NMR, in addition to the single peak at $\delta_2 = +37$ we observe splitting of the phosphorus signal (no ^1H decoupled) as a result of coupling to the eight methylenic protons: ^3J P—H = 14.7 Hz.

(ii) In ^1H NMR (250 Mhz) the spectrum of the four CH_2 groups, shows sixteen peaks that are two pairs of quartets.'The pairs are separated by a chemical shift $\Delta\nu = 5$ Hz (0.02 ppm) revealing a two by two inequivalence of the CH_2 groups. In each quartet we have found the same coupling ^3J H—H = 7.2 Hz with methyl protons. In a pair of quartet the separation due to the phosphorus coupling is ^3J H—P = 14.5 Hz. The twelve protons of the CH_3 groups appear as equivalent, forming a slightly broadened triplet: $\delta = 1.28$, ^3J H—H = 7.2 Hz. Furthermore the ratio resulting from the integration of the three protons signals corresponds accurately to the proposed structure.

(iii) In ^{13}C NMR the coupling constants between phosphorus and methylene carbons (^2J C—P = 6.1 Hz) and also with ortho aryl carbons (^3J C—P = 7.6 Hz) are fully consistent with cation **1** (Table I).

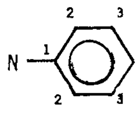
It is important to demonstrate that the Staudinger reaction described actually involve the phosphenium cation and not minute amounts of the corresponding chlorophosphane **1a** which needs to be considered because of the equilibrium (E):



To check this possibility we have studied the reaction of aluminum chloride with chloroiminophosphane **1c** which would be formed in the process. The stoichiometric interaction of **1c** and $AlCl_3$ in CH_2Cl_2 solution at room temperature followed by ^{31}P NMR makes it possible to detect the formation of two phosphorus entities at $\delta_1 = +48.5$ (90%, broad signal) and $\delta_2 = +37.1$ (10%). When this solution is kept at 50°C for 16 hours an irreversible transformation occurs: the broad signal at

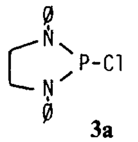
TABLE I

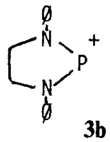
Proton (250 MHz) and carbon (62.86 MHz) NMR data of iminophosphenium cation **1** $(Et_2N)_2P^+$ = NØin solution in $CDCl_3$

	^1H NMR δ ppm (J Hz)	^{13}C NMR δ ppm (J Hz)
—CH_3	1.28 (t) (^3J H—H = 7.2)	13.2 (s)
—CH_2—	$\delta_1 = 3.35$ $\delta_2 = 3.37$ (two pairs of quartets) (^3J H—H = 7.2; ^3J H—P = 14.5)	41.3 (s)
	$7.2 < \delta < 7.3$	C_1: 136.4 (s) C_2: 120.7 (d) (^3J C—P = 7.6) C_3: 129.6 (s) C_4: 125.2 (s)

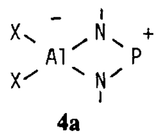
+48.5 decreases while the second peak ($\delta_2 = +37.1$) increases; the relative intensities become 50/50.

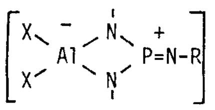
These changes in the spectrum can be interpreted as the formation of an [**1c**-$AlCl_3$] adduct followed by the formation of the cation species. These reactions have been extended to cyclic phosphenium salts **2b** and **3b** yielding similar results (Table II). In particular in the case of **3b** the exclusive participation of the phosphenium entity is most obvious. The chloro aminophosphane **3a** itself does not react with phenyl azide; in contrast, the phosphenium solution of **3b** reacts rapidly quantitatively.


3a


3b

Recently two papers by Niecke *et al.*[6] deal with the reaction of organyl azides with phosphenium salts of type **4a**. In these examples the iminophosphenium species **4** are not detected as intermediates and the final products are the phophonium derivatives **5**, resulting from the reaction of a second mole of azide with the intermediate.


4a


4

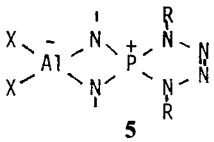
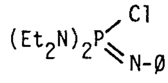
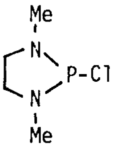
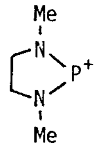
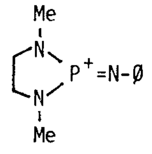
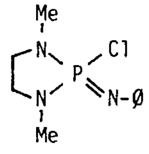
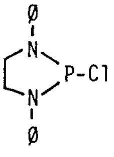
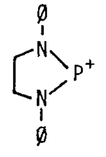
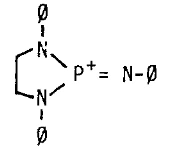
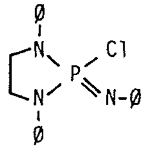
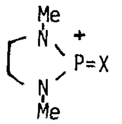

5

TABLE II

Formula and ^{31}P chemical shift of the different entities studied in this work; **3b** is a new phosphenium cation while **3c** is unknown

$(Et_2N)_2P\text{-}Cl$ **1a** + 157	$(Et_2N)_2P^+$ **1b** + 263	$(Et_2N)_2P^+{=}N$-Ø **1** + 37	 $(Et_2N)_2P(Cl){=}N$-Ø **1c** + 11
 **2a** + 169,5	 **2b** + 264	 **2** + 38,5	 **2c** + 6
 **3a** + 137	 **3b** + 254,5	 **3** + 27	 **3c**

It also should be mentioned that in a quite different reaction Light and Paine[7] have characterized in solution species **6** and **7** which also contain tricoordinated tetravalent phosphorus cation centers.



(**6**: X = O; **7**: X = S)

EXPERIMENTAL

Commercial Al_2Cl_6 was purified by sublimation in vacuo, all solvents were dried and distilled prior to use. A solution of phenylazide (0.6 gr; 5 mmol) in CH_2Cl_2 was added to a solution of the phosphenium cation **1b** (1.72 gr, 5 mmol) in CH_2Cl_2 at −20°C. The mixture was stirred for 3 h, during which time the temperature rose to ambient temperature and the expected evolution of nitrogen occurred. The ^{31}P NMR spectrum of the crude material showed the presence of three phosphorus species. Solvent was partially removed and the pure compound **1** crystallized out. The solid was separated, washed with toluol and dried. The same procedure was employed for the preparation of compounds **2** and **3**.

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