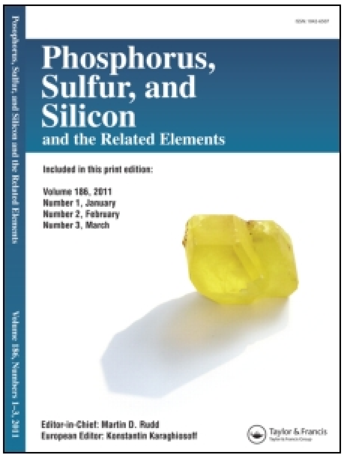


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

New Phosphenium Cations and Bis-phosphocations via Condensation between Chlorophosphines or Chlorophospheniums and Trimethylsilyl Derivatives

Michel Sanchez[a]; Marie-Rose Mazieres[a]; Rainer Bartsch[a]; Robert Wolf[a]; Jean-Pierre Majoral[a]
[a] Laboratoire Synthèse, Structure et Réactivité de Molécules Phosphorées, UA 454, Université Paul Sabatie, Toulouse Cédex, France

To cite this Article Sanchez, Michel , Mazieres, Marie-Rose , Bartsch, Rainer , Wolf, Robert and Majoral, Jean-Pierre(1987) 'New Phosphenium Cations and Bis-phosphocations via Condensation between Chlorophosphines or Chlorophospheniums and Trimethylsilyl Derivatives', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 487 — 490

To link to this Article: DOI: 10.1080/03086648708080626

URL: http://dx.doi.org/10.1080/03086648708080626

Phosphorus and Sulfur, 1987, Vol. 30, pp. 487–490
Photocopying permitted by license only

NEW PHOSPHENIUM CATIONS AND BIS PHOSPHOCATIONS VIA CONDENSATION BETWEEN CHLOROPHOSPHINES OR CHLOROPHOSPHENIUMS AND TRIMETHYLSILYL DERIVATIVES

Michel SANCHEZ, Marie-Rose MAZIERES, Rainer BARTSCH, Robert WOLF and Jean-Pierre MAJORAL
Laboratoire Synthèse, Structure et Réactivité de Molécules Phosphorées, UA 454, Université Paul Sabatier, 118 Route de Narbonne 31062 Toulouse Cédex (France).

Abstract New phosphenium cations of general formula $R_2N\text{-}P^+\text{-}X$, with a variety of X group ($-N{=}P^+R_2$, $-N{=}PR_3$, $-C{\equiv}N$, $-C{=}N{=}S$, OR) are synthesized using trimethylsilyl derivatives as reagents.

Interest in two coordinated phosphorus cations - the phosphenium ions -has grown substantially in recent years [1]. With few exceptions the majority of phosphenium ions $-P^+$ - has been prepared by phosphorus halogen bond heterolysis. Because of the great extend of the chemistry of such species there is a need to diversify the synthetic approach in order to increase the variety of environment around phosphorus.

The reaction of condensation involving silicon-nitrogen, silicon-oxygen or silicon-sulfur derivatives with covalent halides of boron, phosphorus and arsenic has proved to be very useful and is now a classical method. In a particular case, we recently demonstrated [2,3] that a reaction of this type occurs between the chlorophosphenium $\underline{1}$ and trimethylsilylazide :

$$[1] \quad \underset{\underline{1}}{iPr_2N\text{-}\overset{+}{P}\text{-}Cl^-\ \ AlCl_4^-} \xrightarrow{-Me_3SiN_3} \underset{\underline{2}}{iPr_2N\text{-}\overset{+}{P}\text{-}N_3\ \ AlCl_4^-}$$

The azido phosphenium cation $\underline{2}$ has been well characterized as an intermediate ($\delta^{31}P = 280$, at -30°C) ; it reacts on itself or on the chlorophosphenium 1 leading to bicationic species 3a and 3b.

$$iPr_2N-\overset{+}{P}-N=\overset{+}{P}\begin{smallmatrix}X\\ NiPr_2\end{smallmatrix} \quad 2AlCl_4^- \qquad \begin{matrix}\underline{3a} & X = N_3\\ \underline{3b} & X = Cl\end{matrix}$$

By addition of tri n-butylphosphine we have tried to stabilize the phosphenium azide 2 as the adduct 4a ; in this case a Staudinger reaction takes place at room temperature leading to the new phosphenium cation 5a with a tributylphosphazenyl group.

$$[2] \qquad \underset{\underline{4a}}{[n.Bu_3P-P(N_3)NPr^i_2]} \xrightarrow[\text{anion } AlCl_4^-]{-N_2} \underset{\underline{5a}}{n.Bu_3P=N-\overset{+}{P}-NPr^i_2}$$

The cation 5a can be obtained directly by addition of trimethylsilyl azide on the chlorophosphenium adduct 4b :

$$[3] \qquad \underset{\underline{4b}}{[n.Bu_3P-P(Cl)NPr^i_2]} \xrightarrow[\text{anion } AlCl_4^-]{+N_3SiMe_3} \underset{\underline{5a}}{n.Bu_3P=N-\overset{+}{P}-NPr^i_2} + N_2$$

Using triphenyl phosphine instead of $n.Bu_3P$, the phosphenium cation $Ph_3P=N-\overset{+}{P}-NPr^i_2$ 5b has been prepared by reaction [3]. This reaction is more complicated with $(Me_2N)_3P$; however the phosphenium cation 5c has been prepared easily by reaction [4] :

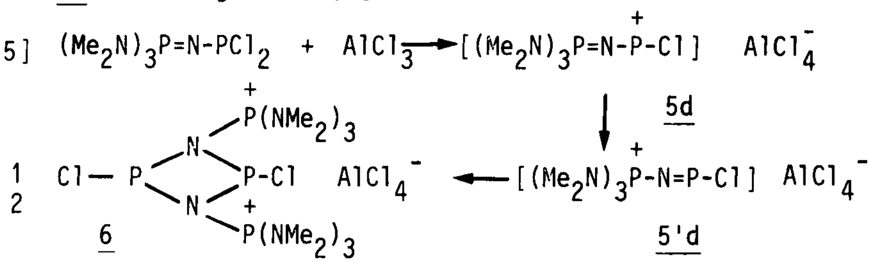
$$[4] \quad (Me_2N)_3P=N-SiMe_3 + Cl-\overset{+}{P}-NPr^i_2 \xrightarrow[\text{anion } AlCl_4^-]{-ClSiMe_3} \underset{\underline{5c}}{(Me_2N)_3P=N-\overset{+}{P}-NPr^i_2}$$

In connection with these phosphazenyl-phosphenium cations, the localisation of the positive charge, deserves to be discussed. So, there are at least three limiting structures for the compounds 5

$$\underset{(I)}{R_3P=N-\overset{+}{P}-NPr^i_2} \qquad \underset{(II)}{R_3\overset{+}{P}-N=P-NPr^i_2} \qquad \underset{(III)}{R_3P=\overset{+}{N}=P-NPr^i_2}$$

In view of the ^{31}P NMR parameters the structure (II) is the most likely. But the non-observation of the well known dimerization[4] of (II) suggests a strong participation of the limiting form (III) with a positive charge on the dicoordinated nitrogen atom.

Incidentally we have found one case where the structure (II)is clearly demonstrated from the attempt to prepare the chlorophosphenium 5d according scheme [5].

[5] 

The structure of the phosphenium cation 5d is that of the phosphonium salt 5'd which dimerizes, as expected, into the diazadiphosphetidine 6.

The preparation of other phosphenium cations (7, 11) has been investigated :

$$[6]\quad {}^{i}Pr_2N{-}\overset{+}{P}{-}Cl\ AlCl_4^- + Me_3Si{-}X \xrightarrow{-ClSiMe_3} {}^{i}Pr_2N{-}\overset{+}{P}{-}X\ \ AlCl_4^-$$

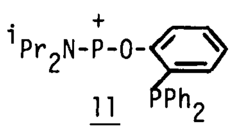
It is of interest to note that no reaction occurs when the Me_3Si-X reagent is added to the starting dichlorophosphine, ${}^{i}Pr_2N{-}PCl_2$, under the same conditions, namely at ambient, in dichloromethane.

$${}^{i}Pr_2N{-}\overset{+}{P}{-}NMe_2 \qquad {}^{i}Pr_2N{-}\overset{+}{P}{-}C{\equiv}N \qquad {}^{i}Pr_2N{-}\overset{+}{P}{-}N{=}C{=}S$$

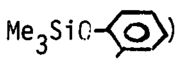
7 8 9

$${}^{i}Pr_2N{-}\overset{+}{P}{-}O{-}CH_2Bu^t$$

10



11

The cations, 7 and 8, have been isolated, whereas 9 and 10, are very unstable and were characterized only in solution. On the other hand in solution, 11 could not be synthesized using reaction [6]: the presence of the diphenyl phosphino group yields to a complicated redox reaction, similar to the one observed by Schmidpeter and al [5]. Thus the triphosphonium salt $(Ph_2ArP{-}P{-}PArPh_2)^+$ $AlCl_4^-$ (Ar = ) is formed among other products.

Finally the existence of the bis (dimethylamino) phosphenium cation with the triflic anion,[6] $CF_3SO_3^-$, encouraged us to use the trimethyl silyl triflate as reagent in presence of the bis (dialkylamino) chlorophosphine :

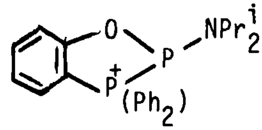
[7] $(R_2N)_2P\text{-}Cl + CF_3SO_3SiMe_3 \xrightarrow{-ClSiMe_3} (R_2N)_2\overset{+}{P}\ \ CF_3SO_3^-$

The phosphenium cations with R = Et, ^iPr, Me-N-CH_2-CH_2-N-Me, have been isolated and the spectroscopic data are the same as the corresponding compounds with $AlCl_4^-$ anion.

It is noteworthy to observe that the alkylamino dichlorophosphines $R_2N\text{-}PCl_2$, do not react with $CF_3SO_3SiMe_3$ even at high temperature ; however addition of $Me_3Si\text{-}C\ N$ in a CH_2Cl_2 solution containing both reagents $^iPr_2N\text{-}PCl_2$ and $CF_3\text{-}SO_3SiMe_3$, gives quantitatively the phosphenium cation 12 which differs from 8 only by the anion. Interestingly, addition of $ArPPh_2$ to a mixture of $^iPr_2N\text{-}PCl_2$ and $CF_3SO_3SiMe_3$ in CH_2Cl_2 solution, leads to aryloxy phosphonium-phosphine cation 13, with the formation of a P-P bond.

$^iPr_2N\text{-}\overset{+}{P}\text{-}C{\equiv}N\ \ \ CF_3SO_3^-$

12



$CF_3SO_3^-$

13

Other examples of this new class of cations have been described [7].

In conclusion we have shown that the use of silyl derivatives provides efficient synthesis of a great variety of original phosphorus cations such as the bis phosphocations (3a and 3b) the phosphazenylphosphenium ions (5a to 5d) and phosphonium-phosphine salt (13).

REFERENCES

1. A.H. Cowley and R.A. Kemp, Chem. Rev., 85, 367 (1985).
2. M.R. Marre, M. Sanchez and R. Wolf, J.C.S. Chem. Comm., 566, (1984).
3. M.R. Mare-Mazieres, M. Sanchez, J. Bellan and R. Wolf, Nouveau Journal de Chimie, 9, 605, (1985).
4. O.J. Scherrer, Nach. Chem. Tech. Lab., 28, 329, (1980).
5. A. Schmidpeter, S. Lochschmidt and W.S. Sheldrick, Angew. Chem. Int. Ed. Engl., 24, 226, (1985).
6. O. Dahl, Tetrahedron Letters, 23, 1493, (1982).
7. R. Bartsch, M. Sanchez and R. Wolf, Submitted to JCS Chem. Comm. (1986).