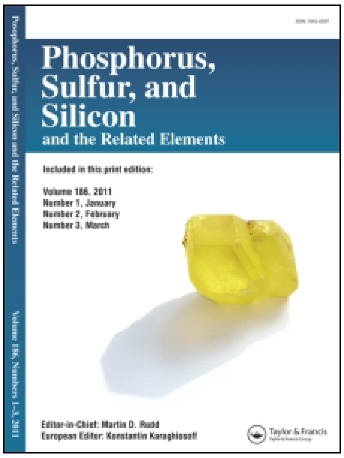

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SYNTHESIS OF NEW HETEROCYCLIC DIPHOSPHORUS MONOCATIONS:

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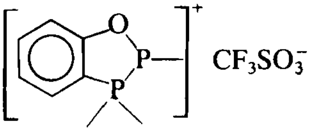
SYNTHESIS OF NEW HETEROCYCLIC DIPHOSPHORUS MONOCATIONS:



RAINER BARTSCH, MICHEL SANCHEZ and ROBERT WOLF
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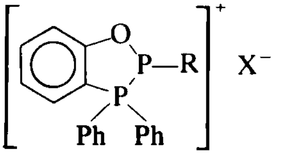
A novel synthetic method has been used to prepare a series of diphosphorus cations (**2**, **6**, **7**, **8**); from their ^{31}P NMR data, these derivatives can be considered as benzo diphospholane cations, but the chemical behaviour of **2** is in agreement with the reactivity of a masked phosphenium cation intramolecularly stabilized.

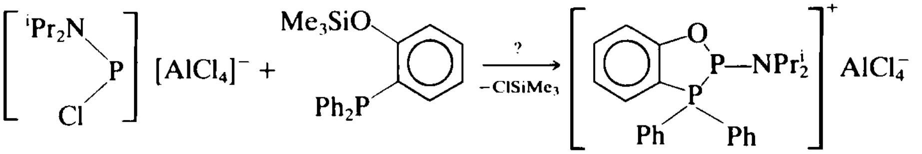
Phosphenium cations were first reported in 1972, and their structures and reactivities have been recently reviewed by Cowley and Kemp.[1] Following up our work in this field, we have observed that no alkoxy or aryloxy phosphenium derivatives such as $[RO—P—NR_2]^+$ or $[ArO—P—NR_2]^+$ have been isolated due to their great instability;[2] however the formation of stable adducts with bases such as phosphines[3] and amines[4] resulting from the Lewis acid properties of the phosphenium cations suggested to us, that the aryloxyphosphenium cations could be stabilized by an intramolecular P—P donor-acceptor bond:



(I)

We now report in this communication the synthesis of four derivatives of type (I) which are new heterocycles with mono cations involving two directly connected phosphorus atoms.

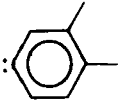
Firstly we have tried to take advantage of the good reactivity of dialkylamino chloro phosphenium cations, e.g. **1** towards silylated derivatives[2] to obtain the phenoxy phosphonium compound **2**



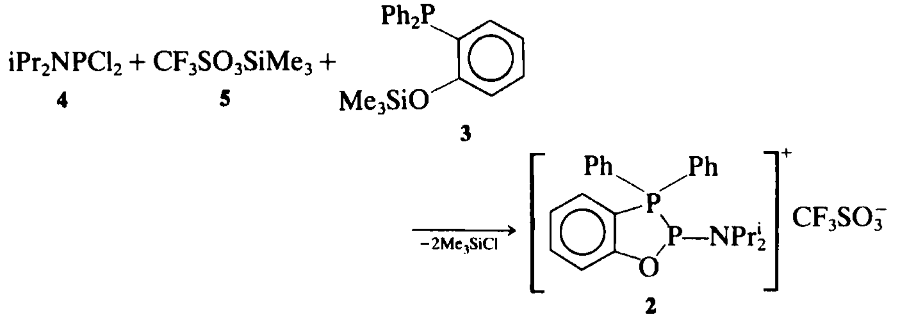
(1)

1 **2**

This experiment was completely unsuccessful; a complicated redox reaction similar to the one observed by Schmidpeter[5] in the $PCl_3/PPh_3/AlCl_3$ system occurred; among the products we have characterised by ^{31}P NMR are the phosphonium cation $(ArPPh_2Cl)^+$ ($\delta = +65$) and the triphosphenium salt $[Ph_2ArP—P—PPh_2Ar]^+$ $[AlCl_4]^-$ ($\delta_1 = 27.9$ $\delta_2 = -172.1$ $^1J_{PP} = 500$ Hz)

(Ar:  OSiMe₃).

In order to avoid the redox reaction due to the presence of $AlCl_3$ in the reaction media[6] we added the silylated reagent **3** to a mixture of the diisopropylamino dichlorophosphine **4** and trimethylsilyl trifluoro methanesulfonate **5**, since several new phosphenium cations were synthetized recently[7] following a similar scheme. Indeed the first benzo diphospholane cation was thus obtained, according to reaction (2).



(2)

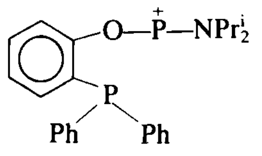
A typical one pot preparation proceeds as follows: a dichloromethane solution (15 ml) of both reagents **4** and **5** (6.67 mmol) is added slowly at room temperature to a CH_2Cl_2 solution of **3** (2.37 g, 6.67 mmol).

The progress of the reaction is followed by ^{31}P NMR; it is complete within 72 hours. The ^{31}P NMR spectra of the reaction mixture show the AX system expected for **2** (90%) and one singulet corresponding to an unknown by-product ($\delta = 51$) (10%). This impurity was eliminated by the addition of toluene and evaporation of the solvent. Compound **2** was obtained in a pure state as a hygroscopic white solid. Elemental analysis was satisfactory,[8] and ^{31}P, ^1H and ^{13}C NMR data are the following.

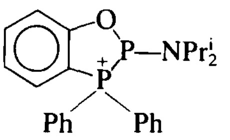
^{31}P (36.44 MHz, CH_2Cl_2, C_6D_6); AX system-$\delta_{P(A)} = 130.9$ doublet ($^1J_{P—P} = 382$ Hz) of triplets ($^3J_{P—H} = 13$ Hz, $\underset{\cdot}{P}NC\underset{\cdot}{H}$) $\delta_{P(X)} = -0.9$ (d, $^1J_{P—P} = 382$ Hz, $Ph_2ArP—$); ^1H (90 MHz, CD_2Cl_2) iPr_2 group: CH_3, $\delta = 1.26$ (d, $^3J_{H—H} = 6.5$ Hz), C—H $\delta = 3.38$ (nonuplet; $^3J_{H—H} = 6.5$ Hz, $^3J_{H—P} = 13$ Hz); $H_{arom.}$ $7 < \delta < 8$; ^{13}C (75.47 MHz, CH_2Cl_2, CD_3CO ext.); iPr_2N group: $\delta = 19.23$ (4C, s, CH_3), $\delta = 48.1$ (2C, s, CH); $CF_3SO_3^-$ $\delta = 121.5$ (1C, q, $^1J_{C—F} = 307.5$ Hz); $C_{arom.}$ $118.9 < \delta < 139.7$ (18 C, m.).

The high coupling constant, $^1J_{P—P} = 382$ Hz proves the existence of the P—P bond; further more the ^{31}P chemical shift, $\delta = 130$ ppm is characteristic of a tricoordinated phosphorus atom. These parameters are consistent with structure,

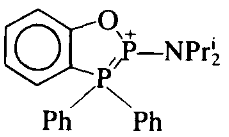
2, and not with the two other possibilities, **2a** and **2b**



2a

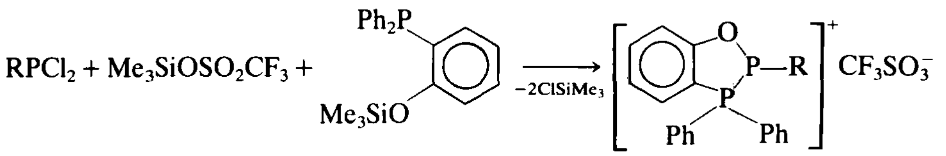


2



2b

Reaction (2) can be extended to the dichlorophosphines, $RPCl_2$ ($R = Ph$ and tBu) and even, surprisingly, to phosphorus trichloride, leading to the new benzodiphospholane salts (**6–8**)



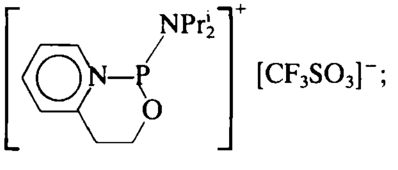
$R = Ph$, t.Bu, Cl

6–8

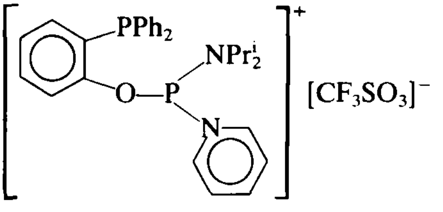
(3)

The ^{31}P NMR data are presented in the table.

Reactions (2) and (3) suggest a general applicability of this scheme, and we have synthetized the pyridinium phospholane **9**, ($\delta^{31}P = 159$ ppm)



9

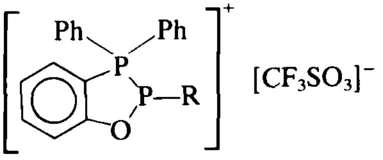


10

Certainly, the most interesting feature of this new class of cations should be their reactivity: they could react as masked phosphenium cations (**2a**) or as phosphines modified by a strongly electropositive group (form **2b**). The first

R	$\delta P(R)$	$\delta P(Ph_2)$	$^1J_{P-P}$(Hz)
$(iC_3H_7)_2N$	130.9	−0.9	385
C_6H_5	91.9	37.9	329
$t \cdot C_4H_9$	136.9	24.3	361
Cl	125.0	40.6	364

Table: ^{31}P NMR data compounds of type,



(CH_2Cl_2 solvent; ref. H_3PO_4).

experiments we have undertaken by progressive addition of pyridine in a CH_2Cl_2 solution of **2**, reveal the cleavage of the P—P bond and the formation of the expected pyridinium salt **10** ($\delta_1 = 156.5$ $\delta_2 = -17$; ${}^4J_{P-P} = 23.6\,Hz$). From this point of view the phosphonium cation **2** must be considered therefore an intramolecularly stabilized phosphenium cation, **2a**.

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$$(t\cdot BuCH_2O{-}PCl{-}NPr^i_2 + AlCl_3 \rightarrow [t\cdot BuCH_2O{-}\overset{+}{P}{-}NPr^i_2]AlCl_4^-,\ \delta = 297)$$

decomposes in CH_2Cl_2 solution, giving several tetracoordinated phosphorus derivatives.

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7. M. Sanchez, M. R. Mazières, R. Bartsch, R. Wolf, and J. P. Majoral, International Congress on Phosphorus Chemistry, Bonn, Sept. 1, 1986; *Phosphorus and Sulfur*, 1987, **30**, 487.
8. Anal. for: $C_{25}H_{28}F_3NO_4P_2S$

	C	H	N	P
Calc:	53.85	5.06	2.51	11.11
Found	52.30	5.05	2.48	10.41