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PHOSPHENIUM CATIONS/IMINOPHOSPHANE REACTIONS. SYNTHESIS OF A SPIRANIC AZADIPHOSPHIRANIUM CATION

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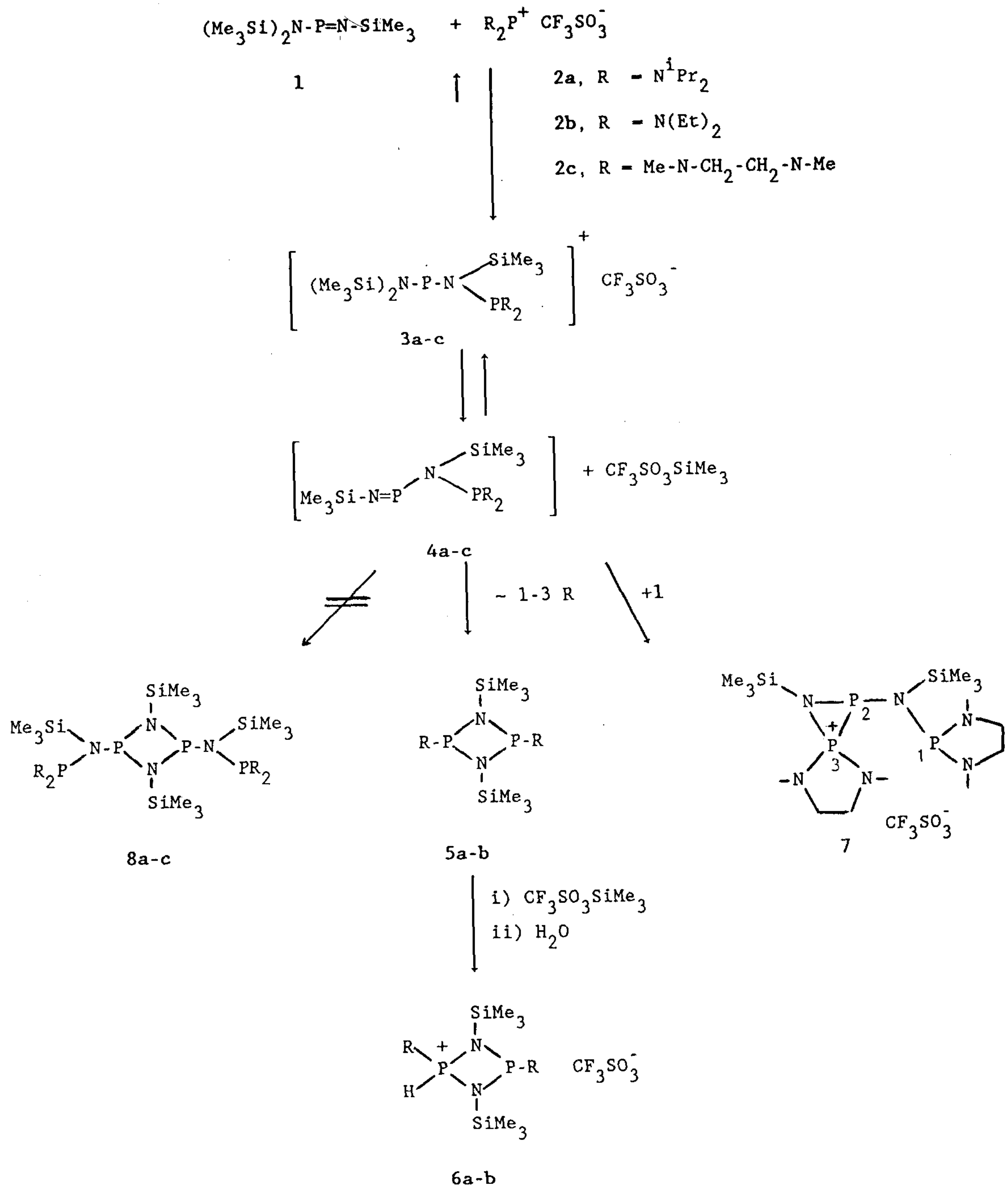
Abstract : The unexpected synthesis of the first spiranic azadiphosphiranium cation is reported, as well as a new entry to diazadiphosphetidine systems.

The versatile chemistry of cationic dicoordinated phosphorus species -phosphenium cations -has recently been the subject of intensive studies [1]. Their reactions with unsaturated organic molecules (dienes, alkynes etc.) afford various phosphorus containing heterocycles. Furthermore phosphenium cations were found to act as Lewis acids since they possess a formal positive charge and a sextet of electrons at phosphorus. These properties are exemplified by the reaction of cations **2a-c** with a neutral dicoordinated phosphorus derivative, the iminophosphane **1**, giving the diazadiphosphetidines **5a-b** or leading to the first charged spiranic compound 7 in which a cationic phosphorus acts as a spiro center between a three and a five membered ring.

Stoechiometric addition of cations **2a-b** to the iminophosphane **1** in dichloromethane at -70°C for 30 mn leads quantitatively to the cis 1,3,2,4 diazadiphosphetidines 5a-5b [2] isolated by pentane extraction in 80% yield. If the resulting mixture is stirred for two additional hours, the trimethylsilyl trifluoromethane sulfonate formed during the reaction reacts further with **5a-b** to give unstable silylated diazadiphosphetidinium cations which are quickly hydrolysed into the corresponding cationic P-H derivatives **6a-b** [3,4] isolated respectively in 60 and 40% yield.

A multi-step mechanism can be postulated to explain the formation of diazadiphosphetidines **5a-b** : i) transient generation of the acyclic cation **3a-b** resulting from the Lewis acid/base complex between the phosphenium cation and the iminophosphane **1** ii) formation of trimethylsilyl trifluoromethane sulfonate and of the iminophosphane-phosphine **4a-b** iii) unusual migration of a diisopropylamino or diethylamino group from the tricoordinated to the dicoordinated phosphorus atom of **4a-b** then cyclisation into the final four membered ring.

On the other hand the reaction of the cyclic phosphenium **2c** with derivative 1 affords the first spiranic aza diphosphirane cation 7 isolated in 30% yield. Interestingly the reaction is slower in this case : the formation of the acid/base adduct 3c is observed by ^{31}P NMR spectroscopy even at room temperature (δ = 209.7 and 190.1 broad lines) ; the transient formation of 4c can also be postulated, but here the migration of the amino group cannot. Indeed the electrophilic attack of the nitrogen phosphorus double bond by the cation **2c** takes place giving rise to 7 [5].


(Me3Si)2N-P=N-SiMe3
1
+ R2P+ CF3SO3-
2a, R = NiPr2
2b, R = N(Et)2
2c, R = Me-N-CH2-CH2-N-Me
CF3SO3-
3a-c
+ CF3SO3SiMe3
4a-c
- 1-3 R
+1
8a-c
5a-b
7
CF3SO3-
i) CF3SO3SiMe3
ii) H2O
CF3SO3-
6a-b

Surprisingly no dimerization of 4 occurs, the 1-3 amino migration in compounds 4a-b or the electrophilic attack of 4c by cation 2c being faster than the formation of dimers 8a-c. Such a behavior is in marked contrast with those of iminophosphane-iminophosphoranes which quickly dimerized even at low temperature into the corresponding diazadiphosphetidines [6].

The composition and constitution of 7 is mainly established from NMR data. The ^{19}F NMR spectrum confirms the presence of the $CF_3SO_3^-$ anion. The ^{31}P NMR spectra appears as a set of three doublet of doublets each phosphorus being coupled with the two others. The large $^1JP_2$-P_3 value (324.6 Hz) is typical for a σ dative P $\longrightarrow$ P bond [1,7] in which the phosphorus atom noted P_2 behaves as a Lewis acid.

In conclusion these reaction show the versatile behavior of phosphenium cations toward the iminophosphane 1. They provide a general synthetic pathway for the synthesis of unstable phosphenium ions or a stable spiranic diphosphiranium cation. Up to now only two examples of the transient generation of phosphenium from dicoordinated phosphorus derivatives were reported : Al_2Cl_6 attack of the phosphorus nitrogen double bond of 1 leading to acyclic and cyclic zwitterions [8] or protic attack of a diphosphene with formation of a phosphenium as the former product [9]. Extension of these reactions (presence or not of trimethylsilyl groups) is underway.

References

[1]. For a review see A.H. Cowley and R.A. Kemp, *Chem. Rev.*, 1985, 367.

2. All the spectroscopic data for 5a and 5b are in agreement with those reported in the literature [10]

[3]. 6a ^{31}P NMR (32.4 MHz, $CDCl_3$, 28 °C, external H_3PO_4) : δ P_1 90.50 (broad d. $^2JP_1$-P_2 = 36.6 Hz) P_2 0.60 (d.m ^1JP-H = 633.4 Hz, $^2JP_2$- P_1 36.6 Hz, ^3JP-H = 16.9 Hz). ^1H NMR (80 MHz, $CDCl_3$,28 °C, internal TMS) δ : 0.19 (s, $SiMe_3$, 9H) 0.21 (s, $SiMe_3$, 9H) 1.07 (d ^2JH-P = 6.70 Hz, N-C-$(CH_3)_2$,12H) 1.15 (d, ^2JH-P = 6.50 Hz, N-C$(CH_3)_2$,6H) 1.17 (d, ^2JH-P= 7.04, N-C$(CH_3)_2$, 6H) 2.87 and 3.52 (m, CH_2 4H). ^{19}F (84.6 MHz, CH_2Cl_2, 28°C, external CCl_3F) δ = 75.7.

6b ^{31}P NMR (32.4 MHz, $CDCl_3$, 28 °C, external H_3PO_4) : P_1 87.23 (broad d. JP_1-P_2= 38.9 Hz) P_2 10.10 (d.m. ^1JP-H $\simeq$ 651.1 Hz $^2JP_2$-P_1= 38.9 Hz ^3JP-H = 14.9 Hz) ^1H NMR (80 MHz, $CDCl_3$, 28 °C, internal TMS) δ : 0.30 (s. 18H, $SiMe_3$) 1.17 (t. ^3JH-H = 6.6 Hz, 6H, N-C- CH_3) 1. 27 (broad t. ^3JH-H = 6.7 Hz, 12H, N-C-CH_3) 3.26 (m. ^3JH-H = 6.6 Hz, ^3JP-H = 14.6 Hz, 8H,CH_2) 4.3, (d.d. ^1JH-P_2 = 651.1 Hz, ^3JH-P_1 = 4 Hz, 1H) ^{19}F (84.6 MHz) CH_2Cl_2, 28 °C,external CCl_3F δ = 75.4.

[4] Synthesis of a similar diazadiphosphetidine cation was recently reported via the acid catalyzed isomerisation of the [2+1] cycloadducts of iminophosphanes [11].

[5] 7 Selected spectroscopic data : $^{31}P|^{1}H|$ NMR (32.2 MHz, $CDCl_3$, 28°C, external H_3PO_4) δP_1 112.4 (d.d $^{2}JP_1$-P_2 = 42.8, $^{3}JP_1$-P_3 = 30 Hz), P_3 61.3 (d.d $^{1}JP_3$-P_2 = 325 Hz, $^{3}JP_3$-P_1= 30Hz), P_2 33.7 (d.d $^{2}JP_2$-P_1 = 42.8 $^{1}JP_2$-P_3 = 325 Hz). ^{1}H NMR (300 MHz, $CDCl_3$, internal TMS, 28°C) :δ 0.22 (s), and 0.25 (d., $^{4}J_{HP}$ = 1.3 Hz) (18 H, $SiMe_3$) 3.2 (m. N-CH_2, 8H) 2.67 (d. ^{3}JH-P_1 = 15 Hz, N-CH_3, 6H) 2.88 (d. ^{3}JH-P_3 = 9.7 Hz, N-CH_3, 3H) 2.79 (d.d ^{3}JH-P = 15 Hz,^{4}JH-P_2 = 4.6 Hz, NCH_3, 3H). ^{19}F (84.6 MHz, CH_2Cl_2, 28°C, external CCl_3F) 75.6.

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