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SPIROPHOSPHAZENES AND THE PARENT TRIAZAPHOSPHOLE : DIFFERENCE AND SIMILARITY IN CHEMICAL REACTIVITY

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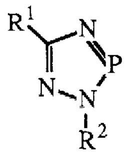
The first step of hydrolysis of compounds 1 , 2 and 4 involves the protonation of the P=N nitrogen atom. 3 does not react with water in the absence of a catalyst . Protonation of compounds 1 - 3 by a strong acid such as CF_3SO_3H is studied by ^{15}N and ^{31}P nmr spectroscopy. In all cases the P=N nitrogen appears to be the strongest basic site .

Introduction

We reported recently the synthesis of spirophosphazenes[1] 2, 3, and 4 . That was done on the supposition that they might react in different ways because of electronic and structural effects. Some differences and similarities are now shown by a study of the first steps of their hydrolysis and protonation by a strong acid.



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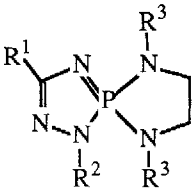

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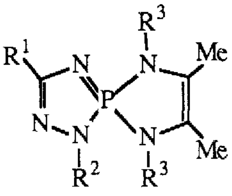

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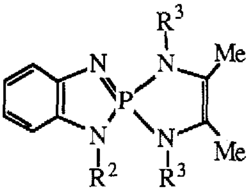

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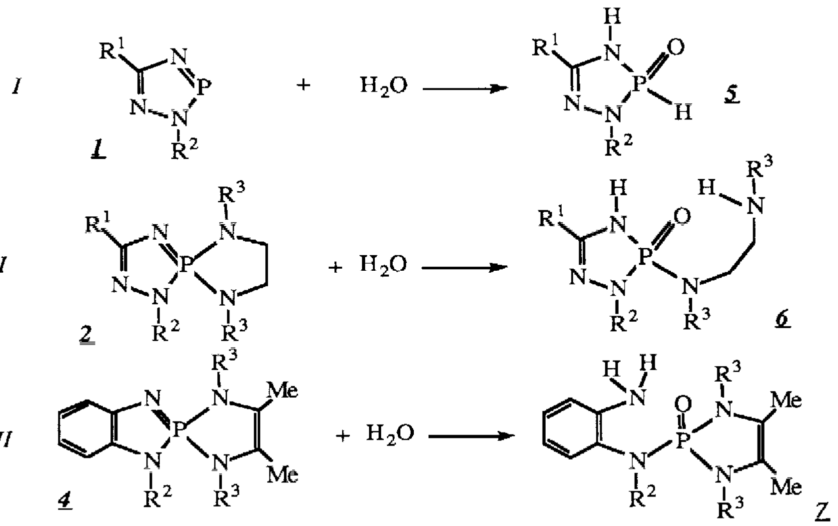
Results and Discussion

HYDROLYSIS:

At room temperature 1 [2], 2 and 4 instantaneously react with water (reactions *I*, *II* and *III*). On the other hand 3 does not react with water unless a strong acid such as HCl is used to catalyse the reaction. This results in the formation of several unidentified phosporus compounds.

The fact that the phosphole ring is readily opened in 4 and preserved in 3 cannot be explained solely by a difference of aromaticity. As a matter of fact , the bare triazaphosphole 1 is readily opened[2]. Obviously there is a stabilization due to the diaza ring in 3 . This stabilization does not have the same extent in both 4 and 3 . This is supported by the fact that compound 2 , which does not have a double bond in its diaza ring , reacts readily with water . On the other hand 3 does not react with water.

Although the hydrolysis process might change from one compound to another , these differences prompted us to make them react with a strong acid such as CF_3SO_3H .



REACTION OF 1 AND 2 AND 3 WITH CF_3SO_3H

The expected reaction is the protonation of the strongest basic sites of these compounds, which should be nitrogen atoms. All the reactions performed were exothermic. The reactive basic site was determined by ^{15}N nmr. The two strongest basic nitrogen atoms were identified in 2 and 3 by adding two molar equivalents of acid to a solution of each compound. ^{15}N nmr spectra of these solutions were scanned before and after each addition. ^{15}N and ^{31}P chemical shifts and some coupling constants are given in Table I[3].

Analysis of the spectra shows that the P=N nitrogen atom N^3 is the strongest base in 1 , 2 and 3 . In fact, in all cases, after addition of one equivalent of acid this nitrogen atom N^3 chemical shift change is at least six times larger than that of the other nitrogen atoms. e.g. in 2 : $|\Delta(\delta^{15}N^3)| = 36.8$ ppm and $|\Delta(\delta^{15}N^2)| = 4.2$ ppm.

As far as the first protonation site is concerned comparison with the hydrolysis process is easy. Supposing that the protonation of N^3 is the first step of the hydrolysis of 1 and 2 and 3 , the latter can be considered as a base weaker than both of the formers as it does not react with water. It should be noticed that N^3 is the hardest basic site in 1 as it is the reactive site with BF_3 , $R\overset{+}{C}=O$ and Pt and Pd complexes[4].

After addition of the second equivalent of CF_3SO_3H , the chemical shift of N^1, in 2 and 3 changes at least twelve times more than that of the other nitrogen atoms. e.g. in 2 : $|\Delta(\delta^{15}N^1)| = 93.5$ ppm and $|\Delta(\delta^{15}N^2)| = 7.5$ ppm.

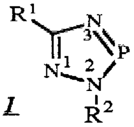
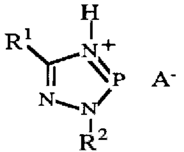
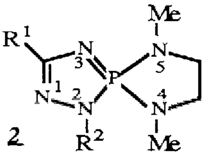
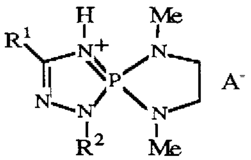
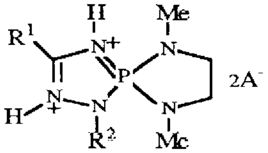
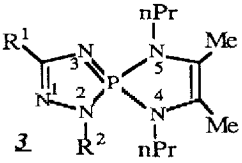
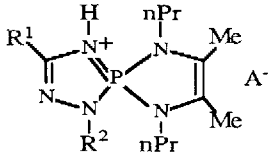
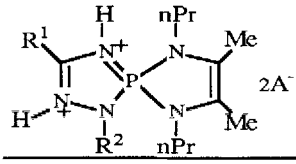
Also the ^{31}P chemical shift change extent in this two step protonation is approximately the same for 2 and 3 . These results are irrelevant in the hydrolysis process but they mean that compounds 2 and 3 behave in the same way in the presence of a strong acid .

It can be inferred from their chemical shift that nitrogen N^4 and N^5 have more sp^2 character in 3 than in 2 :

$\delta^{15}N^4 = \delta^{15}N^5 = -343.1$ ppm in 2 and $\delta^{15}N^4 = \delta^{15}N^5 = -294.4$ ppm in 3 .

This could be accounted for by a partial involvement of N^4 and N^5 lone pairs in a conjugation with the p electrons of the C=C double bond and their partial delocalization into the phosphorus atom unoccupied d orbitals in 3 . This can make the phosphorus atom less electrophilic in 3 than in 2 . N^4 and N^5 should be less basic in 3 than in 2 .

Table I : ^{15}N and ^{31}P nmr chemical shifts (ppm) and coupling constants $J_{P\text{-}N}$ (Hz)
Coupling constants are in parentheses $R^1 = C_6H_5$ $R^2 = Me$ $A^- = CF_3SO_3^-$

	N^1	N^2	N^3	N^4	N^5	P
 1	- 40.8 (5.9)	- 114.9 (86.7)	-97.3 (87.6)			252.9
	-49.8	- 113.9 (80.7)	- 186.6 (70.6)			232.7
 2	- 109.9 (2.71)	- 270.2	- 254.9 (31.2)	- 343.1 (27.1)	- 343.1 (27.1)	54.7
	- 110.9 (11.9)	- 274.4 (20.9)	- 291.7 (33)	- 345.2 (35.2)	- 345.2 (35.2)	37.2
	- 204.4	- 276 (16.3)	- 284.2 (32.6)	- 341 (40.7)	- 341 (40.7)	31.9
 3	- 112.3 (3.3)	- 262.6 (8.11)	- 249.1 (33.2)	- 294.4 (23.8)	- 294.4 (23.8)	50
	- 113.2 (10.5)	- 268 (16.8)	- 284.6 (31.5)	- 295.5 (29.6)	- 295.5 (29.6)	30.5
	- 198.7	- 272.3 (19.8)	-279 (26.9)	- 292.1 (34.7)	- 292.1 (34.7)	24.1

It can be inferred from all these results that **3** is less basic and less electrophilic than **2** . For that reason , whatever the first step of the hydrolysis process may be, either the protonation of one nitrogen atom or the nucleophilic attack of H_2O oxygen upon the phosphorus atom , **3** will be less reactive with water than **2** anyway.

Experimental data : All the spectra were run in dichloromethane if not stated otherwise.^{15}N nmr spectra were recorded on a BRUKER WM250 ($NaNO_3$ as external reference),$Cr(acac)_3$ was used as a relaxation agent in 8 to 10. 10^{-2} molar ratio. ^{31}P and ^{13}C and ^{1}H nmr spectra were recorded on a BRUKER AC80 . All the reactions were performed at room temperature. The required amounts of water or acid were added dropwise to the stirred solutions of phosphorus compounds . ^{31}P nmr spectra of the mixtures show that all the reactions are instantaneous.

5 : R^1=Ph R^2= Me (CDCL3) ^{31}P nmr $\delta = 10.4$ ppm $^1J_{P\text{-}H} = 677$ Hz ; ^{1}H nmr δ 3.2 (d, 3H , $C\underline{H}_3N$, $^3J_{P\text{-}H} = 8.2$ Hz) 7.1 through 7.8 (5H, $C_6\underline{H}_5$) 8.6 (1H, P-H , $^1J_{P\text{-}H} = 677$ Hz) 9.3 (1H , P-N-$\underline{H}$, $^2J_{P\text{-}H} = 16.2$Hz)

6 : R^1=Ph $R^2 = R^3$ =Me ^{31}P nmr $\delta = 21$ ppm ; ^{1}H nmr δ 2.3 (d, 3H , $CH_2NC\underline{H}_3$, $^3J_{PH} = 11$Hz) 2.33 (s, 3H, CH_3NH) 3.1 (d,3H,CH_3NN,$^3J_{PH} = 6.9$ Hz) 2.5 through 3 (CH_2CH_2) 6.5 (NH) 7.1 through 8.2 (5H, C_6H_5) ; ^{13}C nmr δ 32.3 (d, CH_3NN, $^2J_{CP} = 11.5$ Hz) 33.2 (d , $\underline{C}H_3NCH_2$, $^2J_{CP} = 5.4$ Hz) 35.9 (s, $HNCH_3$) 48.9(d, CH_2PN $^2J_{CP} = 4.8$ Hz) 49.5 (s, $HNCH_2$) 144.1 (d, C=N, $^2J_{CP} = 19.5$ Hz) 125 to 130 (C_6H_5)

7 : R^2= Et R^3 =Ph (C_6D_6) ^{31}P nmr $\delta = 20$ ppm; ^{1}H nmr δ 0.56 (t, 3H, $C\underline{H}_3CH_2$, $^3J_{HCCH} = 7.1$ Hz) 1.7 (s,6H, $C\underline{H}_3CNC_6H_5$) 3.1 (q, 2H, $CH_3C\underline{H}_2$, $^3J_{HCCH} = 7.1$ Hz, $^3J_{HP} = 8.9$ Hz) 3.0 (m,NH_2) 6.3 through 7.7 (9H, $C_6\underline{H}_5$ and $C_6\underline{H}_4$) ; ^{13}C nmr δ 11.6 (d, $\underline{C}H_3CNC_6H_5$, $^3J_{CP} = 5.04$ Hz) 13.9 (d , $\underline{C}H_3CH_2$, $^3J_{CP} = 3.98$ Hz) 42.6 (d, $CH_3\underline{C}H_2$, $^2J_{CP} = 5.76$ Hz) 146.2 (d, NC=CN , $^2J_{CP} = 3.8$ Hz) 115 through 147 (C_6H_5 , C_6H_4)

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