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CHARACTERISATION OF THE PARENT PHOSPHOLE AND PHOSPHOLYL ANION AND SOME OF THEIR C-SUBSTITUTED DERIVATIVES BY ^{1}H AND ^{13}C NMR SPECTROSCOPY

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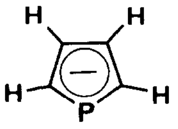
Summary : *The parent phosphole and phospholyl anion as well as some C-substituted derivatives have been characterized by ^{1}H and ^{13}C NMR spectroscopy for the first time ; the two most noteworthy features are the absence of $^{3}J(\underline{H}\text{-}P\text{-}C\text{-}\underline{H})$ couplings for the phospholes and the huge $^{1}J(C\text{-}P)$ couplings for the phospholyl anions.*

Although they are known for many years now [1], phospholyl anions such as 1 have never been characterized by any spectroscopic technique except ^{31}P NMR spectroscopy [2,3]. This is undoubtedly due to their high reactivity and to the difficulty in obtaining them in the pure state . Indeed, they are generally prepared by cleavage of the P-Ph bond of 1-phenylphospholes by alkali metals [1] and thus, are accompanied by phenyl by-products . This situation is obviously unsatisfactory since these anions are both theoretically and practically very interesting [4] . On the other hand, P-unsubstituted phospholes including the parent species 2 have been unambiguously characterized for the first time only very recently [3] . They are obtained by protonation of phospholyl anions at low temperatures and readily rearrange to give 2$\underline{H}$-phosphole [4 + 2] dimers via an easy [1,5] sigmatropic shift of hydrogen from phosphorus to carbon [3] . As phospholyl anions, they have only been characterized by ^{31}P NMR spectroscopy . Very recently, we have devised a technique which allows the preparation of pure phospholyl anions [5] and, consequently, of pure P-H phospholes (eq. 1) .



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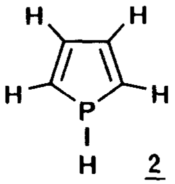

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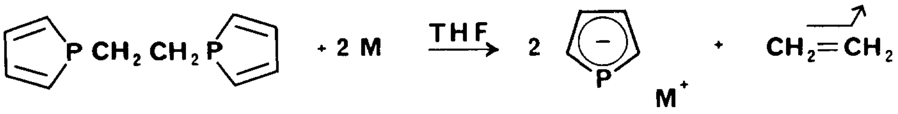

(1)

M = Li , Na , K

This opportunity prompted us to investigate in depth these species by ^{1}H and ^{13}C NMR spectroscopy . The results of this study are reported in Tables I - IV (δ in ppm + for down-field shifts, ref. Me_4Si or H_3PO_4, J in Hz) .

Table I - NMR data : C-unsubstituted phospholes

R	Ph [a]	Li [b]	H [c]
	(CD_2Cl_2)	(C_4H_8O + C_4D_8O)	(C_4D_8O at 183°K)
$\delta\ H_\alpha$	6.94	6.78	7.10
$\delta\ H_\beta$	7.00	6.62	7.33
$^{2}J(H_\alpha - P)$	38.7	40.76	39.8
$^{3}J(H_\beta - P)$	14.5	6.42	14.33
$^{3}J(H_\alpha - H_\beta)$	7.2	5.61	7.05
$^{3}J(H_\beta - H_{\beta'})$	2.2	2.43	2.3
$^{4}J(H_\alpha - H_{\beta'})$	1.1	1.23	1.04
$^{4}J(H_\alpha - H_{\alpha'})$	2.7	3.56	2.78
$\delta\ C_\alpha$	135.78	129.71	131.15
$\delta\ C_\beta$	137.51	119.74	140.68
$^{1}J(C_\alpha - P)$	4.5	46.6	6.1
$^{2}J(C_\beta - P)$	8	4.5	6.1
$\delta\ ^{31}P$	+ 6.57	+ 77.2	- 49.2

[a] The ^{13}C data of 1-phenylphosphole have already been reported [6]

[b] The sodium and potassium derivatives give very similar data

[c] $\delta(P\underline{H})$: 5.19 ; $^{3}J(H_P...H_\alpha)$ 0 ; $^{4}J(H_P...H_\beta)$ 2.3 ; $^{1}J(H\text{-}P)$ 233.1

Table II - NMR data : 3,4-dimethyl-substituted phospholes

R	Ph [a]	Li [b]	H [c]
	($CDCl_3$)	(C_4H_8O + C_4D_8O)	(C_4D_8O at 183°K)
$\delta\ H_\alpha$	6.45	6.36	6.53
$\delta(C\underline{H}_3)$	2.09	2.11	2.24
$^{2}J(H_\alpha - P)$	38.4	39.7	39.8
$^{4}J(C\underline{H}_3...P)$	3.0	0	2.5
$^{4}J(C\underline{H}_3...H)$	0.7	0	-
$\delta\ C_\alpha$	129.47	128.68	124.56
$\delta\ C_\beta$	148.63	127.89	152.18
$\delta\ (\underline{C}H_3)$	17.46	17.42	18.12
$^{1}J(C_\alpha - P)$	4	44	2.4
$^{2}J(C_\beta - P)$	7.8	4.7	6.1
$^{3}J(\underline{C}H_3...P)$	4	0	3.7
$\delta\ ^{31}P$	- 2.5	+ 55.8	- 59.4

[a] The ^{13}C data of 1-phenyl-3,4-dimethylphosphole have been reported elsewhere [7]

[b] These data have been already reported [5]

[c] $\delta(P\underline{H})$: 4.92 ; $^{3}J(H_P...H_\alpha)$ 0 ; $^{5}J(H_P...C\underline{H}_3)$ 2.8 ; $^{1}J(H\text{-}P)$ 215.5

From these data, it is clear that P-unsubstituted phospholes closely resemble P-substituted phospholes as far as ^{1}H and ^{13}C NMR spectroscopy are concerned . We have already discussed the magnitude and the temperature dependence of the $^{1}J(H\text{-}P)$ coupling constants in these species [3] . The only new fact which appears in these Tables concerns the absence of coupling between the protons at phosphorus and at the α-carbons [8] . This $^{3}J(H\text{-}H)$ coupling constant very likely follows a Karplus-like relationship with the H-C-P-H dihedral angle . Thus, this absence of coupling is almost certainly related to the pyramidality at phosphorus which means that this angle is close to 90° . More differences appear between phospholes and phospholyl anions . The most significant one is undoubtedly the drastic increase of the $^{1}J(C\text{-}P)$ coupling constant which is observed when comparing a phosphole and the corresponding phospholyl anion . This increase is certainly related to the increase of the C-P bond order due to the strong aromaticity of phospholyl anions [9] . Indeed, the recent work on phosphaalkenes clearly demonstrates that $^{1}J(C\text{-}P)$ coupling constants increase with the C-P bond order [10]. On the other hand, the β carbons appear to be significantly shifted to high fields in phospholyl anions . It must be recalled here that phospholes more or less behave as vinylphosphines

Table III - NMR data : 2,5-diphenyl-substituted phospholes

R	Ph ($CDCl_3$)	Li (C_4H_8O + C_4D_8O)	H [a] (C_4D_8O at 213°K)
$\delta\ H_\beta$	-	6.92	-
$^3J(H - P)$	-	3.7	-
$\delta\ C_\alpha$	151.58	149.43	146.9
$\delta\ C_\beta$	131.98	118.53	128.28
$^1J(C_\alpha - P)$	0	33.8	0
$^2J(C_\beta - P)$	8.5	0	5
$\delta\ ^{31}P$	+ 0.32	+ 78.75	- 54.16

[a] $\delta(P\underline{H})$: 5.50 ; $^4J(H_P...H_\beta)$ 2.5 ; $^1J(H\text{-}P)$ 227

Table IV - NMR data : 2,3,4,5-tetramethyl-substituted phospholes

R	Ph [13] ($CDCl_3$)	Li (C_4H_8O + C_4D_8O)	H [a] (C_4D_8O at 183°K)
$\delta(\alpha\ C\underline{H}_3)$	1.93	2.18	2.17
$\delta(\beta\ C\underline{H}_3)$	1.93	1.98	2.03
$^3J(\alpha C\underline{H}_3...P)$	10.0	10.2	10.7
$^4J(\beta C\underline{H}_3...P)$	3.6	0	2
$\delta\ C_\alpha$	135.1	134.49	129.89
$\delta\ C_\beta$	142.89	124.84	145.58
$\delta\ (\alpha\ \underline{C}H_3)$	12.7	16.27	13.87
$\delta\ (\beta\ \underline{C}H_3)$	13.85	14.08	14.24
$^1J(C_\alpha - P)$	0	39.7	0
$^2J(C_\beta - P)$	11	0	9.8
$^2J(\alpha\underline{C}H_3...P)$	22.2	29.2	22.0
$^3J(\beta\underline{C}H_3...P)$	2.0	0	2.0
$\delta\ ^{31}P$	+ 12.71	+ 63.02	- 37.0

[a] $\delta(P\underline{H})$: 4.81 ; $^5J(H_P...\ \beta C\underline{H}_3)$ 2.4 ; $^1J(H\text{-}P)$ 207.3

in some cases [11] . This means that the double bonds of phospholes are polarized as follows : $^{+\delta}C_\beta \overset{\cdots}{=} C_\alpha{}^{-\delta} - P$. The aromaticity of phospholyl anions destroys this polarization . Moreover, the coefficients of the π_p HOMO are higher at C_β than at C_α according to theoretical calculations [9b] . Hence, this shielding may be another consequence of the aromaticity of these anions .

Experimental data

The 3,4-dimethylphospholyl anion is synthesized according to eq. 1 . The synthesis is more precisely described in ref. 5 . The parent phospholyl anion is made in the same way . The starting 1,2-bis(phospholyl)ethane has the following characteristics : $\delta^{31}P$ + 9.96 in CD_2Cl_2 ; δH_α 6.76, δH_β 7.03, $\delta C\underline{H}_2$ 1.76 ; $^2J(H_\alpha - P)$ 37.1, $^3J(H_\beta - P)$ 15.3 , $^3J(H_\alpha - H_\beta)$ 7.2, $^4J(H_\alpha - H_{\beta'})$ 1.1, $^4J(H_\alpha - H_{\alpha'})$ 2.8, $^3J(H_\beta - H_{\beta'})$ 2.3 ; δC_α 133.87, δC_β 137.90, $\delta \underline{C}H_2$ 20.0, $^1J(C_\alpha - P)$ 7.3, $^2J(C_\beta - P)$ 7.7 .

Anal. Calcd for $C_{10}H_{12}P_2$: C, 61.86 ; H, 6.18 . Found : C, 62.10 ; H, 6.08 .

The 2,5-diphenylphospholyl anion is obtained via the cleavage of the P-P bond of bis(2,5-diphenylphospholyl) [12] . The 2,3,4,5-tetramethylphospholyl anion is made via the cleavage of 1,4-bis(2,3,4,5-tetramethylphospholyl)butane obtained from 1-phenyl-2,3,4,5-tetramethylphosphole [13] by following the technique depicted in ref. 5 . All the cleavage reactions are run in THF or THF d_8 at room temperature . The protonation of the anions is carried out by CF_3CO_2H (1.5-1.8 eq.) at 183°K, the concentration of the solution is about 0.1 M .

Acknowledgement

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