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Nuclear Magnetic Resonance Structural Study of Phosphonate Anions

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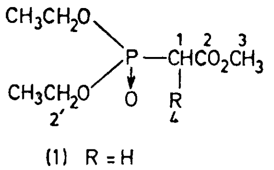
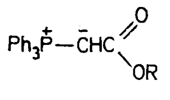
Summary It is shown by ^{31}P, ^{13}C, and ^{1}H n.m.r. spectroscopy that $Bu^{n}Li$ and the phosphonates (1) and (2) in tetrahydrofuran give a single, planar, charge-delocalized species (A), whereas $Bu^{t}OK$ and $Bu^{t}OLi$ and (1) give another species (B) in addition to (A); the structure proposed for (B) is analogous to that of the lithium adducts of phosphorus ylides.

In order to explain the reactivity of phosphonate anions, depending on the associated cation,[1] we have studied by n.m.r. spectroscopy the structure of the species formed in tetrahydrofuran (THF) solution from the phosphonates (**1**) and (**2**) with $Bu^{n}Li$, $Bu^{t}OLi$ and $Bu^{t}OK$ (0·5M solution).



(1) R = H

(2) R = Me



(3)

While the action of $Bu^{n}Li$ leads to single species (**1A**) or (**2A**), the action of $Bu^{t}OLi$ and $Bu^{t}OK$ leads not only to species (**A**), but also to (**B**), the relative ratio (**A**):(**B**) depending on the cation (Li^+ 65:35, K^+ 35:65 at room temperature). The main n.m.r. parameters of these species are in Tables 1 and 2.

In going from the phosphonates (**1**) or (**2**) to the corresponding species (**A**), the following are apparent: a large low-field shift for ^{31}P and a smaller one for C(1) and C(2), and a very large increase in $^{1}J_{PC(1)}$, a large increase in $^{2}J_{PC(2)}$ and $^{1}J_{C(1)H}$, and the appearance of the long-range four-bond coupling $^{4}J_{PC(3)}$.

These results, more specifically the increase in $^{1}J_{C(1)H}$ and $^{1}J_{PC(1)}$, are in line with a change in hybridization of C(1) which becomes planar. Previous results[2] have shown that on going from C–H to C–Li $^{1}J_{CH}$ decreases when carbon remains sp^3 hybridized but increases when it becomes sp^2. Furthermore, a low-field shift of the lithiated carbon resonance is also observed in the latter case. An increase, though smaller, in $^{1}J_{PC(1)}$ has been observed when comparing phosphonium salts with the corresponding ylides, the carbon atom of which being known to be planar.[3,4]

Furthermore, the value of $^{4}J_{PC(3)}$ suggests a W geometry of the four bonds and we attribute to species (**A**) the (*ZZ*) delocalized structure shown. Such a structure is in line with proposals made for related phosphorylated species from i.r. studies[5] and for β-dicarbonyl anionic species from ^{1}H n.m.r. spectra.[6]

In going from the phosphonate (**1**) to species (**1B**)† the following differences are observed compared with (**1A**): smaller low-field ^{31}P and C(1) shifts, and a very small

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† In the case of (2), ^{1}H n.m.r. spectra show that anion formation is incomplete with $Bu^{t}OLi$ or $Bu^{t}OK$.

TABLE 1. Chemical shifts

	δ(H–2′)	δ(^{31}P)^{a}	Δδ(^{31}P)	δC(1)	ΔδC(1)	δC(2)	δC(3)	δC(2′)
(**1**)	4·08	18·6	—	34·5	—	166·7	52·1	62·5
(**2**)	4·06	22·3	—	39·8	—	170·4	52·1	62·7
(**1A**), Li^{+b}	3·95	38·7	+20·1	41·0	+6·5	175·8	50·0	60·6
(**2A**), Li^{+}	3·85	38·9	+16·6	48·0	+8·2	173·3	49·7	60·2
(**1B**), Li^{+}	4·12	27·9	+9·3	36·3	+1·8	171·8	49·9	63·3
(**1B**), K^{+}	4·12	27·9	+9·3	37·6	+3·1	170·7	49·6	62·2

[a] δ(^{31}P) values were determined by double resonance ^{1}H–{^{31}P} experiments and calculated according to the method of R. M. Le-Quan, M. J. Pouet, and M. P. Simonnin, *Org. Magnetic Resonance*, 1975, **7**, 392. [b] Similar parameters were obtained for (**1A**), K^{+}.

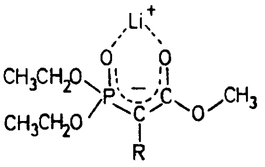
TABLE 2. Coupling constants

	$^{1}J_{PC(1)}$	ΔJ	$^{2}J_{PC(2)}$	ΔJ	$^{2}J_{PC(4)}$	$^{4}J_{PC(3)}$	$^{1}J_{C(1)H}$	ΔJ
(**1**)	132·9	—	5·8	—	—	a	130	
(**2**)	132·5	—	5·0	—	6·3	a	—	—
(**1A**), Li^{+b}	223·1	+90·2	21·7	+15·9	—	3·6	154·4	+24·4
(**2A**), Li^{+}	219·2	+86·7	28·6	+23·6	8·8	2·4	—	—
(**1B**), Li^{+}	134·4	+1·5	3·4	−2·4	—	a	c	—
(**1B**), K^{+}	129·8	−3·1	4·0	−1·8	—	a	c	

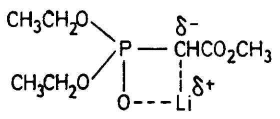
[a] Not resolved. [b] Similar parameters were obtained for (**1A**), K^{+}. [c] Not determined owing to the relative instability of species (**1B**).

change in $^{1}J_{PC(1)}$, a small decrease in $^{2}J_{PC(2)}$, and no long-range coupling $^{4}J_{PC(3)}$. These parameters are not compatible with an (*EZ*) planar charge-delocalized form. However, Gray[7] has interpreted the n.m.r. parameters of ester ylides in terms of an important contribution of the charge-localized form (**3**).

Morover, lithium-associated phosphorus ylides[3,4,8] have been assigned charge-localized adduct structures, with a P–C–Li angle of 90°. For these species, $^{1}J_{PC}$ and the ^{31}P shift are of the same order of magnitude as in the corresponding phosphonium salt. Taking these data into account we propose for (**1B**) the charge-localized structure shown with an Li^{+}–O interaction in order to interpret the ^{31}P downfield shift we have observed.



(A)



(B)

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