

Structural Studies of Carbanionic Species Formed from Phosphonates: Anions of Diethyl Benzyl- and Cyanomethylphosphonates

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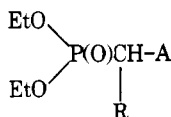
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The structure of anionic species formed from diethyl benzyl- and cyanomethylphosphonates (2 and 3) has been determined by ^1H , ^{13}C , ^{31}P , and ^7Li NMR. From $^1J_{\text{PC}}$, $^1J_{\text{CH}}$, and δ_{C_1} values, as well as the sign of $^2J_{\text{PH}}$, it appears that the anionic carbon is planar and bears a high negative charge, as the corresponding carbon of salt-free P ylides. Some charge delocalization into the phenyl ring takes place for the benzylic derivative $2\text{A}, \text{Li}^+$; however, such a conjugation with the CN group is less efficient for $3\text{A}, \text{M}^+$. In the nitrile case, the cation and solvent effect study shows that loose ion pairs are formed in Me_2SO while in THF and pyridine more or less aggregated tight ones exist. On going from tight ion pairs to loose ones, there is no loss of C_1 planarity as the decrease in $^1J_{\text{CH}}$ is accompanied by an increase in $^1J_{\text{PC}}$.

The reaction of anionic species formed from phosphonates 1 toward aromatic aldehydes or α -enones has been



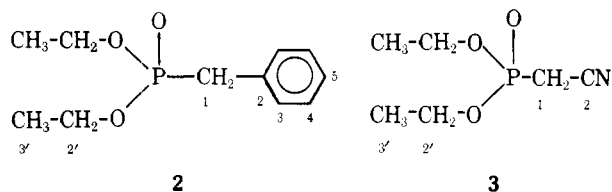
1, R = H, CH_3 ; A = CN

studied in one of our laboratories.¹ It has been observed that the stereoselectivity and regioselectivity of these reactions are highly dependent upon the nature of the cation associated to the base used to generate the anionic species. Therefore, the possibility of the presence of different structural forms has been raised.

Moreover, the structure of phosphorus ylides, which leads to the same type of reactions with carbonyl compounds, has been widely investigated recently. It has been shown that the carbon atom adjacent to phosphorus of these reagents is planar or nearly so by X-ray determination.² However, ^{13}C NMR and photoelectron spectroscopy³⁻⁷ studies indicate a substantial negative charge on this adjacent carbon, which was quite unexpected.

Therefore, it seemed interesting to investigate the structure of anionic species formed from diethyl phosphonates to determine both if there is any relationship between the reagent structure in solution and its chemical reactivity and if the structure of these species is as peculiar as the ylidic one.

In the present paper, we study two types of anionic species in solution by ^1H , ^{13}C , ^{31}P , and ^7Li NMR spectroscopy: one is formed from diethyl benzylphosphonate (2) in order to point



out the influence of the $(\text{EtO})_2\text{P}(\text{O})$ moiety on the charge delocalization into a phenyl ring; the other is formed from diethyl cyanomethylphosphonate (3), which was used in our previous studies.¹ In this latter case, we shall examine the associated cation (Li^+ , K^+ , cryptated K^+) and the solvent (THF, pyridine, Me_2SO) influences on the anionic species structures.

Previously, from a ^1H NMR study in pyridine and IR in the

solid state, Kirilov and Petrov⁸ concluded that several different anionic species can coexist from 3. We have recently published a preliminary communication⁹ on the structure of related anionic species formed from diethyl carbomethoxymethylphosphonate; this study is still under investigation.

Results

The anionic species have been prepared in the same way as for the chemical study: by the action of *n*-BuLi on 2 and *n*-BuLi, LiOt-Bu, or KOt-Bu on phosphonate 3 dissolved in the required protio or deuterated solvent (THF, Me_2SO , or pyridine). [2.2.2]cryptand (1.2 equivalents) was eventually added after formation of the K^+ associated anion. Solution concentrations are from 0.25 to 0.5 M; no important change is observed in this range. Furthermore, these solutions are generally stable at room temperature under anhydrous conditions in an argon atmosphere (up to 5 days), though in some cases precipitation is observed after several hours in THF.

(A) ^1H , ^{13}C , and ^{31}P NMR Spectra. ^{31}P chemical shifts were determined by double resonance $^1\text{H}\{^{31}\text{P}\}$ experiments.¹⁰ By irradiation at a single ^{31}P frequency, the H_1 doublet and H_2 multiplet give rise, respectively to a singlet and a quartet. In some cases, the relative signs of $^1J_{\text{PC}_1}$ and $^2J_{\text{PCH}_1}$ have been obtained by off-resonance $^{13}\text{C}\{^1\text{H}\}$ experiments.¹¹ From ^{13}C proton-coupled and off-resonance decoupled spectra, it is evident that C_1 bears one proton in the anion.

(1) Anionic Species 2A from Diethyl Benzylphosphonate. Using *n*-BuLi in THF or in THF-HMPA (5 or 8 equiv), a single species is observed. ^1H , ^{31}P , and ^{13}C chemical shifts are summarized in Table I and the coupling constants in Table II. Our figures for diethyl benzylphosphonate (2) are very close to those published by Ernst¹² and Gray,¹³ though the spectra were run in a different solvent.

The main features of our results are the following. On going from 2 to 2A, one can notice (a) an upfield shift in H_5 , H_1 , C_3 , and C_5 , a small change in the C_1 chemical shift according to the solvent, and a downfield shift in ^{31}P resonance and (b) a great increase in $^1J_{\text{PC}_1}$ and $^1J_{\text{C}_1\text{H}}$, an increase in $^2J_{\text{PC}_2}$ and $^3J_{\text{PC}_3}$, and a slight change in $^2J_{\text{PC}_2}$ and $^3J_{\text{PC}_3}$. The $^2J_{\text{PCH}_1}$ and $^1J_{\text{PC}_1}$ coupling constants bear the same sign in 2A and have opposite signs in 2.

In the presence of HMPA, the signals are better resolved so that a $^4J_{\text{PC}_4}$ coupling can be observed.

(2) Anionic Species 3A from Diethyl Cyanomethylphosphonate. Using a hexane solution of *n*-BuLi, dried or sublimated LiOt-Bu, or KOt-Bu, a single species is formed

Table I. Chemical Shifts^a of Diethyl Benzylphosphonate (2) and Anionic Species 2A, Li⁺

compd	solvent (base)	$\delta_{31\text{P}}$	δ_{H_1}	δ_{H_5}	δ_{H_2}	δ_{C_1}	δ_{C_2}	δ_{C_3}	δ_{C_4}	δ_{C_5}	δ_{C_6}	δ_{C_7}	concn, M $\frac{\text{H}}{^{13}\text{C}}$
2	THF	25.0	3.06 ₆	~7.24	3.91 ₂	34.1 ₃	133.4 ₃	130.5 ₆	128.7 ₃	127.0 ₂	61.9 ₆	16.6 ₇	0.5 0.5
2A, Li ⁺	THF	44.7	2.24 ₂	6.00	3.87 ₇	34.4 ₇	149.4 ₁	119.5 ₇	128.0	112.2 ₄	60.2 ₇	17.0 ₈	0.25 0.5
	(<i>n</i> -BuLi)	(+19.7)	(-0.82 ₄)	(~-1.24)	(-0.03 ₅)	(+0.3 ₄)	(+15.9 ₈)	(-1.1)	(-0.7 ₃)	(-14.7 ₈)	(-1.6 ₉)	(+0.4 ₁)	
2A, Li ⁺	THF ⁻	40.1	2.29 ₂	5.74	3.85	38.7 ₇	151.5 ₃	118.7 ₃	127.3 ₀	108.6 ₂	58.3 ₆	17.3 ₆	0.4 0.4
	HMPA ^b												
	(<i>n</i> -BuLi)	(+15.1)	(-0.77 ₄)	(-1.50)	(-0.06 ₂)	(+4.6 ₄)	(+18.1 ₀)	(-11.8 ₃)	(-1.4 ₃)	(-18.4 ₀)	(-3.6 ₀)	(+0.6 ₉)	

^a δ_{H} and $\delta_{^{13}\text{C}}$ are in parts per million from internal Me₄Si; $\delta_{31\text{P}}$ is in parts per million relative to external H₃PO₄ (85%). Positive δ values are in the direction of increasing frequency. ^b 8 equiv.

in the three solvents used.⁴⁰ By addition of a few drops of water anion **3a** is not protonated, though addition of two drops of CF₃COOH in the NMR tube gives back only **3**. ¹H, ³¹P, and ¹³C chemical shifts are summarized in Table III and the coupling constants in Table IV. The ¹³C parameters of the nitrile **3** are similar to those previously published without solvent.¹³

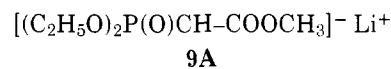
In pyridine-*d*₅, the ¹H spectrum exhibits a well-resolved upfield doublet which has been assigned to H₁ by a ³¹P decoupling experiment. Such a doublet is not observed in Me₂SO-*d*₆; this lack of signal is due to an H-D exchange with solvent, as (a) the formation of partially protiated Me₂SO is observed, (b) the ¹³C spectrum shows that the C₁ doublet is further split into 1:1:1 triplets due to a C-D coupling, and (c) when the anion is generated in protiated Me₂SO, the H₁ doublet is effectively observed; it collapses into a singlet by ³¹P irradiation.

In THF or THF-*d*₈, the H₁ signal is never observed; the C₁ doublet is observed only when noise decoupling of protons is performed. This phenomenon is due to proton exchange, as a broad doublet of doublets can be detected when the ¹³C proton-coupled spectrum is run at -40 °C (**3A**, Li⁺) or at room temperature (**3A**, K⁺). This exchange process did not allow the accurate determination of ¹J_{C₁H₁} in this solvent. As it is not possible to run high temperature spectra in THF, we could not determine if such an exchange involves traces of starting material, dianion, or some species formed from the solvent. Up to our knowledge, such an exchange has not been observed for any lithiated species in THF.

In the presence of [2.2.2]cryptand, all of the different signals can be observed either in the ¹H or ¹³C spectra. Let us quote that in these conditions a better resolution is achieved, and the nonequivalence of the two H₂ protons can be seen in pyridine (ABK₃ system with ³¹P irradiation).

On going from **3** to **3A** the main features of our results are the following: (a) a large upfield H₁ shift in pyridine and Me₂SO even when K⁺ is cryptated; (b) an upfield shift in C₁, and a downfield shift in ³¹P and C₂, the latter being weakly affected by cation and solvent changes; and (c) a great increase in ¹J_{PC₁} (90-100 Hz depending on the associated cation and the solvent), a great increase in ¹J_{C₁H} (25-30 Hz), but no noticeable change in ²J_{PC₂}. As previously, there is a slight change in ²J_{PC₂} and ³J_{PC₃}. Furthermore, ¹J_{PC₁} and ²J_{PCH₁} are of opposite sign in **3** while they bear the same sign in **3A**.

(B) ⁷Li NMR Spectra. The ⁷Li chemical shifts of **2A**, M⁺, **3A**, M⁺, and **9A**, M⁺ (M⁺ = Li⁺) for comparison are reported in Table V in THF and Me₂SO, except for **2A** as the anion could not be generated by the action of *t*-BuOLi on **2** in the latter solvent. All of the signals appear at higher field than the reference values (external LiCl in D₂O 1 M), though they are at lower field than LiClO₄ (0.5 M) in the same solvent. While the three species have different chemical ⁷Li shifts in THF, though very close, **3A** and **9A** have the same chemical shift in Me₂SO.



Discussion

Due to the high concentration used in this work, the species observed are mainly ion pairs which can be more or less aggregated. The improved resolution of the signals in the presence of either HMPA or cryptand suggests the breaking of these aggregates.

It is generally admitted¹⁴ that ¹J_{CH} values mainly depend upon carbon hybridization. For instance, when comparing hydrocarbons and the corresponding organolithium compounds, a flattening of the lithiated carbon induces an increase in ¹J_{CH} (Ph₂CH₂ → Ph₂CHLi). However, a decrease in ¹J_{CH}

Table II. Coupling Constants (Hz) of Diethyl Benzylphosphonate (2) and Anionic Species 2A, Li⁺

compd	solvent (base)	¹ J _{PC₁}	² J _{PC₂}	³ J _{PC₃}	⁴ J _{PC₄}	⁵ J _{PC₅}	² J _{PC_α}	³ J _{PC_β}	² J _{PH₁}	¹ J _{C₁H₁}	concn, M ¹ H ¹³ C	
2	THF	+137.4 ^a	8.7	7.2	2.5	3.6	6.2	5.9	-21.7 ^a	127.0	0.5	0.5
2A, Li ⁺	THF	+224.8 ^b	13.5	15.7	c	<1.2	3.7	8.1	+17.8 ^b	150.5	0.25	0.5
	(<i>n</i> -BuLi)	(+87.4)	(+4.8)	(+8.5)			(-2.5)	(+2.2)	(+39.5)	(+23.5)		
2A, Li ⁺	THF-	+226.6 ^b	12.8	16.0	1.8	<1.2	4.0	8.1	+17.8		0.4	0.4
	HMPA											
	(<i>n</i> -BuLi)	(+89.2)	(+4.1)	(+8.8)	(-0.7)		(-2.2)	(+2.2)	(+39.5)			

^a From ¹³C {¹H} off-resonance experiments, ¹J_{PC₁} and ²J_{PH₁} are of opposite sign in phosphonate 2. ^b From ¹³C {¹H} off-resonance experiments, ¹J_{PC₁} and ²J_{PH₁} bear the same sign in anionic species 2A, Li⁺. ^c Unresolved.

has been interpreted in terms of no hybridization change but an increase of effective nuclear charge (CH₄ → CH₃Li). This conclusion is in agreement with X-ray determinations, which indicate that the lithiated carbon is indeed pyramidal for C₂H₅Li.¹⁵

The ¹³C NMR data concerning tetracoordinated phosphorus compounds indicate that ¹J_{PC} is mainly dependent upon carbon hybridization,^{3-6,10a,16} more specifically, a comparison of phosphonium salts with the corresponding ylides, the C₁'s of which are planar,² shows a great increase in ¹J_{PC}.³⁻⁶ By theoretical calculations, Albright¹⁶ directly related the magnitude of this coupling constant with the percent *s* character in the hybrid orbital on the carbon comprising the P-C bond.

Furthermore, literature data^{3a,17} indicate that the sign of ²J_{PCH} depends upon the central carbon hybridization: if this carbon is sp³ hybridized, ²J_{PCH} is negative;^{17a} if it is sp² hybridized, ²J_{PCH} is positive.^{17b-d} As for tetracoordinated phosphorus derivatives, ¹J_{PC} is positive, whatever the carbon hybridization is.^{3a,10a,17a,18} It follows that ¹J_{PC} and ²J_{PCH} will be of opposite sign if the carbon is sp³ hybridized and of the same sign if it is sp² hybridized.^{3a}

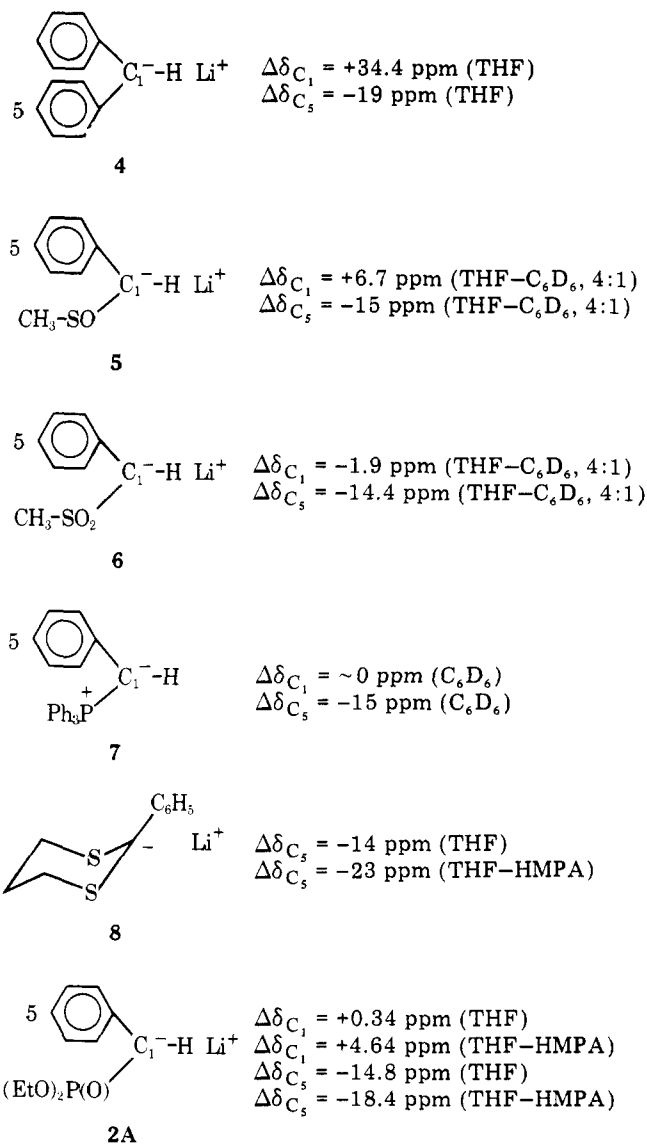
Therefore, we have three criteria at our disposal to evaluate the planar or pyramidal geometry of the anionic carbon: Δ¹J_{PC}, Δ¹J_{CH}, and the sign of ²J_{PCH}.

For a carbon atom, in a given hybridization state, numerous attempts have been made to correlate ¹³C shift with electron density.¹⁹ However, this has been strongly questioned recently, but it seems that the validity of such a correlation is well established for para carbons of aromatic rings;²⁰ we shall then discuss the values of the other ¹³C chemical shifts in a qualitative way.

(A) **Lithiated Diethyl Benzylphosphonate (2A).** The three criteria, based on coupling constants, all indicate that the carbanionic C₁ is planar. Therefore, it can safely be compared with diphenylmethyl lithium (4),^{21a,b} lithiated sulfoxide 5²² or sulphone 6,²² and phosphorus ylide 7,^{5c,6d} for which C₁ is also planar. For a comparison of these various species, we shall examine the chemical shift differences (Δδ) between the lithiated or ylidic species and the parent protonated ones.

If the chemical shifts variations in C₁ and C₅, as indicated, are very similar for 2A, 6, and 7, slightly different for 5, they are quite different from those of diphenylmethyl lithium (4). In this latter case, C₁ is strongly shifted to lower field while the high field shift of the two equivalent para carbons suggests that the negative charge is strongly delocalized into the aromatic rings (2Δδ_{C₅} = -38 ppm). For 2A, 5, and 6, it seems that charge delocalization from C₁ to the aromatic ring is rather limited; the C₁ chemical shifts of 2A, 5, and 6, imply that these sp² hybridized carbons should bear a large amount of negative charge.

In the case of 2A, the loosening of anion-cation interaction by HMPA addition induces a slight low field shift in C₁ and a high field shift in C₅, but smaller than that observed by Eliel²³ for dithiane anion 8. Therefore, the presence of a



phosphoryl moiety α to the carbanionic carbon inhibits somewhat charge delocalization into an aromatic ring, an effect which is reminiscent of the ylidic case 7^{5c,6d} and might suggest a P⁺-C⁻ type of stabilization of these two kinds of species as proposed by Bernardi, Wolfe, and co-workers by ab initio calculations.²⁴ Such an analogy is in line with the ³¹P chemical shift, as we observe an important downfield shift on going from 2 to 2A (+20 ppm), which could partly be attributed to a positive charge increase. On going from a phosphonium salt to the corresponding ylide, where no P hybridization or important charge changes occur, one observes a slight high field ³¹P shift (-5 to -10 ppm).^{5c,25}

The HMPA addition effect shows that in THF there is an interaction of Li⁺ with the p C₁ orbital which polarizes the π

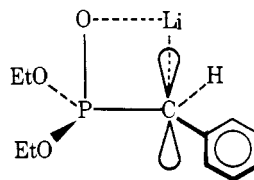
Table III. Chemical Shifts^a of Diethyl Cyanomethylphosphonate (3) and Anionic Species 3A, M⁺

compd	solvent (base)	δ_{31P}	δ_{H_1}	δ_{H_2}	δ_{C_1}	δ_{C_2}	$\delta_{C_2'}$	$\delta_{C_3'}$	concn, M $\frac{[H]}{[C]}$
3	THF	15.0	3.13	4.17 ₄	15.8 ₈	113.9 ₆	63.6 ₉	16.5 ₉	
	py-d ₅	15.4	3.67	4.22 ₂	16.3 ₀	114.5 ₅	63.5 ₉	16.3 ₄	0.26 0.51
	Me ₂ SO-d ₆	15.9	3.55	4.12	14.9 ₅	114.4 ₆	62.8 ₁	16.0 ₃	0.25 0.47
3A, K ⁺	THF	44.1 (+29.1)	3.89 ₄ (-0.28)	3.89 ₄ (-0.28)	3.4 ₉ (-12.3 ₉)	135.1 ₆ (+21.2)	60.8 ₂ (-2.8 ₇)	16.7 ₆ (+0.1 ₇)	0.25 1.0
	(t-BuOK)	44.7 (+29.3)	1.51 (-2.16)	4.11 ₆ (-0.10 ₆)	3.9 ₁ (-12.3 ₉)	134.9 ₃ (+20.4 ₄)	60.5 ₆ (-3.0 ₃)	16.6 ₁ (+0.2 ₇)	0.25 0.5
	(t-BuOK)	43.0 (+27.6)	1.61 (-2.06)	4.35 ₄ ^b (+0.13 ₂)	4.4 ₃ (-11.8 ₇)	131.9 ₃ (+17.3 ₈)	59.6 ₀ (-3.9 ₉)	17.0 ₈ (+0.7 ₄)	0.25 0.5
3A, Li ⁺	Me ₂ SO	41.9 (+26.0)	0.66 (-2.89)	3.76 ₅ (-0.35 ₅)	3.5 ₇ (-11.3 ₈)	131.3 ₆ (+16.9)	58.8 ₀ (-4.0 ₁)	16.3 ₉ (+0.3 ₆)	0.37 0.5
	(t-BuOK)	41.8 (+25.9)		3.74 (-0.38)	3.5 ₇ (-11.3 ₈)	130.8 ₂ (+16.3 ₆)	58.5 ₆ (-4.2 ₅)	16.4 ₅ (+0.4 ₂)	0.37 0.5
	(t-BuOK)	42.8 (+27.8)		3.94 ₁ (-0.23 ₃)	3.3 ₇ (-12.5 ₁)	132.8 ₀ (+18.8 ₄)	60.5 ₉ (-3.1 ₀)	16.8 ₄ (+0.2 ₆)	0.5 0.37
3A, Li ⁺	THF	42.4 (+27.4)		3.93 (-0.24 ₄)	3.5 ₁ (-12.3 ₇)	132.6 ₂ (+18.6 ₅)	60.6 ₂ (-3.0 ₇)	16.8 ₇ (+0.2 ₈)	0.25 0.37
	Me ₂ SO	41.6 (+25.7)	0.70 ₄ (-2.84 ₆)	3.79 ₅ (-0.32 ₅)	3.3 ₈ (-11.5 ₇)	130.6 ₄ (+16.1 ₈)	59.0 ₄ (-3.7 ₇)	16.3 ₄ (+0.3 ₁)	0.37 0.5
	(t-BuOLi)								

^a δ_{H_1} and δ_{H_2} are in parts per million from internal Me₄Si; δ_{31P} is in parts per million relative to external H₃PO₄ (85%). Positive δ values are in the direction of increasing frequency. ^b Inequivalent; ² J_{AB} = -10.2₇ Hz. ^c Run in the presence of 1.2 equiv of [2.2.2]cryptand.

system toward this carbon,²⁶ thus accounting for its shielding in the absence of HMPA. However, from ⁷Li chemical shifts, the possibility of an interaction with the aromatic π system, according to literature data for benzyl lithium,^{14b} can be ruled out as a high field ⁷Li shift for related compounds is not observed in the present case.^{14b,27}

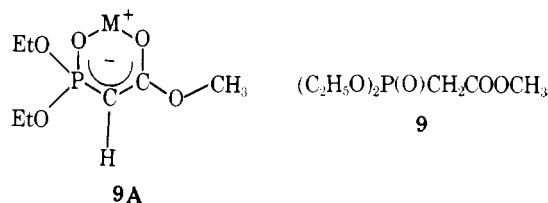
Therefore, in THF a structure analogous to α -lithio sulfonides²⁸ can be assigned, probably involving an O...Li inter-



action, as evidenced by the upfield ³¹P chemical shift observed when weakening ion pair interaction which occurs on HMPA addition.

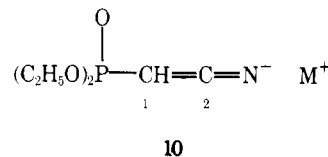
(B) Anionic Species 3A from Diethyl Cyanomethylphosphonate. The results, on the whole, especially the very large increase in ¹ J_{PC} (90–100 Hz) and ¹ J_{CH} (25–30 Hz) when compared to starting material 3 as well as the ² $J_{PC,H}$ sign change, show that C₁ is planar or nearly so in 3A, M⁺.

The large upfield shift of this sp² carbon atom (δ_{C_1} 3.5, $\Delta\delta$ = -12 ppm) indicates that C₁ bears a large electron density. A further confirmation that the high shielding of C₁ is mainly due to a charge increase and not to a ΔE variation comes from the fact that H₁ proton shielding also increases ($\Delta\delta_{H_1}$ = -2 to -3 ppm). The C₁ negative charge appears to be higher in 3A than in 2A ($\Delta\delta_{C_1}$ = +4 to ~0 ppm, $\Delta\delta_{H_1}$ = -0.8 ppm). This result is suggesting that the CN moiety is less efficient than Ph in delocalizing the negative charge; it is also less efficient than the ester group, as we have shown⁹ that for chelate 9A

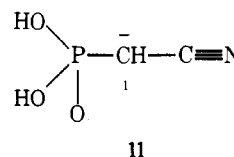


C₁ is shifted downfield (+5–6 ppm) when compared to starting material 9. Such a poor electron-withdrawing effect for the CN moiety has already been observed in the ¹³C NMR spectrum of the cyanobenzyl carbanion.²⁹

From the C₂ chemical shift in 3A, M⁺, it appears that the contribution of the resonance allenic form 10, as suggested by Kirilov and Petrov,⁸ seems to have a negligible weight since this carbon should be strongly deshielded.³⁰



An ab initio calculation of species 11 also indicates that when



C₁ is planar, the nitrile bond remains short, as expected for a triple bond (1.17 Å).³² The ³¹P chemical shift variation to low field ($\Delta\delta$ = 25–30 ppm) suggests that there is some positive charge on this atom, though an angular change can also intervene.³⁹ The fact that the screening constants decrease for ³¹P, C₂, and C₃ but increase for C₁ and C₂ favors a charge alternating structure³³ such as 12.

Table IV. Coupling Constants (Hz) of Diethyl Cyanomethylphosphonate (3) and Anionic Species 3A,M⁺

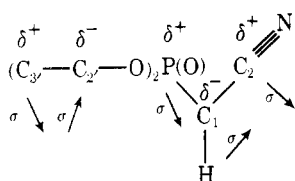
compd	solvent (base)	¹ J _{PC₁}	² J _{PC₂}	² J _{PC_{2'}}	³ J _{PC_{3'}}	² J _{PH₁}	¹ J _{C₁H₁}	concn, M	
								¹ H	¹³ C
3	THF	+141.7	11.3	6.1	5.3	-21.1	135.4		
	py- <i>d</i> ₅	+140.4	11.3	6.2	5.3	-20.8		0.26	0.51
	Me ₂ SO- <i>d</i> ₆	+138.8 ^a	11.1	6.3	6.0	-20.8 ^a		0.25	0.47
3A,K ⁺	THF (<i>t</i> -BuOk)	233.5 (+91.8)	12.4 (+1.1)	4.9 (-1.2)	7.5 (+2.2)		166 (+30.6)	0.25	1.0
	py- <i>d</i> ₅ (<i>t</i> -BuOK)	234.0 (+93.6)	12.0 (+0.7)	5.0 (-1.2)	7.5 (+2.2)	+5.1 (+25.9)	163.8 (+28.4)	0.25	0.5
	py- <i>d</i> ₅ ^c (<i>t</i> -BuOK)	+236.5 ^b (+96.1)	10.8 (-0.5)	5.0 (-1.2)	7.5 (+2.2)	+5.0 ^b (+25.8)	160.8 (+25.4)	2.8	0.25
	Me ₂ SO (<i>t</i> -BuOK)	+235.5 ^b (+96.7)	11.0 (-0.1)	5.0 (-1.3)	7.2 (+1.2)	+5.0 ^b (+25.8)	161.3 (+25.9)	2.9	0.37
	Me ₂ SO ^c (<i>t</i> -BuOK)	235.7 (+96.9)	10.3 (-0.8)	5.0 (-1.3)	7.2 (+1.2)		160.4 (+25.0)	0.37	0.5
	THF (<i>n</i> -BuLi)	242.5 (+100.8)	12.5 (+1.2)	4.9 (-1.2)	7.5 (+2.2)			0.5	0.37
3A,Li ⁺	THF (<i>t</i> -BuOLi)	241.8 (+100.1)	11.7 (+0.4)	4.5 (-1.6)	7.5 (+2.2)			0.25	0.37
	Me ₂ SO (<i>t</i> -BuOLi)	238.7 (+99.9)	11.2 (+0.1)	5.2 (-1.1)	7.5 (+1.5)	+4.9 (+25.7)	161.5 (+26.1)	3.1	0.37

^a From ¹³C {¹H} off-resonance experiments, ¹J_{PC₁} and ²J_{PH₁} are of opposite sign in phosphonate 3. ^b From ¹³C {¹H} off-resonance experiments, ¹J_{PC₁} and ²J_{PH₁} bear the same sign in anionic species 3A,K⁺. ^c Run in the presence of 1.2 equiv of [2.2.2]cryptand.

Table V. ⁷Li Chemical Shifts ^a of 2A,Li⁺, 3A,Li⁺, and 9A,Li⁺

compound solvent	LiClO ₄		2A,Li ⁺	3A,Li ⁺		9A,Li ⁺	
	THF	Me ₂ SO	THF ^b	THF ^b	Me ₂ SO ^c	THF ^b	Me ₂ SO ^c
δ	-1.0	-1.3	-0.5	-0.9	-0.3	~0	-0.3
W _{1/2} (Hz)	2.5	2.5	11	6.5	8.5	<5	7

^a δ_{Li} is in parts per million from external LiCl/D₂O (c = 1 M). Negative δ values are in the direction of decreasing frequency. Concentrations are 0.5 M in the indicated solvent. ^b *n*-BuLi was used to generate the anion. ^c *t*-BuOLi was used to generate the anion.



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This fits with Bell's proposal³¹ that anions α to nitriles should be stabilized by an electrostatic >C^{δ-}—δ⁺C≡N^{δ-} interaction rather than by charge delocalization into the triple bond. However, the infrared vibration ν P → O is nearly the same for 3 and 3A,M⁺;³⁴ this lack of variation is not in accordance with a P⁺—O⁻ structure for the 3A,M⁺ phosphoryl moiety. This disagreement between NMR and IR results remains still unexplained.

The cation and solvent effects are not very large, but it is known that NMR parameters are not very sensitive to these phenomena.^{26,38}

(1) In the case of K⁺ as the associated cation, the NMR parameters of the anionic moiety are similar in Me₂SO in the absence and presence of [2.2.2]cryptand as well as in pyridine in the presence of [2.2.2]cryptand. Therefore, in these cases, the anion-cation interaction is weak, indicative of a loose ion pair in Me₂SO. In THF and pyridine, the variations of the parameters suggest the presence of more or less aggregated tight ion pairs.

¹J_{PC} and ¹J_{CH} variations indicate that for loose ion pairs Δ¹J_{PC} is maximum (+97 Hz) while Δ¹J_{CH} is minimum (+25 Hz); the reverse is true for tight ion pairs (Δ¹J_{PC} = +92 Hz, Δ¹J_{CH} = +30.6 Hz). At first sight, the decrease in ¹J_{CH} on going from tight ion pairs to loose ones could have been attributed to a pyramidalization of C₁.^{14b} However, the parallel increase in ¹J_{PC} is not consistent with such an interpreta-

tion.^{2b,16} Both variations indicate a change in the valency angles around C₁, which still remains planar.

The C₂ and ³¹P chemical shift variations on going from loose to tight ion pairs might be due either to deaggregation phenomena or to intramolecular effects, and they are difficult to discuss at the present time.

(2) In the case of Li⁺ as the associated cation, the parameters of the anionic species in Me₂SO are very close to those of 3A,K⁺ in the same solvent; one is also dealing with loose ion pairs, a fact which is confirmed by ⁷Li chemical shifts, which are independent of the associated anion nature. However, ¹J_{PC} is a little larger than with K⁺ (3 Hz). It is even larger in THF, although it is minimum when M = K⁺. This anomalous behavior is in contrast with C₂ chemical shift variation, the Δδ of which increases for both 3A,Li⁺ and 3A,K⁺ on going from Me₂SO to THF. Both trends suggest that the cation-anion interaction is different for the two kinds of tight ion pairs; the interaction of Li⁺ with the CN group should probably be stronger than with K⁺, in line with previous results of the literature on Li⁺ affinity for nitriles³⁵ and on the effect of the CN moiety on the structure of Na⁺ and Li⁺ 9-cyano-fluorenyl ion pairs in THF or DME.³⁶

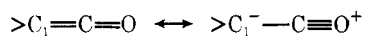
Conclusion

From NMR results, it appears that the stable phosphonate carbanions formed from benzyl- (2) and cyanomethyl phosphonates (3) have structures which are analogous to P ylides; C₁ is planar and bears a high negative charge, with the pπ-dπ interaction, if it exists, being unable to promote an effective charge delocalization.^{3c} The stabilization of these species seems to involve a P⁺—C⁻ interaction.²⁴ Such a structure is rather unexpected in light of the usual concepts of organic chemistry as it is generally admitted that the stability of charged species increases with charge delocalization.

The benzylic species 2A,Li⁺ structure is very similar to the

lithiated benzyl sulfoxide one^{22,28} in THF. Though the C₁ carbon is planar, its negative charge is only partly delocalized into the aromatic ring, even in the presence of HMPA.

In the nitrile case, the anion keeps nearly the same geometry whatever the associated cation and solvent are. The C₁⁻-δ⁺C₂≡Nδ⁻ moiety has a structure which is very reminiscent



of ketenes and diazoalkanes,³⁰ with the C₁ nucleus nearly as strongly shielded as that of ketene (δ_{C₁} 2.5).

In Me₂SO, 3A, M⁺ are loose ion pairs, while in pyridine and THF they are tight and more or less aggregated in the range of concentrations used.

In THF, the location of the cation seems to be different for Li⁺ and K⁺. This leads to an interpretation of the different stereoselectivities we previously observed when reacting a cyanomethylphosphonate anion with benzaldehyde^{1b,c} using either Li⁺ in THF and K⁺ in HMPA or K⁺ in THF. In the first two cases, the cation is unable to participate in the approach of the aldehyde to the anionic site, as it is too far from the reactive carbon; in the later case, a cationic bridge can take place between the aldehyde carbonyl and the anion so that the relative orientation of the two approaching reagents can be different.³⁷

Experimental Section

NMR Spectra. ¹H and ¹³C spectra were recorded on a Varian XL-100-12 W.G. spectrometer. The temperature of the probe was 31 ± 2 °C. ¹H and ¹³C chemical shifts were measured with Me₄Si as an internal reference. ¹H spectra (100 MHz, 5-mm tubes) were studied using the CW mode. The ¹H resonance of Me₄Si was used to provide the field frequency lock. Heteronuclear double resonance experiments ¹H-³¹P were performed by irradiating ³¹P at 40.5 MHz with the XL gyrocode decoupler. The ³¹P irradiating frequency was determined using an Eldorado-Varian frequency counter, and ³¹P chemical shifts relative to H₃PO₄ were calculated as previously described.¹⁰

¹³C spectra (25.17 MHz, 10-mm tubes, ²H lock) were collected using the Fourier transform technique. The instrument was equipped with a 620 L-100-16 K on line computer. A capillary filled with D₂O served as an internal lock when using protio solvents. Spectral widths of 5000 or 2500 Hz were used (digital resolution, 1.25 or 0.68 Hz/point). Proton-coupled ¹³C spectra were obtained with gated proton decoupling.

⁷Li spectra were recorded on a Varian FT-80 spectrometer (30.912 MHz, 10-mm tubes, ²H lock) using the Fourier transform technique. A 4-mm tube filled with a 1 M solution of LiCl in D₂O, located inside the 10-mm tube, was used for the ²H internal lock and ⁷Li external reference. No magnetic susceptibility correction was applied. A spectral width of 2000 Hz was used (digital resolution, 0.5 Hz/point).

Materials. Tetrahydrofuran (Merck pure) was distilled over LiAlH₄ and kept under argon. Me₂SO was freshly distilled over CaH₂. Merck *n*-BuLi solutions (1.6 M in hexane) were standardized by acid-base titration before use. *t*-BuOK (Merck) was sublimated before use; *t*-BuOLi was prepared from Li and freshly distilled *t*-BuOH, vacuum dried after solvent evaporation, and kept under an argon atmosphere. Deuterated solvents were commercial.

Preparation of Solutions. Starting material (0.001 mol) was weighed in a drybox into a carefully dried tube containing a small magnetic rod. It was then septum-capped after argon introduction. Solvent (2 mL, or 1.4 mL if the base used was *n*-BuLi) was introduced by a syringe, and the solution was then magnetically stirred. *n*-BuLi (0.7 mL) in hexane was added by a syringe or 0.0012 mol of *t*-BuOK or *t*-BuOLi under argon. The solution was stirred again for 45 min and then centrifuged. A 0.5-mL amount of this solution was taken via a syringe and introduced under an argon atmosphere into a 5-mm NMR tube containing Me₄Si. A 60 MHz ¹H NMR spectrum was run to check the solution, and the remaining 1.5 mL of solution was similarly transferred into a 10-mm NMR tube for a ¹³C NMR spectrum. Similar procedures were run in half amounts for the 100 MHz ¹H NMR spectra.

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Registry No.—2, 1080-32-6; 2A, 67393-38-8; 3, 2537-48-6; 3A (M⁺ = K⁺), 67393-39-9; 3A (M⁺ = Li⁺), 67393-40-2; 4, 881-42-5; 5, 29284-50-2; 6, 60188-42-3; 7, 21655-89-0; 7 (uncharged form), 16721-45-2; 8, 53178-41-9; 9A (M⁺ = Li⁺), 67393-41-3.

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