spectrum, found *m/e* 327.1464 (M^+), $C_{19}H_{21}NO_4$ requires *m/e* 327.1465.

2-Allyl-3-methoxy-1,4-naphthoquinone (45). The hydroquinone dimethyl ether **26** (0.67 g, 1.9 mmol) in 25 mL of CH_2Cl_2 was shaken with 10 mL of 6 M HNO_3 for 1 min. The layers were separated, the aqueous layer was washed with CH_2Cl_2 (3×), and the combined organic phase was washed, dried, and evaporated to give 0.52 g of an orange oil. Chromatography (25 g of silica, CH_2Cl_2) gave **45** as a solid which was recrystallized from hexane/EtOAc: 0.062 g (14%); mp 80–81 °C; NMR δ 3.29 (d, J = 6 Hz, $C\mathbf{H}_2CH{=}CH_2$), 4.05 (s, OCH_3), 5.1 (m, $CH{=}C\mathbf{H}_2$), 5.9 (br m, $C\mathbf{H}{=}CH_2$), 7.6, 8.0 (2 m, 3 H, 1 H, ArH); IR (Nujol) 1690, 1640, 1600, 1590, 1570 cm^{-1}; UV λ_{max} 391 nm (ϵ 1750), 333 (3040), 278 (18 300), 274 (19 700), 256 (sh, 20 900), 251 (23 100). Anal. Calcd for $C_{14}H_{12}O_3$: C, 73.7; H, 5.3. Found: C, 73.3; H, 5.3.

Registry No. 3, 72881-45-9; **7**, 13243-65-7; **8**, 72866-61-6; **9**, 72866-62-7; **10**, 59641-26-8; **13**, 72866-63-8; **14**, 72866-64-9; **15**, 72866-65-0; L-**19**, 69940-12-1; **20**, 2065-37-4; L-**21**, 72866-66-1; (*S*)-**24**, 72866-67-2; (*S*)-**25**, 72866-68-3; L-**26**, 72866-69-4; (*S*)-**27**, 72866-70-7; (*S*)-**28**, 72866-71-8; [*S*(*cis*)]-**29**, 72881-46-0; [*S*(*trans*)]-**29**, 72866-72-9; (*S*)-**30**, 72866-73-0; L-**31**, 72866-74-1; L-**33**, 72866-75-2; L-**34**, 72866-76-3; L-**37**, 72866-77-4; L-**38**, 72866-78-5; L-**39**, 72866-79-6; *cis*-**40**, 72866-80-9; **44**, 72866-81-0; **47**, 72866-82-1; **48**, 72881-47-1; **49**, 72881-48-2; **50**, 72866-83-2; **51**, 72866-84-3; **52**, 72866-85-4; **53**, 72866-86-5; **54**, 72866-87-6; **55**, 72866-88-7; **56**, 72866-89-8; **57**, 72866-90-1; *cis*-**58**, 72866-91-2; *trans*-**58**, 72866-92-3; **59**, 72866-93-4; **60**, 72866-94-5; **61**, 72866-95-6; **62**, 72866-96-7; **63**, 72866-97-8; ketene dimethyl acetal, 922-69-0; pyrrolidine, 123-75-1; 1,4-naphthoquinone, 130-15-4; L-proline methyl ester, 2577-48-2; allyl bromide, 106-95-6; hydroxylamine hydrochloride, 5470-11-1; methoxyamine hydrochloride, 593-56-6; trimethyl orthoformate, 149-73-5; phenyl chloroformate, 1885-14-9; ethyl 2-pyrroleacetate, 4728-25-0; ethyl 3-pyrroleacetate, 71616-57-4; homoproline ethyl ester acetate, 72866-98-9.

Structural Study of Carbanionic Species α to a Phosphoryl Group. The Anion of Diethyl [(Carbomethoxy)methyl]phosphonate. Comparison with Phosphorus-Ylidic Esters and Acetoacetic Ester Anions

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The structure of the anion of diethyl [(carbomethoxy)methyl]phosphonate in solution has been studied by ^1H, ^{13}C, and ^{31}P NMR and by IR. Two slowly interconverting species, **2a** and **2b**, can be observed when the gegenion K^+ is complexed to [2.2.2]cryptand in THF, pyridine, and Me_2SO. From the various coupling constants and IR frequencies it appears that, for these two species, the carbon α to phosphorus is planar, and the carbon–carbon and carbon–oxygen bonds are partially double; the ΔG_c^{*} value indicates that their interconversion takes place by rotation around the partial C–C double bond. All these characteristics show a close similarity with phosphorus ylidic ester **3**. In the three examined solvents (Me_2SO, pyridine, and THF), either an externally solvated chelate **2A** (Li^+/Me_2SO; c = 0.5 M), occasionally accompanied by free ion (K^+/Me_2SO; c = 0.5 M), or aggregates (Li^+ or K^+/THF; c = 0.5 M) are observed, thus showing a similarity with acetoacetate anion **4** under similar conditions. From the determined dissociation coefficient in Me_2SO, it can be concluded that K^+ is as strongly chelated by the anion formed from diethyl [(carbomethoxy)methyl]phosphonate as by the acetoacetate anion, though its carbon α to phosphorus bears more negative charge.

The reactivity of Wittig–Horner reagents,[1] i.e., anionic species **1** (where R is alkoxy or aryl and A is an electron-withdrawing group) formed from electron-withdrawing substituted phosphonates and phosphine oxides, has been shown to be dependent on the solvent and the associated cation.[2] In order to understand this behavior, we have undertaken a structural study of these species in solution by NMR and IR spectroscopy.

$$[R_2P(O){-}CH{-}A]^-M^+$$

1

In a previous work[3] on nitrile and benzylic phosphonate anions (**1**, R = OC_2H_5, A = CN or Ph), a striking similarity between the structures of these species and of the corresponding P ylides has been shown. In the present work, we examine the structure of the phosphono ester anion **2** (**1**, R = OC_2H_5, A = $COOCH_3$) according to solvent and associated cation.

$$[(C_2H_5O)_2P(O)CHCOOCH_3]^-M^+$$

2

This species could be expected to chelate a cation by two oxygen atoms: such a possibility has already been suggested by Kirilov and Petrov[4] and by ourselves in a preliminary communication.[5] Thus, the structure of **2** will be compared not only to that of ylidic analogue **3**[6] but also

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to acetoacetic ester anions **4**, the structure of which has been recently investigated by NMR,[7] IR,[8] and X-ray[8,9] methods.

$Ph_3\overset{+}{P}\overset{-}{CH}COOCH_3$

3

$[CH_3COCHCOOC_2H_5]^-M^+$

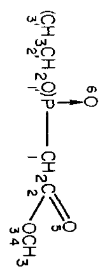
4

Previous work on compound **2** deals with ^1H NMR spectra in pyridine and IR spectra in the solid state.[4] However, more comprehensive structural information can be gained from ^{13}C and ^{31}P NMR data, as well as from NMR and IR data in more or less associating conditions.

Therefore, a systematic investigation of the solvent (THF, pyridine, Me_2SO) and the associated cation nature influence (Li^+, K^+, K^+ [2.2.2]crypt) was undertaken by ^1H, ^{13}C, and ^{31}P NMR and IR. The IR and Raman spectra of phosphonate **5** and the IR spectrum of anionic species **2** in the solid state were simultaneously investigated.[10a] Moreover, we were able to observe the formation of an intermediate species when less than 1 equiv of base is used to generate **2** in THF or pyridine: its structure will be discussed in a forthcoming publication.[10b]

Results and Interpretation

The anionic species **2** was prepared under argon in the same way as for the chemical study by action of a slight excess of *n*-BuLi, LiO-*t*-Bu or KO-*t*-Bu on the corresponding phosphonate **5** dissolved in the required protio



5

or deuterated solvent. [2.2.2]Cryptand ([2.2.2]crypt, 1.2 equiv) was occasionally added after formation of the K^+ associated anion.

(1) NMR Data. The formation of anionic species was deduced from the intensity of H_1 in the proton spectrum; it was also checked by the multiplicity of the C_1 signal in off-resonance ^{13}C spectra: doublet of triplets in starting phosphonate **5**, doublet of doublets in the anion **2**. Addition of CF_3COOH to a solution of **2** regenerates starting phosphonate **5**.

The ^{13}C signal assignments were straightforward from their multiplicity in ^1H-coupled or off-resonance ^{13}C spectra and from splitting with ^{31}P. ^{31}P chemical shifts were determined from $^1H\{^{31}P\}$ double resonance experiments. The relative signs of $^1J_{PC_1}$ and $^2J_{PH_1}$ were determined from ^{13}C spectra by using the off-resonance tech-

Table I. Chemical Shifts[a] of Diethyl [(Carbomethoxy)methyl]phosphonate (**5**) and Anionic Species **2**,M^+

compd	solvent (base)	$\delta_{^{31}P}$	δ_{C_1}	δ_{C_2}	δ_{C_4}	$\delta_{C_2'}$	$\delta_{C_3'}$	δ_{H_1}	δ_{H_4}	$\delta_{H_2'}$	$\delta_{H_3'}$
5	THF	18.6	34.4	166.7	52.1	62.5_5	16.6_0	2.93	3.64_5	4.08	
5	py-*d*$_5$	19.2	34.4_5	166.7_5	52.5_5	62.60	16.4_0	3.31	3.65	4.20_5	1.24
5	Me_2SO-*d*$_6$	19.2	33.2_5	166.1_5	52.0_5	61.9_5	16.0_5	3.11	3.64_5	4.04_5	
2A,Li^+	THF (*n*-BuLi)	38.7 (+20.1)	41.0 (+6.6)	175.7_5 ($+9.0_5$)	50.0	60.6_0	16.7_0	2.63 (−0.30)	3.43	3.94	1.19_8
2A,Li^+	THF (LiO-*t*-Bu)		41.1_8 ($+6.7_8$)	175.4_7 ($+8.7_7$)	49.9_7	60.3_5	16.5_8				
2A,K^+	THF (KO-*t*-Bu)	38.7 (+20.1)	39.0_5 ($+4.6_5$)	174.2_0 (+7.5)	50.2_0	60.5_5	16.7_0	2.58 (−0.35)	3.36	3.84	1.18
{**2a**,K^+ [b]	THF (KO-*t*-Bu)	37.9 (+19.3)	38.4_5 ($+4.0_5$)	170.1_5 ($+3.4_5$)	47.8_5	59.2_5	17.3_5	2.26_5 (-0.66_5)	3.22	3.88	1.14
{**2b**,K^+ [b]		36.4 (+17.8)	40.1_0 (+5.7)	170.5_0 (+3.8)	48.1_5	id.	id.	2.03 (−0.90)	3.28_5	id.	1.12_5
2A,K^+	py (KO-*t*-Bu)	38.9 (+19.7)	39.6_5 (+5.2)	173.8_7 ($+7.1_2$)	49.9_8	60.2_5	16.5_5	3.12_4 (-0.18_6)	3.59_6	4.02_7	1.22_2
{**2a**,K^+ [b]	py (KO-*t*-Bu)	38.9 (+19.7)	39.3_5 (+4.9)	170.5_0 ($+3.7_5$)	48.3_0	59.4_5	17.3_0	3.26_5 (-0.04_5)	3.69_6	4.41_7	1.33_2
{**2b**,K^+ [b]		37.6 (+18.4)	40.9_0 ($+6.4_5$)	171.0_5 (+4.3)	48.7_0	59.3_0	17.2_0	3.03_6 (-0.27_4)	3.73_9	4.21_2	1.31
2A,Li^+	Me_2SO (LiO-*t*-Bu)	38.4 (+19.2)	39.6_5 (+6.4)	172.8_4 ($+6.6_9$)	48.6_0	59.0_6	16.2_6	2.36 (−0.75)	3.33	3.80	1.15
{(**2A** + **2a**),K^+	Me_2SO (KO-*t*-Bu)	37.5 (+18.3)	39.2_0 ($+5.9_5$)	170.7_0 ($+4.5_5$)	48.1_0	58.7_0	16.4_0	2.26 (−0.85)	3.24	3.74_5	1.13
{**2b**,K^+		36.3 (+17.1)						1.88_5 (-1.22_5)	id.	3.72	1.10_5
{**2a**,K^+ [b]	Me_2SO (KO-*t*-Bu)	37.4 (+18.2)	38.4_5 (+5.2)	168.7_5 (+2.6)	47.4_0	58.2_5	16.6_0	2.11 (−1.00)	3.16_5	3.75	1.10
{**2b**,K^+ [b]		36.0 (+16.8)	39.9_0 ($+6.6_5$)	169.3_0 ($+3.1_5$)	47.7_5	58.2_5	16.6_0	1.82 (−1.29)	3.22	3.71	1.10

[a] $\delta_{^1H}$ and $\delta_{^{13}C}$ are in parts per million from internal Me_4Si; $\delta_{^{31}P}$ is in parts per million relative to external H_3PO_4 (85%). Positive δ values are in the direction of increasing frequency. Variations of δ (δ in **2** minus δ in **5**) are indicated in parentheses. [b] Run in the presence of 1.2 equiv of [2.2.2]cryptand.

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Table II. Coupling Constants (hertz) of Diethyl [(Carbomethoxy)methyl]phosphonate (**5**) and Anionic Species **2**,M$^+$

compd	solvent (base)	$^1J_{PC_1}$ [d]	$^2J_{PC_2}$ [d]	$^4J_{PC_4}$	$^2J_{PC_2'}$	$^3J_{PC_3'}$	$^1J_{C_1H}$ [d]	$^2J_{PH_1}$
5	THF	132.6	5.5	<1.2	5.4	5.8	130	−21.6[b]
5	py-d_5	132.4[a]	5.2	<1.2	5.9	6.0	130.3[a]	−21.7
5	Me$_2$SO-d_6	131.3	6.3	<1.2	5.6	6.2	130.6	−21.3
2A,Li$^+$	THF (*n*-BuLi)	223.1 (+90.5)	21.7 (+16.2)	3.6	4.5	7.3	154.4 (+24.4)	13.2
2A,Li$^+$	THF (LiO-*t*-Bu)	220.8 (+88.2)	21.4 (+15.9)	3.7	4.3	7.4	153.7 (+23.7)	
2A,K$^+$	THF (KO-*t*-Bu)	218.0 (+85.4)	21.9 (+16.4)	3.8	5.2	7.1	155.4 (+25.4)	15.6[c]
2a,K$^+$ [e]	THF (KO-*t*-Bu)	219.7 (+87.1)	21.3 (+15.8)	3.7	4.2	7.5	151 (+21.0)	15.5
2b,K$^+$ [e]		215.0 (+82.4)	12.8 (+7.3)	<1.2	id.	id.		15.1
2A,K$^+$	py (KO-*t*-Bu)	218.5 (+86.1)	22.4 (+17.2)	3.7	5.4	7.2	155.4 (+25.1)	15.3[c]
2a,K$^+$ [e]	py (KO-*t*-Bu)	219.7 (+87.3)	21.2 (+16.0)	3.7	3.7	7.5	152.6 (+22.3)	15.7[c]
2b,K$^+$ [e]		214.9 (+82.5)	12.6 (+7.4)	<1.2	4.1	7.4	152.3 (+22.0)	15.4[c]
2A,Li$^+$	Me$_2$SO (LiO-*t*-Bu)	219.6 (+88.3)	22.6 (+16.3)	3.3	4.6	7.0	153.1 (+22.5)	13.8
(**2A** + **2a**),K$^+$	Me$_2$SO (KO-*t*-Bu)	221.3 (+90.0)	22.5 (+16.2)	3.8	4.9	7.4	153.0 (+22.4)	15.2[c]
2b,K$^+$								15.2
2a,K$^+$ [e]	Me$_2$SO (KO-*t*-Bu)	219.8 (+88.5)	21.0 (+14.7)	3.9	4.5	7.4	152.3 (+21.7)	15.8
2b,K$^+$ [e]		214.1 (+82.8)	7.5 (+1.2)	<0.7	4.5	7.4		15.3

[a] From $^1H\{^{31}P\}$ double-resonance experiments; $^1J_{PC_1}$ and $^1J_{C_1H}$ bear the same sign. [b] From $^{13}C\{^1H\}$ off-resonance experiments; $^1J_{PC_1}$ and $^2J_{PH_1}$ are of opposite signs. From $^{13}C\{^1H\}$ off-resonance experiments; $^1J_{PC_1}$ and $^2J_{PH_1}$ bear the same sign. [d] Variations of J (J in **2** minus J in **5**) are indicated in parentheses. [e] Run in the presence of [2.2.2]cryptand.

nique described by Jakobsen.[11] ^1H, ^{31}P, and ^{13}C chemical shifts are given in Table I and J_{PH}, J_{PC}, and J_{CH} coupling constants in Table II, as well as those of phosphonate **5** for comparison purposes.

The ^{13}C data for phosphonate **5** are similar to those given by Gray[12] for the ethyl ester. We have checked by heteronuclear $^1H\{^{31}P\}$ selective double irradiation experiments that $^1J_{PC_1}$ and $^1J_{C_1H_1}$ bear the same sign; i.e., $^1J_{PC_1}$ is positive.[13] Moreover, $^1J_{PC_1}$ and $^2J_{PH_1}$ are of opposite signs; i.e., $^2J_{PH_1}$ is negative. Long-range coupling constants can be observed in the ^1H spectrum: $^5J_{PH_4} = +0.65$ Hz and $|^5J_{H_1H_4}| = 0.25$ Hz.

When the anionic species **2** is generated with *n*-BuLi in THF, LiO-*t*-Bu in THF or Me$_2$SO,[29] or KO-*t*-Bu in THF and pyridine, a single species, **2a**, is observed. H_1 proton exchange between phosphonate **5** and anion **2a** is slow in Me$_2$SO, but it becomes fast in THF or pyridine if a sufficient amount of **5** is added, as shown by averaging of the H_1 shift and the lack of $^2J_{PH_1}$. In Me$_2$SO, with KO-*t*-Bu as a base, two sets of signals coexist in the ^1H spectrum: one corresponds to **2a** and the other to a second species **2b**, the ratio of **2a** to **2b** being 9:1. These two species are also seen when K$^+$ is complexed to [2.2.2]cryptand in the three solvents, **2a** to **2b** being in a 3:1 ratio. Both species are characterized by large $^1J_{C_1H_1}$ and $^1J_{PC_1}$ coupling constants; moreover, $^2J_{PH_1}$ and $^1J_{PC_1}$ bear the same sign, thus showing that the sign of one of those coupling constants changes on going from phosphonate **5** to anions **2a** and **2b**.

Literature data indicate that $^1J_{CH}$ depends mainly upon carbon geometry; the same conclusion holds for $^1J_{PC}$ in the case of tetracoordinated phosphorus compounds: on going from pyramidal to planar carbon, along a given series, one observes an increase in both coupling constants.[3,6d,e,16] The sign of $^2J_{PH}$ also depends upon central carbon geometry: when this carbon is pyramidal, $^2J_{PH}$ is negative[13] while $^2J_{PH}$ is positive when the central carbon is planar.[17] As for tetracoordinated phosphorus derivatives, $^1J_{PC}$ is positive, independent of carbon hybridization.[13,18,19] The $^1J_{PC}$ and $^2J_{PH}$ coupling constants will bear opposite signs if the central carbon is pyramidal and the same sign if this carbon is planar.

From these data, it may be concluded that C_1 becomes planar or nearly so in **2a** and **2b**. This conclusion is in line with the parameters found for vinylic phosphonates **6**. In

$$(C_2H_5O)_2P(O)C_1H{=}CHCOOCH_3$$

6 (*Z* or *E*)

our case $^1J_{PC_1}$ is even larger (215–223 Hz) than $^1J_{PC_1}$ in compounds **6** (184–186 Hz), while $^1J_{C_1H_1}$ is smaller in the former case (151–155 Hz) than in the latter (160–162 Hz).[20]

Although C_1 is planar or nearly so in **2a** and **2b**, this carbon appears to bear a relatively high negative charge, as it resonates around 40 ppm, while in the vinylic phosphonates **6**, C_1 resonates at significantly lower field (129–132 ppm).[20] This conclusion is confirmed by the H_1 upfield shift in **2a** and **2b** when compared to the shift in **5**.

The downfield ^{31}P shift on going from phosphonate **5** to anionic species **2** is similar to that observed in the previously studied cases;[3] this effect could be due to an angular change around the phosphorus atom.[22]

Variable-temperature ^1H NMR in pyridine as a solvent, when K$^+$ is complexed to [2.2.2]cryptand, showed a reversible coalescence between the two sets of signals of **2a** and **2b**. For H_4 signals, the coalescence temperature was 54 °C. From this temperature and the peak separation (4.3 Hz) at 15 °C a free energy of activation $\Delta G_c^{\ddagger} \simeq 17.7$ kcal/mol was calculated from the approximate Gutowsky–Holm formula.[14] Such an interconversion can take place by rotation either around the PC_1 bond or around the C_1C_2 bond. The barrier magnitude is in agreement with a hindered rotation around a partially double carbon–carbon bond.[6h,23] It disfavors a hindered rotation

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(17) J. E. Lancaster, *Spectrochim. Acta, Part A*, **23**, 1449 (1967); R. M. Lequan and M. P. Simonnin, *Bull. Soc. Chim. Fr.*, 2365 (1973); M. P. Simonnin and C. Charrier, *Org. Magn. Reson.*, **1**, 27 (1969).

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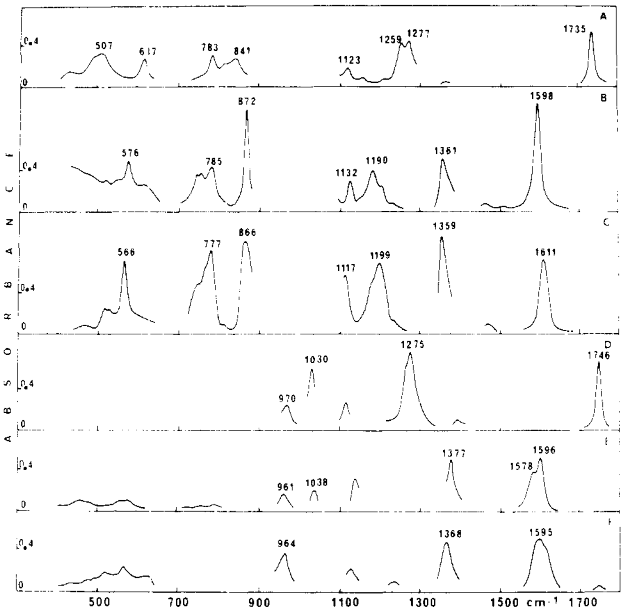
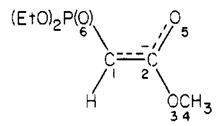


Figure 1. Infrared spectra of starting compound **5** (A, D) and carbanionic species (B, C, E, F) dissolved in Me_2SO (A, B, C) and in THF (D, E, F). Carbanionic species are prepared with LiO-*t*-Bu (B), *n*-BuLi (E), and KO-*t*-Bu (C, F). The concentration of the compound is 0.37 M. The cell thickness is 0.0030 cm. For band frequencies, see Table III.

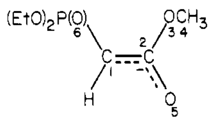
around a PC bond as the already known rotation barriers, even for compounds with bulky substituents, are significantly lower[24] (6–10 kcal/mol) except in α tricarbonyl phosphorus(III) derivatives.[25]

Moreover, the presence of a long-range $^4J_{PC_4}$ coupling constant in **2a**, which is absent in **2b** and in starting phosphonate **5**, is in favor of a W arrangement of the $P\text{-}C_1\text{-}C_2\text{-}O_3\text{-}C_4$ fragment solely in **2a**.[21]

Therefore, the following structures can be assigned to the anionic framework of **2a** and **2b**; nevertheless, the geometry around phosphorus remains undetermined at least for the K^+[2.2.2]crypt anionic moiety.



2a (*Z*)



2b (*E*)

(2) IR Data. Cation and Solvent Effects on Solution Structure. It is well-known that NMR spectroscopy gives detailed information on the electronic structure and on the geometrical framework of a molecule. However, it is poorly sensitive to its external environment, e.g., ionic association[15] or aggregate formation. Such information can be deduced from IR data.[8] The results are given in Table III.

(a) Me_2SO Solutions. Instead of the ν(C=O) at 1735 cm^{-1} and $\nu(P{\to}O)$ at 1259–1277 cm^{-1} in starting phosphonate **5**,[10a] lithium- and potassium-associated species **2** show intense absorptions around 1600, 1360, and 1190 cm^{-1} which are assigned to vibrational modes $\nu(C_2 \overline{\cdots} O_5)$, $\nu(C_1 \overline{\cdots} C_2)$, and $\nu(P \overline{\cdots} O_6)$, respectively, as justified by comparison with the vibrational spectra of related species[10a] (Figure 1). The $\nu(C_2{-}O_3)$, corresponding to medium-intensity bands at 1132 cm^{-1} (Li^+) and 1117 cm^{-1} (K^+), shows a slight

Table III. IR Bands[a] (cm^{-1}) of Diethyl [(Carbomethoxy)methyl]phosphonate (5) and Anionic Species 2,M^+

	in Me_2SO				in THF				
	5	2,K^+[2.2.2]crypt	2,K^+	2,Li^+	5	2,K^+	2,Li^+	$(2,K^+)_n$	$(2,Li^+)_n$
$\nu(C_2 \overline{\cdots} O_5)$	1735				1746				
$\nu(C_2 \overline{\cdots} O_5)$		1620 (+115)[c]	1611 (+124)	1598 (+137)		(1612)[b] (+134)	1596 (+150)	1595 (+151)	1578 (+168)
$\delta(CH_3)$		1478	1471	1472					
	1365				1393				
$\nu(C_1 \overline{\cdots} C_2)$		1355	1359	1361		1368	1377		
	1277				1275				
$\nu(P{\to}O_6)$ + comb	1259				(1265)				
	1217								
		1238	1235	1235					
$\nu(P \overline{\cdots} O_6)$ + comb		(1199)	1199	(1210)					
		1185	(1185)	1190					
$\rho(CH_3)$	1161								
$\nu(C_2{-}O_3)$	1123		1117 (+6)	1132 (−9)	1118	1128 (−10)	1138 (−20)		
$\nu(O_{1'}{-}C_{2'})$					1030		1038 (−8)		
$\nu(C_{2'}{-}C_{3'})$					970	964 (+6)	961 (+9)		
$\nu(O_3{-}C_4)$			866	872					
	841		777	785			793		
$\nu(P{-}O_{1'})$ and $\nu(P{-}C_1)$	(815)		(764)	759			759		
	783		749	750			725		
δ or $\gamma(C_2 \overline{\cdots} O_5)$	617			621		626			
	507		566	576		567	576		
$\delta(O_6PO_{1'})$ or $\delta(O_6PC_1)$	(489)		526–517	551		519	559		
	428		470	519		490	446		

[a] ν values in cm^{-1}. [b] Shoulders are indicated by numbers in parentheses. [c] Variations, $\Delta\nu$ (ν in 5 minus ν in 2), are indicated by numbers with a sign in parentheses.

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(24) J. B. Robert and J. D. Roberts, *J. Am. Chem. Soc.*, **94**, 4902 (1972); C. H. Bushweller and J. A. Brunelle, *Tetrahedron Lett.*, 893 (1974); *J. Am. Chem. Soc.*, **95**, 5949 (1973).

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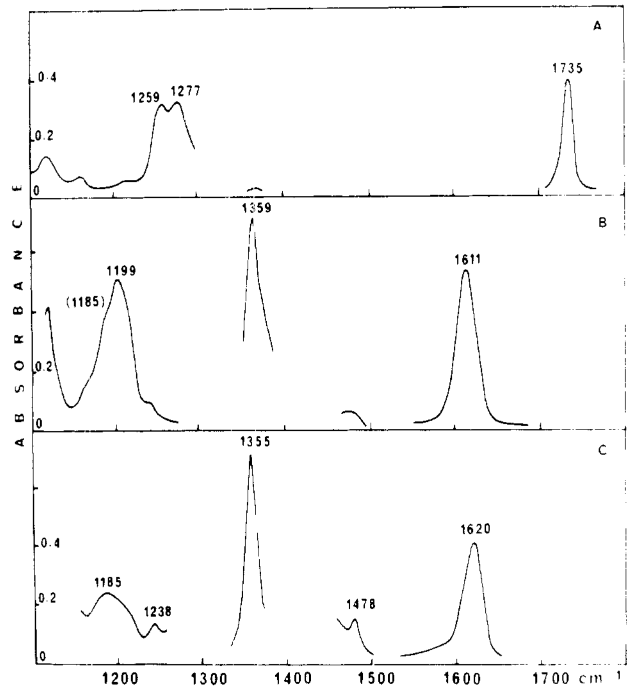
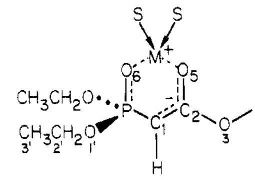


Figure 2. Influence of [2.2.2]cryptand addition on the infrared spectra of carbanionic species prepared with KO-*t*-Bu in Me$_2$SO: (A) compound **5**, concentration 0.37 M, cell thickness 0.0030 cm; (B) potassium salt 0.37 M, 0.0030 cm; (C) potassium salt plus 1.2 equiv of [2.2.2]cryptand, 0.37 M, 0.0030 cm.

frequency perturbation relative to that of starting phosphonate **5** (1123 cm^{-1}).

The cation dependence of $\nu(C_2{\overset{\cdots}{-}}O_5)$ and $\nu(P{\overset{\cdots}{-}}O_6)$ indicates that even in this dissociating solvent, the cation is interacting with the two O$_5$ and O$_6$ oxygen atoms so that the species existing in Me$_2$SO solution is mainly the externally Me$_2$SO-solvated chelate **2A**. Furthermore, the



2A

large $\Delta\nu(P{\overset{\cdots}{-}}O_6)$ (Table III) observed, compared to the small $\Delta\nu(P{\rightarrow}O_6) \simeq 3$ cm^{-1} when a Li$^+$ salt is added to starting phosphonate **5**, shows that there is a lengthening of the $P{\overset{\cdots}{-}}O_6$ bond through carbanion formation. The frequencies of perturbations of the $\nu(PO_{1'})$ and $\nu(PC_1)$ modes may be indicative of a small hybridization change of the phosphorus atom.[10a] This small hybridization change and the negative charge increase on both O$_5$ and O$_6$ in the carbanionic species **2A**, which may have opposite effects on the $\delta_{^{31}P}$, could be responsible for the observed NMR shift ($\Delta\delta_{^{31}P} \simeq +19$ ppm) which is smaller than that in the previously studied diethyl (cyanomethyl)phosphonate anion ($\Delta\delta_{^{31}P} \simeq +26$ ppm).[3]

Although the NMR spectra exhibit distinct sets of signals for the *Z* and *E* isomers of anion **2**, nearly all the observed IR absorptions correspond to single bands (Figure 2). The K$^+$[2.2.2]crypt anion exhibits a $\nu(C_2{\overset{\cdots}{-}}O_5)$ absorption at 1620 cm^{-1}, and the $\nu(C_1{\overset{\cdots}{-}}C_2)$ mode appears at 1355 cm^{-1}. The $\nu(P{\overset{\cdots}{-}}O_6)$ vibration is a broad band at 1185 cm^{-1} with a shoulder at 1199 cm^{-1}. The small frequency shift of $\nu(C_2{\overset{\cdots}{-}}O_5)$ and $\nu(C_1{\overset{\cdots}{-}}C_2)$ observed through complexation of the K$^+$ cation as well as the large intensity change of the $\nu(P{\overset{\cdots}{-}}O_6)$ mode (Figure 2) shows the probable formation of a free anion as already observed for potassium ethylacetoacetate enolate.[8] The relative intensity change of the components at 1185 and 1199 cm^{-1} through complexation could correspond to the existence of the two isomers, observed by NMR; in any case, a Fermi resonance or a coupling with another vibration mode cannot be excluded.

For the K$^+$ salt in Me$_2$SO, the shoulder at 1185 cm^{-1} present on the 1199-cm^{-1} $\nu(P{\overset{\cdots}{-}}O_6)$ band may be indicative of the coexistence of free anion conformers **2a** and **2b** and externally Me$_2$SO-solvated chelate **2A**. The band at 1199 cm^{-1} is tentatively assigned to $\nu(P{\overset{\cdots}{-}}O_6)$ of both **2A** and **2a** and the shoulder at 1185 cm^{-1} to **2b**. The relative intensities of these two bands with or without [2.2.2]cryptand suggest that the molar extinction coefficients are different for species **2A**, **2a**, and **2b**, since from ^{1}H NMR integration the dissociation coefficient in Me$_2$SO is about $\alpha = 0.33$ ($c = 0.5$ M) if one admits that the populations of **2a** and **2b** of the free anion are those observed for the K$^+$[2.2.2]crypt anionic moiety.

The Li$^+$-associated species only exists as a chelate in this solvent, as only one absorption is observed.

As shown in Table III, the frequency shift decreases for the $\nu(C_2{\overset{\cdots}{-}}O_5)$ mode and increases slightly for the $\nu(C_1{\overset{\cdots}{-}}C_2)$ mode in the following order: free K$^+$[2.2.2]crypt anion, K$^+$ ion pair, Li$^+$ ion pair. This is consistent with NMR data for which a slight upfield variation of δ C$_2$ is seen: Li$^+$ > K$^+$ > K$^+$[2.2.2]crypt. Furthermore, the high similarity between the stretching vibrations of chelated ion pair **2A** and free anions **2a** and **2b** shows a very close electronic delocalization which might explain the fact that ^{1}H NMR parameters are very close for **2A** and **2a**.

(b) THF Solutions. The solvent absorption does not allow the observation of the region corresponding to $\nu(P{\overset{\cdots}{-}}O_6)$ for the anionic species (Figure 1). Generation of the lithium-associated species by action of either *n*-BuLi or LiO-*t*-Bu has no effect on the solution structure as shown by NMR and IR data for **2**, thus showing that the equivalent amount of *t*-BuOH formed when LiO-*t*-Bu is used has no influence. The ν(OH) vibration of *t*-BuOH confirms that this alcohol is associated to THF. This agrees with former results on acetoacetate anion **4**, as important amounts of *t*-BuOH are necessary to observe the alcohol-solvated enolate ion pair in THF.[26]

The $\nu(C_2{\overset{\cdots}{-}}O_5)$ absorption, which has the largest cation dependence in Me$_2$SO, shows two maxima at 1578–1596 cm^{-1} (Li$^+$) and 1595–1612 cm^{-1} (K$^+$). The fact that this vibrational mode corresponds to a single band in Me$_2$SO (Li$^+$, 1598 cm^{-1}; K$^+$, 1611 cm^{-1}) makes improbable the existence of a Fermi resonance. The dilution of the solution induces a great change of the relative intensities of these two bands (Figure 3). For the Li$^+$-associated species, a decrease in concentration involves an enhancement of the 1596-cm^{-1} component at the expense of the 1578-cm^{-1} one. By analogy with the Me$_2$SO case, the 1596-cm^{-1} band can be attributed to an externally THF-solvated chelate ion pair **2A** while the 1578-cm^{-1} one, the relative intensity of which increases with concentration, is probably due to the formation of aggregates such as ion pairs and dimers in this poorly polar solvent. Such an aggregation has already been observed for lithium thiocyanate.[27] This is further shown by the close value observed for the $\nu(C_2{\overset{\cdots}{-}}O_5)$ frequency in this species and in the solid compound.[10a] The formation of triple ions, as already observed for lith-

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[26] P. Sarthou, Thèse, de Doctorat, Université Paris XI, Orsay, France, 1978; P. Sarthou, F. Guibe, G. Bram, and J. Corset, submitted for publication.

[27] D. Paoli, M. Luçon, and M. Chabanel, *Spectrochim. Acta*, in press; J. Vaes, M. Chabanel, and M. L. Martin, *J. Phys. Chem.*, in press.

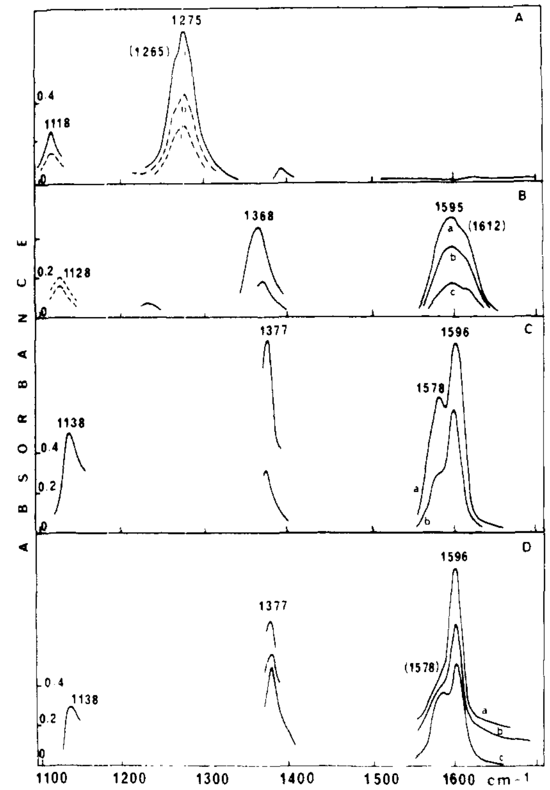


Figure 3. Influence of concentration of carbanionic species (B, C, D) and of phosphonate **5** (A) on the infrared spectra of THF solutions. Carbanionic species are prepared with KO-*t*-Bu (B), LiO-*t*-Bu (C), and *n*-BuLi (D). Concentration and cell thickness: for A–D, (a) 0.25 M, 0.0053 cm, (b) 0.12 M, 0.0092 cm; for A and B, (c) 0.03 M, 0.0220 cm; for D, (c) 0.06 M, 0.0220 cm.

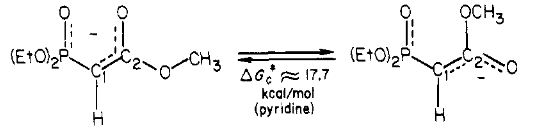
ium trifluoroacetate[28] or lithiated ethylacetoacetate anion,[8b] is improbable in this solvent of low dielectric constant.[28b] The effect of dilution on the $\nu(C_2 \underset{\cdots}{-} O_5)$ value for the K^+-associated species is less important than when $M^+ = Li^+$. However, the 1612-cm^{-1} shoulder, by analogy with the 1611-cm^{-1} band observed in Me_2SO, is attributable to the externally THF-solvated K^+ chelate **2A**, while the intense 1595-cm^{-1} band is due to aggregation; furthermore, Li^+ is more strongly solvated by THF than K^+.[30]

The external solvation of the ion pair **2A** is strongly suggested through comparison of observed frequencies for species **2A** in both solvents (Table III). The frequency shifts are larger in THF than in Me_2SO as already shown for CF_3COOLi ion pairs.[28] This is also observed for $\nu(C_2–O_3)$, $\nu(C_{3'}–C_{2'})$, and $\nu(O_{1'}–C_{2'})$ which show that as in the solid compound[10a] the ethoxy and methoxy groups participate in the electronic delocalization inside the carbanion. While, in THF solution, only one species can be seen by NMR, corresponding to the **2a** framework, infrared data point out the coexistence of externally solvated chelates, analogous to those observed in Me_2SO, and aggregates. Aggregation is more important for the K^+-associated species than for the Li^+-associated one (Figure 3).

Discussion

Comparison with Phosphorus Ylides and Acetoacetic Anions. Our results will be discussed in two respects: on one hand, the structure of the free anion **2**, which is observed when K^+ is complexed to [2.2.2]cryptand, will be compared to structures of ylide **3** and free anion **4**; on the other hand, the anion–cation association according to the solvent will be discussed in comparison with acetoacetate anion **4** under the same conditions.

(1) Structure of the Free Anion. The two conformers **2a** and **2b** which are observed in the three solvents have structures similar to those of ylidic analogues **3a** and **3b**.



2a (*Z*, 70%) **2b** (*E*, 30%)

3a (*Z*, 82%) **3b** (*E*, 18%)

$$\nu(C_1 \underset{\cdots}{-} C_2) = 1334\ \mathrm{cm}^{-1}$$
$$\nu(C_2 \underset{\cdots}{-} O) = 1620\ \mathrm{cm}^{-1}$$

The interconversion barriers are nearly the same,[6h] indicative of a similar double bond character of the C_1C_2 bonds in both types of compounds. However, neither NMR nor IR data allow one to determine if the PC_1 bond has partial double bond character, so we sketch this bond as a single one.

This analogy is confirmed by the IR data for $\nu(C_1 \underset{\cdots}{-} C_2)$ and $\nu(C_2 \underset{\cdots}{-} O)$.[61] In both cases the *Z* form is the most populated. Such a parallelism may be extended to *J* and δ values: $^1J_{PC}$ is larger in **2a** and **3a** (219.7 and 130 Hz) than in **2b** and **3b** (214.9 and 117 Hz).[6d] The H_1 proton is 0.3 ppm more shielded in **2b** and **3b** than in **2a** and **3a**.[6a–c,h] Though C_1 is nearly planar in both cases, it resonates at a relatively high field (**2**, ~40 ppm; **3**, 28.9 ppm[6f]), thus showing that the negative charge is poorly delocalized. There is a small difference in both cases: in the case of **2**, on going from phosphonate **5** to the anionic species, C_1 is deshielded ($\Delta\delta = +6$ ppm) while on going from phosphonium salt **7** to ylide **3**, C_1 is slightly shielded

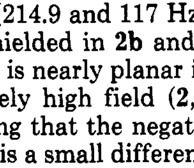
$$(Ph)_3P^+CH_2COOCH_3,X^-$$

7

($\Delta\delta = -3.7$ ppm).[6f] Therefore, all these results show the strong structural similarity between anionic species **2** and P ylide **3**.

However, ^{31}P chemical shift behavior is quite different: a low-field shift is observed on going from phosphonate **5** to species **2** ($\Delta\delta = +20$ ppm) while a very small change is observed between **7** and **3** ($\Delta\delta = +3$ ppm).[6e] This may be explained through the electronic delocalization observed by IR.

The comparison of the phosphono ester free anion with acetoacetate analogue **4** shows noticeable differences: the free anion **4** only adopts the (*Z,E*)-**4b** conformation,[8] like the acetoacetonate anion,[31] while in the case of **2**, the



(*Z,E*)-**4b**

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[28] (a) A. Regis and J. Corset, *Chem. Phys. Lett.*, **32**, 462 (1975). (b) A. Regis, Thèse de Doctorat, Université Pierre et Marie Curie, Paris VI, France, 1977.

[29] In Me_2SO-d_6, proton deuterium exchange takes place at C_1.

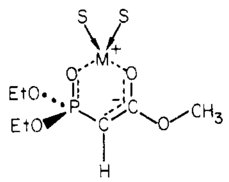
[30] M. Szwarc, "Ions and Ion Pairs in Organic Reactions", Wiley, New York, 1972.

[31] (a) M. Raban, E. A. Noe, and G. Yamamoto, *J. Am. Chem. Soc.*, **99**, 6527 (1977); (b) M. Raban and D. Haritos, *J. Chem. Soc., Chem. Commun.*, 965 (1978).

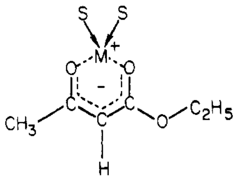
analogous conformation **2b** is the less populated one. The predominance of the **2a** conformer in the free anion seems, at first sight, rather unexpected, as oxygen–oxygen repulsion should disfavor such a conformation, like in the acetoacetate or acetoacetonate anion case.[31] Since the P–O and C–O bond lengths are not equal, the through-space repulsion should be lower; moreover, as the P–C_1 rotation barrier is low, skewed forms are probably highly populated.

The central carbon chemical shift is at a significantly lower field in **4** than in **2** (**4**, $\Delta\delta \approx +30$ ppm;[32] **2**, $\Delta\delta \approx +6$ ppm), thus showing a better charge delocalization in the acetoacetate anion moiety.

(2) Anion–Cation Interaction. The cation–anion interactions in THF and Me_2SO are very similar for phosphono ester anion **2** and acetoacetate anion **4**. In THF, externally solvated chelates **2A** as well as aggregates can be observed from the dilution effect on the relative intensities of the $\nu(C_2\overset{\cdot\cdot}{-}O_5)$ absorption bands, as previously shown with acetoacetate-chelated species **4A**.[8] In Me_2SO, with Li^+ as a counterion, only the presence of externally solvated chelate **2A**, M = Li^+, can be deduced from NMR and IR data, as in the case of Li^+-associated acetoacetate anion **4A**, M = Li^+, in Me_2SO.[8]



2A



4A

However, in both cases, when K^+ is the gegenion, free ions **2a** + **2b** and **4b** as well as externally solvated chelates **2A**,K^+ and **4A**,K^+ do coexist. The estimated dissociation coefficients (0.33 for **2A** and 0.25 for **4A**)[8] in that solvent seem to indicate a similar cation–anion interaction in the phosphonate **2A** chelated species and in **4A**.

Conclusion

The structure of the free ionic species formed from phosphono ester **5** and observed in the presence of [2.2.2]cryptand in THF, pyridine, or Me_2SO is very similar to that of ylide ester **3**. Two slowly interconverting conformers **2a** and **2b** do coexist, and the carbon–carbon ($C_1\overset{\cdot\cdot}{-}C_2$) and carbon–oxygen ($C_2\overset{\cdot\cdot}{-}O_5$) bonds have partial double bond character, a proposal which is different from those of Kirilov and Petrov.[4] As in ylide **3**, the carbon α to phosphorus in **2** is planar or nearly so, and its negative charge is poorly delocalized.

However, the presence of the phosphoryl group makes possible the formation of a chelate, **2A**, so that comparable results are obtained for solutions of phosphono ester anion **2** and acetoacetate anion **4** in similar media. In Me_2SO, with Li^+ as a gegenion, only chelates are observed in both cases, while with K^+, free ions and chelates coexist. In THF, externally solvated chelates and aggregates can be seen for **2** as well as for **4**.

The high stability of the Li^+-associated chelate **2A** in THF, due to the strong O–Li association, explains the lack of reactivity previously observed toward α enones.[2d] The K^+-associated one, although more aggregated than the lithium salt, is reactive, because the O–K interaction is weaker.

The interpretation given by Shatenstein and Kabachnik[33] about the cation and solvent influence on the pK_a of phosphono ester **5** and analogous compounds is in line with the present work. The pK_a of **5** in DME, with Li^+ as a counterion, is 12.2 while it is 19.2 in Me_2SO with K^+ as a counterion.[33] These data have been interpreted in terms of chelate coordination of the metal cation with the phosphoryl and carbethoxyl groups of the carbanion in a contact ion pair in DME. Since the solvent properties of DME are very close to those of THF,[30] our results point out the formation of a tight chelate with strong Li^+–anion electrostatic interactions in THF, while with K^+ in Me_2SO the existence of free ions, which are quite less stabilized than the chelate, has been shown.

Experimental Section

NMR Spectra. ^1H and ^{13}C spectra were recorded on a Varian XL-100-12 WG spectrometer, as previously described.[3]

IR Spectra. Infrared spectra have been scanned on a Beckman IR 12 spectrometer. The spectral slit width is usually 2 cm^{-1}, and the frequencies are given with a precision of at least ±1 cm^{-1} for sharp bands. The cells with fixed thickness are equipped with CaF_2 or KBr windows. The solvent spectra were subtracted from the solution spectra so that the figures show the absorption of the solute. The cells were filled in a drybox, and the anion solutions were checked by running a ^1H NMR spectrum at 60 MHz.

Materials and Preparation of Solutions. Purification of materials and preparation of solutions (c = 0.5 M) are identical with those described in our previous work[3] under strictly moisture- and oxygen-free conditions.

Acknowledgment. We thank Mrs. A. Cordaville for running ^1H NMR spectra and performing variable-temperature experiments at 60 MHz on a Varian A-60 spectrometer.

Registry No. **2A**,Li^+, 67393-41-3; **2a**,K^+, 67393-41-3; **2a**,K^+-[2.2.2]cryptand, 72726-72-8; **5**, 1067-74-9.

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(32) The δ 50 shift of the central carbon atom of methyl acetoacetate was determined on the pure liquid (CFT-20 spectrometer) with Me_4Si as an internal reference.

(33) E. S. Petrov, E. N. Tsvetkov, M. I. Terekhova, R. A. Malevannaya, A. I. Shatenstein, and M. I. Kabachnik, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 517 (1976).