Formation of Phosphonoacetate Carbanions by Lithiated Bases or by the Conjunction of a Lithium Salt and an Amine: Structural Study of Intermediate Species.

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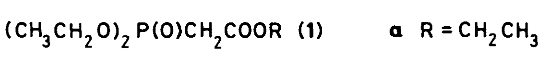
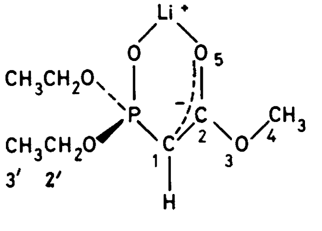
In THF, the anionic species (**2**) formed from methyl diethylphosphonoacetate (**1b**) by the action of Li bases coexist as aggregates (**2A**) and externally solvated monomeric ion pair (**2M**), while in CH_3CN triple ions (**2T**) and small amounts of free ions ($\mathbf{2}^-$) are also characterized. When (**1b**) is in slight excess, relative to the lithiated base, these four species coexist in both solvents, together with other species (**I**). From n.m.r. and i.r. data, it appears that the intermediate species (**I**) include a neutral phosphonate (**1b**) moiety, as a Li^+ cation bidentate ligand, the two other lithium solvation sites being occupied either by ($\mathbf{2}^-$), or by (**1b**) as a monodentate and a solvent molecule, or else by two solvent molecules. The structure of (**1b**) in this intermediate species is strongly perturbed as deduced from variations in ^{31}P and ^{13}C carbonyl shifts as well as that of ν_{CO}. Furthermore, a fast proton exchange takes place between the anionic species (**2**) and free (**1b**) as shown by ^1H n.m.r., but (**I**) does not participate in this exchange phenomenon. When (**2**) is formed by action of diazabicycloundecene (DBU) in the presence of LiCl, aggregates (**2A**), monomeric ion pair (**2M**), and small amounts of (**2T**) as well as two intermediate species (**I**) are characterized by i.r. or ^{31}P n.m.r. spectroscopy. The role of DBU is manifold: it deaggregates LiCl or (**2A**), it deprotonates (**1b**) within (**I**), and it facilitates proton exchange between (**2**) and (**1b**), the relative importance of such effects depending upon the DBU concentration.

Recently, Masamune *et al.*[1] and Rathke[2] have performed the Horner–Wadsworth–Emmons modification of the Wittig reaction in the presence of an amine and lithium or magnesium salts. The former authors observed in the reagent so generated from triethylphosphonoacetate (**1a**) in CD_3CN, next to a broad ^{31}P n.m.r. signal at δ *ca.* 34 p.p.m., a sharp resonance at δ 29.5 p.p.m.; no precise assignment was made. These observations were reminiscent of results described by our group for the deprotonation of methyl diethylphosphonoacetate (**1b**) by less than equimolar amounts of n-butyl-lithium in tetrahydrofuran (THF)[3]. ^1H, ^{13}C, and ^{31}P n.m.r. spectra showed that, next to the signals for the anionic part of the chelated ion pair (**2**), another set of signals, different from those of (**1b**), was present. This set disappeared when adding a small excess of base, to the benefit of the signals of (**2**).



$$\underset{3'}{CH_3}\underset{2'}{CH_2}O)_2P(O)\underset{1}{CH_2}\underset{2}{COOR} \quad (\mathbf{1}) \qquad \mathbf{a}\ R = CH_2CH_3 \quad \mathbf{b}\ R = CH_3$$



(**2**) S = solvent

This paper reports a study of such intermediates in THF and in acetonitrile (CH_3CN), as well as that of the species formed from reagent (**1b**) in Masamune's conditions.

(1) *Species formed from Compound* (**1b**) *by Action of Lithium t-Butoxide or n-Butyl-lithium in THF or* CH_3CN.—Solutions of phosphonate (**1b**) in THF or $[^2H_8]$THF of known concentrations were treated by increasing amounts either of solid $LiOBu^t$ or of a 1.6M-$LiBu^n$ solution in hexane. The THF solutions were evaporated and the solvent was replaced by CH_3CN or CD_3CN. All these operations were performed in a drybox under argon. The ^1H, ^{13}C, and ^{31}P n.m.r. and the i.r. spectra of these solutions were recorded at least 30 min after their preparation. When 0.75 equivalent of base was used, two sets of signals were observed in the ^1H and ^{13}C n.m.r. spectra in both solvents: one of them corresponds to the anionic part of the chelated ion pair (**2**), the other, which is different from that of (**1b**), can be ascribed to the presumed intermediate(s) (**I**). The main chemical shifts and coupling constants are given in Table 1. The ^{31}P spectra exhibit three to five signals (see Table 2) according to the nature of the base and its relative concentration (ρ = base:total phosphonate molar ratio). Two of the signals are due to (**1b**) and (**2**), suggesting the presence of several intermediate species (**I**). The i.r. spectra of these solutions also show, next to the absorptions characteristic of phosphonate (**1b**) and the chelated ion pair (**2**),[3] several other absorptions: characteristic i.r. spectra are in Figures 1 and 2.

Other experiments were also run: to (**2**), which is the only species observed in n.m.r. when a slight excess of base was used (ρ > 1, exp. 9, Table 2), increasing amounts of (**1b**) were added. The n.m.r. and i.r. spectra of these solutions were recorded: the

Table 1. ^{13}C and ^{31}P chemical shifts and coupling constants of phosphonate (**1b**) and chelate (**2**) in CD_3CN and of intermediate species (**I**) in CD_3CN and $[^2H_8]THF$[a]

Product	Solvent	δ_P	$\delta_{C(1)}$	$\delta_{C(2)}$	$\delta_{C(4)}$	$\delta_{C(2')}$	$\delta_{C(3')}$	$^1J_{PC(1)}$/Hz
(**1b**)	CD_3CN	19.1	34.5	167.4	52.9	63.3	16.6	132.7
(**2**)	CD_3CN[b]	38.8	41.8	175.8	51.3	61.4	16.7	222.0
(**I**)	CD_3CN[c]	28.1	35.9	172.5	49.9	63.9	16.7	133.3
(**I**)	$[^2H_8]THF$[d]	28.5	36.2	171.7	50.0	63.3	16.7	134.4[e]

[a] δ_P (solvent CH_3CN) in p.p.m. relative to external H_3PO_4 (85%), δ_C in p.p.m. relative to internal Me_4Si, J values in Hz. [b] The anionic species were formed by action of 1.1 equiv. of $LiBu^n$ on (**1b**) in THF; the solvents were evaporated under argon; the resulting solid was dissolved in CD_3CN. [c] As *b*, followed by adding 0.3 equiv. of (**1b**). [d] The (**I**) + (**2**) mixture was formed by action of 0.5 equiv. of $LiOBu^t$ on (**1b**) in $[^2H_8]THF$ [e] Other J_{PC} coupling constants: $^2J_{PC(2)}$ 3.4, $^2J_{PC(2')}$ 6.2, $^3J_{PC(3')}$ 7.6 Hz.

Table 2. Characterization by ^{31}P n.m.r.[a] and i.r. of the different species obtained by action of lithium bases on phosphonate (**1b**) according to the solvent and the base concentration

	Base				Phosphonate (**1b**)		Chelated anion (**2**)		Intermediates (**I**)		I.r. data
No.	C_B[b,c]	Solvent	C_P[d]	ρ[e]	δ_P	C(**1b**)[f]	δ_P	C(**2**)[f]	δ_P	C(**I**)[f]	C(**1b**)[g]
	$LiBu^n$	THF									
1	0.13	THF	0.42	0.31	19.6	0.26	39.9	0.13	28.5	0.03	0.32
2	0.15	THF	0.40	0.37_5	19.6	0.19	39.8	0.15	28.4	0.06	
3	0.22	THF	0.57	0.38	19.7	0.22	39.7	0.22	26.5 28.4 29.4	0.02 0.06 0.05	
4	0.34	THF	0.67	0.51	20.2	0.25	39.7	0.34	26.3 28.5 29.7	0.02 0.03 0.03	0.31
5	0.31	THF	0.53	0.58	20.0	0.10	39.6	0.31	26.4 28.4 29.4	0.02 0.05 0.05	
6	0.35	THF	0.50	0.70	20.4	0.04	39.6	0.35	26.2 28.5 29.7	0.02 0.05 0.04	0.06
7	0.35	THF	0.46	0.76	*h*		39.6	0.35	26.4 28.5 29.9	0.02 0.05 0.04	0.01
8	0.32	THF	0.36	0.88	*h*		39.7	0.32	26.4 28.4 29.6	0.01 0.01 0.02	
9	0.40	THF	0.37	1.08	*h*		39.5	0.37	*h*		
	$LiBu^n$	CH_3CN									
10	0.34	CH_3CN	0.67	0.51	19.7	0.24	38.9	0.34	26.5 28.2 29.1	0.02 0.05 0.02	0.26
11	0.35	CH_3CN	0.53	0.66	19.7	0.05	38.8	0.35	26.5 28.0 29.1	0.02 0.08 0.03	0.07
12	0.35	CH_3CN	0.46	0.76	*h*		38.8	0.35	26.4 28.1 29.2	0.02 0.06 0.03	0.01
	$LiOBu^t$	THF									
13	0.14	THF	0.45	0.31	19.7	0.29	39.9	0.14	28.5	0.02	0.38
14	0.27	THF	0.45	0.60	20.0	0.16	39.8	0.27	28.5	0.02	0.21
15	0.41	THF	0.45	0.91	20.3	0.03	39.8	0.41	28.5	0.01	0.06

[a] δ_P in p.p.m. relative to external H_3PO_4(85%). [b] All concentrations are in mol l^{-1}. [c] C_B is the added base concentration. [d] C_P is the total phosphonate concentration. [e] $\rho = C_B/C_P$. [f] The concentration of chelate (**2**) is postulated to be equal to that of added base, the relative concentrations in free phosphonate (**1b**) and intermediate species (**I**) are estimated from integration of ^{31}P n.m.r. spectra. [g] C(**1b**) estimated from intensity measurement of the $\nu_{C=O}$ band at 1 744 cm^{-1} in THF or at 1 740 cm^{-1} in CH_3CN. [h] Not observed.

results are in Table 2. However, when the amount of (**1b**) was high enough, proton spectra indicated a fast exchange between (**1b**) and (**2**) as shown *inter alia* by averaging of the H(1) signals and the absence of $^2J_{PH(1)}$.[3]

(a) *N.m.r.* From the n.m.r. data, it appears that while C(1) is planar[3] in (**2**) in both solvents ($^1J_{PC(1)}$ 222 Hz), it remains pyramidal in (**I**) ($^1J_{PC(1)}$ 133 Hz); moreover, the off-resonance ^{13}C spectrum confirms that C(1) bears two protons in (**I**) as it produces a doublet of triplets as expected for a PCH_2 fragment. However, ^1H (100 MHz) and ^{13}C (62.5 MHz) spectroscopy are unable to differentiate the various species (**I**) which were characterized by ^{31}P n.m.r. (32.4 MHz) (Table 2). These results suggest that part of the organic framework of these intermediates (**I**) has a structure close to that of the neutral phosphonate (**1b**); this moiety should strongly interact with a Li^+ cation, through its P–O and C=O oxygens, as ^{31}P and $^{13}C(2)$ are the most perturbed resonances in (**I**) relative to (**1b**). The slight differences observed in δ_P, for the various species (**I**),

Table 3. I.r. ν(C=O) and ν(P ⟶ O) frequencies (cm^{-1}) of the different observed species

Species		(**1b**) free	(**2M**)	(**2A**)	(**2T**)	(**2**) free	(**I**)
$\nu(C_2O_5)$	THF	1 744	1 597	1 578	1 634	1 525	1 675
	CH_3CN	1 740	1 592	1 575	1 632	1 525	1 668
ν(P ⟶ O)	THF	1 277 1 259 sh		1 185			1 259
	CH_3CN	1 277 1 257 sh		1 185			1 256

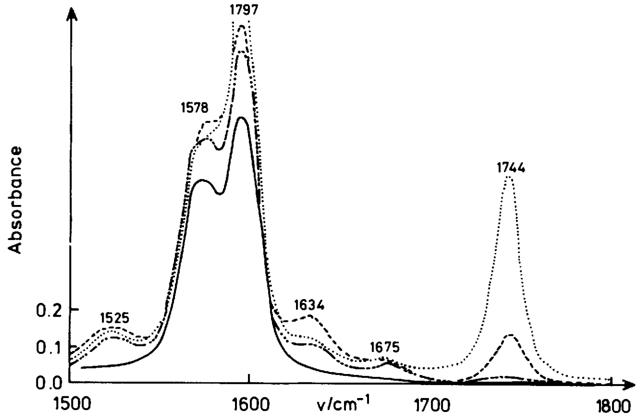


Figure 1. I.r. spectra of 0.35M solutions of (**2**) in THF with (**1b**) added. Concentration ratio, $\rho = C_B/C_P$: —— 1.08; —···— 0.76; ——— 0.66; ···· 0.51

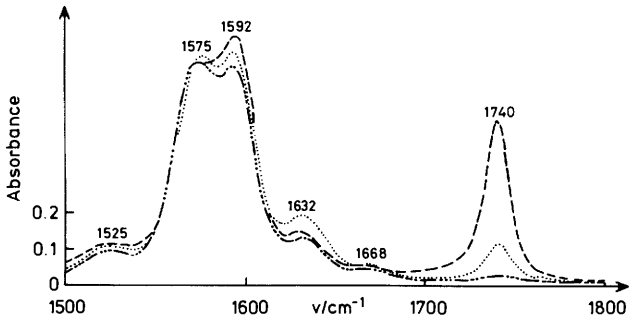
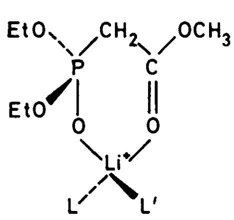


Figure 2. I.r. spectra of 0.35M solutions of (**2**) in CH_3CN with (**1b**) added. Concentration ratio, $\rho = C_B/C_P$: —··· —0.76; ···· 0.66; ——— 0.51



(**I**)

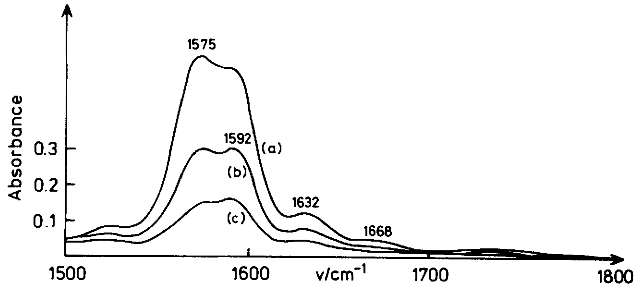
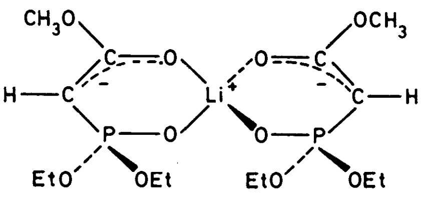


Figure 3. Variation with concentration of the i.r. spectra of (**2**) in CH_3CN: a, 0.33M; b, 0.20M; c, 0.10M

could be attributed to the nature of the other ligands L and L′ around the Li^+ cation, as it is well known that ^{31}P chemical shifts of phosphine oxides are very sensitive to the phosphoryl group environment.[4]

(b) *I.r.* The i.r. spectra of a solution of anionic species (**2**) obtained in CH_3CN, as well as in THF,[3] by use of a nearly equimolar amount of base ($\rho \sim 1$) show the disappearance of the 1 740 cm^{-1} $\nu_{C=O}$ band of (**1b**) and suggest that the chelated ion pairs (**2**) coexist as externally solvated monomers (**2M**) ($\nu_{C(2)\cdots O(5)}$ 1 592 cm^{-1} in CH_3CN, 1 597 cm^{-1} in THF) and aggregates (**2A**) (1 575 cm^{-1} in CH_3CN, 1 578 cm^{-1} in THF) (Table 3). These assignments were confirmed by dilution experiments by solvent addition which showed a decrease in the relative intensity of the absorption at 1 575 cm^{-1} in CH_3CN at higher dilutions (Figure 3). For a given concentration in (**2**), the aggregates proportion is lower in THF (Figure 3, ref. 3) than in CH_3CN (Figure 3, this work). Furthermore, in CH_3CN only, two other absorptions at 1 525 and 1 632 cm^{-1} are observed in these conditions ($\rho \sim 1$). Their intensity decreases less with dilution by solvent addition than that of the bands assigned to monomeric or aggregated ion pairs. The 1 632 cm^{-1} absorption can be attributed to triple ions (**2T**), formed at the expense of externally solvated chelated ion pairs (**2M**); this finding is in line with results previously published on the structure of lithium trifluoroacetate solutions[5] or those of lithium enolate of ethyl acetoacetate,[6] triple ions being particularly stable in CH_3CN.



(**2T**)

The 1 525 cm^{-1} absorption might tentatively be assigned to a very small amount of free anion. Unfortunately, the low intensities of the bands and the solvent absorption do not allow the observation of related bands in the ν_{P-O} stretching vibration region.

When less than one equivalent of base was used, or when increasing amounts of phosphonate (**1b**) were added to the lithiated phosphonate anion solution (**2**) ($\rho < 1$, Table 2), other absorptions than those attributed to aggregated (**2A**) or monomeric chelated ion pairs (**2M**) in THF, or to these entities as well as triple or free ions in CH_3CN, can be observed. They appear in the $\nu_{C=O}$ region at 1 675, 1 634, and 1 525 cm^{-1} in THF and at 1 668 cm^{-1} in CH_3CN, next to a band at 1 744 cm^{-1} in THF and 1 740 cm^{-1} in CH_3CN due to free (**1b**). The relative intensities of all these absorptions vary according to the amount and nature of the base used and its total concentration as seen in Figures 1 and 2. A striking observation is the fact that addition of 0.3 mol. equiv. of (**1b**) to a 0.35M solution of anionic species (**2**) (ρ 0.76) either in THF or in CH_3CN (Experiments 7 and 12) induces a very weak absorption at *ca.* 1 740 cm^{-1}, characteristic of $\nu_{C=O}$ of free (**1b**), whose intensity is therefore much lower than expected from the amount of added (**1b**). In other conditions (experiments 4, 5, 6, 10, and 11) the intensity of this band is also lower than expected. These results confirm, as proposed from the n.m.r. data, the formation of a species (**I**) in which phosphonate (**1b**) is no longer free, and is chelating a lithium cation. Its $\nu_{C=O}$ absorption could lie between that of free (**1b**) and that of anionic species (**2**): such a band is observed at 1 675 and 1 668 cm^{-1} in THF and CH_3CN respectively. In the ν_{P-O} stretching region, the absorption at 1 259 cm^{-1} in THF and 1 256 cm^{-1} in CH_3CN could also be assigned to (**I**), while that of free (**1b**) is located at 1 277 cm^{-1};[3] that of (**2**) is too weak to be observed.[3]

However, at low Li^+ concentration (ρ 0.3, experiment 1) or when the base used in THF to generate the anionic species was LiOBu^t (experiments 13—15), the amount of intermediate species (**I**) is very low as a very small absorption at 1 675 cm^{-1} can be seen, in agreement with the ^{31}P n.m.r. spectrum which indicates that the concentration in (**I**) is <0.03M.

In all the experiments in which neutral (**1b**) and anionic species (**2**) coexist, enhancement of the absorptions assigned to free and triple ions at 1 525 and 1 632 cm^{-1} in CH_3CN or at 1 525 and 1 634 cm^{-1} in THF is observed. Their intensities related to those of ion pairs and aggregates are at a maximum when 0.4—0.5 mol. equiv. of neutral (**1b**) was added to a 0.35M preformed solution of anionic species ($\rho \sim 0.7$, experiments 6 and 11). When $\rho < 0.7$, the main change in the i.r. spectrum is an increase in intensity of the band assigned to externally solvated chelated ion pair (**2M**) at the expense of aggregates (**2A**).

In THF and CH_3CN, when anion (**2**) is the only species in solution ($\rho > 1$), an equilibrium between aggregated (**2A**) and externally solvated chelated ion pairs (**2M**) is settled, as summarized in equilibrium (1). In CH_3CN, two other equilibria participate, involving free (2^-) and triple ions (**2T**), which are not observed in THF solution in similar conditions ($\rho > 1$) [equilibra (2) and (3)]. The presence of free phosphonate

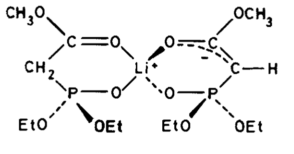
$$(\mathbf{2A}) \underset{\text{solvent}}{\rightleftharpoons} n\,(\mathbf{2M}) \qquad (1)$$

$$(\mathbf{2M}) \underset{\text{solvent}}{\rightleftharpoons} (2^-)_{\text{solv}} + Li^+{}_{\text{solv}} \qquad (2)$$

$$(\mathbf{2M}) + (2^-) \rightleftharpoons (\mathbf{2T}) + 2\ \text{solvent} \qquad (3)$$

(**1b**) generates another equilibrium in which (**1b**) is involved to chelate the lithium cation of (**2M**): the structure for the intermediate is ($\mathbf{I_1}$) in which L and L′ are the anionic framework of (**2**).

$$(\mathbf{2M}) + (\mathbf{1b}) \rightleftharpoons (\mathbf{I_1}) + 2\ \text{solvent} \qquad (4)$$



(I_1)

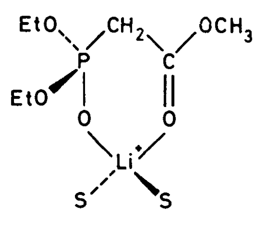
When LiOBu^t is used to generate the anionic species, the so-formed Bu^{t}OH can interact with (**1b**) by hydrogen-bonding: the concentration in ($\mathbf{I_1}$) becomes very low as (**1b**) is no longer available to shift equilibrium (4) to the right. The formation of ($\mathbf{I_1}$) is entropically favoured since two solvent molecules in (**2M**) are replaced by one chelating neutral phosphonate. Furthermore, the Li^+-solvating ability of the P–O and C=O oxygens of this bidentate ligand is certainly stronger than that of the two solvent molecules, so that the ionic moiety in ($\mathbf{I_1}$) is more easily dissociated than in (**2M**). This leads to an increasing amount of free ions in CH_3CN or to their appearance in THF, as well as to another intermediate ($\mathbf{I_2}$) where L and L′ should be two solvent molecules according to equilibrium (2′). The displacement of

$$(\mathbf{I_1}) \underset{\text{solvent}}{\rightleftharpoons} (2^-)_{\text{solv}} + (\mathbf{I_2}) \qquad (2')$$

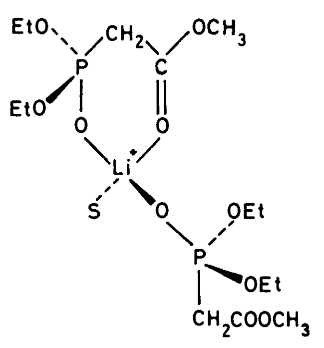
this equilibrium to the right also induces the formation of triple ions (**2T**) in THF according to equilibrium (3) or an increase in their concentration in CH_3CN. Therefore, at lower concentrations of (**1b**) ($\rho \geqslant 0.7$) the overall phenomenon observed becomes a stationary low concentration in free ions and an increase in that of triple ions, while there is nearly no modification in the relative ratio of aggregates and externally solvated ion pairs. At higher concentrations of (**1b**) ($\rho < 0.7$), free (**1b**) is observed: it probably acts as a monodentate ligand of lithium in (**2M**) and possibly participates in (**I**)–Li^+ solvation as ($\mathbf{I_3}$) where L and L′ are the monodentate (**1b**) molecule and a solvent molecule [equilibrium (4′)]. The main phenomenon

$$(\mathbf{I_2}) + (\mathbf{1b}) \rightleftharpoons (\mathbf{I_3}) + \text{Solvent} \qquad (4')$$

observed when $0.7 > \rho > 0.3$ is thus the increase in externally solvated ion pairs at the expense of aggregates.



(I_2)



(I_3)

The significant spectroscopic perturbations of the framework of (**1b**) seen in (**I**) are worthy of comment. Indeed, addition of 0.5 mol. equiv. of $(EtO)_2P(O)CH_3$(δ_P 31.4 p.p.m. in THF) to a solution of anionic species (**2**) in THF, gives rise to two ^{31}P signals at δ 39.5 [corresponding to (**2**)] and 33.0 p.p.m.: therefore, P–O monodentate lithium solvation, if it occurs, has only a slight influence on the ^{31}P chemical shift. Similar slight effects are observed in i.r. for monodentate P–O–Li^+ or C=O–Li^+ interactions, 10 or 25 cm^{-1} low-frequency shifts respectively.[7] The *ca.* 10 p.p.m. downfield ^{31}P chemical shift and the 18 and 70 cm^{-1} stretching vibrations low-frequency displacement of the P–O and C=O stretching vibrations between (**I**) and (**1b**) show an important structural reorganization of the phosphonate moiety when it acts as a rigid bidentate ligand.

Related i.r. perturbations have been previously observed in the formation of a bidentate complex between LiBr and ketophosphine oxide (3) ($\Delta\nu$P–O 25 cm^{-1}; $\Delta\nu$C=O 45 cm^{-1}).[8]

Table 4. Characterization by ^{31}P n.m.r.[a] and i.r. of the different species obtained by addition of DBU to an equimolar solution of phosphonate (**1b**) and lithium chloride in CH_3CN

				^{31}P N.m.r. data						I.r. data
						(I)				
No.	DBU C_{DBU}[b]	Total P C_P[b]	ρ'[c]	$\langle\delta\rangle$[d]	molar ratio (**1b**)/(**2**)	δ_P	C(I)[e]	C(**1b**)[e]	C(**2**)	C(**1b**)[f]
16	0	0.4	0							0.4
17	0.04_6	0.37	0.12_4	20.5_6	12.70	28.0	0.01_7	0.32_7	0.02_6	0.27
18	0.09_2	0.37	0.24_8	21.3_9	7.70	28.0	*g*	*g*	*g*	0.25
19	0.18	0.36	0.5	25.6	2.05	28.0 24.8	*g*	*g*	*g*	0.2
20	0.27	0.36	0.75	28.1	1.20	28.1 24.8	*g*	*g*	*g*	0.17
21	0.36	0.36	1.0	30.5_7	0.72	28.1 24.8	*g*	*g*	*g*	0.12
22	0.52	0.36	1.44_4	31.5_3	0.59	28.2 24.8	0.03_6 0.02_4	0.11_1	0.18_9	0.12
23	0.68	0.34	2.0	32.7_5	0.45	28.2 24.8	0.02_9 0.02_9	0.08_7	0.19_5	0.09
24	0.96	0.32	3.0	34.1_8	0.31	28.3 24.8	0.02_8 0.03_5	0.06_1	0.19_6	0.08

[a] δ_P in p.p.m. relative to external H_3PO_4 (85%). [b] All concentrations are in mol l^{-1}. [c] $\rho' = C_{DBU}/C_P$. [d] $\langle\delta\rangle$ is the ^{31}P averaged chemical shift due to a fast proton exchange between phosphonate (**1b**), δ(**1b**) 19.1_2, and chelate (**2**), δ(**2**) 38.8_5. The molar ratio [(**1b**)/(**2**)] was calculated from $\langle\delta\rangle$ = P(**1b**)δ(**1b**) + P(**2**)δ(**2**). [e] Relative concentrations estimated from integration of ^{31}P n.m.r. spectra. [f] C(**1b**) estimated from intensity measurement of the $\nu_{C=O}$ band at 1 740 cm^{-1}. [g] The relative concentrations of the different species could not be estimated due to overlap of the signals.

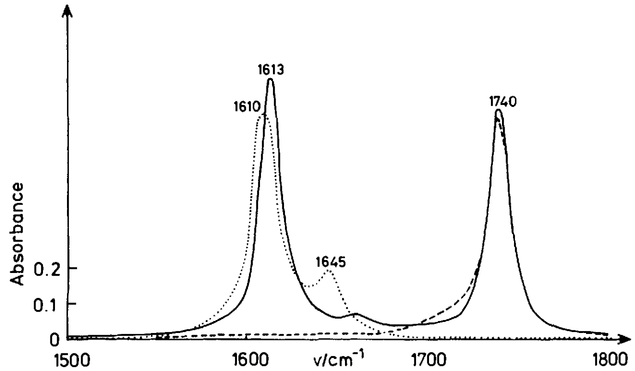
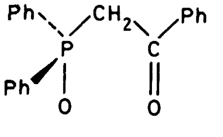
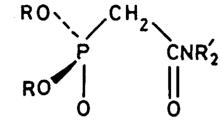


Figure 4. I.r. spectra of solutions in CH_3CN: —— (**1b**) 0.36M + DBU; – – – (**1b**) 0.37M + LiCl; ···· DBU 0.35M + LiCl

The complexes formed between lanthanide salts and phosphonoacetamides (**4**) also show similar low-frequency i.r. shifts ($\Delta\nu$P–O *ca.* 50 cm^{-1}; $\Delta\nu$C=O *ca.* 30 cm^{-1}).[9]



(3)



(4)

(2) *Study of the Deprotonation of* (**1b**) *by Lithium Chloride and 1,5-Diazabicyclo*[5.4.0]*undec-5-ene (DBU) in Acetonitrile*.—Preliminary experiments showed that the ^{31}P n.m.r. and i.r. spectra of (**1b**) in CH_3CN solution are not significantly altered by addition of either DBU or LiCl, which is solubilized to some extent (Figure 4). LiCl, which is poorly soluble in CH_3CN, can be solubilized up to 0.35M by a 0.5M solution of DBU in this solvent. The i.r. spectrum of this solution shows a slight shift of the DBU $\nu_{C=N}$ band from 1 613 to 1 610 cm^{-1} and the appearance of a new one at 1 645 cm^{-1} which corresponds to the DBU–LiCl interaction. Increasing amounts of DBU (from 0.12 to 3 equiv.: ρ') were added to a 0.37M solution of phosphonate (**1b**) in the presence of 0.37M solid LiCl which is totally solubilized in all the cases.

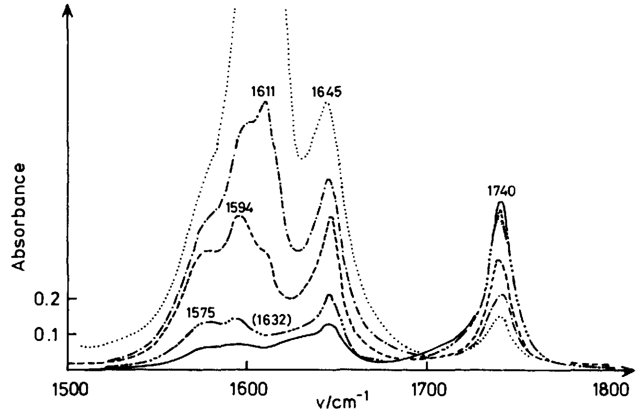


Figure 5. I.r. spectra of an equimolar solution of LiCl and phosphonate (**1b**), 0.37M in CH_3CN, in the presence of DBU. Concentration ratio, $\rho' = C_{DBU}/C$(**1b**): —— 0.12; —···— 0.25; – – – 0.75; —·—· 1.5; ···· 3

(a) *I.r.* The modification of the $\nu_{C=O}$ region of the i.r. spectra of these solutions is shown in Figure 5. Addition of DBU induces a progressive decrease in the intensity of the 1 740 cm^{-1} absorption due to free (**1b**) and the appearance of those assigned to aggregated (**2A**) and externally solvated chelate (**2M**) at 1 575 and 1 594 cm^{-1}, as well as that of triple ions (**2T**) at 1 632 cm^{-1} although very weak. Formation of chelate (**2**) is confirmed by the decrease in intensity of the ν_{O-CH_3} band of (**1b**) at 1 118 cm^{-1} to the benefit of ν_{O-CH_3} of (**2**) at 1 137 cm^{-1}. When the

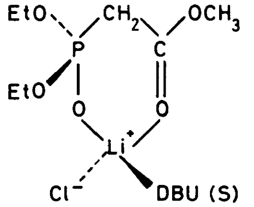
DBU concentration increases (ρ′ > 0.5), the intensity of the band due to externally solvated species (**2M**) grows at the expense of those of aggregates (**2A**) and of free (**1b**). However, at high DBU concentration (ρ′ 3), deprotonation of (**1b**) is not complete since the 1 740 cm^{-1} absorption still exists. On the other hand, for low concentrations in DBU (ρ′ < 1), only the band due to associated DBU at 1 645 cm^{-1} has an appreciable intensity, while, at higher DBU content (ρ′ ⩾ 2), a band is observed at 1 610 cm^{-1}, the intensity of which increases with DBU concentration, showing that free DBU is present. The 1 645 cm^{-1} band obscures the region where the absorption of (**I**) should be expected. The measurement of the intensity of the 1 740 cm^{-1} $\nu_{C=O}$ absorption allows the concentration in free (**1b**) to be determined (Table 4).

(b) *N.m.r.* The ^{31}P n.m.r. spectra of these solutions consist of one or two sharp signals at δ 28.0 and 24.8 p.p.m. whose chemical shifts are close to those of intermediates (**I**) and a broad one, the chemical shift of which varies between δ 20.6 and 34.2 p.p.m. according to the DBU concentration. This observation, together with the absence of signals due to the anionic part of chelate (**2**) at δ 38.8 p.p.m. and to free phosphonate (**1b**) at δ 19.1 p.p.m., which are present in solution according to the i.r. spectra, indicate that the broad signals correspond to average ones due to a fast proton exchange between (**2**) and (**1b**). The relative populations of (**2**) and (**1b**) can be deduced from the chemical shift of the coalesced signal. The ability of DBU to increase the rate of exchange between (**2**) and (**1b**) was proven by an independent experiment: the sharp and distinct ^{31}P signals, observed for (**2**) and (**1b**) without DBU, broaden in THF and coalesce in CH$_3$CN by addition of 1 mol. equiv. of this base. However, the signal(s) of (**I**), observed in such solutions, still remain sharp, thus showing that (**I**) does not participate in the exchange process.

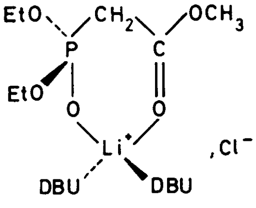
At low DBU content (ρ′ < 0.5) a single intermediate (**I$_4$**) is observed at δ 28.0 p.p.m. while a second one (**I$_5$**) appears when the amount of added DBU increases. In analogy with the previous results, namely ^{31}P chemical shifts, both entities certainly include a neutral phosphonate moiety in the lithium cation first solvation shell. From the ^{31}P n.m.r. spectra, the relative concentrations of the different species can be estimated, when there is no overlap of the signals (ρ′ 0.12 or ⩾ 1.4): these results are gathered in Table 4. Despite the low precision of these methods, there is good agreement between the estimations in free (**1b**) concentrations determined by n.m.r. and i.r. These concentrations decrease rapidly with DBU addition until ρ′ 1 and vary more slowly beyond this value.

The fact that the concentration in (I$_4$) is always low and nearly constant and that its ^{31}P chemical shift is close to that of the intermediates observed previously suggests that in (I$_4$) a negatively charged ligand is co-ordinated to the cation in its first solvation shell: therefore L and L′ in (I$_4$) could be either the anionic moiety of chelate (**2**) *i.e.* (I$_4$) = (I$_1$) or Cl$^-$ and either DBU or a solvent molecule (I$_{4a}$).

The amount of (I$_5$) increases with DBU concentration: therefore DBU is certainly involved in Li$^+$ co-ordination. The ^{31}P upfield shift related to (I$_4$) probably reflects a change in charge distribution around the cation: the anion associated to Li$^+$ should not be included in its first solvation shell, suggesting the formation either of a DBU separated ion pair as in (**I$_5$**) or of the corresponding free ions.



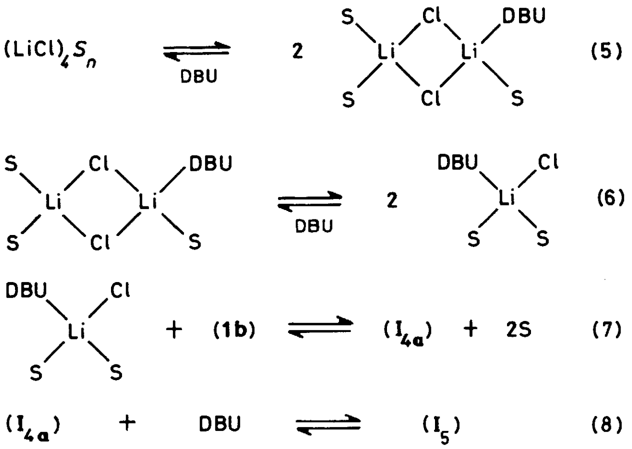
(I$_{4a}$)



(I$_5$)

From the literature,[10] it is known that lithium bromide is strongly soluble in ethereal solvents as solvated tetramers. In solvents having a higher dielectric constant, such as dimethyl or diethyl carbonate, it exists as dimeric ion pairs in equilibrium with monomeric ones.[11] LiCl is poorly soluble in low polar aprotic solvents and is certainly even more aggregated than is LiBr. In the presence of phosphonate (**1b**), it can be solubilized into CH$_3$CN to some extent: the i.r. spectrum of (**1b**), which only shows a very slight perturbation in the $\nu_{C=O}$ region, suggests that the aggregates or the tetramers should not be disrupted by (**1b**) in these conditions. DBU also can solubilize LiCl in CH$_3$CN, to a larger extent than (**1b**): this solubilization induces a noticeable perturbation of the i.r. spectrum of DBU. This interaction is indicative of a deaggregation of the salt, as exemplified in equilibria (5) and (6).

In the presence of both DBU and (**1b**) the activated salt should be able to co-ordinate to phosphonate (**1b**) even at low DBU concentration as in (I$_{4a}$) (experiments 17 and 18) [equilibrium (7)] so that its deprotonation by DBU could take place, leading to chelate (**2**). However, when the spectra are run after equilibration of the different species in solution, it is impossible to discriminate the ligands L and L′ in (I$_4$), as far as some chelate (**2**) is formed. At higher DBU concentrations (experiments 19—24) (I$_5$) certainly intervenes in the process [equilibrium (8)].



From the i.r. spectra (Figure 4), it appears that chelate (**2**) does exist as aggregates (**2A**) and externally solvated monomeric ion pair (**2M**) next to a small amount of triple anion (**2T**). When the DBU content increases, the amount in (**2**) also increases but favouring (**2M**) by deaggregation of (**2A**) according to an equilibrium analogous to equilibrium (6), next to the shift of equilibria (1)—(3). Therefore the role of DBU is manifold in these processes: (a) it solubilizes and deaggregates LiCl, thus forming activated LiCl ion pairs [equlibria (5) and (6)]; (b) it deprotonates Li$^+$ chelated phosphonate (**1b**) in intermediates (I$_{4a}$) or (I$_5$); (c) it deaggregates (**2A**) into (**2M**); (d) it accelerates the proton exchange between (**2M**) and free (**1b**). Rigid bidentate phosphonate included in the various intermediates (**I**) is not involved in this fast proton exchange, although it certainly bears a very acidic proton. This is a very unexpected observation and therefore a proton jump from *sp*^{3} to *sp*^{2} carbons within (I$_1$) may be excluded.

Conclusion.—Methyl diethylphosphonacetate (**1b**) is able to act as a bidentate ligand of lithium cation, provided that the corresponding salts are not too highly aggregated. In THF and in CH_3CN, the n.m.r. and i.r. spectra of the framework of (**1b**) in these chelates are strongly perturbed by co-ordination to the lithium cation, the carbonyl group being more affected than the phosphoryl one. Deprotonation of (**1b**) by an amine in the presence of LiCl in acetonitrile, as recently proposed for the Horner–Wadsworth–Emmons modification of the Wittig reaction,[1,2] certainly takes place with such lithiated chelated intermediates.

Experimental

Materials.—Methyl diethylphosphonoacetate (Janssen) was distilled under reduced pressure and kept under argon. Diethyl methylphosphonate (Aldrich) was used without purification. Tetrahydrofuran (Merck pure) was distilled over $LiAlH_4$ and kept under argon. Acetonitrile (Merck) was dried over molecular sieves (Merck 3 or 4 Å). 1,5-Diazabicyclo[5.4.0]undec-5-ene (Janssen) was used without purification. n-Butyllithium solutions (Merck; 1.6M in hexane) were standardized by acid–base titration before use. Lithium t-butoxide was prepared from Li and freshly distilled Bu^tOH, vacuum dried after solvent evaporation, and kept under argon. Lithium chloride (Merck) was dried under vacuum at 120 °C during 8 h. Deuteriated solvents were commercial.

Preparation of Solutions.—Solutions were prepared in a dry box or in a glove bag under argon. Two different procedures were used to prepare THF solutions: (a) increasing amounts of $LiBu^n$ were added to a solution of (**1b**) in THF (experiments 1, 2, 3, 5, 8, and 9), concentrations are in Table 2; (b) anionic species (**2**) was initially formed by adding one equivalent of $LiBu^n$ to a solution of (**1b**) in THF. Various amounts of (**1b**) were then added to the preformed anionic species (**2**) (experiments 4, 6, and 7).

Solutions in CH_3CN were prepared by evaporating the former THF solutions under argon at room temperature and adding the same volume of CH_3CN (experiments 10—12). Solutions used in experiments 13—15 were obtained by adding increasing amounts of dried $LiOBu^t$ to a solution of (**1b**) in THF.

The solutions used in experiments 16—24 of Table 3 were prepared by adding increasing amounts of DBU to an equimolar solution of (**1b**) and LiCl in CH_3CN.

I.r. Spectra.—I.r. spectra were scanned on a Perkin-Elmer 983 spectrometer. The resolution was usually 3 cm^{-1} and the frequencies are given with a precision of at least ± 1 cm^{-1}. The cell of 0.003 cm thickness was equipped with CaF_2 windows.

N.m.r. Spectra.—^{31}P Spectra were recorded at 80.13 MHz on a Bruker WP-80 spectrometer, using Fourier transform mode and ^1H noise decoupling. A capillary filled with $(CD_3)_2CO$ served as a ^2H internal lock. Spectral width of 10 kHz was used (digital resolution: 2.5 Hz per point).

^{13}C Spectra were recorded at 62.9 or 25.17 MHz on a Bruker AM-250 spectrometer or a Varian XL-100 instrument, using the Fourier mode and ^1H noise decoupling. The ^2H resonance of the solvent (CD_3CN or $[^2H_8]THF$) was used to provide a ^2H internal lock. Spectral width of 15 kHz was used (digital resolution: 1.85 Hz per point) for the 62.9 MHz spectra. Spectral widths of 5 or 2.5 kHz were used for the 25.17 MHz spectra (digital resolution: 1.25 or 0.68 Hz per point).

^1H Spectra were recorded on a Varian XL-100 spectrometer using the continuous wave mode. The ^1H resonance of Me_4Si was used to provide the field frequency lock.

N.m.r. data of phosphonate (**1b**) and chelate (**2**) have been previously published[3] (solvents THF, Me_2SO, and pyridine). ^1H N.m.r. data for intermediate (**I**) ($[^2H_8]THF$—$LiOBu^t$): δ 2.85 (1-H), 3.27 (4-H), 4.16 (2′-H), and 1.27 (3′-H) ($^2J_{PH}$ -20.3 Hz).

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