Spectroscopic studies of the structure of carbanionic species in nonaqueous solutions: Identification of reactive intermediates

J. CORSET

Laboratoire de Spectrochimie Infrarouge et Raman
CNRS - 2, rue Henri Dunant - 94320 Thiais - France

<u>Abstract</u> — The comparison of the structure of the chelated carbanions of acetylacetone, acetylacetate, keto and esterphosphonate through X-ray, IR and NMR data shows that the oxygen atom α to the carbonyl ester group plays an important role in the stability of the chelated ion pair. The charge delocalization between the carbonyl oxygen atoms and the central carbon atom is more sensitive to the cation field effect in esters as the extra cycle oxygen atom may participate in that delocalization. The phosphorus atom reinforces this effect as it already drains the electrons from this oxygen in the parent phosphonate ester. In the corresponding free anions like in the neutral phosphorus ylids, the activation barrier relating the Z and the E conformer is higher in the ketonic compounds than in esters where the C_1-C_2 bond has a lower double bond character due to the larger delocalization possibilities and also to the lower oxygen charge repulsion in phosphonates compounds.
The analysis through IR and NMR of the formation mechanism of the ester phosphonate from an organic base or from an "amine (DBU) activated" lithium salt shows the formation of different intermediate species <u>I</u>. The underprotonated phosphonate is strongly bonded as a bidentate ligand to the lithium cation of the activated lithium salt in these species. Although the protons of the neutral phosphonate part of <u>I</u> becomes more acidic than those of the free ligand, this intermediate species does not participate to the fast exchange observed between the free ligand and the anionic species in the presence of DBU. Such intermediates seem not to be formed with ketophosphonates (study underway) probably due to the lower basicity of its carbonyl group or to the larger stability of the derived carbanionic chelated ion-pair.
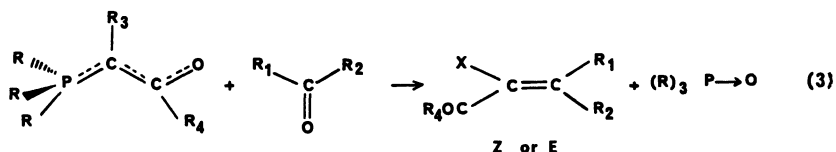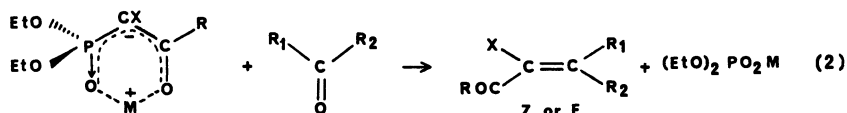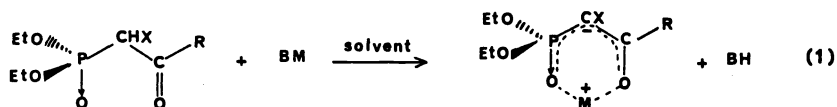
INTRODUCTION

The development of "fine chemical" processes needs a precise understanding of the various steps of the reaction mechanism. The knowledge of the elementary molecular or ionic steps of the reaction may be a guide for the discovery of milder or easier reaction conditions, for the use of cheaper reagents or for getting a better control of the stereochemistry of the products. Carbanionic species in solutions have a very large place in that field as they are important reaction intermediates mainly in the formation of carbon-carbon bonds.

Vibrational spectroscopy is an important tool often complementary to NMR for the structural analysis of carbanionic species (ref. 1, 2). Both techniques allow determination of the species formed in solutions through analysis of the internal vibration frequency shifts or of the NMR chemical shifts and coupling constant variations between the parent carbon acid and the carbanionic species. More accurate structural information may be obtained through vibrational spectroscopy when model compounds may be crystallized in order to obtain X-ray structures which give information on the geometries. The spectra of these models may indeed be compared to those of the species formed in solutions. This type of analysis has been particularly successful for the identification of dicarbonyl enolate ion-pairs which may be crystallized through use of strong complexing agents of the cations such as tetramethylene diamine TMEDA (ref. 3), crown ethers

(ref. 4). Triple anions have been crystallized through encapsulation of one
potassium or lithium cation by the 222 or 211 cryptands (ref. 5). These
spectroscopic studies have largely contributed to a better understanding of
the structure of the carbanions in solutions and of the reactivity and the
regioselectivity of their alkylation compared to that of free anions which
are formed in dissociating solvents, such as DMSO, HMPA, or through cryptation
of the potassium cation (ref. 1, 2, 6—8).

Vibrational and NMR spectroscopy are also complementary as they have very
different characteristic observation time scales, and may then give
methods on the lifetime of the species formed in these solutions. They
may thus through this dynamical approach allow to characterize important
reaction intermediates.

We shall mainly focus in this topic on the use of these complementary
information for the study of reaction mechanism. As several examples of the
reactivity of isolated carbanionic ion—pairs have been reported, we shall now
draw attention to the aggregation and solvation state of these organometallic
compounds in solution and to their influence on the reactivity. For a long
time, we have been involved in the study of carbanionic species α to a phosphoryl
group (ref. 9, 10). These are important reagents on the way to the formation
of carbon—carbon double bonds (ref. 11) through the Wittig—Horner reaction.
They allow, for instance, to synthesize important biological compounds
including αβ unsaturated ketones or esters.

$$\text{EtO}_{\prime\prime\prime\prime}\overset{}{\underset{\text{EtO}}{P}}\overset{\text{CHX}}{\underset{\text{O}}{|}}\overset{}{\underset{\text{O}}{C}}\text{—R} \quad + \quad \text{BM} \quad \xrightarrow{\text{solvent}} \quad \text{(1)} \quad + \quad \text{BH} \qquad (1)$$

$$\text{(2)}$$

$$\text{(3)}$$

We shall first recall how spectroscopy leads to demonstrate the structural
analogy of the keto or ester phosphonates anions with acetylacetonates and
acetylacetates anions as well as with the corresponding phosphorus ylids. We
shall discuss in details the mechanism of formation of these anions according
to the solvent and the nature of the organic bases BM used to generate them,
equ. (1). We shall further show how this mechanism allows to explain their
generation in milder conditions from simple lithium salts and an appropriate
solvating agent as has been recently reported by Masamume et al. (ref. 12)
and by Rathke and Nowack (ref. 13).

STRUCTURE AND PROPERTIES OF THE CARBANIONIC SPECIES OF DIETHYL [(CARBOMETHOXY)METHYL]PHOSPHONATE

Structure of the chelated carbanion in the ion-pairs and aggregates

Most of the carbanionic species are formed by reaction of the parent neutral
compound with relatively strong organic bases BM (eq. 1), such as
n—butyllithium, potassium t—butoxide or sodium hydride which are the most
commonly used ones. The choice of the solvent is limited by its reactivity
with BM compared with the carbon acidity of the parent compound. The solvents
used are therefore non—polar or weakly polar (class A or B, ref. 1) and have
very weak carbon acidity (ref. 35), and low acceptor number (ref. 36), so
that the carbanionic species formed remain associated with the cation and
often form aggregates (A). Even in the presence of strong complexing agents
of the cations such as crown—ethers (ref. 37) or cryptands (ref. 38), they
still form contact, or solvent separated ion—pairs, and keep a very similar
structure in the solutions (ref. 7). The bidentate carbanions such as
acetylacetonate 1, acetylacetate 2, ketophosphonate 3 and esterphosphonates
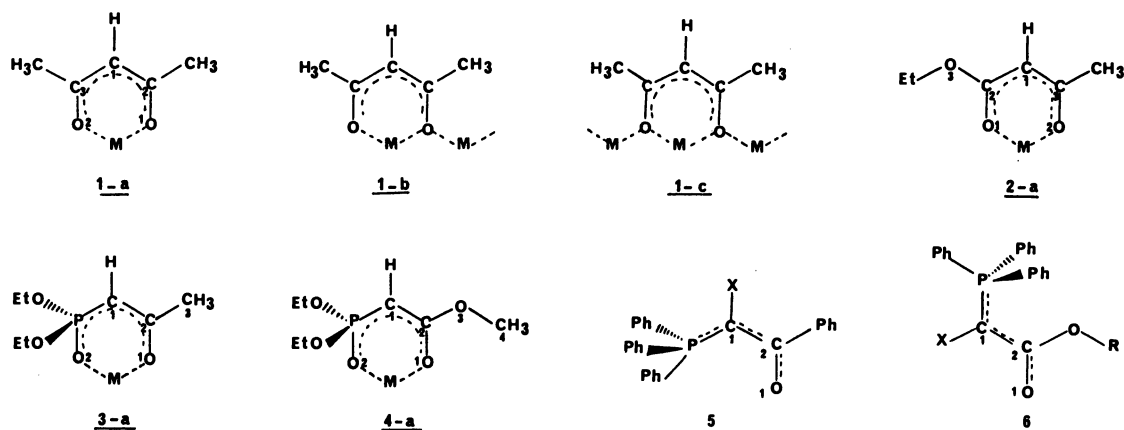4, form with alkali or alkaline—earth metals cation chelated ion pairs,

Fig. 1 : Model structure for carbanions : acetylacetonates **1**, acetylacetates **2**, ketophosphonate **3**, esterphosphonate **4** and for phosphorus ylidic ketone **5** and ester **6**. a, b and c indicates different metal anion interactions.

dimers of ion-pairs, or higher aggregates. The anion cation environment may be slightly different in the ion-pair a, in the trimers b or in the aggregates c (see Fig; 1). Selected X-ray bond lengths and angles, infrared (IR) frequencies and NMR chemical shifts or coupling constants which characterize the structure of these chelated anions are summarized in Tables 1 to 4. For comparison, we have also introduced some divalent transition metal cations like Cu, Co or Pt associated species, although they may introduce some disymmetry in the ligand field even with the most symmetric **1** as in **1aCu(II)**. In order to compare the frequency shifts, for the stretching vibrations of the chelated cycle of the carbanions, Tables 1 and 2 give the $\nu_m(CO)$ and the $\nu_m(CC)$ frequencies. The assignments of $\nu_s(CO)$, $\nu_a(CO)$, $\nu_a(CCC)$ and $\nu_s(CCC)$ follows those of Junge and Musso (ref. 15) which are based on isotopic $^{16}O/^{18}O$, $^{12}C/^{13}C$ and $^{1}H/^{2}H$ substitution. The $\nu_m(CO)$ and $\nu_m(CC)$ frequencies give approximate values of the CO and CC stretching vibrations in spite of the slight asymmetries previously underlined and of the slight participation of the $\delta(CH)$ vibration coordinate to the $\nu_a(CCC)$ and $\nu_a(CO)$ modes as well as of the $\nu(C-CH_3)$ vibration coordinate to the $\nu_s(CCC)$ as shown by the calculation of the form of normal modes by Behnke and Nakamoto (ref. 19). We shall only consider the mean CC or CO bond lengths as it is almost impossible to discriminate between $\nu(C=O)$ frequencies of the ketone and the ester group

Table 1 : X-ray data and IR frequencies for some acetylacetonates **1**

comp	ref[*]	$\nu_s(CO)$ $\nu_a(CO)$ / $\nu_m(CO)$		$\nu_a(CC)$ $\nu_s(CC)$ / $\nu_m(CC)$		ref	C_1C_2 C_1C_3 / $(CC)_m$		C_2O_1 C_3O_2 / $(CO)_m$	
1bMg	(15)	1612	1263	1519	1196	(14)	139	142	130	125
			1437.5		1357.5			140		127.5
1cLi	(15)	1602	1263	1517	1199	(16)	140	140	126	126
			1432.5		1358			140		126
1aK	(15)	1617	1234	1506	1198	(34)	141	141	126	126
			1425.5		1352			141		126
1aCuII	(15)(18)	1578	1397	1527	1281	(17)	145	150	124	129
			1487.5		1400.5			147.5		126.5
1aPtClK	(19)	1563	1380	1538	1380	(19)	139	139	128	128
			1450.5		1413			139		128

[*]$\nu_m=(\nu_a+\nu_s)/2$; $(CC)_m=(C_1C_2+C_1C_3)/2$ and $(CO)_m=(C_2O_1+C_3O_2)/2$

Table 2 : X-ray data and IR frequencies for some acetylacetates $\underline{2}$

comp	ref*	$\nu_s(CO)$ $\nu_m(CO)$	$\nu_a(CO)$	$\nu_\alpha(CC)$ $\nu_m(CC)$	$\nu_s(CC)$	ref	C_1C_3 $(CC)_m$	C_1C_2	C_3O_2	C_2O_1 $(CO)_m$	C_2O_3
$\underline{2b}$Mg	(20)	1635 1585	1535	1589 1434	1279						
$\underline{2a}$Li K(222)	(21) (5)	1638.5 1566	1494	1506 1380	1234						
$\underline{2c}$Li	(15)	1643 1566.5	1488	1500 1369	1238						
$\underline{2a}$K(18C6)	(21) (7)	1664.5 1567	1472	1528 1369	1210	(7)	142 141	140	122	122 122	137
$\underline{2a}$Na(15C5)	(7) (21)	1657 1565.5	1473	1518.5 1367.5	1217	(7)	139 137.5	136	117	120 118.5	141
$\underline{2a}$K(18C6)	(21) (7)	1664.5 1567	1472	1528 1369	1210	(7)	142 141	140	122	122 122	137
$\underline{2a}$Cu(II)	(21)	1601 1570.5	1540	1559 1425	1291	(22)	131 135	139	132	128 130	131

*see note Table 1

Table 3 : X-ray, NMR data and IR frequencies for some ketophosphonates $\underline{3}$ and phosphorus ylidic ketones $\underline{5}$*

comp **	ref	$\nu(PO)$	$\nu(CC)$	$\nu(CO)$	ref	$\delta^{31}P$	$\delta^{13}C$	^1JPC	ref	P_2O	P_1C	C_1C_2	C_2O_1
$\underline{3b}$Mg	(23)	1196 (−64)	1420	1557 (−153)					(14)	148	172	136	132
$\underline{3a}$Li	(26)	1198 (−62)	1431	1535 (−182)									
$\underline{3a}$Na	(24)	1193 (−67)	1425	1530 (−180)			38 (−13)						
$\underline{3a}$K	(26)	1192 (−68)	1418	1522 (−195)	(25)	33.3 (−14)	63.3 (−21)	194.9 (−70)					
$\underline{3b}$CoII	(24)	1185 (−75)	1403	1544 (−166)					(27)	146	173	136	130
$\underline{5}$(X=Cl)	(29)		1470 (−205)		(29)	19.8 (+3)			(28)		173	136	130
$\underline{5}$(X=H)	(26)		1390 (−140)	1520	(30)	16.8 (+5)	50.4 (−12)	111.7 (−50)					

*numbers between parenthesis are : $\Delta\nu=\nu(\underline{7})-\nu(\underline{3})$; $\Delta\delta=\delta(\underline{7})-\delta(\underline{3})$; $\Delta J=J(\underline{7})-J(\underline{3})$ excepted for $\underline{5}$ where in the $\Delta\delta$ $\underline{7}$ and $\underline{3}$ are replaced by the corresponding phosphonium salt and $\underline{5}$ respectively.
$\delta^{31}P$ in ppm relative to external H_3PO_4 (85%), $\delta^{13}C$ in ppm from internal Me_4Si, positive δ values are in the direction of increasing frequency.

**IR and NMR data observed for $\underline{3b}$–Mg in solutions, $\underline{3a}$–Na and $\underline{3a}$–CoII benzene solution, $\underline{3a}$K pyridine or Me_2SO solutions, $\underline{3a}$Li in THF solution.

TABLE 4 : X-ray, NMR data and IR frequencies for some ester phosphonates 4 and phosphorus ylidic esters 6*

| Comp	IR frequencies(cm⁻¹)				NMR Chem. shifts δ(ppm) and coup. const. J(Hz)				X-ray bond lengths pm			
**	ref	$\nu(PO)$	$\nu(CC)$	$\nu(C_2O_1)$	ref	$\delta^{31}P$	$\delta^{13}C_1$	$^1JPC_1$	P_1C	C_1C_2	C_2O_1	C_2O_3
4bMg	(31)	1205 (-70)	1410	1580 (-160)								
4cLi	(9)		1377	1596 (-150)	(9)	38.7 (-20.1)	41.0 (-6.6)	223.1 (-90.5)				
4aLi		1190 (-78)	1361	1598 (-137)		38.4 (-19.2)	39.6 (-6.4)	219.6 (-88.3)				
4cK			1368	1612 (-134)		38.7 (-20.1)	39.0 (-4.6)	218.0 (-85.4)				
4aK		1192 (-76)	1359	1611 (-124)		37.5 (-18.3)	39.2 (-5.9)	221.3 (-90.0)				
6 R=Me(32) X=CH₂CO₂Bu				1620			36.0	130	171	141	122	138
6 X=H (33) R=Me ou Et			1336	1615	(30)	17.8 (+3.2)	29.8 (-11.3)	126.7 (-67.9)				

*See footnote table 3, where 4, 8 and 6 replace respectively 3, 7 and 5.
**IR and NMR data observed for 4bMg in nujol mull, for 4cLi and K in THF solutions and for 4aLi and K in DMSO solutions.

in the acetylacetonate anion. The Δν or Δδ are the IR frequency variations or the variations of the chemical shifts from those of the parent molecule 7 and 8 or from the corresponding phosphonium salts for 5 and 6.

$$(EtO)_2\ PO\ CH_2\ CO\ CH_3 \qquad\qquad (EtO)_2\ PO\ CH_2\ COO\ CH_3$$
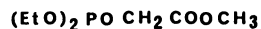
$$\underline{7} \qquad\qquad\qquad\qquad \underline{8}$$

For acetylacetonates 1 (table 1), the lengthening of the C=O bond from 121.5pm in acetone (ref. 39) to a mean value of 127pm in 1 correspond to a 275cm⁻¹ lowering of the mean ν(C⋯O) frequency at 1435cm⁻¹ compared to that of the acetone (ref. 40) when the alkaline or alkaline earth cations (M) are concerned. The ν(C=O) frequency of the acetone is indeed very close of that of the acetylacetonate at 1727cm⁻¹. A corresponding shortening of the C-C bond from 151.5pm in acetone to a mean value of 140pm corresponds to an increase of the mean ν(C⋯C) frequency at 1355cm⁻¹. The interaction with softer cations such as CuII or PtII gives a slightly smaller ν(C⋯O) and higher ν(C⋯C) increase (∼50cm⁻¹) than in 1aM. This effect shows a stronger electron delocalization inside the chelate cycle, where the C⋯C bonds have a larger π character, when the C-M bonds become more covalent. The points corresponding to these frequencies and bond lengths are close to the straight line drawn on Fig. 2 for data from neutral molecules. There is however an exception for the C-C bond length in 1aCu but this discrepancy may come from a lack of refinement of the structure as already pointed out (ref. 41).

For acetylacetates 2a, a similar trend of frequencies is noticed, with nevertheless a smaller lowering of the νm(C-O) frequency from 1747cm⁻¹ for the methylacetate (ref. 42) to about 1570cm⁻¹, that is to say about 180cm⁻¹ compared to 275cm⁻¹ for 1. The increase of the νm(C-C) frequency in 2 is only slightly higher than 1. This frequency increase of the bonds of the chelate cycle is certainly due to the electron draining off the C₂O₃ bond. This bond is indeed lengthened in ionic compounds like 2aK(18C6) and 2aNa(15C5) compared to the value of 133pm in the methylacetate (ref. 43) and its frequency decreases from 1248cm⁻¹ (ref. 42) to 1152cm⁻¹ (ref. 7). This larger electron delocalization in the chelate cycle and the C₂O₃ bonds make the charge delocalization more variable with the cation field strength. This effect is clearly seen through comparison of 2aK(18C6) and 2aNa(15C5) where the shortening of the bonds of the cycle is compensated by a lengthening of the C₂O₃ bond. For 2aCu the larger delocalization in the chelate cycle is also related to a larger lengthening of the C=O bonds
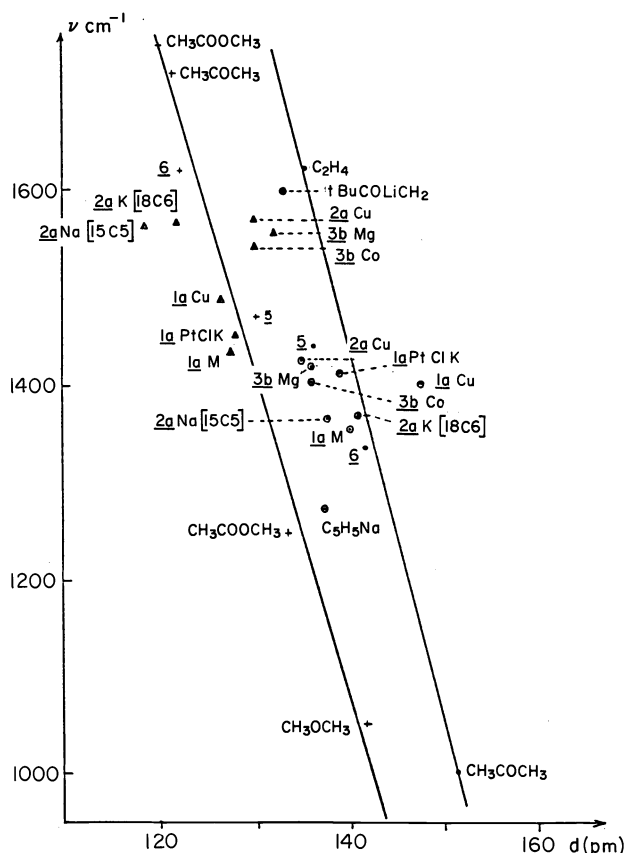
Fig. 2 : ν(CO) frequencies of molecules [+] or carbanions [▲] and ν(CC) or ν_m(CC) frequencies of molecules [●] or carbanions [⊙] against CO or CC bond lengths d.

and an unsymmetric shortening of the C=C bonds. There is almost no participation of the electrons of the C_2O_3 bond. The larger double bond character of the C=C bonds when the OM bond becomes more covalent, is thus confirmed. This overall effect as well as the smaller ν_m(C-O) frequency shift and lengthening in 2aM compounds than in 1aM is probably due to the stronger polarity of the C=O bond in esters than in ketones shown by bond moments or IR intensity measurements (ref. 44).

For ketophosphonates 3, we have less X-ray data (table 3) but a comparison may be made for 3bMg and 3bCo with compounds 1. Similarly, the chelate cycle formation leads to a C=O and P→O lengthening from 121.5pm in acetone and 143pm for instance in $(C_6H_5O)_3$P→O (ref. 45) to 131 and 147pm respectively. The compound 7 has indeed ν(C=O) and ν(P→O) frequencies very close to those of the acetone and of $(C_6H_5O)_3$PO. A concomitant shortening of the PC_1 and C_1-C_2 bonds from 180pm (ref. 45) and 151pm for single bonds to 173 and 136pm respectively is observed. These bond lengths variations are clearly related to the ν(C=O) and ν(P→O) frequency lowering. Like in 2 compared to 1, the ν(C=O) frequency shifts are slightly smaller in 3 than in 4 due to the leveling off effect of the polar P→O bond (fig. 2). There is also a good consistency in the comparison of the ν_m(CC) frequency in 1 and of the ν(CC) frequency in 3. These trends are also nicely confirmed by the NMR chemical shifts of ^{31}P and $^{13}C_1$ nuclei which show a clear deshielding, shown as Δδ, and a large increase of the $^1JPC_1$ coupling constants which are in line with a trend of the C_1 carbon hybridization change from planar to pyramidal (ref. 9, 25).

For the ester phosphonate 4, all the data (table 4) indicate a structure very close to 3 but with a shorter C≔O bond and a longer C=C bond, as indicated by the infrared frequencies and their shifts. This difference is already noticed for the parent compounds 8 and 7. Indeed while $\delta^{31}P$, 19.2 and 19.5ppm, are similar for 8 and 7, the carbon C_1 is more deshielded in 8 than in 7 ($\delta^{13}C_1$=33.2 and 42.3ppm). This is in line with the assignment of the $\nu(C_2O_3)$ vibration frequency to a band at 1123cm^{-1} in 8 at a quite lower frequency than expected around 1200cm^{-1} (ref. 46) for an alkylester. This behaviour indicates that the phosphorus atom attracts the electrons of the C_2O_3 bond in 8 while in 7 this attraction takes place from the oxygen lone pairs of the carbonyl group with a participation of the C_1C_2 bond to this delocalization.

For carbanionic species **1**, **2**, **3** are given in tables 1 to 3. References for frequencies and bond lengths are respectively for : CH_3COOCH_3 (ref. 42, 43) CH_3COCH_3 (ref. 40, 39), CH_3OCH_3 (ref. 47, 48), C_2H_4 (ref. 49), $tBuCOLiCH_2$ (ref. 50, 51), C_5H_5Na (ref. 52, 53).

This electron delocalization, which takes place probably at the expense of the oxygen O_1 lone pairs, explains the similar $\nu(C=O)$ frequency in the ketophosphonate and in the acetone, as already pointed out, as well as the smaller $\delta^{13}C$ in **8** than in **7**. When going from **8** to **4**, only a very small increase (10 to 20cm^{-1}((ref. 9) of the $\nu(C_2O_3)$ frequency is observed. The larger deshielding of $^{13}C_1$ and the smaller one of ^{31}P when going from **7** and **8** to **3** and **4** is in line with a shorter C_1C_2 bond length in **7** than in **8**.

For phosphorus ylids **5** and **6**, the structural data (Table 3, 4 and Fig. 2) compare very well with those of the related phosphonates **3** and **4**, the $C \cdots O$ and $C \cdots C$ bond lengths and frequencies are very close. Although the phosphorus ylid **6** conformation is Z or *trans* to the C_1C_2 bond while that of **5** is E or *cis*, the same trend is observed for the $PC_1C_2O_2$ delocalization when going from **5** to **6** as that observed between phosphonates **3** and **4**. The lengthening of the C_2O_4 bond being compensated by that of the C_2O_3 bond in the ester **6**. A smaller C_1C_2 double bond character in **6** than in **5** is also shown by a smaller $\nu(C-C)$ frequency like in phosphonates **4** and **3**. Furthermore as it may be seen in Fig. 2, the points for **6** are close to the straight line drawn through the points obtained for neutral molecules, while for points **5** and carbanionic species **1**, **2**, the distances from points to the line may be due to the charge delocalization. Indeed the $\nu_m(CC)$ frequency for the allyl sodium C_5H_5Na where the ionic charge is delocalized on the two CC bonds of the allyl anion (ref. 52) is quite lower than expected from the CC bond length d (ref. 53). For the lithium pinacolone t-BuCOLiCH$_2$ where the anionic charge remains localized on the oxygen atom (ref. 51), the point for the C-C bond is close to the line with a $\nu(C=C)$ frequency close to that of ethylene (ref. 50).

Structure of the free anion or cryptate separated ion pair

In more polar solvents (class C, ref. 1) like DMSO these carbanions at the concentration of 0.37M form essentially solvated ion pairs in equilibrium with free ions. In these solvents or in pyridine with addition of 1.2 equivalent of cryptand (222) to the potassium salt two types of anions, slowly, exchanging, are observed for **3** (ref. 25) and **4** (ref. 9) ; these anions are the most clearly observed by NMR as it seems that the monomeric ion pair **4M** and the free anion **4** have very close $\nu(C_2 \cdots O_1)$ and $\nu(P\rightarrow O)$ frequencies. The two types of NMR signals are assigned to the Z and E forms of the free anion or cryptate separated ion-pair mainly through δ or ^1J, ^2J and $^4J(PC)$ comparison (ref. 25, 9). Variable temperature ^1H NMR allows us to deduce, from the coalescence temperature and the separation of the two sets of signals observed for the methyl protons of the EtO group in **3** and of the ester group in **4**, a free energy of activation $\Delta G^\#$ for the interconversion of these two conformers, using the approximate Gutowsky–Holm formula (ref. 54). The interconversion barriers are very similar (Fig. 3) for **4** and **6** which both exist as Z and E conformers, the Z form being the most populated. The increases of the barrier for **3**$^-$ and the existence of only the Z conformer for **5** (ref. 55) are indicative of a higher double bond character of the $C_1 \cdots C_2$ bond in **3** and **5** than in **4** and **6** as already noticed from the structure of the ion pairs. The free anion **2**$^-$ only adopts the ZE conformation (ref. 7, 21), like the **1**$^-$ anion (ref. 56). This seems to indicate that the charge repulsion of the oxygen prevails in these anions, with shorter $O_1 \cdots O_2$ distances.

$$\underline{3}^- Z \quad \xrightarrow[\text{DMSO}]{\Delta G^\# \simeq 92 \text{ KJmol}^{-1}} \quad \underline{3}^- E$$

$$\underline{4}^- Z \quad \xrightarrow[\text{Pyridine}]{\Delta G^\# \simeq 74 \text{ KJmol}^{-1}} \quad \underline{4}^- E$$
70%　30%

$$\underline{6} Z \quad \xrightarrow[\text{CDCl}_3]{\Delta G^\# \simeq 71 \text{ KJmol}^{-1}} \quad \underline{6} E$$
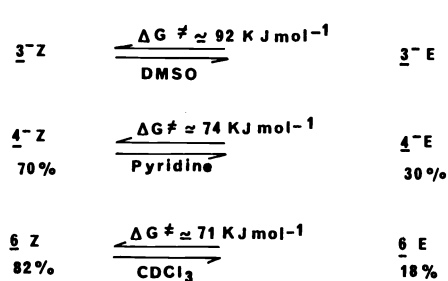82%　18%

Fig. 3 : Equilibria between Z and E conformers of **3**$^-$ (ref. 25), **4**$^-$ (ref. 9) and **6** (ref. 47) in solutions.
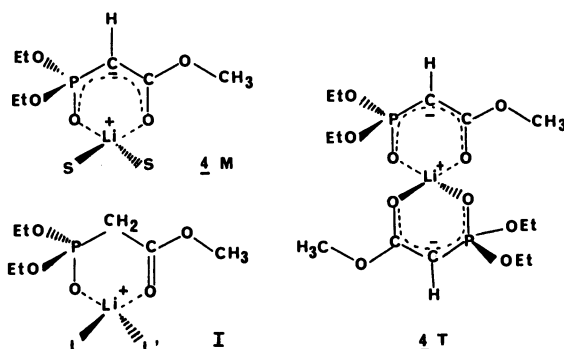
Fig. 4 : Structures for the monomeric solvated ion-pair **4M**, the triple anion **4T** and the intermediates **I**.

TABLE 5 : ^{13}C and ^{31}P chemical shifts and coupling constants[a] of the intermediate species $\underline{I}$ compared to those of phosphonate $\underline{8}$ and chelate $\underline{4}$ in CD_3CN

Product	$\delta^{31}P$	δC_1	δC	δC_4	$^1JPC_1$
$\underline{8}$	19.1	34.5	167.4	52.9	132.7
$\underline{4}$[b]	38.8	41.8	175.8	51.3	222.0
$\underline{I}$[c]	27.7	35.9	172.5	49.9	133.3

[a]See caption and footnote table 3

[b]The anionic species were formed by addition of 1.1 equiv. of LiBu^n to $\underline{8}$ in THF ; the THF was evaporated under argon and replaced by CD_3CN

[c]Same process as for b followed by addition of 0.3 equiv. of $\underline{8}$ to obtain a $\underline{I}+\underline{4}$ mixture.
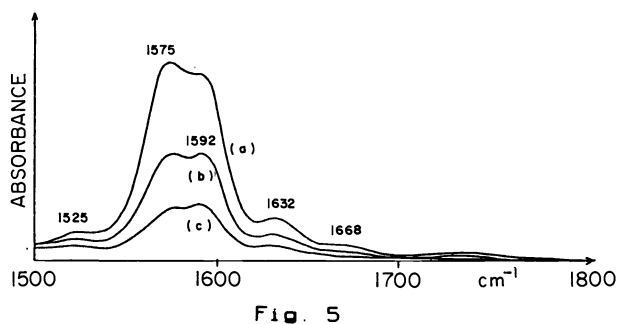

Fig. 5

Fig. 5 : Variation with concentration of the IR spectra of $\underline{4}$ Li in CH_3CN.
(a) 0.33 M, (b) 0.20 M, (c) 0.10 M. Cell thickness 0.003 cm.
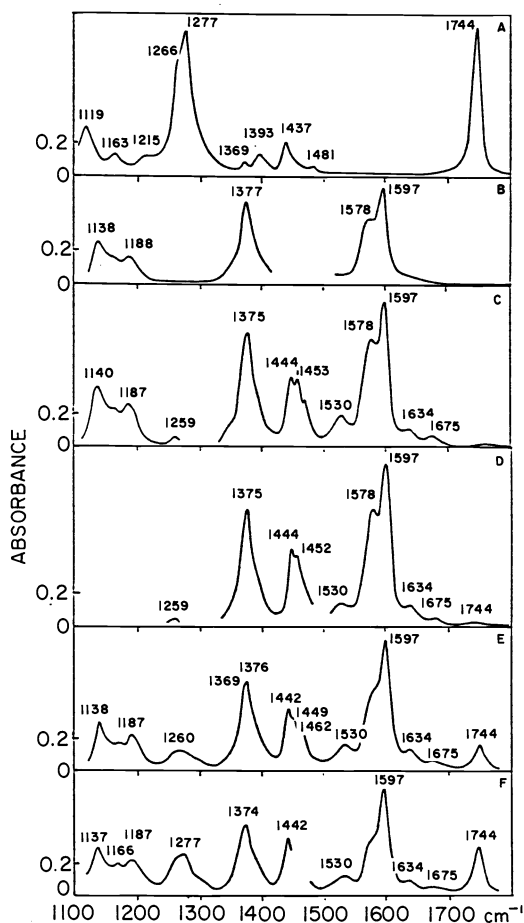

Fig. 6

Fig. 6 : IR spectra of a 0.5 M solution of $\underline{8}$ in THF or THF-d_8, without A or with additions of n-BuLi B to F. Concentration ratio for n-BuLi/$\underline{8}$: B:1.2, C:0.93, D:0.95, E:0.66, F:0.5. Cell thickness 0.003 cm

Formation of triple anions in acetonitrile

In THF, IR spectra shows for the lithium salt of $\underline{8}$, only the presence of ion pair aggregates ($\underline{4A}$) in equilibrium with monomeric externally solvated ion-pairs ($\underline{4M}$) (Fig. 4) which are characterized mainly by their $\nu(C_2 \overset{\cdots}{=} O_1)$ stretching vibrations at 1578cm^{-1} and 1597cm^{-1} respectively (Fig. 3, ref. 9). In acetonitrile, a solvent with intermediate dissociating power between THF and DMSO (Fig. 5), besides the two intense $\nu(C_2 \overset{\cdots}{=} O_1)$ bands at 1575cm^{-1} and 1592cm^{-1} related to $\underline{4A}$ and $\underline{4M}$ three other less intense bands are observed at 1525, 1632 and 1668cm^{-1}. The relative intensity of the different bands vary only slowly with the concentration variation between 0.1 and 0.33M. A slight change of the relative intensities of the bands at 1575 and 1592cm^{-1} is however noticed, in agreement with the shift of equilibrium (4) already observed in THF, but with a quite different position. As shown by the band intensities, $\underline{4A}$ is in similar amount as $\underline{4M}$ in CH_3CN while in THF at the same concentration $\underline{4M}$ predominates. This behaviour has already been observed for lithium trifluoroacetate (ref. 57) or for the lithium acetylactate (ref. 5, 21), the formation of lithium triple anions with bidentate anions being favoured in that solvent through equilibria (5) and (6). We then assign the 1525 and 1632cm^{-1} bands respectively at the free anion ($\underline{4}^-$) and to the triple anion ($\underline{4T}$) (Fig. 4). The carbanion $\underline{4}$ cannot be formed directly in CH_3CN as in equation (1) because of the solvent acidity (ref. 35). Also it is first formed in THF with a slight excess of $\underline{8}$, the THF being further evaporated and replaced by CH_3CN (see experimental conditions, ref. 58). The band at 1668cm^{-1} is then related to a new species formed in the presence of a slight excess of $\underline{8}$ and will be discussed hereafter.

FORMATION MECHANISM OF THE ESTER PHOSPHONATE ANION THROUGH REACTION OF PARENT PHOSPHONATE WITH AN ORGANIC BASE BM

The carbanions **4** are usually prepared as in equation (1) by addition of solid LiOBut or of a 1.6M LiBu^n solution in hexane to a solution of **8** in THF. When a slight excess of the base BM (>1.1 equivalent) is added only two sets of signals are observed in NMR or IR (see Fig. 6, curve B) for THF solutions. When less than 1.1 equivalent of base is used in THF as well as in CH$_3$CN or when **8** is added to a carbanion **4** solution, two or three sets of signals are observed in the ^{1}H, ^{13}C and sometimes up to five in ^{31}P NMR spectra (table 5, 6) and six in the carbonyl stretching region in IR spectra (Fig. 6, 7).

In NMR ^{1}H, ^{13}C and ^{31}P, the two first set of signals correspond to the neutral starting phosphonate **8** or to the anionic part of **4**, the third one in ^{1}H, ^{13}C and ^{31}P and the three others , when observed in ^{31}P, are ascribed to intermediate species **I** already mentioned (ref. 9). From these results, it appears that while C$_1$ is planar in **4** (ref. 9) (^{1}JPC$_1$=222Hz), it remains pyramidal in **I** (^{1}JPC$_1$=133Hz) ; moreover, the off resonance ^{13}C spectrum for C$_1$ in **I** shows a doublet of triplets as expected for a P–CH$_2$ group. ^{1}H(100MHz), ^{13}C(62.5MHz) spectroscopies are unable to differentiate the various species **I** which have been characterized (table 6) by ^{31}P NMR (32.4MHz) in line with its large chemical shifts scale. These results suggest that a part of the organic framework of **I** has a structure close to that of **8**. This moiety should be strongly interacting with a Li$^+$ cation by the P→O and C=O oxygens as ^{31}P and ^{13}C$_2$ are the most perturbed resonances in **I** (table 5). The slight differences observed in δ^{31}P for the various species **I** (table 6) could be attributed to the nature of the other ligands L and L´ around the Li$^+$ cation (Fig. 4)(ref. 5B).

In IR when less than 1 equivalent of base was used (Fig. 6), or when increasing amounts of **8** were added to the **4** Li solution (Fig. 7), other bands than those already assigned to **4A**, **4M** in THF, and to **4A**, **4M**, **4T** and **4⁻** in CH$_3$CN, appear. They are observed at 1668cm^{-1} in CH$_3$CN and at 1675cm^{-1} in THF, next to the bands at 1741 and 1744cm^{-1} due to free **8** in these two solvents. The relative intensities of all these absorptions vary with the amount of **8** and BM as well as with the nature of BM (ref. 5B). It is noticeable for instance that the addition of 0.3 molar equivalent of phosphonate **8** to a 0.35M solution of **4** (ρ=0.76, Fig. 7 and table 6) induces only a very weak absorption around 1741cm^{-1} characteristic of free **8**. In other conditions (table 6, Fig. 6, 7) the intensity of this band is also lower than expected. These results confirm that, as proposed form the NMR data, a species **I** is formed in which **8** is no longer free and is chelating a lithium cation. Its υ(C=O) frequency is expected between that of free **8** and that of **4** : such a band is observed at 1675cm^{-1} and 1668cm^{-1} in THF and CH$_3$CN respectively. In δ^{31}P in ppm relative to external H$_3$PO$_4$ (85%) ; C$_b$ added base concentration, C$_p$ is the total phosphonate concentration added, C$_8$, C$_4$ and C$_I$ are the concentration of species **8**, **4** and **I**. All concentrations are in mol.l^{-1} ; they are obtained from ^{31}P NMR by postulating C$_4$ equal to C$_B$ and estimating C$_8$ and C$_I$ from integrated NMR intensities. The C$_8$ IR concentration is deduced from the intensity of the band υ(C=O) of species **8**, ρ is the molar ratio C$_B$ over C$_p$.

$$(\underline{4}\ A) \xrightleftharpoons[\ 3\ ]{} n\ (\underline{4}\ M) \qquad (4)$$

$$(\underline{4}\ M) \xrightleftharpoons{} (\underline{4}^-) + (Li^+) \qquad (5)$$

$$(\underline{4}M) + (\underline{4}^-) \xrightleftharpoons{} \underline{4}\ T + 2\ S \qquad (6)$$

$$(\underline{4}M) + \underline{8} \xrightleftharpoons{} I_1 + 2\ S \qquad (7)$$

$$I_1 \xrightleftharpoons{} (\underline{4}^-) + I_2 \qquad (5')$$
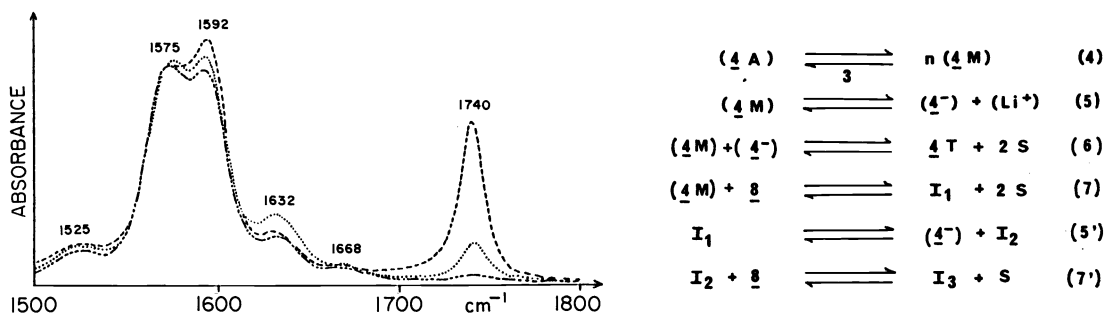
$$I_2 + \underline{8} \xrightleftharpoons{} I_3 + S \qquad (7')$$

Fig. 7 : IR spectra of solutions 0.35 M of **4Li** in CH$_3$CN with **8** added. concentration ratios: **4Li**/**8** : ————— 0.76 ;.......... 0.66 ;_ _ _ _ _ 0.51.

For THF in the $\nu(P\rightarrow O)$ stretching region, the absorption at 1259cm^{-1} could also be assigned to $\underline{I}$ while that of the free $\underline{8}$ is located at 1277cm^{-1}. At low C_{DBU} concentration in DBU, ρ' is the molar ratio C_{DBU} over C_p $\langle\delta\rangle$ is the ^{31}P average chemical shift due to rapid exchange between phosphonate $\underline{8}$ ($\delta_8=19.1$) and chelate $\underline{4}$ ($\delta_4=38.8$). ρ'' is the C_8 over C_4, molar ratio calculated from $(C_8+C_4)\langle\delta\rangle=C_8\delta_8+C_4\delta_4$. C_I, C_8 and C_4 are estimated from integration of ^{31}P NMR spectra. C_8 IR is also estimated from the intensity of the $\nu(C=O)$ band at 1740cm^{-1}. All concentrations are given in mol.l^{-1}.

LiBun concentration or when the base used is LiOBut (table 6), the amount of the intermediate species $\underline{I}$ is very low. When neutral $\underline{8}$ and anionic species do coexist, the enhancement of the absorptions assigned to free and triple anions in CH_3CN or their appearance at 1525 and 1634cm^{-1} in THF are observed. For a 0.35M solution of anionic species their intensities, related to those of $\underline{4A}$ and $\underline{4M}$ absorptions, are maximum when 0.5 molar equiv. phosphonate ($\rho=0.7$), is added. When $\rho>0.7$ (Fig. 7), or when the base concentration decreases (Fig. 6), the main change in the IR spectra is an intensity increase of the $\underline{4M}$ band at the expense of that of aggregates $\underline{4A}$.

When the free phosphonate $\underline{8}$ is added to the solution of the aggregated carbanion equations (4) to (6), a new equilibrium takes place (equation 7) in which $\underline{8}$ is involved to chelate the lithium cation of $\underline{4M}$: this moiety is observed as intermediate $\underline{I_1}$ (L and L', Fig. 4, being the anionic part of $\underline{4}$). When LiOBu-t is used to generate the anionic species, the formed t-BuOH can hydrogen bond the highly basic oxygen of the $P\rightarrow O$ group of $\underline{8}$. The concentration of $\underline{I_1}$ becomes then very low as $\underline{8}$ is no longer available to shift equilibrium (7) to the right. The formation of $\underline{I_1}$ is indeed entropically favored since two S solvent molecules in $\underline{4M}$ are replaced by one chelating neutral phosphonate. Furthermore, the solvating power of the $P\rightarrow O$ and $C=O$ oxygens of this bidentate ligand is certainly stronger than that of the two solvent molecules, so that the ionic moieties in $\underline{I_1}$ are more easily dissociated than in $\underline{4M}$, leading thus to an increased amount of free anion $\underline{4}^-$

TABLE 6 : Characterization by IR, $\nu(C=O)$, intensity and by ^{31}P NMR δ and integrated intensity of different species formed by action of lithium base BLi on phosphonate $\underline{8}$ according to the solvent and BLi or $\underline{8}$ concentrations

Base Solvent	C_B	C_P	ρ	$\underline{8}$ $\delta^{31}P$	C_8	$\underline{4}$ $\delta^{31}P$	C_4	$\underline{I}$ $\delta^{31}P$	C_I	C_8 IR
LiBun THF	0.13	0.42	0.31	19.6	0.26	39.9	0.13	28.5	0.03	0.32
	0.34	0.67	0.51	20.2	0.25	39.7	0.34	26.3	0.02	0.31
								28.5	0.03	
								29.7	0.03	
	0.34	0.48	0.71	20.4	0.04	39.6	0.34	26.2	0.02	0.06
								28.5	0.05	
								29.7	0.04	
	0.34	0.45	0.76	–	–	39.6	0.34	26.4	0.02	0.01
								28.5	0.05	
								29.9	0.04	
LiBun	0.34	0.67	0.51	19.7	0.24	38.9	0.34	26.5	0.02	0.26
								28.2	0.05	
								29.1	0.02	
	0.35	0.53	0.66	19.7	0.05	38.8	0.35	26.5	0.02	0.07
								28.0	0.08	
								29.1	0.03	
	0.35	0.46	0.76	–	–	38.8	0.35	26.4	0.02	0.01
								28.1	0.06	
								29.2	0.03	
LiOBut THF	0.14	0.45	0.31	19.7	0.29	39.9	0.14	28.5	0.02	0.38
	0.27	0.45	0.60	20.0	0.16	39.8	0.27	28.5	0.02	0.21
	0.41	0.45	0.91	20.3	0.03	39.8	0.41	28.5	0.01	0.06

and to another intermediate I_2 (where L and L' should be two solvent molecules) according to equation (5'). This equilibrium favors the formation of triple anion $\underline{4T}$ along to equation (6). At higher phosphonate concentration, $\rho > 0.7$, free $\underline{8}$ is observed through its free $\nu(C=O)$ band, it probably acts as a monodentate ligand (Equation 7') to give an intermediate I_3 (where L and L' are a monodentate $\underline{8}$ and a solvent molecule). The main phenomenon observed is then the deaggregation of $\underline{4A}$ through equation (4).

The important spectroscopic perturbations of the phosphonate $\underline{8}$ framework seen in $\underline{I}$ are worthy of comment. They are quite higher than those observed for corresponding monodentate ligands (ref. 58). The 9ppm downfield ^{31}P chemical shift and the $18 cm^{-1}$ and $66 cm^{-1}$· $\nu(P \rightarrow O)$ and $\nu(C=O)$ low frequencies displacement show a strong structural reorganization of the phosphonate moiety when it acts as a rigid bidentate. Related effects have already been observed (ref. 59) for a bidentate complex formed between ketophosphine oxide and lithium bromide in the solid state where similar low frequencies displacements, $25 cm^{-1}$ and $45 cm^{-1}$, have been observed for the $\nu(P \rightarrow O)$ and $\nu(C=O)$ frequencies respectively.

FORMATION MECHANISM OF THE ESTER PHOSPHONATE ANION THROUGH REACTION OF PARENT PHOSPHONATE WITH ACTIVATED LITHIUM CHLORIDE

Lithium chloride is only slightly soluble in acetonitrile, and its solubility may be increased by the presence of $\underline{8}$ or of DBU (ref. 58). For mixtures of $\underline{8}$ and LiCl in acetonitrile, the infrared spectrum of $\underline{8}$ is only very slightly perturbed but the solubility of LiCl is increased. For mixtures of DBU and LiCl in acetonitrile, the $\nu(CN)$ band of free DBU in CH_3CN at $1610 cm^{-1}$ comes with a new band at $1646 cm^{-1}$ which corresponds to the LiCl-DBU association. In the presence of both phosphonate $\underline{8}$ and DBU, LiCl may be solubilized at the concentration of 0.37M with an equimolecular amount of $\underline{8}$ and about 0.12 equivalent of DBU (Table 7 and Fig. 8). Through the addition of DBU, the intensity of the $1741 cm^{-1}$ absorption due to $\underline{8}$ decreases and new bands appear at 1575, 1594 and $1634 cm^{-1}$ which are due to the species $\underline{4A}$, $\underline{4M}$ and $\underline{4T}$ respectively and at $1645 cm^{-1}$ which is due to the LiCl-DBU association. The formation of the chelate anion $\underline{4}$ is confirmed by the intensity decrease of the $\nu(O-CH_3)$ band of $\underline{8}$ at $1118 cm^{-1}$ (ref. 9) to the benefit of the $\nu(O-CH_3)$ band of $\underline{4}$ at $1137 cm^{-1}$. When the DBU concentration increases, $\rho > 0.5$, the intensity of the band due to $\underline{4M}$ grows at the expense of the band due to $\underline{4A}$ and $\underline{8}$. However, at high DBU concentration ($\rho = 3$), deprotonation of $\underline{8}$ is not complete since the $1741 cm^{-1}$ band still exists. At DBU concentrations, $\rho' < 1$, all the DBU is associated, while for $\rho' > 1$, a new band appears at $1610 cm^{-1}$ showing the presence of free DBU.

TABLE 7 : Characterization by IR and ^{31}P NMR of the different species obtained by addition of DBU to solutions of DBU to an almost equimolecular solution of phosphonate $\underline{8}$ and lithium chloride in CH_3CN

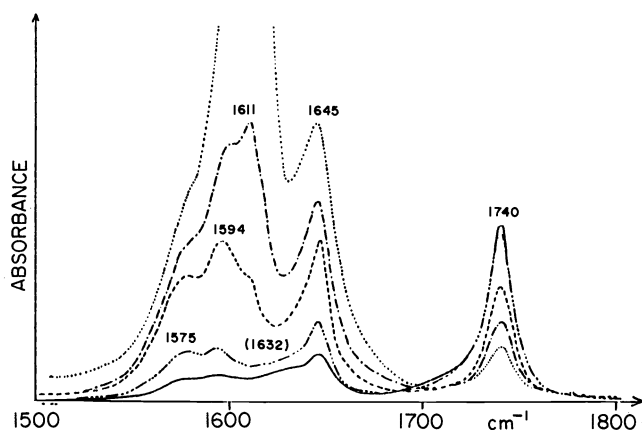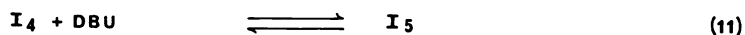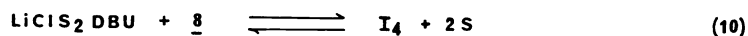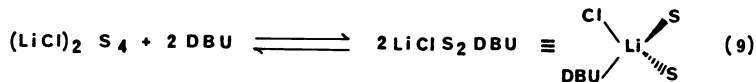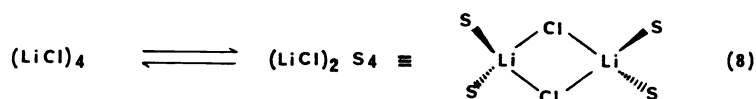| C_{DBU}	ρ'	$<\delta>$	$\rho^{\bullet}$	NMR data				IR data
				$\delta^{31}P$	$C_{\underline{I}}$	$C_{\underline{8}}$	$C_{\underline{4}}$	$C_{\underline{8}}$
0								0.4
0.05	0.12	20.6	12.70	28.0	0.02	0.33	0.03	0.27
0.09	0.25	21.4	7.70	28.0				0.25
0.18	0.50	25.6	2.05	28.0 24.8				0.20
0.27	0.75	28.1	1.20	28.1 24.8				0.17
0.36	1.0	30.6	0.72	28.1 24.8				0.12
0.52	1.44	31.5	0.59	28.2 24.8	0.04 0.02	0.11	0.19	0.12
0.68	2.0	32.7	0.45	28.2 24.8	0.03 0.03	0.09	0.19	0.09
0.96	3.0	34.2	0.31	28.3 24.8	0.03 0.03	0.06	0.19	0.08

Fig. 8 : IR spectra of an
equimolar solution of LiCl
and phosphonate **8**,0.37M in
CH_3CN, in the presence of
DBU Ratio of DBU over **8**
concentrations : —— 0.12 ;
——·——— 0.25 ; —————— 0.75
—·——··1.5 ; ···········... 3.

The ^{31}P NMR spectra of these mixtures consist of one or two sharp signals at
28.0 and 24.8ppm whose chemical shifts are close to those of the
intermediates **I** and a broad one, the chemical shift of which varies between
20.6 and 34.2ppm according to the DBU concentration. These chemical shifts
<Δ> are given in table 7. This observation and the absence of signals due to
the anionic part **4** at 39.7ppm and free phosphate **8** at 19.6ppm which are
present in the solutions according to the IR spectra indicate that the broad
band corresponds to an average signal due to a fast proton exchange between **4**
and **8**. The ability of DBU to increase the rate of exchange between **8** and **4**
was checked independently. The sharp and distinct signals observed for **8** and
4 without DBU broaden in THF and coalesce in CH_3CN at room temperature by
addition of one equivalent of this base. However, the signals of **I** still
remains sharp showing that this entity does not participate in the exchange
process. At low DBU content (ρ'<0.5) a single intermediate I_3 is observed at
28.0ppm, while the second one I_4 appears when the amount of DBU increases.
The analogy of the chemical shifts namely ^{31}P (table 5, 6 and 7) suggest that
I_4 and I_5 contains a neutral phosphonate molecule in a lithium cation first
solvation shell. As shown in table 7, the concentrations of the different
species are estimated from <Δ>, integrated intensities in the absence of
overlap and from the total phosphorus concentration (table 7). Despite the
low precision of the method, there is a good agreement between the
concentration in free **8** estimated from NMR and IR data. This concentration
decreases rapidly with DBU addition until ρ=1 and varies more slowly over
this value.

$$(LiCl)_4 \quad \rightleftharpoons \quad (LiCl)_2 \; S_4 \; \equiv \quad \text{[structure]} \qquad (8)$$

$$(LiCl)_2 \; S_4 + 2\,DBU \quad \rightleftharpoons \quad 2\,LiCl\,S_2\,DBU \; \equiv \quad \text{[structure]} \qquad (9)$$

$$LiCl\,S_2\,DBU + \underline{\textbf{8}} \quad \rightleftharpoons \quad I_4 + 2\,S \qquad (10)$$

$$I_4 + DBU \quad \rightleftharpoons \quad I_5 \qquad (11)$$

From these results, it appears that LiCl is strongly aggregated when
dissolved in CH_3CN where it is only slightly soluble. It probably forms
tetramers in equilibrium with dimers equation (8). LiCl is indeed more
aggregated than LiBr (ref. 60) which forms tetramers in diethylether (ref.
61). These dissociate into dimers in equilibrium with ion-pairs in weakly
polar solvents (ref. 62). These aggregates cannot be disrupted by phosphonate
8 since neither intermediate **I** nor any anionic species **4** can be observed in
such conditions. The addition of DBU induces firstly deaggregation of LiCl to
form very polar DBU solvated ion pairs (equation 9), the DBU ν(C=N) frequency
being shifted, by 33cm^{-1} to high frequency in these complexes. Thus the activated

lithium salt is then able to be coordinated by the bidentate phosphonate **8** leading to intermediate **I₄** (where L and L', figure 4, are one DBU and one solvent molecule, equation 10). This species can then be deprotonated and lead to chelate **4**. However, with the reported spectra being run after equilibration of the different species in solution, it is not possible for the moment to discriminate between the ligands L and L' in **I** because some chelate **4** is formed. At higher DBU concentrations, a new species **I₅** (where L and L' are due two DBU molecules) may be formed from **I₄** by replacement of Cl⁻ by one DBU (equation 11) leading to a loose ion-pair. From the IR spectra (Fig. 8), chelate **4** exists as aggregates **4A**, ion pairs **4M** and triple anion **4T** at low DBU concentration. At higher DBU concentrations, the deaggregation of **4A** (equation 4) is favoured through solvation of **4M** by DBU (S, Figure 4, being replaced by DBU). It is important to point out from these results that as shown by NMR, ³¹P, the most acidic species **I₄** or **I₅**, does not participate in the fast exchange between **8** and **4**. Comparison of these results with the behaviour of the ketophosphonate **7** in such media are in progress and seems to indicate that intermediate species **I** involving **7** are not formed. This is probably due to the lower basicity of the ketocarbonyl group and to the larger stability of the derived carbanionic chelated ion-pair **3** as seen in the first part.

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