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Lithiated anions derived from (alkenyl)pentamethyl phosphoric triamides: an accurate study of the carbanion formation mechanism

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Abstract

The mechanism of the formation of lithiated carbanions derived from (alkenyl) pentamethyl phosphoric triamides has been elucidated. Whereas a few initial ambident allylphosphoramide anion was formed with *n*-BuLi, both reversible α-reprotonation and not reversible γ-reprotonation simultaneously occurred as a result of the reaction between the ambident carbanion formed and the starting enephosphoramide. A such autocatalytic process led partially to the transposed allylphosphoramide isomer. In the case of α-phenyl substituent the transposed phosphoramide was not a difficulty because it was further γ-deprotonated in situ with the *n*-BuLi still present, provided finally the expected ambident anion. With α-methyl and α-propyl substituent the transposed enephosphoramide formed in the autocatalytic process was not γ-deprotonated and consequently was prejudicial to the preparation of the target ambident carbanion. In these last cases, adapted experimental conditions avoided the autocatalytic process and allowed the preparation of the corresponding anions.

Keywords: Enephosphoramide; Allylic transposition; Lithium reagents; Alkenyl pentamethyl phosphoric triamides; Ambident anions

1. Introduction

The heteroatom-assisted γ-deprotonation of allylic group is a convenient and efficient strategy for the preparation of aldehyde homoenolate synthons [1]. Heterosubstituent is used to stabilize the allylic anion and to generate a masked carbonyl group after γ-reaction with electrophilic reagents. Heterosubstituted allyl anions belong now to the synthetically important group of reversed polarity synthons and are versatile tools for further synthetic transformations [2].

The use of allylic anions as ketone homoenolate equivalents however is far less documented. It brings new problems: difficult or impossible access to the starting material, reduced stability of the allyl anions and not easy hydrolysis of the γ-adduct [3].

As part of a program aimed at developing new homoenolate synthons we have previously reported the synthetic utility of lithium anions derived from allylphosphoramides as aldehyde [4] and recently ketone homoenolate equivalents [5]. In this work, we describe accurately the different interesting facts observed during the formation of the ketone homoenolate equivalents derived from *N*-[(1-alkyl or 1-aryl)-2-propenyl] phosphoramides.

2. Results and discussion

2.1. Stability of lithiated carbanions 3 and ^{1}H and ^{31}P NMR data of starting enephosphoramides 2, carbanions 3 and transposed enephosphoramides 4 (Z/E)

The starting compounds (alkenyl) pentamethyl phosphoric triamides **2** and the lithiated anions derived

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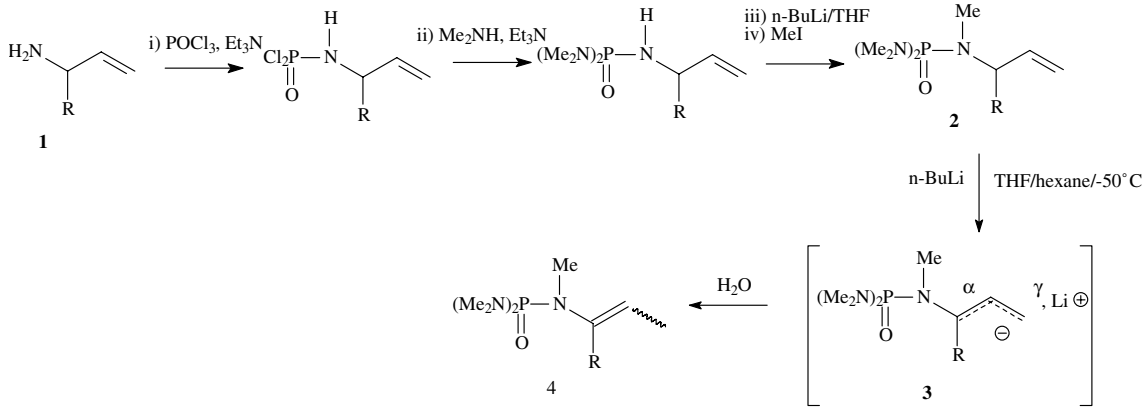


Scheme 1.

3 were prepared according to Scheme 1 as previously described [5].

^{31}P RMN established the quantitative formation of anions **3**: the signal of anions **3** was ~1 ppm downfield from that of the phosphoramides **2** in THF (Table 1).

The stability of the anions **3** was very temperature-dependent. The metallation of **2c** could be achieved smoothly at −10 °C leading to the anion **3c** which was perfectly stable at 20 °C and kept at 20 °C during 4 h without degradation. As expected, the anions **2a** and **2b** were less stable and it was obliged to keep the reaction medium at low temperature (Table 2).

Hydrolysis or deuterolysis at one sweep at −50 °C of carbanions **3** gave exclusively the fully transposed enephosphoramides **4** contrary to lithiated α-unsubstituted enephosphoramides (R = H) which were known to lead after hydrolysis to a mixture of transposed and not transposed enephosphoramide products. The double bond configuration of transposed enephosphoramides **4a-b** depended on the hydrolysis temperature. Rapid hydrolysis at −50 °C gave the (Z) enephosphoramides **4a-b** which are the kinetic products (Scheme 2). Those results could be explained by an internal lithium chelating stabilising effect of the phosphoramide group into **3a-b**. Temperature increase or addition of HMPA prevented the stabilisation and led to a mixture of (Z) and (E) products. In the case of **3c** the sole transposed (Z) **4c** was obtained whatever the hydrolysis temperature, the phenyl hindrance forced the (Z) **3c** configuration which was maintained after hydrolysis.

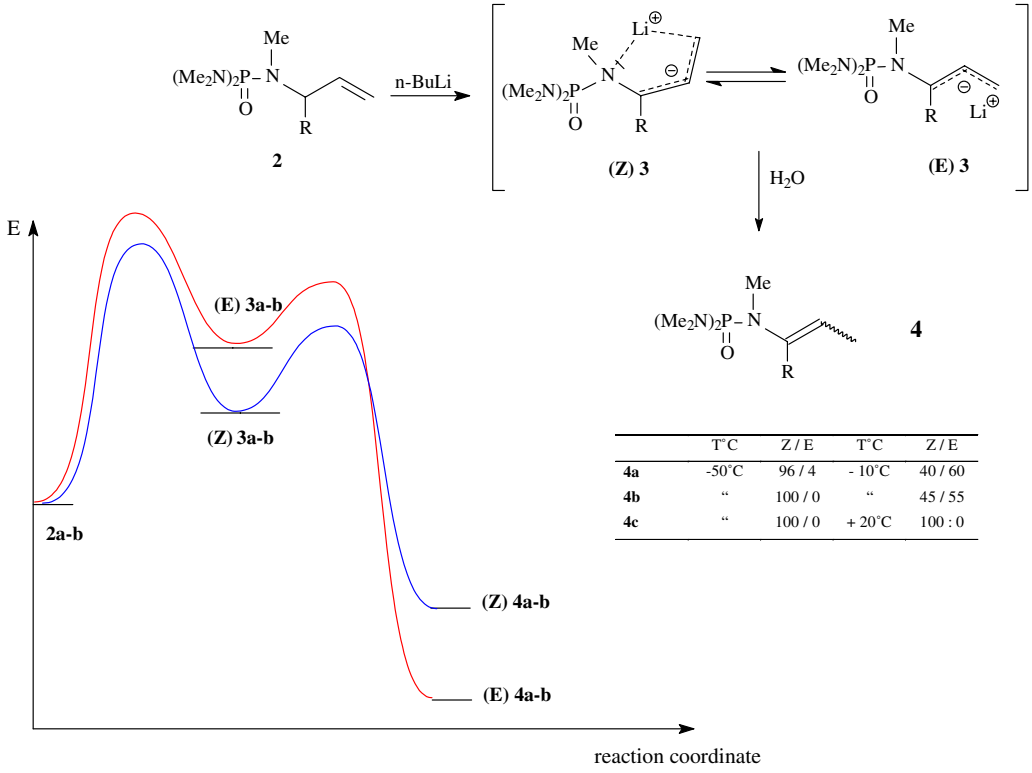
Table 2
Stability of the anions **3**

Entry	3	R	Temperature (°C)	Time
1	**3a**	Me	−50	>2 h
2	**3a**	Me	−10	A few minutes
3	**3a**	Me	+20	Immediate degradation
4	**3b**	Pr	−50	>2 h
5	**3b**	Pr	−20	2 h
6	**3b**	Pr	0	1 h
7	**3b**	Pr	+20	Immediate degradation
8	**3c**	Ph	−50	>2 h
9	**3c**	Ph	+20	>4 h
10	**3c**	Ph	+58	1 h

^{1}H and ^{31}P NMR spectra allowed a clear identification of transposed **4** and not transposed **2** enephosphoramides. In the ^{31}P NMR spectra (in $CDCl_3$) a singlet was observed at 22.68–22.80 ppm for the starting enephosphoramides **2** whereas in the transposed product **4**, this signal appeared in all cases upfield at 18.00–19.57 (Table 1, Fig. 1). Moreover the distinction between **2** and **4** was facilitated by the observation of the Cα–N–*Me* chemical shift which constituted an efficient internal probe. In the ^{1}H NMR spectra the Cα–N–*Me* signal appeared as a doublet at 2.42–2.46 ppm for **2** ($^{3}J_{H-P}$ = 8.9–9.5 Hz) whereas in the transposed product

Table 1
^{31}P NMR chemical shifts of **2**, **3** and **4**

Entry	R	2	δ (ppm)		3	δ (ppm) (THF)	4	δ (ppm)	
			($CDCl_3$)	(THF)				($CDCl_3$)	(THF)
1	Me	**2a**	22.7	21.0	**3a**	21.9	(Z) **4a**	18.19	
							(E) **4a**	19.40	
2	Pr	**2b**	22.7	21.0	**3b**	22.3	(Z) **4b**	18.13	
							(E) **4b**	19.57	
3	Ph	**2c**	22.8	20.9	**3c**	22.7	(Z) **4c**	18.00	16.5
							(E) **4c**		17.4



	T°C	Z / E	T°C	Z / E
4a	-50°C	96 / 4	- 10°C	40 / 60
4b	"	100 / 0	"	45 / 55
4c	"	100 / 0	+ 20°C	100 : 0

Scheme 2.

4 it was observed in all cases at 2.72–2.94 ppm ($^3J_{H-P} = 8.0–8.7$ Hz) (Fig. 2).

The configuration of the double bond into the transposed enephosphoramides **4** was also assigned from the ^1H and ^{31}P NMR spectra as exemplified in the case of (Z) **4a** and (E) **4a** as well as in the case of (Z) **5a** obtained by methylation of the carbanion **3a** with iodomethane (Fig. 1 and 2).

In ^{31}P NMR (in $CDCl_3$) the signal of (Z) **4a** was located at 18.19 ppm whereas that of (E) **4a** was slightly deshielded at 19.4 ppm (Table 1, Fig. 1). The observation of the ^4J allylic coupling in ^1H NMR of the two split signals (d) and (f) is also characteristic of (Z) or (E) **4a** (Fig. 2). The signal (d) of pure (Z) **4a** appeared as a quadruplet mainly resulting from a ^3J coupling with the *Me* (e). The *cis* ^4J allylic coupling between (d) and (f) was poor and did not appear. On the contrary, the same signal (d) into (E) **4a** presented a multiplet corresponding to both coupling $^3J_{H-Me\,(e)}$ and $^4J_{H-Me\,(f)}$. This observation was confirmed by new splitting of signals (f) and (e).

It was also noteworthy that the both appearance of the signal (d) and the disappearance of the signal of the hydrogen (c) are of great utility to estimate the conversion into the transposed alkylation product as **5a**. Although the chemical shifts of (d) were very close into **4a** (product of hydrolysis of the carbanion **3a** having not reacted with the alkylating reagent) and **5a** (alkylation product) the splitting of this signal was characteristic of the alkylation product. If it presented as a quadruplet it was the transposed enephosphoramide resulting of the hydrolysis of the not reacted carbanion **3a**. If this signal appeared as a triplet it was the alkylation product **5a**.

*2.2. More accurate ^{31}P NMR study of the reaction mechanism between n-BuLi and enephosphoramides **2a-c** for the obtention of carbanions **[3a-c]** at −50 °C*

*2.2.1. Reaction between n-BuLi and enephosphoramide **2c***

Addition of *n*-BuLi to the enephosphoramide **2c** at −50 °C in THF led to the immediate and total formation of carbanion **[3c]** as it could be observed from the presence of the sole signal at 22.7 ppm in ^{31}P NMR just after the total introduction of one equivalent of *n*-BuLi (Table 2, Fig. 3, D). However the monitoring of the reaction according to the amount of *n*-BuLi added, shown two phases.

During the first half of the addition, it was observed a continue chemical shift variation from the initial signal at 20.9 ppm characteristic of **2c** towards that of **[3c]** at 22.7 ppm, indicating a coalescence between the two signals. In the same time, two new signals appeared at 17.40 and 16.50 ppm, respectively, assigned to transposed enephosphoramides (E) **4c** and (Z) **4c**. Until half-addition these signals progressively increased at these invariable chemical shifts (Fig. 3, A–C). At half-addition

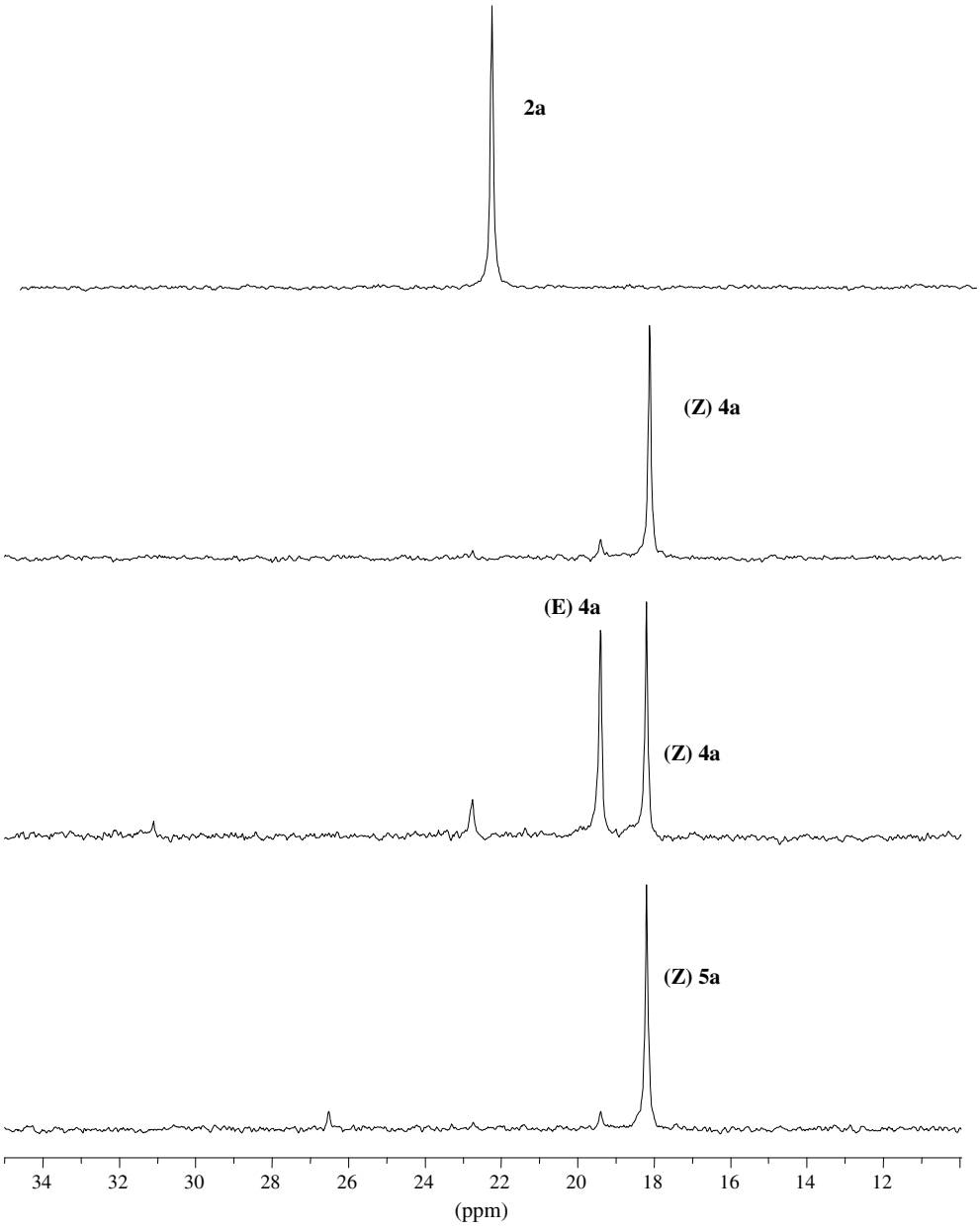


Fig. 1. ^{31}P NMR spectra ($CDCl_3$) of enephosphoramides **2a** (starting compound), **4a** (transposed product), **5a** (methylation product).

of *n*-BuLi the reaction medium contained approximately 50% of carbanion **[3c]** and 50% of enephosphoramide **4c**. The addition going on, the signals of **4c** progressively disappeared and at the end of addition have completely disappeared (Fig. 3, D).

These different observations could be explained by the following mechanism (Fig. 4).

During the first period the ambident carbanion **[3c]** behaved as a transposition catalyst. The coalescence of signals of **2c** and **[3c]** shows that an acid–base equilibrium occurs between **2c** and **[3c]** and that the α-reprotonation of **[3c]** with **2c** is entirely reversible. It indicates also that the hydrogen exchange rate between both species is faster than the relaxation time of phosphorus atom. Appearance of transposed enephosphoramide (E, Z) **4c** can be explained by a partial irreversible γ-reprotonation of **[3c]** with **2c**. An other experience consisting in the addition of a small amount of **2c** to the sole carbanion **[3c]** proves such a supposition. In that attempt it was effectively observed an upfield shift variation of the signal of **[3c]** from 22.7 to 22.4 ppm and the signal of (E) **4c** at 17.40 ppm as expected. It has to note that the formation of major (E) **4c** in the reaction medium during the first part of addition of *n*-BuLi seems contrary to the result of hydrolysis of the carbanion **[3c]** which provides (Z) **4c** as related above. Consequently we suppose that the starting compound **2c** can induce a destabilising effect,

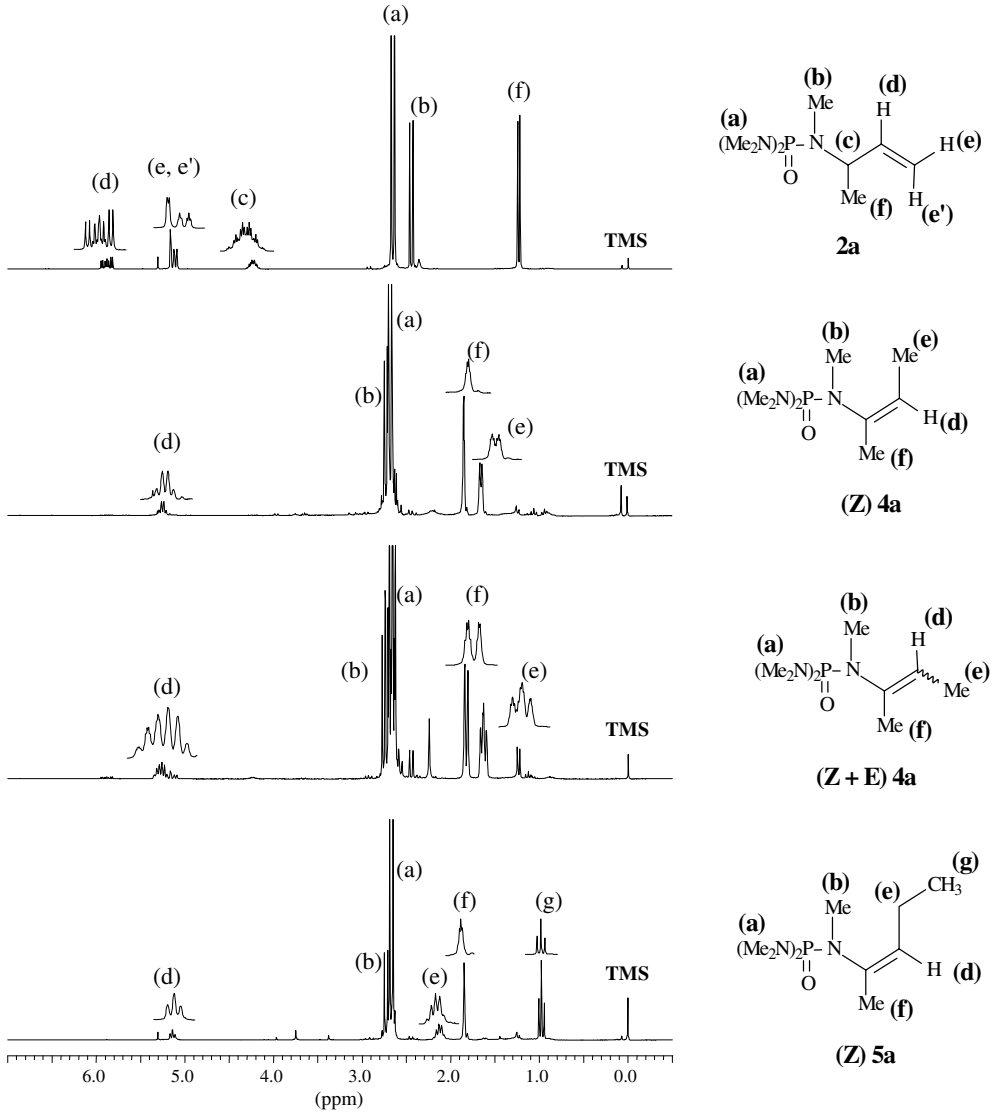


Fig. 2. ^{1}H NMR spectra ($CDCl_3$) of **2a** (starting compound), (Z) (E) **4a** (transposed products), (Z) **5a** (methylation product).

like HMPA, on the intermediate (Z) **[3c]** which would lead to (E) **4c**, in situ.

After the half-equivalence, the progressive disappearance of signals **4c** was observed without any change in the chemical shift of **[3c]** which remained the unique signal at the end of addition. At this time, one equivalent of *n*-BuLi was added and 100% of carbanion **[3c]** was sole present in the medium.

That means that the addition of *n*-BuLi from half-reaction only used to deprotonate the transposed phosphoramide **4c** into the ambident anion **[3c]**. This was verified in a parallel experience consisting to test the ability for *n*-BuLi to effect the γ-deprotonation of pure **4c** followed by a subsequent deuterolysis that afforded γ-deuterated transposed enephosphoramide **4c**.

The absence of coalescence between the signals of **[3c]** and **4c** cannot sole constituted a sufficient prove to establish that neither reversible reaction exist between both species. A smallest proton rate exchange between **[3c]** and **4c** compared to the relaxation time of phosphorus atom could also explained this fact. The coalescence signal which reached its maximum at 22.7 ppm at half-addition and which maintained this value until the end of addition was the best argument. A reprotonation of **[3c]** by **4c** after the half-addition would produce again **2c** in the reaction medium and consequently a new coalescence between the signals of **2c** and **[3c]** would exist involving an upfield variation of that signal, that was not the case.

Finally it has to be noted that this study that revealed the presence of different intermediates during the metallation of **2c** can induce the idea of a long time metallation. It is not the case. With a synthetic aim, carbanion **[3c]** was fully formed at −50 °C in THF after addition in

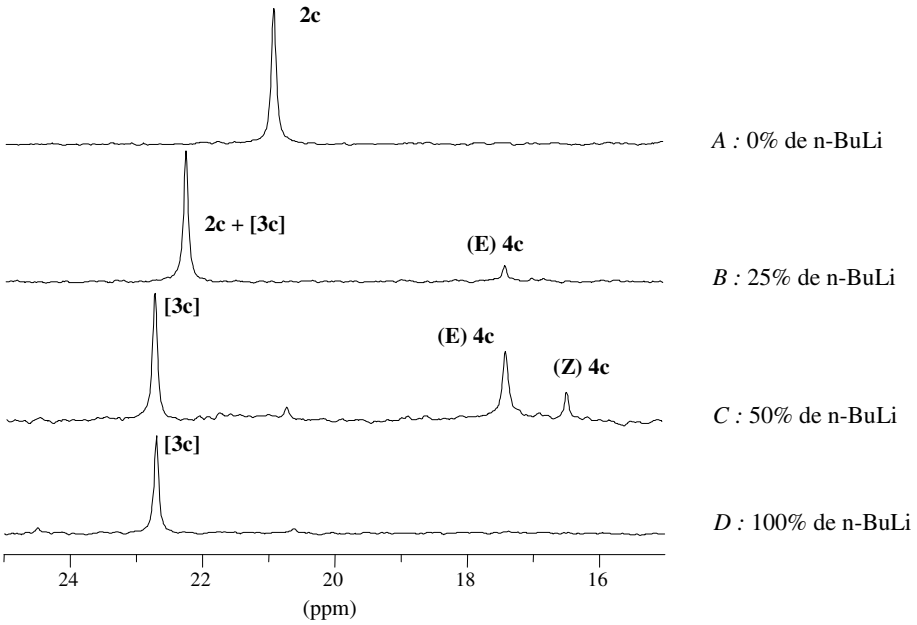


Fig. 3. *n*-BuLi addition-evolution of different species observed in the reaction with enephosphoramide **2c** at −50 °C (^{31}P NMR in THF in mode sweep-off).

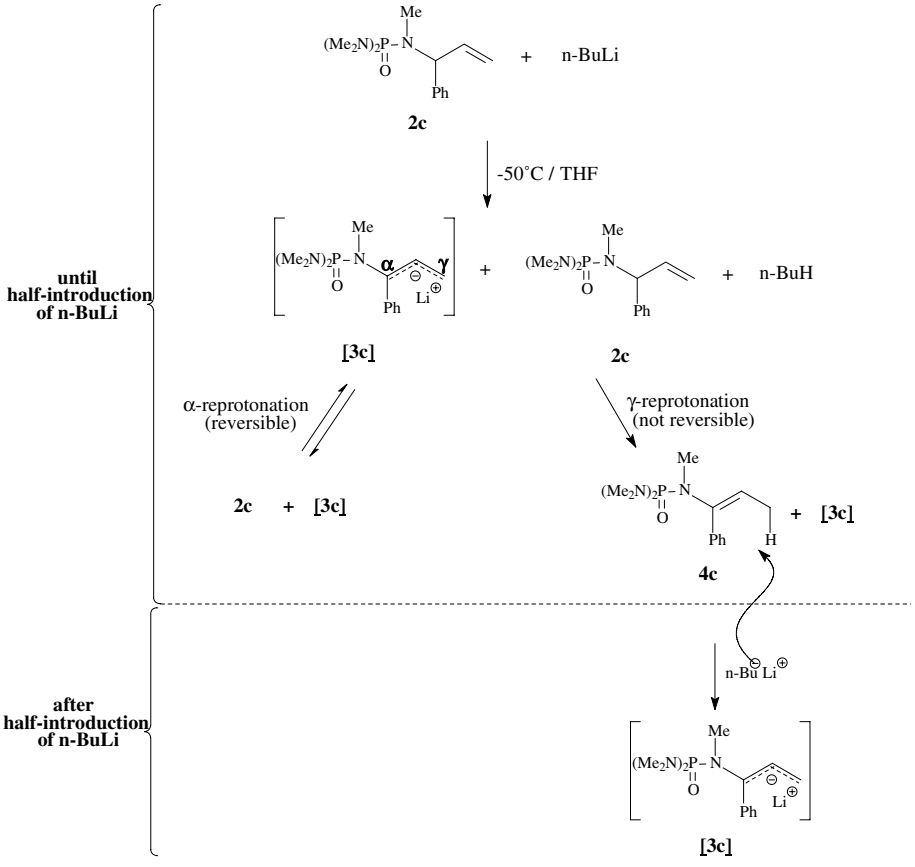


Fig. 4. Mechanism of the reaction of enephosphoramide **2c** with *n*-BuLi.

1 min. of 2 ml of *n*-BuLi (2.5 M in hexane, 5 mmol, 1.1 equiv.) to 4.5 mmol of enephosphoramide **2c** in 35 ml of THF. Immediate deuterolysis of the reaction mixture or methylation with iodomethane respectively yielded 100% of transposed γ-deuterated (Z) **4c** or 100% of (Z) **5c**.

*2.2.2. Reaction between n-BuLi and enephosphoramide **2a***

The metallation of **2a** with *n*-BuLi was as swift as **2c** in the same precedent conditions since after addition of *n*-BuLi in 1 min to **2a** and subsequent immediate deuterolysis, 100% of transposed γ-deuterated (Z) **4a** was obtained.

When *n*-BuLi was added *slowly* at −50 °C, ^{31}P NMR monitoring sweep-off of the metallation shown that carbanion **[3a]** behaved as a transposition catalyst like **[3c]**. For instance, hydrolysis of the reaction mixture at half-addition afforded 100% of transposed enephosphoramide **4a**. That means that 50% of **4a** was the result of the autocatalytic process. But in contrast with the precedent case of **4c**, *n*-BuLi was unable to deprotonate in situ the transposed enephosphoramide **4a**. There is here an essential difference in the formation of **[3a]** compared to that of **[3c]**: in the case of **[3c]** the formation of transposed product **4c** which accompanied **[3c]** at half-addition was not a problem since the enephosphoramide **4c** was entirely retransformed into **[3c]** in the second part of the addition of *n*-BuLi, and this whatever the addition rate of *n*-BuLi. As a result, 100% of added *n*-BuLi provided 100% of **[3c]**. In contrast, a slow metallation of **2a** produced enephosphoramide **4a** at the expense of **[3a]** that therefore could not be obtained in 100% yield. Consequently a very fast addition of *n*-BuLi is recommended in this case, so that α-deprotonation of **2a** provides **[3a]** faster than autocatalysis leading to transposed enephosphoramide **4a**.

*2.3. Reaction between n-BuLi and enephosphoramide **2b***

2.3.1. Metallation at −50 °C (Fig. 5)

Whereas the metallation of enephosphoramides **2a** and **2c** was extremely rapid at −50 °C, complete deprotonation of **2b** needed 1 h at this temperature after the complete addition of *n*-BuLi. ^{31}P NMR monitoring sweep-off of the metallation at −50 °C shown that coalescence did not exist between the signals of enephosphoramide **2b** at 21.0 ppm and that of corresponding carbanion **[3b]** at 22.6 ppm whatever the amount of *n*-BuLi added. Either the reversible α-deprotonation of **2b** with **[3b]** was not possible or the rate of the exchange of α-hydrogen between these species was slower than the relaxation time of phosphorus atom in ^{31}P NMR.

Otherwise, the in situ γ-reprotonation of **[3b]** into **4b** was never observed at −50 °C in contrast with the metallation of **2a** or **2c**: in this case the transposed enephosphoramide **4b** was not present in situ at half-addition of *n*-BuLi. The sole noted change in the ^{31}P NMR spectra of the reaction medium relatively to the *n*-BuLi added was the gradual appearance of the carbanion signal **[3b]** and the concomitant, then complete, disappearance of the signal **2b**.

2.3.2. Metallation at −50 °C/1 h, then gradual warming of the reaction mixture to 0 °C

In this experience 0.25 equiv. of *n*-BuLi was added to 1 equiv. of **2b** at −50 °C. After 1 h at this temperature, a sample was taken and analysed by ^{31}P NMR

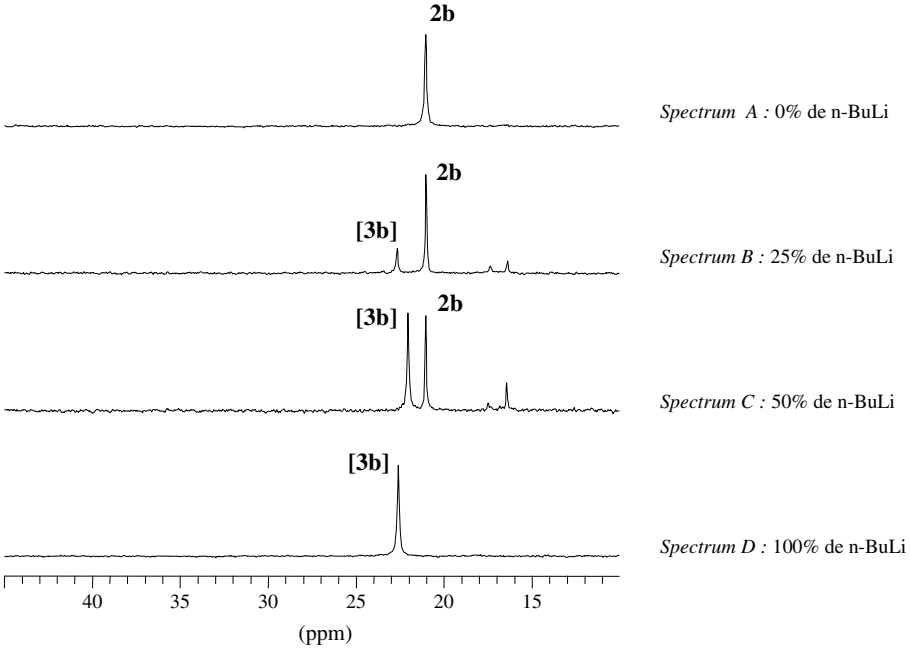


Fig. 5. *n*-BuLi addition-evolution of different species observed in the reaction with enephosphoramide **2b** at −50 °C (^{31}P NMR in THF in mode sweep-off).

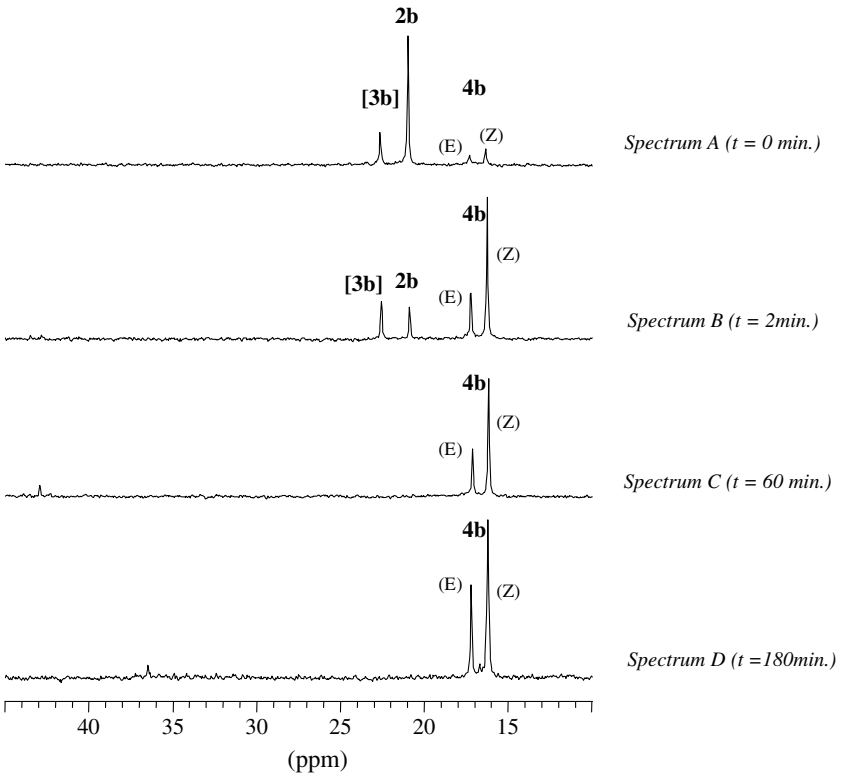


Fig. 6. Evolution of different species observed in the reaction between enephosphoramide **2b** (1 equiv.) and *n*-BuLi (0.25 equiv.) between −50 and 0 °C (^{31}P NMR in THF in mode sweep-off).

(without hydrolysis). The presence of 25% of **[3b]**, 75% starting compound **2b** and traces of **4b** was observed. The reaction mixture was allowed to gradually warm to 0 °C with successive analyses at different temperatures. Neither change occurred until −30 °C but after 1 h at −20 °C, 10% of **4b** was present. Increasing of the temperature enhanced the autocatalytic process. After 1 h at −10 °C 33% of **4b** was noted, and 100% of **4b** was finally observed at 0 °C before hydrolysis. Fig. 6 illustrates this evolution at different times with a sample taken at −50 °C and placed in the not thermostat probe of the NMR apparatus allowing it to warm to ambient temperature.

In summary, the carbanion **[3b]** (R = Pr) presented a similar behaviour that **[3a]** (R = Me) and **[3c]** (R = Ph) as transposition catalyst, but it distinguished from these carbanions by a greater auto catalysis temperature that only efficiently occurred between −10 and 0 °C.

This auto catalysis temperature was of great importance in the preparation of carbanion **[3b]** since once formed **4b**, *n*-BuLi was unable to deprotonate **4b** into **[3b]** (like with **4a** where *n*-BuLi was unable to deprotonate **4a** into **[3a]**). A parallel attempt shown indeed that the reaction between **4b** and *n*-BuLi followed by subsequent quenching with D_2O afforded 100% of not deuterated **4b**.

As a result it was necessary to rigorously maintain the temperature of the metallation of **2b** with *n*-BuLi at −50 °C for 1 h to obtain 100% of carbanion **[3b]**.

3. Conclusion

The ^{31}P NMR study of the reaction of metallation of α-substituted enephosphoramides **2a-c** (R = Me, Pr, Ph) with *n*-BuLi allows to establish the best conditions for the preparation of the lithiated corresponding carbanions and determine their stabilities. The formation of α-methyl **[3a]** and α-phenyl **[3c]** substituted carbanions is immediate at −50 °C in THF, whereas 1 h is necessary for the metallation of **2b** (R = Pr) at this temperature. The stability of these ambident anions vary according to their structure. The α-phenyl **[3c]** substituted carbanion is by far the most stable since it can refluxed in THF for 1 h without any degradation. The α-propyl **[3b]** begins to degrade after 1 h at 0 °C whereas the α-methyl **[3a]** is the less stable and fast degrades within a few minutes at −10 °C.

A fine autocatalytic reaction has been revealed during these different metallations leading to a plausible reaction mechanism. It was established that the formed carbanions **[3a-c]** behaves like bases towards the starting enephosphoramides **2a-c** as the *n*-BuLi addition proceeds. In this way these ambident anions are able to repronate at the α- or at the γ-position to respectively afford again **2a-c** or transposed enephosphoramides **4a-c**.

It was demonstrated that α-reprotonation is reversible at $T \geqslant -50$ °C in the case of α-substituted phenyl enephosphoramide **[3c]** and not reversible for **[3b]** whatever the temperature between −50 and 0 °C. As a result of the

great fragility of **[3a]**, the monitoring of the reaction medium in a not thermostat ^{31}P NMR probe being not possible without degradation, the eventual coalescence between the signals of **2a** and **[3a]** could not been observed. Consequently, the reversibility of α-deprotonation remains a not resolved question in the case of **2a**. On the other hand, γ-reprotonation of **[3a-c]** is not reversible whatever the nature of the carbanion, and constitutes an auto catalysis process providing, in situ, transposed enephosphoramides **4a-c**. This phenomena has to be absolutely avoided in the cases of α-methyl and α-propyl enephosphoramides **2a-b** during the metallation leading to **[3a-b]** whereas it is not a problem in the metallation of **2c**.

4. Experimental

IR spectra were obtained using a Nicolet 210 spectrometer and are given in cm^{-1}. ^1H NMR/^{13}C NMR/^{31}P NMR spectra were recording on a Bruker AC250. Data for ^1H NMR spectra are reported in δ units downfield from internal Me_4Si. ^{13}C NMR spectra were referenced to the $CDCl_3$ peak at 77 ppm relative to Me_4Si. Orthophosphoric acid (85%) was used as an external standard for ^{31}P NMR. Multiplicities are reported as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Mass spectra (EI, 70 eV and CI) were obtained on a Fison Trio 1000 spectrometer. Analytical chromatography was performed on silica gel 60 F254 plates. TLC plates were developed with spraying sulfuric acid followed by calcination, by iodine, or by UV. Preparative chromatographic separations were carried out on Merck silica gel 60 (230–400 mesh). Et_2O was distilled over P_2O_5 and stored over Na. THF was freshly distilled from Na/naphtalene prior to use. Benzene was distilled over Na and stored over molecular sieves (3 Å). *N*-Butyllithium was purchased from Aldrich and was titrated using the Watson–Eastham procedure.

4.1. Preparation of ene phosphoramides *2*, *4*, and *5*

Typical procedures for the preparation of ene phosphoramides **2**, **4**, and **5** were described previously with the corresponding analytical data [5].

4.2. Reaction between n-BuLi and transposed enephosphoramide *4c*

To a stirred solution of transposed enephosphoramide [5] **4c** (4.5 mmol) in THF (10 ml) at −50 °C was added a solution of *n*-BuLi (2.0 ml, 5 mmol, 2.5 M in hexane). After stirring under nitrogen atmosphere at −50 °C for 5 min, the mixture was rapidly hydrolysed with deuterium oxide (1.5 ml) at this temperature followed by an addition of 15 ml of a NaCl aqueous saturated solution. The aqueous layer was extracted with dichloromethane (3×20 ml). The combined organic layers were dried ($MgSO_4$) and the solvent was removed under reduced pressure to afford the γ-deuterated phosphoramide **4c**. This compound was identical to γ-deuterated phosphoramide **4c** obtained according to the same experimental conditions applied to the starting enephosphoramide **2c** [5].

[(1-phenyl-1-propen-3d$_1$-1-yl)pentamethyl phosphoric triamide] ***4c***. Yield: 100%; pale yellow oil; (Z/E: 100/0); IR (NaCl plates)/cm^{-1}: $\nu_{max} = 3026, 2923, 2151, 1637, 1592, 1490, 1454$ and 1299; ^1H NMR (250.13 MHz, $CDCl_3$): $\delta_H = 1.92$ (m, 2H, C=CH–CH_2–D), 2.55 [d, $^3J_{H-P} = 9.0$ Hz, 12H, [(CH_3)$_2$N]$_2$PO], 2.93 [d, $^3J_{H-P} = 8.6$ Hz, 3H, CH_3–N–CH(Ph)], 5.82 [t, $^3J_{H-H} = 6.8$ Hz, 1H, C(Ph)=C*H*–CH_2D], 7.19–7.51 (m, 5H, *Ph*); ^{13}C NMR (62.896 MHz, $CDCl_3$): $\delta_C = 13.6$ (t, $^1J_{C-D} = 19.0$ Hz, C=CH–*C*H_2D), 36.7, 36.8 [[(CH_3)$_2$N]$_2$PO and CH_3–N–CH(Pr)], 122.6 (d, $^3J_{C-P} = 5.0$ Hz, C=*C*H–CH_2D), 126.0, 126.9, 127.8, 140.4 (*Ph*), 143.3 [N–*C*(Ph)=CH–CH_2D]; ^{31}P NMR (101.256 MHz, $CDCl_3$): $\delta_P = 17.97$; MS (EI^+) m/z calculated for $C_{14}H_{23}DN_3OP$ $[M]^+$ 282.3 found 282 [$[M]^+$, 70%], 147 [$[M–(Me_2N)_2PO]^+$, 78%], 135 [$[(Me_2N)_2PO]^+$, 100%].

4.3. ^{31}P NMR monitoring of the reaction between n-BuLi and enephosphoramides *2*

To a stirred solution of transposed enephosphoramide **2** (4.5 mmol) in THF (10 ml) at −50 °C was added in 0.5 ml equal shares a solution of *n*-BuLi (2.0 ml, 5 mmol, 2.5 M in hexane). After each addition of *n*-BuLi, a sample was taken off at −50 °C, placed in a NMR tube under nitrogen atmosphere, and rapidly analysed by ^{31}P NMR in mode sweep-off in a not thermostat probe. Consequently it was not possible to assign the exact analysis temperature which was probably greater than −50 °C. However, these conditions were compatible with the stability of **[3b-c]** in the probe so that the different recorded spectra could be considered significant for the mechanism determination. In the case of the fragile carbanion **[3a]** samples were cut off, then hydrolysed before NMR analysis.

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