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Sigmatropic [2,3]-Wittig Rearrangement of α-Allylic-Heterosubstituted Methylphosphonates. Part 2[1] : Rearrangement in the Nitrogen Series

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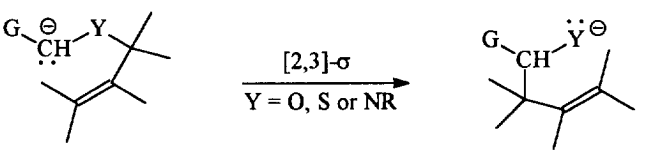
Abstract : Whereas the lithiated carbanion derived from the diethyl (*N*-allyl, *N*-phenyl)-amino methylphosphonate **1** failed to undergo the [2,3]-Wittig shift, ammonium salts resulting from the quaternization of diisopropyl (*N,N*-diethyl)-aminomethylphosphonate **8** with allylic bromides, were conveniently rearranged into the α-(*N,N*-diethylamino)-alkenylphosphonates **11**, in the presence of *t*-BuOK, in DMF, at -40°C.

INTRODUCTION

The sigmatropic [2,3]-Wittig rearrangement[2-5] of α-anions of allylic ethers[6] and thioethers[7] is a very well known reaction which has found many applications in organic synthesis. In contrast, the aza analogue [2,3]-shift appears to be rare and difficult[8-10], possibly owing to the low stability and the high basicity of the resulting amide anion as compared to the alkoxide or the sulfide ones (Scheme 1).



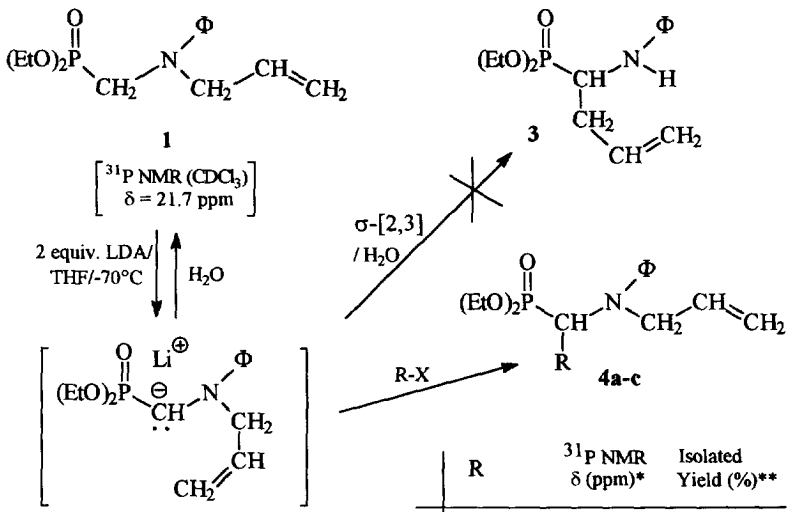
I **II**

Scheme 1

On the other hand, whereas various functional groups G have served to stabilize the α-hetero substituted carbanion **I**, the use of a phosphonate group had not been reported until our recent studies in the α-allyloxymethyl[1] and α-allylthiomethyl[11] phosphonate series. Pursuing our work in this area, we have now studied the behaviour of α-(*N*-allylic substituted) aminomethylphosphonate carbanions.[12]

RESULTS AND DISCUSSION

In the first set of experiments, we studied the carbanion **2** derived from the diethyl (*N*-allyl-*N*-phenylaminomethyl)phosphonate **1** (Scheme 2). The treatment of **1** with a two-fold excess of lithium diisopropylamide (LDA) in tetrahydrofuran (THF) at -70°C gave anion **2** [^{31}P NMR (THF), δ = 43 ppm], quantitatively formed after about 2 h. The rearranged product **3** was not detected after 4 h at -70°C nor at room temperature. Instead, trapping the generated anion **2**, at -70°C, with water or various other electrophiles led to phosphonate **1** or to the α-substituted phosphonates **4**, respectively.



	R	^{31}P NMR δ (ppm)*	Isolated Yield (%)**
a	$SiMe_3$	25.1	79
b	$SnBu_3$	28.2	52
c	SΦ	16.2	60
d	CH_3	24.5	70

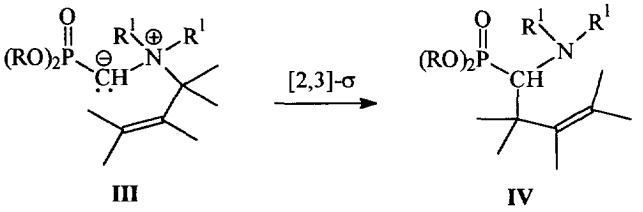
* In $CDCl_3$ ** Purified by column chromatography (over neutral Al_2O_3; eluent, ether/hexane : 1/1)

Scheme 2

These results showed that the α-metallated *N*-allylaminomethylphosphonic ester **2** failed to undergo the [2,3]-sigmatropic rearrangement observed with the oxides[1] or sulfides[11] counterparts.

Another useful [2,3]-sigmatropic shift of α-allyl heterosubstituted carbanions is the rearrangement of ammonium ylides[13-15] that provides homoallylic dialkyl amines, and whose driving force very likely lies in the charge annihilation process. To the best of our knowledge, no example of such rearrangement has been described so far in the phosphonic series.

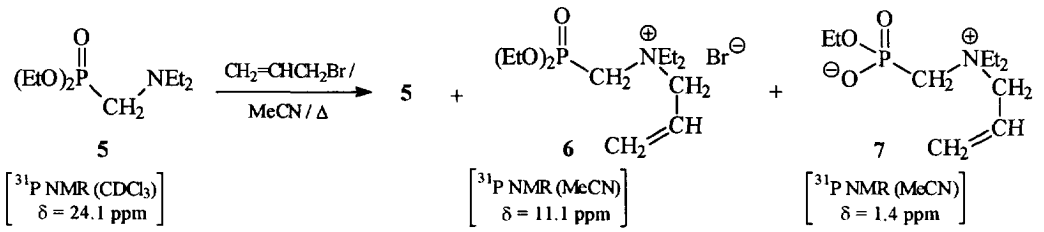
In the second part of our study, we investigated the rearrangement of allyl dialkylphosphonomethyl ammonium ylides **III** into α-dialkylamino-γ,δ-unsaturated phosphonates **IV** (Scheme 3).



III IV

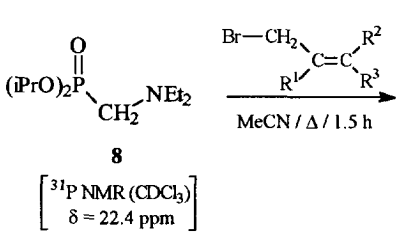
Scheme 3

First, all our attempts to quaternize allylic amine **1** with methyl iodide or dimethyl sulfate in refluxing acetonitrile failed, probably because of the low nucleophilicity of the *N*-phenylated nitrogen atom in **1**. Then, we decided to study the quaternization of the readily available diethyl (*N,N*-diethylaminomethyl)phosphonate **5**[16] with allyl bromide in boiling acetonitrile. The reaction was uncomplete after 2 h, and besides the expected ammonium salt **6**, we observed (by ^{31}P and ^{1}H NMR spectroscopy) the progressive formation of the O-dealkylated zwitterion **7**, which became the major product (~80%) in the mixture after 8 h (Scheme 4). Moreover, the formation of this undesirable product was accelerated when the reaction was carried out in the presence of one equivalent of sodium iodide.



Scheme 4

The facile monodealkylation of unbranched alkyl esters of alkylphosphonic acids, when treated by nucleophilic anions as halides or sulfides, is well established.[17-19] In contrast, branched dialkyl esters as diisopropyl alkylphosphonates are quite resistant to the same nucleophilic attacks.[18,20] In order to avoid the formation of by-products such as **7**, we studied the quaternization of the diisopropyl(*N,N*-diethylamino methyl)phosphonate **8**[21] with various allylic bromides, in refluxing acetonitrile (Scheme 5).



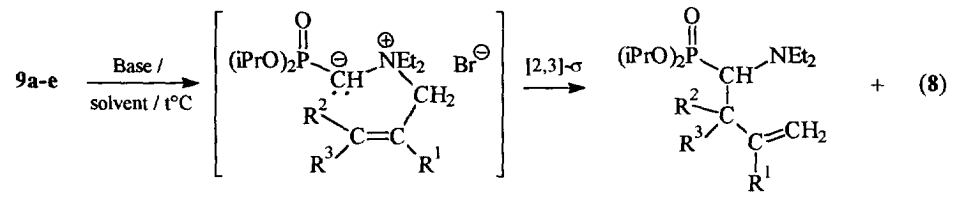
	R^1	R^2	R^3	^{31}P NMR δ (ppm)*
9a	H	H	H	9.5
9b	H	H	CH_3	10.0
9c	H	H	C_6H_5	9.9
9d	CH_3	H	H	10.3
9e	H	CH_3	CH_3	9.6

* In $CDCl_3$

Scheme 5

After elimination of the volatile products under reduced pressure the crude ammonium salts **9** were obtained quantitatively as brown viscous pastes, and their purity was determined by ^{31}P and ^{1}H NMR spectroscopy.

The crude phosphonates **9** were then submitted to deprotonation using various bases. The progress of the reaction was monitored by ^{31}P NMR spectroscopy, measuring the intensity of the peak of product **11** and comparing to that of the starting phosphonate **9**. In any case, the ylide **10** intermediate was not detected (Scheme 6).



10 **11**

Scheme 6

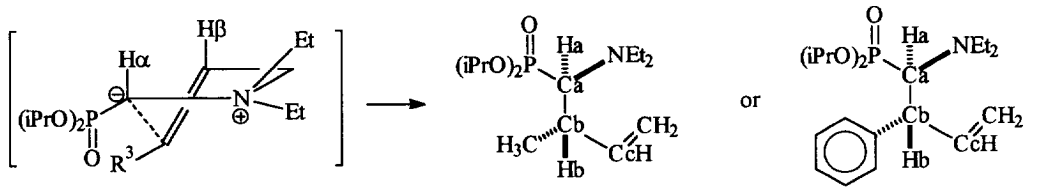
Using LDA (2 equiv.) as the base, in THF, at -70°C or at room temperature, the progress of the rearrangement was estimated to be ~15%, after 3h of reaction. This disappointing result might be attributed to the very low solubility of the salts **9** in THF. With the same amount of LDA, using a 1/1 mixture of THF and dimethylformamide (DMF) as solvent, the extent of the reaction attained ~50%, at the same temperature. We also examined the role of the anion of the ammonium salt; when **9a** was shaken with 1.2 equiv. of $AgBF_4$ in acetonitrile for 1.5 h, at room temperature, complete replacement of Br^- by BF_4^- was observed [as proved by ^{31}P NMR (δ = 9.1 ppm in $CDCl_3$) and ^{19}F NMR (δ = −153 ppm in $CDCl_3$) spectroscopy], giving the corresponding ammonium tetrafluoroborate **9'a**, soluble in THF. When **9'a** was treated with 2 equiv. of LDA in THF at -70°C, the progress of the rearrangement was only 50%, after 3 h of reaction. Finally, the best results were obtained by treating **9** with potassium *tert*-butoxide (*t*-BuOK, 2 equiv.) in DMF at -40°C, for about 1.5 h (Table 1).

Table 1. Rearrangement of Phosphonic Ammonium Salts **9** into Phosphonates **11**, under Basic Conditions.

Entry	R^1	R^2	R^3	Rearranged product	^{31}P NMR ($CDCl_3$) of **11** δ (ppm)	Yield of pure **11**[a] (%)	% of **8** in the crude mixture[b]
1	H	H	H	**11a**	24.6	71	10
2	H	H	CH_3	**11b**	24.4 / 24.3[c]	77	5
3	H	H	C_6H_5	**11c**	23.5[d]	72	10
4	CH_3	H	H	**11d**	24.7	71	5
5	H	CH_3	CH_3	**11e**	25.2	51	40

[a] Purified by colum chromatography (over neutral Al_2O_3, eluent : ether / hexane : 1/1).
[b] Determined by ^{31}P NMR spectroscopy.
[c] Two diastereoisomers in the 10 / 1 ratio, respectively.
[d] Any trace of a second diastereoisomer was not observed.

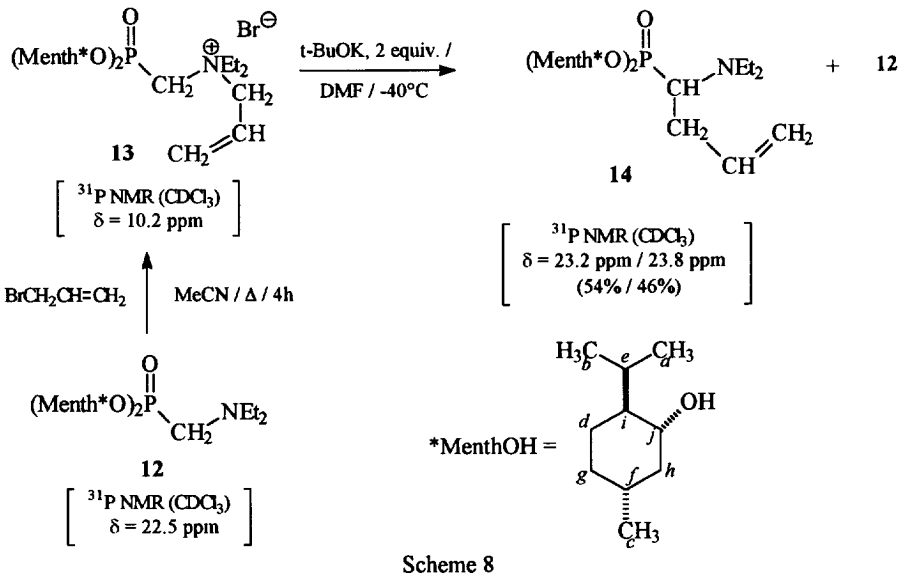
In all experiments, the crude product was contaminated with phosphonate **8** resulting from the nucleophilic attack of the base on the allylic moiety of **9**. Phosphonates **11** were purified by column chromatography and isolated in good yields (Table 1). The very good diastereoselectivities observed in the rearrangement of the crotyl (de = 82%, Entry 3) and of cinnamyl (de = 100%, Entry 4) derivatives deserve to be underlined.[22] The stereochemistry of **11c** was assigned from ^{1}H NMR ($^3J_{HaHb}$ = 8.1 Hz)[23] and $^{13}C\{^1H\}$ NMR ($^3J_{PCc}$ = 11.5 Hz)[24] data which are in good agreement with a *trans*-arrangement of the Ha-Ca-Cb-Hb and the P-Ca-Cb-Cc bonds. The same relative configuration was assigned to the major isomer of **11b** from $^{13}C\{^1H\}$ NMR ($^3J_{PCc}$ = 11 Hz) data.[25] This high level of diastereoselection is reasonably interpreted as the result of the small Hα-Hβ pseudo-1,3-diaxial repulsion in the well accepted chair-like model **T** for the transition state[4] (Scheme 7).



T **11b** (major isomer) **11c**

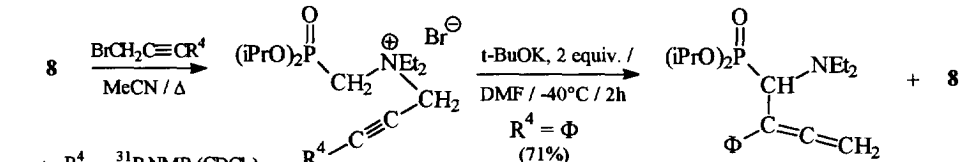
Scheme 7

In order to examine the effect of a chiral auxiliary on the stereocontrol of the reaction, we studied the rearrangement of the dimenthoxyphosphonyl ammonium salt **13**, readily prepared from the dimenthyl (diethylamino)methylphosphonate **12** (Scheme 8). In contrast to the oxide series[26], a very low diastereoselectivity (de = 8%) was observed; moreover, about 25% of the deallylated phosphonate **12** was recovered in the crude mixture.



Scheme 8

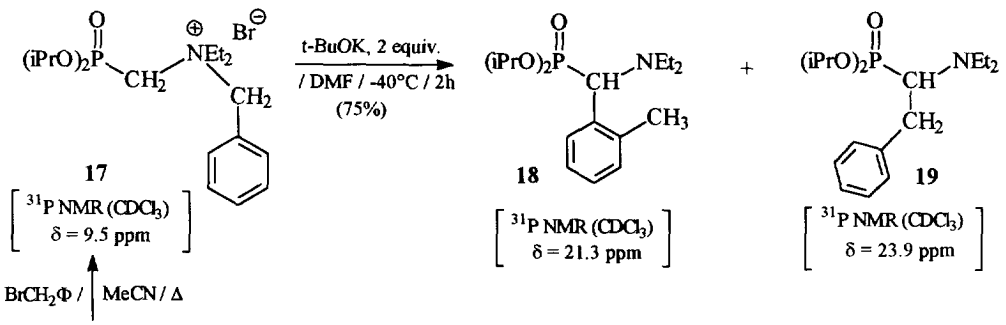
We then extended the study to some propargylic and benzylic derivatives. The two phosphonic ammonium salts **15** of the propargylic series were quantitatively prepared by quaternization of **8**, then submitted to the *t*-BuOK / DMF system. As expected, the terminal alkyne **15a** was recovered unchanged after work up. On the other hand, the phenyl substituted derivative **15b** was quantitatively rearranged into the allenyl phosphonate **16b** (Scheme 9).



	R^4	^{31}P NMR ($CDCl_3$) δ (ppm)
15a	H	9.6
15b	Φ	9.2

Scheme 9

Finally, the benzylic ammonium salt **17**, quantitatively prepared from **8** and benzyl bromide, was treated with 2 equiv. of *t*-BuOK in DMF, at -40°C; a 8 / 1 mixture of the [2,3]-rearranged α-(*o*-tolyl)-phosphonate **18** and the [1,2]-rearranged α-(benzyl)-phosphonate **19** was obtained, as shown by ^{31}P and ^{1}H NMR spectroscopy (Scheme 10). For the benzylic series, it is well known that the [1,2]-shift (often referred to as the "Stevens rearrangement"), usually competes with the [2,3]-shift (referred to as the "Sommelet-Hauser rearrangement").[27,28] Replacing the *t*-BuOK/DMF system by the LDA (2 equiv., -70°C) /THF-DMF system led to a 2/1 mixture of **18** and **19**, respectively, as determined by ^{31}P NMR spectroscopy and by gas chromatography.



Scheme 10

In conclusion, this work reports the first study of the aza-[2,3]-Wittig rearrangement of the carbanions derived from methylphosphonates bearing an amino or an ammonium group at the α-position . Whereas any rearrangement was not observed for the carbanion derived from the diethyl (*N*-allyl *N*-phenyl)-aminomethyl-phosphonate **1**, ammonium salts resulting from the quaternization of the diisopropyl (*N,N*-diethyl)-amino-methylphosphonate **8** with various allylic bromides conveniently rearranged into the corresponding α-(*N,N*-diethyl)-amino alkenylphosphonates **11**, in the presence of *t*-BuOK, in DMF, at -40°C. The reaction was then extended to the propargylic and benzylic series. Current efforts are made in order to use an adapted version of this rearrangement as a key-step for a new synthesis of α-amino alkenylphosphonic acids.

EXPERIMENTAL SECTION

General : Melting points were taken on a Kofler apparatus and are uncorrected. Gas chromatography (GC) was performed on a Girdel 300 chromatograph equipped with a 2m OV17 column. Elemental microanalyses were carried out on a Carlo Erba 1106 analyser.The NMR spectra were recorded in $CDCl_3$, on a Brucker AC-200 spectrometer; the chemical shifts (δ) are expressed in ppm relative to tetramethylsilane for ^1H and ^{13}C nuclei and to H_3PO_4 for ^{31}P nucleus; the coupling constants (J) are given in Hz; conventional abbreviations are used. Solvents were dried and distilled just before use. All metallation reactions were carried out under dry inert gas.

Preparation of phosphonates **4**. *General procedure :* To a 1.6 M solution of *n*-BuLi (0.02 mol) in hexane at -20°C, was dropped a solution of diisopropylamine (2 g, 0.02 mol) in THF (15 mL). The mixture was stirred for 15 mn at -20°C, then cooled to -60°C. A solution of phosphonate **1**[29] (2.8 g, 0.01 mol) in THF (10 mL) was dropped at -60°C and stirring continued for about 2 h until complete formation of anion **2**, as proved by ^{31}P NMR spectroscopy. A solution of the electrophile RX (0.012 mol) in THF (10 mL) was then added and the mixture was stirred for 1 h at -60°C, then for 1.5 h at room temperature. After quenching with water (15 mL), the aqueous layer was extracted with ether (20 mL), then CH_2Cl_2 (2x20 mL). The combined organic layers were dried ($MgSO_4$). The solvent was evaporated under reduced pressure to give the crude product, which was purified by column chromatography over neutral Al_2O_3 (eluent : hexane/ether = 1/1) leading to the pure product **4**.

Diethyl 1-(N-allyl-N-phenyl)amino-1-trimethylsilyl-methylphosphonate (**4a**) : 2.8 g, 79% yield; ^{31}P NMR : 25.1; ^1H NMR : 0.2 (s, 9H, $(C\underline{H}_3)_3Si$); 1.2 & 1.25 (2t, J = 6.2, 6H, 2 × $C\underline{H}_3CH_2O$); 3.8 (d, J = 24, 1H, $PC\underline{H}N$); 4.0-4.2 (m, 6H, 2 × $OC\underline{H}_2CH_3$, $C\underline{H}_2CH{=}CH_2$); 5.05-5.25 (m, 2H, $C\underline{H}_2{=}CH$); 5.7-5.8 (m, 1H, $C\underline{H}{=}CH_2$); 6.6-7.3 (m, 5H, $C_6\underline{H}_5$).

Diethyl 1-(N-allyl-N-phenyl)amino-1-tri-n-butylstannyl-methylphosphonate (**4b**) : 2.9 g, 52% yield; ^{31}P NMR : 28.2 ($^2J_{P^{119}Sn}$ = 96.4, $^2J_{P^{117}Sn}$ = 95.8); ^1H NMR : 0.7-1.5 (m, 33H, 2 × $C\underline{H}_3CH_2O$ & 3 × $C_4\underline{H}_9$); 3.8-4.2 (m, 7H, 2 × $OC\underline{H}_2CH_3$ & $C\underline{H}_2CH{=}CH_2$ & $PC\underline{H}N$); 5.0-5.3 (m, 2H, $C\underline{H}_2{=}CH$); 5.7-6.0 (m, 1H, $C\underline{H}{=}CH_2$); 6.6-7.3 (m, 5H, $C_6\underline{H}_5$).

Diethyl 1-(N-allyl-N-phenyl)amino-1-phenylsulfinyl-methylphosphonate (**4c**) : 2.3 g, 60% yield; ^{31}P NMR : 16.2 ; ^1H NMR : 1.1-1.4 (m, 6H, 2 × $C\underline{H}_3CH_2O$); 3.8 (d, J = 5.5, 2H, $C\underline{H}_2CH{=}CH_2$); 4.0-4.4 (m, 4H, 2 × $OC\underline{H}_2CH_3$); 5.1-5.3 (m, 2H, $C\underline{H}_2{=}CH$); 5.5 (d, J = 20.5, 1H, $PC\underline{H}N$); 5.7-6.1 (m, 1H, $C\underline{H}{=}CH_2$); 6.6-7.6 (m, 10H, $C_6\underline{H}_5$-N & $C_6\underline{H}_5$-S).

Diethyl 1-(N-allyl-N-phenyl)amino-ethylphosphonate (**4d**) :2.1 g, 70% yield; ^{31}P NMR : 24.5; ^1H NMR : 1.2 & 1.3 (2t, J = 7.1, 6H, 2 × $C\underline{H}_3CH_2O$); 1.45 & 1.55 (dd, J = 16.8 & 7.3, 3H, $C\underline{H}_3CHP$); 3.9-4.2 (m, 6H, 2 × $OC\underline{H}_2CH_3$ & $C\underline{H}_2CH{=}CH_2$); 4.2 & 4.25 (dq, J = 18.3 & 7.3, 1H, $PC\underline{H}CH_3$); 5.1-5.35 (m, 2H, $C\underline{H}_2{=}CH$); 5.75-6.0 (m, 1H, $C\underline{H}{=}CH_2$); 6.7-7.3 (m, 5H, $C_6\underline{H}_5$).

Preparation of Dimenthyl N,N-diethylamino-methylphosphonate (**12**): A 37% aqueous solution of formaldehyde (2mmol) was rapidly added to a stirred mixture of diethyl amine (1.46 g, 2mmol) and dimenthyl phosphite[23] (7.16 g, 2mmol).The mixture was refluxed for 4 h, then cooled and dried ($MgSO_4$). The crude product was purified by column chromatography over basic Al_2O_3 (eluent : ether), leading to the pure phosphonate **12**.

Dimenthyl N,N-diethylamino-methylphosphonate (**12**) : 5.3 g, 60% yield; ^{31}P NMR : 22.5; ^{1}H NMR : 0.8 (d, J = 7.1, 6H, 2 × $\underline{H}_3C$*c*); 0.9 (d, J = 6.8, 12H, 2 × $\underline{H}_3C$*a,b*); 1.0 (t, J = 7.2, 6H, $(C\underline{H}_3CH_2)_2N$); 1.1-2.4 (m, 18H, $\underline{H}$C*e,f,i*, $\underline{H}_2$C*d,g,h*); 2.7 (q, J = 7.2, 4H, $N(C\underline{H}_2CH_3)_2$); 2.8 (d, J = 10.5, 2H, $PC\underline{H}_2N$); 4.1-4.3 (m, 2H, 2 × $\underline{H}$C*j*O); ^{13}C NMR (in C_6D_6) : 9.4 (s, $\underline{C}H_3CH_2N$); 13.6 & 13.8 (2s, $\underline{C}$*a*); 19.02 (s, $\underline{C}$*b*); 19.9 (s, $\underline{C}$*c*); 20.8 & 20.9 (2s, $\underline{C}$*d*); 23.3 & 23.4 (2s, $\underline{C}$*e*); 29.3 & 29.4 (2s, $\underline{C}$*f*); 32.1 (s, $\underline{C}$*g*), 41.4 & 42.1 (2s, $\underline{C}$*h*), 46.1 (d, J = 9.7, $\underline{C}$*i*), 46.8 (d, J = 12, $N\underline{C}H_2CH_3$); 49.05 (d, J = 167.8, $P\underline{C}H_2N$); 73.9 & 74.6 (2d, J = 7.5, $\underline{C}$*j*).

Attempt at quaternizing phosphonate **5** : A solution of phosphonate **5**[16] (2.2 g, 1mmol) and of allyl bromide (1.6 g, 1.3 mmol) in acetonitrile (30 mL) was refluxed and the reaction was monitored by ^{31}P NMR spectroscopy. After 2 h, phosphonates **5**, **6** and **7** were in a ratio of 1:8:1, respectively; after 8 h, the ratio was 1:1:8. The mixture was then evaporated under reduced pressure, giving the crude product, in which the major component **7** was clearly characterized by ^{31}P and ^{1}H NMR spectroscopy.

Ethyl 1-(N-allyl-N,N-diethyl)ammonium-methylphosphonate (**7**) : as the major product of the crude mixture; ^{31}P NMR : 1.4 ; ^{1}H NMR : 1.1 (t, J = 7.4, 3H, $C\underline{H}_3CH_2O$); 1.3 (t, J = 8.3, 6H, $(C\underline{H}_3CH_2)_2N^+$); 3.2 (d, J = 11.9, 2H, $PC\underline{H}_2N^+$); 3.3-3.6 (m, 4H, $N^+(C\underline{H}_2CH_3)_2$); 3.9 (q, J = 7.4, 2H, $OC\underline{H}_2CH_3$); 4.1 (d, J = 7.1, 2H, $C\underline{H}_2CH{=}CH_2$); 5.6-5.75 (m, 2H, $C\underline{H}_2{=}CH$); 5.8-6.0 (m, 1H, $C\underline{H}{=}CH_2$).

Preparation of ammonium salts **9**, **13**, **15** and **17**. *General procedure :* A solution of phosphonate **8**[21] or **12** (0.01 mol) and of an allylic bromide (0.013 mol) in acetonitrile (30 mL) was refluxed for 1.5 h. Evaporation of the volatiles under reduced pressure gave quantitatively the corresponding ammonium salt **9**, **13**, **15** or **17**, whose purity was controlled by ^{31}P, ^{1}H and ^{13}C NMR spectroscopy. These phosphonates were used in the crude state for the following step.

(N-Allyl-N,N-diethyl-N-diisopropoxyphosphonylmethyl)ammonium bromide (**9a**) : 3.7 g of a paste; ^{31}P NMR : 9.5; ^{1}H NMR : 1.3-1.45 (m, 12H, 2 × $(C\underline{H}_3)_2CHO$); 1.5 (t, J = 7.8, 6H, $(C\underline{H}_3CH_2)_2N^+$); 3.6 (q, J = 7.8, 4H, $N^+(C\underline{H}_2CH_3)_2$); 4.1 (d, J = 13.7, 2H, $PC\underline{H}_2N^+$); 4.4 (d, J = 5.9, 2H, $C\underline{H}_2CH{=}CH_2$); 4.7-5.0 (m, 2H, 2× $OC\underline{H}(CH_3)_2$); 5.7-5.9 (m, 2H, $C\underline{H}_2{=}CH$); 5.9-6.1 (m, 1H, $C\underline{H}{=}CH_2$); ^{13}C NMR : 8.1 (s, $\underline{C}H_3CH_2N^+$); 23.3 (s, $(\underline{C}H_3)_2CHO$); 52.1 (d, J = 150.1, $P\underline{C}H_2N^+$); 55.6 (s, $N^+\underline{C}H_2CH_3$); 61.4 (s, $N^+\underline{C}H_2CH{=}CH_2$); 72.6 (s, $(CH_3)_2\underline{C}HO$); 123.8 (s, $\underline{C}H_2{=}CH$); 128.6 (s, $\underline{C}H{=}CH_2$).

[N-(E)-Crotyl-N,N-diethyl-N-diisopropoxyphosphonylmethyl)ammonium bromide (**9b**) : 3.8 g of a paste; ^{31}P NMR : 10.0; ^{1}H NMR : 1.2-1.4 (m, 12H, 2 × $(C\underline{H}_3)_2CHO$); 1.5 (t, J = 6.5, 6H, $(C\underline{H}_3CH_2)_2N^+$); 1.8 (d, J = 6.4, 3H, $(C\underline{H}_3CH)$); 3.6 (q, J = 6.5, 4H, $N^+(C\underline{H}_2CH_3)_2$); 3.9 (d, J = 13.7, 2H, $PC\underline{H}_2N^+$); 4.3 (d, J = 7.7, 2H, $C\underline{H}_2CH{=}CH$); 4.7-4.9 (m, 2H, 2× $OC\underline{H}(CH_3)_2$); 5.45-5.55 (m, 1H, $C\underline{H}CH_3$); 6.2-6.4 (m, 1H, $C\underline{H}{=}CH{-}CH_3$); ^{13}C NMR : 8.06 (s, $\underline{C}H_3CH_2N^+$); 17.8 (s, $\underline{C}H_3CH{=}CH$); 23.3 (s, $(\underline{C}H_3)_2CHO$); 51.8 (d, J = 150.3, $P\underline{C}H_2N^+$); 55.1 (s, $N^+\underline{C}H_2CH_3$); 61.1 (s, $N^+\underline{C}H_2CH{=}CHCH_3$); 72.6 (s, J = 6.9, $(CH_3)_2\underline{C}HO$); 116.5 (s, $CH_3\underline{C}H{=}CH$); 141.1 (s, $\underline{C}H{=}CHCH_3$).

(N-Cinnamyl-N,N-diethyl-N-diisopropoxyphosphonylmethyl)ammonium bromide (**9c**) : 4.4 g of a solid, Mp ~ 45 °C; ^{31}P NMR : 9.9; ^{1}H NMR :1.2-1.4 (m, 12H, 2 × $(C\underline{H}_3)_2CHO$); 1.5 (t, J = 7.8, 6H, $(C\underline{H}_3CH_2)_2N^+$); 3.7 (q, J = 7.8, 4H, $N^+(C\underline{H}_2CH_3)_2$); 4.05 (d, J = 15.6, 2H, $PC\underline{H}_2N^+$); 4.6 (d, J = 9.2, 2H, $C\underline{H}_2CH{=}CH$); 4.7-4.9 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 6.2-6.4 (m, 2H, $C\underline{H}{=}C\underline{H}Ph$); 7.1-7.5 (m, 5H, $C_6\underline{H}_5$); ^{13}C NMR : 8.2 (s, $\underline{C}H_3CH_2N^+$); 23.3 (d, J = 2.9, $(\underline{C}H_3)_2CHO$); 52.3 (d, J = 150, $P\underline{C}H_2N^+$); 55.5 (s, $N^+\underline{C}H_2CH_3$); 61.5 (s, $N^+\underline{C}H_2CH{=}CHPh$); 72.6 (d, J = 6.7, $(CH_3)_2\underline{C}HO$); 113.8 (s, $C_6H_5\underline{C}H{=}CH$); 126.6; 128; 128.5; 134.1 (4s, $\underline{C}$arom); 142.2 (s, $\underline{C}H{=}CHPh$).

(N,N-Diethyl-N-diisopropoxyphosphonylmethyl-N-methallyl)ammonium bromide (**9d**) : 3.8 g of a paste; ^{31}P NMR : 9.6; ^{1}H NMR : 1.2-1.4 (m, 12H, 2 × ($C\underline{H}_3$)$_2$CHO); 1.5 (t, J = 7.4, 6H, ($C\underline{H}_3CH_2$)$_2N^+$); 2.1 (s, 3H, $C\underline{H}_3C$); 3.7 (q, J = 7.4, 4H, $N^+(C\underline{H}_2CH_3)_2$); 4.1 (d, J = 12.9, 2H, $PC\underline{H}_2N^+$); 4.4 (s, 2H, $C\underline{H}_2CCH_3$); 4.6-4.9 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 5.5 & 5.6 (2s, 2H, $C\underline{H}_2$=CCH_3); ^{13}C NMR : 9.1 (s, $\underline{C}H_3CH_2N^+$); 10.3 (s, $\underline{C}H_3C$=CH_2); 23.9 (d, J = 2.9, ($\underline{C}H_3$)$_2$CHO); 53.2 (d, J = 150, $P\underline{C}H_2N^+$); 56.75 (s, $N^+\underline{C}H_2CH_3$); 65.1 (s, $N^+\underline{C}H_2C(CH_3)$=$CH_2$); 73.2 (d, J = 6.9, ($CH_3$)$_2\underline{C}$HO); 126.7 (s, $\underline{C}H_2$=C); 132.5 (s, $\underline{C}(CH_3)$=CH_2).

(N,N-Diethyl-N-diisopropoxyphosphonylmethyl-N-prenyl)ammonium bromide (**9e**) : 4 g of a solid, Mp = 116°C; ^{31}P NMR : 10.3; ^{1}H NMR : 1.3-1.5 (m, 12H, 2 × ($C\underline{H}_3$)$_2$CHO); 1.5 (t, J = 7.1, 6H, ($C\underline{H}_3CH_2$)$_2N^+$); 1.9 (s, 6H, ($C\underline{H}_3$)$_2$C); 3.7 (q, J = 7.1, 4H, $N^+(C\underline{H}_2CH_3)_2$); 4.1 (d, J = 12.5, 2H, $PC\underline{H}_2N^+$); 4.3 (d, J = 7.1, 2H, $C\underline{H}_2CH$=C); 4.7-5 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 5.3 (t, J = 7.1, 1H, $CH_2C\underline{H}$=C); ^{13}C NMR : 8.4 (s, $\underline{C}H_3CH_2N^+$); 18.8 & 26.1 (2s, ($\underline{C}H_3$)$_2$C=CH); 23.5 & 23.6 (2d, J = 2.3, J = 3.4, ($\underline{C}H_3$)$_2$CHO); 52.3 (d, J = 150, $P\underline{C}H_2N^+$); 55.6 (d, J = 4.5, $N^+\underline{C}H_2CH_3$); 58.4 (d, J = 4.4, $N^+\underline{C}H_2CH$=C); 72.9 (d, J = 6.8, (CH_3)$_2\underline{C}$HO); 109.9 (s, $\underline{C}$=CH); 147.2 (s, $\underline{C}$H=C).

(N-Allyl-N,N-diethyl-N-dimenthoxyphosphonylmethyl)ammonium bromide (**13**) : 5.6 g of a paste; ^{31}P NMR : 10.2; ^{1}H NMR : 0.7-1.0 (m, 18H, 2 × $\underline{H}_3C^c$, 2 × $\underline{H}_3C$*a,b*); 1.0-2.3 (m, 18H, $\underline{H}C$*e,f,i*, $\underline{H}_2C$*d,g,h*); 1.4 (t, J = 7.1, 6H, ($C\underline{H}_3CH_2$)$_2N^+$); 3.6-3.8 (m, 6H, $N^+(C\underline{H}_2CH_3)_2$, $PC\underline{H}_2N^+$); 4.1-4.3 (m, 2H, 2 × $H\underline{C}$O); 4.4 (d, J = 6.0, 2H, $N^+C\underline{H}_2CH$=CH_2); 5.7-6.1 (m, 3H, $C\underline{H}_2$=CH, $C\underline{H}$=CH_2); ^{13}C NMR (in C_6D_6) : 7.5 (s, $\underline{C}H_3CH_2N^+$); 15.3 & 15.4 (2s, $\underline{C}$*a*); 20.6 & 20.8 (2s, $\underline{C}$*b*); 21.5 &21.6 (2s, $\underline{C}$*c*); 22.5 (s, $\underline{C}$*d*); 25.2 & 25.5 (2s, $\underline{C}$*e*); 31.4 (s, $\underline{C}$*g*); 33.4 & 33.5 (2s, $\underline{C}$*f*); 42.2 & 43.1 (2s, $\underline{C}$*h*), 48.1 & 48.25 (2d, J = 6.4, $\underline{C}$*i*), 52.5 (d, J = 148.5, $P\underline{C}H_2N^+$); 55.8 (s, $N^+\underline{C}H_2CH_3$); 61.5 (s, $N^+\underline{C}H_2CH$=CH_2); 79.3 & 79.6 (2d, J = 7.3, $\underline{C}$*j*); 124.6 (s, $\underline{C}H_2$=CH); 128.3 (s, $\underline{C}$H=CH_2).

(N,N-Diethyl-N-diisopropoxyphosphonylmethyl-N-propargyl)ammonium bromide (**15a**) : 3.7 g of a paste; ^{31}P NMR : 9.6; ^{1}H NMR : 1.3-1.5 (m, 12H, 2 × ($C\underline{H}_3$)$_2$CHO); 1.5 (t, J = 7.1, 6H, ($C\underline{H}_3CH_2$)$_2N^+$); 2.9 (t, J = 2, 1H, C≡C$\underline{H}$), 3.8-4.0 (m, 4H, $N^+(C\underline{H}_2CH_3)_2$); 4.2 (d, J = 13.7, 2H, $PC\underline{H}_2N^+$); 4.7-4.9 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 4.9 (d, J = 2, 2H, $N^+C\underline{H}_2C$≡CH); ^{13}C NMR : 8.5 (s, $\underline{C}H_3CH_2N^+$); 23.4 (d, J = 3.8, ($\underline{C}H_3$)$_2$CHO); 50.6 (d, J = 4.8, $N^+\underline{C}H_2C$≡CH); 56.6 (d, J = 4.4, $N^+\underline{C}H_2CH_3$); 58.8 (d, J = 149.2, $P\underline{C}H_2N^+$); 70.6 (s, $\underline{C}$H≡C); 73.1 (d, J = 6.7, (CH_3)$_2\underline{C}$HO); 81.8 (s, $\underline{C}$≡CH).

[N,N-diethyl-N-diisopropoxyphosphonylmethyl-N-(3-phenyl-2-propynyl)]ammonium bromide (**15b**) : 4.4g of a paste; ^{31}P NMR : 9.2; ^{1}H NMR : 1.3-1.5 (m, 12H, 2 × ($C\underline{H}_3$)$_2$CHO); 1.6 (t, J = 6.3, 6H, ($C\underline{H}_3CH_2$)$_2N^+$); 3.9 (q, J = 6.3, 4H, $N^+(C\underline{H}_2CH_3)_2$); 4.2 (d, J = 14.2, 2H, $PC\underline{H}_2N^+$); 4.7-4.9 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 5.05 (s, 2H, $N^+C\underline{H}_2C$≡CPh); 7.3-7.5 (m, 5H, $C_6\underline{H}_5$); ^{13}C NMR : 8.5 (s, $\underline{C}H_3CH_2N^+$); 23.35 (d, J = 3.8, ($\underline{C}H_3$)$_2$CHO); 51.5 (s, $N^+\underline{C}H_2C$≡CPh); 52.9 (d, J = 140.6, $P\underline{C}H_2N^+$); 56.3 (s, $N^+\underline{C}H_2CH_3$); 72.8 (d, J = 6.5, (CH_3)$_2\underline{C}$HO); 75.8 (s, $\underline{C}$Ph≡C) ; 91.1 (s, $\underline{C}$≡CPh); 119.5, 127.9, 129.3 & 131.3 (4s, $\underline{C}$arom).

(N-Benzyl-N,N-diethyl-N-diisopropoxyphosphonylmethyl)ammonium bromide (**17**) : 4.2g of a solid, Mp = 139°C; ^{31}P NMR : 9.5; ^{1}H NMR : 1.4 (d, J = 5.5, 12H, 2 × ($C\underline{H}_3$)$_2$CHO); 1.6 (t, J = 7.5, 6H, ($C\underline{H}_3CH_2$)$_2N^+$); 3.5-3.8 (m, 4H, $N^+(C\underline{H}_2CH_3)_2$); 4.1 (d, J = 15, 2H, $PC\underline{H}_2N^+$); 4.8-5 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 5.1 (s, 2H, $N^+C\underline{H}_2$Ph); 7.55-7.65 (m, 5H, $C_6\underline{H}_5$); ^{13}C NMR : 8.8 (s, $\underline{C}H_3CH_2N^+$); 23.4 (d, J= 4.6, ($\underline{C}H_3$)$_2$CHO); 52.1 (d, J = 149.2, $P\underline{C}H_2N^+$); 55.5 (d, J = 4.4, $N^+\underline{C}H_2CH_3$); 62.9 (s, $N^+\underline{C}H_2$Ph); 72.9 (d, J = 6.9, $O\underline{C}H(CH_3)_2$); 126.6, 128.7, 130.3 & 132.3 (4s, $\underline{C}$arom).

Preparation of phosphonates **11**, **14**, **16b** and **18/19** *by [2,3]-Wittig rearrangement of metallated corresponding ammonium salts* **9**, **13**, **15b** and **17**. *General procedure :* To a solution of *t*-BuOK (0.9 g, 8 mmol) in DMF (10 mL), placed in a four-necked flask, equipped with a mechanical stirrer, an addition funnel, a low temperature thermometer and a nitrogen inlet tube, was dropped, at -40°C, a solution of ammonium salt (4 mmol) in DMF (10 mL). Stirring was continued at the same temperature for 1.5 h. The mixture was allowed to warm to room temperature, then quenched with water (20 mL). Aqueous layer was extracted with CH_2Cl_2 (3x20 mL). The combined organic layers were dried ($MgSO_4$), then evaporated to give the crude product, which was purified by column chromatography over neutral Al_2O_3 (eluent : ether), leading to the pure phosphonate **11**, **14**, **16b** or the mixture of phosphonates **18** and **19** in a ratio of 8:1, respectively.

Diisopropyl 1-(N,N-diethylamino)-3-butenylphosphonate (**11a**) : 0.8 g, 71% yield; ^{31}P NMR : 24.6; ^{1}H NMR : 1.05 (t, J = 6.9, 6H, $(C\underline{H}_3CH_2)_2N$); 1.22 & 1.23 (2d, J = 6.2, 12H, 2 × $(C\underline{H}_3)_2CHO$); 2.3-2.5 (m, 2H, $C\underline{H}_2CH=CH_2$); 2.6-2.9 (m, 4H, $N(C\underline{H}_2CH_3)_2$); 2.9-3.1 (m, 1H, $PC\underline{H}N$); 4.6-4.8 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 4.95-5.1 (m, 2H, $C\underline{H}_2=CH$); 5.8-6.0 (m, 1H, $C\underline{H}=CH_2$); ^{13}C NMR : 14.2 (s, $\underline{C}H_3CH_2N$); 23.7 & 24.1 (2d, J= 12, $(\underline{C}H_3)_2CHO$); 31.4 (d, J =7.8, $\underline{C}H_2CH=CH_2$); 44.7 (d, J = 4.4, $N\underline{C}H_2CH_3$); 57.5 (d, J = 144, $P\underline{C}H$); 69.1 & 69.8 (2d, J = 7.5, $O\underline{C}H(CH_3)_2$); 115.4 (s, $\underline{C}H_2=CH$); 136.5 (d, J = 13.4, $\underline{C}H=CH_2$). Anal. Found: C, 57.8; H, 10.4; N, 4.8 ($C_{14}H_{30}O_3NP$ requires C, 57.77; H, 10.37; N, 4.80).

Diisopropyl 1-(N,N-diethylamino)-2-methyl-3-butenylphosphosphonate (**11b**) : 0.9 g, 77% yield; ^{31}P NMR : 24.4 & 24.3 (ratio 10/1); ^{1}H NMR : 1.05 (t, J = 6.9, 6H, $(C\underline{H}_3CH_2)_2N$); 1.2 (d, J = 6.4, 3H, $C\underline{H}_3CH$); 1.3 (d, J = 6.4, 12H, 2 × $(C\underline{H}_3)_2CHO$); 2.6-2.9 (m, 6H, $PC\underline{H}N$, $C\underline{H}CH_3$, $N(C\underline{H}_2CH_3)_2$); 4.6-4.8 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 4.9-5 (m, 2H, $C\underline{H}_2=CH$); 5.9-6.0 (m, 1H, $C\underline{H}=CH_2$); ^{13}C NMR : 13.9 (s, $\underline{C}H_3CH_2N$); 17.9 (d, J = 4.7, $\underline{C}H_3CH$); 23.3 & 23.5(2d, J = 4.9, J = 3.1, $(\underline{C}H_3)_2CHO$); 37.0 (d, J = 9.5, $\underline{C}HCH_3$); 44.7 (d, J = 2.9, $N\underline{C}H_2CH_3$); 63.2 (d, J = 133, $P\underline{C}H$); 68.1 & 68.7 (2d, J = 8.2 , J = 7.6, $O\underline{C}H(CH_3)_2$); 111.7 (s, $\underline{C}H_2=CH$); 142.2 (d, J = 11, $\underline{C}H=CH_2$). Anal. Found: C, 58.6; H, 10.7; N, 4.4 ($C_{15}H_{32}O_3NP$ requires C, 58.99; H, 10.56; N, 4.58).

Diisopropyl 1-(N,N-diethylamino)-2-phenyl-3-butenylphosphonate (**11c**) : 1.05 g, 72% yield; ^{31}P NMR : 23.6; ^{1}H NMR : 1.05 (t, J = 6.9, 6H, $(C\underline{H}_3CH_2)_2N$); 1.15 & 1.16 (2d, J = 5.5, 12H, 2 × $(C\underline{H}_3)_2CHO$); 2.9 (q, J = 8.1, 4H, $N(C\underline{H}_2CH_3)_2$); 3.3 (dd, J = 18.9 , J = 8.1 , 1H, $PC\underline{H}N$); 3.7-3.9 (m, 1H, $C\underline{H}C_6H_5$); 4.4-4.6 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 4.8-5.0 (m, 2H, $C\underline{H}_2=CH$); 6.1-6.3 (m, 1H, $C\underline{H}=CH_2$); 7.2-7.3(m, 5H, $C_6\underline{H}_5$); ^{13}C NMR : 14.1 (s, $\underline{C}H_3CH_2N$); 23.5 & 23.6 (2d, J = 9, $(\underline{C}H_3)_2CHO$); 45.1 (s, $N\underline{C}H_2CH_3$); 50.4 (d, J = 10, $\underline{C}HC_6H_5$); 63.5 (d, J= 132.2, $P\underline{C}H$); 68.8 & 69.1 (2d, J = 7.9, $O\underline{C}H(CH_3)_2$); 113.9 (s, $\underline{C}H_2=CH$); 125.9 , 127.7 & 128.3 (3s, *o,m,p*-$\underline{C}$arom); 140.5 (d, J = 11.5, $\underline{C}H=CH_2$); 142.4 (s, *ip*-$\underline{C}$arom). Anal. Found: C, 65.0; H, 9.6; N, 3.7 ($C_{20}H_{34}O_3NP$ requires C, 65.37; H, 9.32; N, 3.81)..

Diisopropyl 1-(N,N-diethylamino)-3-methyl-3-butenylphosphonate (**11d**) : 0.85 g, 71% yield; ^{31}P NMR : 24.7; ^{1}H NMR : 1.05 (t, J = 6.6, 6H, $(C\underline{H}_3CH_2)_2N$); 1.15 & 1.16 (2d, J = 6.5, 12H, 2 × $(C\underline{H}_3)_2CHO$); 1.8 (s, 3H, $C\underline{H}_3C$); 2.3-2.4 (m, 2H, $C\underline{H}_2C=CH_2$); 2.6-2.8(m, 4H, $N(C\underline{H}_2CH_3)_2$); 3.1-3.3 (m, 1H, $PC\underline{H}N$); 4.6-4.8 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 4.8 (s, 2H, $C\underline{H}_2=C$); ^{13}C NMR : 14.2 (s, $\underline{C}H_3CH_2N$); 21.6 (s, $\underline{C}H_3C$); 23.7 & 23.9 (2d, J= 11, $(\underline{C}H_3)_2CHO$); 35.2 (d,J = 8, $\underline{C}H_2C=CH_2$); 44.5 (d, J = 6, $N\underline{C}H_2CH_3$), 56.4 (d , J = 142, $P\underline{C}H$); 69 & 69.8 (2d, J = 8, $O\underline{C}H(CH_3)_2$); 112.6 (s, $\underline{C}H_2=C$); 142.6 (d, J = 14, $\underline{C}=CH_2$). Anal. Found: C, 59.0; H, 10.6; N, 4.7 ($C_{15}H_{32}O_3NP$ requires C, 58.99; H, 10.56; N, 4.58).

Diisopropyl 1-(N,N-diethylamino)-2,2-dimethyl-3-butenylphosphonate (**11e**) : 0.65 g, 51% yield; ^{31}P NMR : 25.3; ^{1}H NMR : 1.05 (t, J = 6.3, 6H, $(C\underline{H}_3CH_2)_2N$); 1.1 & 1.15 (2s, 6H, $(C\underline{H}_3)_2C$); 1.2 (d, J = 6.4, 12H, 2 × $(C\underline{H}_3)_2CHO$); 2.6-2.8 (m, 4H, $N(C\underline{H}_2CH_3)_2$); 2.9 (d, J = 14.8, 1H, PC<u>H</u>N), 4.6-4.8 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 4.9-5.1 (m, 2H, $C\underline{H}_2$=CH); 6.1-6.3 (m, 1H, C<u>H</u>=CH_2); ^{13}C NMR : 15 (s, $\underline{C}H_3CH_2N$); 24.1 & 24.2 (2d, J = 3, J = 2.2, $(\underline{C}H_3)_2CHO$); 24.9 (d, J = 14.5, $(\underline{C}H_3)_2C$); 26.9 (d, J = 7.1, $\underline{C}(CH_3)_2$); 49.9 (d, J = 11.8, $N\underline{C}H_2CH_3$); 68.6 (d, J = 126, P<u>C</u>H); 69.3 & 69.4 (2d, J = 3.7, J = 3, $O\underline{C}H(CH_3)_2$); 110.7 (s, $\underline{C}H_2$=CH); 145.9 (d, J = 3.7, <u>C</u>H=CH_2). Anal. Found: C, 60.0; H, 11.0; N, 4.1 ($C_{16}H_{34}O_3NP$ requires C, 60.16; H, 10.72; N, 4.38).

Dimenthyl 1-(N,N-diethylamino)-3-butenylphosphonate (**14**) : 1.1 g, 61% yield; ^{31}P NMR : 23.2 & 23.8 (ratio 54/46); ^{1}H NMR : 0.7-1.0 (m, 20H, 2 × $\underline{H}_3C$*c*, 2 × $\underline{H}_3C$*a,b*); 1.0-1.15 (t, 6H, $(C\underline{H}_3CH_2)_2N$); 1.2-2.4 (m, 18H, <u>H</u>C*e,f,i*, $\underline{H}_2C$*d,g,h*); 2.6-2.9 (m, 5H, $N(C\underline{H}_2CH_3)_2$, PC<u>H</u>N); 4.1-4.3 (m, 2H, 2 × H<u>C</u>O); 4.95-5.1 (m,2H, $C\underline{H}_2$=CH); 5.8-6.1 (m, 1H, C<u>H</u>=CH_2); ^{13}C NMR (in C_6D_6) : 11.2 (s, $\underline{C}H_3CH_2N$); 14.4-15.6 (4s, <u>C</u>*a*); 20.6 (s, <u>C</u>*b*); 20.9 (s, <u>C</u>*c*); 21.0 & 21.7 (2s, <u>C</u>*d*); 22.5-22.7 (4s, <u>C</u>*e*); 31.2-31.48 (m, <u>C</u>*f*); 32.5-33.7 (m, $\underline{C}H_2CH$=CH_2); (33.9 (s, <u>C</u>*g*), 43.2-43.9 (m, <u>C</u>*h*); 44.9-45.2 (m, <u>C</u>*i*); 48.78 (d, J = 5.8, $N\underline{C}H_2CH_3$); 58.95 & 59.9 (2d, J = 134.7,J = 139.3, P<u>C</u>HN); 76.08-76.9 (m, <u>C</u>*j*); 115.2 (s, $\underline{C}H_2$=CH); 137.2 & 137.5 (2d, J = 13.2, J = 13.4, C<u>H</u>=CH_2). Anal. Found: C, 68.9; H, 10.9; N, 2.9 ($C_{28}H_{54}O_3NP$ requires C,69.52; H, 11.25; N, 2.89).

Diisopropyl 1-(N,N-diethylamino)-2-phenyl-2,3-butadienylphosphonate (**16b**) : 1.0 g, 70% yield; ^{31}P NMR : 19.2; ^{1}H NMR : 0.9 & 0.92 (2t, J = 6, 6H, $(C\underline{H}_3CH_2)_2N$); 1.2-1.4 (m, 12H, 2 × $(C\underline{H}_3)_2CHO$); 2.4-2.6 & 2.9-3.1 (2m, 4H, $N(C\underline{H}_2CH_3)_2$); 4.1 (dd, J = 26.3 , J = 2.9, 1H, PC<u>H</u>N); 4.6-4.8 (m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 5.1 & 5.2 (2d, J = 2.9 , J = 4.3, 2H, $C\underline{H}_2$=C=C); 7.2-7.3 (m, 5H, $C_6\underline{H}_5$); ^{13}C NMR : 13.5 (s, $\underline{C}H_3CH_2N$); 23.8 & 24.1 (2d, J = 6.2 , J = 10.9, $(\underline{C}H_3)_2CHO$); 45.4 (d, J = 7.7, $N\underline{C}H_2CH_3$); 58.5 (d, J = 168, P<u>C</u>HN); 69.6 & 70.4 (2d, J = 7.6, $O\underline{C}H(CH_3)_2$); 78.6 (s, $\underline{C}H_2$=C); 99.4 (s, <u>C</u>Ph=C); 126.4, 128.1, 128.5 & 138 (4s, <u>C</u>arom); 211 (d, J = 5, C=<u>C</u>=CH_2). Anal. Found: C, 65.8; H, 9.0; N, 3.7 ($C_{20}H_{32}O_3NP$ requires C,65.73; H, 8.82; N, 3.83).

Diisopropyl 1-(N,N-diethylamino)-1-o-tolyl-methylphosphonate (**18**), as the major product of the **18/19** mixture : ^{31}P NMR : 21.3; ^{1}H NMR : 1.1 (t, J = 7.8, 6H, $(C\underline{H}_3CH_2)_2N$); 1.2-1.5 (m, 12H, 2 × $(C\underline{H}_3)_2CHO$); 2.4 (s, 3H, $C\underline{H}_3C_6H_4$); 2.4-2.8 (m, 4H, $N(C\underline{H}_2CH_3)_2$); 4.3 (d, J = 21.2, 1H, PC<u>H</u>N), 4.2-4.4 & 4.6-4.9 (2m, 2H, 2 × $OC\underline{H}(CH_3)_2$); 7.0-7.2 (m, 4H, $C_6\underline{H}_4$).

Diisopropyl 1-(N,N-diethylamino)-2-phenyl-ethylphosphonate (**19**), as the minor product of the **18/19** mixture : ^{31}P NMR : 23.9; ^{1}H NMR : 0.7 & 1.1 (2d, J = 5.8, 12H, 2x$(C\underline{H}_3)_2CHO$); 0.9 (t, J = 7.1, 6H, $(C\underline{H}_3CH_2)_2N$); 2.5-3.0 (m, 6H, $N(C\underline{H}_2CH_3)_2$ & $C\underline{H}_2C_6H_5$); 3.0-3.3 (m, 1H, PC<u>H</u>N); 4.6-4.9 (m, 2H, 2x$(CH_3)_2C\underline{H}O$); 7.0-7.2 (m, 5H, $C_6\underline{H}_5$).

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