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### THERMAL REARRANGEMENT OF A PHOSPHORUS YLIDE: METHANOLYSIS AND HYDROLYSIS OF THE OBTAINED PHOSPHORANES

L. Labaudinière<sup>a</sup>; R. Burgada<sup>a</sup>

<sup>a</sup> Laboratoire de Chimie des Organo-éléments, UA473, Université P. et M. Curie, Paris Cédex, France

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# THERMAL REARRANGEMENT OF A PHOSPHORUS YLIDE: METHANOLYSIS AND HYDROLYSIS OF THE OBTAINED PHOSPHORANES

L. LABAUDINIÈRE and R. BURGADA

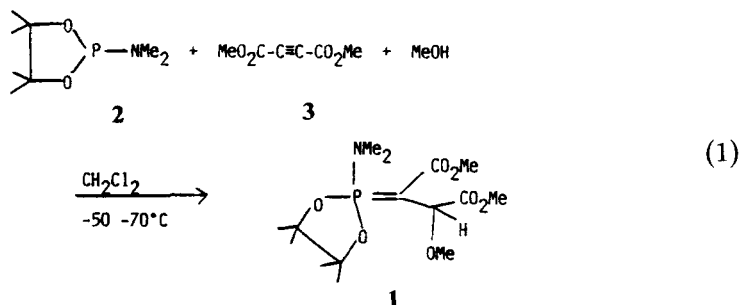
*Laboratoire de Chimie des Organo-éléments, UA473, Université P. et M.  
Curie, tour 44-45, 4 place Jussieu 75230 Paris Cédex 05, France*

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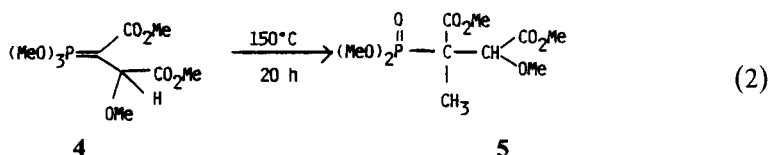
The thermal reactivity of ylide **1** at 140–150°C is reported. It affords a  $\beta, \gamma$  unsaturated phosphorane **6** which gives rise to an  $\alpha, \beta$  unsaturated phosphorane **7**. At room temperature, **6** reacts readily with methanol or water while **7** undergoes only hydrolysis. A mechanism is proposed to explain the formation of both phosphoranes.

## INTRODUCTION

In a previous work,<sup>1</sup> we described the synthesis of ylide **1**, from the aminophosphine **2** and acetylene dimethylcarboxylate **3** (1).



Trimethylphosphite leads to ylide **4** by an analogous reaction; **4** rearranges at 150°C to afford phosphonate **5** as a mixture of two diastereoisomers<sup>2</sup> (2).

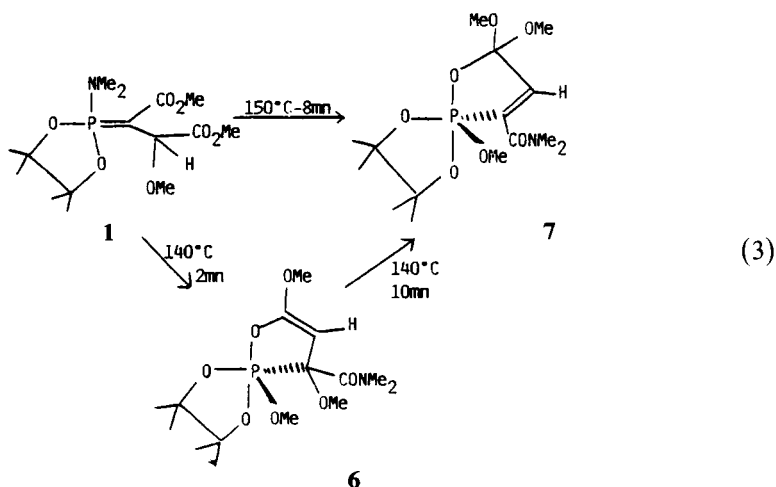


We report herein the results concerning the thermal reactivity of ylide **1**, which cannot undergo an internal Arbuzov reaction such as **4**.

## RESULTS

When ylide **1** is heated 2 mn at 140°C,\* without solvent, it gives rise mainly to a spirannic five-coordinate phosphorous compound **6** (3). Structural assignment for **6** is based on NMR and IR analysis. Its chemical shift in  $^{31}\text{P}$  NMR is  $-12.4$  ppm. This value is in agreement with a five-coordinate and spirannic phosphorous species.<sup>3</sup> The uncoupled spectrum shows a doublet ( $J = 29.3$  Hz) of quadruplets ( $J = 14.7$  Hz) arising from the coupling with proton  $\beta$  to the phosphorus atom, and with a methoxy group linked to the phosphorus respectively. The IR spectrum shows a large and strong absorption at  $1640\text{ cm}^{-1}$ , characteristic of an amide group. The vinylic proton of **6** appears in  $^1\text{H}$  NMR as a doublet ( $J = 29$  Hz) at 4.47 ppm. In  $^{13}\text{C}$  NMR, the carbon  $\alpha$  to the phosphorus is a doublet at 63.5 ppm with a high coupling constant  $J_{\text{PC}} = 214.8$  Hz. The  $^{13}\text{C}$  NMR spectra obtained by SFORD<sup>4</sup> and  $J$  modulated spin echo Fourier transform<sup>5</sup> methods are typical for a quaternary carbon atom. Under these conditions, other products are observed beside **6**: spirophosphorane **7** (15%;  $\delta^{31}\text{P} = 30.4$  ppm) and several other phosphonates (10%; signals appearing between  $+31$  and  $+13$  ppm in  $^{31}\text{P}$  NMR).

Spirophosphorane **7** is obtained almost quantitatively (90%) when **1** is heated for longer time, or when **6** is heated again. That means, that the rearrangement  $1 \rightarrow 7$  proceeds via **6**.



In this case too, the proposed structure for **7** has been assigned on NMR and IR data. In  $^{31}\text{P}$  NMR, the chemical shift, negative and lower than that of **6**, agrees with a bicyclic  $\alpha$ - $\beta$  unsaturated phosphorane.<sup>4</sup> The uncoupled spectrum shows a doublet ( $J = 57.4$  Hz) of quadruplet ( $J = 13.4$  Hz P—OMe). The wide coupling constant for the doublet means that the proton must belong to a cyclic  $\alpha$ , $\beta$  unsaturated system, P and H being *trans* to each other.<sup>6</sup> The vinylic proton appears as a doublet ( $J = 58$  Hz) at 6.60 ppm in  $^1\text{H}$  NMR. The carbonyl absorption for amide still appears on the IR spectrum ( $1638\text{ cm}^{-1}$ ). The  $\alpha$ , $\beta$  unsaturated bond is

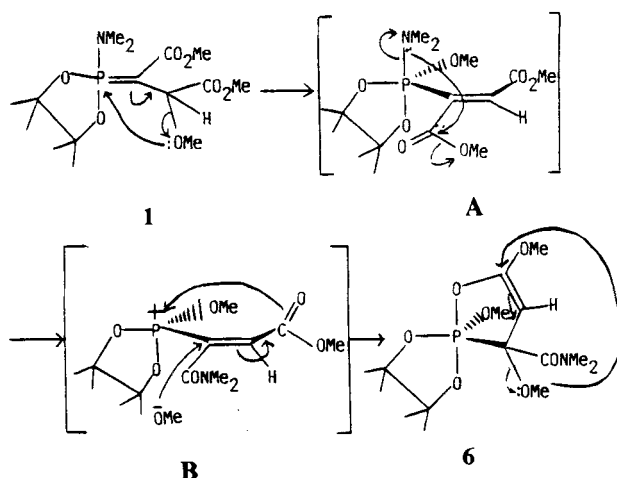
\*Condition for about 1.0 g of ylide **1**.

obvious in  $^{13}\text{C}$  NMR: each carbon atom gives a doublet in the  $\text{sp}^2$  region.  $\delta = 143.2$  ppm ( $J = 186.0$  Hz) and  $\delta = 139.7$  ppm ( $J = 16.8$  Hz). The first signal is attributed to the carbon  $\alpha$  to the phosphorus, because of the great value of the coupling constant. The quaternary carbon atom, which bears three oxygen atoms and one carbon atom, gives a doublet ( $J = 24.9$  Hz) at 111.4 ppm. The two methoxy groups on this quaternary carbon atom have a different chemical shift: in  $^1\text{H}$  NMR, 2 singlets at 3.40 and 3.37 ppm; in  $^{13}\text{C}$  NMR, 2 singlets at 50.7 and 49.9 ppm. These two methoxy groups are not equivalent due to their different environment.

Phosphorane **6** may be isolated by addition of any anhydrous solvent (except alcohol) and diethyl ether to the reaction mixture. It yields white and very hygroscopic crystals. Attempts to dissolve them in usual solvents (except alcohols) failed and lead only to the degradation of **6** into phosphonates.

## DISCUSSION

In order to explain the formation of phosphoranes **6** and **7** from ylide **1**, the following mechanism may be suggested (Scheme 1). No intermediate was seen between **1** and **6**.



SCHEME 1

We propose, first the formation of phosphorane **A** from ylide **1** since the thermal evolution: ylide  $\rightarrow$  phosphorane has often been observed in this kind of compound.<sup>1,7</sup> The resulting methoxy phosphoranes are thermally stable, contrary to **A**, which possesses a  $\text{P}-\text{N}$  bond,\* more labile than a  $\text{P}-\text{O}$  bond. Consequently **A** should

\*At this temperature,  $\text{NMe}_2$  is probably in the apical position. It is the less energetic bond, therefore the easiest to break.

evolve to a phosphorane, in which the phosphorus atom is surrounded by a maximum of oxygen atoms (symbiotic effect).

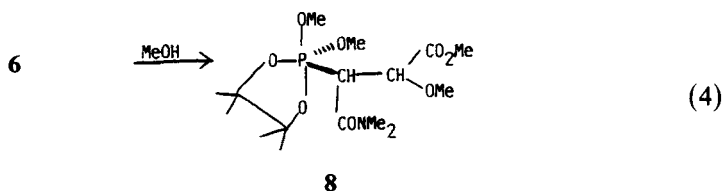
Considering compound **A** after P—N bond break, the free  $\text{Me}_2\text{N}^-$  attacks the hardest electrophilic centre: the carbonyl the nearest to  $\text{P}^+$  to afford **B**.

Attack on the ethylenic carbon  $\alpha$  to the  $\text{P}^+$  by  $\text{MeO}^-$ , has already been observed<sup>8</sup> with a phosphonium salt and can be explained by the activation of this carbon atom substituted by two attractive groups:  $\text{P}^+$  and  $\text{C}=\text{O}$ . In the case of **B**, since P is surrounded by oxygen atoms (phosphite structure), attack by  $\text{MeO}^-$  allows the formation of a five-membered ring, which increases the stability of the phosphorane.

The rearrangement **6**  $\rightarrow$  **7** may probably be explained by the increase of stability due to the conjugation between the amide, the double bond and the *d* orbitals of the phosphorus atom. We have already synthesized several monocyclic  $\alpha,\beta$  unsaturated phosphoranes which are quite stable compounds.<sup>1</sup>

#### Methanolysis of phosphoranes **6** and **7**.

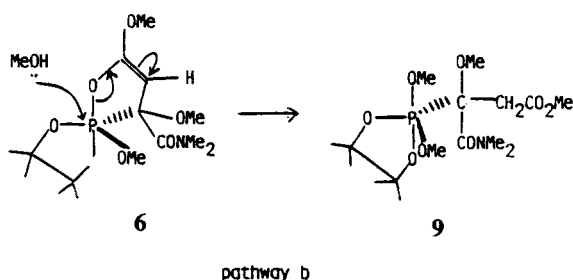
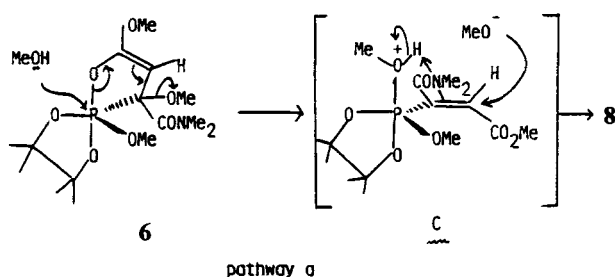
While phosphorane **7** does not immediately react with methanol at room temperature, phosphorane **6** affords quickly the saturated monocyclic phosphorane **8** (4).



This new compound is probably a mixture of two diastereoisomers  $\delta_a = -38.8$  ppm (83%) and  $\delta_b = -41.1$  ppm (17%). The  $^{31}\text{P}$  NMR shifts agree with saturated monocyclic five coordinate structures. IR spectrum of the reaction mixture (after removal of excess methanol) shows two strong absorption bands at  $1735\text{ cm}^{-1}$  ( $\text{CO}_2\text{Me}$ ) and  $1630\text{ cm}^{-1}$  ( $\text{CONMe}_2$ ). The product has the structure **8** not **9** which was also possible for the methanolysis of **6** (Scheme 2). H, IR and undecoupled  $^{31}\text{P}$  spectra are too complex to choose between structure **8** and **9**.

Whatever the case,  $^{13}\text{C}$  NMR spectrum shows a doublet at 82.5 ppm ( $J = 6.7$  Hz) and another one at 54.6 ppm ( $J = 182.6$  Hz). The second one may be attributed to the carbon  $\alpha$  to the phosphorus atom. The chemical shift is too weak for a quaternary atom, substituted by one oxygen atom and one phosphorus atom. Furthermore, in the off resonance spectrum, each doublet at 82.5 and 54.6 ppm is dedoubled, which is typical for tertiary carbon atoms. Consequently, the methanolysis should follow pathway a\* and not pathway b (Scheme 2).

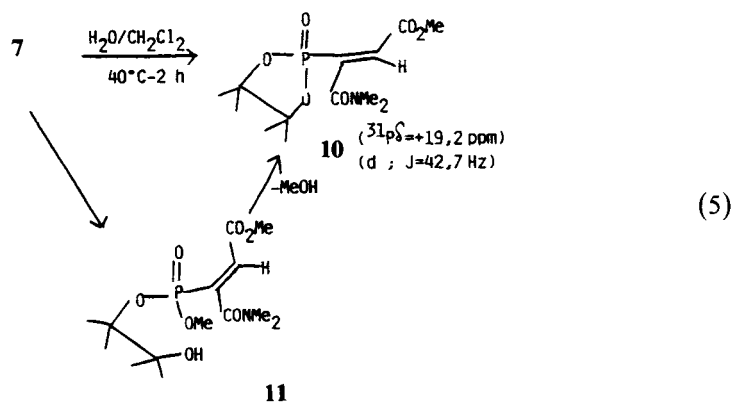
\* $\text{MeO}^-$  and not  $\text{MeOH}$  attacks the carbon atom  $\beta$  to the phosphorus in **C**, while  $\alpha,\beta$  unsaturated  $\text{PV}$  do not add methanol even in excess, at room temperature.



SCHEME 2

### Hydrolysis of phosphoranes **6**, **7** and **8**

Hydrolysis of **7** with excess water at 40°C in dichloromethane yields phosphonate **10** **Z** (**5**) (overall yield 70%, after recrystallization in Et<sub>2</sub>O).

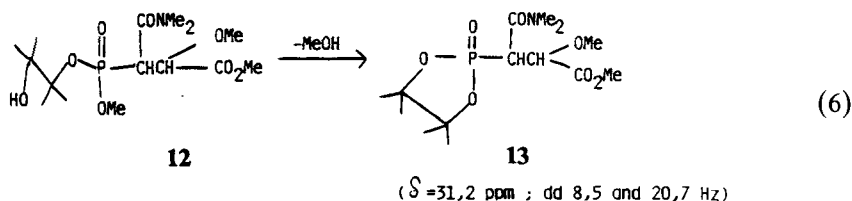


The isomerisation **10** **Z** → **10** **E** does not occur with benzoic acid.

Compound **11** (δ = +4.9 ppm dq 43.9 and 11.6 Hz) is an intermediate during the hydrolysis of **7**. The pinacol ring closes in about 14 hours at room temperature to afford **10** (one may observe this phenomenon, when the hydrolysis is done at room temperature).

When hydrolyzed at room temperature, phosphoranes **6** and **8** give rise in 10 min to a mixture of phosphonates and phosphate. The main product is a linear phosphonate **12** obtained, after column chromatography, in 48% overall yield (from **1**). The mechanism for hydrolysis and methanolysis is probably the same.

After four days at room temperature or 2 h 30 at 55°C, **12** affords mainly cyclic phosphonate **13** (70%) (**6**)



## CONCLUSION

The results described herein show the quite particular thermal reactivity of ylide **1**. While ylide **4** yields in 20 h at 150°C phosphonate **5**, ylide **1** is more reactive: in less than 15 min at the same temperature, it affords the  $\beta,\gamma$  unsaturated phosphorane **6**, then the  $\alpha,\beta$  unsaturated **7**. This evolution agrees with observations made in previous works:

- (1) The vinylic phosphoranes with a P—NMe<sub>2</sub> bond are unstable.
- (2) Spirannic phosphoranes are more stable than the monocyclic ones.
- (3)  $\alpha,\beta$  unsaturated spirannic phosphoranes are stable, isolable compounds and do not add methanol, even in excess, at room temperature, such as the analogous monocyclic structures.

## EXPERIMENTAL

<sup>1</sup>H NMR spectra were recorded on a Jeol MH100 instrument at 100 MHz with TMS as an internal reference; IR spectra were recorded on Perkin Elmer 157G. <sup>31</sup>P and <sup>13</sup>C NMR spectra were taken on a Jeol FX90Q instrument, using H<sub>3</sub>PO<sub>4</sub> and TMS as internal standards. (CDCl<sub>3</sub>). Melting points were obtained on a büchi SMP-20 instrument.

The synthesis of ylide **1** has been already described.<sup>1</sup> <sup>13</sup>C NMR spectra of **1**, **7**, **8**, **10** and **12** are in Table I.

**Synthesis of the phosphorane 6.** 1.1 g (3.0 mmoles) of ylide **1** is placed 2 min in a heating bath at 140°C. The cold reaction mixture is then analyzed in <sup>31</sup>P NMR:  $\delta = -12.4$  ppm (75%) **6**;  $\delta = -30.4$  ppm (15%) **7**;  $\delta = +31.4$  ppm (10%); undecoupled spectrum of **6**: dq: 29.3 and 14.7 Hz; <sup>1</sup>H NMR: 4.47 (d,  $J = 29$  Hz, 1 H, C=CH), 3.78 (s, 3 H, OMe), 3.75 (d,  $J = 15$  Hz, 3 H, P—OMe), 3.42 (s, 3 H, OMe), 3.03 (s, 6 H, NMe<sub>2</sub>), 1.68–1.05 (ma, 12 H, pinacolic H); IR  $\nu_{\text{C=O}}$  1640 cm<sup>-1</sup> (amide).

**Synthesis of phosphorane 7.** As for **6**, 1.1 g (3.0 mmoles) of **1** is placed 8 min in a bath at 150°C (or **6**, obtained from **1**, is placed again 10 min at 140°C). The cold mixture is analyzed in <sup>31</sup>P NMR:  $\delta = -30.4$  ppm (90%) **7**;  $\delta = +13.6$  ppm (5%), other P=O compounds (5%). Undecoupled spectrum of **7**: dq 57.4 and 13.4 Hz. <sup>1</sup>H NMR 6.60 (d,  $J = 58$  Hz, 1 H, =CH—), 3.75 (d,  $J = 13.5$  Hz, 3 H, P—OMe), 3.40 and 3.37 (2s, 2 × 3 H, C(OMe)<sub>2</sub>), 3.01 (s, 6 H, NMe<sub>2</sub>), 1.47–1.03 (mu, 12 H, pinacolic H). IR:  $\nu_{\text{C=O}}$  = 1638 cm<sup>-1</sup> (amide).

TABLE I  
<sup>13</sup>C spectra of **1**, **6**, **7**, **8**, **10**, **12** δ (ppm) *J* (Hz)

Ci	COMPOUNDS					
	1	6	7	8	10	12
1	173.4 (d <i>J</i> = 8.7)	172.8 (d <i>J</i> = 13.4)	167.6 (d <i>J</i> = 13.4)	172.4 (d <i>J</i> = 20.8)	165.3 (d <i>J</i> = 11.4)	170.8 (d <i>J</i> = 18.1)
2	170.7 (d <i>J</i> = 21.5)	168.5 (s)	143.2 (d <i>J</i> = 186.0)	169.7 (d <i>J</i> = 6.1)	164.0 (d <i>J</i> = 10.1)	166.8 (d <i>J</i> = 5.4)
3	88.4 (s) 87.4 (s)	82.2 (s) 81.6 (s)	139.7 (d <i>J</i> = 16.8)	82.5 (d <i>J</i> = 6.7)	145.8 (s <i>J</i> = 165.2)	92.6 (d <i>J</i> = 11.4)
4	78.7 (d <i>J</i> = 12.1)	75.3 (d <i>J</i> = 11.8)	111.4 (d <i>J</i> = 24.9)	77.7 (s)	130.7 (s)	79.9 (d <i>J</i> = 5.4)
5	55.5 (s)	63.5 (d <i>J</i> = 214.8)	81.1 (s) 77.9 (s)	58.9 (s)	89.2 (s)	74.6 (d <i>J</i> = 5.4)
6	51.5 (s)	55.6 (s)	54.6 (d <i>J</i> = 10.7)	54.7 (d <i>J</i> = 10.8)	52.4 (s)	59.2 (s)
7	50.2 (s)	54.5 (d <i>J</i> = 7.4)	50.7 (s)	52.5 (d <i>J</i> = 8.7)	38.4 (s)	53.7 (d <i>J</i> = 6.0)
8	49.5 (d <i>J</i> = 221.6)	51.6 (s)	49.9 (s)	54.6 (d <i>J</i> = 182.6)	34.8 (s)	52.3 (s)
9	37.5 (d <i>J</i> = 5.4)	37.5 (s)	38.4 (s)	51.7 (s)	24.9; 24.7 23.8; 23.6 (4s)	46.1 (d <i>J</i> = 139.0)
10	25.5–25.4 (m)	24.2 (m)	34.5 (s)	38.1 (s)		38.1 (s)
11			25.2–22.0 (m)	35.9 (s)		35.9 (s)
12				24–22 (m)		24.5–23.3 (m)

**Methanolysis of 6 to 8.** To the freshly obtained cold reaction mixture (from 3 mmoles of ylide **1**), 2 ml of anhydrous methanol are added and the excess of methanol is removed under reduced pressure at room temperature. The residue is analyzed in <sup>31</sup>P NMR: δ = −38.8 ppm and −41.4 ppm (75%) **8**. Ratio of diastereoisomers: 83/17; δ = −30.4 ppm (15%) **7**; other products P=O (10%); <sup>1</sup>H NMR: 4.80–4.24 (m, CH—CH), 4.20–3.40 (m, OMe), 3.3 and 3.0 (2s, NMe<sub>2</sub>), 1.67–1.00 (m, pinacolic H). IR: 1735 cm<sup>−1</sup>  $\nu_{C=O}$  (ester); 1630 cm<sup>−1</sup>  $\nu_{C=O}$  (amide).

**Hydrolysis of 7 to 10.** Crude **7** (obtained from 3 mmoles of **1**) is dissolved in 3 ml CH<sub>2</sub>Cl<sub>2</sub> and 1 ml water. After refluxing for 2 h, the organic phase is separated and the aqueous phase extracted twice with 5 ml CH<sub>2</sub>Cl<sub>2</sub>. The organic phases are combined, dried (MgSO<sub>4</sub>) and the solvent is removed under reduced pressure. The residue crystallizes at room temperature. The crystals are filtered and washed with Et<sub>2</sub>O. 0.55 g of **10** (overall yield 70%); (The mother liquor contains mainly phosphate (Me<sub>2</sub>C—O)<sub>2</sub>P(O)OMe (δ = 13.6; 9.11 Hz) F = 163 − 4°C. <sup>31</sup>P: δ = +19.2; uncoupled spectrum d *J* = 42.7 Hz. <sup>1</sup>H: 6.51 (d, *J* = 44 Hz, 1 H, C=CH), 3.91 (s, 3 H, CO<sub>2</sub>Me), 3.18 and 3.06 (2s, 2 × 3 H, NMe<sub>2</sub>), 1.53 and 1.20 (2s, 2 × 6 H, pinacolic H). IR (KBr)  $\nu_{C=O}$  1735 cm<sup>−1</sup> (ester);  $\nu_{C=O}$  1640 cm<sup>−1</sup> (wide) (conjugated amide).

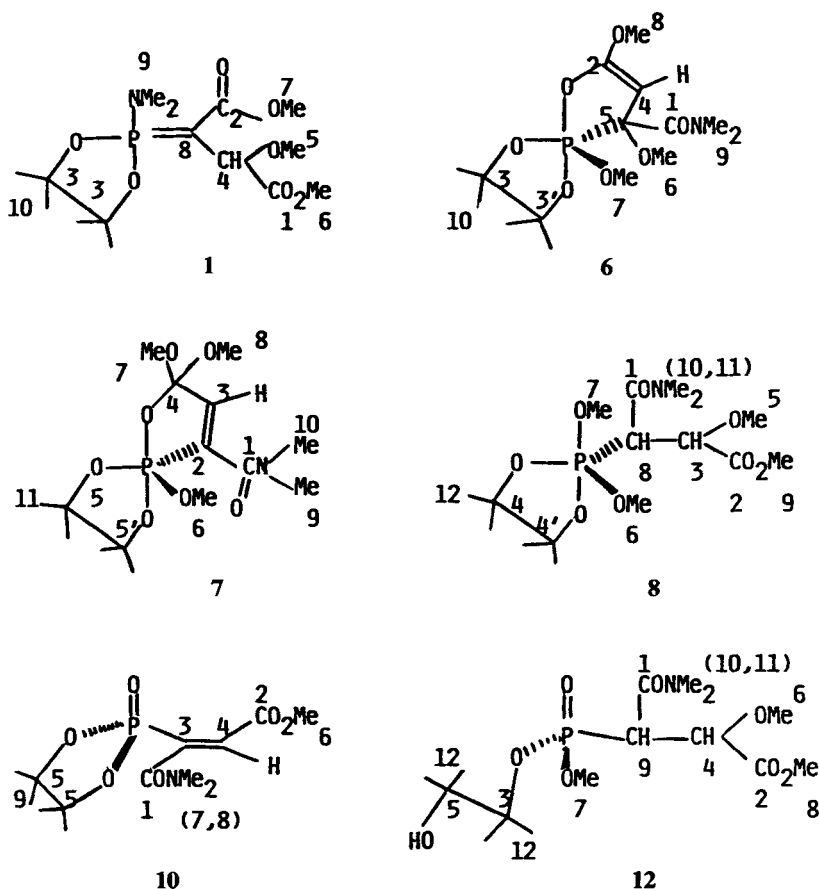
**Hydrolysis of 6 and 8 to 12.** To freshly prepared **6** or **8** from **1** (3 mmoles) are added 3 ml CH<sub>2</sub>Cl<sub>2</sub> and 1 ml H<sub>2</sub>O. The solution is stirred 10 min at room temperature then worked up as above. The residue (~ 1.0 g) is purified by column chromatography (30 g—SiO<sub>2</sub>). Eluent: CH<sub>2</sub>Cl<sub>2</sub>/MeOH (95/5). Phosphonate **8** migrates just after the coloured fraction 0.55 g (overall yield 48%) of **8** is obtained.

<sup>31</sup>P: +17.1 ppm. Uncoupled spectrum: ddq *J* = 7.9; 9.8 and 20.1 Hz. <sup>1</sup>H: 4.41 (dd, <sup>2</sup>*J*<sub>PH</sub> = 8 Hz, <sup>3</sup>*J*<sub>RH</sub> = 8 Hz, P—CH), 3.81 (d, *J* = 10 Hz, P—OMe), 3.79 (s, CO<sub>2</sub>Me), 3.56 (s, COMe), 3.22 and 2.99 (2s, NMe<sub>2</sub>); 1.58, 1.51, 1.24 and 1.17 (4s, pinacolic H).

The proton β to the phosphorus is partially masked by the methoxy signals. The extreme parts of the signal are separated by 28 Hz and appear at 4.09 and 3.64 ppm.

**Cyclization of 12 in 13.** A sample of **12** in CDCl<sub>3</sub> is left 4 days at room temperature, then analyzed by <sup>31</sup>P NMR: δ = +31.2 ppm (70%) **13**; δ = +11.8 (15%) (Me<sub>2</sub>C—O)<sub>2</sub>P(O)H. Others P=O (15%);





STRUCTURES off-resonance spectra of 6 and 12: signals of C<sub>3</sub> and C<sub>5</sub> are unchanged.

undecoupled spectrum of 13 dd  $J = 8.5$  Hz and 20.8 Hz.  $^1\text{H}$ : 4.68–4.00 (m, P—CH—CH), 3.83 (s, CO<sub>2</sub>Me), 3.63 (s, C—OMe), 3.22 and 3.00 (2s, NMe<sub>2</sub>), 1.56 and 1.44 (m, pinacolic H). Small impurities at 3.85; 3.52; 3.50; 3.08 and 1.35 ppm.

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