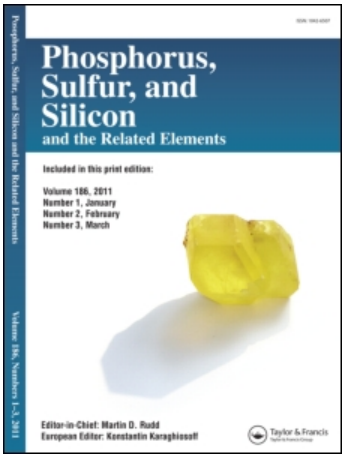

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PHTHALIMIDE DERIVATIVES TOWARDS PHOSPHORYLATED REACTANTS: UNEXPECTED, BUT INTERESTING, REACTIONS

J. Guervenou[a]; J. -P. Gourvès[a]; H. Couthon[a]; B. Corbel[a]; G. Sturtz[a]; N. Kervarecy[ab]
[a] Laboratoire de Chimie Hétéro Organique, Université de Bretagne Occidentale U.F.R. Sciences et Techniques, Brest Cedex [b] NMR department, UBO, Brest Cedex

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PHTHALIMIDE DERIVATIVES TOWARDS PHOSPHORYLATED REACTANTS: UNEXPECTED, BUT INTERESTING, REACTIONS

J. GUERVENOU*, J.-P. GOURVÈS, H. COUTHON, B. CORBEL, G. STURTZ and N. KERVAREC†

Laboratoire de Chimie Hétéro Organique, Université de Bretagne Occidentale U.F.R. Sciences et Techniques, BP 809, 6 Avenue Le Gorgeu, F-29285 Brest Cedex

(Received April 06, 1999)

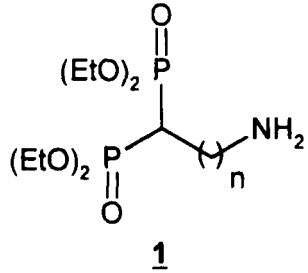
This paper describes several reactions involving either phthalimide or some of its N-(bromoalkyl) or N-(hydroxyalkyl) derivatives towards phosphorylated compounds. Though sometimes unexpected, these reactions can lead especially to diethylphosphono-substituted polyheterocycles or vinyles.

Keywords: Phthalimide; N-methylphthalimide; N-(bromoalkyl)phthalimide; N-(hydroxalky) phthalimide; tetraethyl ethenylidene-1,1-bisphosphonate; tetraethyl methylidene-1,1-bisphosphonate; diethylphosphite; MICHAEL addition; HORNER-WADSWORTH-EMMONS

INTRODUCTION

Over the last years the synthesis of tetraethyl ω-aminoalkylidene-1,1-bisphosphonates, **1**, has been one of the aims of our laboratory[1] Indeed, these structures display two important capabilities; first, they can be used as entity in the treatment of some bone-, teeth- or calcium metabolism-diseases[2,3]; secondly, thanks to the amine function they carry, they can be involved in an original concept of pharmacological targeting-delivery[4].

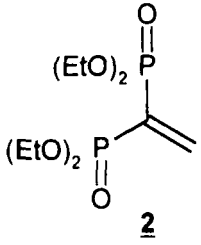
* To whom correspondence should be addressed. e-mail: Joel.Guervenou@univ-brest.fr
† NMR department: UBO, BP 809, 6 av. Le Gorgeu, F-29285 Brest Cedex



1

FIGURE 1

While keeping this goal in mind, we attempted to make some phthalimide derivatives react towards classical reactants used in our laboratory like tetraethyl ethenylidene-1,1-bisphosphonate, **2**, tetraethyl methylidene-1,1-bisphosphonate, **3**, and diethylphosphite, **4**.



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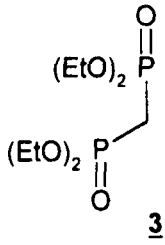

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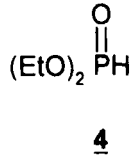


4

FIGURE 2

The various experiments carried out led to interesting, though unexpected, results. This paper describes the most typical of them.

RESULTS AND DISCUSSION

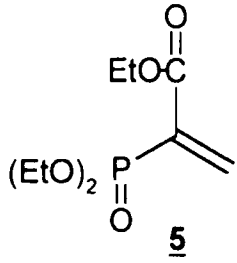
Our experimental knowledge of bisphosphonates chemistry has led us to think that tetraethyl ω-aminoalkylidene-1,1-bisphosphonates, **1**, could be classically synthesized through either a MICHAEL addition on tetraethyl ethenylidene-1,1-bisphosphonate, **2**, or a nucleophilic substitution of halogenated derivatives by the carbanion of tetraethyl methyli-

dene-1,1-bisphosphonate, **3**, or a MICHAELIS-BECKER reaction of diethylphosphite, **4**, on bromated derivatives. We will also follow this order to describe our experimental results. One should note that ^{31}P NMR allows one to easily follow how reactions are developing, which enabled us to quickly elucidate the proposed mechanisms.

Towards tetraethyl ethenylidene-1, 1-bisphosphonate 2

It is well-known that tetraethyl ethenylidene-1,1 -bisphosphonate **2** is a good MICHAEL acceptor[5,6]. In previous papers[7] we showed that tetraethyl ethenylidene-1,1-bisphosphonate **2** could be used in a tandem MICHAEL/HORNER-WADWORTH-EMMONS reaction involving ketonic alcohols or amines and leading to diethylphosphono-substituted heterocycles.

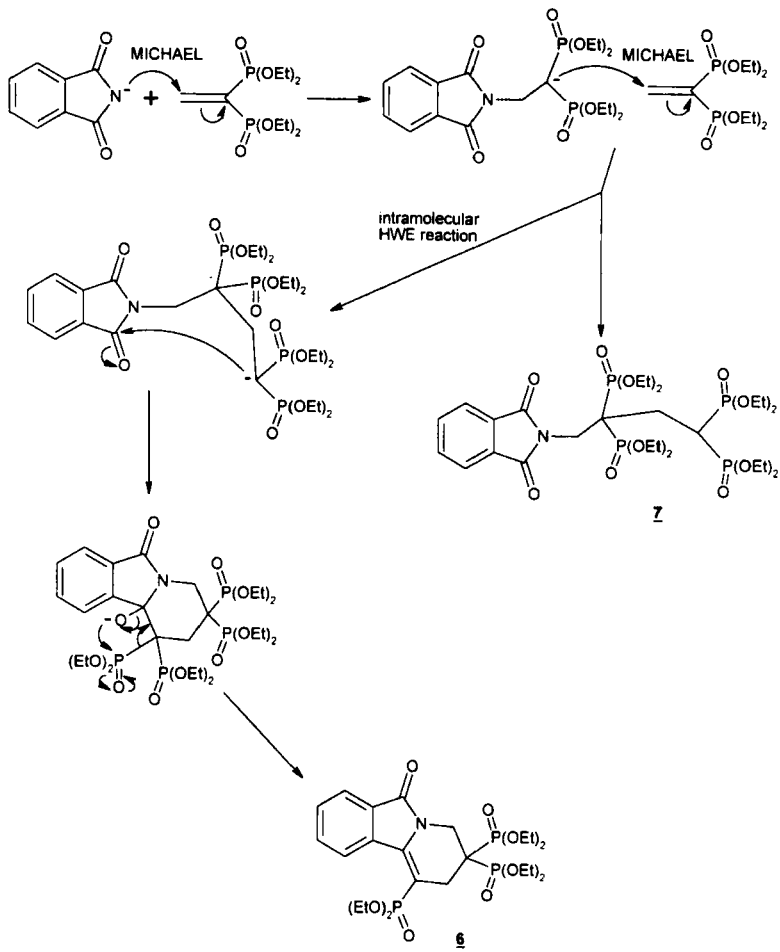
Later, from both the works on diethyl(α-ethoxycarbonylvinyl)phosphonate **5** reported by MINAMI[8] and our own ones on acylpyroles[7(b)], we logically tried to add the phthalimide anion onto tetraethyl ethenylidene-1, 1-bisphosphonate **2**.



5

FIGURE 3

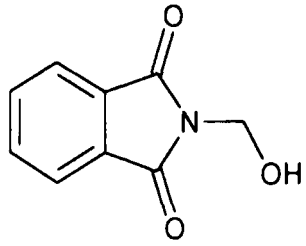
MINAMI has described the obtention of a 'three-component annulation compound' via a sequential MICHAEL-MICHAEL ring closure (MIMIRC) reaction. Under similar conditions, we caused two molecules of tetraethyl ethenylidene-1,1-bisphosphonate **2** to react with phthalimide. Like MINAMI and according to scheme I, we got a three-component annulation compound, 4,4,6-tris(diethylphosphono)-2,3,4,5-tetrahydro[2,3a]-isoindolin-1-one, **6**.



SCHEME I

However, our reaction yield (27%) from tetraethyl ethenylidene-1,1-bisphosphonate **2** was far much lower than the one (92%) reported by MINAMI from diethyl (α-ethoxycarbonylvinyl)phosphonate **5**. Our low yield can be explained by a HORNER-WADWORTH-EMMONS (HWE)-induced cyclization, more difficult to achieve since, at the end of this reaction, we also isolated the uncyclized addition compound (MIMI) **7** in high amount (30%).

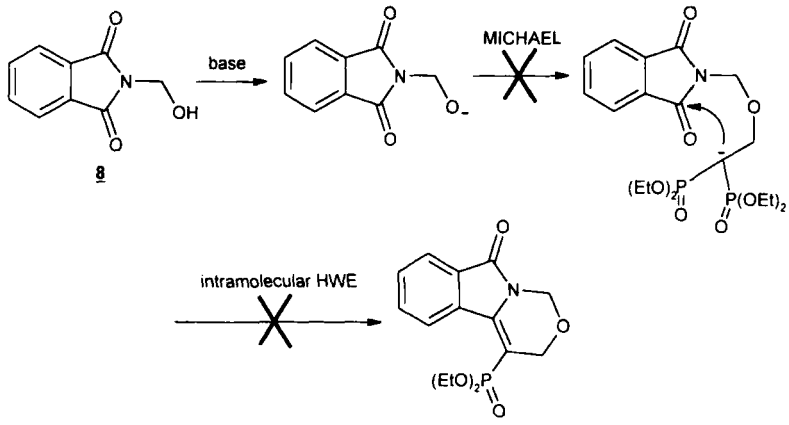
Pursuing the same logics we wished to apply the know-how acquired from our previous work[7(a)] using N-(hydroxymethyl)phthalimide, **8**.



8

FIGURE 4

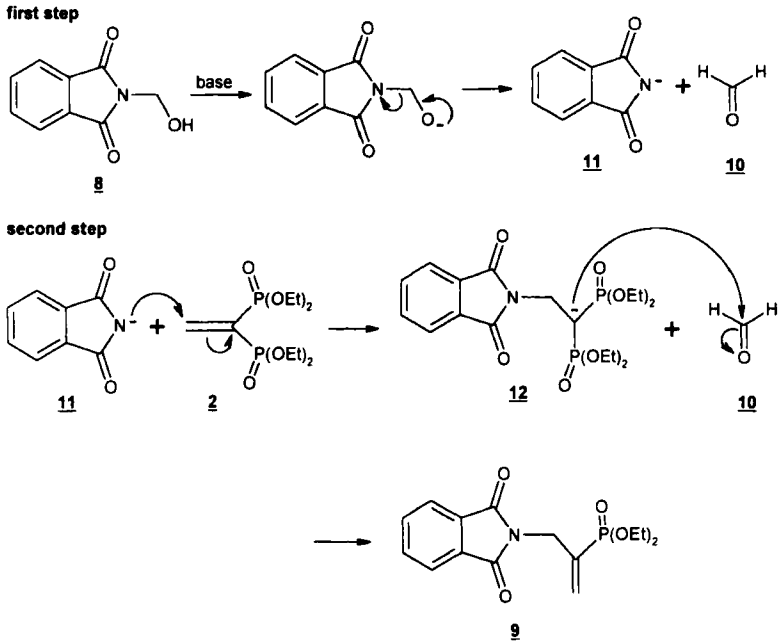
Once the oxanion had been formed we were entitled to expect a MICHAEL addition onto tetraethyl ethenylidene-1,1-bisphosphonate **2** followed by a HORNER-WADWORTH-EMMONS intramolecular cyclization on one of the carbonyl functions of imide **8** according to scheme II.



SCHEME II

In fact, the pathway followed differed since, at the end of the reaction, we obtained 2-diethylphosphono-3-phthalimidoprop-1-enylidene **9** in quantitative amount. According to scheme III, alcohol **8** reacts with a base

to generate *in situ* formaldehyde **10** along with phthalimide anion **11**. The latter, **11**, can react with tetraethyl ethenylidene-1,1 -bisphosphonate **2** through a MICHAEL process once **2** has been introduced into the reaction mixture. Then, through a HORNER-WADSWORTH-EMMONS reaction with formaldehyde **10** contained in the reaction mixture, the resulting carbanion, **12**, leads to vinylphosphonate **9**.

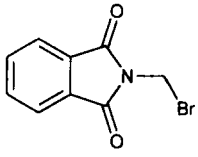


SCHEME III

Towards tetraethyl methylidene-1, 1-bisphosphonate 3

Still focusing on the synthesis of various tetraethyl ω-aminoalkylidene-1,1-bisphosphonates **1**, we made tetraethyl methylidene-1,1-bisphosphonate carbanion **3'** to react on the three following N-(ω-bromoalkyl)phthalimides, *i.e.* N-(bromomethyl)- **13**, N-(2-bromoethyl)- **14** and N-(3-bromopropyl)-phthalimide **15**.

No nucleophilic substitution was observed with N-(bromomethyl)phthalimide **13**, but, octaethylpropylidene- 1,1,3,3-tetrakisphosphonate **16** was made.



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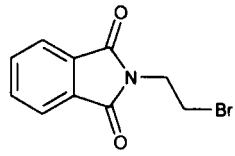

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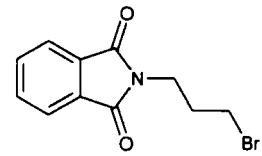
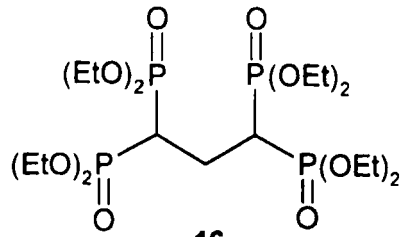


15

FIGURE 5



16

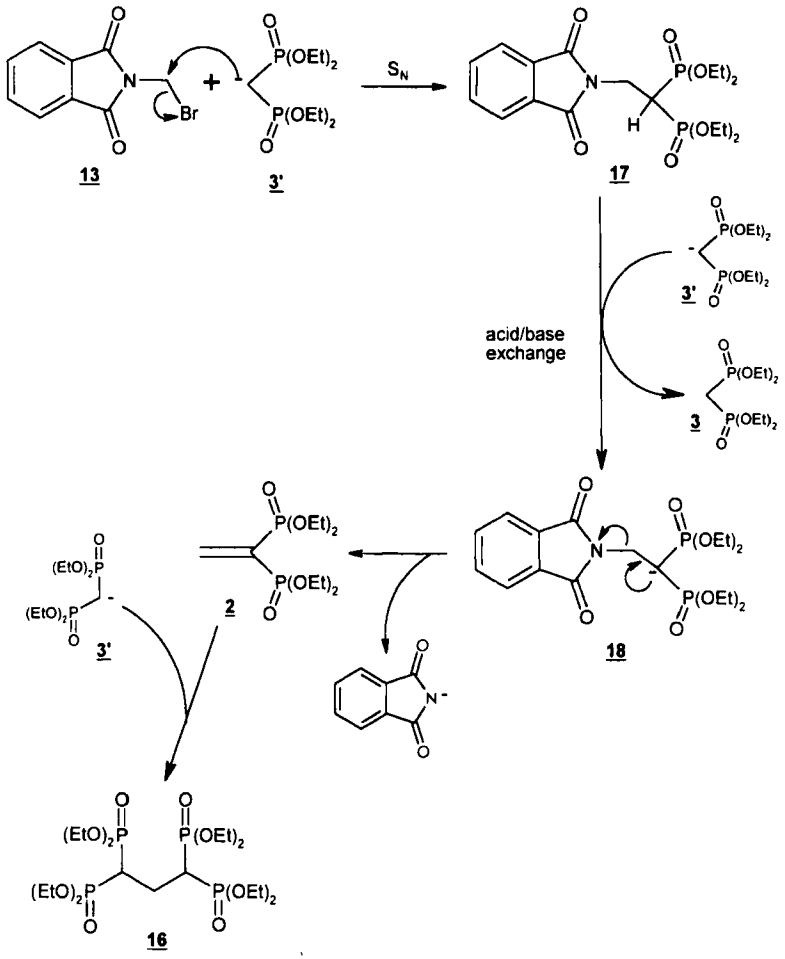
FIGURE 6

We assumed that compound **16** was formed through the mechanism depicted in scheme IV.

According to this scheme a carbanion-induced nucleophilic substitution of the bromo atom on compound **13** took place first; then, the resulting bisphosphonate, **17**, was attacked by another carbanion **3'** to give a new but unstable carbanion, **18**, which rearranged to form *in situ* tetraethyl ethenylidene-1,1-bisphosphonate **2**. Then, one carbanion **3'** reacted with this tetraethy ethenylidene-1,1-bisphosphonate[6] through a MICHAEL addition to give tetrakisphosphonate **16** in a 50% yield.

N-(2-bromoethyl)phthalimide **14** did not give rise to any nucleophilic substitution, but gave N-vinylphthalimide **19**. There, carbanion **3'** acted only as a base by removing H^+ from the methylene group on the nitrogen atom. The following elimination gave the vinyl compound, **19**. Scheme V depicts the corresponding mechanism.

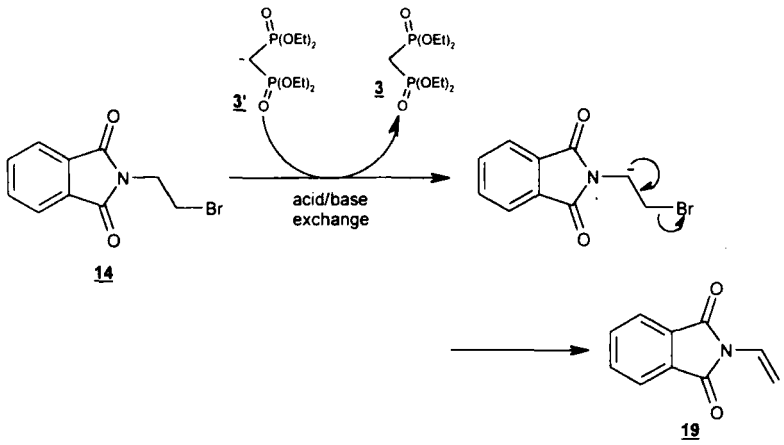
The third compound, N-(3-bromopropyl)phthalimide **15** did not lead either to the expected nucleophilic substitution product, **20**, but gave one heterocycle, 6-(diethylphosphono)-2,3,4,5-tetrahydro-[2,3a]-isoindolin-1-one **21**.



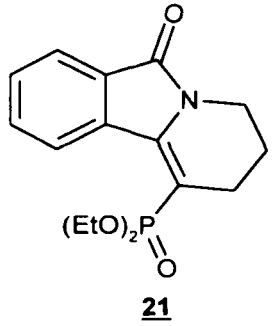
SCHEME IV

We explained its synthesis through the mechanism reported in scheme VI.

A preliminary attack of carbanion on the carbonyl was excluded because tetraethyl methylidene-1,1-bisphophonate carbanion **3'** did not react with N-methylphthalimide. This result indicated an initial nucleophilic substitution. Then, *via* an acid-base exchange, the substitution product prompted the intramolecular HORNER-WADSWORTH-EMMONS reaction which is made easier because of the formation of the 6-ring compound[9], **21**.



SCHEME V



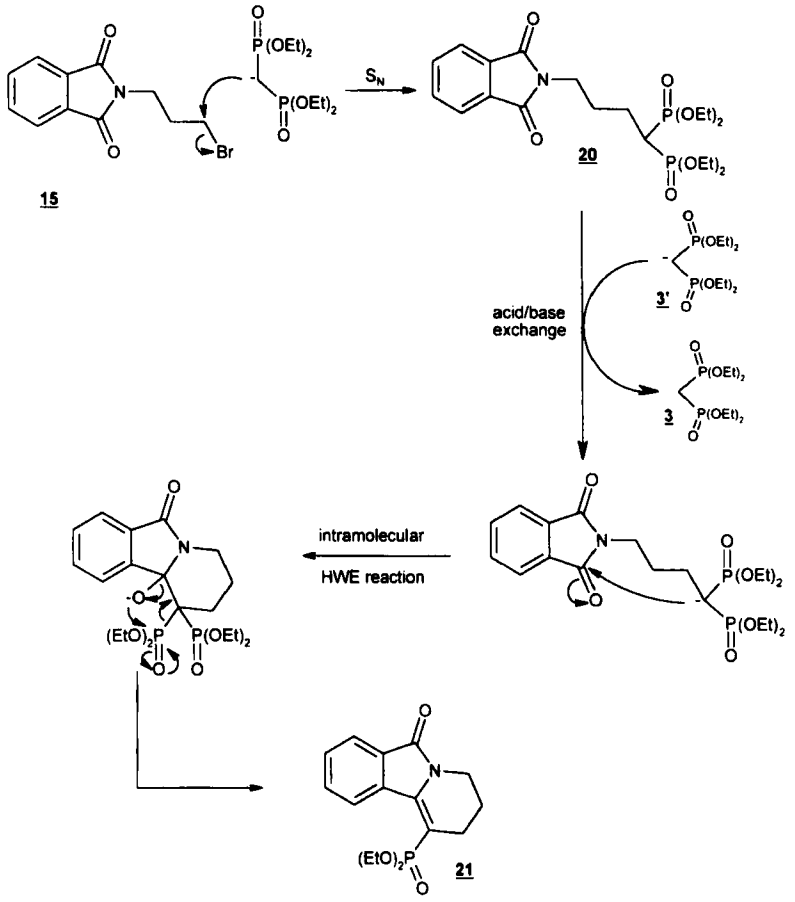
21

FIGURE 7

Towards diethylphosphite 4

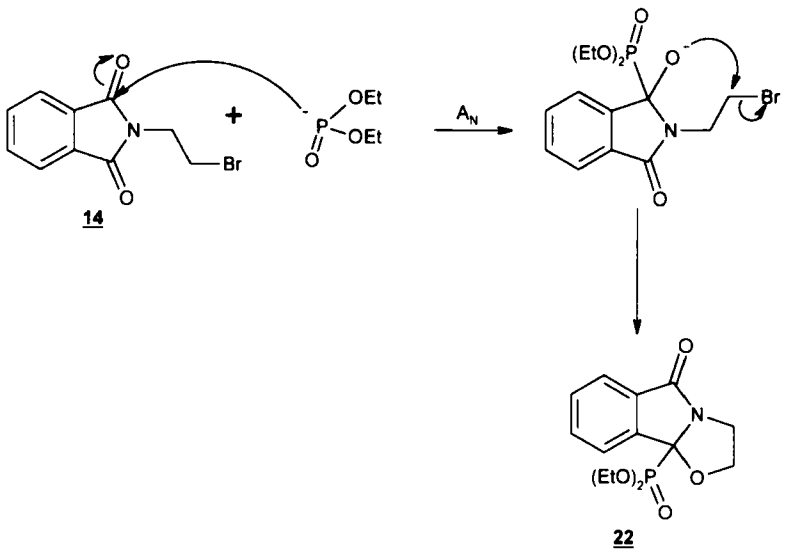
Another pathway to tetraethyl ω-aminoalkylidene-1,1-bisphosphonates, **1**, consisted in carrying out a MICHAELIS-BECKER reaction on N-(bromoalkyl)phthalimides followed by the condensation of the monophosphorylated-compound carbanion with diethylchlorophosphate.

Once again, with N-(2-bromoethyl)phthalimide **14**, the reaction pathway followed an unexpected course, described in scheme VII, and gave 5a-(diethylphosphono)-5-oxapyridido-[2,3-a]-isoindolin-1-one **22**.



SCHEME VI

^{31}P-NMR monitoring evidenced the very fast occurrence of a unique compound whose chemical shift (δ = 14.7 ppm) was not the one expected ($\delta \approx 31$ ppm) for this type of alkylphosphonate. Thus, it seems that the first step was a nucleophilic addition followed by a second step where the formed oxanion acted in place of the bromo atom, carried by compound **14**, by an intramolecular nucleophilic substitution.



SCHEME VII

CONCLUSION

This work highlighted that some phthalimide derivatives can undergo interesting reactions leading to various vinyls or heterocycles. Some of the compounds described here are novel. Synthetic applications of these novel molecules are now under investigation.

We thank Dr *M.P. Friocourt* for assistance in the writing of the English manuscript.

EXPERIMENTAL SECTION

The primary chemicals used were from commercial origin. The solvents were distilled prior to both reactions and chromatography. The purity of products and the reaction progress were monitored on TLC plates ($60F_{254}$ Merck); liquid chromatography was carried out on a silica gel column (Merck 60, 70–230 mesh). TLC plates were investigated under UV-light (254 nm) or with iodine and/or DITTMER.

1-D NMR spectra were recorded either on a BRUKER AC 300 spectrometer equipped with a dual 5-mm $^{1}H/^{13}C$ probehead, or on a BRUKER DRX 400 spectrometer equipped with an indirect 5-mm $^{1}H\{BB\}$ gradient probehead. The probe temperature was 298 K; samples were dissolved in $CDCl_3$. Chemical shifts (δ) are expressed in ppm by reference to TMS as external standard (^{1}H, ^{13}C NMR) or to phosphoric acid as reference (85 % H_3PO_4 in D_2O) with positive values downfield (^{31}P NMR). The coupling constants J are expressed in Hertz (Hz).

2-D NMR spectra were acquired with non-spinning samples with deuterium frequency locking. For heteromultiple quantum coherence (HMQC) experiments the raw data sets consisted of 1024 (F2) × 700 (F1) complex data points zero-filled to 1 k in the F1 dimension prior to Fourier transform with spectral widths of 170000 and 3546 Hz in the Fl and F2 dimensions respectively and for heteromultiple band coherence (HMBC) experiments the raw data sets consisted of 1024 (F2) × 405 (F1) complex data points zero-filled to 1 k in the Fl dimension prior to Fourier transform with spectral widths of 170000 and 3546 Hz in the F 1 and F2 dimensions respectively.

Tetraethyl ethenylidene-1, 1-bisphosphonate 2

Prepared according to literature procedures[10].

^{31}P NMR δ: 12.7

Tetraethyl methylidene-1, 1-bisphosphonate 3

Prepared according to literature procedures[11].

^{31}P NMR δ: 19.3 *(41 ppm for sodium salt in THF solution)*

Diethylphosphite 4

From commercial origin.

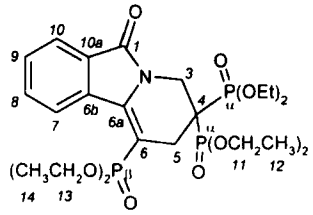
^{31}P NMR δ: 6.9 *(131 ppm for sodium salt in THF solution)*

4,4,6-tris(diethylphosphono)-2,3,4,5-tetrahydro-[2,3a]-isoindolin- 1-one 6

To a suspension of NaH (0.24 g, 10 mmol) in THF (30 mL) a solution of phthalimide (1.47 g, 10 mmol) in THF (10 mL) was added under nitrogen

and at room temperature. The mixture was stirred for 1 h 30. Then, a solution of **2** (6.00 g, 20 mmol) in THF (5 mL) was added before allowing the mixture to stand for 72 hours at room temperature under stirring. The mixture was hydrolysed with a saturated aqueous solution of NH_4Cl (15 mL) and extracted three times with ethyl acetate (30 mL). The combined organic layers were dried over Na_2SO_4, then the solvent was removed under reduced pressure. The residue was purified by chromatography on silica gel column (AE/E: 9/1 to 3/1). Yield: 27 %. Physical and spectral data are summarized in Table I.

TABLE I Physical and spectral data of **6**



$C_{24}H_{38}NO_{10}P_3$

593.5 g.mol^{-1}

C ± 0.36 ; H ± 0.19

Rf (AE/E : 9/1) = 0.25

RMN ^{1}H	
H_{12} & H_{14} :	1.2-1.4 (m, 18H)
H_5 :	3.2 (dt, $^3J_{HPa}$ = 7.1, $^3J_{HPb}$ = 14.7, 2H)
H_3, H_{11} & H_{13} :	4.1-4.2 (m,14 H)
H_9 :	7.5 (dd, ;1H)
H_8 :	7.6 (dd, 1H)
H_{10} :	7.8 (d, 1H)
H_7 :	8.7 (d, 1H)

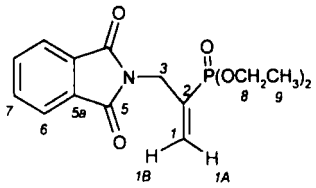
RMN ^{31}P	
P_α :	22.9
P_β :	17.3

RMN ^{13}C	
C_{12} & C_{14} :	15.9 & 16.0
C_5 :	28.6 (dt, $^2J_{CP}$ = 4.5, $^2J_{CP}$ = 4.1)
C_3 :	38.9
C_4 :	39.2 (td, $^1J_{CP}$ = 135.0, $^3J_{CP}$ = 8.2)
C_{13} :	61.8
C_{11} :	62.9
C_6 :	101.2 (dt, $^1J_{CP}$ = 197.1, $^3J_{CP}$ = 10.8)
C_{10} :	122.5
C_7 :	125.8
C_{10a} :	19.5
C_9 :	129.9
C_8 :	132.1
C_{6b} :	133.2
C_{6a} :	142.9 (d, $^2J_{CP}$ = 19.8)
C_1 :	165.4

2-diethylphosphono-3-phthalimidoprop-1-enylidene 9

To a suspension of NaH (0.29 g, 12 mmol) in THF (30 mL) a solution of **8** (1.77 g, 10 mmol) in THF (10 mL) was added under nitrogen and at room temperature. The mixture was stirred for 1 h. Then, a solution of **2** (3.00 g, 10 mmol) in THF (5 mL) was added, before keeping the mixture under stirring for 2 h 30 at room temperature. The mixture was quenched with a saturated aqueous solution of NH_4Cl (15 mL) and extracted three times with ethyl acetate (30 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel column (AE/H: 1/1). Quantitative yield. Physical and spectral data are summarized in Table II.

TABLE II Physical and spectral data of **9**



$C_{15}H_{18}NO_5P$

323.3 g.mol^{-1}

C ± 0.37 ; H ± 0.20

Rf (AE/H : 1/1) = 0.56

RMN ^{1}H		RMN ^{13}C	
H_9 :	1.3 (t, 6H)	C_9 :	16.2
H_8 :	4.0-4.2 (m, 4H)	C_3 :	38.8 (d, $^2J_{CP}$ = 16.5)
H_3 :	4.5 (td, $^3J_{CP}$ = 6.3, $^4J_{HH}$ = 1.1, 2H)	C_8 :	62.1
H_{1B} :	5.8 (dt, $^3J_{CP}^{trans}$ = 44.1, $^4J_{HH}$ = 1.1, 1H)	C_6 & C_7 :	123.3 & 134.1
H_{1A} :	6.2 (dt, $^3J_{CP}^{cis}$ = 21.8, $^4J_{HH}$ = 1.1, 1H)	C_1 :	130.8 (d, $^2J_{CP}$ = 8.1)
H_6 & H_7 :	7.7-7.9 (m, 4H)	C_{5a} :	131.9
		C_2 :	133.7 (d, $^1J_{CP}$ = 174.9)
RMN ^{31}P		C_5 :	167.5
16.7			

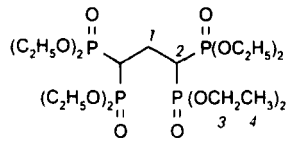
Octaethylpropylidene-1,1,3,3-tetrakisphosphonate 16

To a suspension of NaH (0.24 g, 10 mmol) in THF (20 mL) a solution of **3** (2.88 g, 10 mmol) in THF (10 mL) was added under nitrogen at room temperature. The temperature was allowed to reach 30°C and the mixture

stirred for 10 min. Then, a solution of **13** (2.40 g. 10 mmol) in THF (5 mL) was added, before allowing the mixture to stand under stirring for 2 h at room temperature. The mixture was quenched with a saturated aqueous solution of NH_4Cl (15 mL) and extracted three times with chloroform (30 mL). The combined organic layers were dried over Na_2SO_4 and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel column (pure AE). Yield 50%. Physical and spectral data are summarized in Table III.

TABLE III Physical and spectral data of **16**

Table III



$C_{19}H_{44}O_{12}P_4$

588.4 g.mol^{-1}

C ± 0.29 ; H ± 0.20

Rf (AE) = 0.27

bp 120°C/0.025 mm Hg

RMN ^{1}H		RMN ^{13}C	
H_3 :	1.3 (t, 24H)	C_4 :	15.6
H_1 :	2.5 (tqn, 2H)	C_1 :	21.0 (tt, $^2J_{CP}$ = 3.8)
H_2 :	3.4 (tt, $^2J_{HP}$ = 23.9, 2H)	C_2 :	33.2 (tt, $^1J_{CP}$ = 131.8, $^3J_{CP}$ = 6.8)
H_3 :	4.15 (dq, 16H)	C_3 :	61.7

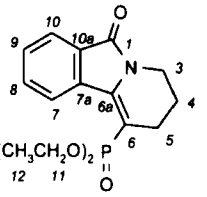
RMN ^{31}P
22.7

6-(diethylphosphono)-2,3,4, 5-tetrahydro-[2,3a]-isoindolin- 1-one 21

To a suspension of NaH (0.48 g, 20 mmol) in THF (30 mL) a solution of **3** (2.88 g, 10 mmol) in THF (10 mL) was added under nitrogen at room temperature. The temperature was allowed to reach 45°C. The mixture was stirred for 10 min. Then, a solution of **15** (2.68 g, 10 mmol) in THF (10 mL) was added before heating under reflux for 12h. The mixture was hydrolysed with a saturated aqueous solution of NH_4Cl (20 mL) and extracted for three times with chloroform (30 mL). The combined organic

layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by silica gel column chromatography (AE/H : 1/1). Yield : 85%. Physical and spectral data are summarized in Table IV.

TABLE IV Physical and spectral data of **21**



$C_{16}H_{20}NO_4P$

321.3 g.mol^{-1}

C ± 0.30 ; H ± 0.19

Rf (AE/H : 1/1) = 0.21

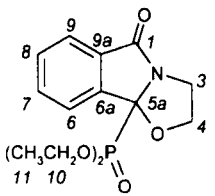
RMN ^{1}H		RMN ^{13}C	
H_{12} :	1.3 (t, 6H)	C_{12} :	15.9
H_4 :	2.0 (tt, 2H)	C_4 :	20.1
H_5 :	2.6 (dt, $^3J_{HP}$ = 5.7, 2H)	C_5 :	25.6
H_3 :	3.8 (t, 2H)	C_3 :	38.2
H_{11} :	4.1 (dq, $^3J_{HP}$ = 6.9, 4H)	C_{11} :	61.1
H_8 & H_9 :	7.4 & 7.6 (dd, 1H & 1H)	C_6 :	104.0 (d, $^1J_{CP}$ = 195.5)
H_{10} & H_7 :	8 & 8.5 (d, 1H & 1H)	C_7, C_8, C_9, C_{10} :	123.0, 125.7, 130.1, 131.8
		C_{6b} :	125.9
RMN ^{31}P		C_{10a} :	133.5
17.9		C_{6a} :	143.0 (d, $^2J_{CP}$ = 22)
		C_1 :	166.1

5a-(diethylphosphono)-5-oxapyrididido-[2,3-a]-isoindolin-1-one 22

Sodium (0.50 g, 22 mmol) was stored in THF (20 mL) under nitrogen. Then, diethylphosphite **4** (3.04 g, 22 mmol) was added dropwise at room temperature. The mixture was kept under strirring, until hydrogen release stopped. Then, a solution of **14** (6.15 g, 24 mmol) in THF (10 mL) was added, before the mixture was allowed to stand with stirring for 3 hours at room temperature. The mixture was hydrolysed with a saturated aqueous solution of NH_4Cl (15 mL) and extracted for three times with chloroform (30 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed under reduced pressure. The residue was purified by

silica gel column chromatography (AE/H : 1/1). Yield 86 %. Physical and spectral data are summarized in Table V.

TABLE V Physical and spectral data of **22**



$C_{14}H_{18}NO_5P$

311.3 g.mol^{-1}

C ± 0.31 ; H ± 0.18

Rf (AE/H : 1/1) = 0.31

RMN ^{1}H		RMN ^{13}C	
H_{11} :	1.2 (t, 6H)	C_{11} :	16.3
H_3, H_4 & H_{10} :	4.5 (m, 8H)	C_3 :	41.8
H_6, H_7, H_8 & H_9 :	7.5-8.0 (m , 4H)	C_{10} :	61.9
		C_4 :	70.1
RMN ^{31}P		C_{5a}	99.8 (d, $^1J_{CP}$ = 205.1)
14.7		C_6, C_7, C_8 & C_9 :	127.1, 128.5, 131.7, 132.8
		C_{6a} :	132.7 (d, $^2J_{CP}$ = 4.5)
		C_{9a} :	133.2
		C_1 :	168.7

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