Pergamon

Tetrahedron Vol. 51, No. 35, pp. 9625-9632, 1995

0040-4020/95 $9.50+0.00

0040-4020(95)00537-4

Synthesis and Reactivity of 1,2 λ^5-Azaphosphinines

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Key words : Azaphosphinines, oxidation, phosphine oxides, isomerization.

***Abstract** : The synthesis of 1,2 λ^5-azaphosphinines has been achieved in three steps starting from the readily available 1,2-dihydro-1,2 λ^3-azaphosphinines. The oxidation and hydrolysis of 1,2 λ^5-azaphosphinines on exposure to air give functionalized phosphine oxides.*

The synthesis of λ^3-azaphosphinines has received recent attention [1,2], but there are few reports on the preparation and synthetic applications of λ^5-azaphosphinines. 4,4-Diphenyl-1,4 λ^5-azaphosphinines [3], 3,3-diethoxy-1,3 λ^5-azaphosphinines [4], 2,2-dialkoxy-1,2 λ^5-azaphosphinines [5] and recently a new 1,4 λ^5-azaphosphinine [6] have been prepared. However, the methods of preparation are not general. We would like to describe the synthesis and the reactivity of a series of new 1,2 λ^5-azaphosphinines [7].

Results and discussion

The 1-tert-butyl-1,2-dihydro-1,2 λ^3-azaphosphinines **1** and 1-tert-octyl-1,2-dihydro-1,2 λ^3-azaphosphinine **2** were easily prepared by the reaction of dichlorophenylphosphine with imines [8,9]. Alkylation of azaphosphinines **1** and **2** with methyl iodide in toluene gave the phosphonium salts **3** and **4** in good yields. The thermolysis of these salts yielded isobutene and phosphonium salts **5** in an excellent yield (table 1). The easy formation of isobutene by thermolysis of 1-tert butylazaphosphinines **1** and 1-tert-octyl azaphosphinines **2** has been previously reported [2]. Treatment of a solution of salts **5** in ether-acetonitrile under nitrogen at room temperature with potassium carbonate produced 1,2 λ^5-azaphosphinines **6**. The structure of the λ^5-azaphosphinines was determined by ^{1}H-NMR and ^{13}C-NMR spectroscopy (table 2).

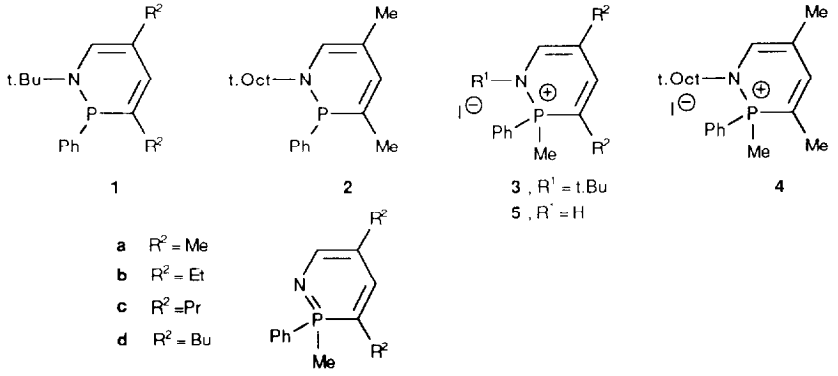


Table 1. Thermolysis of salts **3** and **4**.

Compd.	**3a**	**3b**	**3c**	**3d**	**4**
Temp (°C)	235	220	215	205	207
Time (min.)	30	30	20	20	15
Yield of **5** (%)	98	98	96	93	96

According to their NMR spectra, particularly the large high-field shifts of carbons 3 and 5 and the large values of the $^1J_{PC3}$, the 1,2 λ^5-azaphosphinines **6** can be classified as six π-electron phosphorus ylides [10]. But, while 3,4,5,6-tetrahydro-1,2 λ^5-azaphosphinine can give Wittig olefination [11], 1,2 λ^5-azaphosphinine gave no reaction with benzaldehyde in refluxing diethyl ether. The 1,2 λ^5-azaphosphinines **6** were air sensitive.

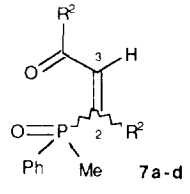
Table 2. Selected NMR spectral data of 1,2 λ^5-azaphosphinines **6**.

Compd.	Yield (%)[a]	$\delta^{31}P$	δC_3 (J_{PC})	δC_4 (J_{PC};$^1J_{CH}$)	δC_5 (J_{PC})	δC_6 (J_{PC},$^1J_{CH}$)	δP-Me (J_{PC},$^1J_{CH}$)	others
6a	94	21.8	91.8 (74.8)	146.1 (4.5;146.1)	104.5 (28)	146.5 (10.2;171)	15.7 (78.7;129)	17.5,18.2,129.8, 128.7,131.3
6b	86	21.7	97.9 (73.3)	143.2 (5.6;148.8)	111.8 (28.7)	146.1 (10.4;167.6)	16.3 (77.8;129)	14.3,16.5,24.3,26.4, 128.7,130.0,131.3
6c	80	22.1	95.7 (73.2)	144.4 (5.9;148.4)	109.8 (28.7)	146.9 (10.0;168)	16.2 (78.1;129)	13.5,13.7,23.1,25.0, 33.6,35.4,128.6, 129.9,131.3
6d	83	22.0	96.1 (75)	144.3 (5.6;154)	110.2 (28.0)	146.5 (9.8;164)	16.2 (78.5;129)	13.8,14.0,22.1,22.3, 32.1,33.0,31.2,34.1, 128.6,129.9,131.3

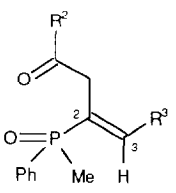
[a] Isolated yield based on the amount of **3**.

1,2 λ^5-Azaphosphinines **6** were slowly oxidized and hydrolyzed on exposure to air, even in the dark, to give formamide (detected by ^1H NMR on the crude product) and a mixture of phosphine oxides **7Z**, **8E** and **9Z**. The product ratios of **7**, **8** and **9** are shown in table 3. The time of complete air oxidation was 40 h and the time of oxidation in oxygen atmosphere was 17-18 h. The oxidation of azaphosphinines **6** can be also achieved by treatment with hydrogen peroxide. In these conditions, **6d** gave **8d** in 80 % yield. Compounds **7**, **8** and **9** were separated by chromatography on silica gel and the structures were determined by IR, ^1H-NMR, ^{31}P-NMR, ^{13}C-NMR and MS spectral analyses.

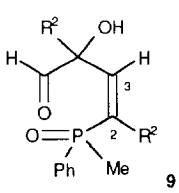
A slow isomerization of **7Z** into **7E** was observed in solution at room temperature. The structure of isomers **7E** and **7Z** was established by ^1H NMR spectroscopy. The coupling constant $^3J_{PH3}$ was higher when H_3 and the phosphorus atom are in trans position ($^3J_{PH3}$ = 33-36 Hz for **7Z**) than in cis position ($^3J_{PH3}$ = 20-21 Hz for **7E**)[12].



7a-d



8b R^2 = Et, R^3 = Me
8c R^2 = Pr, R^3 = Et
8d R^2 = Bu, R^3 = Pr



9c,d

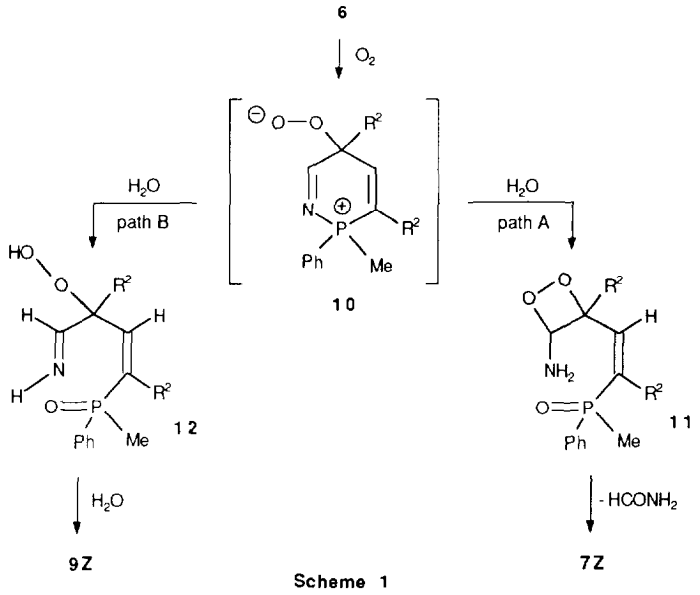
Table 3. Product ratios in the air oxidation of azaphosphinines **6** in CH_2Cl_2 for 40 h [a]

Starting product	7Z (%)	8E (%)	9Z (%)
6a	100	0	0
6b	88	12	0
6c	76	12	12
6d	50	20	30

[a] Product ratios determined by ^1H NMR.

Phosphine oxides **7b-d** rearranged quantitatively to phosphine oxides **8b-d** in the presence of base as sodium hydroxide, potassium carbonate or barium oxide. In these conditions **7Z** gave quantitatively **7E**. The structure of phosphine oxides **8** was very likely E, because $^3J_{PH3}$ = 20 Hz as in **7E**. Two diastereoisomers **9c,d** of configuration Z were obtained ($^3J_{PH3}$ = 37 Hz).

The following scheme 1 shows plausible pathways for conversions of azaphosphinines **6** into phosphine oxides **7** and **9**. The oxidation can proceed through a peroxi anion **10**, as in the oxidation of alkyliden phosphoranes [13-15] or the oxidation of naphtoxide [16] or enamines [17]. Hydrolysis of **10** leads to the intermediate **12**, precursor of **9Z** (path B). The cyclization of **10** into dioxetane **11**, precursor of **7Z** and formamide, seems to be assisted by the steric bulk of the R^2 group (table 3) (path A).



Scheme 1

In conclusion, we have developed a facile route to 1,2 λ^5-azaphosphinines starting from readily available 1,2-dihydro-1,2 λ^3-azaphosphinines. λ^5-Azaphosphinines are easily oxidized and hydrolyzed to give functionalized phosphine oxides.

Experimental section

General. ^1H, ^{31}P and ^{13}C NMR spectra were recorded on a Bruker AC 300 spectrometer operating at 300, 121 and 75 MHz respectively. Deuteriochloroform was used as the solvent. IR spectra were obtained using a Perkin Elmer 1420 instrument. Mass spectra were recorded under electron impact at 70 eV on a Varian MAT 311 instrument of the Centre de Mesures Physiques, Rennes.

General procedure for the preparation of salts 3 and 4

To a solution of azaphosphinine **1** or **2** (8 mmol) in dry toluene (20 ml) under nitrogen was added dropwise a solution of iodomethane (2.27 g, 16 mmol) in dry toluene (20 ml). The mixture was stirred at the refluxing temperature for 1 h. The solvent was removed in vacuo. Trituration of the residue with diethylether yielded yellow crystals recrystallized from ethyl acetate.

1-tert.Butyl-2-phenyl-2,3,5-trimethyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***3a.*** 47 %. mp 163°C. ^{1}H NMR δ 1.39 (s, 9H), 1.80 (d, 3H, J_{PH} = 16 Hz), 1.95 (s, 3H), 2.88 (d, 3H, J_{PH} = 12.8 Hz), 6.59 (d, 1H, J_{PH} = 20 Hz), 6.92 (d, 1H, J_{PH} = 34 Hz), 7.77-8.17 (m, 5H). ^{13} C NMR δ 16.81, 17.42, 19.21, 30.93, 63.46, 108.01, 110.14, 126.70, 127.43, 130.50, 132.05, 135.36, 144.23. ^{31}P NMR δ 35.9. Anal. calcd for $C_{17}H_{25}NPI$: C, 50.87 ; H, 6.23 ; N, 3.49 ; P, 7.73 ; I, 31.67. Found : C, 50.59 ; H, 6.36 ; N, 3.54 ; P, 7.78 ; I, 32.03.

1-tert.Butyl-3,5-diethyl-2-methyl-2-phenyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***3b.*** 67 %, mp 86°C. ^{1}H NMR δ 0.96 (t, 3H, J_{HH} = 7 Hz), 1.11 (t, 3H, J_{HH} = 7 Hz), 1.40 (s, 9H), 1.95 (m, 2H), 2.27 (m, 2H), 2.87 (d, 3H, J_{PH} = 12 Hz), 6.56 (d, 1H, J_{PH} = 22 Hz), 6.91 (d, 1H, J_{PH} = 34 Hz), 7.72-8.12 (m, 5H). ^{31}P NMR δ 34.9. **3b** was crystallized with water which comes probably from water saturated ether. Anal. calcd for $C_{19}H_{29}NPI$, $2H_2O$: C, 49.03 ; H, 7.09 ; N, 3.01 ; P, 6.66 ; I, 27.31. Found : C, 48.85 ; H, 6.85 ; N, 2.88 ; P, 6.44 ; I, 27.17.

1-tert.Butyl-3,5-dipropyl-2-methyl-2-phenyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***3c.*** 61 %, mp 140°C. ^{1}H NMR δ 0.76 (t, 3H, J_{HH} = 7 Hz), 0.91 (t, 3H, J_{HH} = 7 Hz), 1.40 (m, 4H), 1.41 (s, 9H), 2.14 (m, 4H), 2.91 (d, 3H, J_{PH} = 12 Hz), 6.53 (d, 1H, J_{PH} = 21.6 Hz), 6.88 (d, 1H, J_{PH} = 34 Hz), 7.75-8.15 (m, 5H). ^{31}P NMR δ 34.6. Anal. calcd for $C_{21}H_{33}NPI$: C, 55.14 ; H, 7.27 ; N, 3.06 ; P, 6.77 ; I, 27.74. Found : C, 54.56 ; H, 7.15 ; N, 3.15 ; P, 6.55 ; I, 27.66.

1-tert.Butyl-3,5-dibutyl-2-methyl-2-phenyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***3d.*** 63 %. mp 156-160°C. ^{1}H NMR δ 0.71 (t, 3H, J_{HH} = 7 Hz), 0.92 (t, 3H, J_{HH} = 7 Hz), 1.32 (m, 8H), 1.42 (s, 9H), 2.22 (m, 4H), 2.89 (d, 3H, J_{PH} = 12 Hz), 6.55 (d, 1H, J_{PH} = 20 Hz), 6.90 (d, 1H, J_{PH} = 35 Hz), 7.75-8.20 (m, 5H). ^{31}P NMR δ 34.6. Anal. calcd for $C_{23}H_{37}NPI$: C, 56.90 ; H, 7.68 ; N, 2.88 ; P, 6.38 ; I, 26.14. Found : C, 57.10 ; H, 7.89 ; N, 2.93 ; P, 6.33 ; I, 25.91.

1-tert.Octyl-2-phenyl-2,3,5-trimethyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***4.*** 83 %. mp 64°C. ^{1}H NMR δ 0.94 (s, 9H), 1.47 (s, 3H), 1.55 (s, 3H), 1.72 (s, 2H), 1.82 (d, 3H, J_{PH} = 17.6 Hz), 2.01 (s, 3H), 2.92 (d, 3H, J_{PH} = 12 Hz), 6.55 (d, 1H, J_{PH} = 22.4 Hz), 6.96 (d, 1H, J_{PH} = 32.8 Hz), 7.70-7.80 (m, 5H). ^{13}C NMR δ 17.0, 17.5, 19.3, 30.3, 31.5, 31.8, 54.8, 66.1, 108.0, 110.0, 126.5, 127.8, 130.4, 132.0, 135.3, 144.4. ^{31}P NMR δ 34.2. Anal. calcd for $C_{21}H_{33}NPI$: C, 55.14 ; H, 7.27 ; N, 3.06 ; P, 6.77 ; I, 27.74. Found : C, 55.08 ; H, 7.13 ; N, 3.16 ; P, 6.80 ; I, 27.79.

General procedure for the thermolysis of salts 3 and 4

A flask (25 ml) was filled with salts **3** or **4** (5 mmol) and was heated in a oil bath at a stable temperature (± 4°C) and for a time given in table 1. The salts **5a-c** were obtained and used without further purification.

2-Phenyl-2,3,5-trimethyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***5a.*** Black oil. ^{1}H NMR δ 1.82 (s, 3H), 2.00 (d, 3H, J_{PH} = 16 Hz), 2.66 (d, 3H, J_{PH} = 14,4 Hz), 6.52 (dd, 1H, J_{PH} = 22 Hz, J_{HH} = 6 Hz), 7.01 (d, 1H, J_{PH} = 33.6 Hz), 7.65 - 7.95 (m, 5H), 9.10 (t, 1H, J_{PH} = J_{HH} = 6 Hz). ^{31}P NMR δ 29.7.

3,5-Diethyl-2-methyl-2-phenyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***5b.*** Black oil. ^{1}H NMR δ 1.06 (t, 3H), 1.11 (t, 3H), 2.11 (m, 4H), 2.70 (d, 3H, J_{PH} = 14.4 Hz), 6.50 (dd, 1H, J_{PH} = 23 Hz,

J_{HH} = 6 Hz), 7.04 (d, 1H, J_{PH} = 34 Hz), 7.65 - 7.95 (m, 5H), 9.12 (t, 1H, $J_{PH} = J_{HH}$ = 6 Hz). ^{31}P NMR δ 29.4.

3,5-Dipropyl-2-methyl-2-phenyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***5c*** . Black oil, ^1H NMR δ 0.87 (m, 6H), 1.44 (m, 4H), 2.12 (m, 4H), 2.68 (d, 3H, J_{PH} = 13.6 Hz), 6.55 (dd, 1H, J_{PH} = 22 Hz, J_{HH} = 6 Hz), 7.03 (d, 1H, J_{PH} = 35 Hz), 7.67 - 7.92 (m, 5H), 9.19 (t, 1H, $J_{PH} = J_{HH}$ = 6 Hz). ^{31}P NMR δ 29.2.

3,5-Dibutyl-2-methyl-2-phenyl-1,2-dihydro-1,2 λ^5-azaphosphininium iodide ***5d***. mp 88°C (AcOEt). ^1H NMR δ 0.85 (t, 3H), 0.90 (t, 3H), 1.37 (m, 8H), 2.15 (m, 4H), 2.69 (d, 3H, J_{PH} = 14.4 Hz), 6.54 (dd, 1H, J_{PH} = 22.8 Hz, J_{HH} = 6 Hz), 7.01 (d, 1H, J_{PH} = 34.4 Hz), 7.67-7.92 (m, 5H), 9.25 (t, 1H, $J_{PH} = J_{HH}$ = 6 Hz). ^{31}P NMR δ 29.2. Anal. calcd for $C_{19}H_{29}NPI$: C, 53.15 ; H, 6.81 ; N, 3.26 ; P, 7.21 ; I, 29.56. Found : C, 52.92 ; H, 6.90 ; N, 3.01 ; P, 6.98 ; I, 29.70.

Preparation of 1,2 λ^5-azaphosphinines 6

To a solution of crude salt **5** obtained from **3** (5 mmol) in dry acetonitrile (50 ml) and ether (50 ml) was added, under nitrogen, finely powdered K_2CO_3 (4 g). The mixture was stirred for 30 min. at 20°C. After filtration and solvent evaporation, the residue was dissolved in $CHCl_3$ (25 ml). The solution was filtrated, then evaporated to dryness. Crude azaphosphinine was used for the next step without further purification. ^{31}P NMR spectra of **6** show a good purity.

2-Phenyl-2,3,5-trimethyl-1,2 λ^5-azaphosphinine ***6a***. Yellow oil. ^1H NMR δ 1.78 (s, 3H), 1.85 (d, 3H, J_{PH} = 13 Hz) ; 1.97 (d, 3H, J_{PH} = 13.3 Hz), 6.76 (d, 1H, J_{PH} = 28.6 Hz) ; 7.07 (d, 1H, J_{PH} = 46 Hz), 7.5-7.6 (m, 5H). HRMS m/z calcd for $C_{13}H_{16}NP$ 217.10203, found 217.1024.

3,5-Diethyl-2-methyl-2-phenyl-1,2 λ^5-azaphosphinine ***6b***. Yellow oil. ^1H NMR δ 1.03 (t, 3H), 1.06 (t, 3H), 1.98 (d, 3H, J_{PH} = 13.3 Hz), 2.10 (m, 4H), 6.83 (dd, 1H, J_{HH} = 1.2 Hz, J_{PH} = 29.4 Hz), 7.09 (dd, 1H, J_{PH} = 46 Hz, J_{HH} = 1.2 Hz), 7.47 (m, 3H), 7.58 (m, 2H). HRMS, m/z calcd for $C_{15}H_{20}NP$ 245.1333, found 245.1321.

3,5-Dipropyl-2-methyl-2-phenyl-1,2 λ^5-azaphosphinine ***6c***. Yellow oil. ^1H NMR δ 0.86 (t, 3H), 0.87 (t, 3H), 1.40 (m, 4H), 1.92 (d, 3H, J_{PH} = 14 Hz), 2.04 (m, 4H), 6.79 (d, 1H, J_{PH} = 29 Hz), 7.08 (d, 1H, J_{PH} = 47 Hz), 7.47 (m, 3H), 7.60 (m, 2H). HRMS calcd for $C_{17}H_{24}NP$: 273.16463. Found 273.1641.

3,5-Dibutyl-2-methyl-2-phenyl-1,2 λ^5-azaphosphinine ***6d***. Yellow oil. ^1H NMR δ 0.81 (t, 3H), 0.87 (t, 3H), 0.95 (m, 8H), 1.95 (d, 3H, J_{PH} = 13 Hz), 2.05 (m, 4H), 6.77 (dd, 1H, J_{PH} = 29 Hz, J_{HH} = 1.3 Hz), 7.04 (dd, 1H, J_{PH} = 45 Hz, J_{HH} = 1.3 Hz), 7.45-7.60 (m, 5H). HRMS calcd for $C_{19}H_{28}NP$: 301,19592, found 301,1952.

Oxidation of azaphosphinines 6. Preparation of phosphine oxides 7Z and 9Z.

A stream of oxygen was bubbled through a solution of azaphosphinine **6** (3 mmol) in dry CH_2Cl_2 (20 ml) for 15 min, then the solution was allowed to stand at room temperature overnight. The solvent was evaporated in vacuo to leave crude products which were chromatographed on silica gel.

2-(methylphenylphosphinyl)-2-penten-4-one ***7aZ***. Oil purified by silica gel column chromatography (chloroform/acetone, 1 : 1), 47 %. ^1H NMR δ 1.93 (d, 3H, J_{PH} = 13 Hz), 2.04 (d, 3H, J_{PH} = 11 Hz), 2.17 (s, 3H), 6.68 (dt, 1H, J_{PH} = 34 Hz, J_{HH} = 1 Hz), 7.75-7.52 (m, 5H). ^{13}C NMR δ 15.26, 21.83, 30.63, 128.50, 130.00, 131.70, 133.51, 139.92, 143.33, 199.30. δ ^{31}P 31.80. IR (Nujol) ν 1690 cm^{-1}. MS m/z (rel. intensity) 222 (M^+ 50), 207 (60), 179 (24), 157 (37), 140 (100). HRMS calcd for $C_{12}H_{15}O_2P$ 222.08096. Found : 222.0802. Anal. calcd for $C_{12}H_{15}O_2P$: C, 64.86 ; H, 6.80. Found : C, 64.58 ; H, 6.92.

3-(methylphenylphosphinyl)-3-hepten-5-one ***7bZ***. The crude product was chromatographed over silica gel column and eluted with 12:9 chloroform/acetone to give **7bZ**. Oil, 46 %. ^{1}H NMR δ 0.90 (t, 3H), 1.11 (t, 3H), 1.96 (d, 3H, J_{PH} = 14 Hz), 2.42 (m, 4H), 6.59 (dt, 1H, J_{PH} = 35.2 Hz, J_{HH} = 1 Hz), 7.40-7.86 (m, 5H). ^{13}C NMR δ 7.44, 13.18, 15.53, 27.06, 36.60, 128.40, 130.16, 131.70, 133.40, 138.08, 148.40, 203.00. ^{31}P NMR δ 30.67. IR (Nujol) ν 1680 cm^{-1}. MS m/z (rel. intensity) 250 (M^+, 10), 235 (24), 221 (100), 193 (21), 157 (24), 140 (52), 139 (73), 125 (35), 77 (33). HRMS calcd for $C_{14}H_{19}O_2P$ 250.11226. Found 250.1138. Anal. calcd for $C_{14}H_{19}O_2P$: C, 67.18 ; H, 7.66. Found : C, 66.97 ; H, 7.88.

The crude product of oxidation of **6c** was chromatographed over silica gel with 3:2 chloroform/acetone as eluent to give **9c** and **7c**. First eluted was **9c**.

4-(Methylphenylphosphinyl)-4-nonen-6-one ***7cZ***. Oil, 44 %. ^{1}H NMR δ 0.71 (t, 3H), 0.86 (t, 3H), 1.40 (m, 4H), 1.94 (d, 3H, J_{PH} = 12.8 Hz), 2.32 (m, 4H), 6.59 (dt, 1H, J_{PH} = 35.2 Hz, J_{HH} = 1 Hz), 7.37-7.82 (m, 5H). ^{13}C NMR δ 13.5, 13.7, 15.8, 17.00, 22.40, 36.40, 45.20, 128.20, 130.20, 131.40, 133.80, 138.00, 149.00, 201.61. ^{31}P NMR δ 32.50. IR (Nujol) ν 1685 cm^{-1}. MS m/z (rel. intensity) : 278 (M^+, 46), 249 (81), 235 (94), 208 (50), 207 (100), 173 (34), 140 (61), 139 (81), 125 (36), 77 (31). HRMS Calcd for $C_{16}H_{23}O_2P$ 278.14356. Found 278.1426.

The major diastereoisomer **9c** was purified by flash chromatography on silica gel with chloroform/acetone 4:3 as eluent.

4-(methylphenylphosphinyl)-4-nonen-6-ol-6-carboxaldehyde ***9cZ***. Colorless oil, 8 %. ^{1}H NMR δ 0.87 (t, 3H), 0.92 (t, 3H), 1.42 (m, 4H), 1.87 (d, 3H, J_{PH} = 12.8 Hz), 1.90 (m, 5H), 6.50 (d, 1H, J_{PH} = 36.8 Hz), 7.50-7.60 (m, 5H), 9.71 (s, 1H). ^{13}C NMR δ 13.6, 14.2, 14.5, 22.4, 22.6, 35.6, 41.2, 79.3, 128.8, 130.4, 131.4, 132.3, 135.3, 149.3, 204.6. ^{31}P NMR δ 36.17. IR (Nujol) ν 3100-3500, 1720 cm^{-1}. MS m/z (rel. intensity) 279 ($(M-CHO)^+$, 100), 278 (33), 157 (13), 146 (10), 140 (21), 139 (43), 125 (15), 77 (12). HRMS calcd for $C_{16}H_{24}O_2P$ $(M-CHO)^+$ 279.15138, found 279.1505.

The crude product of oxidation of **6d** was chromatographed (silica gel, chloroform/acetone 19:12) to give **7d** and **9d**. First eluted was **9d**.

5-(methylphenylphosphinyl)-5-undecen-7-one ***7dZ***. *Colorless oil, 45 %.* ^{1}H NMR δ 0.88 (m, 6H), 1.41 (m, 8H), 1.98 (d, 3H, J_{PH} = 13.6 Hz), 2.40 (m, 4H), 6.60 (dt, 1H, J_{PH} = 35.2 Hz, J_{HH} = 1 Hz), 7.40-7.85 (m, 5H). ^{13}C NMR δ 13.8, 13.9, 15.7, 22.0, 23.0, 25.5, 31.3, 34.2, 42.9, 128.2, 130.2, 131.4, 133.6, 138.2, 148.8, 201.6. ^{31}P NMR δ 32.2. IR (Nujol) ν 1700 cm^{-1}. MS m/z (rel. intensity) 306 (M^+, 12), 263 (53), 249 (21), 222 (56), 221 (100), 140 (70), 139 (91), 125 (42), 91 (29), 77 (31). HRMS calcd for $C_{18}H_{27}O_2P$ 306.17486, found 306.1750.

5-(Methylphenylphosphinyl)-5-undecen-7-ol-7-carboxaldehyde ***9dZ***. Major diastereomer purified by flash chromatography (silica gel, chloroform/acetone 15 : 10). Colorless oil, 9 %. ^{1}H NMR δ 0.87 (m, 6H), 1.25 (m, 13H), 1.88 (d, 3H, J_{PH} = 12 Hz), 6.48 (d, 1H, J_{PH} = 36.8 Hz), 7.5-7.8 (m, 5H), 9.69 (s, 1H). ^{13}C NMR δ 13.7, 13.8, 14.0, 22.1, 23.1, 25.0, 33.1, 33.5, 38.5, 79.2, 128.8, 130.4, 132.0, 132.4, 135.0, 148.7, 204.6. ^{31}P NMR δ 35.77. IR (CCl_4) ν 3580, 3160, 1720 cm^{-1}. MS m/z (rel. intensity) 307 $(M-CHO)^+$ (100), 292 (13), 140 (42), 139 (61), 125 (22), 77 (10). HRMS calcd for $C_{18}H_{28}O_2P$ $(M-CHO)^+$: 307.18268, found 307.1776. Anal. calcd for $C_{19}H_{29}O_3P$: C, 67.83 ; H, 8.69 ; found C, 68.01 ; H, 8.75.

Isomerization of 7Z into 7E

A solution of **7bZ**, **7cZ** or **7dZ** (1 mmol) in CH_2Cl_2 (10 ml) was stored at room temperature for 8 days. Removal of the solvent gave a mixture of Z and E isomers **7** (ratio 3:2) analyzed by NMR.

7bE. ^{31}P NMR δ 33.68. ^{1}H NMR δ 7.01 (d, 1H, J_{PH} = 21 Hz, H-4).

7cE. ^{31}P NMR δ 33.20. ^{1}H NMR δ 6.99 (d, 1H, J_{PH} = 21 Hz, H-5).

7dE. ^{31}P NMR δ 33.20. ^{1}H NMR δ 7.00 (d, 1H, J_{PH} = 20 Hz, H-6).

Reaction of phosphine oxides 7Z with sodium hydroxide

To a solution of **7Z** (2 mmol) in dichloromethane (5 ml) was added 1N NaOH (5 ml). The mixture was stirred at room temperature for 3 h. The organic phase was washed with water (10 ml) and dried (Na_2SO_4). After evaporation, the crude product was purified by flash chromatography (silica gel, chloroform/acetone 3:2). (The same reaction can be performed with powdered barium oxide (2 g). The mixture was stirred at room temperature for 2 h).

*2-(methylphenylphosphinyl)-2-penten-4-one **7aE***. Yellow oil, 90 %. ^{1}H NMR δ 1.86 (d, 3H, J_{PH} = 12.8 Hz), 2.04 (dd, 3H, J_{PH} = 14.4 Hz, J_{HH} = 2.4 Hz), 2.26 (s, 3H), 7.07 (dq, 1H, J_{PH} = 20 Hz, J_{HH} = 1 Hz), 7.42-7.82 (m, 5H). ^{13}C NMR δ 13.1, 14.7, 31.9, 128.9, 130.0, 131.0, 132.3, 135.2, 146.4, 198.6. ^{31}P NMR δ 33.1. Anal. calcd for $C_{12}H_{15}O_2P$: C, 64.86 ; H, 6.80. Found : C, 64.62 ; H, 7.01.

*3-(methylphenylphosphinyl)-2-hepten-5-one **8bE***. Yellow oil, 73 %. ^{1}H NMR δ 0.90 (t, 3H), 1.73 (dd, 3H, J_{HH} = 7.2 Hz, J_{PH} = 3.2 Hz), 1.74 (d, 3H, J_{PH} = 12.8 Hz) ; 2.30 (m, 2H), 3.33 (d, 2H, J_{PH} = 13.6 Hz), 6.55 (dq, 1H, J_{PH} = 20 Hz, J_{HH} = 7 Hz), 7.42-7.82 (m, 5H). ^{31}P NMR δ 34.00. IR (Nujol) ν 1715 cm^{-1}. HRMS calcd for $C_{14}H_{19}O_2P$ 250.11226. Found 250.1130.

*4-(methylphenylphosphinyl)-3-nonen-6-one **8cE***. Yellow oil, 57 %. ^{1}H NMR δ 0.75 (t, 3H), 0.99 (t, 3H), 1.30 (m, 2H), 1.71 (d, 3H, J_{PH} = 12 Hz), 1.97 (m, 2H), 2.20 (t, 2H), 3.27 (d, 2H, J_{PH} = 16 Hz), 6.44 (dt, 1H, J_{PH} = 20 Hz, J_{HH} = 7.2 Hz), 7.40-7.82 (m, 5H). ^{13}C NMR δ 12.9, 13.6, 15.0, 17.1, 23.0, 40.5, 44.3, 126.0, 127.0, 129.3, 130.0, 131.3, 148.8, 206.1. ^{31}P NMR δ 34.04. IR (Nujol) ν 1715 cm^{-1}. MS (rel. intensity) : 278 (M^+, 1), 208 (100), 199 (22), 140 (39), 139 (44), 112 (61), 77 (54). HRMS calc for $C_{16}H_{23}O_2P$: 278.14356, found 278.1435.

Oxidation of azaphosphinine with hydrogen peroxide. Preparation of 5-(methylphenylphosphinyl)-4-undecen-7-one 8dE.

To a solution of azaphosphinine **6d** (0.6 g, 2 mmol) in toluene (15 ml) was added dropwise hydrogen peroxide (35 wt % solution in water, 1.5 ml). The mixture was stirred at room temperature for 15 min. The organic phase was washed with water (2 x 10 ml) and dried (Na_2SO_4). After evaporation, the phosphine oxide **8d** was purified by flash chromatography (silica gel, chloroform/acetone 1:1).

Light yellow oil, 80 %. ^{1}H NMR δ 0.90 (m, 6H), 1.32 (m, 6H), 1.76 (d, 3H, J_{PH} = 13.6 Hz), 2.12 (m, 2H), 2.27 (t, 2H), 3.31 (d, 2H, J_{PH} = 14.4 Hz), 6.50 (dt, 1H, J_{PH} = 20.8 Hz, J_{HH} = 8 Hz), 7.42-7.82 (m, 5H). ^{31}P NMR δ 33.50. IR (Nujol) ν 1700 cm^{-1}. MS m/z (rel. intensity) 306 (M^+, 4), 291 (5), 263 (7), 222 (100), 221 (28), 207 (22), 194 (17), 193 (33), 157 (12), 140 (41), 139 (55), 125 (23), 85 (8), 77 (13). HRMS calcd for $C_{18}H_{27}O_2P$: 306.17486, found : 306.1750. Anal. calcd for $C_{18}H_{27}O_2P$: C, 70.56 ; H, 8.88. Found : C, 70.41 ; H, 8.93.

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(*Received in Belgium* 26 *April* 1995; *accepted* 26 *June* 1995)