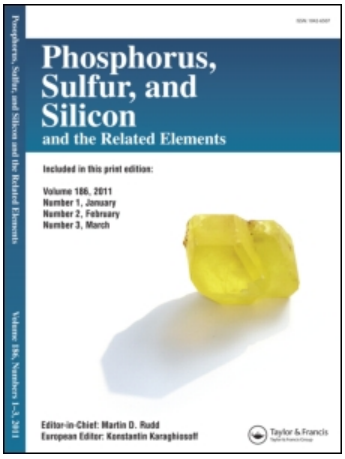

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FROM SILYLPHOSPHANES AND 2-BENZAL-1-INDANONES TO NEW PHOSPHANES, PHOSPHANE OXIDES OR SULFIDES AND PHOSPHONIUM SALTS

M. El Mkadmi[a]; M. Lazraq[a]; A. Kerbal[a]; J. Escudie[b]; C. Couret[b]; H. Ranaivonjatovo[b]
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FROM SILYLPHOSPHANES AND 2-BENZAL-1-INDANONES TO NEW PHOSPHANES, PHOSPHANE OXIDES OR SULFIDES AND PHOSPHONIUM SALTS

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Diethyl(trimethylsilyl)phosphane **1** reacts with the conjugated carbonyl moiety of 2-benzal-1-indanones **2–6** to afford exclusively 1,4-adducts **2a–6a**. Subsequent oxydation or sulfuration of most of the adducts leads to the corresponding phosphane oxides or sulfides. Further hydrolysis or reaction with HCl involves the desilylation with the formation of new (thio)phosphorylated ketones or phosphonium salts.

Keywords: Silylphosphanes; 2-benzal-1-indanones; phosphane oxides; phosphane sulfides; phosphonium salts; 1,4-additions

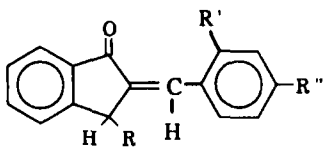
INTRODUCTION

Organophosphorus compounds play a vital role in all life forms; the compounds the most usually found are the phosphate esters, whereas there are a few derivatives with phosphorus-carbon bonds which are noteworthy for their rarity[1]. On the contrary organophosphorus poisons used in agrochemistry (pesticides) often present the RR'P(O)X moiety with phosphorus-carbon bonds and heterocyclic structures. Thus, the introduction of a phosphorus group on a carbon atom of various substrates is important in the goal to synthesize new potentially active

*Corresponding author.

derivatives. For this introduction, silylphosphanes $R_3SiPR'_2$ are convenient reagents since they easily react with α,β-ethylene carbonyl compounds; the further deprotection of the adducts (elimination of the silicon moiety) gives the phosphorus substrates.

We describe in this paper the reactivity of the silylphosphane Me_3SiPEt_2 **1** with various 2-benzal-1-indanones **2–6** and the reactivity of the adducts toward hydrolysis, oxydation, sulfuration and with HCl.

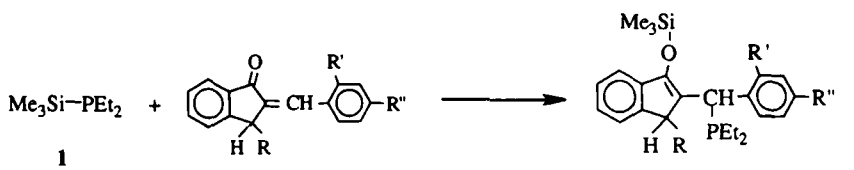


2-6

RESULTS AND DISCUSSION

Reactions of Silylphosphane 1 with 2–6

Reactions of diethyl(trimethylsilyl)phosphane **1**[2] with 2-benzal-1-indanones **2–6** lead to 1,4-adducts **2a–6a** in good yields. Only the 1,4-adducts have been obtained; the formation of the 1,2-adducts involving only the carbonyl group has never been observed:



1

R : H, R' : H, R" : OMe,	**2**
R : H, R' : H, R" : Me,	**3**
R : Me, R' : Cl, R" : H,	**4**
R : Me, R' : NO_2, R" : H,	**5**
R : Me, R' : H, R" : OMe,	**6**

R : H, R' : H, R" : OMe,	**2a**
R : H, R' : H, R" : Me,	**3a**
R : Me, R' : Cl, R" : H,	**4a**
R : Me, R' : NO_2, R" : H,	**5a**
R : Me, R' : H, R" : OMe,	**6a**

These results are in agreement with those previously reported with other α-ethylene ketones for which only the 1,4-additions have been observed[3]; note that on the contrary 1,2 and 1,4-additions sometimes occur in the reactions between **1** and α-ethylene aldehydes, although 1,4-additions are more frequent[3]. Similar 1,4-additions have also been reported by Wolfsberger et al.[4] in the reactions between the silylphosphanes Ph(R)P-$SiMe_3$ and acrylic esters CH_2 =

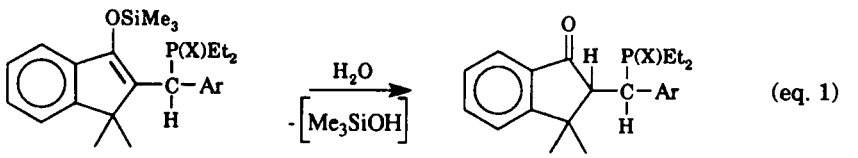
$C(R')CO_2Me$ (R': H, Me). However, in some cases, when the steric hindrance round phosphorus was high, 1,2-additions on the C=C double bond were also observed, but in minor ratio.

Adducts **4a**, **5a** and **6a** with two asymetric carbons, should be obtained in the form of two diastereoisomers: it is the case for **4a** and **6a**, whereas **5a**, according to ^{31}P NMR of the crude solution performed immediately after reaction, was obtained in the form of only one diastereoisomer. However, even when two diastereoisomers are obtained, one of them is very predominant (**4a**: 95/5, **6a**: 90/10), and only the major one could be isolated and characterized by ^{1}H and ^{13}C NMR or mass spectroscopy.

All these adducts are air- and moisture-sensitive and must be handled under inert atmosphere.

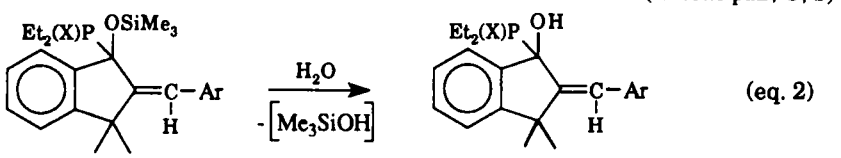
Reactivity of 2a–6a

The hydrolysis of the enoxysilane moiety leads to β-phosphorylated ketones and proves the 1,4-process of the addition (eq. 1), since in the case of a 1,2-addition (eq. 2), alcohols would be formed instead of ketones:



2a - 6a (eq. 1)

(X: lone pair, O, S)

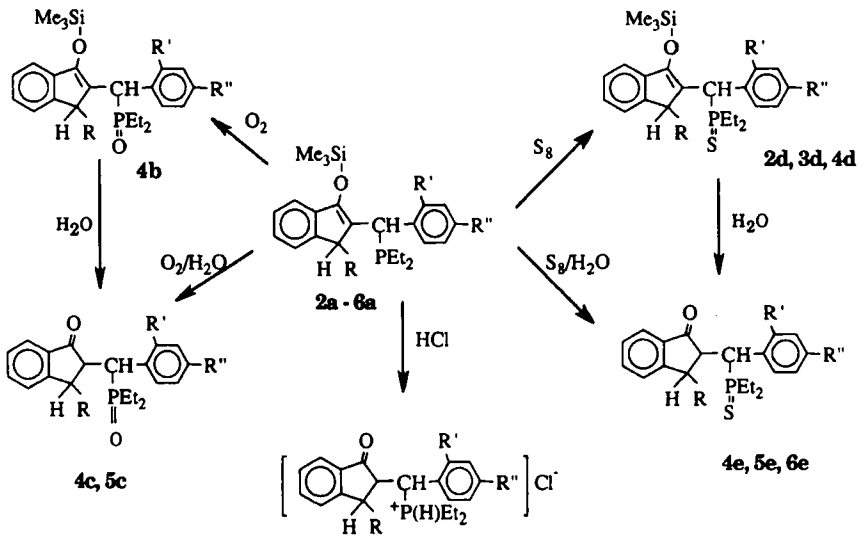


(eq. 2)

By hydrolysis a new chiral carbon is formed (carbon 2, bonded to the carbonyl group). However, only one diastereoisomer was obtained, at least in the limits of the precision of the NMR spectroscopy.

The reactivity of adducts **4a** has been thoroughly studied towards oxygen, and sulfur, in anhydrous conditions or not, and hydrochloric acid. Some of these reactions have also been performed from the other adducts **2a, 3a, 5a** and **6a.** Oxygen or sulfur give the corresponding phosphane oxides or sulfides, without

loss of the trimethylsilyl group. The desilylation, corresponding to a deprotection of the carbonyl group, can be easily obtained by hydrolysis or by reaction with hydrochloric acid to form the corresponding phosphonium salts.



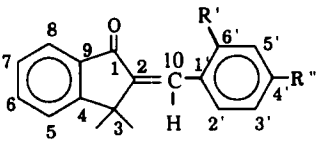
2f, 4f

R : H, R' : H, R" : OMe, 2
R : H, R' : H, R" : Me, 3
R : Me, R' : Cl, R" : H, 4
R : Me, R' : NO_2, R" : H, 5
R : Me, R' : H, R" : OMe, 6

Physicochemical Studies

^{1}H NMR Data:

Carbons are numbered according to the following scheme:



SCHEME I

The 1,4-addition was easily proved from ^1H NMR owing to the chemical shift (~4.5 ppm) and the multiplicity of the signal (doublet due to the ^2J coupling with phosphorus) for the proton bonded to carbon 10; in the case of an 1,2-adduct on the carbonyl group this proton should give a singlet at lower field since it would be on an ethylenic carbon.

In adducts **2a** and **3a**, the two protons bonded to carbon 3 give as expected an AB spectrum. When the phosphorus is tetracoordinated (compounds **2d** and **3d**) the chemical shift difference between these two protons is much larger, around 1 ppm.

The ethyl groups on phosphorus appear as a very complex multiplet in adducts **a** (generally between 0.8 and 1.5 ppm) but they become rather different when the phosphorus is tetracoordinated: in this case, the methyl and methylene groups give a wider multiplet, between ~0.8 and 2.5 ppm; moreover, methyls and methylenes are even sometimes separated (**2d**, **2f**, **4d**, **4e**, **4f**, **6e**); as the two ethyl groups are diastereotopic, each methyl appears as a doublet of triplet (coupling with phosphorus and with the protons of the methylene). Methylenes are still very complicated since their two protons are diastereotopic; thus, 64 peaks are expected for the four protons!

In two cases, **4e** and **6e**, an extremely surprising phenomenon was observed: one of the four methylenic proton resonates between 2.10 and 2.90 ppm (**4e**) or 2.61 and 2.83 ppm (**6e**) and is completely separated of the multiplets of the three other methylenic protons by about 1 ppm. This surprising signal is unambiguously attributed to one of the four methylenic protons on the basis of the integration and of decoupling experiments. Such a phenomenon, which is not observed in **5e**, is difficult to explain.

^{13}C NMR

The 1,4-addition is also proved in ^{13}C NMR since the spectra of **2a–6a** do not display any CH ethylenic carbon; the signals between 120 and 150 ppm correspond only to aromatic CH. In all compounds the $^3JC_3P$ coupling constant is larger than the $^2JC_2P$ coupling constant; the assignment of these two carbons can be made by comparison with the spectra of derivatives **2a**, **2d**, **2f** and **3a**, **3d** in which C_3 is a CH_2 instead of a CH.

^{31}P NMR

Chemical shifts are found in the normal range for compounds **a** (generally between 0 and −2 ppm, the only exception being **6a** at −8.50 and −10.12 ppm)

and for tetracoordinated phosphorus **b** or **c** (55–56 ppm) and **d** or **e** (60–63 ppm). As expected, no appreciable chemical shift difference is observed between ketones and enoxysilanes. Phosphonium salts **f** are found in the range 31–33 ppm.

EXPERIMENTAL SECTION

As the starting silylphosphane **1** and some adducts are highly air- and moisture-sensitive, their synthesis and handling require high-vacuum techniques and the use of carefully deoxygenated solvents which must be freshly distilled from sodium benzophenone.

^{1}H NMR spectra were recorded on Bruker AC 80, AC 200 and AC 250 instruments at 80.1, 200.1 and 250.1 MHz (reference: TMS) respectively; ^{13}C NMR spectra were recorded on Bruker AC 200 and AC 250 instruments at 50.3 and 62.9 MHz (reference TMS), respectively. ^{31}P NMR spectra were recorded on a Bruker AC 80 and AC 200 at 32.4 and 81.0 MHz (reference H_3PO_4), respectively. The NMR solvent was $CDCl_3$ except when another solvent is reported.

IR spectra were recorded on a Perkin-Elmer 1600 FT instrument. Mass spectra were measured on a Hewlett-Packard 5989 A spectrometer by EI at 70 eV. Melting points were determined on a Leitz microscope heating stage 350. Elemental analyses, performed by the "Service de Microanalyse de l'Ecole de Chimie de Toulouse, France" gave satisfactory results within 0.4% error and are not reported.

The starting ketones have been prepared according to: **2**[5], **3**[6], **4**[7], **5**[7], **6**[8]

Synthesis of 2a

1.35 g (5.40 mmol) of **2** was dissolved in THF (15 ml); 0.88 g (5.40 mmol) of **1**, in solution in 5 ml of the same solvent was added and the reaction mixture refluxed for 1 h. After elimination of solvents in vacuo, recrystallization from pentane gave 1.49 g (67%) of pure **2a** (mp: 90–95°C).

^{1}H NMR: 0.36 (s, $SiMe_3$), 0.70–1.70 (m, CH_3CH_2P), 3.26 (AB system, $^2J_{HH}$: 22.0 Hz, $C_{(3)}\underline{H_A}H_B$), 3.60 (AB system $^2J_{HH}$: 22.0 Hz, $C_{(3)}H_A\underline{H_B}$), 3.78 (s, OCH_3), 4.22 (d, $^2J_{HP}$: 6.9 Hz, CHP), 6.81–7.44 (m, arom. H).

^{31}P NMR: −2.0 ppm.

Synthesis of 2d

One equivalent of sulfur was added to a solution of 1.54 g (3.74 mmol) of **2a** in THF (20 ml). After 1 h at 60°C, elimination of THF and recrystallization from pentane afforded 0.96 g (58%) of **2d** (mp: 134–136°C).

^{1}H NMR: 0.33 (s, $SiMe_3$), 0.95 (dt, $^3J_{HH}$: 7.8, $^3J_{HP}$: 9.6 Hz, $C\underline{H_3}CH_2P$), 1.18 (dt, $^3J_{HH}$: 7.8, $^3J_{HP}$: 10.4 Hz, CH_3CH_2P), 1.25–2.15 (m, CH_2P), 3.39 (dd, $^2J_{HH}$: 17.6 $^4J_{HP}$: 3.6 Hz, $C_{(3)}\underline{H_A}H_B$), 3.77 (s, OMe), 4.34 (dd, $^2J_{HH}$: 17.6, $^4J_{HP}$: 3.6 Hz, $C_{(3)}H_A\underline{H_B}$), 4.55 (d, $^2J_{HP}$: 10.4 Hz, $C_{(10)}H$), 6.80–7.94 (m, arom H).

^{31}P NMR: 59.8 ppm.

MS: 372 (M, 1), 340 (M - S, 1), 310 (M - S - Et - 1), 251 (M - Et_2PS + 1, 100), 121 (Et_2PS, 80).

Synthesis of 2f

A twofold excess of HCl in solution in Et_2O (5.5 M) was added to a solution of **2a** (1.54 g, 3.74 mmol) in THF (20 ml). After elimination of solvents in vacuo, recrystallization from acetone gave 0.82 g (58%) of **2f** (mp: 162–164°C).

^{1}H NMR: 1.12 (dt, $^3J_{HH}$: 7.8, $^3J_{HP}$: 20.0 Hz, CH_3CH_2P), 1.40 (dt, $^3J_{HH}$: 7.8, $^3J_{HP}$: 20.8 Hz, CH_3CH_2P), 2.11–4.05 (m, CH_2P, $C_{(3)}H_2$ and $C_{(2)}H$), 3.68 (s, OMe), 5.58 (dd, $^2J_{HP}$: 20.4, $^3J_{HH}$: 5.3 Hz, CHP), 6.67–7.76 (m, arom H).

^{13}C NMR: 8.33 (d, $^1J_{CP}$: 5.3 Hz, $\underline{C}H_3CH_2P$), 8.66 (d, $^2J_{CP}$: 5.8 Hz, $\underline{C}H_3CH_2P$), 11.81 (d, $^1J_{CP}$: 48.8 Hz, CH_2P), 12.91 (d, $^1J_{CP}$: 43.3 Hz, CH_2P), 30.18 (d, $^3J_{CP}$: 11.8 Hz, C_3), 38.00 (d, $^1J_{CP}$: 44.8 Hz, C_{10}), 47.99 (C_2), 55.30 (OMe), 115.30 (C_3·$C_{5'}$), 122.63 (d, $^2J_{CP}$: 4.4 Hz, $C_{1'}$), 123.94 (C_7), 126.69 (C_8), 127.81 (C_5), 130.79 (d, $^3J_{CP}$: 16.1 Hz, C_2·$C_{6'}$), 135.58 (C_9), 136.10 (C_6), 155.03 (C_4), 160.17 ($C_{4'}$), 209.08 (C_1).

^{31}P NMR: 31.7 ppm.

IR: ν (PH): 2419, ν(CO): 1643 cm^{-1}.

MS: 340 (M, 20), 311 (M - Et, 1), 250 (M - Et_2PH, 100), 235 (M - Et_2PH - Me, 50).

Synthesis of 3a

1.08 g (4.62 mmol) of **3** was dissolved in 10 ml of THF; one equivalent of **1** (0.75 g) in solution in THF (5 ml) was added, and the reaction mixture was heated for 1 h at reflux. THF was eliminated in vacuo, and the crude resulting **3a** was recrystallized from pentane. 1.48 g (81%) of pure **3a** was obtained; mp: 118–120°C.

^{1}H NMR: 0.32 (s, $SiMe_3$), 0.50–1.65 (m, CH_3CH_2P), 2.29 (s, p-Me), 3.14 (AB system, $^2JH_AH_B$: 21.2 Hz, $C_{(3)}\underline{H_A}H_B$), 3.49 (AB system, $^2JH_AH_B$: 21.2 Hz, $C_{(3)}H_A\underline{H_B}$), 4.25 (d, $^2J_{HP}$: 7.8 Hz, $\overline{CH}P$), 7.16–7.95 (m, arom H).

^{31}P NMR: −1.8 ppm.

Synthesis of 3d

Sulfur (0.14 g, 25% excess) was added to 1.40 g (3.54 mmol) of **3a**, prepared as previously described, in solution in THF. After 4 h at room temperature, and 1/2 h at reflux, the solvent was eliminated in vacuo. Recrystallization from pentane afforded yellow crystals of **3d** (1.04 g, 69%; mp: 138–140°C).

^{1}H NMR: 0.33 (s, $SiMe_3$), 0.83–2.14 (m, CH_3CH_2P), 2.32 (s, p-Me), 3.34 (dd, $^2J_{HH}$: 22.3, $^4J_{HP}$: 3.2 Hz, $C\underline{H_A}H_B$), 4.35 (dd, $^2J_{HH}$: 22.4, $^4J_{HP}$: 3.2 Hz, $CH_A\underline{H_B}$), 4.59 (d, $^2J_{HP}$: 11.2 Hz, $\overline{CH}P$), 7.11–7.70 (m, arom. H).

^{13}C NMR: 1.22 ($SiMe_3$), 6.65 (d, $^2J_{CP}$: 4.4 Hz, $\underline{C}H_3CH_2P$), 7.07 (d, $^2J_{CP}$: 4.9 Hz, $\underline{C}H_3CH_2P$), 21.13 (p-Me), 22.84 (d, $^1J_{CP}$: 51.1 Hz, CH_2P), 23.53 (d, $^1J_{CP}$: 47.4 Hz, CH_2P); 36.45 (C_3), 44.13 (d, $^1J_{CP}$: 46.6 Hz, C_{10}), 118.00, 123.98, 125.09 and 125.30 (arom CH), 119.69 (d, $^2J_{CP}$: 7.0 Hz, C_2), 129.31 ($C_{3'}C_{5'}$), 129.72 (d, $^3J_{CP}$: 6.2 Hz, $C_{2'}C_{6'}$), 132.89 (d, J_{CP}: 3.4 Hz) and 137.26 and 140.54 (d, J_{CP}: 3.5 Hz) and 142.29 (C_9, $C_{1'}$, C_6, $C_{4'}$), 151.50 (C_1).

^{31}P NMR: 59.9 ppm.

MS: 428 (M, 2), 413 (M - Me, 2), 355 (M - $SiMe_3$, 2), 307 (M - Et_2PS, 100), 121 (Et_2PS, 40), 73 ($SiMe_3$, 85).

Synthesis of 4a:

To a solution of 0.50 g (1.85 mmol) of **4** in THF (20 ml) was added at room temperature one equivalent of silylphosphane **1** (0.30 g) in 5 ml of THF. Then the reaction mixture was heated at reflux of THF: the solution turned from yellow to colorless. A ^{31}P NMR showed the formation of two diastereoisomers of **4a** at δ: −2.0 (95%) and −2.8 (5%). After elimination of THF in vacuo, recrystallization from pentane gave 0.64 g (81%) of crystals of the major diastereoisomer (mp: 103–105°C).

^{1}H NMR: 0.51 (s, $SiMe_3$), 0.87–1.45 (m, $P(CH_2CH_3)_2$), 1.08 (d, $^3J_{HH}$: 7.4 Hz, $CH\underline{Me}$), 3.74 (q, $^3J_{HH}$: 7.4 Hz, $C\underline{H}Me$), 4.74 (d, $^2J_{HP}$: 6.4 Hz, CHP), 6.95–7.40 and 7.98–8.05 (m, arom H).

^{13}C NMR: 1.92 ($SiMe_3$), 9.37 (d, $^2J_{CP}$: 11.7 Hz, $\underline{C}H_3CH_2P$), 9.96 (d, $^2J_{CP}$: 14.4 Hz, $\underline{C}H_3CH_2P$), 17.34 (d, $^1J_{CP}$: 17.8 Hz, CH_2P), 17.60 ($CH\underline{C}H_3$), 17.68 (d, $^1J_{CP}$: 16.3 Hz, CH_2P), 38.70 (d, $^1J_{CP}$: 16.8 Hz, C_{10}), 41.72 (d, $^3J_{CP}$: 3.9 Hz, C_3),

117.91, 122.59, 124.89, 126.17, 126.78, 127.31 and 129.41 (arom CH), 127.40 (d, $^2J_{CP}$: 3.0 Hz, C_2), 132.12 (d, $^3J_{CP}$: 18.3 Hz, $C_{2'}$), 134.06 (d, $^3J_{CP}$: 2.6 Hz, $C_{6'}$), 139.85 (d, $^2J_{CP}$: 9.9 Hz, $C_{1'}$), 140.55 (C_9), 147.87 (C_4), 148.35 (d, $^3J_{CP}$: 3.1 Hz, C_1).

^{31}P NMR: −2.0 ppm.

Synthesis of 4b

Dry oxygen was bubbled through a solution of 0.79 g (1.84 mmol) of **4a** in THF (10 ml). After 10 min. stirring at room temperature, a ^{31}P NMR analysis showed the formation of oxide **4b**, which was also characterized by ^{1}H NMR. **4b** could not be obtained in completely pure form by crystallization.

^{1}H NMR: 0.40 (s, $SiMe_3$), 0.64 (d, $^3J_{HH}$: 7.2 Hz, CHMe), 0.90–2.30 (m, CH_3CH_2P), 4.31 (qd, ^{3}JHH: 7.2, $^4J_{HP}$: 4.0 Hz, CHMe), 5.60 (d, $^2J_{HP}$: 12.3 Hz, CHP), 7.16–7.70 and 9.15–9.45 (m, arom H).

^{31}P NMR: 55.9 ppm.

Synthesis of 4c

An excess of wet oxygen was bubbled through a solution of 0.79 g of **4a** (1.84 mmol) in THF (10 ml), then the reaction mixture was refluxed for 1 h. Purification was made by using a chromatotron with Et_2O as eluant. Recrystallization from Et_2O gave **4c** but not completely pure (purity: 95%); however **4c** was identified by its physicochemical data.

^{1}H NMR: 0.75–2.10 (m, CH_3CH_2P), 1.30 (d, ^{3}JHH: 6.9 Hz, CHMe), 2.72 (ddd, $^3J_{HH}$: 3.3 and 4.5, $^3J_{HP}$: 18.0 Hz, CHCO), 3.70–4.01 (m, CHMe), 4.34 (dd, $^3J_{HH}$: 3.3, $^2J_{HP}$: 12.0 Hz, CHP), 7.10–8.05 (m, arom H).

^{13}C NMR: 5.84 (d, $^2J_{CP}$: 5.1 Hz, CH_3CH_2P), 5.94 (d, $^2J_{CP}$: 4.5 Hz, CH_3CH_2P), 19.92 (d, $^1J_{CP}$: 66.3 Hz, CH_2P), 20.31 (CHMe), 20.70 (d, $^1J_{CP}$: 64.0 Hz, CH_2P), 36.66 (d, $^3J_{CP}$: 6.4 Hz, C_3), 38.91 (d, $^1J_{CP}$: 60.3 Hz, C_{10}), 58.28 (d, $^2J_{CP}$ 1.5 Hz, C_2), 123.78, 125.35, 127.39, 127.69, 128.95, 130.11 and 125.50 (arom CH), 131.88 (d, $^3J_{CP}$: 3.6 Hz, $C_{2'}$), 135.13 (C_9), 158.60 (C_4), 205.04 (C_1).

^{31}P NMR: 56.3 ppm.

MS: 374 (M, 5), 269 (M–Et_2PO, 46), 230 ($Et_2P(O)CH_2PhCl$, 100).

Synthesis of 4d

To a solution of 1.50 g (3.48 mmol) of **4a**, prepared as previously described, in solution in THF (30 ml), was slowly added 0.14 g (4.37 mmol) of sulfur. After

the end of the addition, the reaction mixture was refluxed during 2 h, and then the THF was eliminated in vacuo. A ^{31}P NMR analysis showed the formation of only one product. Crystallization from pentane afforded 1.14 g (71%) of **4d** (mp: 110–113°C).

^{1}H NMR: 0.41 (s, $SiMe_3$), 0.65 (d, $^{3}J_{HH}$: 7.2 Hz, HC<u>Me</u>), 0.93 (dt, $^{3}J_{HH}$: 7.8, $^{3}J_{HP}$: 12.1 Hz, $\underline{CH_3}CH_2P$), 1.16 (dt, $^{3}J_{HH}$: 7.8, $^{3}J_{HP}$: 13.1 Hz, $\underline{CH_3}CH_2P$), 1.64–2.11 (m, CH_2P), 4.27 (qd, $^{3}J_{HH}$: 7.2, $^{4}J_{HP}$: 3.5 Hz, C<u>H</u>Me), 5.30 (d, $^{2}J_{HP}$: 12.0 Hz, HCP), 7.14–7.60 and 9.03–9.15 (m, arom H).

^{13}C NMR: 1.53 ($SiMe_3$); 6.62 (d, $^{2}J_{CP}$: 4.3 Hz, $\underline{C}H_3CH_2P$), 7.15 (d, $^{2}J_{CP}$: 4.9 Hz, $\underline{C}H_3CH_2P$), 18.75 (CH<u>Me</u>), 22.76 (d, $^{1}J_{CP}$: 52.5 Hz, CH_2P), 23.77 (d $^{1}J_{CP}$: 46.0 Hz, CH_2P), 38.90 (d, $^{1}J_{CP}$: 48.7 Hz, C_{10}), 42.02 (C_3), 121.91 (d, $^{2}J_{CP}$: 8.1 Hz, C_2), 118.16, 122.84, 125.50, 125.96, 126.57, 128.95 and 129.95 (arom CH), 132.13 (d, $^{3}J_{CP}$: 6.2 Hz, $C_{2'}$), 132.89 (C_9), 134.59 (d, $^{2}J_{CP}$: 9.8 Hz, $C_{1'}$), 138.59 (d, $^{3}J_{CP}$: 4.2 Hz, $C_{6'}$), 149.75 (C_4), 150.35 (d, $^{3}J_{CP}$: 4.0 Hz, C_1)

^{31}P NMR: 63.4 ppm.

MS: 462 (M, 1), 447 (M–15, 1), 427 (M–Cl, 1), 355 (M–Me_3Si–Cl + 1, 3), 341 (M–Et_2PS, 100), 217 (M–CHP(S)Et_2PhCl, 5).

Synthesis of 4e

To 1.01 g of **4d** (2.19 mmol) in solution in THF was added two equivalents of water. After 1 h stirring, a ^{1}H NMR spectrum showed the formation of hexamethyldisiloxane proving the completion of the hydrolysis. Crystallization from pentane of the residue obtained after elimination of THF afforded 0.63 g (74%) of **4e** (mp: 125–128°C).

^{1}H NMR: 1.14 (td, $^{3}J_{HH}$: 7.5, $^{3}J_{HP}$: 17.6 Hz, $\underline{CH_3}CH_2P$), 1.15 (td, $^{3}J_{HH}$: 7.5, $^{3}J_{HP}$: 19.0 Hz, $\underline{CH_3}CH_2P$), 1.34–1.99 (m, 3 H of $\underline{CH_2}P$), 1.47 (d, $^{3}J_{HH}$: 6.9 Hz, CH<u>Me</u>), 2.10–2.90 (m, 1 H of CH_2P), 3.38 (qdd, $^{3}J_{HH}$: 6.9, $^{4}J_{HP}$: 1.8 Hz, C<u>H</u>Me), 3.60 (ddd, $^{3}J_{HH}$: 4.6 and 6.9, $^{3}J_{HP}$: 13.0 Hz, CHCO), 4.36 (dd, $^{3}J_{HH}$: 4.6, $^{2}J_{HP}$: 18.4 Hz, CHP), 7.07–7.90 (m, arom H).

^{13}C NMR: 7.04 (d, $^{2}J_{CP}$: 8.9 Hz, $\underline{C}H_3CH_2P$), 7.15 (d, $^{2}J_{CP}$: 8.0 Hz, $\underline{C}H_3CH_2P$), 18.72 (CH<u>Me</u>), 22.99 (d, $^{1}J_{CP}$: 51.3 Hz, CH_2P), 23.01 (d, $^{1}J_{CP}$: 48.8 Hz, CH_2P), 37.18 (d, $^{2}J_{CP}$: 9.6 Hz, C_3), 42.22 (d, $^{1}J_{CP}$: 47.2 Hz, C_{10}), 58.10 (C_2), 131.77 (d, $^{3}J_{CP}$: 3.4 Hz, $C_{2'}$), 123.65, 124.89, 127.37, 127.64, 129.12, 130.21, 135.20 (arom CH), 133.60 (d, J_{CP}: 1.4 Hz), 135.20 and 135.80 (C_9, $C_{1'}$ and $C_{6'}$), 157.71 (C_4), 204.81 (C_1).

^{31}P NMR: 62.4 ppm.

MS: 390 (M, 3), 355 (M–Cl, 70), 269 (M–Et_2PS, 100), 233 (M–Et_2PS–Cl–1, 85), 211 ($Et_2P(S)CHPh$ + 1, 90).

Synthesis of 4f

To a solution of **4a** (0.79 g, 1.84 mmol) in THF (10 ml) was added a threefold excess of HCl in solution in Et_2O (10 ml). After 1 h stirring at room temperature, solvents were eliminated in vacuo; crude **4f** was recrystallized from Et_2O and was obtained in the form of white needles: 0.50 g, 69%, mp: 114–116°C.

^{1}H NMR: 1.13 (td, $^3J_{HH}$: 7.8, $^3J_{HP}$: 19.9 Hz, CH_3CH_2P), 1.44 (td, $^3J_{HH}$: 7.8, $^3J_{HP}$: 21.5 Hz, CH_3CH_2P), 1.60 (d, $^3J_{HH}$: 6.9 Hz, CHMe), 2.18–3.65 (m, CH_2P, and CHCO), 5.67 (dd, $^2J_{HP}$: 21.3 Hz, $^3J_{HH}$: 5.5 Hz, CHP), 7.15–7.64 (m, arom H). **^{13}C NMR**: 7.92 (d, $^2J_{CP}$: 5.8 Hz, CH_3CH_2P), 8.58 (d, $^2J_{CP}$: 5.3 Hz, CH_3CH_2P), 11.92 (d, $^1J_{CP}$: 47.8 Hz, CH_2P), 13.47 (d, $^1J_{CP}$: 44.4 Hz, CH_2P), 16.18 (CHMe), 33.31 (d, $^1J_{CP}$: 46.7 Hz, C_{10}), 36.81 (d, $^3J_{CP}$ 11.1 Hz, C_3), 56.72 (C_2), 123.73–136.35 (arom C), 158.67 (C_4), 207.24 (C_1).

^{31}P NMR: 32.5.

IR: ν(PH): 2276 cm^{-1}, ν(CO): 1706 cm^{-1}.

Synthesis of 5c

To 0.87 g (3.12 mmol) of **5** in solution in THF (15 ml) was added a solution of 0.51 g (3.12 mmol) of silylphosphane **1** in THF (10 ml); then the reaction mixture was refluxed for 1 h: a ^{31}P NMR analysis showed the complete disappearance of **1** and the formation of the expected adduct **5a** was proved by its chemical shift in ^{31}P NMR (δ: −0.5 ppm) and by ^{1}H NMR:

0.51 (s, $SiMe_3$), 0.56–1.80 (m, CH_3CH_2P), 1.07 (d, $^3J_{HH}$: 7.2 Hz, CHMe), 3.37 (q, $^3J_{HH}$: 7.2 Hz, CHMe), 4.86 (d, $^2J_{HP}$: 5.9 Hz, CHP), 7.05–7.80 and 8.11–8.17 (m, arom H).

However, **5a** could not be obtained in pure form by recrystallization; thus, it was oxidized directly by an excess of wet oxygen which was bubbled through the reaction mixture; after elimination of THF in vacuo, **5c** was purified with a chromatotron, using Et_2O as eluant. Recrystallization from pentane gave 0.71 g (59%) of **5c**, mp: 105°C.

^{1}H NMR: 0.83–1.95 (m, CH_3-CH_2P), 1.37 (d, $^3J_{HH}$: 6.9 Hz, CHMe), 2.95 (ddd, $^3J_{HP}$: 18.9 Hz, $^3J_{HH}$: 4.80, CHCO), 4.12 (qd, $^3J_{HH}$: 4.8 and 6.9 Hz, CHMe), 4.38 (dd, $^3J_{HH}$: 4.8, $^2J_{HP}$: 13.2 Hz, CHP), 7.24–8.45 (m, arom H).

^{13}C NMR: 5.77 (d, $^2J_{CP}$: 5.3 Hz, CH_3CH_2P), 5.97 (d, $^2J_{CP}$: 4.5 Hz, CH_3CH_2P), 20.00 (d, $^1J_{CP}$: 52.2 Hz, CH_2P), 21.01 (CHMe), 21.30 (d, $^1J_{CP}$: 49.6 Hz, CH_2P), 36.88 (d, $^3J_{CP}$: 5.0 Hz, C_3), 37.50 (d, $^1J_{CP}$: 47.9 Hz, C_{10}), 58.62 (C_2), 123.93, 124.90, 125.42, 125.63, 128.48, 132.62 and 125.58 (arom CH), 131.31 ($C_{1'}$), 134.89 (C_4), 158.39 ($C_{6'}$), 204.25 (C_1).

^{31}P NMR: 55.2 ppm.

Synthesis of 5e

A solution of **1** (0.52 g, 3.18 mmol) in THF (10 ml) was added to a solution of **5** (0.89 g, 3.18 mmol) in THF. A ^{31}P NMR analysis showed the formation of the expected adduct **5a** (δ: −0.5 ppm). After 1 h stirring at room temperature, 0.12 g of sulfur was added; the reaction mixture was refluxed for 1 h, and then hydrolyzed. Recrystallization from Et_2O of the residue obtained after elimination of THF gave 0.45 g of pure **5e** (61%, mp: 123°C).

^{1}H NMR: 0.94–2.45 (m, CH_3CH_2P), 1.53 (d, $^3J_{HH}$: 6.7 Hz, CHMe), 3.33–3.68 (m, CHMe and CHCO), 4.30 (dd, $^2J_{HP}$: 13.3 Hz, $^3J_{HH}$: 5.4 Hz, CHP), 7.24–8.15 (m, arom H).

^{13}C NMR: 6.62 (d, $^2J_{CP}$: 4.5 Hz, CH_3CH_2P), 7.12 (d, $^2J_{CP}$: 4.7 Hz, CH_3CH_2P), 20.09 (CHMe), 23.05 (d, $^1J_{CP}$: 50.3 Hz, CH_2P), 24.30 (d, $^1J_{CP}$: 50.1 Hz, CH_2P), 37.86 (d, $^3J_{CP}$: 6.7 Hz, C_3), 40.05 (d, $^1J_{CP}$, 42.0 Hz, C_{10}), 57.88 (C_2), 123.88–135.51 (arom CH), 129.88 ($C_{1'}$), 135.38 (C_4), 157.91 ($C_{6'}$), 160.96 (C_5), 204.88 (d, $^3J_{CP}$: 4.6 Hz, C_1).

^{31}P NMR: 61.9 ppm.

MS: 355 (M—NO_2, 1), 256 ($NO_2PhCHP(S)Et_2$, 100).

Synthesis of 6a

To a solution of **6** (0.97 g, 3.88 mmol) in THF was added a solution of **1** (0.63 g, 3.88 mmol). A 1h reflux was necessary for the completion of the reaction. A ^{31}P NMR showed the formation of the expected adduct **6a** in the form of two diastereoisomers (ratio: 90/10). After elimination of THF, recrystallization in pentane gave 1.13 g (71%) of the mixture of the two diastereoisomers which were not separated; the major one was unambiguously characterized by NMR.

^{1}H NMR: 0.47 (s, $SiMe_3$), 0.75–1.48 (m, CH_3CH_2P), 1.08 (d, $^3J_{HH}$: 6.5 Hz, CHMe), 3.52 (q, $^3J_{HH}$: 6.5 Hz, CHMe), 3.75 (s, OMe), 4.28 (d, $^2J_{HP}$: 7.6 Hz, CHP), 6.80–7.67 (m, arom H).

^{31}P NMR: −8.5 ppm (10%), −10.1 ppm (90%).

Synthesis of 6e

To a solution of 1.21 g (2.94 mmol) of **6a**, prepared as previously described, was added one equivalent of sulfur. The reaction mixture was refluxed for 1 h and then hydrolyzed. After extraction with Et_2O and drying on Na_2SO_4, recrystallization from Et_2O gave pure **6e** (0.70 g, 64%; mp: 135–138°C).

^{1}H NMR (250 MHz): 1.14 (td, $^3J_{HH}$: 7.7, $^3J_{HP}$: 18.2 Hz, CH_3CH_2P), 1.21 (td, $^3J_{HH}$: 6.7, $^3J_{HP}$: 16.5 Hz, CH_3CH_2P), 1.46 (d, $^3J_{HH}$: 6.5 Hz, CHMe), 1.50–2.01

(m, 3 H of CH_2P), 2.61–2.83 (m, 1 H of CH_2P), 3.23 (qd, $^3J_{HH}$: 5.5 and 6.5 Hz, CHMe), 3.47 (dd, $^3J_{HH}$: 3.4, $^2J_{HP}$: 19.2 Hz, CHP), 3.60 (ddd, $^3J_{HH}$: 3.4 and 5.5 Hz, $^3J_{HP}$: 10.8 Hz, CHCO), 3.71 (s, OMe), 6.73–7.70 (m, arom H).

^{13}C NMR: 6.63 (d, $^2J_{CP}$: 4.8 Hz, CH_3CH_2P), 6.99 (d, $^2J_{CP}$: 4.9 Hz, CH_3CH_2P), 18.31 (CHMe), 22.06 (d, $^1J_{CP}$: 51.9 Hz, CH_2P), 22.76 (d, $^1J_{CP}$: 49.2 Hz, CH_2P), 37.57 (d, $^3J_{CP}$: 10.6 Hz, C_3), 47.76 (d, $^1J_{CP}$: 44.2 Hz, C_{10}), 55.23 (OMe), 57.51 (C_2), 114.32 ($C_{3'}$, $C_{5'}$), 123.65 (C_5 or C_7), 124.83 (C_7 or C_5), 126.51 (d, $^2J_{CP}$: 2.9 Hz, $C_{1'}$), 127.61 (C_8), 131.53 (d, $^3J_{CP}$: 5.20 Hz, $C_{2'}C_{6'}$), 135,10 (C_6), 136.06 (C_9), 157.76 ($C_{4'}$), 158.17 (C_4), 205.27 (C_1).

^{31}P NMR: 61.1 ppm.

MS: 386 (M, 1), 265 (M - Et_2PS, 90), 121 (Et_2PS, 100).

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