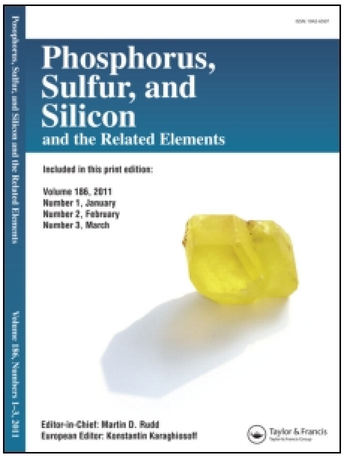

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Synthesis and Reactivity of a New 1,1-Diphenyl 2,5-Dihydrophospholium Salt

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SYNTHESIS AND REACTIVITY OF A NEW 1,1-DIPHENYL 2,5-DIHYDROPHOSPHOLIUM SALT

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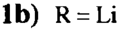
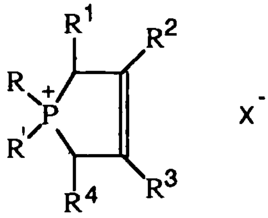
We describe the first synthesis of an unsatured cyclic diphenyl phosphonium salt of type **2**, the 1,1-diphenyl 2,5-dihydrophospholium salt **2d**. The method involves a cyclo-addition of the diphenyl halophosphine to the corresponding diene. The salt **2d** allowed the access to interesting alkadienyl phosphine oxides **4** and trienes **6**.

Key words: 2,5-Dihydrophospholium salt; alkadienyl phosphine oxides; substituted hexa-1,3,5-triene; Wittig reaction; Wittig-Horner reaction; ylide; diylide.

In the course of our investigations[1] on the optimization of Wittig reactions using the high nucleophilicity of lithium diphenyl phosphonium diylide **1b** instead of the parent classical monoylide **1a**, we now turned our attention to the chemistry of the mono and diylide derivatives of the salt **2d**. The cyclic structure would favour particular interactions between the unsaturation and the carbanionic charges resulting, respectively, of the mono- and bis-deprotonation of this starting material **2d** (the presence of two phenyl instead of alkyl groups on the phosphorus simplifies the study).

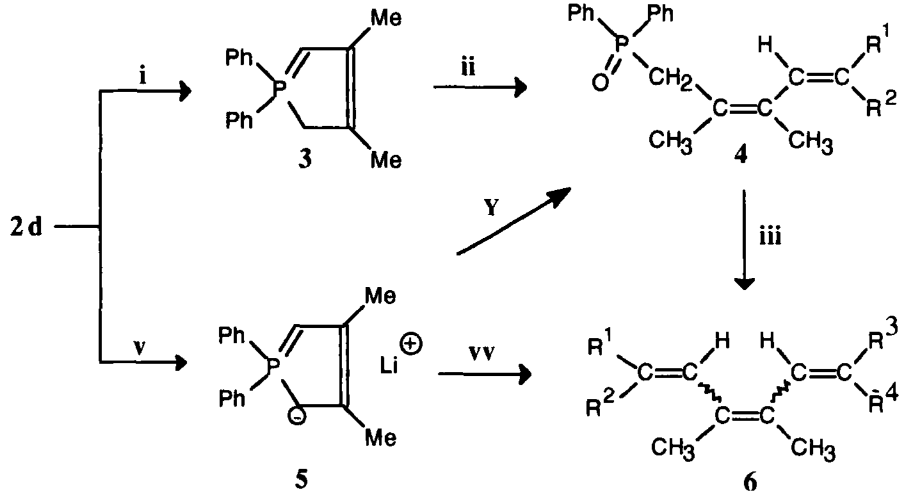


1a) R = H
1b) R = Li



2a) R = Me, R' = Bz, R^1, R^2, R^3, R^4 = H,^{ref3} Me;$^{ref\,2}$ X = Br
2b) R = R' = Me, R^1, R^2, R^3, R^4 = H,$^{ref\,6}$ Me,$^{ref\,6}$ X = Cl, I
2c) R = Ph, R' = Bz, R^1, R^3, R^4 = H; R^2= Me;$^{ref\,6}$ X = Br
2d) R = R' = Ph, R^1, R^4 = H; R^2, R^3= Me; X = Cl, I or BPh_4

It was forty years ago that the first examples of 1,1-dialkyl and 1-phenyl, 1-benzyl-2,5-dihydrophospholium salts **2** were described.[2–5] Most of them were prepared as shown by McCormack,[5] by reaction of phenyl or alkyl dihalophosphine with 1,3-dienes followed by successive reactions of hydrolysis, reduction of the obtained phospholene oxide and alkylation of the corresponding phosphine. Using the same strategy Green[6] obtained the 1,1-dimethyl and 1,1,2,5-tetramethyl 2,5-dihydrophospholium chlorides by condensation of the dimethyl phosphinous chloride with the buta-1,3-diene and the hexa-(**2E**, **4E**)-diene, respectively.



SCHEME I **1)** 1.0 eq. nBuLi in THF or 1.0 eq. tBuOK in THF; **ii)** 1.3 eq. R^1COR^2; **iii)** 1.0 eq. nBuLi in THF; 1.3 eq. R^3COR^4; **vv)** 2.0 eq. R^1COR^2 (in the obtained **6** R^1, $R^2{=}R^3$, R^4; **Y)** 1.0 eq. R^1COR^2.

In 1983, the efficient preparation of 1,1-diamino 2,5-dihydrophospholium salts was demonstrated by SooHoo[7] and Cowley,[8] as the result of the rapid 1,4-addition of different stabilized diaminophosphenium ions to 1,3-butadienes. Unfortunately this interesting synthesis does not open the way to the 1,1-diphenyl-2,5-dihydrophospholium salts 2, our challenge. Indeed the necessary diphenyl phosphenium ion was unknown,[9] and all our attempts to obtain it were unfruitful.

In this paper we wish to report a new modification of the two component cycloadditions leading to 1,1-diphenyl salt **2d**, and the first results obtained in the study of reactivity of its monoylide and diylide derivatives.

Concerning the reactivity of the monoylide **3**, it must be pointed out that Lednicer[10] already described a synthesis of trienes starting from the salt **2b** ($R{=}R'{=}Me$; $R^1{=}R^2{=}R^3{=}R^4{=}H$, $X = I$) and using consecutive Wittig (**ii**) and Wittig-Horner (**iii**) reactions; but, the yields were rather low (8–19%) and the stereochemistry undetermined.

Starting from **2d**, we hoped that the presence of the two phenyl groups linked to the phosphorus atom instead of the methyl substituents in **2b**, will allow better results. Furthermore, the salt **2d** affords the possibility to use the corresponding diylide **5** (way **y** or **vv**): the yields and stereochemistry of the resulting dienyl phosphine oxides **4** or trienes **6** may be greatly affected[1] by the different nucleophilicity of the species **3** or **5**.

Thus the 1,1-diphenyl-3,4-dimethyl-2,5-dihydrophospholium chloride (**2d**) was prepared by direct condensation of diphenyl chlorophosphine and 2,3-dimethylbuta-1,3-diene in the presence of copper stearate. This 1,4-addition goes smoothly and gives **2d** in satisfactory yields (70%), as evidenced by detailed NMR spectroscopy, microanalysis data as well as by comparison with known products **2**.

The diphenyl chlorophosphine seems to be less reactive than its analogous dimethyl compound. So the cyclization of dimethyl chlorophosphine with buta-1,3-

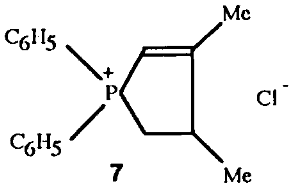
TABLE I

Products **2d** and **7** prepared from the reactions of Ph_2PCl with a diene

Product	diene[a]	r[b]	Conditions Solvent	 Temp. (°C)	 Time (d)[c]	Yield %
2d	A	1	none	60	10	30
2d	A	1	none	84	12	70
2d	A	1	toluene	84	11	30
2d	A	2	none	84	6	70
7[d]	A	1	toluene	120	11	99
7[d]	A	2	toluene	120	6	99

[a] A = 2,3-dimethyl buta-1,3-diene.
[b] Molar ratio: diene/Ph_2PCl.
[c] d = day.
[d] 7 was not obtained pure but mixed with **2d** in the ratio: 7/**2d**: 45/55.

diene in respective proportions 2.3/1.0 gives a 95% yield, after 8 days at room temperature in a sealed tube.[5] In our case the best result (Table I) was obtained at 84°C, using a particularly good candidate for Diels-Alder reaction, the 2,3-dimethylbuta-1,3-diene (ratio: 2.0/1.0). This reaction does not give better yields in a sealed tube, or at higher temperature. Moreover, the last factor may affect the stability of the prepared salt **2d**. At 120°C we observed a migration (55/45) of the double bond from the 3- to the 2-position of the dihydrophospholium ring to give the salt 7.

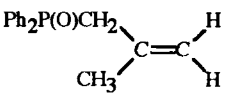

7

7- ^{1}H-nmr δppm : 7.6-8.5 (m, 10H, Ph); 6.3 (d, $^3J_{HP}$ =44Hz, 1H,CH); 3.9 (m, 2H,CH_2); 2.3 (s, 3H, CH_3); 1.4 (d, $^1J_{HH}$ =7Hz, 3H, CH_3). ^{31}P-nmr δppm : 45. 24

The new vinyl phosphonium salt 7 was identified based on ^{1}H and ^{31}P n.m.r. spectra of the mixture of the salts **2d** and **7**. At room temperature, a comparable rearrangement was described[11] in the case of the salt **2c** (R=Cl, R′=Ph, R^1=R^3=R^4=H; R^2=Me; X^- = Cl) into the corresponding vinylic salt but initiated by the basicity of the chloride anion.

The overall tested transformation of the salt **2d** can be rationalized as shown in Tables II and III. The corresponding alkadienyl diphenyl phosphine oxide **4** was obtained in a straightforward manner via a Wittig reaction.

Most of the addition of an aldehyde or a ketone to the ylide **3** afforded in good yields the corresponding alkadienyl phosphine oxide and with a good stereoselectivity the (**2Z**)-isomer. For instance regio- and stereoselective olefination was observed when the electrophile was the benzophenone and the alkadienyl phosphine oxide (**2Z**)-**4c** was obtained (Table II).



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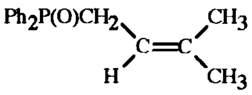

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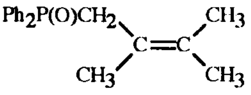


10

8- ^{1}H-nmr δppm (CH_3 m. 1.60-1.94); **9** ^{1}H-nmr δppm (CH_3 d. 1.64 (J = 5Hz) and CH_3 d. 1.45 (J = 3Hz); **10**-^{1}H-nmr δppm (CH_3 d. 1.34 (J = 2Hz) and CH_3 dd 1.67 (J = 2Hz and J = 1Hz) and CH_3 d.1.60 (J = 5Hz).

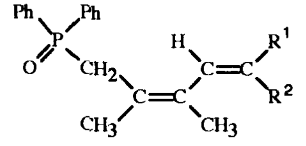
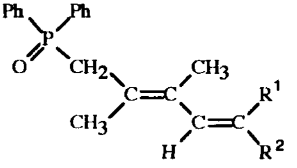
However, the benzaldehyde afforded a mixture 9:1 of two phosphine oxides **(2Z, 4Z)-4a** and **(2Z, 4E)-4a′**, respectively, and in the same manner the p-nitrobenzaldehyde afforded a mixture 3:1 of **(2Z, 4E)-4b** and **(2E, 4E)-4′b**, respectively; the isolation in pure form of the major isomer was possible in each case. The stereoselectivity could be ameliored in regard to the true basicity of the solution of nBuLi,[12] since we observed the possible isomerisation of the compound **(2Z, 4E)-4b** into the phosphine oxide **(2E, 4E)-4′b**, in basic conditions.

The different isomers **4** are identified by ^{1}H nmr spectroscopy, in accordance with the literature for the phosphine oxides **8** and **9**,[13] and for the presently synthesized phosphine oxide **10**. This new compound was prepared by basic hydrolysis of the salt **2d**. In the case of the phosphine oxides **(2Z, 4Z)-4a** and **(2Z, 4E)-4a′**, using in the way **i)** tBuOK instead of nBuLi we obtained a mixture of these two isomers in the ratio 71/29 with an easily analysable spectrum.

Now, concerning the way **iii**, the anion from the phosphine oxide **(2Z)-4c** was formed by addition of 1.0 eq. of n-butyllithium at −78°C in THF. Reacting it with benzophenone gave the pure (3Z)-3,4-dimethyl 1,1,6,6-tetraphenyl hexa-1,3,5-triene (**6c$_1$**). The same anion gave on reaction with benzaldehyde a crude product which was chromatographed on silica gel to afford a mixture of two isomers the (3Z, 5E)-3,4-dimethyl 1,1,6-triphenyl hexa-1,3,5-triene, (**6c$_2$**) and the (3E, 5E)-3,4-dimethyl

TABLE II

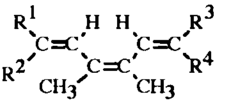
Alkadienyl phosphine oxides **4** obtained

Products	 **4**			 **4′**		
	R^1	R^2	Yld%	R^1	R^2	Yld%
(2Z,4Z)-4a	H	Ph	59^a			
(2Z,4E)-4a′	Ph	H	6^b			
(2Z,4E)-4b	$pNO_2C_6H_4$	H	53^a			
(2E,4E)-4′b				H	$pNO_2C_6H_4$	17^b
(2Z)-4c	Ph	Ph	70^a			
(2E)-4′c				Ph	Ph	10^c

[a]Obtained by the way **ii** using nBuLi as base and isolated as pure compounds.
[b]Obtained by the way **ii** using nBuLi as base and not isolated.
[c]Obtained by the way **iii** as by-product and isolated as pure compound.

TABLE III

Synthesis of trienes **6** from alkadienyl phosphine oxide **4** (way **iii**) or from diylide **5** (way vv)



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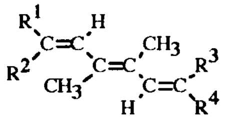

6'

Starting Compound	Electrophile (n. eq)^{a}	Obtained trienes	R^1	R^2	R^3	R^4	%^{c}
(2Z) - **4c**	Ph C(O) Ph (1.3 eq)	**(3Z)-6 c_1)**^{b}	**Ph**	**Ph**	**Ph**	**Ph**	75
(2Z) - **4c**	Ph C(O) H (1.3 eq)	**(3Z,5E)-6 c_2)**^{b} **(3E,5E)-6'c_2**	**Ph** **Ph**	**Ph** **Ph**	**Ph** **Ph**	**H** **H**	60
(2Z) - **4c**	p.MeOPh C(O) Ph (1.3 eq)	**(3Z,5E)-6 c_3)**^{b} **(3E,5E)-6' c_3**	**Ph** **Ph**	**Ph** **Ph**	**pMeOPh** **pMeOPh**	**H** **H**	85
5	Ph C(O) H (2.5 eq)	**(1E,3Z,5E)-6 a)**^{b}	**Ph**	**H**	**Ph**	**H**	25
5	Ph C(O) Ph (2.5 eq)	**(3Z)-6 c_1)**^{b}	**Ph**	**Ph**	**Ph**	**Ph**	16
5	9-Fluorenone (2.5eq)	**(3Z)-6 d)**^{b}	**9-fluorenyl**		**9-fluorenyl**		8

[a] n = molar ratio; electrophile/starting material.
[b] The triene was isolated in pure form.
[c] Yield.

1,1,6-triphenyl hexa-1,3,5-triene, (**6'**c_2) in 80% overall yield. The presence in the molar ratio /84/16/ of (**3Z, 5E)-6**c_2 and (**3E, 5E)-6'**c_2, respectively, were revealed by CPV/mass and ^1H nmr spectra. The recrystallisation in a mixture of benzene and ethanol allowed the isolation of the major isomer (**3Z, 5E)-6**c_2. In the same manner, Horner-Wittig olefination of (**2Z)-4c** with p-methoxybenzaldehyde afforded a mixture of the following derivatives: the (**3Z, 5E**)-1,1-diphenyl 6-(p-methoxyphenyl) 3,4-dimethyl hexa-1,3,5-triene (**6**c_3) and the (**3E, 5E**)-1,1-diphenyl 6-(p-methoxyphenyl) 3,4-dimethyl hexa-1,3,5-triene (**6'**c_3); the major isomer (**3Z, 5E)-6**c_3 was isolated in high yield. The study of the reactivity of the corresponding anions of other synthesized alkadienyl phosphine oxides **4** is still in progress.

An alternative route to trienes **6** was attempted (way v) by conversion of **2d** into the diylide **5**, followed by the reaction of the obtained diylide with two equivalents of benzaldehyde (way vv). But ^{31}P nmr spectra of the resulting compounds of the reaction of 2.0 eq. of nBuLi with 1.0 eq. of salt **2d**, showed that partial bis-deprotonation of the phosphonium salt **2d** had occurred. Indeed the signal of the monoylide **3** (well identified by a singlet at -25 ppm) was present (40%), and the lithiated reagent **5** (perhaps existing in different types of complexes)[14] gave rise to several signals centered at -8 (± 0.2) ppm. We are searching the best conditions in order to obtain exclusively one signal at -8 ppm. In this present condition the way **vv**) gave three compounds. The major one was the phosphine oxide **(2Z, 4Z)-4a** (40%) accompanied by the (2,3,5-trimethyl hexa-2,4-diene) diphenyl phosphine oxide (**10**) and in low yield (24%) the (**1E, 3Z, 5E**)-3,4-dimethyl 1,6-diphenyl hexa-1,3,5-triene (**6a**) isolated as a pure compound. Nevertheless, this result is promising. The assignment of (**1E, 3Z, 5E**) geometry to this triene **6a** was based on the chemical shift of their vinylic protons.

In the same manner, the addition of two equivalents of benzophenone to the diylide **5** furnished after chromatography the (**3Z**)-3,4-dimethyl 1,1,6,6-tetraphenyl hexa-1,3,5-triene, (**6c$_1$**) in 16% yield and the two phosphine oxides (**2Z, 4E**)**-4b** (35%) and **10** (30%).

Further studies are now in progress to improve the synthesis of the diylide **5** and the stereoselectivity of these one-pot consecutive Wittig reactions.

EXPERIMENTAL

Diphenylchlorophosphine was used immediately after distillation. Solvents were purified and dried by standard methods before use. All reactions that required an inert atmosphere were carried out under dry nitrogen. NMR spectra were obtained from Bruker AC at 250 MHz or Bruker AC at 200 MHz for ^{1}H with TMS as an external standart and from Bruker WP at 81 MHz for ^{31}P with 85% H_3PO_4 as an external standart, and from Bruker WP at 50.32 MHz for ^{13}C with $CDCl_3$ as an internal standart. Mass spectra were obtained on a Jeol JMS-DX-300 and GC was carried out on a Hewlett Packard-5890 instrument equipped with a OV-17 capillary column (30 m × 0.25 mm).

*Synthesis of the 1,1-diphenyl 3,4-dimethyl 2,5-dihydrophospholium chloride, or iodide, or tetraphenylborate (**2d**).* 20 ml (0.11 mol) of diphenylchlorophosphine, 24.8 ml (0.22 mol) of 2,3-dimethyl butadiene, and 5 mg of copper stearate were stirred six days at 84°C; the white adduct was centrifugated under nitrogen stream, then washed with 100 ml of pentane. The product was dried under vacuum (50°C, 80 mmHg). Analytical sample was obtained as tetraphenylborate exchanging the anion Cl^- by Ph_4B^-, using $NaPh_4B$ in methanolic solution. In the same manner, using an aqueous sodium iodide, the anion Cl^- was exchanged by I^- in chloroformic solution and the iodide obtained was recrystallized from $CHCl_3$/EtOAc ($C_{18}H_{20}PI$):

Yield: 70%. m.p. = 143.8°C; ^{31}P NMR ($CDCl_3$): δ ppm; s, 34.2, ^{1}H NMR ($CDCl_3$): δ ppm 8.30–7.80 (m, 4H, Ph), 7.70–7.60 (m, 6H, Ph), 3.9 (d, $^2J_{PH}$ = 10.0 Hz, 4H, CH_2), 1.8 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$): δ ppm; 135.2 (d, $^4J_{PC}$ = 3.2 Hz, 2C, Cp), 133.1 (d, $^3J_{PC}$ = 12.9 Hz, 4C, Cm), 130.7 (d, $^2J_{PC}$ = 10.6 Hz, 4C, Co), 128.7 (d, $^2J_{PC}$ = 6.9 Hz, 2C, C_2), 119.1 (d, $^1J_{PC}$ = 82.1 Hz, 2C, Ci), 35.4 (d, $^1J_{PC}$ = 54.3 Hz, 2C, C_1), 16.8 (d, $^3J_{PC}$ = 13.0 Hz, 2C, C_3). F.A.B.$^+$ m/z = 267. Analysis ($C_{42}H_{40}BP$) m.p. = 193.9°C; %Calc.: C 86.0, H 6.9, %Found.: C 86.1, H 7.0.

*Synthesis of 1,1-diphenyl 3,4-dimethyl 2H-phosphole (**3**):* ^{n}Butyllithium (1.6 M. in hexane, 6.2 ml, 10 mmol), was added to **2d** (4.0 g, 10 mmol) in dry tetrahydrofuran (THF, 40 ml) at -80°C and after 30 min of stirring at this temperature, a sample of **3** was analyzed; ^{31}P NMR (THF) δ ppm: s, -25.0.

*Other synthesis of 1,1-diphenyl 3,4-dimethyl 2H-phosphole (**3**):* tBuOK (0.28 g, 25 mmol) was added to **2d** (1.0 g, 25 mmol) in dry tetrahydrofuran (THF, 40 ml) at -80°C and after 30 min of stirring at this temperature, a sample of **3** was analyzed; ^{31}P NMR (THF) δ ppm: s, -25.0.

*Synthesis of dienyl phosphine oxides (**4a–4c**): General procedure.* The solution of **3** (obtained by the nBuLi method) was cooled to -50°C and the electrophile (15 mmol) added. The mixture was allowed to warm to room temperature and to react 72 h. After neutralization with aqueous NH_4Cl (saturated), THF was evaporated, then the aqueous solution was extracted with ether (3 × 100 ml). After drying and evaporation of the solvent of the organic phase, crude **4** was obtained. In most of the cases pure **4** was isolated by column chromatography (Silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$).

*(**2Z, 4Z**)-1,1-diphenyl 2,3-dimethyl 5-phenyl pentadi-2,4-enyl phosphine oxide (**4a**):* Using benzaldehyde (1.52 ml; 15 mmol), the crude product obtained was a mixture (9:1) of two isomers (**2Z, 4Z**)**-4a** and (**2Z, 4E**)**-4a′** Yield: 70%. Pure (**2Z, 4Z**)**-4a** was obtained by column chromatography:

Yield: 55%. ^{31}P NMR ($CDCl_3$): δ ppm 30.8; ^{1}H NMR ($CDCl_3$): δ ppm 8.09–7.68 (m, 4H, Ph); 7.55–7.33 (m, 6H, Ph); 7.32–7.15 (m, 5H, Ph); 6.21 (d, $^3J_{HH}$ = 11.1 Hz, 1H, =CH); 5.80 (d, $^3J_{HH}$ = 11.0 Hz, 1H, =CH); 3.22 (d, $^2J_{PH}$ = 14.3 Hz, 2H, CH_2); 1.87 (d, $^4J_{PH}$ = 1.1 Hz, 3H, CH_3); 1.65 (d, $^5J_{PH}$ = 4.8 Hz, 3H, CH_3); GC/MS m/z = 372. Analysis ($C_{25}H_{25}OP$); %Calc.: C 80.62, H 6.77, O 4.30; %Found.: C 80.62, H 6.90, O 4.80.

*Mixture of the (**2Z, 4Z**)-1,1-diphenyl 2,3-dimethyl 5-phenyl pentadi-2,4-enyl phosphine oxide (**4a**) and the (**2Z, 4E**)-1,1-diphenyl 2,3-dimethyl 5-phenyl pentadi-2,4-enyl phosphine oxide (**4a'**):* Adding to the ylide **3** (2.5 mmol) obtained by the tBuOK method, benzaldehyde (0.25 ml; 2.5 mmol), a mixture (6:4) of two isomers (**2Z, 4Z**)-**4a** and (**2Z, 4E**)-**4a'** was obtained by column chromatography (Silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$):

Yield: 73%. ^{31}P NMR ($CDCl_3$): δ ppm 30.3 and 29.5; ^{1}H NMR ($CDCl_3$): δ ppm 8.09–7.68 (m, 4H, Ph); 7.55–7.33 (m, 6H, Ph); 7.32–7.15 (m, 5H, Ph); 6.21 (d, $^3J_{HH}$ = 11.1 Hz, 1H, =CH); 5.80 (d, $^3J_{HH}$ = 11.0 Hz, 1H, =CH); 3.22 (d, $^2J_{PH}$ = 14.3 Hz, 2H, CH_2); 1.87 (d, $^4J_{PH}$ = 1.1 Hz, 3H, CH_3); 1.65 (d, $^5J_{PH}$ = 4.8 Hz, 3H, CH_3); and 8.09–7.68 (m, 4H, Ph); 7.55–7.33 (m, 6H, Ph); 7.32–7.15 (m, 5H, Ph); 6.80 (d, $^3J_{HH}$ = 15.6 Hz, 1H, =CH); 6.37 (d, $^3J_{HH}$ = 15.6 Hz, 1H, =CH); 3.43 (d, $^2J_{PH}$ = 14.7 Hz, 2H, CH_2); 1.96 (d, $^4J_{PH}$ = 4.7 Hz, 3H, CH_3); 1.85 (d, $^5J_{PH}$ = 3.7 Hz, 3H, CH_3); GC/MS m/z = 372.

*(**2Z, 4E**)-1,1-diphenyl 2,3-dimethyl 5-(p-nitrophenyl) pentadi-2,4-enyl phosphine oxide (**4b**):* Using p-nitro benzaldehyde (2.25 g; 1.5 mmol), the crude product obtained was a mixture (2:1) of two isomers (**2Z, 4E**)-**4b** and (**2E, 4E**)-**4'b**:

Yield: 70%. Pure (**2Z, 4E**)-**4b** was obtained by recrystallisation (acetone); m.p. °C = 192, ^{31}P NMR ($CDCl_3$): δ ppm 29.2; ^{1}H NMR ($CDCl_3$): δ ppm 8.11 (d, $^3J_{HH}$ = 9.0 Hz, 2H, pNO_2Ph); 7.82–7.71 (m, 4H, Ph); 7.47–7.39 (m, 6H, Ph); 7.30 (d, $^3J_{HH}$ = 9.0 Hz, 2H, pNO_2Ph); 7.01 (d, $^3J_{HH}$ = 15.8 Hz, 1H, =CH); 6.37 (d, $^3J_{HH}$ = 15.8 Hz, 1H, =CH); 3.48 (d, $^2J_{PH}$ = 14.8 Hz, 2H, CH_2); 1.91 (d, $^5J_{PH}$ = 4.7 Hz, 3H, CH_3); 1.88 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): 146.0 (s, 1C, $C_{p'}$); 144.8 (s, 1C, $C_{i'}$); 132.7 (d, $^1J_{PC}$ = 97.6 Hz, 2C, C_i); 132.3 (d, $^4J_{PC}$ = 4.9 Hz, 1C, C_4); 131.9 (d, $^4J_{PC}$ = 2.8 Hz, 2C, C_p); 131.0 (d, $^3J_{PC}$ = 10.1 Hz, 1C, C_3), 130.9 (d, $^2J_{PC}$ = 9.2 Hz, 4C, C_o); 129.6 (d, $^2J_{PC}$ = 11.8 Hz, 1C, C_2); 128.5 (d, $^3J_{PC}$ = 11.6 Hz, 4C, C_m); 126.6 (s, 2C, $C_{m'}$), 124.9 (d, $^5J_{PC}$ = 3.1 Hz, 1C, C_5), 123.8 (s, 2C, $C_{o'}$); 37.6 (d, $^1J_{PC}$ = 65.0 Hz, 1C, C_1); 22.9 (d, $^4J_{PC}$ = 2.1 Hz, 1C, $C_{4'}$); 14.6 (d, $^3J_{PC}$ = 2.9 Hz, 1C, $C_{3'}$); GC/MS m/z = 417.

*(**2Z**)-1,1-diphenyl 2,3-dimethyl 5,5-diphenyl pentadi-2,4-enyl phosphine oxide (**4c**):* Using benzophenone (2.73 g; 15 mmol), the pure product was obtained by chromatography:

Yield: 70%. ^{31}P NMR ($CDCl_3$): δ ppm 29.6; ^{1}H NMR ($CDCl_3$): δ ppm; 7.83–6.84 (m, 20H, Ph); 6.34 (s, 1H, =CH); 3.30 (d, $^2J_{PH}$ = 14.4 Hz, 2H, CH_2); 1.86 (d, $^4J_{PH}$ = 2.9 Hz, 3H, CH_3); 1.36 (d, $^5J_{PH}$ = 4.9 Hz, 3H, CH_3); ^{13}C NMR ($CDCl_3$): 143.7–126.1 (m, 28 C, Ph, C_2, C_3, C_4, and C_5); 37.5 (d, $^1J_{PC}$ = 67.7 Hz, 1C, C_1); 20.7 (d, $^4J_{PC}$ = 1.5 Hz, 1C, $C_{2'}$); 18.9 (d, $^3J_{PC}$ = 2.7 Hz, 1C, $C_{3'}$); GC/MS m/z = 448.

*1,1-diphenyl 2,3-dimethyl but-2-enyl phosphine oxide (**10**).* ^{n}Butyllithium (1.6 M in hexane, 3.1 ml, 5 mmol) was added to **2d** (2.0 g, 5 mmol) in dry THF (40 ml) at −80°C and after 30 min of stirring at this temperature, the mixture was warmed to room temperature and hydrolyzed by 0.1 N HCl (50 ml) to give, after column chromatography (Silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$), phosphine oxide **10** with 80% yield:

^{31}P NMR ($CDCl_3$): δ ppm 29.9; ^{1}H NMR ($CDCl_3$): δ ppm 8.00–7.41 (m, 10H, Ph); 3.20 (d, $^2J_{PH}$ = 14.2 Hz, 2H, CH_2); 1.71 (s, 3H, CH_3); 1.62 (d, $^4J_{PH}$ = 5.2 Hz, 3H, CH_3); 1.35 (s, 3H, CH_3).

*Synthesis of trienes **6c**: General procedure (way **iii**):* ^{n}Butyllithium (1.4 ml, 2.2 mmol, 1.6 M in hexane) was added to a solution of (**2Z**)-**4c** (1.0 g, 2.2 mmol) in dry tetrahydrofuran (THF, 20 ml) at −50°C and after 30 min of stirring at this temperature, the electrophile added. The mixture was allowed to warm to room temperature and to react 72 h. After neutralization with aqueous NH_4Cl (saturated), THF was evaporated then the aqueous solution was extracted with ether (3 × 100 ml). After drying and evaporation of the solvent of the organic phase, most of the part of crude **6** was isolated by precipitation in acetone and purified by recrystallization in benzene/ethanol. The acetone solutions were concentrated to dryness. The residue was taken up in CH_2Cl_2 and column chromatographed (Silicagel, CH_2Cl_2/C_6H_{14}) yielding a second crop of the triene **6c**.

*Synthesis of trienes **6a**, **6c** and **6d**. General procedure (way **vv**):* A solution of **5** was obtained by adding ^{n}Butyllithium (1.6 M in hexane, 12.4 ml, 20 mmol) to a suspension of salt **2d** (4.0 g, 11 mmol) in dry tetrahydrofuran (40 ml) maintained at −80°C during 30 min. Then the solution was warmed to −50°C and the electrophile (25 mmol) was added. The mixture was allowed to warm to room temperature and to react 72 h. After neutralization with aqueous NH_4Cl (saturated), THF was evaporated, then the aqueous solution was extracted with ether (3 × 200 ml). After drying and evaporation of the solvent of the organic phase, most of the part of crude **6** was isolated by precipitation in acetone and purified by recrystallization in benzene/ethanol. The acetone solutions were concentrated to dryness. The residue was taken up in CH_2Cl_2 and chromatographed (Silicagel, CH_2Cl_2/C_6H_{14}) yielding a second crop of the triene **6**.

*Synthesis of (***3Z***)-1,1,6,6-tetraphenyl 3,4-dimethyl hexatri-1,3,5-ene (***6c**$_1$*):* As indicated in the general procedure (way **iii**), using **(2Z)-4c** (1.0 g; 2.2 mmol) and as electrophile benzophenone (0.6 g; 3.3 mmol), was obtained the alkadienyl phosphine oxides **4c** and **4'c**; accompanied by the trienyl compound **(3Z)-6c**$_1$, isolated by column chromatography (Silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$) as a pure compound.

Yield: 75% m.p. °C = 114.6; ^1H NMR ($CDCl_3$): δ ppm 7.4–7.2 (m, 20H, Ph); 6.7 (s, 2H, =CH); 1.5 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$): 143.6 (s); 142.0 (s); 141.1 (s); 133.3 (s); 130.6 (s); 130.2 (s); 128.0 (s); 127.9 (s); 127.8 (s); 127.2 (s); 127.1 (s); 19.3 (s, 2C, CH_3); GC/MS m/z = 412; Analysis $C_{32}H_{28}$; %Calc.: C 92.16, H 6.84; %Found.: C 92.26, H 6.90.

*(***2E***)-1,1-diphenyl 2,3-dimethyl 5,5-diphenyl pentadi-2,4-enyl phosphine oxide (***4'c***):* In the preceding synthesis there was formation of the alkadienyl phosphine oxide **4'c**, isolated by chromatography:

Yield: 10%. ^{31}P NMR ($CDCl_3$): δ ppm 30.6; ^1H NMR ($CDCl_3$): δ ppm 7.83–6.84 (m, 20H, Ph); 6.34 (s, 1H, =CH); 3.30 (d, $^2J_{PH}$ = 14.4 Hz, 2H, CH_2); 1.77 (d, $^4J_{PH}$ = 1.0 Hz, 3H, CH_3); 1.30 (s, 3H, CH_3); GC/MS m/z = 448.

*Synthesis of the (***3Z, 5E***)-1,1,6-triphenyl-3,4-dimethyl hexatri-1,3,5-ene (***6c**$_2$*):* As indicated in the general procedure (way **iii**), using **(2Z)-4c** (1.0 g; 2.2 mmol) and as electrophile benzaldehyde (0.34 ml; 3.3 mmol) was obtained with 80% yield a mixture (21/4) of trienes **(3Z, 5E)-6c**$_2$ and **(3E, 5E)-6'c**$_2$, respectively. The triene **(3Z, 5E)-6c**$_2$ was isolated and purified by recrystallization m.p. °C = 130.9 (benzene/ethanol):

Yield: 60%. ^1H NMR ($CDCl_3$) δ ppm: 7.5–7.2 (m, 16H, Ph and =CH); 6.8 (s, 1H, =CH); 6.6 (d, J_{HH} = 16 Hz, 1 H, =CH); 1.98 (s, 3H, CH_3); 1.73 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): 18.2 (s, 1C, CH_3) 15.3 (s, 1C, CH_3). GC/MS m/z = 336.

*Synthesis of the (***3Z, 5E***)-1,1-diphenyl 6-(p-methoxyphenyl) 3,4-dimethyl hexatri-1,3,5-ene (***6c**$_3$*):* As indicated in the general procedure (way **iii**), using **(2Z)-4c** (1.0 g; 2.2 mmol) and as electrophile p-methoxybenzaldehyde (0.41 ml; 3.3 mmol) was obtained with 97% yield a mixture of **(3Z, 5E)-6c**$_3$ and **(3E, 5E)-6'c**$_3$, respectively 90/10. The pure **(3Z, 5E)-6c**$_3$ was isolated by recrystallization m.p.°C = 107.1 (benzene/ethanol):

Yield: 85%. ^1H NMR ($CDCl_3$): δ ppm 7.3–7.2 (m, 14H, Ph); 7.1 (d, $^3J_{HH}$ = 15.3 Hz, 1H, =CH); 6.9 (s, 1H, =CH); 6.6 (d, $^3J_{HH}$ = 15.7 Hz, 1H, =CH); 3.8 (s, 1H, OCH_3); 1.95 (s, 3H, CH_3); 1.69 (s, 3H, CH_3); GC/MS m/z = 366. Analysis $C_{27}H_{26}O$; %Calc.: C 88.48, H 7.15, O 4.37; %Found.: C 88.64, H 7.05, O 4.35.

*Essay of preparation of a solution of lithium 1,1-diphenyl 2,4-dimethyl 2H-phosphol-2-ylide (***5***):* ^{n}Butyllithium (1.6 M in hexane, 12.4 ml, 20 mmol) was added to **2d** (4.0 g, 11 mmol) in dry tetrahydrofuran (THF, 40 ml) at −80°C and after 1 h of stirring at this temperature a sample of **5** was analyzed:

^{31}P NMR (THF) δ ppm: (m, −8.5) and (s, −25.0).

*Synthesis of the (***1E, 3Z, 5E***)-3,4-dimethyl 1,6-diphenyl hexatri-1,3,5-ene (***6a***):* As indicated in the general procedure (way **vv**), using the solution containing **5** and as electrophile benzaldehyde (1.93 ml; 19 mmol) was obtained, after column chromatography:

With 25% yield the triene **(1E, 3Z, 5E)-6a** m.p. °C = 182; ^1H NMR ($CDCl_3$) δ ppm: δ 7.6–7.1 (m, 10H, Ph); 6.5 (d, J_{HH} = 16.2 Hz, 1H, =CH); 5.9 (d, J_{HH} = 16.2 Hz, 1H, =CH); 1.5 (s, 3H, CH_3); 1.4 (s, 3H, CH_3); GC/MS m/z = 260, Analysis $C_{20}H_{20}$; %Calc.: C 92.31, H 7.70; %Found.: C 92.26, H 7.87.

*Synthesis of (***3Z***)-1,1,6,6-tetraphenyl hexatri-1,3,5-ene (***6c**$_1$*):* As indicated in the general procedure (way **vv**), using the solution containing **5** and as electrophile benzophenone (3.46 g; 19 mmol) was obtained with 16% yield the sole compound **(3Z)-6c**$_1$.

Synthesis of the (3Z)-3,4-dimethyl 1,1,6,6-bis(9,9-fluorenyl) hexatri-1,3,5-ene **(6d)**. As indicated in the general procedure (way **vv**), using the solution containing **5** and 9-fluorenone as electrophile (3.4 g; 19 mmol) was obtained:

With 8% yield the triene **(3Z)-6d** m.p. °C = 228 (PhH/C_2H_5OH); ^1H NMR ($CDCl_3$) δ ppm: δ 7.9–7.3 (m, 18H, Ph, and =CH); 2.1 (s, 6H, CH_3); GC/MS m/z = 408. Analysis: %Calc.: C 94.12, H 5.88; %Found.: C 94.01, H 5.96.

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