Heteroatom Chemistry
Volume 7, Number 6, 1996

Behavior of 1,1-Diphenyl-2,5-dihydrophospholium Salts toward Bases: Ylide Formation or Ring Opening

Henri-Jean Cristau,* Jerôme Grenier, Patricia Lezouret, and Eliane Torreilles*

Laboratoire de Chimie Organique, Unité de Recherche associée au CNRS (ESA 5076), Ecole Nationale Supérieure de Chimie de Montpellier. 8, Rue de l'Ecole Normale, 34053 Montpellier Cedex, France

Received 28 May 1996

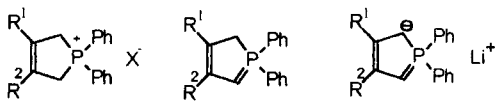
ABSTRACT

Efficient procedures are described leading to pure 3,4-R^1,R^2-substituted 1,1-diphenyl-2,5-dihydrophospholium salts ($R^1 = R^2 = CH_3$, H; $R^1 = CH_3$, R^2 = H). Their behaviors toward bases such as n*BuLi and* t*-BuOK in THF or DMSO have been examined. According to the nature of the substituents R^1 and R^2, the complete monodeprotonation of these salts leads either to the corresponding pure five-membered cyclic ylide (and, in some cases, its prototropic isomer) or to a dienylphosphine resulting from a ring opening. The reactivity of the 3,4-dimethyl-disubstituted salt was especially studied. The corresponding monoylide functions as a good Wittig reagent, allowing stereoselective access to interesting alkadienylphosphine oxides and subsequently to trienes. However, in the presence of alkylating electrophiles, it reacts under an open dienylphosphine form giving rise to P-alkylated phosphonium salts. Nevertheless, this monoylide does not undergo further deprotonation into the corresponding cyclic diylide. Most of the synthetisized derivatives are original.*

INTRODUCTION

In earlier work [1], we justified our synthetic interest in the 1,1-diphenyl-2,5-dihydrophospholium salt **1a**, its monoylide **2a**, and, moreover, its diylide **3a** (Scheme 1), expected to be a super ylide, owing to an increased nucleophilicity attributable to the presence of a negative charge in the β position [2].

Salts **1a–b** were prepared by an adaptation of a strategy previously described by McCormack [2] and Quin [3]. As depicted in Scheme 2, the chelotropic cycloaddition between diphenylchlorophosphine and 2,3-dimethyl or 2-methylbuta-1,3-diene gave good yields, respectively, of salts **1a** (70%) or **1b** (75%), after 6 or 36 days at 80°C. In the second case, the reaction was carried out in a sealed tube. We observed, accompanying **1b**, a small amount (2%) of the isomer **1'b** resulting from a migration of the double bond from the 3- to the 2-position. The salt **1b**



1 **2** **3**

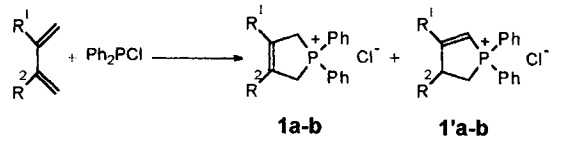
a) $R^1 = R^2$ = Me
b) R^1 = Me, R^2 = H
c) $R^1 = R^2$ = H

SCHEME 1

Dedicated to Prof. Louis D. Quin on the occasion of his retirement from the University of Massachusetts at Amherst.

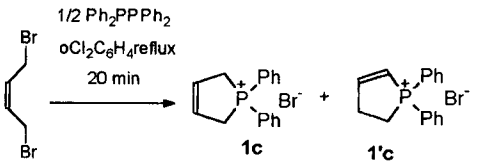
*To whom correspondence, should be addressed.

1042-7163/96/060471-10



a) $R^1 = R^2 = Me$
b) $R^1 = Me$, $R^2 = H$

SCHEME 2



SCHEME 3

was obtained in pure form after a simple recrystallization.

With an unactivated diene, the long reaction time is an obvious disadvantage of this latter method. So, to obtain salt **1c** ($R^1 = R^2 = H$), we tested another method, originally reported by Märkl [4] to provide the salt **1c** in 18% yield, after 20 minutes, by reacting tetraphenyldiphosphine with *cis*-1,4-dibromo-but-2-ene in *o*-dichlorotoluene under reflux. However, we found that, under these conditions, the salt **1c** was formed in only 2% yield, together with its isomer **1'c** (8%) and other unidentified salts (Scheme 3).

Still with the aim to synthesize **1c**, other phosphines were tried (Table 1). The use of Ph_2PSiMe_3 in *a,a'-o*-dichloroxylene had been successfully carried out by Schmidbaur [5] in the preparation of the salt **4** (Scheme 4). The best result (85% yield of pure **1c**) obtained by us was realized when Ph_2PSiMe_3 was caused to react with *cis*-1,4-dibromobut-2-ene instead of *cis*-1,4-dichlorobut-2-ene. In the latter case, a mixture (65% yield) of salt **1c** and **1'c** (in the ratio 76/24) was obtained. Poor results were observed in other attempts with Ph_2PLi or Ph_2PH.

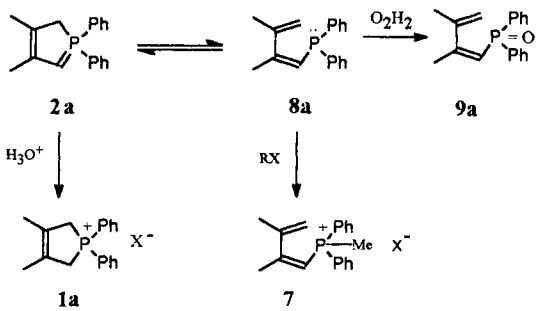
The structures of **1b** and **1c** were confirmed by classical analytical methods (IR, ^1H and ^{31}P-NMR spectroscopies and elemental analysis). They were expected to be similar to the structure of the analogous salt **5**, prepared by Quin [3b,d], by alkylation of the corresponding phosphine. Indeed, the coupling constants in the spectra of **1b** and **1c** ($^2J_{HH} \sim 0$ Hz between methylenic and vinylic protons as well as $^3J_{HP} = 27$–32 Hz between vinylic protons and phosphorus atom) were found to be very close to the coupling constants observed for the salt **5**.

TABLE 1 Synthesis of Salt **1c** via the Reaction: Ph_2P-Y + *cis*-1,4-Dibromobut-2-en

Y	*T* (°C)	*Time* (*h*)	*Yield*[a] (%)
$SiMe_3$	20	72	40[b]
$SiMe_3$	110	12	85[b]
Li	20	72	3
Li	110	12	32[b]
H	20	72	0
H	110	12	30[b]

[a]Calculated yield from ^{31}P-NMR spectra.
[b]Isolated yield.

SCHEME 4



SCHEME 5

RESULTS AND DISCUSSION

Monoylide of the Salt 1a

Presently, we believe, in opposition to the report in our preliminary publication [1], that the monodeprotonation, by a base, of the salt **1a** gives both the ylide **2a** and the phosphine **8a** in equilibrium (Scheme 5). This point of view does not change the validity of the published results on the Wittig reaction, but it is more consistent with other new results.

As indicated by the ^{31}P-NMR spectra, equimolar amounts of **1a** and *n*BuLi in THF gave one signal at $\delta = -25$, assumed to be characteristic of the ylide **2a** ($R^1 = R^2 = Me$) [1]. Indeed, in the reaction mixture, the presence of the conjugate base of **1a** was expected, since, by adding one equivalent of acid, the signal of the starting salt **1a** was quantitatively reobtained at $\delta = 35$. The existence of the ylide **2a** was also proved through its reactivity as a Wittig reagent

(Table 2). We report here an extension of the Wittig reaction to synthesize previously unknown 2,4-dienylphosphine oxides **6** (Scheme 6). With *p*-methoxybenzaldehyde, the reaction afforded in nearly quantitative yield (98%) and with complete stereoselectivity, the phosphine oxide (2*Z*,4*Z*)-**6** (R^1 = $pMeOC_6H_4$, R^2 = H). A comparable result was obtained with benzaldehyde that gave (2*Z*,4*Z*)-**6** (R^1 = Ph, R^2 = H) [1].

A mixture of (2*Z*,4*E*)-**6**/(2*E*,4*E*)-**6′** (R^1 = p-$NO_2C_6H_4$, R^2 = H) in the ratio 72/28 was obtained when *p*-nitrobenzaldehyde was used as the electrophile. The main product was isolated by column chromatography. The formation of (2*E*,4*E*)-**6** (R^1 = $pNO_2C_6H_4$, R^2 = H) is assumed to be due to the presence of base in the medium and subsequent isomerization of the compound (2*Z*,4*E*)-**6** (R^1 = p-$NO_2C_6H_4$, R^2 = H). Such basic isomerization favored by the electron-withdrawing effect of the *p*-nitrophenyl group was corroborated by a control experiment, as described in the Experimental section.

The reaction of **2a** with 9-fluorenone (Table 2) also afforded a mixture of two isomers (2*Z*)-**6**/(2*E*)-**6′** (R^1, R^2 = *o*,*o*′-biphenyl) (ratio 64/36), obtained in 98% yield (chromatography allowed the isolation of the main compound).

In contrast, benzophenone gave only the corresponding phosphine oxide (2*Z*)-**6** (R^1 = R^2 = Ph).

No isomerization occurred in the case of the reaction with heptanal; only (2*Z*,4*Z*)-**6** (R^1 = C_6H_{13}, R^2 = H) was obtained in 68% yield. The stereoselectivity was not so good with acetophenone; equimolar amounts of two phosphine oxides **6** (R^1 = Ph, R^2 = Me) were obtained (the respective stereochemistry was not established).

Finally, no reaction occurred when **2a** was treated with $PhCO_2Et$ or chalcone, and the reprotonation of each reaction mixture gave the salt **1a**.

In contrast to our expectations, *α*-alkylation of the ylide **2a** was not observed when the reaction mixture was treated with alkyl halides. ^{31}P- and ^1H-NMR spectra revealed the formation of an acyclic P-alkylated phosphonium salt **7** (Scheme 7), and the corresponding yields depended on the nature of the alkyl group (Table 3). In all cases, a complex mixture was obtained. With MeI, the major compound was the P-methylated salt **7** (R = CH_3), accompanied by a small amount of salt **1a** (5%). With a more acidic alkylating reagent, the formation of **1a** was predominant (entry 5). Furthermore, in the case of hindered alkyl halides, no reaction occurred at room temperature (entries 6 and 7), even at 45°C for *t*BuCl. At this temperature, after 5 days of contact with *i*PrBr, the protonation of **2a** was complete, and a mixture of salts **1a** and **1a′** was obtained (ratio: 73/27).

These observations support the concept of the existence of an equilibrium between the cyclic monoylide **2a** and an open form such as the dienylphosphine **8a** (Scheme 5). It must be pointed out that the signal at δ ^{31}P = −25. 0 is at higher field than the one at −12.5 of the P-spiran diphospholanium ylide known in the literature to be the most shielded [6].

No obvious temperature effect, in the −80 to +50°C range, was observed in the ^{31}P-NMR spectra on the signal at δ = −25.0; only at −40°C, a small signal at δ = −16.0 (8%) appeared and remained during all of the experiment.

However, the formation of the phosphine oxide **9a** when H_2O_2 was added to the product of the deprotonation of **1a**, is evidence of the presence of the dienylphosphine **8a**. ^1H-NMR spectra were in accord with this hypothesis, affording apparently only the signals compatible with the structure of **8a** obtained when the deprotonation of the salt **1a** by *n*BuLi was conducted in THF-(d_8).

Also, the behavior of **1a** was studied in THF in the presence of *t*BuOK. The same result was observed, with the appearance of one signal at δ ^{31}P = −25 that became two singlets at 27.4 and −26.0 in the ratio 1:4, when DMSO was added. These two signals were also present when the deprotonation of **1a** was carried out by *n*BuLi in DMSO. In all cases, the two signals mentioned earlier vanished by addition of one equivalent of benzoic acid, and then the spectra exhibited only the signal at δ = 35 corresponding to the salt **1a**. In DMSO, the downfield signal revealed, probably, the occurrence of a slow equilibrium between ylide **2a** and its conjugate acid, the dimsylate **1a**.

Monoylide of the Salt **1b**

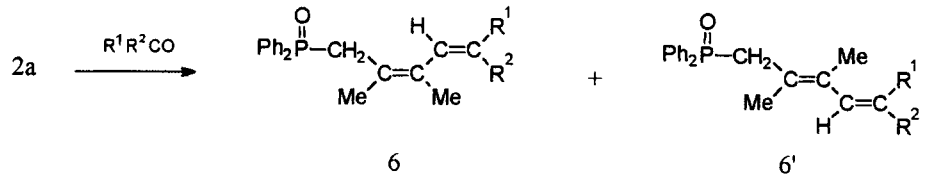
Subsequently, the reaction of one equivalent of *n*-BuLi with **1b** in THF was investigated. ^{31}P-NMR spectra exhibited three signals at δ = −18.9, −25.3, and −30.3 in the ratio 20/18/62. The last two signals vanished when one equivalent of $PhCO_2H$ was added, and two new signals appeared at δ = 43.0 and 52.0 in the ratio 90/10. They were identified as, respectively, the salts **1b** and **1′b** by co-injection of authentic synthesized samples. These salts resulted from the protonation of the corresponding regio-isomeric ylides **2b** and **2′b** (Scheme 8). Never was the salt **1″b** detected after acidification of the crude reaction product.

The signal at δ ^{31}P = −18.9 was insensitive to the acidity of the solution; it disappeared when H_2O_2 was added to give a signal at δ ^{31}P = 32.0 due to the formation of the phosphine oxide **11** that was later isolated and identified by its ^{13}C- and ^1H-NMR spec-

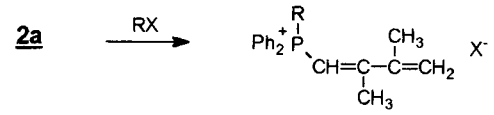
TABLE 2 Alkadienyl Phosphine Oxides **6** and **6'** Obtained via the Wittig Reaction of the Ylide **2a** (Scheme 6)

	6			**6'**		
Products	R^1	R^2	*Yield (%)*	R^1	R^2	*Yield (%)*
(2*Z*,4*Z*)-**6**	H	*p*MEOC$_6$H$_4$	98[a]			
(2*Z*,4*Z*)-**6**	H	C_6H_{13}	68[a]			
(2*Z*)-**6**	o,o'-biphenylen		64[a]			
(2*E*)-**6'**				o,o'-biphenylen		36[b]
(2*Z*,4*Z*)-**6**	H	Ph	92[a]			
(2*Z*,4*E*)-**6'**				H	Ph	6[b]
(2*Z*,4*E*)-**6**	*p*NO$_2$C$_6$H$_4$	H	72[a]			
(2*Z*,4*E*)-**6'**				H	*p*NO$_2$C$_6$H$_4$	28[b]
(2*Z*)-**6**	Ph	Ph	98[a]			

[a]Isolated as pure compound.
[b]Not isolated.



SCHEME 6



SCHEME 7

TABLE 3 Synthesis of Salts **7** at Room Temperature by Alkylation of Ylide **2a**

Entry	*RX*	**7**	**1a** (%)[a]	**1'a**
1	MeI	87	5	
2	Et I	67	23	
3	Et Br	25	54	
4	Ph CH_2 Br	47	15	
5	CO_2ME CH_2 Br		100	
6	*i*PrBr		73	27
7	*t*BuCl		100[b]	

[a]Calculated yield from ^{1}H-NMR spectra of the crude mixture.
[b]After acidification.

tra. Accordingly, the signal at δ ^{31}P = −18.9 may be attributed to the nonisolated phosphine **10** (Scheme 8).

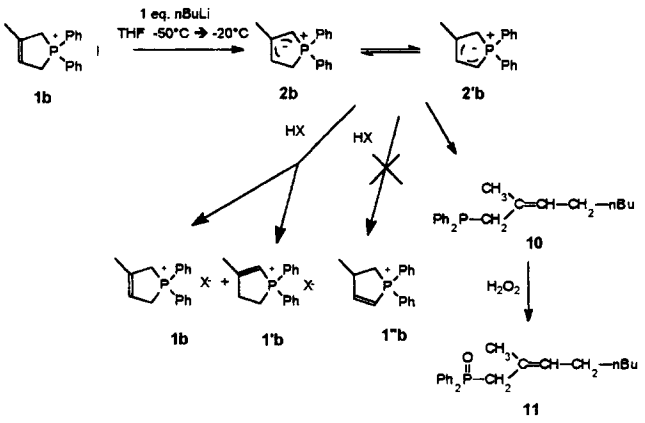
To explain the formation of **11**, various pathways are proposed in Scheme 9. In the pathway **A**, **1b** undergoes a nucleophilic substitution of the *n*-butyl anion on the less hindered methylene group, resulting in ring opening. The pathway **B**, more speculative, involves (the unobserved) *n*-butylphosphorane formation, followed by a [1,2]-anionotropic migration to the less hindered *α*-methylene group and a subsequent ring opening. Concerning the plausible attacks of *n*-butyl anion on the double bond of **1b**, as in the pathways **C** and **D**, it can be concluded that they do not occur because they would provide the phosphine **12a** or **12b** that was not observed in their corresponding phosphine oxides **13a** or **13b**, after oxidation of the crude reaction product.

Using a less nucleophilic base as *t*BuOK instead of *n*BuLi, the ^{31}P-NMR spectra exhibit only the two signals at δ = −25.3 and −30.3 (ratio: 13/87), identified as the ylides of the salts **1b** and **1'b**, in the same manner as in the preceding example.

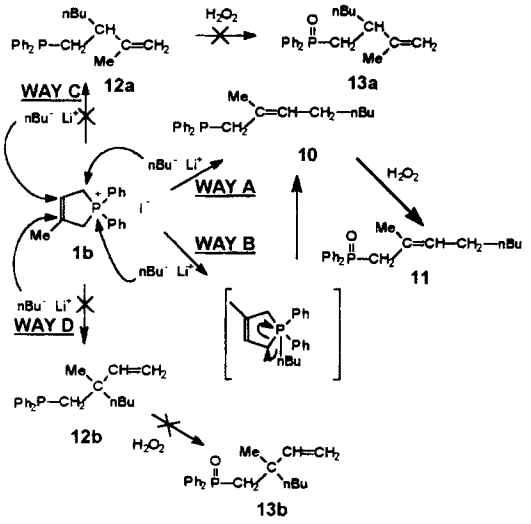
Finally, the main product of the monodeprotonation of the salt **1b** is the ylide **2b**, accompanied by its regio-isomer **2'b**. As mentioned for the ylide **2a**, the signals corresponding to the ylides **2b** and **2'b** appear at surprisingly high fields.

Monoylide of the Salt **1c**

In the same way, the monodeprotonation of **1c** was performed with one equivalent of base, *n*-butyllithium or *t*BuOK, in THF. With *n*BuLi, two signals



SCHEME 8



SCHEME 9

rapidly appeared in the ^{31}P-NMR spectra at δ = −29.3 and −15.9 (ratio: 87/13). With *t*BuOK, only the first one at −29.3 appeared. Both signals are insensitive to acidification, and they are assigned, respectively, to the phosphines **14** and **16**. Indeed, their oxidation by H_2O_2 gave the corresponding phosphine oxides **15** and **17**, isolated and chemically (but not stereochemically) well characterized.

$Ph_2P\text{-}CH_2\text{-}CH = CH\text{-}CH_2\text{-}nC_4H_9$ (**14**) $\quad Ph_2P(O)\text{-}CH_2\text{-}CH = CH\text{-}CH_2\text{-}nC_4H_9$ (**15**)

$Ph_2P\text{-}CH = CH\text{-}CH = CH_2$ (**16**) $\quad Ph_2P(O)\text{-}CH = CH\text{-}CH = CH_2$ (**17**)

It seems that either the two bases *n*BuLi and *t*BuOK gave the monoylide **2c** that underwent a rapid ring opening by an E1cB elimination mechanism or the ring opening by cleavage of the phosphorus group was simultaneous with the basic proton abstraction in an E2′ mechanism.

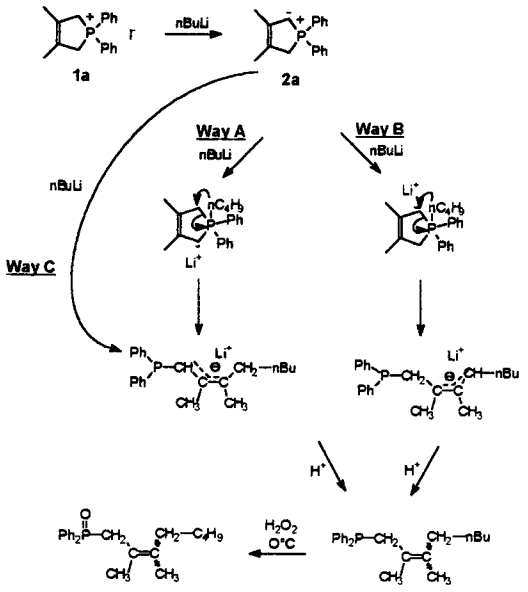
In the case of *n*BuLi, the last reaction occurred in competition with the nucleophilic substitution by *n*-butyl anion, as in the earlier example, and **16** resulted. Thus, the short-lived **2c** does not seem to be viable.

Attempts to Prepare the Diylide 3a

The mixtures in THF, with or without TMEDA, of two equivalents of *n*BuLi (in hexane or ether) and salt **1a**, at temperatures lower than −40°C, are unhomogeneous. They become homogeneous when the temperatures are higher than −40°C. Then, the ^{31}P-NMR spectra show several broad signals. The most important (70%) is at −7.8 ± 3, accompanied by signals at δ = −17.4 ± 0.8 (9%), −23.0 ± 0.5 (6%), −27.0 ± 0.5 (7%), and 11.2 (8%). The following chemical tests revealed that the expected diylide **3a** was not present in the reaction solution:

- The formation of the monoylide **2a** (δ = −25) was not observed when one equivalent of $PhCO_2H$ was added. The absence of **2a** was corroborated by a second addition of $PhCO_2H$ that only induced a change in the ratios of the above-mentioned signals, without the appearance of the signal characteristic of salt **1a** at δ ^{31}P = 35.
- On the other hand, the addition of one equivalent of H_2O_2 to the monoacidified solution produced a deshielding of all the signals plotted at δ ^{31}P = 33.2 ± 1.3 (28%), 28.7 ± 1.0 (47%), and 20.7 ± 1.3 (25%). The attempts to separate by column chromatography the different components of the oxidized crude mixture were unsuccessful. It was only possible to isolate the fraction giving rise to the second signal in the ^{31}P-NMR spectra. This fraction was a mixture of the two isomeric phosphine oxides 2*Z* and 2*E*-**18** (ratio 3/2). The other components were also *n*-butyl–substituted phosphine oxides as indicated by quantitative analysis of ^{1}H-NMR spectra.

These results may be explained as follows (Scheme 10): the monoylide **2a** (obtained by monodeprotonation of **1a** by one equivalent of *n*BuLi) reacts with the second equivalent of *n*BuLi under ring opening and formation of *n*-butylbutenylphosphines. This hypothesis is supported by the fact that, in the first state of the reaction at −80°C, the ylide **2a** is present and is associated with one equivalent of *n*BuLi, as an insoluble aggregate in the THF. This is proved by the two following chemical reactions: The addition of two equivalents of $PhCO_2H$ gave exclusively the salt **1a** (assigned by co-injection in the



SCHEME 10

^{31}P-NMR spectroscopy), and the addition of one equivalent of N,N-dimethylbenzamide gave quantitatively *n*-butylphenyl ketone, indicating the presence of one equivalent of *n*BuLi, liberated from the aggregate (Scheme 11).

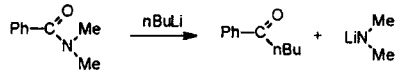
Reactivity of the Phosphine Oxide (2Z)-6 (R^1 = R^2 = Ph)

As reported by Mathey [7] and Kauffman [8], the penta-2,4-dienylphosphine oxides provide good intermediates for the preparation of 1,3,5-trienes. We have already shown [1] the possible stereoselective preparation of such trienes **19** by the Horner reaction with aldehydes (PhCHO, *p*-MeOPhCHO), or a ketone (PhCOPh), starting from the *α*-lithiated phosphine oxide (2*Z*)-**20** (R^1 = R^2 = Ph) (Scheme 12).

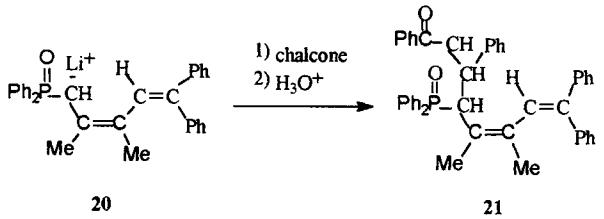
$$(R^1)(R^2)C = CH\text{–}CMe = CMe\text{–}CH = C(R^3)(R^4)$$
19

Now, we have observed that, when the lithiated anion **20** reacts with an *α,β*-unsaturated ketone such as a chalcone, a 1,4-addition takes place with formation in 83% yield of a mixture of keto-dienylphosphine oxides (2*Z*/2*E*)-**21** in a ratio of 69/31. The major isomer (2*Z*)-**21** was isolated in pure form.

In our attempts to prepare "one pot" 1,3,5-trienes from the salt **1a**, we have also shown [1] that consecutive Wittig and Horner reactions occur only to a small extent when the salt **1a** in THF is in the presence of two equivalents of *n*BuLi and of benzaldehyde. In all cases, after hydrolytic treatment, a



SCHEME 11



SCHEME 12

mixture of compounds was formed, of which the triene (1*E*,3*Z*,5*E*)-**19** (R^1 = R^3 = Ph; R^2 = R^4 = H) was isolated in 25% yield.

When the same reaction was repeated, using *t*BuOK instead of *n*BuLi, a mixture of trienes stereochemically nonidentified (66%) corresponding to the general formula **19** (R^1 = R^3 = Ph; R^2 = R^4 = H), and the phosphine oxide **8a** (44%) were isolated. The presence of the compound **8a** confirms the possible opening of the ylide **2a** into **8a**.

CONCLUSION

This work concerns the preparation and behavior of new 1,1-diphenyl-2,5-dihydrophospholium salts **1**. Their syntheses complete the important series beginning with 1-chloro 2,5-dihydrophospholium chloride synthesized by Quin [3].

The results obtained show that the +I effect of the two methyl groups linked to the double bond stabilizes to some extent the ylide of the unsaturated phosphonium salt **1a**. Such an ylide **2a** is a useful Wittig reagent, giving rise to new dienylphosphine oxides, which are good precursors for the stereoselective preparation of trienes [1]. This ylide **2a** is apparently in rapid equilibrium with the corresponding 1,3-dienylphosphine **8a**, which can be trapped by alkylation or oxidation.

With only one methyl group present on the double bond, the mesomeric ylides **2b** and **2'b** corresponding to the salt **1b** can be prepared using *t*BuOK as base. But, in the case of salt **1c**, without a methyl substituent, the reactions with bases result only in ring opening.

EXPERIMENTAL

Solvents and commercial reagents were purified by conventional methods before use. All reactions that

required an inert atmosphere were carried out under dry nitrogen. NMR spectra were recorded in $CDCl_3$ solution with a Bruker AC instrument at 200 MHz (^1H), 50.32 MHz (^{13}C), and 81 MHz (^{31}P). Reference substances were $SiMe_4$ (TMS) ext. (^1H, ^{13}C) and 85% H_3PO_4 ext. (^{31}P). Mass spectra were recorded on a JEOL JMS-DX-300, IR spectra were taken on a Perkin-Elmer 377, and GC was carried out on a Hewlett Packard-5890 instrument equipped with an OV-17 capillary column (30 m × 0.25 mm). Melting points were determined by an METTLER FP5 apparatus and are uncorrected. The synthesis of the salt **1a** was described in Ref. 1.

Synthesis of 1,1-Diphenyl-3-methyl-2,5-dihydrophospholium Iodide **1b**

An amount of 15 mL (83 mmol) of diphenylchlorophosphine, 8.35 mL (170 mmol) of isoprene, and 0.23 g of copper stearate were stirred for 26 days at 80°C inside a sealed tube. The vitreous product formed was isolated after decantation, dissolved in $CHCl_3$, and the anion Cl^- was exchanged for I^- by washing twice with an aqueous sodium iodide solution; the iodide obtained was recrystallized from $CHCl_3$/EtOAc to give **1b** (23.8 g, 62.3 mmol, 75%): mp 169.5°C. ^1H-NMR ($CDCl_3$) δ: 8.30–7.80 (m, 4H, Ph); 7.70–7.60 (m, 6H, Ph); 5.80 (d, $^3J_{PH}$ = 32.0 Hz, 1H, CH=); 4.00 (d, $^2J_{PH}$ = 9.0 Hz, 4H, CH_2); 2.00 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$): δ: 43.0; ^{13}C-NMR ($CDCl_3$) δ: 137.3 (d, $^2J_{PC}$ = 10.1 Hz, C =, 1C); 134.6 (d, $^4J_{PC}$ = 3.1 Hz, C_p, 2C); 130.1 (d, $^3J_{PC}$ = 12.9 Hz, C_m, 4C); 132.5 (d, $^2J_{PC}$ = 10.6 Hz, C_o, 4C); 120.3 (d, $^2J_{PC}$ = 5.3 Hz, CH =, 1C); 118.4 (d, $^1J_{PC}$ = 81.4 Hz, C_i, 2C); 33.4 (d, $^1J_{PC}$ = 55.4 Hz, CH_2, 1C); 30.4 (d, $^1J_{PC}$ = 52.3 Hz, CH_2, 1C); 19.1 (d, $^3J_{PC}$ = 11.0 Hz, CH_3, 1C); IR (KBr) ν cm^{-1}: 1435 (P–Ph); FAB$^+$:$[M]^+$ = 253. Anal. calcd for $C_{17}H_{18}IP$: C, 53.70; H, 4.77. Found: C, 53.68; H, 4.68.

Synthesis of 1,1-Diphenyl-3-methyl-2,3-dihydrophospholium Chloride or Iodide **1'b**

The treatment of the preceding reaction involves a decantation. The solution resulting from the decantation was collected, and the solvent was evaporated. The residue was dissolved in $CHCl_3$, and the resulting solution was caused to produce a precipitate by pouring it into ether, and **1'b** was obtained as a brown oil. ^1H-NMR ($CDCl_3$) δ: 7.88–7.77 (m, 4H, Ph); 7.71–7.61 (m, 6H, Ph); 6.43 (d, $^2J_{PH}$ = 30.0 Hz, 1H, CH=); 3.34 (m, 4H, CH_2); 2.30 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$): δ: 52.4; ^{13}C-NMR ($CDCl_3$) δ: 137.3 (d, $^2J_{PC}$ = 10.1 Hz, C=, 1C); 134.6 (d, $^4J_{PC}$ = 3.1 Hz, C_p, 2C); 131.6 (d, $^2J_{PC}$ = 11.0 Hz, C_o, 4C); 129.0 (d, $^3J_{PC}$ = 13.0 Hz, C_m, 4C); 119.0 (d, $^1J_{PC}$ = 85.2 Hz, C_i, 1C); 105.5 (d, $^1J_{PC}$ = 86.6 Hz, CH=, 1C); 55.1 (d, $^2J_{PC}$ = 22.1 Hz, CH_2, 1C); 36.6 (d, $^2J_{PC}$ = 6.3 Hz, CH_2, 1C); 20.7 (d, $^3J_{PC}$ = 17.2 Hz, CH_3, 1C); IR (KBr) ν cm^{-1}: 1435 (P–Ph); FAB$^+$: $[M]^+$ = 253.

Synthesis of 1,1-Diphenyl-2,5-dihydrophospholium Bromide **1c**

An amount of 2.6 g (10.1 mmol) of trimethylsilyldiphenylphosphine and 1.13 mL (10.1 mmol) of *cis*-1,4-dibromobut-2-ene were simultaneously added dropwise to 20 mL of toluene under refluxing, and the mixture was stirred for 12 hours. After filtration of the reaction mixture, the white precipitate was washed twice with ether and dissolved in warm MeOH. The recrystallized impurities were filtered off, and the solution after evaporation was caused to produce a precipitate by addition to ether to give **1c** (2.7 g, 8.5 mmol, 85%): mp 158.0°C. ^1H-NMR ($CDCl_3$) δ: 8.03–7.91 (m, 4H, Ph); 7.65–7.58 (m, 6H, Ph); 6.18 (d, $^3J_{PH}$ = 29.5 Hz, 2H, CH=); 3.99 (d, $^2J_{PH}$ = 9.4 Hz, 4H, CH_2); ^{31}P-NMR ($CDCl_3$) δ: 42.0; ^{13}C-NMR ($CDCl_3$) δ:135.1 (d, $^4J_{PC}$ = 3.2 Hz, C_p, 2C); 133.0 (d, $^2J_{PC}$ = 10.7 Hz, C_o, 4C); 130.4 (d, $^3J_{PC}$ = 12.9 Hz, C_m, 4C); 127.3 (d, $^2J_{PC}$ = 8.7 Hz, CH=, 2C); 118.1 (d, $^1J_{PC}$ = 81.7 Hz, C_i, 2C); 31.1 (d, $^1J_{PC}$ = 53.9 Hz, CH_2, 2C); IR (KBr) ν cm^{-1}: 1435 (P–Ph); FAB$^+$: $[M]^+$ = 239.

1,1-Diphenyl-2,3-dihydrophospholium Iodide **1'c**

An amount of 2.6 g (10.1 mmol) of trimethylsilyldiphenylphosphine and 0.90 mL (10.1 mmol) of *cis*-1,4-dichlorobut-2-ene were simultaneously added dropwise to 20 mL of toluene under refluxing, and the mixture was stirred for 12 hours. After filtration of the reaction mixture, the yellow precipitate was washed twice with ether and then with CH_2Cl_2. After filtration of the resulting solution, and evaporation of the solvent from the filtrate, the crude product obtained in 64% yield was a mixture (76/24), respectively, of salts **1c** and **1'c**. Spectral data obtained for **1'c** are ^1H-NMR ($CDCl_3$) δ: 8.03–7.91 (m, 4H, Ph); 7.65–7.58 (m, 8H, Ph, CH=); 3.38 (m, 4H, CH_2); ^{31}P-NMR ($CDCl_3$) δ: 52.2.

Synthesis of 1,3-Dienylphosphine Oxides **6** *through Wittig Reactions*

General Procedure. *n*-Butyllithium (1.6 M in hexane, 1.6 mL, 2.5 mmol) was added to **1a** (1.0 g, 2.5 mmol) in dry tetrahydrofuran (THF, 20 mL) at −80°C, and, after 30 minutes of stirring at −50°C, the carbonyl compound (2.5 mmol) was added. The

mixture was allowed to warm to room temperature and to react for 3–6 days. After neutralization with 0.1 N HCl at 0°C, extraction with CH_2Cl_2 (2 × 50 mL), drying, and evaporation of the solvent, crude **6** was obtained. In most cases, pure **6** was isolated by column chromatography (silicagel, CH_2Cl_2/$CH_3CO_2C_2H_5$: 80/20).

(2Z,4Z)-1,1-Diphenyl-2,3-dimethyl-5-p-methoxyphenylpentadi-2,4-enylphosphine Oxide **6** *(R^1 = H, R^2 = $pMeOC_6H_4$)*

Mp 198.0°C. ^{1}H-NMR ($CDCl_3$) δ: 7.77–7.67 (m, 4H, Ph); 7.53–7.35 (m, 6H, Ph); 7.11 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *p*-$MeOC_6H_4$); 6.77 (d, $^3J_{HH}$ = 8.7 Hz, 2H, *p*-$MeOC_6H_4$); 6.14 (d, $^3J_{HH}$ = 12.1 Hz, 1H, CH=); 5.70 (d, $^3J_{HH}$ = 12.1 Hz, 1H, CH=); 3.79 (s, 3H, CH_3); 3.21 (d, $^2J_{PH}$ = 14.3 Hz, 2H, CH_2); 1.87 (d, $^5J_{PH}$ = 1.0 Hz, 3H, CH_3); 1.65 (d, $^4J_{PH}$ = 4.8 Hz, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 30.6; ^{13}C-NMR ($CDCl_3$) δ: 158.6 (s, $C_{p'}$, 1C); 133.6 (d, $^1J_{PC}$ = 96.9 Hz, C_i, 2C); 131.5 (d, $^4J_{PC}$ = 2.8 Hz, C_p, 2C); 131.5 (d, $^2J_{PC}$ = 11.47 Hz, C=, 1C); 131.0 (d, $^2J_{PC}$ = 9.2 Hz, C_o, 4C); 130.1 (d, $^4J_{PC}$ = 3.4 Hz, CH=, 1C); 130.1 (s, C_i, 1C); 129.8 (s, $C_{m'}$, 2C); 128.38 (d, $^3J_{PC}$ = 11.5 Hz, C_m, 4C); 128.2 (d, $^5J_{PC}$ = 2.3 Hz, CH=, 1C); 123.5 (d, $^3J_{PC}$ = 10.3 Hz, C=, 1C); 113.5 (s, $C_{o'}$, 2C); 55.2 (s, OCH_3, 1C); 37.5 (d, $^1J_{PC}$ = 68.1 Hz, CH_2, 1C); 19.8 (d, $^4J_{PC}$ = 1.8 Hz, CH_3, 1C); 18.3 (d, $^3J_{PC}$ = 2.6 Hz, CH_3, 1C); UV (cyclohexane): λ_{max} nm: 220 and 272; D.O.: 0.59 and 0.41; ε (1 mol^{-1} cm^{-1}): 20,996 and 14,590; FAB$^+$: $[M + H]^+$ = 403; $[Ph_2PO]^+$ = 201; anal. calcd for $C_{17}H_{18}IP$: C, 77.59; H, 6.76; O, 7.95. Found: C, 76.88; H, 6.64; O, 8.30.

(2Z,4Z)-1,1-Diphenyl-2,3-dimethyl-5-hexylpentadi-2,4-enylphosphine Oxide **6** *(R^1 = H, R^2 = C_6H_{13})*

^{1}H-NMR ($CDCl_3$) δ: 7.75–7.65 (m, 4H, Ph); 7.48–7.40 (m, 6H, Ph); 5.32 (d, $^3J_{HH}$ = 13.0 Hz, 1H, CH=); 5.20 (m, 1H, CH=); 3.17 (d, $^2J_{PH}$ = 14.4 Hz, 2H, CH_2); 1.82 (d, $^5J_{PH}$ = 1.4 Hz, 3H, CH_3); 1.61 (d, $^4J_{PH}$ = 5.0 Hz, 3H, CH_3); 1.23 (m, 10H, CH_2); 0.85 (m, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 28.8; IR (KBr) ν cm^{-1}: 1435 (P–Ph), 1120 (P = O); FAB$^+$: $[M + H]^+$ = 381.

(2Z)-1,1-Diphenyl-2,3-dimethyl-5-o,o'-biphenylenpentadi-2,4-enylphosphine Oxide **6** *(R^1,R^2 = o,o-biphenylen)*

^{1}H-NMR ($CDCl_3$) δ: 7.92–7.05 (m, 19H, Ph, CH=); 3.40 (d, $^2J_{PH}$ = 14.3 Hz, 2H, CH_2); 1.86 (s, 3H, CH_3); 1.73 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 28.6; ^{13}C-NMR ($CDCl_3$) δ: 140.6–136.9 (s, 4 C=); 135.1 (d, $^5J_{PC}$ = 3.4 Hz, C=, 1C); 133.7 (d, $^1J_{PC}$ = 97.8 Hz, C_i, 2C); 131.9 (d, $^4J_{PC}$ = 2.7 Hz, C_p, 2C); 131.0 (d, $^2J_{PC}$ = 9.3 Hz, C_o, 4C); 130.9 (d, $^2J_{PC}$ = 10.4 Hz, C=, 1C); 128.7 (d, $^3J_{PC}$ = 11.5 Hz, C_m, 4C); 128.7 (d, $^4J_{PC}$ = 3.8 Hz, C=, 1C); 128.1–119.4 (s, 8 CH=); 124.8 (d, $^3J_{PC}$ = 10.6 Hz, C=, 1C); 37.1 (d, $^1J_{PC}$ = 67.2 Hz, CH_2, 1C); 22.2 (d, $^4J_{PC}$ = 1.7 Hz, CH_3, 1C); 19.0 (d, $^3J_{PC}$ = 2.9 Hz, CH_3, 1C); IR (KBr) ν cm^{-1}: 1435 (P–Ph), 1140 (P = O); FAB$^+$: $[M \pm H]^+$ = 447; $[Ph_2PO]^+$ = 201; $[Ph_2POC_4H_9 + H]^+$ = 283.

(2E)-1,1-Diphenyl-2,3-dimethyl-5-o,o'-biphenylenpentadi-2,4-enylphosphine Oxide **6'** *(R^1, R^2 = o,o-biphenylen)*

^{1}H-NMR ($CDCl_3$) δ: 7.92–7.05 (m, 18H, Ph); 6.25 (s, 1H, CH=); 3.24 (d, $^2J_{PH}$ = 13.9 Hz, 2H, CH_2); 2.14 (s, 3H, CH_3); 1.90 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 31.3.

Mixture of Two Isomers: 1,1-Diphenyl-2,3-dimethyl-5-methyl-5-phenylpentadi-2,4-enylphosphine Oxide **6** *(R^1 = CH_3, R^2 = C_6H_5)*

^{1}H-NMR ($CDCl_3$) δ: 7.72–7.03 (m, 15H, Ph); 5.77 (s, 1H, CH=); 3.20 (d, $^2J_{PH}$ = 14.3 Hz, 2H, CH_2); 1.97 (d, $^4J_{PH}$ = 5.4 Hz, 3H, CH_3); 1.63 (d, $^5J_{PH}$ = 1.4 Hz, 3H, CH_3); 1.46 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 27.2.

^{1}H-NMR ($CDCl_3$) δ: 7.72–7.03 (m, 15H, Ph); 5.69 (s, 1H, CH=); 3.15 (d, $^2J_{PH}$ = 13.9 Hz, 2H, CH_2); 1.76 (s, 3H, CH_3); 1.60 (d, $^4J_{PH}$ = 3.7 Hz, 3H, CH_3); 1.34 (s, 3H, CH_3); ^{31}P NMR ($CDCl_3$) δ: 27.4.

Synthesis of P-Alkylated Salts **7**

General Procedure. *n*-Butyllithium (1.6 M) in hexane (1.6 mL, 2.5 mmol) was added to **1a** (1.0 g, 2.5 mmol) in dry tetrahydrofuran (THF, 20 mL) at −80°C and, after 30 minutes of stirring at −50°C, the alkylating agent (2.5 mmol) was added. The mixture was allowed to warm to room temperature and to react during 12 hours. After evaporation of THF, the crude reaction mixture was dissolved in CH_2Cl_2 (2 × 50 mL). The organic layer was poured into ether, so that crude **7** was obtained as a precipitate and isolated by filtration. In all cases, pure **7** cannot be isolated by recrystallization.

1,1-Diphenyl-1-methyl-(2,3-dimethyl)-buta-1,3-dienylphosphonium Iodide **7** *(R = CH_3)*

Purity: 87%. ^{1}H-NMR ($CDCl_3$) δ: 7.88–7.63 (m, 10H, Ph); 6.37 (d, $^2J_{PH}$ = 22.3 Hz; 1H, CH=); 4.70 (s, 1H, CH=); 4.63 (s, 1H, CH=); 2.78 (d, $^2J_{PH}$ = 13.4 Hz;

3H, CH_3); 2.30 (s, 3H, CH_3); 1.56 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 11.1, FAB$^+$: $[M]^+$ = 281; $[Ph_2PMe]^+$ = 200.

1,1-Diphenyl-1-ethyl-(2,3-dimethyl)-buta-1,3-dienylphosphonium Iodide **7** *(R = C_2H_5)*

Purity: 67%. ^{1}H-NMR ($CDCl_3$) δ: 7.78–7.64 (m, 10H, Ph); 6.51 (d, $^2J_{PH}$ = 22.2 Hz; 1H, CH=); 4.63 (s, 1H, CH=); 4.60 (s, 1H, CH=); 3.15 (m, $^2J_{PH}$ = 12.6 Hz; $^3J_{HH}$ = 7.6 Hz; 2H, CH_2); 2.32 (s, 3H, CH_3); 1.30 (s, 3H, CH_3); 1.17 (m, $^3J_{PH}$ = 20 Hz; $^3J_{HH}$ = 7.5 Hz; 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 17.5, FAB$^+$: $[M^+]$ = 295.

1,1-Diphenyl-1-benzyl-(2,3-dimethyl)-buta-1,3-dienylphosphonium Iodide **7** *(R = CH_2Ph)*

Purity: 47%. ^{1}H-NMR ($CDCl_3$) δ: 7.78–6.90 (m, 15H, Ph); 6.48 (d, $^2J_{PH}$ = 23.9 Hz; 1H, CH=); 4.56 (d, $^2J_{PH}$ = 14.6 Hz; 2H, CH_2Ph); 4.52 (s, 1H, CH=); 4.43 (s, 1H, CH=); 2.28 (s, 3H, CH_3); 1.16 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 14.3, FAB$^+$: $[M^+]$ = 357.

1,1-Diphenyl-2,3-dimethyl-buta-1,3-dienylphosphine Oxide **8a**

First method: *n*-butyllithium (1.6 M in hexane, 1.6 mL, 2.5 mmol) was added to **1a** (1.0 g, 2.5 mmol) in dry tetrahydrofuran (THF, 20 mL) at −80°C, and, after 30 minutes of stirring at −50°C, the mixture was allowed to warm to 0°C (^{31}P-NMR spectral monitoring verifies that, during this warming, the spectrum of the reaction mixture was inchanged). Then H_2O_2 (2.5 mmol) was added. After 15 minutes with ^{31}P-NMR monitoring, THF was evaporated, and the crude reaction mixture was dissolved in CH_2Cl_2 (2 × 50 mL). The organic layer was concentrated and poured into ether. After filtration, the filtrate obtained was evaporated to afford a product that was purified by column chromatography (silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$: 80/20). Pure **8a** was isolated as an oil. 80% yield. ^{1}H-NMR ($CDCl_3$) δ: 7.79–7.69 (m, 4H, Ph); 7.47–7.35 (m, 6H, Ph) 6.11 (d, $^2J_{PH}$ = 23.4 Hz; 1H, CH=); 5.38 (s, 1H, CH=); 5.22 (s, 1H, CH=); 2.21 (d, $^4J_{PH}$ = 2.1 Hz, 3H, CH_3); 1.95 (s, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 23.6 FAB$^+$: $[M + H]^+$ = 283.

Second method: Synthesis of the trienes **19** (R^1 = R^3 = Ph; R^2 = R^4 = H) and of the 1,1-diphenyl-2,3-dimethyl-buta-1,3-dienylphosphine oxide **8a**.

*t*BuOK (0.56 g, 5.0 mmol) was added to **1a** (1.0 g, 2.5 mmol) in dry tetrahydrofuran (THF, 20 mL) at 20°C and, after 30 minutes of stirring at this temperature, benzaldehyde 0.51 mL (5.0 mmol) was added. After 72 minutes of stirring, the mixture was neutralized by addition of HCl (0.1 N), and the THF was evaporated. From the crude reaction mixture, the organic products were extracted by CH_2Cl_2 (2 × 50 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and evaporated to afford the crude product, which was purified by column chromatography (silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$: 80/20):

-eluent: hexane/CH_2Cl_2 (60/40) give a mixture of trienes **19** (R^1 = R^3 = Ph; R^2 = R^4 = H) (66%), ^{1}H-NMR ($CDCl_3$) δ: 7.78–7.21 (m, 10H, Ph); 6.84–6.49 (m, 4H, CH=); 2.34–1.95 (m, 6H, CH_3); GC/M − 260.

-eluent: ACOEt/CH_2Cl_2 (80/20) give **8a** (44%).

1,1-Diphenyl-1-(2-methyl)-octa-2-enylphosphine Oxide **11**

n-Butyllithium (1.6 M in hexane, 1.6 mL, 2.5 mmol), was added to **1b** (0.95 g, 2.5 mmol) in dry tetrahydrofuran (THF, 20 mL) at −80°C and, after 30 minutes of stirring at −20°C, benzoic acid (0.3 g, 2.5 mmol) was added. After evaporation of THF and extraction of the organic phase with CH_2Cl_2 (2 × 50 mL), the mixture was precipitated in ether to give 0.79 g salts **1b/1b'** in a ratio of 90/10. To the ether layer, one equivalent of H_2O_2 was added. Then, after removal of the solvent, the crude reaction mixture was dissolved in CH_2Cl_2 (2 × 50 mL) and purified by column chromatography (silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$: 80/20) to give **11** (0.12 g, 0.4 mmol, 15%), ^{1}H-NMR ($CDCl_3$) δ: 7.78–7.72 (m, 4H, Ph); 7.50–7.41 (m, 6H, Ph); 5.07 (m, 1H, CH=); 3.11 (d, $^2J_{PH}$ = 13.6 Hz, 2H, CH_2); 1.88 (m, 2H, CH_2); 1.69 (s, 3H, CH_3); 1.21–1.06 (m, 6H, CH_2); 0.82 (t, $^3J_{HH}$ = 6.4 Hz, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 32.0; ^{13}C-NMR ($CDCl_3$) δ: 132.8 (d, $^1J_{PC}$ = 97.9 Hz, C_i, 2C); 131.6 (d, $^4J_{PC}$ = 2.7 Hz, C_p, 2C); 131.1 (d, $^2J_{PC}$ = 9.1 Hz, C_o, 4C); 128.5 (d, $^3J_{PC}$ = 11.6 Hz, CH=, 1C); 128.4 (d, $^3J_{PC}$ = 11.6 Hz, C_m, 4C); 125.3 (d, $^2J_{PC}$ = 10.0 Hz, C=, 1C); 41.1 (d, $^1J_{PC}$ = 67.8 Hz, CH_2, 1C); 31.2 (s, CH_2, 1C); 29.0 (d, $^4J_{PC}$ = 3.5 Hz, CH_2, 1C); 28.0 (d, $^5J_{PC}$ = 2.5 Hz, CH_2, 1C); 22.5 (s, CH_2, 1C); 18.0 (d, $^3J_{PC}$ = 2.5 Hz, CH_3, 1C); 14.0 (s, CH_3, 1C); FAB$^+$: $[M]^+$ = 326; $[Ph_2PO]^+$ = 201.

1,1-Diphenyl-1-buta-1,3-dienylphosphine Oxide **15**

*t*BuOK (0.45 g, 4.2 mmol) was added to **1c** (1.3 g, 4.2 mmol) in dry tetrahydrofuran (THF, 20 mL) at 20°C, and, after 30 minutes of stirring at this temperature, H_2O_2 (4.2 mmol) was added. After evaporation of THF, the crude reaction mixture was dissolved in CH_2Cl_2 (2 × 50 mL) and purified by column chro-

matography (silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$: 80/20), giving **15** (0.95 g, 3.8 mmol, 90%), mp 103°C. ^{1}H-NMR ($CDCl_3$) δ: 7.74–7.64 (m, 4H, Ph); 7.44–7.40 (m, 7H, Ph, CH=); 7.02 (m, 1H, CH=); 6.03 (dd, $^2J_{PH}$ = 23.9 Hz, $^3J_{HH}$ = 6.1 Hz, 1H, CH=); 5.46 (d, $^3J_{HH}$ = 5.3 Hz, 1H, CH_2=); 5.39 (d, $^3J_{HH}$ = 0.2 Hz, 1H, CH_2=); ^{31}P-NMR ($CDCl_3$) δ: 22.9; ^{13}C-NMR ($CDCl_3$) δ: 149.3 (d, $^4J_{PC}$ = 1.4 Hz, =CH_2, 1C); 134.1 (d, $^1J_{PC}$ = 105.7 Hz, C_i, 2C); 133.8 (d, $^2J_{PC}$ = 9.6 Hz, CH=, 1C); 131.7 (d, $^4J_{PC}$ = 2.8 Hz, C_p, 2C); 131.0 (d, $^2J_{PC}$ = 9.9 Hz, C_o, 4C); 128.6 (d, $^3J_{PC}$ = 12.0 Hz, C_m, 4C); 125.5 (d, $^3J_{PC}$ = 2.1 Hz, CH=, 1C); 121.2 (d, $^1J_{PC}$ = 98.9 Hz, CH=, 1C); IR (KBr): ν cm^{-1}: 1435 (P–Ph); 1180 (P=O), FAB$^+$: $[M + H]^+$ = 255; $[Ph_2PO]^+$ = 201.

1,1-Diphenyl-octa-2-enyl-phosphine Oxide 17

n-Butyllithium (1.6 M in hexane, 0.6 mL, 1.6 mmol) was added to **1c** (0.5 g, 1.6 mmol) in dry tetrahydrofuran (THF, 20 mL) at −60°C, and, after 30 minutes of stirring at this temperature, H_2O_2 (1.6 mmol) was added. After evaporation of THF, the crude reaction mixture was dissolved in CH_2Cl_2 (2 × 50 mL) and purified by column chromatography (silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$: 80/20), giving **17** (0.4 g, 1.8 mmol, 80%). ^{1}H-NMR ($CDCl_3$) δ: 7.76–7.66 (m, 4H, Ph); 7.49–7.42 (m, 6H, Ph); 5.43 (m, 2H, CH=); 3.06 (dd, $^2J_{PH}$ = 14.7 Hz, $^3J_{HH}$ = 6.3 Hz, 2H, CH_2); 1.92 (m, 2H, CH_2); 1.15 (m, 6H, CH_2); 0.81 (t, $^3J_{HH}$ = 6.3 Hz, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 28.7; ^{13}C-NMR ($CDCl_3$) δ: 137.5 (d, $^2J_{PC}$ = 11.8 Hz, CH=, 1C); 132.7 (d, $^1J_{PC}$ = 98.1 Hz, C_i, 2C); 131.7 (d, $^4J_{PC}$ = 2.7 Hz, C_p, 2C); 131.0 (d, $^2J_{PC}$ = 9.1 Hz, C_o, 4C); 128.4 (d, $^3J_{PC}$ = 11.6 Hz, C_m, 4C); 117.9 (d, $^3J_{PC}$ = 9.2 Hz, CH=, 1C); 34.9 (d, $^1J_{PC}$ = 69.6 Hz, CH_2, 1C); 32.5 (d, $^5J_{PC}$ = 2.2 Hz, CH_2, 1C); 31.1 (s, CH_2, 1C); 28.7 (d, $^4J_{PC}$ = 3.0 Hz, CH_2, 1C); 22.4 (s, CH_2, 1C); 13.9 (s, CH_3, 1C); FAB$^+$: $[M]^+$ = 311; $[Ph_2PO]^+$ = 201.

1,1-Diphenyl-1-(2,3-dimethyl)-octa-2-enylphosphine Oxide 18

n-Butyllithium (1.6 M in hexane, 3.16 mL, 5.0 mmol) was added to **1a** (1 g, 2.5 mmol) in dry tetrahydrofuran (THF, 20 mL) at −60°C. After 2 hours of stirring at 0°C, benzoïc acid (2.5 mmol) was added, and then, after 30 minutes more of stirring at 0°C, H_2O_2 (2.5 mmol) was added. After evaporation of THF, the crude reaction mixture was dissolved in CH_2Cl_2 (2 × 50 mL) and purified by column chromatography (silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$: 80/20), giving two isomers **18** in ratio 1/1 (0.17 g, 0.5 mmol, 20%). ^{1}H-NMR ($CDCl_3$) δ: 7.78–7.68 (m, 4H, Ph); 7.49–7.38 (m, 6H, Ph); 3.13 (d, $^2J_{PH}$ = 14.3 Hz, 2H, CH_2); 1.69 (s, 3H, CH_3); 1.65 (d, $^4J_{PH}$ = 2.3 Hz, 3H, CH_3); 1.32–1.07 (m, 8H, CH_2); 0.88–0.82 (m, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 28.3.

(2Z)-1,1-Diphenyl-1-(1,3-diphenyl-3-oxo-propanyl)-2,3-dimethyl-5-diphenylpenta-2,4-dienylphosphine Oxide 21

Formation of the Carbanion **20**. To a solution of phosphine oxide (2Z)-**6** (R^1 = R^2 = Ph), and 1.0 g (2.2 mmol) of **1** in THF (30 mL) maintained at −50°C, *n*Buli (1.55 mL, 2.2 mmol) was added. Under stirring, the solution was allowed to warm to room temperature during one night. The mixture was cooled to 0°C and neutralized by addition of (0.1 N) HCl. After evaporation of THF, the aqueous layer was extracted with CH_2Cl_2 (2 × 50 mL), and the combined organic layers were dried (Na_2SO_4), the solvent was removed, and the phosphine oxide **21** was isolated by column chromatography (silicagel, $CH_2Cl_2/CH_3CO_2C_2H_5$: 80/20). Mp 222°C, ^{1}H-NMR ($CDCl_3$) δ: 8.01–6.50 (m, 30H, Ph); 5.91 (d, J = 4.3 Hz, 1H, CH=); 4.19 (m, 2H, CH_2CO); 3.73 (dd, $^2J_{PH}$ = 14.5 Hz, $^3J_{HH}$ = 2.5 Hz, 1H, CH_α); 2.82 (m, ^{1}H, CHPh); 1.79 (s, 3H, CH_3); 1.14 (d, $^4J_{PH}$ = 1.7 Hz, 3H, CH_3); ^{31}P-NMR ($CDCl_3$) δ: 32. FAB$^+$: $[M]^+$ = 657; $[Ph_2PO]^+$ = 201.

REFERENCES

[1] H.-J. Cristau, J. Grenier, E. Torreilles, *Phosphorus, Sulfur, and Silicon, 89,* 1994, 163.

[2] W. B. McCormack, U.S. Patents, 2, 663, 737, 1953, and, 2, 663, 738, 1953.

[3] (a) L. D. Quin, D. A. Mathews, *J. Org. Chem., 29,* 1964, 836. (b) L. D. Quin, J. A. Peters, C. E. Griffin, M. Gordon, *Tetrahedron Lett., 48,* 1964, 3689. (c) L. D. Quin, T. P. Barket, *Chem. Commun.,* 1967, 914. (d) L. D. Quin, J. P. Gratz, T. P. Barket, *J. Org. Chem., 33,* 1968, 1034.

[4] G. Märkl, *Angew. Chem. Int. Ed. Engl., 2,* 1963, 620.

[5] H. Schmidbaur, A. Mörtl, *J. Organomet. Chem., 250,* 1983, 171.

[6] J. G. Verkade, L. D. Quin: *Phosphorus-31 NMR Spectroscopy in Stereochemical Analysis,* VCH, Weinheim, p. 647 (1987).

[7] C. C. Santini, F. Mathey, *Can. J. Chem., 61,* 1983, 21.

[8] T. Kauffman, K.-R. Gaydoul, *Tetrahedron Lett., 26,* 1985, 4071.