

A GENERAL METHOD FOR PREPARING DIPHOSPHIRANES

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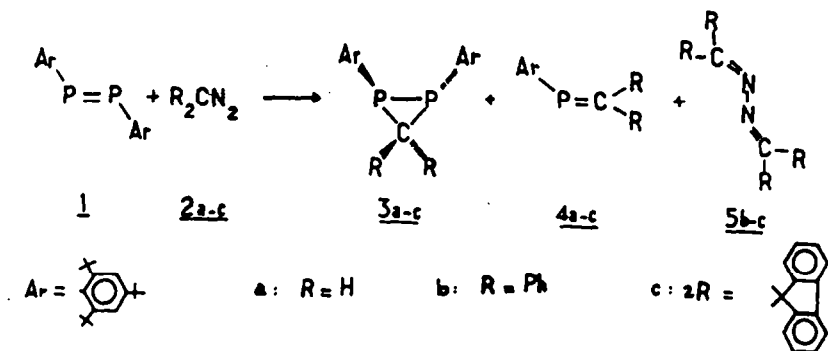
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Abstract : Diphosphiranes 3a-3f are obtained by action of diazo derivatives and carbenes on the trans-diphosphene 1. The structures are elucidated by spectroscopic methods. In all cases the cycloaddition reaction is stereoselective.

Resume : Les diphosphiranes 3a-3f sont obtenus par action des dérivés diazo et des différents carbenes sur le trans diphosphène 1. Les structures ont été établies par différentes méthodes spectrographiques. Dans tous les cas, la réaction de cycloaddition est stéréosélective.

The chemistry of diphosphiranes, phosphorus analogues of cyclopropanes, has only been developed in recent years (1-2). In particular, M. Baudler (1) and I.F. Lutsenko (2) have synthesized this type of compound from diphosphides and from dichlorodiphosphines. The reactions of diazo derivatives or of carbenes on multiple bonds (cyclopropanation reaction), when transposed over to diphosphenes, suggested to us a new way of preparing these strained models.

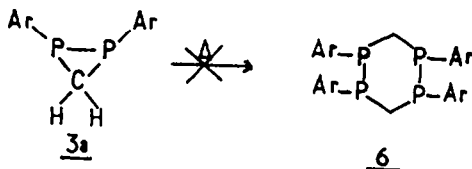
We have generalized the previously described (3) reaction of trans-diphosphene 1 on diazomethane 2a (scheme 1)



Scheme 1

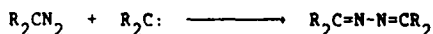
The addition of the diazomethane **2a** on **1** leads after 48h to the diphosphirane **3a** as well as small quantities (< 10%) of the phosphalkene **4a** (4, 5) (table 1) which were separated and purified on pre-coated P.L.C plates.

Heating the solution of **3a** in C_7D_8 does not produce the 1,2,4,5-tetraphosphacyclohexane **6** observed for the unsubstituted dialkyldiphosphiranes, prepared by other methods (1,2). The diphosphirane **3a** remains unchanged after heating :



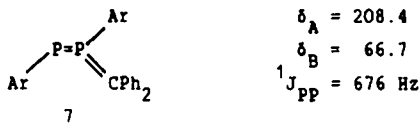
Diphenyldiazomethane **2b** is less reactive than diazomethane **2a** towards the diphosphene **1**. At 65 °C in degassed benzene in the presence of an excess of **2b**, it produces the diphosphirane **3b** (80 %), the phosphalkene **4b** (20 %) and the diazine **5b**, which were separated and purified on silica plates (tables 1-2).

This diazine **5b** (as **5c**) results of the action of the diazo derivative on the corresponding carbene.



Owing to the formation of large amounts of diazine, we have added a large excess of diphenyldiazomethane.

We have not observed the [2 + 3] cycloadduct detected during the reaction of diazoderivatives on phosphalkenes (**6**) but only the intermediary $\lambda^5\sigma^3$ -phosphorane **7**.

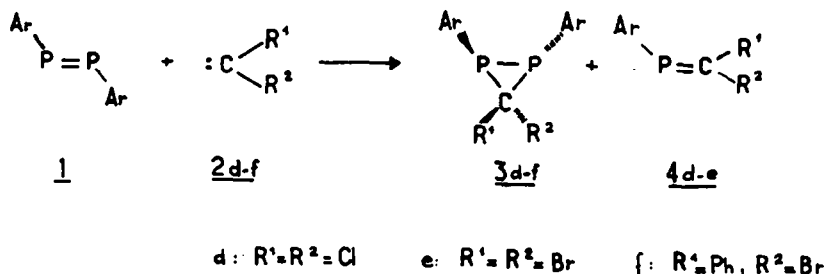


Irradiation of a mixture of **2b** with **1** at 253 nm in degassed benzene also gave rise to the formation of **3b**, **4b** and **5b**. On the other hand, the formation of $\lambda^5\sigma^3$ -phosphorane **7** was not observed.

Irradiation under the same conditions of 9-diazofluorene **2c** with **1** leads to the formation of the analogous derivatives **3c** (70 %), **4c** (30 %) and **5c** (tables 1-2).

As the reactivity of **2c** is slower than the thermal decomposition of **1**, it is not possible to perform the cycloaddition by heating.

The action on the diphosphene **1**, at low temperature of 10 equivalents of halogenocarbene **2d-2f** gives rise to the diphosphiranes **3d-3f** (tables 1-2) and to the phosphalkenes **4d** (10 %) and **4e** (20 %) (7) (scheme 2).



Scheme 2

In the case of the monohalogenocarbene 2f the corresponding phosphalkene 4f is not observed.

Substances 3d, 4d and 4e were purified on silica plates.

The values of $\delta^{31}\text{P}$ and $\delta^{13}\text{C}$ for the phosphorus atoms and for the intracyclic carbon C_9 are strongly shifted towards high field as in the case of the cyclopropanes and their analogues (1, 8,) (tables 1-2) : - 141 < $\delta^{31}\text{P}$ < -49 29.8 < $\delta^{13}\text{C}$ < 30.8

Compounds <u>3</u>	$\delta^{31}\text{P}$	m/z	Compounds <u>4</u>	$\delta^{31}\text{P}$	m/z
<u>3a</u>	- 141.0 ($^2\text{J}_{\text{P-C-H}} = 14 \text{ Hz}$)	566	<u>4a</u>	289	290
<u>3b</u>	- 74	718	<u>4b</u>	241	442
<u>3c</u>	- 59.2	716	<u>4c</u>	253.5	440
<u>3d</u>	- 68.8	635(^{35}Cl) (m+1/z)	<u>4d</u>	232	358(^{35}Cl)
<u>3e</u>	- 70.35	722(^{79}Br)	<u>4e</u>	269	446(^{79}Br)
<u>3f</u>	$\delta_{\text{A}} = - 49.2$ $\delta_{\text{B}} = - 77.9$ ($^1\text{J}_{\text{PP}} = 168 \text{ Hz}$)	720(^{79}Br)			

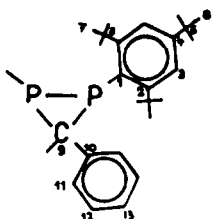
Table 1 : $\delta^{31}\text{P}$ NMR parameters and mass spectra (FD) of diphosphiranes 3 and phosphalkenes 4

The cyclopropane structure is confirmed by the equivalence of the two phosphorus atoms (3a-3d) and by the triplet observed in NMR ^{13}C of the carbon C_9 ($^1\text{J}_{\text{CP}} \sim 20 \text{ Hz}$).

The non equivalence of the phosphorus atoms in 3f, the equivalence of the hydrogens attached to the C-9 (NMR ^1H (^{31}P)) of the compound 3a and of the ipso carbons ($\delta = 131.1$, t, $^2\text{J}_{\text{CP}} = 8.8 \text{ Hz}$) for the compound 3b imply that the Ar substituents retain their trans configuration. Thus the cycloaddition reaction is stereoselective.

The diphosphiranes prepared are particularly stable and no decomposition of 3b into phosphalkene, for example, is observed after heating at 60 °C for 20 h. Likewise 3b does not react with the sulfur in refluxing toluene during 3 days. As the reactions for the formation of the diphosphiranes 3a, 3d and 3e take place at low temperature, the corresponding phosphalkenes are apparently obtained from the intermediate analogous to 7.

We have not elucidated the mechanism of the reaction of diazomethane on 1, but the absence of the cycloaddition adduct [2+3] and the fact that the cyclopropanation reactions only take place under conditions in which diphenyl and fluorenylidene carbenes are formed (heating and/or irradiation of the diazo derivatives), lead us to consider the diphosphiranes 3 b-f probably as the result of the attack of the carbenes on the diphosphene.



Compounds	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉
<u>3a</u>	137.4	157.3	123.6	148.7	39.6	32.2	34.5	31.8	30.5 (¹ J _{PC} =24Hz)
<u>3b</u> *	137.0	157.0	123.4	148.0	38.8	34.2	34.7	31.6	29.8 (¹ J _{PC} =20Hz)
<u>3d</u>		157.9	123.5	150.2	39.3	34.2	35.7	31.7	30.8
	* C ₁₀ 131.1	(J _{CP} = 8.8 Hz)		C ₁₁ 126.4		C ₁₂ 121.8		C ₁₃ 124.9	

Table 2 : NMR ¹³C parameters of the diphosphiranes obtained

Experimental

All NMR spectra (¹H, ¹³C, ³¹P) are recorded on a Bruker AC 80 in C₆D₆ as solvent. Mass spectra (FD) are recorded on a Varian-MAT 311 A. All experiments are carried out under argon with anhydrous solvents.

1,2-bis(2,4,6-tri-*tert*-butylphenyl)diphosphirane (3a).

A solution of diazomethane in ether 0.2 M (15 ml) is added at 0 °C to diphosphene **1** (0.16 g, 0.29 mmol) dissolved in THF (10 ml). The mixture, gradually warmed to room temperature (48h), is concentrated. Diphosphirane **3a** is purified on pre-coated plate (silica gel 60F254-hexane as eluent) as a pale yellow solid.

Yield : 80% ; R_f = 0.31 (hexane) ; m.p 180-182 °C ; ³¹P NMR (C₆D₆) δ : -141 (²J_{P-C-H} = 14 Hz) ; MS (FD) m/z : 566.

1,2-bis(2,4,6-tri-*tert*-butylphenyl)phosphaalkene (4a)

Compound **4a** present in small amounts in reaction mixture is isolated and purified on silica plate (hexane as eluent).

Yield : 10 % ; R_f = 0.15 (hexane) ; ³¹P NMR (C₆D₆) δ : 289 ; MS (FD) m/z : 290.

1,2-bis(2,4,6-tri-*tert*-butylphenyl)3,3-diphenyl diphosphirane (3b)

Thermal procedure

In a sealed tube, a mixture of **1** (0.055g, 0.1 mmol) and diphenyldiazomethane **2b** (10) (0.39 g, 2 mmol) was dissolved in degassed benzene (1.5 ml). The solution is heated at 65 °C for 24 h. The precipitate of the diazine **5b** is separated by filtration and the diphosphirane **3b** is purified on silica plate (hexane as eluent).

Yield : 80% ; R_f = 0.51 (hexane) ; m.p. = 154-155 °C ; ³¹P NMR (C₆D₆) δ : -74 ; MS (FD) m/z : 718.

Photochemical procedure

To a solution of diphosphene **1** (0.067 g, 0.12 mmol) in degassed benzene (1.5 ml) is added the diphenyl diazomethane **2b** (0.37 g, 1.92 mmol). The solution is irradiated at 253 nm for 24h. The purification of diphosphirane **3b** is performed as described above.

(2,4,6-tri-*tert*-butylphenyl)diphenyl phosphaalkene (4b)

Compound **4b** obtained as a by-product, is separated and purified on silica plate (hexane as eluent).

Yield : 20 % ; R_f = 0.22 (hexane) ; ³¹P NMR (C₆D₆) : 241 ; MS (FD) m/z : 442.

1,2-bis(2,4,6-tri-tert-butylphenyl)3,3-dichloro diphosphirane (3d).

To a stirred suspension of **1** (0.055 g, 0.1 mmol) and tBuOK (0.078g, 0.66 mmol) in pentane (2 ml) maintained at 0 °C, are added 10 equivalents of chloroform dissolved in pentane (0.5 ml). The mixture let to come to the room temperature. The solvent is removed and the residue extracted by benzene (1.5 ml) is purified on silica plates.

Yield : 80% ; $R_f = 0.54$ (hexane) ; $^{31}\text{P NMR}$ (C_6D_6) δ : -68.8 ; MS (FD) m/z : 635 (^{35}Cl).

(2,4,6-tri-tert-butylphenyl)dichlorophosphaalkane (4d)

Compound **4d** obtained as a by-product is purified on silica plate (hexane as eluent).

Yield : 10% ; $R_f = 0.10$ (hexane) ; $^{31}\text{P NMR}$ (C_6D_6) δ : 232 ; MS (FD) m/z : 358 (^{35}Cl).

1,2-bis(2,4,6-tri-tert-butylphenyl)3,3-dibromo diphosphirane (3e)

The same procedure as described above is used. The diphosphirane **3e**, obtained in a crude form, (80%) decomposes during the purification on silica plate. Only, the phosphoalkene **4e** is purified : $R_f = 0.55$ (hexane) ; $^{31}\text{P NMR}$ (C_6D_6) δ : 269 ; MS (FD) m/z : 446 (^{79}Br).

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