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A GENERAL METHOD FOR PREPARING DIPHOSPHIRANES

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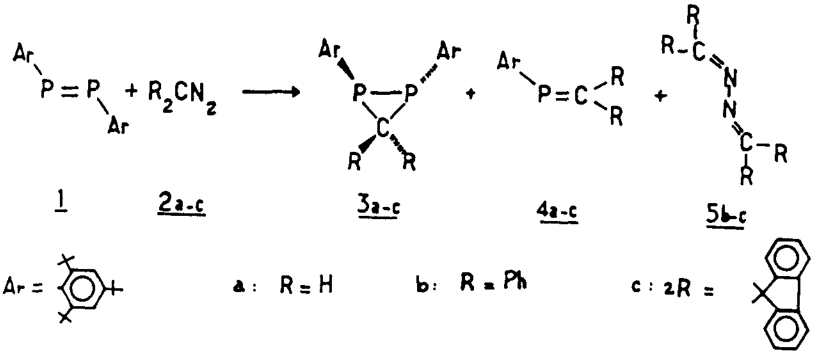
Abstract : Diphosphiranes 3a-3f are obtained by action of diazo derivatives and carbenes on the trans-diphosphene 1. The structures are elucidated by spectroscopic methods. In all cases the cycloaddition reaction is stereoselective.

Resume : Les diphosphiranes 3a-3f sont obtenus par action des dérivés diazo et des différents carbènes 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 synthesize 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.

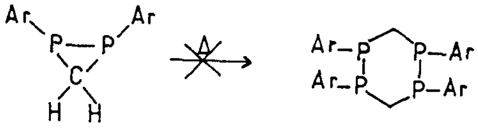
We have generalized the previously described (3) reaction of trans-diphosphene 1 on diazomethane 2a (scheme 1)



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 phosphaalkene 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 :



3a 6

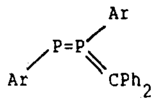
Diphenyldiazomethane 2b is less reactive than diazomethane 2a towards the diphosphene 1. At 65 °C in degassed benzene in the presence of an excess of 2b, it produces the diphosphirane 3b (80 %), the phosphaalkene 4b (20 %) and the diazine 5b, which were separated and purified on silica plates (tables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

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

$$R_2CN_2 + R_2C: \longrightarrow R_2C{=}N{-}N{=}CR_2$$

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 phosphaalkenes (6) but only the intermediary $\lambda^5\sigma^3$-phosphorane 7.



7

$\delta_A = 208.4$

$\delta_B = 66.7$

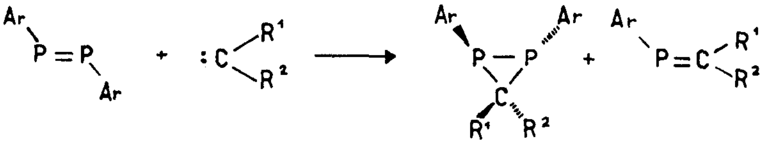
${}^1J_{PP} = 676$ Hz

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 λ^5 σ^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 phosphaalkenes 4d (10 %) and 4e (20 %) (7) (scheme 2).



1 2d-f 3d-f 4d-e

d : $R^1=R^2=Cl$ e: $R^1=R^2=Br$ f: $R^1=Ph$, $R^2=Br$

Scheme 2

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

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

The values of $\delta^{31}P$ and $\delta^{13}C$ 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) : $- 141 < \delta^{31}P < -49$ $29.8 < \delta^{13}C < 30.8$

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

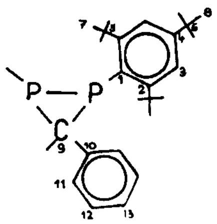
Table 1 : $\delta^{31}P$ NMR parameters and mass spectra (FD) of diphosphiranes 3 and phosphaalkenes 4

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 ($^1J_{CP} \sim 20$ Hz).

The non equivalence of the phosphorus atoms in 3f, the equivalence of the hydrogens attached to the C-9 (NMR ^{1}H {^{31}P}) of the compound 3a and of the ipso carbons (δ = 131.1 , t, $^2J_{CP}$ = 8.8 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 phosphaalkene, 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 phosphaalkenes 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
3a	137.4	157.3	123.6	148.7	39.6	32.2	34.5	31.8	30.5 ($^1J_{PC}$=24Hz)
3b*	137.0	157.0	123.4	148.0	38.8	34.2	34.7	31.6	29.8 ($^1J_{PC}$=20Hz)
3d		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 ^{13}C parameters of the diphosphiranes obtained

Experimental

All NMR spectra (^1H, ^{13}C, ^{31}P) are recorded on a Bruker AC 80 in C_6D_6 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 ; ^{31}P NMR (C_6D_6) 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) ; ^{31}P NMR (C_6D_6) 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 ; ^{31}P NMR (C_6D_6) 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) ; ^{31}P NMR (C_6D_6) : 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}P NMR (C_6D_6) δ : -68.8 ; MS (FD) m+1/z : 635 (^{35}Cl).

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

Compound 4d obtained as a by-product is purified on silica plate (hexane as eluent).
Yield : 10 % ; R_f = 0.10 (hexane) ; ^{31}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 phosphaalkene 4e is purified : R_f = 0.55 (hexane) ; ^{31}P NMR (C_6D_6) δ : 269 ; MS (FD) m/z : 446 (^{79}Br).

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