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NEW METHOD OF OBTAINING A STABLE DIPHOSPHIRANE

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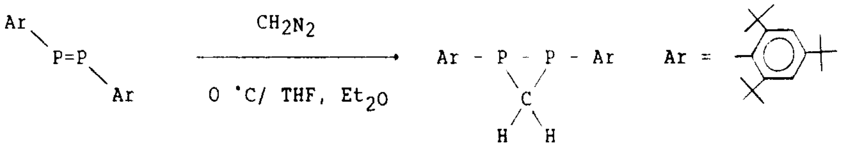
*Abstract. The stable monomer diphosphirane **2** is produced by the reaction of the diazomethane on the diphosphène **1**.*

Following our study of the reactivity of the diphosphenes (1) and in the light of results obtained on the diazenes (2) and the phosphaalkenes (3), we have reacted diazomethane with the trans-diphosphene **1** in the following reaction :



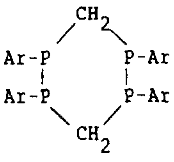
1 **2**

The product obtained (yield 80% for a ten fold excess of diazomethane), purified on a pre-coated P.L.C. plate (silica gel 60F 254 - hexane as eluent) was a pale yellow solid, M.P. = 180-182 °C. The field desorption mass spectrum (m/e = 566) corresponds to the monomeric form. The ^{31}P {^{1}H} NMR spectrum in C_6D_6 is a singlet at $\delta = -141$, whereas without decoupling of the proton, one observes a pseudo-triplet (J_{PCH} = 14 Hz).

The ^{13}C {^{1}H} spectrum gives a pseudo-triplet at $\delta = 30.5$ (4) for the methylene carbon atom, whereas the ^{1}H {^{31}P} shows that the two hydrogen atoms linked to the carbon are equivalent ($\delta = 1.61$) (4).

These results allow us to conclude to the formation of the diphosphirane 2,on which the ring phosphorus atoms and the methylene hydrogen atoms, observed at 250 MHz, are magnetically equivalent.

Heating the solution in C_7D_8 does not produce the 1,2,4,5-tetraphosphacyclohexane 3 observed for the unsubstituted dialkyldiphosphiranes, prepared by other methods (5).



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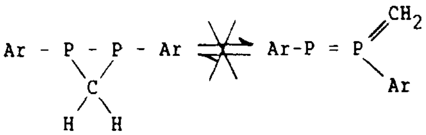
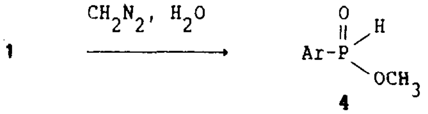
The diphosphirane **2** remains unchanged after heating. When the solution is cooled to -80 °C, no non-equivalence of the phosphorus atoms is observed in ^{31}P NMR. This excludes, in the temperature range considered, the equilibrium diphosphirane $\rightleftharpoons$ methylenediphosphene :



Substance **2** represents the first example of a stable non-complexed and non-C-substituted diphosphirane (6).

When we extend the reaction time, hydrolysis of **1** in the presence of CH_2N_2 leads to the formation of compound **4** (7).



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Finally, we note that the cis diphosphene isomer (1a) obtained by laser irradiation does not react on CH_2N_2 at - 78 °C.

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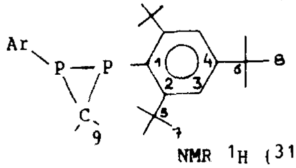
4 - Compound **2** : NMR ^{13}C {^1H} : δ C(1) 137.37 (t, $^1J_{CP}$ + $^2J_{CP}$=32.5Hz) C(2) 157.26 (t, $^2J_{CP}$+$^3J_{CP}$= 3Hz) C(3) 123.64 (s);C(4) 148.68(s) C(5) 39.58(s) ; C(6) 32.20(s) ; C(7) 34.51(t, $^4J_{CP}$=4.8Hz) C(8) 31.75(s) ; C(9) 30.54 (t, $^1J_{CP}$ + $^2J_{CP}$ =24Hz)



NMR ^1H {^{31}P} : 1.23 (18H, s) ; 1.61 (2H,s) ; 1.71 (36H,s) ; 7.36 (4H,s)

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7 - Compound **4** : NMR ^{31}P : δ = +26.95, J_{PH} = 559 Hz. Masse (FD) m/e = 324. NMR ^1H : 1.20 (9H, s), 1.57 (18H, s), 3.32 (3H, d, J_{POCH} = 11Hz), 1.49 (2H, m), 8.0 3 (1H, d, J_{HP} = 559 Hz).

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