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First 1-Phospha-1,3-dienes Unsubstituted in the Carbon Chain by Pyrolysis of Diallylphosphines: A Novel Route to the Phosphorus–Carbon Double Bond

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ABSTRACT

Allylic phosphine systems were studied as phosphorus–carbon double bond precursors. 1-Phenyl and 1-butyl-1-phospha-1,3-dienes were generated by pyrolysis at 350–460°C of the corresponding diallyl phosphines in a stirred-flow reactor. The unsubstituted phosphadienes generated in this manner dimerized; the formation of [4 + 2] *cycloaddition products was confirmed by NMR and mass spectroscopic analysis.* ^{31}P *NMR data of the 1-phospha-1,3-dienes were obtained.*

INTRODUCTION

In the last few years, some 1-phospha-1,3-dienes have been synthesized [1–3]. In general they are unstable and lead to dimerization or intermolecular Diels-Alder reaction [1]. Some of them have been stabilized by bulky substituents [1, 2] or "masked" as organometallic complexes [2, 4]. Until now, no description of the synthesis of a 1-phosphadiene without substituents on the carbon chain has been reported in the literature. We describe here the generation of the first unsubstituted 1-phospha-1,3-dienes by pyrolysis of diallylphosphines. This reaction represents a novel access to phosphaalkenes.

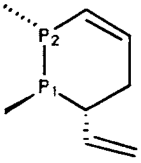
Numerous studies have been published on the thermal decomposition of allylic systems of type I (Scheme 1) [5, 6], which leads to the formation of double bonds.

Kinetic studies [5, 6] showed that this reaction involves a 6 center 1,5-H shift retroene reaction mechanism.

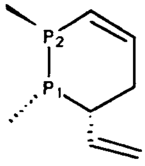
The pyrolysis of *t*-butyl (**1a**) or phenyl (**1b**) diallyl phosphine (Scheme 2), in a stirred-flow reactor [8] at 350–460°C and at pressures between 5–15 torr, led to the formation of a mixture of 1,2-diphospha-3-cyclohexene isomers (**3-3'a**; **3-3'b**) in 20–50% yield.

The gas chromatography analysis of the gaseous products formed during the pyrolysis showed that propene was formed in 98% yield, as expected from Scheme 2. The $^{31}P(H)$ NMR spectra of the mixture showed essentially two AB systems (Table 1) with a large J_{PP} and different integral ratios according to the substituents. The values of the chemical shifts and the large $^{1}J_{PP}$, which are typical of P^{III}–P^{III} direct coupling, agree with those published in the literature for this kind of compound [1]. The presence of these products was also confirmed by mass spectroscopy.

Compound 3 has three asymmetric centers: thus the four possible diastereoisomers (A, B, C, and D forms and their enantiomers) are possible products.



A



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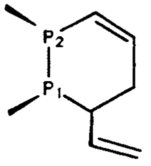
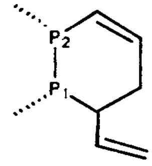


C



D

However, as mentioned above, we observed only two of the racemates. This experimental fact is at

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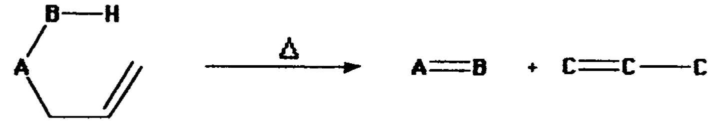
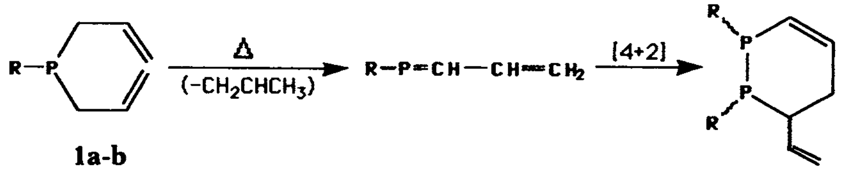


I
A = N, O, CO, S
B = Alkyl

SCHEME 1



1a-b
a: R = tBu; b: R = Ph

2-2'a; 2-2'b

3-3'a; 3-3'b

SCHEME 2

present difficult to explain. We suggest that, because of steric reasons, the R substituents on the P atoms are in the trans position, while the vinyl group on the C6 atom may be in the trans or cis position with respect to the P1 atom, i.e. in our case, structures A and B. Examination of models offered support for this concept.

For R = tBu, selective formation of one isomer was observed, the A form should be the sterically favored one. It has been possible to enrich the mixture to more than 95% in this product, enough to characterize it unambiguously [7a]. In the case of R = phenyl the steric hindrance is not so important, and the two isomers **3b**, **3'b** (A and B forms) were present in nearly the same amount. In this case, the structures have been established by ^{31}P NMR and mass spectroscopy [7b]. Addition of elemental sulfur led to the formation of two new compounds having AB systems in the same proportion, which were assigned to the corresponding 1,2-dithio-1,2-diphospha-3-cyclohexenes (**4-4'b**). Chemical shift, $^{1}J_{PP}$, and mass spectra [16] are analogous to those reported in the literature for similar compounds [1]. All attempts to separate these compounds were unsuccessful.

When the products were collected at low temperature (−78°C), the ^{31}P NMR spectra showed, in addition to the signals corresponding to the diphosphacyclohexenes, two new signals at low field (Table 2) that disappeared slowly when warmed to room temperature. Comparing the ^{31}P chemical shift with those reported by Hamelin [3] and Appel [1], we concluded that these signals correspond to the unsubstituted 1-phospha-1,3-diene **2-2'**. It is well known that Z and E isomers in phosphaalkene may have different chemical shifts [9–13], and this fact can explain the presence of two signals in the typical region for phosphaalkene resonances.

It is also well known that proton–phosphorus coupling constants are very sensitive to the geometrical disposition of one atom with respect to the other [9, 15], and a wide range of $^{n}J_{PH}$ for phosphaalkenes have been reported [1, 9–15]; this can explain the multiplet patterns observed in the proton-coupled ^{31}P NMR spectra of **2** and **2'** (Table 2). All attempts to trap the phosphadienes by use of classical diene traps failed.

In conclusion, the presence of propene in more than 98% yield in the gases produced during the pyrolysis and the unambiguous formation of the 1,2-diphospha-3-cyclohexenes are in good agreement with the novel generation of the 1-phospha-1,3-dienes, represented in Scheme 2. A kinetic study and generalization of this novel reaction leading to phosphorus–carbon double bond formation are being carried out with satisfactory preliminary results.

TABLE 1 ^{31}P NMR (CDCl$_3$) Data of the Diphosphacyclohexenes **3-3'**; **3-3'b**

R	δ P$_1$	δ P$_2$	$^{1}J_{PP}$	%
tBu	−32.6	−18.2	254.4	90
	−66.4	−41.6	230.4	10
Ph	−64.2	−34.8	255.9	60
	−21.4	3.5	230.6	40

TABLE 2 ^{31}P NMR (CDCl$_3$) Data of the Phosphabutadienes **2-2'a**; **2-2'b**

R	δ ^{31}P	$^{2}J_{PH}$	$^{3}J_{PH}$	$^{4}J_{PH}$
tBu	205.7	44.75	33.4	—
	204.4	37.2	37.2	8.56
Ph	205.7	36.6	—	—
	191.5	36.1	36.1	9.0

EXPERIMENTAL

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on a Bruker AM-300 instrument. Mass spectra were obtained on a kratos GLCMS RFA25 instrument. *t*-Butyl-dichloro-phosphine was obtained by a published method [19] and dichloro-phenyl-phosphine from Aldrich Co.

General Procedure for the Synthesis of the Diallyl Phosphines **1a** *and* **1b** [17]

A filtered solution of 0.242 mol of allylmagnesium bromide (obtained from 0.242 mol of allyl bromide and 0.484 mol of magnesium turnings in 200 mL of freshly distilled ether [18]) was added dropwise to a stirred solution of 0.11 mol of the dichloro phosphine in 100 mL of freshly distilled ether cooled to −10°C. When the addition had been finished the mixture was stirred at room temperature for 2 h, filtered, and the solvent evaporated. The diallylphosphine was distilled under reduced pressure in a 15-cm vigreux column (70–90% yield).

t-Butyl Diallyl Phosphine **1a**. Selected data: liq bp: 67°C/0.1 torr. ^{31}P{^{1}H} NMR (121.496 MHz, $CDCl_3$, H_3PO_4 ext.) $\delta = -4.72$. ^{13}C{^{1}H} NMR (75.469 MHz, $CDCl_3$, TMS ext.). $\delta = 27.44$ (d, $^{2}J_{PC} = 12.64$, $(CH_3)_3C$) $\delta = 28.41$ (d, $^{1}J_{PC} = 15.03$, $(CH_3)_3C$) $\delta = 29.19$ (d, $^{1}J_{PC} = 19.18$, PCH_2–) $\delta = 115.9$ (d, $^{3}J_{PC} = 9.6$, $CH_2{=}CH$) $\delta = 135.45$ (d, $^{2}J_{PC} = 10.34$, $CH_2{=}CH$). ^{1}H NMR (300.133 MHz, $CDCl_3$, TMS ext.) $\delta = 1.01$ (d, $^{3}J_{PH} = 11.47$, $(CH_3)_3C$, 9H) $\delta = 2.18$ (m, CH_2P, 4H) $\delta = 4.96$ (m, $CH_2{=}CH$, 4H) $\delta = 4.96$ (m, $CH_2{=}CH$, 4H) $\delta = 5.77$ (m, $CH_2{=}CH$–, 2H).

Diallyl Phenyl Phosphine **1b**. Selected data: liq bp: 52°C/0.1 torr. ^{31}P{^{1}H} NMR (75.469 MHz, $CDCl_3$, H_3PO_4 ext.) $\delta = -28.4$. ^{13}C{^{1}H} NMR (75.469 MHz, $CDCl_3$, TMS ext.) $\delta = 31.6$,b (d, $^{1}J_{PC} = 15.4$, PCH_2) $\delta = 116.7$ (d, $^{3}J_{PC} = 8.8$, $CH_2{=}CH$) $\delta = 128.1$ (d, $^{3}J_{PC} = 6.4$, *m*-C) $\delta = 128.1$ (s, *p*-C) $\delta = 132.1$ (d, $^{2}J_{PC} = 18.2$, $CH_2{=}CH$) $\delta = 132.8$ (d, $^{2}J_{PC} = 6.9$, *o*-C) $\delta = 137.1$ (d, $^{1}J_{PC} = 17.7$, arom. *C*P), ^{1}H NMR (300.133 MHz, $CDCl_3$, TMS ext.) $\delta = 2.5$ (m, CH_2P, 4H) $\delta = 5.0$ (m, $CH_2{=}CH$, 4H) $\delta = 5.7$ (m, $CH_2{=}CH$, 2H) $\delta = 7.3$–7.5 (m, arom. 5H).

The pyrolyses were carried out in a 265-mL stirred-flow reactor [8]. The outflow from the reactor was trapped at −190°C. It was then fractionated and warmed to room temperature. The involatile fraction containing phosphorated products remained in the first trap. The gases were collected at −190°C and analyzed by GPC in a 10-m × 0.0122-m activated Al_2O_3 80/100 mesh column at 170°C, using an FID detector.

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[7] (a) Selected data for **3a**: ^{31}P{^{1}H} NMR (121.496 MHz, $CDCl_3$, H_3PO_4 ext., AB system) $\delta_{P_1} = 32.6$, $\delta_{P_2} = -18.2$, $^{1}J_{P_2P_2} = 254.4$. ^{13}C{^{1}H} NMR (75.469 MHz, $CDCl_3$ 13.03, $^{3}J_{PC} = 7.76$, $(CH_3)_3C$), $\delta = 31.34$ (bs, CH_2) $\delta = 34.18$ (d, $^{1}J_{PC} = 27.09$) $\delta = 134.92$ ($^{2}J_{PC} = 2.9$, PC*H*CH$=$CH$_2$), $\delta = 142.3$ (d, $^{2}J_{PC} = 19.4$, PCH$=$*C*H) ^{1}H NMR (300.133 MHCDCl$_3$, TMS ext.) $\delta = 1.16$ (d $^{3}J_{PH} = 12.21$, (C*H*$_3$)$_3$C, 18H) $\delta = 2.1$ (m, PCHC*H*$_2$, 1H) $\delta = 2.51$ (m, PC*H*CH$_2$, 1H), $\delta = 2.76$ (m, PCHC*H*$_2$, 1H), d $= 4.97$ (m, C*H*, 1H). Assignments made by normal spectra, Dept. and HH.2D experiments. Mass spectrum *m/e* (%) 256 (2.6, M$^+$), 215 (9.9, M-C_3H_5), 199 (7.1, M-tBu), 143 (37.3, M/2), 57(100, tBu); (b) Mass spectrum for **3**, **3'b**: *m/e* (%) 296 (25, M$^+$), 256 (71, M–PhP–H), 77 (72, Ph).

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[16] The isomeric mixture of **3b** and **3'b** reacted with elemental sulfur led to formation of the corresponding 1,2-dithio-1,2-diphosphacyclohexenes. ^{31}P NMR **4b** (60%) δ P$_1$ $= 18.72$, δ P$_2$ $= 32.17$, $^{1}J_{PP} = 52.18$; **4'b** (40%) δ P$_1$ $= 16.12$, δ P$_2$ $= 31.79$, $^{1}J_{PP} = 53$. Mass spectrum *m/e* (%): 360 (34, M$^+$), 328 (20, M–S), 296

(9, M–2S), 220 (40, M–PhPs), 188 (97, M–PhP2S), 174 (28, M–2Ph–S), 107 (50, PhP–H), 91 (33), 77 (57, Ph).

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