SYNTHESIS AND REACTIVITY OF A NEW DIBENZOBICYCLIC PHOSPHORANE
OF UNUSUAL HIGH STABILITY:1-PHENYL-5-AZA-2,8-DIOXA-1-PHOSPHA^V-
DIBENZO[c,f]BICYCLO[3.3.0]OCTANE

Rosalinda Contreras[/][*], Apolonia Murillo[/], Guillermo Uribe[/], and Alain Klaébé[#]

[/]Centro de Investigación y de Estudios Avanzados del I.P.N. De-
partamento de Química. Apartado Postal 14-740. 07000-México,D.F.
[#]Unité Associee au CNRS No. 454, Université Paul Sabatier.
31062 Toulouse Cedex, France

Abstract — The title compound was synthesized, and its structure
and reactivity were studied. It shows a remarkable stability.

The study of structure and reactivity of bicyclic phosphoranes led to interesting
results. One of these is the opening of the bicyclic compound 2 with borane di-
methylsulfur (BH$_3$.SMe$_2$), compound 2 does not bear basic centers, however it reacts
rapidly with the Lewis acid to afford a very stable bis-adduct 3 of its tautomeric
phenylphosphonite 2'[1] (scheme 1). Another result was the fact that compound 2 is
capable to exchange its hydrogen bonded to phosphorus with deuterium oxide. This
exchange is catalyzed by para-toluensulfonic acid[2] (scheme 1).
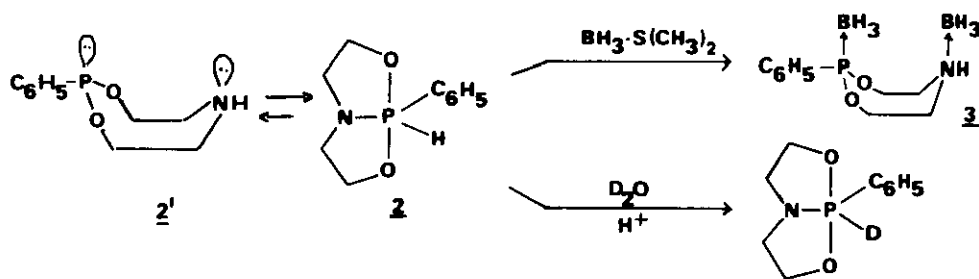
Scheme 1

In order to understand more about these systems we decided to prepare the dibenzo-
bicyclic phosphorane 1 and to investigate the reactivity of this new structure
with two Lewis acids BH$_3$SMe$_2$ and BH$_3$THF, and the acidic character of the hydrogen
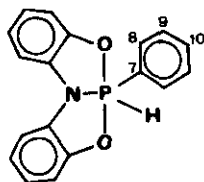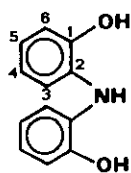bonded to phosphorus.
The compound 1 was prepared from reaction of 2,2'-diphenolamine 4 and bis-(dime-
thylamino)-phenylphosphane 5 (scheme 2).

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*To whom correspondence should be addressed.
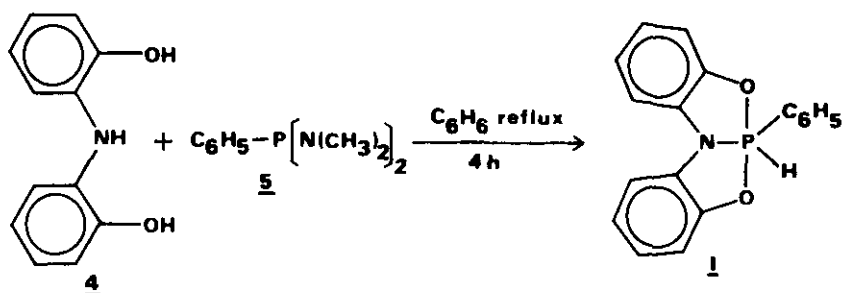
Scheme 2

A white crystalline compound was obtained in 90% yield with the following data:

^{1}H NMR (TMS, CDCl$_3$) δ= 8.9 (d, 1H, J_{H-P}= 769 Hz); δ= 6.6-8 ppm (m, 13 H). ^{31}P NMR (85% H$_3$PO$_4$, DMSO) δ= -37.4 ppm (d, J_{P-H}= 769 Hz).

^{13}C NMR

COMPOUNDS	ATOMS	1	2	3	4	5	6	7	8	9	10
1^a	δ ppm=	146.1	137	110.3	121.6	120.6	110.7	c	129.9	128.7	131.9
	J(Hz)=	(4.8)		(11)			(19.6)		(13.3)	(14.6)	(3.6)
4^b	δ=	148.1	131.7	120.7	123.5	121.5	115.3				

a) In DMSO. b) In CDCl$_3$. c) Non attributed.
Mass spectrum M$^+$= 307.1 (62.8); 230(100); 201.2 (39.8). IR (KBr) ν_{PH} 2400 cm^{-1}.
MP 113°C

Compound 1 is stable in the presence of water, opposed to the behaviour of phosphorane 2. No deuterium exchange of the hydrogen bonded to phosphorus was observed in deuterium oxide even in presence of triethylamine or para-toluensulfonic acid. Treatment of 1 with sodium hydride followed by methyl iodide in CHCl$_3$ did not substitute the hydrogen bonded to phosphorus by a methyl group. These facts show that compound 1 has a remarkable stability. Compound 2 reacts instantaneously and vigorously with BH$_3$SMe$_2$ to give 3. But no appreciable reaction occurs in 48 h between compound 1 and BH$_3$SMe$_2$. After seven days a small signal ($\approx$20%) of a P-BH$_3$ group was detected in ^{11}B nmr at δ= -40 ppm.

The reaction of 1 with one equivalent of BH$_3$THF in CH$_2$Cl$_2$ showed after two days, two small broad signals in ^{11}B nmr, besides the one of the BH$_3$THF, one at δ= -40 ppm characteristic of a P→BH$_3$ function, and another at -16 ppm attributed to a borate probably from a slight decomposition of BH$_3$THF. After one week some BH$_3$THF

($\approx$20%) remained and three signals were observed, one at -40 ppm ($\approx$35%), a broad single band at +17 ppm ($\approx$10%) and a doublet at +26 ppm (35%; J= 160Hz), similar to the signal of compound 9 described elsewhere[3], no N$\rightarrow$BH$_3$ band was observed. The ^{31}P nmr of the same reaction mixture showed three bands a doublet at -37.4 ppm of phosphorane 1 ($\approx$20%), a broad signal of a phosphorus coupled with boron at +143 ppm (30%) attributed to a borane adduct of a phenylphosphonite similar to compound 10[4], also it was observed a broad doublet at +105 ppm (J= 390 Hz, 45%). This doublet was coupled with boron and with one hydrogen, it was deduced that this signal must belong to a phosphorus with a borane, a hydrogen, a phenyl plus another substituent as oxygen or nitrogen, the coupling constant corresponds to a tetracoordinated phosphorus, we could not find in the literature the nmr spectra of other similar phosphorus compound that could help us to support the assignment, but in base of nmr data we propose two structures, 6 and 7 for the products of the reaction of compound 1 with BH$_3$THF in CH$_2$Cl$_2$ (scheme 3).
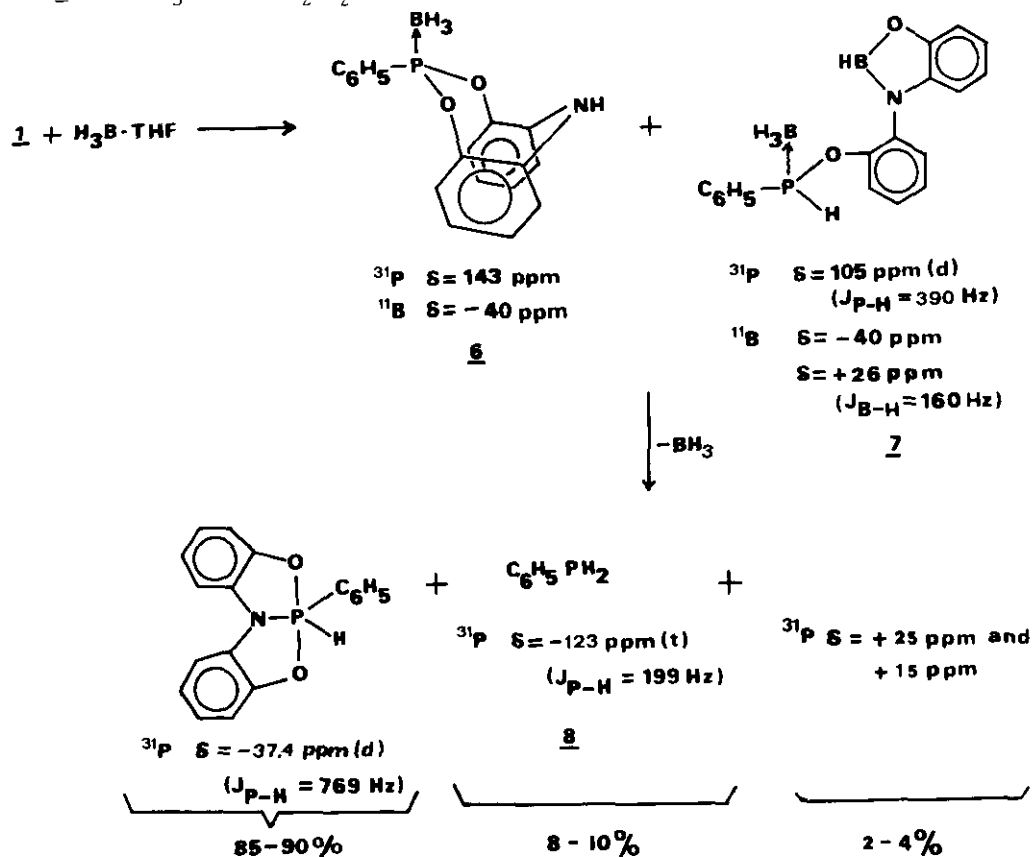

Scheme 3

The reaction mixture of 1 with BH₃THF was evaporated under vacuum, it afforded a white powdered solid wich was dissolved again in a solvent mixture of methylene chloride and DMSO, the ^{11}B and ^{31}P spectra were recorded again, ^{31}P nmr spectrum showed that the reaction mixture was converted to phosphorane 1 in ≈85-90%, some other signals appeared but none of them showed boron-phosphorus coupling indicating that the borane was lost by vacuum evaporation, one of these signals (-123 ppm, J= 199Hz; ≈8-10%) was phenylphosphine 8 and other two at +25 ppm and +15 ppm (2-4%) could be attributed to some phosphonates. The ^{11}B nmr spectrum showed that the P-BH₃ and B-H signals have disappeared and only a borate signal was observed at +18 ppm probably due to a small decomposition of borane.

^{11}B δ=+28ppm
J=170 Hz
9

^{31}P δ = + 133 ppm
10
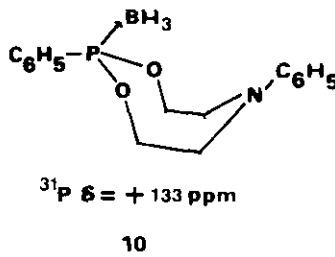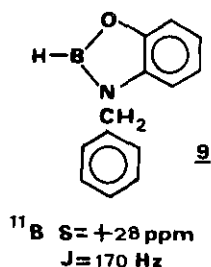
The analysis of the above results lets us to assume that the four cycles of compound 1 must be coplanar due to steric strain of the system which can be easily shown with Dreiding models. This planar conformation allows a strong delocalisation of the nitrogen electron pair with the π system of the benzo substituents and toward the empty d orbital of the phosphorus atom. The nitrogen-phosphorus donation is well admitted as the involvement of the nitrogen lone pair into π bonding to the π-acid phosphorus atom[5]. In phosphoranes it is known that equatorial nitrogen can be retrocoordinated to phosphorus when it adopts a trigonal geometry coplanar with the axial phosphorus substituents[6]. This π bonding must be particularly favored in compound 1 because of its bicyclic structure. The recently reported X-ray structure determination of a bicyclic three coordinated phosphorus 11 containing two ethylenic intracyclic patterns, shows a planar conformation which is an argument for the proposed planar structure of compound 1[7].

Another experimental result indicating the high stability of this bicyclic phosphorane is the mass spectrum analysis of 1 where the base peak corresponds to structure 12, the similar structure was not the base peak in the fragmentation of phosphorane 2.

11

m/e   230 (100 %)
12
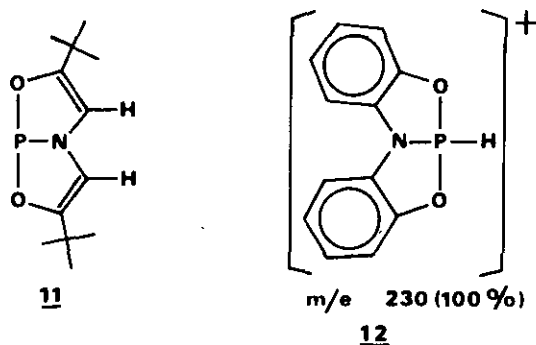
Also the nitrogen electrons donation to phosphorus promoted by the coplanarity of
compound 1 can account the absence of deuterium-hydrogen exchange of the hydrogen
bonded to phosphorus, even in the presence of base, the phosphorane structure must
be extremely stable and rule out any equilibrium with an open phosphonite form as
for 2. The π delocalisation can be observed in ^{13}C nmr, it shows for carbon 2,
binded to nitrogen, of compound 1 a five ppm downfield shift compared with the same
carbon in diphenolamine 4, this shift indicates an electron deficiency in carbon 2
caused by attraction towards the nitrogen atom.

The borane coordination have been used as a test for the determination of the
basic centers in molecules [1,4] and also for the degree of N-P electron donation[8].
In this case, the low reactivity of phosphorane 1 with borane can be attributed
to an absence of basic sites in 1 and to the high stability of 1 compared to its
tautomers 13 and 14 (no one of them was observed in ^{31}P nmr of 1).

13   **1**   **14**
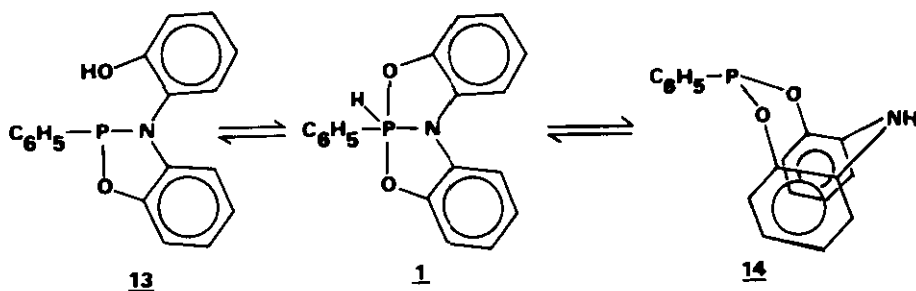
Addition of borane did not give $N-BH_3$ adducts, only the $P-BH_3$ mono-adducts <u>6</u> and <u>7</u> of tautomers <u>13</u> and <u>14</u> were observed. It is remarkable that compounds <u>6</u> and <u>7</u> can easily afford the phosphorane <u>1</u> by loss of BH_3 moiety. This phenomenon shows the extraordinary stability of phosphorane <u>1</u> compared with its opened phenylphosphonite tautomers.

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