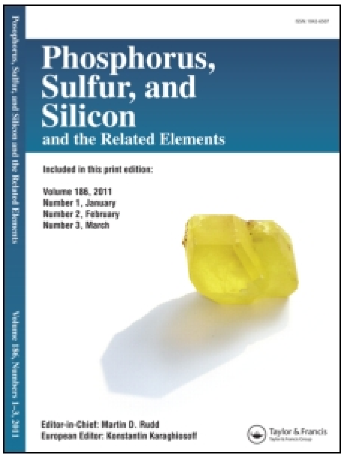

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UNUSUAL BEHAVIOR OF 2-CYCLOPENTADIENYL-1,3-DIOXAPHOSPHOLANE

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UNUSUAL BEHAVIOR OF 2-CYCLOPENTADIENYL-1,3-DIOXAPHOSPHOLANE

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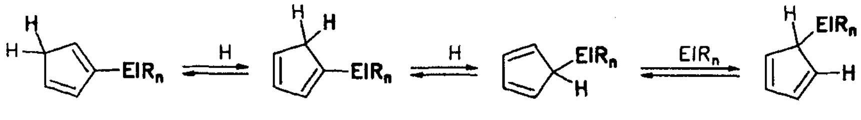
It has been found that 2-cyclopentadienyl-1,3-dioxaphospholane (**2**) and 2-cyclopentadienyl-1,3-dioxaphosphorinane (**3**) demonstrate different fluxional behavior. While **3** represents a mixture of three isomers **3a–c**, **2** exists in only the allylic form **2a**. The relative stability, molecular structure and the fast rate of [1,5]-phosphotropic shifts in **2a** indicate that the efficiency of σ-π-conjugation is increased with a decrease in the O-P-O angle in dialkyl esters of cyclopentadienylphosphorous acids.

Key words: Phosphorylated cyclopentadienes; sigmatropic rearrangements; σ-π-conjugation.

INTRODUCTION

The heteroatomic substituted cyclopentadienes represent so- called "fluxional" compounds. Allylic isomers **1a** are able to undergo [1,5]-sigmatropic (elementotropic and/or prototropic) intramolecular rearrangements. Either degenerate allylic **1a**′ or vinylic isomers **1b** and **1c** can be formed. It is postulated that the rate of rearrangement **1a** $\rightleftarrows$ **1a**′ increases with an increase of the effective magnitude of σ-π-conjugation in the allylic isomer **1a**. Elementotropic shifts were found to take place in the cyclopentadienyl derivatives of Si, Ge, Sn, P, B and other elements[1] (Scheme I).

Some phosphorylated cyclopentadienes have been synthesized.[2–5] These compounds have been found to be rather unstable, with the vinylic isomers being dominant (except for cyclopentadienyldifluorophosphine[4]) in the equilibrium mixtures. Only phosphorylated pentamethylcyclopentadienes, in which prototropic shifts are impossible, represent a suitable model for elucidation of the **1a** $\rightleftarrows$ **1a**′ process.[6]



1c 1b 1a 1a'

SCHEME I

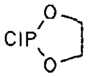
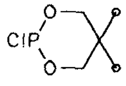
In the course of our current investigations we have found it possible to prevent prototropic shifts in **1a** and to isolate phosphorylated cyclopentadiene in a pure allylic form by means of regulating the environment of the phosphorus atom.

RESULTS

We have synthesized 2-cyclopentadienyl-1,3-dioxaphospholane (**2**) and 2-cyclopentadienyl-1,3-dioxaphosphorinane (**3**) and compared their NMR spectral behavior. Compounds **2** and **3** were easily prepared from thallium cyclopentadienide and the corresponding chloride (Scheme II).

We have found only the allylic isomer of phospholanous compound **2** to be present (there are some impurities, but their structures can't be proved owing to their small concentrations) while three isomers of the phosphorinane derivatives **3a–c** were observed in the equilibrium mixture of **3**.

The temperature dependence of NMR spectra of **2** and **3** have been studied (Figs. 1 and 2). Compound **2a** (Fig. 1) displays no dynamic properties below −65°C. An increase of temperature up to −5°C causes the collapse of the cyclopentadienyl proton signals. This signal sharpens on heating but we have failed to observe the formation of a sufficiently sharp singlet belonging to the cyclopentadienyl protons even at 60°C because further heating resulted in dimerization of **2**. The NMR spectra of **3** are more complicated. This substance is a mixture of three isomers (Fig. 2). It is remarkable that the difference between the collapse temperatures for **2a** and **3a** (−5°C and 50°C respectively) is about 55°. Therefore the σ-π-conjugation in **2a** seems to be more pronounced than in **3a**.

ClP(OR)$_2$		a	b	c
	(2)	>98%	<1%	<1%
	(3)	38%	42%	20%

SCHEME II

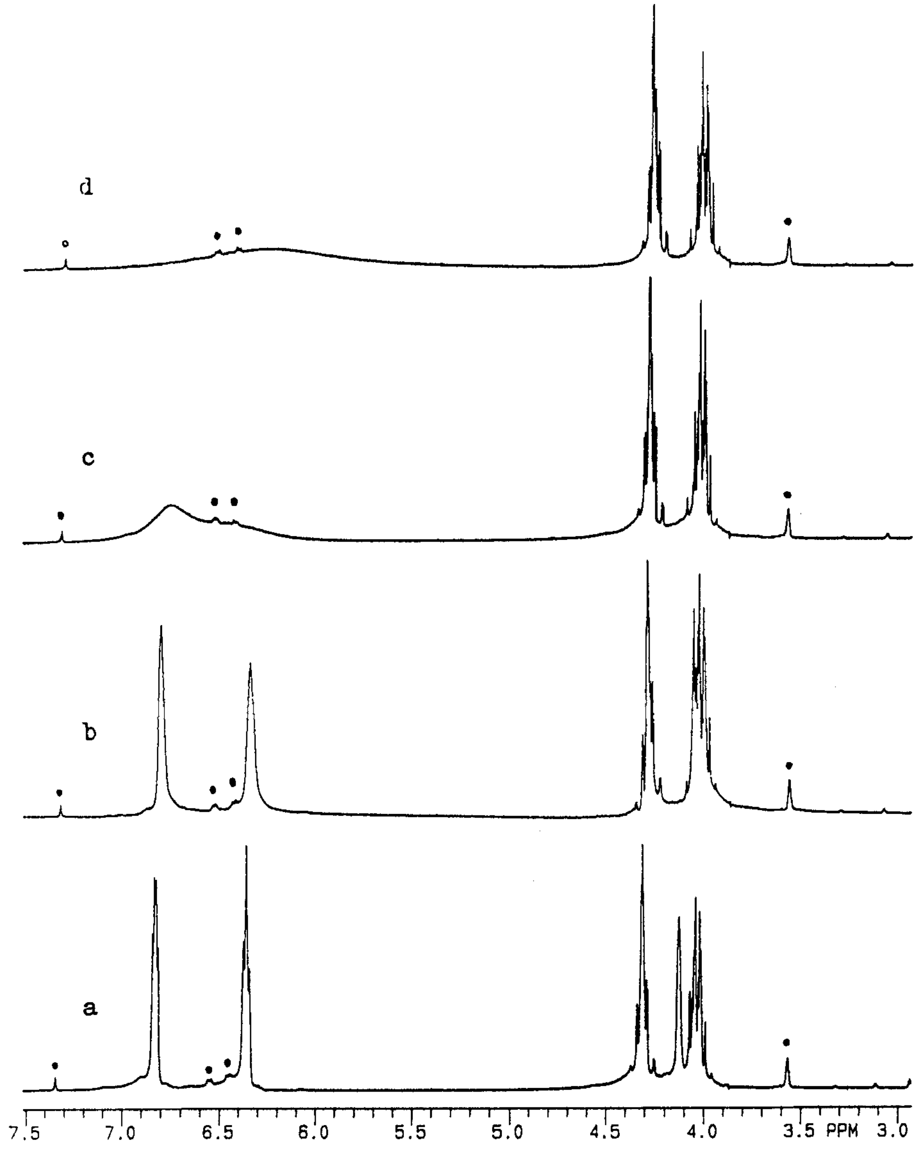


FIGURE 1 The NMR spectra of **2a**: a) −65°C; b) −35°C; c) −5°C; d) 25°C (the signals of solvent and impurities are marked by ●).

We have determined the molecular structure of **2a** (Fig. 3). Atomic coordinates, bond lengths and bond angles are presented in the Tables I–IV. A characteristic feature of the structure of **2a** is the nearly parallel orientation of cyclopentadienyl and dioxaphospholane rings (the angle between the average planes is equal to 8.8°). The phosphorus ring has an envelope conformation with the phosphorus atom displaced by 0.419Å from the O(1),O(2),C(6),C(7) plane towards the other ring. The envelope angle is 22.2°. The cyclopentadienyl ring carbon atoms are complanar within 0.025Å. The torsion angles O(1)—P(1)—C(1)—C(5) and O(2)—P(1)—

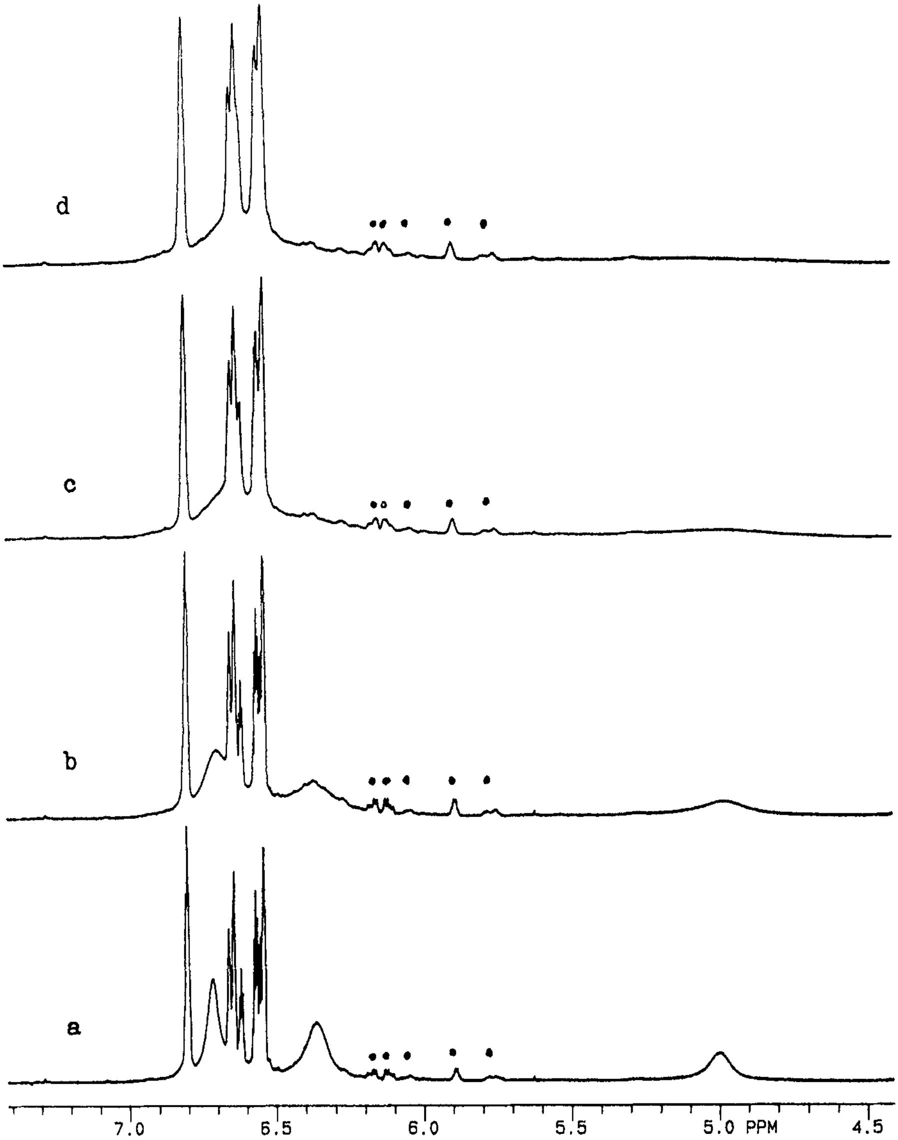


FIGURE 2 The NMR spectra of **3**: a) 30°C; b) 40°C; c) 52°C; d) at 60°C is caused by the beginning of prototropic process in **3** (the signals of solvent and impurities are marked by ●).

C(1)—C(2) that characterize the mutual orientation of the rings are −77.6° and 78.7°, respectively. The non-bonded intramolecular distances H . . . O(1,2) are 2.93 and 2.85Å, which is too long to assume H . . . O interactions. The phosphorus atom has a pyramidal geometry with the usual bond angles sum of 299.2°.[7] The angle between the P(1)—C(1) bond and the plane of the cyclopentadienyl ring is 77.1°. The last value indicates the great effectivity of σ-π-conjugation in **2a** (the previously observed angles in all structurally studied element substituted cyclopentadienes are smaller[1]).

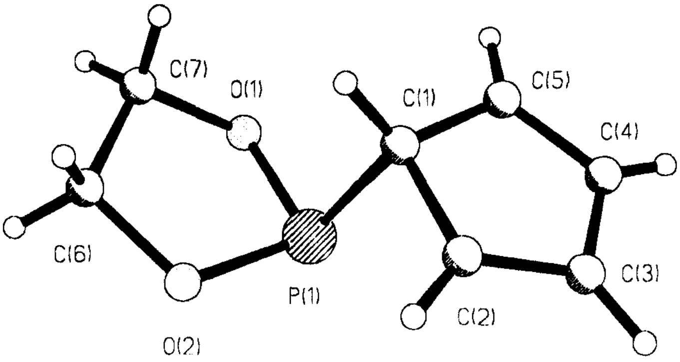


FIGURE 3 Molecular structure of **2a**.

TABLE I

Atom coordinates (× 10^4) and temperature factors (Å^2 × 10^3) of non-hydrogen atoms in **2a**

Atom	X	Y	Z	U*
P(1)	1360(1)	1331(1)	9818(1)	24(1)
O(1)	3108(1)	2463(3)	9795(1)	28(1)
O(2)	4355(1)	2698(4)	11005(1)	34(1)
C(1)	3760(1)	3417(4)	8769(2)	23(1)
C(2)	4391(1)	2419(4)	8895(2)	26(1)
C(3)	4186(1)	718(5)	8066(2)	29(1)
C(4)	3437(1)	613(5)	7333(2)	31(1)
C(5)	3175(1)	2290(5)	7701(2)	27(1)
C(6)	4084(1)	4782(5)	11288(2)	28(1)
C(7)	3295(1)	4830(4)	10410(2)	28(1)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U(i;j) tensor.

DISCUSSION

It is clear that the decrease of the angle between two P—X bonds in Cp—PX$_2$ can lead to the increase of p-character of hybridized phosphorus orbital interacting

TABLE II

Bond length (Å) in **2a**

P(1)-O(1)	1.638(2)	O(2)-C(6)	1.477(3)	C(3)-C(4)	1.441(3)
P(1)-O(2)	1.634(1)	C(1)-C(2)	1.491(4)	C(4)-C(5)	1.354(4)
P(1)-C(1)	1.892(3)	C(1)-C(5)	1.481(2)	C(6)-C(7)	1.530(3)
O(1)-C(7)	1.445(3)	C(2)-C(3)	1.352(3)		

TABLE III

Bond angles (deg.) in **2a**

O(1)-P(1)-O(2)	94.4(1)	C(2)-C(1)-C(5)	103.8(2)
O(1)-P(1)-C(1)	102.9(1)	C(1)-C(2)-C(3)	108.5(2)
O(2)-P(1)-C(1)	101.9(1)	C(2)-C(3)-C(4)	109.3(2)
P(1)-O(1)-C(7)	111.0(1)	C(3)-C(4)-C(5)	109.5(2)
P(1)-O(2)-C(6)	112.9(1)	C(1)-C(5)-C(4)	108.5(2)
P(1)-C(1)-C(2)	100.1(1)	O(2)-C(6)-C(7)	107.3(2)
P(1)-C(1)-C(5)	100.8(2)	O(1)-C(7)-C(6)	106.9(2)

TABLE IV

Hydrogen atom coordinates ($\times 10^3$) and temperature factors ($Å^2 \times 10^2$) in **2a**

Atom	X	Y	Z	U
H(1)	377(1)	323(6)	892(2)	5(1)
H(2)	487(1)	286(5)	953(2)	3(1)
H(3)	448(1)	-24(6)	799(2)	4(1)
H(4)	321(1)	-12(6)	676(2)	4(1)
H(5)	271(1)	258(5)	741(2)	3(1)
H(6)a	429(1)	630(5)	1126(2)	4(1)
H(6)b	421(1)	446(5)	1203(2)	4(1)
H(7)a	318(1)	618(5)	991(2)	4(1)
H(7)b	302(1)	500(6)	1072(2)	5(1)

TABLE V

NMR data of **2** and **3** (THF-d_8, 20°C, TMS for ^{1}H, ^{13}C and 85% H_3PO_4 for ^{31}P as a reference standard)

Compound		NMR data
2a	$^1H^a$	δ 6.84(m, 2H); 6,38(m, 2H); 4.33(m, J_{HP}=1.9 Hz, 2H); 4.13(s, 1H); 4.05(m, J_{HP}=6.7Hz, 2H)
	$^{13}C^a$	δ 136.6(d, J_{CP}=4.9Hz); 130.0(d, J_{CP}=9.8Hz); 65.9(d, J_{CP}=9.4Hz); 64.1(d, J_{CP}=48.6Hz)
	$^{31}P^b$	δ 162.3(s)
3a	^1H	δ 6.72(br.s, 2H); 6.36(br.s, 2H); 4.98(br.s, 1H); 4.17(dd, J_{HP}=6Hz, 2H); 3.58(m, J_{HP}=11Hz, 2H); 1.19(s, 3H); 0.89(s, 3H)
	^{13}C	δ 135.4(br.s); 131.0(br.s); 55.7(br.d, J_{CP}= 50Hz); 72.31(d, J_{CP}=3.4Hz); 33.18(d, J_{CP}= 4.2Hz); 22.54(s).
	$^{31}P^b$	δ 141.5(s)
3b	^1H	δ 6.85-6.53(m, 3H); 3.84(dd, J_{HP}=6Hz, 2H); 3.44(m, J_{HP}=13.5Hz, 2H); 3.10(m, 2H); 1.20 (s, 3H); 0.64(s, 3H)
	^{13}C	δ 148.81(d, J_{CP}=46.4Hz); 139.60(d, J_{CP}=16.8 Hz); 137.90(d, J_{CP}=5.6Hz); 132.81(d, J_{CP}= 4.0Hz); 72.19(d, J_{CP}=3.5Hz); 42.70(d, J_{CP}= 11.8Hz); 33.68(d, J_{CP}=4.3Hz); 22.68(s)
	$^{31}P^b$	δ 146.3(s)
3c	^1H	δ 6.68-6.53(m, 3H); 3.80(dd, J_{HP}=6Hz, 2H); 3.42(m, J_{HP}=13.5Hz, 2H); 3.15(dd, J_{HP}=18.0 Hz, 2H); 1.23(s, 3H); 0.60(s, 3H)
	^{13}C	δ 147.80(d, J_{CP}=45.0Hz); 138.85(d, J_{CP}=15.0 Hz); 135.19(d, J_{CP}=2.9Hz); 132.31(d, J_{CP}= 13.6Hz); 72.15(d, J_{CP}=3.5Hz); 43.89(d, J_{CP}=2.3Hz); 33.71(d, J_{CP}=4.3Hz); 22.58(s)
	$^{31}P^b$	δ 143.1(s)

[a] at -65°C; [b] in Et_2O.

with cyclopentadienyl ring and thus to the increase of the σ-π-conjugation in this molecule.

We have compared two phosphorylated cyclopentadienes: **2** in which the geometry of the phosphorus environment is distored (the angle O—P—O in **2a** is 94.4°) and **3** in which the phosphorus geometry should be almost normal (the angle O—P—O in dioxaphosphorinanes and in acyclic phosphites is near 100°[7]).

We have found that the decrease of the angle between two P—O bonds dramatically results in both an increase of the phosphotropic shift rate and an increase of the relative stability of allylic form **a** (allylic form **a** has not been found in acyclic cyclopentadienyl phosphites[3]).

This result can be applied to the synthesis of stable phosphorylated cyclopentadienes. Since the vinylic isomers of the type **b** and **c** are more active in the Diels-Alder reaction, phosphorylated cyclopentadienes with a five-membered phosphorus heterocycle must be more stable with respect to dimerization. In fact, compound **2** can be stored in solution without dimerization for several days. On the contrary, the dimerization of **3** proceeds more rapidly. A detectable quantity of its dimer appears in one hour. Besides, phosphorylated silacyclopentadienes, which undoubtly contain substituents in the allylic position, are significantly more stable than their non-sililated analogs.[5]

EXPERIMENTAL

Compounds **2** and **3** are very instable in air, all operations were carried out under dry argon. The NMR spectra were recorded on a Varian VXR-300 instrument. Quantitative analyses were performed on the Carlo Erba analyser. The X-ray diffraction experiment was carried out with a four-circle automated Syntex-P2$_1$ diffractometer at −120°C (λMo-K$_\alpha$, graphite monochromator, $\theta/2\theta$ scan, $2\theta \leq 50°$). Crystals of **2a** are monoclinic, space group C2/c, a = 23.699(3), b = 5.246(1), c = 14.716(2)Å, β = 125.83(3)°, V = 1483(1)Å^3, Z = 8. 2446 reflections were measured, of them 1028 independent reflections with $|F| \geq 8\sigma$ were used in calculations and refinement. The structure was solved by the direct method and refined by least-squares technique in anisotropic-isotropic (for hydrogen atoms) approximations to R = 0.040, R$_w$ = 0.044, GOF = 1.46. All calculations were performed with IBM PC/AT, using the SHELXTL PLUS programs.

Synthesis of compounds **2** *and* **3**. 10 mmol of corresponding chloride diluted in 10 ml of Et$_2$O was added dropwise to a suspension of 3.00 g (11 mmol) of CpTl[8] in 20 ml of Et$_2$O. The mixture was stirred for about 1 hour, then the solution was filtered, and the solvent was removed. The crystalline residue can be recrystallized from pentane. NMR data for **2** and **3** are given in Table V. (Compound **3** exists at room temperature as an inseparable equilibrium mixture of three isomers **3**(**a**–**c**). Nevertheless their mole fractions are not equal so that it is possible to pick out their NMR signals). Compound **2** can be sublimed at 80°C (10^{-2} torr), compound **3** boils at 52°C (10^{-2} torr).

Found for **2**: C 53.29; H 5.68.
Calculated for $C_7H_9O_2P_1$: C 53.86; H 5.81.

Found for **3**: C 60.43; H 7.51.
Calculated for $C_{10}H_{15}O_2P_1$: C 60.70; H 7.63.

REFERENCES

1. P. Jutzi, *Chem. Rev.*, **86**, 983 (1986).
2. M. I. Kabachnik and E. N. Tsvetkov, *J. Obsch. Khim.*, **30**, 322 (1960).
3. F. Mathey and J. P. Lampin, *Tetrahedron*, **31**, 2685 (1975); F. Mathey and J. P. Lampin, *J. Organomet. Chem.*, **128**, 297 (1977); B. Deschamps and F. Mathey, *Phosphorus and Sulfur*, **17**, 317 (1983).
4. J. E. Bentham, E. A. V. Ebsworth and H. Moretto, *Angew. Chem.*, **11**, 640 (1972); R. T. Raine,

R. W. Light and D. E. Maier, *Inorg. Chem.*, **18,** 368 (1979).

5. P. Jutzi and H. Saleske, *Chem. Ber.*, **110,** 1269 (1977).
6. P. Jutzi and H. Saleske, *Ibid.*, **117,** 222 (1984); D. Guidat, E. Niecke, B. Krebs and M. Dartmann, *Chimia,* **39,** 277 (1985); P. Jutzi, U. Meyer, B. Krebs and M. Dartmann, *Angew. Chem.*, **98,** 894 (1986).
7. V. A. Naumov and L. V. Vilkov, *Molecular structures of organophosphorus compounds* (Nauka, Moscow, 1986), pp. 23–86.
8. H. Meister, *Angew. Chem.*, **69,** 533 (1957).