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### INVESTIGATIONS IN THE SYSTEM PHOSPHORUS TRICHLORIDE/1,3-PROPANEDIOL

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# INVESTIGATIONS IN THE SYSTEM PHOSPHORUS TRICHLORIDE / 1,3-PROPANEDIOL

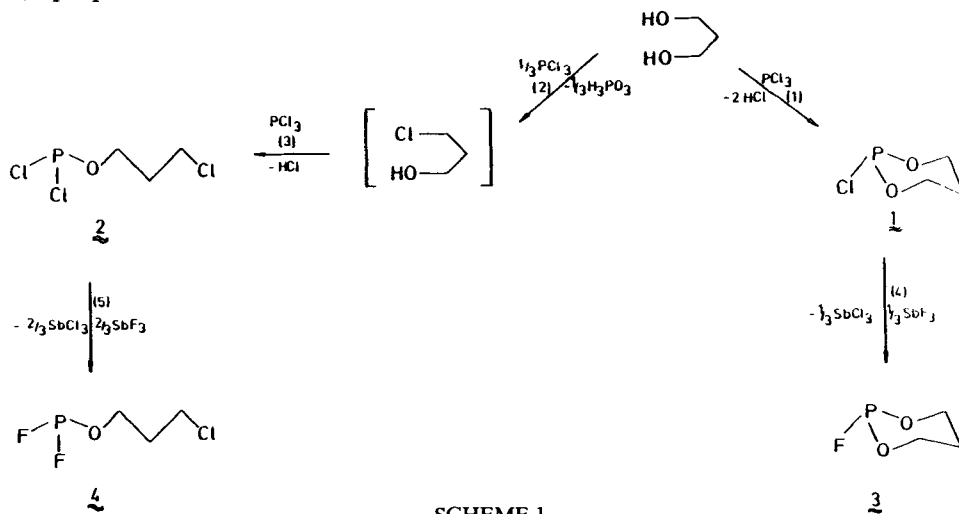
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The reaction of phosphorus trichloride and 1,3-propanediol was reinvestigated. Besides 2-chloro-1,3,2-dioxaphosphorinane **1** 3-chloropropyl-dichlorophosphite **2** was formed. Compound **1** and **2** were fluorinated to give the corresponding phosphorinane **3** and the phosphite **4**, respectively. Proton NMR spectra were recorded at 360.08 MHz and simulated for **1** and **3**. The 4-H and 6-H signals were treated not as first order but as AA'XX' systems.

The importance of 1,3,2-dioxaphosphorinanes in biological processes has initiated intense activity in preparative phosphorus chemistry and research on structural and mechanistic properties, respectively.<sup>1</sup> Our interest in 2-fluoro-1,3,2-dioxaphosphorinane led us to reinvestigate the reaction of phosphorus trichloride and 1,3-propanediol.<sup>2</sup>



SCHEME 1

## RESULTS

Two phosphorus compounds, the known<sup>1</sup> 2-chloro-1,3,2-dioxaphosphorinane **1** (eq. 1) (48%) and 3-chloropropyl-dichlorophosphite **2** (5%) (eq. 2, 3) were isolated upon

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TABLE I  
Shifts in ppm (diagonal) and scalar couplings in Hz (off diagonal) of **1** (lower left) and **3** (upper right).  
**3** (X = F)

	P	2-Hal	4-H <sub>a</sub>	4-H <sub>c</sub>	5-H <sub>a</sub>	5-H <sub>c</sub>	6-H <sub>a</sub>	6-H <sub>c</sub>
<b>1</b> (X = Cl)								
P	120.84							
	154.8	1172.0	3.2	10.4	0.6	2.3	3.2	10.4
2-Hal		-61.9	1.1	0.1	0.7	0.5	1.1	0.1
4-H <sub>a</sub>			4.401					
	5.6	4.596	4.596	-11.0	12.5	2.4	1.2	-0.8
4-H <sub>c</sub>				3.856				
	10.5		-11.1	3.990	4.5	2.2	-0.8	1.8
5-H <sub>a</sub>			13.0	4.6	2.437	-14.5	12.5	4.5
	1.5				2.488			
5-H <sub>c</sub>						1.624		
	2.6		2.5	1.7	-14.5	1.654	2.4	2.2
6-H <sub>a</sub>							4.401	
	5.6		<sup>a)</sup>	<sup>a)</sup>	13.0	2.5		-11.0
6-H <sub>c</sub>							4.596	
	10.5		<sup>a)</sup>	2.0	4.6	1.7	-11.1	3.856
								3.990

<sup>a)</sup> Values < 0.2 Hz, not determined uniquely.

reacting phosphorus trichloride and 1,3-propanediol. 3-Chloro-1-propanol (eq. 2) was formed probably as an intermediate furnishing **2** in the presence of phosphorus trichloride (eq. 3). 1,3-Dichloropropane,<sup>3</sup> but no 3-chloro-1-propanol was found in the reaction mixture. The two phosphorus(III) derivatives **1** and **2** could be separated by distillation (**1**: 34°C/4 Torr, **2**: 72°C/4 Torr). The corresponding fluorophosphites **3** and **4** were obtained easily by Cl/F exchange reaction with antimony trifluoride (eq. 4, 5). All four compounds were colourless, air and moisture sensitive liquids.

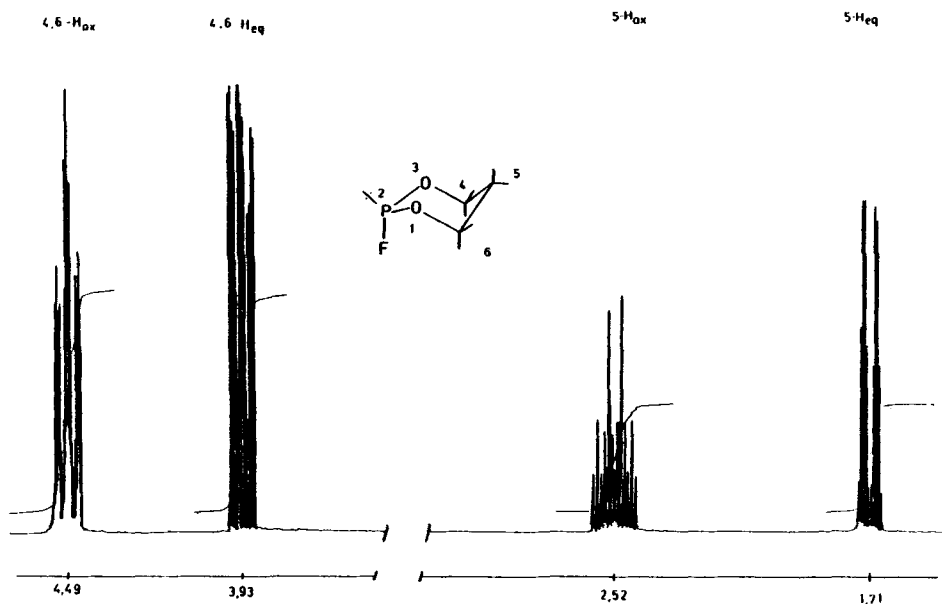


FIGURE 1A Proton n.m.r. spectrum of **3**.

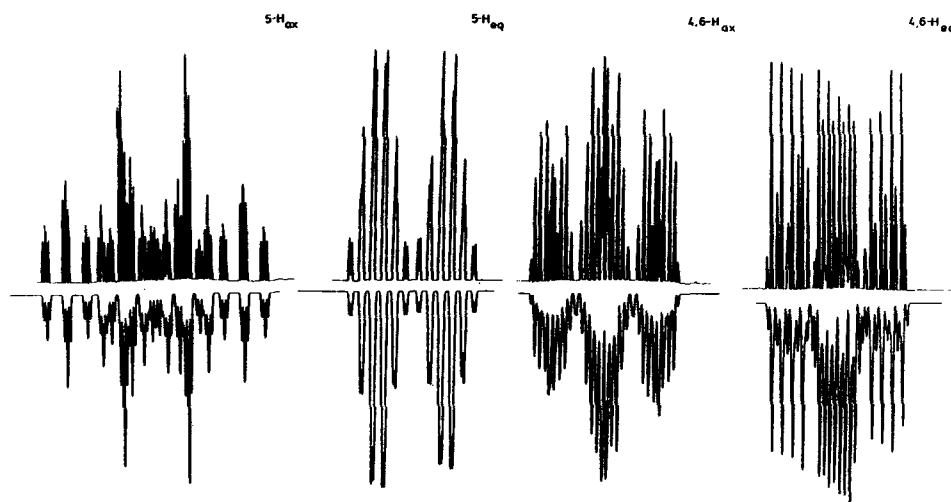


FIGURE 1B Expanded portions of the experimental (upper trace; negative intensities obtained under the experimental conditions applied are omitted) and the simulated spectrum (lower trace).

The 70 eV mass spectra of **2**, **3** and **4** exhibit fragments like  $M^+$  (**2**, **3**, **4**),  $M^+-X$  (**2**,  $X = Cl$ ; **4**,  $X = F$ ),  $M^+-C_2H_2$  (**3**),  $C_3H_2O^+$  (**3**),  $PX_2^+$  (**2**, **4**),  $F_2POCH_2^+$  (**4**),  $C_3H_2Cl^+$  (**2**, **4**),  $C_3H_5Cl^+$  (**2**) and  $C_3H_5^+$  (**2**, **4**) as characteristic ions.

The  $^1H$ -NMR spectrum of **1** has been recorded at low field and analyzed recently.<sup>4-13</sup> Our data (Table I, lower left) were obtained at 360 MHz and agree with the earlier reports.

Methyl substituted 2-fluoro-1,3,2-dioxaphosphorinanes were studied (5-dimethyl<sup>6,11</sup>, 4-methyl<sup>14</sup>) but not compound **3**, however. The spectra (Table I, upper right; Figure 1) were treated as first order, except the 4-H and 6-H signals of **1** and **3** which were analyzed as  $AA'XX'$  systems. The synthetic spectra<sup>15</sup> fitted the experimental

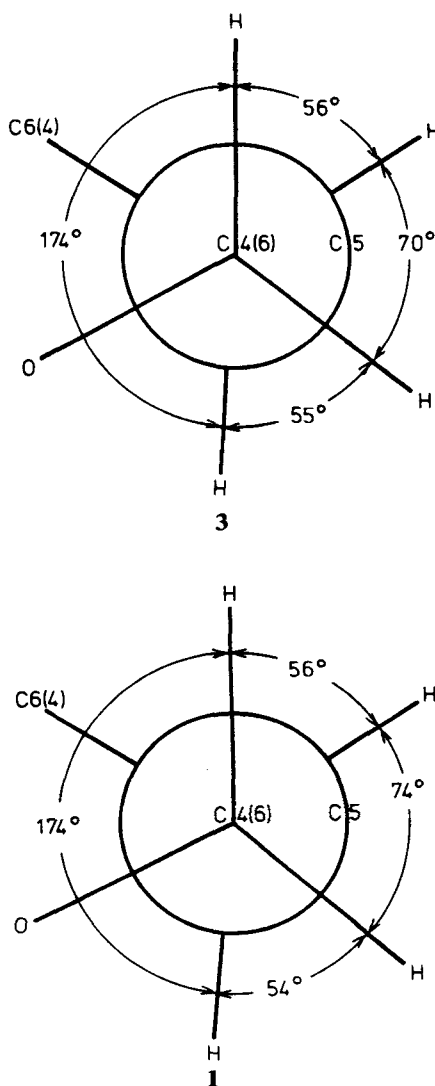


FIGURE 2 Dihedral angles along C4-C5 and C5-C6 in **1** and **3** (calculated from  $^3J_{HH}$ , lit. 19).

ones closely with substantial  $^4J_{aa}$  and  $^4J_{ac}$ .  $J_{FH}$  values were assumed positive.<sup>16-18</sup> Using a multi-parameter approach accounting for nonproton substituents on the H—C—C—H fragment,<sup>19</sup> we transformed  $^3J_{HH}$  values into dihedral angles (cf. Figure 2).

The angles add up to 358°C for **1** and 355°C for **3** close to the full turn of 360°C proving the validity of the calculation. Both, **1** and **3** exist almost exclusively as a single conformer, the propylene fragment being pronouncedly chair-shaped. According to Dreiding models, the slight inflection of the axial protons towards the ring center might indicate a partial flattening of the chair in the OPO fragment.

The  $^1J_{PF}$  value (1172.0 Hz) is somewhat at variance with lit. **14** (1156 Hz), but in agreement with lit. **6** (1180 Hz).  $^4J_{FH}$  is a geometric indicator for fluorine in axial position  $^4J_{ee}$  being one magnitude larger than  $^4J_{ac}$ , a relation similar to that found in cyclohexanes.<sup>20</sup>

The  $^1\text{H-NMR}$  spectra of **2** and **4** were similar showing a triplet of triplets (merging to give a quintet) for the CH<sub>2</sub> group, a triplet for the ClCH<sub>2</sub> substituent and a doublet of triplets for the OCH<sub>2</sub> fragment (data see Experimental Part).

## EXPERIMENTAL

The appropriate precautions in handling moisture and oxygen-sensitive compounds were observed throughout this work.

Solvents were dried by standard procedures. Mass spectra were recorded on a Varian MAT CH-7 instrument at 70 eV. NMR spectra were obtained on a Bruker WH 360 spectrometer at 360.08 MHz ( $^1\text{H}$ , internal TMS), 338.68 MHz ( $^{19}\text{F}$ , external CCl<sub>3</sub>F) and 145.72 MHz ( $^{31}\text{P}$ , external 85% H<sub>3</sub>PO<sub>4</sub>). Chemical shifts were reported as downfield positive. Solutions ca. 10% (V/V) in CDCl<sub>3</sub> were measured.

**2-Chloro-1,3,2-dioxaphosphorinane<sup>2</sup> (1) and 3-chloro-*n*-propyl-dichlorophosphite (2).** 41.0 g (0.54 mole) 1,3-Propanediol was added dropwise to 95.0 g (0.69 mole) phosphorus trichloride in 100 ml methylene chloride within 1 h and stirred for 1 h at ambient temperature. The mixture was distilled two times at 20 Torr and 4 Torr, respectively, to give 36.4 g (48%) **1** and 5.7 g (5%) (b.p. 72°C/4 Torr) **2**.

Characterization of **2**: MS: 194 ( $\text{M}^+$ , 5%), 159 ( $\text{M}^+ - \text{Cl}$ , 50), 118 ( $\text{PCl}_2\text{OH}^+$ , 25), 101 ( $\text{PCl}_2^+$ , 18), 77 ( $\text{C}_3\text{H}_6\text{Cl}^+$ , 73), 76 ( $\text{C}_3\text{H}_5\text{Cl}^+$ , 100), 42 ( $\text{C}_3\text{H}_6^+$ , 11), 41 ( $\text{C}_3\text{H}_5^+$ , 82) and other fragments (intensities based on  $^{35}\text{Cl}$ ). NMR:  $^1\text{H}$ :  $\delta$  = 2.80 (—CH<sub>2</sub>—, 2 H,  $^3J_{HH}$  = 5.9, tt), 3.70 (ClCH<sub>2</sub>—, 2 H,  $^3J_{HH}$  = 5.9, t), 4.40 (2 H,  $J_{PH}$  = 8.3,  $^3J_{HH}$  = 5.9 Hz, dt);  $^{31}\text{P}$ :  $\delta$  = +179.9.  $\text{C}_3\text{H}_6\text{Cl}_3\text{OP}$  (195, 41) Calc: C, 18.44%; H, 3.09%. Found: C, 18.52; H, 3.04.

**2-Fluoro-1,3,2-dioxaphosphorinane (3).** 2.4 g (0.017 mole) **1** was reacted with 6.0 g (0.034 mole) dry antimony trifluoride for 2 h at ambient temperature. Distillation yielded 2.1 g (95%) **3** (b.p. 62°C).

MS: 124 ( $\text{M}^+$ , 74%), 98 ( $\text{M}^+ - \text{C}_2\text{H}_2$ , 32), 94 ( $\text{M}^+ - \text{OCH}_2$ , 28), 58 ( $\text{C}_3\text{H}_6\text{O}^+$ , 100), 41 ( $\text{C}_3\text{H}_5^+$ , 42) and other fragments.  $\text{C}_3\text{H}_6\text{FO}_2\text{P}$  (124, 05): Calc: C, 23.70%; H, 1.33%; F, 54.15. Found: C, 23.57; H, 1.10; F, 53.90.

**3-Chloro-*n*-propyl-difluorophosphite (4).** 3.2 g (0.016 mole) **2** was reacted with 6.5 g (0.036 mole) dry antimony trifluoride for 4 h at ambient temperature. Distillation yielded 2.4 g (96%) **4** (b.p. 71°C).

MS: 161 ( $\text{M}^+$ , 0.1%), 142 ( $\text{M}^+ - \text{F}$ , 0.1), 127 ( $\text{M}^+ - \text{Cl}$ , 0.1), 99 ( $\text{F}_2\text{POCH}_2^+$ , 37), 77 ( $\text{C}_3\text{H}_6\text{Cl}^+$ , 89), 69 ( $\text{PF}_2^+$ , 62), 41 ( $\text{C}_3\text{H}_5^+$ , 100) and other fragments. NMR:  $^1\text{H}$ :  $\delta$  = 2.14 (—CH<sub>2</sub>—, 2 H,  $^3J_{HH}$  = 5.9, tt), 3.69 (ClCH<sub>2</sub>—, 2 H,  $^3J_{HH}$  = 6.2 t), 4.28 (—OCH<sub>2</sub>—, 2 H,  $^3J_{PH}$  = 6.5,  $^3J_{HH}$  = 5.9 Hz, dt);  $^{19}\text{F}$ :  $\delta$  = -49.4 ( $^1J_{PF}$  = 1289 Hz);  $^{31}\text{P}$ :  $\delta$  = +113.9.  $\text{C}_3\text{H}_6\text{ClF}_2\text{OP}$  (162, 50): Calc: C, 22.57%; H, 3.72%; F, 23.38. Found: C, 22.26; H, 3.60; F, 23.10.

## ACKNOWLEDGMENT

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## REFERENCES AND NOTES

1. B. Maryanoff, R. Hutchins and C. Maryanoff, *Top. Stereochem.* **11**, 187 (1979).
2. H. J. Lucas, F. W. Mitchell and C. N. Scully, *J. Am. Chem. Soc.* **72**, 5491 (1950).
3. Characterized by its  $^1\text{H}$ -NMR spectrum ( $\delta_{\text{H}}(-\text{CH}_2-)=2.20$  ( $^3J_{\text{HH}}=5.90$ ),  $\delta_{\text{H}}(\text{ClCH}_2-)=3.72$ , ( $^3J_{\text{HH}}=5.90$  Hz)) and b.p. 120–122°C.
4. K. Bergesen and P. Albrigtsen, *Acta. Chem. Scand.* **26**, 1680 (1972).
5. C. L. Bodkin, and P. Simpson, *J. Chem. Soc. (B)* **1971**, 1136.
6. D. W. White, R. D. Bertrand, G. K. McEwen and J. G. Verkade, *J. Am. Chem. Soc.* **92**, 7125 (1970).
7. M. Haemers, R. Ottinger, J. Reisse and D. Zimmermann, *Tetrahedron Lett.* **1971**, 461.
8. W. G. Bentrude and J. H. Hargis, *J. Am. Chem. Soc.* **92**, 7136 (1970).
9. J. H. Hargis and W. G. Bentrude, *Tetrahedron Lett.* **1968**, 5365.
10. K. Bergesen, and P. Albrigtsen, *Acta. Chem. Scand.* **25**, 2257 (1971).
11. D. Gagnaire, J. B. Roberts and J. Verrier, *Bull. Chim. Soc. Fr.* **1968**, 2392.
12. V. Mark, C. H. Dungan, M. M. Crutchfield and J. R. van Wazer, *Top. Phosphorus Chem.* **5**, 227 (1967).
13. D. W. White, G. K. McEwen, R. D. Bertrand and J. G. Verkade, *J. Magn. Reson.* **4**, 123 (1971).
14. A. Okruszek and W. J. Stec, *Z. Naturforsch.* **31b**, 354 (1976).
15. The simulation was carried out using the program PANIC from the Bruker software package.
16. W. McFarlane and R. R. Dean, *Chem. Commun.* **1967**, 840.
17. H. Dreeskamp, C. Schumann and R. Schmutzler, *Chem. Commun.* **1970**, 617.
18. J. P. Albrand, A. Cogne, D. Gagnaire, J. Martin, J. B. Robert and J. Verrier, *Org. Magn. Reson.*, **3**, 75 (1971).
19. C. A. G. Haasnoot, F. A. A. M. de Leeuw and C. Altona, *Tetrahedron* **36**, 2783 (1980).
20. W. Offermann and D. Leibfritz, private communication.