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CONFIGURATIONAL STABILITY IN SOME 3-COORDINATE PHOSPHORUS COMPOUNDS[1]

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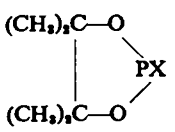
Abstract—PMR spectra of a variety of 4,4,5,5-tetramethyl-1,3,2-dioxaphospholanes, bearing different substituents at phosphorus, have been determined at different temperatures. There is no inversion at phosphorus detectable. The P-chloro compound undergoes a chemical exchange process the rate of which is concentration dependent.

THERE has been considerable recent interest in configurational stability of three-coordinate phosphorus compounds, and studies involving organo-phosphorus compounds have shown that tertiary phosphines are configurationally stable enough to be prepared in optically active form;[2] in addition, geometrical isomers of cyclic phosphines differing in configuration about phosphorus have been separated.[3]

In an earlier study[4] it was shown that configurational stability at phosphorus in 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane (I, X = Cl) could be demonstrated by PMR spectroscopy. This method has the limitation that it can only place limits on the rates of processes which fall outside its useful range, but it has the advantage of being nondestructive and applicable to compounds bearing sensitive groups on phosphorus which might not survive the rigors of separation or resolution procedures.

In the present work an attempt has been made to examine the effect of substituents on the rate of inversion at phosphorus for a series of P-substituted 4,4,5,5-tetramethyl-1,3,2-dioxaphospholanes (I). The substituents include chloro, methoxy, phenoxy, dimethylamino and phenyl.



$X = Cl, OCH_3, OC_6H_5, N(CH_3)_2, C_6H_5$

I

The PMR spectra of compounds I have been examined at varying temperatures. With the exceptions of the dimethylamino and chloro compounds the results of the PMR studies were immediately clear; within the temperature range studied (see Table 1) there was no change in the chemical shifts of the *two* peaks observed for the CH_3 groups attached to the ring carbon atoms. Earlier work[4] showed that the two

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[1] This investigation was supported by a grant from the Los Angeles State College Foundation.

[2] L. Horner, H. Winkler, A. Rapp, A. Mentrup, H. Hoffman and P. Beck, *Tetrahedron Letters*, 161 (1961).

[3] L. D. Quin and H. E. Shook, Jr., *Tetrahedron Letters*, 2193 (1965).

[4] H. Goldwhite, *Chem. and Ind.* 494 (1964).

peaks are due to chemical shift differences between methyl groups *cis*- and *trans*- to the substituent on phosphorus and not to any unusually large spin–spin coupling effect. The compounds I, X = OCH_3, OC_6H_5, C_6H_5, are therefore configurationally stable at phosphorus in the sense that they are not inverting rapidly at phosphorus at the highest temperatures studied.

TABLE 1. PMR SPECTRA* OF 2-SUBSTITUTED-4,4,5,5-TETRAMETHYL-1,3,2-DIOXAPHOSPHOLANES

2-Substituent	Solvent	δ (ppm downfield from internal (CH_3)4Si) for CH_3-C*	Other peaks*	Maximum temp. (°C) of observations
Cl	Neat	1·40		See Table 2
Cl	Benzene	0·62		See Table 2
	(10% soln)	0·27		
OCH_3	Neat	1·07	$POCH_3$, δ = 3·27	148
		1·19	Doublet	
			$J_{H\text{-}O\text{-}O\text{-}P}$ = 13 c/s	
OC_6H_5	Dioxan	1·11	P-OC_6H_5, δ = 6·8–7·6	148
	(25% soln)	1·30	P-C_6H_5, δ = 7·25–81	130
C_6H_5	Neat	0·91	Multiplet	
		1·05		
$N(CH_3)_2$	Neat	1·09	P-$N(CH_3)_2$, δ = 2·45	151
		1·15	Doublet	
			$J_{H\text{-}O\text{-}N\text{-}P}$ = 6 c/s	

* Spectra run at ambient probe temperature, 32°C.

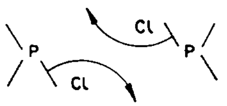
The dimethylamino compound has a PMR spectrum which is solvent dependent. The neat compound shows two peaks for the 4,4,5,5-methyl groups which coalesce into one peak on dilution with benzene or toluene, but which remain separate in cyclohexane, hexane, or dioxan over a range of temperatures. This effect is not due to any abnormal association or dissociation in the aromatic solvents, since the molecular weight of the compound as determined from freezing point depression, is normal in benzene (as in cyclohexane). A careful study showed that the observed singlet is due to an accidental coincidence of the expected two peaks; the low-field peak has a solvent dependent chemical shift and, on dilution with benzene or toluene moves upfield until it coincides with the high-field peak which shows no such solvent dependence. The variable temperature studies on the neat compound indicate that it is not undergoing rapid inversion at the highest temperature studied.

The PMR spectrum of the 2-chlorophospholane (I, X = Cl) is a singlet in the neat liquid at room temperature, which broadens and finally splits into two peaks if the temperature is lowered or if the liquid is diluted with an inert solvent (benzene, toluene, chloroform, or dioxan). The observed coalescence temperatures, Tc, of the neat liquid and a number of solutions are listed in Table 2; the dependence of the chemical shift difference on concentration is shown in Table 3. The marked dependence of the coalescence temperature and the chemical shift difference on concentration indicates that the single peak observed at higher temperatures is not the result of purely thermal inversion process at phosphorus, which ought to be a concentration independent process. It is likely that the process which leads to exchange

Table 2. Coalescence temperature Tc for the CH$_3$-C PMR of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane

Solvent	Mole fraction of phospholane	Tc(°C)
None	1·00	−23
Toluene	0·48	3
Toluene	0·33	100

of the proton magnetic environments is a chemical exchange process, formulated below, of a kind which has been previously observed in P-halo compounds.[5] The



rate of this chemical exchange would be concentration dependent if it occurs by the suggested bimolecular process.[6] The coalescence of the two peaks into one upon exchange indicates that the exchange process is taking place with inversion at phosphorus, which is consistent with the four-center transition state which has been suggested for this reaction.

Thus, it can be concluded that in the 4,4,5,5-tetramethyl-1,3,2-dioxaphospholane series, with a wide variety of different substituent types at phosphorus, inversion of configuration at phosphorus is a slow process—a result which is consistent with the earlier observations on phosphines.[3]

Table 3. Chemical shifts for the CH$_3$-C protons of 2-chloro-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane at various concentrations in benzene at 32°

Mole fraction of phospholane	δ for CH$_3$-C peaks (ppm downfield from (CH$_3$)$_4$Si)	Chemical shift difference (ppm)
1	1·40	0
0·62	1·20 1·00	0·20
0·35	0·99 0·72	0·27
0·12	0·77 0·44	0·33
0·057	0·62 0·27	0·35
0·082	0·59 0·24	0·35
0·005	0·57 0·20	0·37

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[5] E. Fluck, J. R. VanWazer and L. C. D. Groenweghe, *J. Amer. Chem. Soc.* **81**, 6363 (1959).

[6] J. Lockhart, *Chem. Rev.* **64**, 147 (1964).

EXPERIMENTAL

PMR spectra were determined on a Varian A-60 spectrometer equipped with a variable temperature probe. Temperatures were measured by determining the separation between the resonance peaks of MeOH (low temp) or ethylene glycol (high temp) samples. P compds were handled in a glove-bag filled with dry N_2.

4,4,5,5-*Tetramethyl*-1,3,2-*dioxaphospholanes*

(i) *The* 2-*chloro compd* was prepared by a modification of the published procedure[7] using N,N-diethylaniline as the base. Yields were always low (~40%); the product had b.p. 79·5–80·5°/13·5mm. (Found: Cl, 19·1; calcd. for $C_6H_{12}ClO_2P$; Cl, 19·4%.)

(ii) *Preparation of the* 2-*methoxy compd.* A solution of 6·42 g (36 mmoles) of the 2-chloro compound in 20 ml ether was dropped slowly into a stirred, N_2 blanketed solution of 1·16 g (35 mmoles) of MeOH and 5·38 g (36 mmoles) N,N-diethylanine in 50 ml ether, which was cooled in an ice bath. After the addition the solution was stirred for 1 hr, the solid was removed by filtration through a Skau tube, and the solvent was evaporated under red. press. The residual liquid was twice distilled to yield the 2-*methoxy compd* (3·2 g, 18 mmoles, 51%) b.p. 38–39°/1 mm. (Found: P, 16·8; $C_7H_{15}PO_3$ requires P, 17·4%.)

(iii) *Preparation of the* 2-*phenoxy compd.* The method was analogous to the above; the yield on a 17·5 mmolar scale was 45% of the 2-*phenoxy compd.* b.p. 88–90°/2 mm. (Found: P, 12·3; $C_{12}H_{17}PO_3$ requires P, 12·9%.)

(iv) *Preparation of the* 2-*phenyl compd.* Phenyl phosphonous dichloride (7·70 g, 43 mmoles) was slowly dropped into an ice-cooled, stirred, N_2-blanketed solution of 4·99 g (42 mmoles) pinacol, and 12 g (86 mmoles) triethylamine in 100 ml pet. ether (b.p. 40–60°). The solid was removed by filtration through a Skau tube. Evaporation of the solvent under red. press. left a solid residue which was best purified by vacuum sublimation to yield the 2-*phenyl* compd, m.p. 103–104° (2·6 g, 11·6 mmoles, 27%.) (Found: P, 13·2; $C_{12}H_{17}PO_2$ requires P, 13·7%.)

(v) *Preparation of the* 2-*dimethylamino compd.* A solution of 2·07 g (11 mmoles) of the 2-chloro compd in 5 ml benzene was added dropwise to 4 ml benzene saturated with dimethylamine at 0° (about 26% dimethylamine, 2-fold excess). The solid was removed by filtration through a Skau tube; evaporation of the solvent followed by distillation gave the 2-*dimethyl-amino compd* (1·2 g, 6·6 mmoles, 60%). (Found: P. 15·5; mol.wt. (cryoscopic in benzene) 178, (cryoscopic in cyclohexane) 192. $C_8H_{18}NO_2P$ requires P, 16·2; mol.wt. 191.)

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[7] B. A. Arbuzov and M. M. Azanovskaya, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk* 473 (1949).