Configurational Assignments to 2-X-2-Y-4-methyl-1,3,2-dioxaphosphorinans

W. J. Stec, R. Kinas, and A. Okruszek
Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, 90–362 Łódź, Poland

(Z. Naturforsch. **31 b**, 393–395 [1976]; received July 17, 1975)

Dioxaphosphorinans, Configuration, Conformation

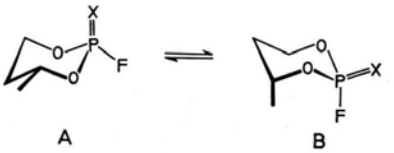
It has been reported from this Laboratory that $^1J_{PH}$ and $^1J_{PSe}$ absolute values showed the clear dependence on the spatial orientation of H and Se substituents in several pairs of ring C-substituted 2-X-2-Y-1,3,2-dioxaphosphorinans and may therefore provide information about conformation of the ring and configuration at phosphorus atom[1].

In this communication we wish to report further examples of usefulness of this observation to the *cis-trans*-geometry assignment of several new pairs of 2-X-2-Y-4-methyl-1,3,2-dioxaphosphorinans. Thirteen pairs of them were prepared and spin-spin coupling values between directly bonded phosphorus and selenium-77, fluorine-19 and carbon-13, respectively, were measured. Preliminary *cis-trans* assignments were concluded from deductive reasonings concerning stereochemical course of reactions in which they were obtained and also from the analysis of their ^1H, ^{13}C and ^{31}P NMR spectra. Results of measurements are collected in the Table.

Inspection of the Table reveals that the difference in spin-spin coupling between directly bonded phosphorus and selenium-77 can be applied as useful criterium for *cis-trans* assignment in diastereoisomeric pairs of **2**, **3**, **4**, **5**, **6**, **7**, **8** and **12**. It has to be emphasized that the structure of both *cis*- and *trans*-2-*tert*-butylamino-2-seleno-4-methyl-1,3,2-dioxaphosphorinans (**7**) were determined by X-ray crystallography[8] and in the solid state both isomers possess equatorially orientated 4-methyl group and selenium atom axial in *cis*-**7** and equatorial in *trans*-**7**, respectively. It is also worthwhile to mention that the equatorial P = Se bond is shorter (*trans*-**7**, 2.080 and 2.082 Å) than that in the axial disposition (*cis*-**7**, 2.086 Å).

Although the solid state structure determination did not elucidate the conformation of both isomers in solution, our preliminary ^1H NMR analysis confirmed that the *cis*-isomer is conformationally stable (C_6D_6 solution, 25°) and it has the same conformation as determined by X-ray technique. The *trans*-**7** in the same experimental conditions exists in the chair-chair equilibrium with *ca.* 70% of conformation with both 4-methyl and selenium atom equatorially orientated. Conformational mobility of *trans*-**7** may be responsible for the lower than average value of $\Delta J/J$ min and suggests also the similar situation in pair of **6**, where detailed ^1H NMR analysis has not been performed due to the complexity of spectra recorded at 90 MHz.

Pairs of **8**, **9** and **10** represent the case, when the criterium of absolute values of direct spin-spin couplings between directly bonded phosphorus-31 and carbon-13 can be applied to cyclic phosphonates. Again, spin-spin coupling between directly bonded phosphorus and carbon-13 atoms has higher absolute value when the alkyl group is equatorially orientated. Additionally, pair of **8** shows the complementary character of spin-spin coupling constants between phosphorus and carbon-13 or selenium-77. Thus $|^1J_{PSe}|$ *cis* $<|^1J_{PSe}|$ *trans* and $|^1J_{PC}|$ *cis* $>|^1J_{PC}|$ *trans*. Pairs of **1**, **11**, **12** and **13** represent the dependence of $^1J_{PF}$ absolute values on the spatial orientation of fluorine atom in dioxaphosphorinanyl ring system. The striking feature of these pair is the lower than in the case of other X substituents ΔJ value. In pairs **1**, **11** and **12** always $|^1J_{PF}|$ axial $<|^1J_{PF}|$ equatorial. In pair **13** the situation is reversed. This case requires of special comment. As it has been shown in our previous work[2], there is a lot of evidence that the *cis*-isomers of **1**, **11**, **12** and **13** exist in the chair-chair equilibrium



X = l.p., O, S, Se.

and it is very probable that in the case of **13** (X = O) the equilibrium is shifted towards B.

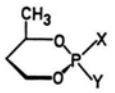
This fact suggests that the direct spin-spin coupling can be used for estimation of the conformational equilibria. Work on this problem is in progress. However, the case of **13** warns against the use of $|^1J_{PX}|$ value as the only criterium for the *cis-trans* geometry assignment in family of compounds under consideration.

Recent literature reports confirm the usefulness of our empirical rule $|^1J_{XY}ax| < |^1J_{XY}eq|$ to other cyclic systems like phosphorinans and cyclohexane derivatives. Quin reported the synthesis and conformational assignments to several substituted phosphorinans and their sulphides. In the case of sulphides $^1J_{P-C}$ for the equatorial phosphorus substituent is higher than for the axial one[12]. However, for the corresponding trivalent compounds[13] the situation is reversed.

Bock and Pedersen pointed out that one-bond coupling between anomeric carbon and proton in α- and β-hexapyranoses are different and always

Requests for reprints should be sent to Doz. Dr. W. J. Stec, Polish-Academy of Sciences, Centre of Molecular and Macromolecular Studies, *90–362 Łódź*, Boczna 5, Poland.

Table. ^{31}P NMR parameters* of 2-X-2-Y-4-methyl-1,3,2-dioxaphosphorinans (**1–13**).



Compound		X	Y	δ ^{31}P [H_3PO_4]	$\Delta\delta$ [ppm]	$^1J_{P-X}$ [Hz]	$^1J_{P-Y}$ [Hz]	ΔJ [Hz]	$\frac{100\,\Delta J}{J\,min}$	Solvent	Reference
1	*trans*	l.p.	F	—98.5	1.0	–	1180	24	2.0	Neat	2
	cis	F	l.p.	—99.5		1206	–				
2	*trans*	Se	SMe	—88.5	5.5	960	–	65	7.3	Benzene	3
	cis	SMe	Se	—94.0		–	895				
3	*trans*	S	SeMe	—78.5	9.0	–	435	75	17.3	Benzene	4
	cis	SeMe	S	—87.5		510	–				
4	*trans*	Se	NMe_2	—76.0	—1.0	960	–	30	3.2	Benzene	5
	cis	NMe_2	Se	—75.0		–	930				
5	*trans*	Se	NHPh	—60.0	2.5	942	–	55	6.2	Dioxane	6
	cis	NHPh	Se	—62.5		–	887				
6	*trans*	Se	NMePh	—65.2	7.3	941	–	16	1.7	Benzene	7
	cis	NMePh	Se	—72.5		–	925				
7	*trans*	Se	$NHBu^t$	—58.7	7.8	916	–	16	1.8	C_6D_6	8
	cis	$NHBu^t$	Se	—66.5		–	900				
8	*trans*	Se	CH_2Ph	—92.0	4.9	909	78	7 (P–C)	9.0 (P–C)	C_6D_6	9
	cis	CH_2Ph	Se	—96.9		85	883	26 (P=Se)	2.9 (P=Se)		
9	*trans*	O	CH_2Ph	—19.0	5.5	–	128.0	10.3	8.0	$CDCl_3$	9
	cis	CH_2Ph	O	—24.5		138.3	–				
10	*trans*	O	CH_3	—23.0	5.0	–	133	12	9.0	$CDCl_3$	10
	cis	CH_3	O	—28.0		145	–				
11	*trans*	S	F	—57.2	0.4	–	1130	10	0.9	Benzene	11
	cis	F	S	—57.6		1140	–				
12	*trans*	Se	F	—60.8	0.2	1122	1202	14 (P–F)	1.2 (P–F)	Benzene	2
	cis	F	Se	—61.0		1216	1110	12 (P=Se)	1.1 (P=Se)		
13	*trans*	O	F	+17.5	0.1	–	1030	6	—0.6	Benzene	2
	cis	F	O	+17.4		1024	–				

* Proton-decoupled ^{31}P NMR spectra were taken on a JEOL C-60H or Bruker HX-72 (Fourier transform) spectrometer and are referenced to external 85% H_3PO_4. Standard deviation ± 3 Hz. Proton-decoupled Fourier transform ^{13}C spectra were obtained on a Bruker HX-72 system at 22.63 MHz. C–P coupling constants are ± 1.5 Hz.

$|^1J_{eq}| > |^1J_{ax}|$ [14]. Very recently SUBBOTIN and SERGEYEV have determined the direct spin-spin couplings between carbon-13 and fluorine-19 in fluorocyclohexane and found at —100 °C the values 167.0 Hz for axial and 172.2 Hz for equatorial fluorine[15].

At the same temperature in cyclohexane $^1J_{C-H}$ for the axial proton is 122.6 Hz and for equatorial one 126.6 Hz [16]. ANET *et al.* found also the meaningful difference in values of $^1J_{C13-Hg119}$ in cyclohexyl mercurials depending on the spatial orientation o mercury atom. In all cases $|J_{axial}| < |J_{equatorial}|$ [17].

Presented above informations are indicative of the generality of the criterium of absolute value of direct spin-spin coupling between the central atom and exocyclic substituent in diastereoisomeric pairs of cyclic compounds for determination of axial/equatorial orientation of exocyclic substituent and thus, may form the basis for configurational assignment.

[1] W. J. Stec, Z. Naturforsch. **29b,** 109 [1974].
[2] W. J. Stec and A. Okruszek, Z. Naturforsch. **31b,** 354 [1976].
[3] A. Okruszek and W. J. Stec, Z. Naturforsch. **30b,** 430 [1975].
[4] W. J. Stec, A. Okruszek, K. Lesiak, B. Uznański, and J. Michalski, J. Org. Chem., in press.
[5] W. J. Stec, A. Okruszek, and J. Michalski, J. Org. Chem., in press.
[6] W. J. Stec and A. Okruszek, J. Chem. Soc., Perkin I, **1975,** 1828.
[7] W. J. Stec and R. Kinas, unpublished results.
[8] T. J. Bartczak, A. Christensen, R. Kinas, and W. J. Stec, Cryst. Str. Comm. (Pharma) **4,** 701 [1975].
[9] W. J. Stec, K. Lesiak, D. Mielczarek, and B. Stec, Z. Naturforsch. **30b,** 710 [1975].
[10] B. A. Arbusov, R. P. Arshinova, Yn. M. Mareev, and W. S. Vinogradova, Dokl. Acad. Nauk, USSR, **208,** 849 [1973].
[11] M. Mikołajczyk, J. Krzywański, and B. Ziemnicka, Tetrahedron Letters **1975,** 1607.
[12] S. I. Featherman and L. D. Quin, Tetrahedron Letters **1973,** 1955.
[13] L. B. Quin, A. T. McPhail, S. O. Lee, and K. D. Onan, Tetrahedron Letters **1974,** 3473.
[14] a) K. Bock, I. Lundt, and C. Pedersen, Tetrahedron Letters **1973,** 1037; b) K. Bock and C. Pedersen, J. Chem. Soc., Perkin II, **1974,** 293.
[15] O. A. Subbotin and N. M. Sergeyer, J. Amer. Chem. Soc. **97,** 1080 [1975].
[16] F. A. L. Anet and R. Anet, in "Determination of Organic Structures by Physical Methods," Vol. III, p. 396, Academic Press, New York 1971.
[17] W. Kitching, D. Preager, D. Doddrell, F. A. L. Anet, and J. Krane, Tetrahedron Letters **1975,** 759.