Acceleration of the Pseudorotation Rates in Pentacoordinated Phosphorus Compounds. Conformational Transmission versus Hexacoordinated Zwitterionic Intermediates

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A variable-temperature ^{13}C NMR study, accompanied by a high-resolution ^{1}H NMR conformational analysis study, on a series of monocyclic oxyphosphoranes is reported. The selected compounds enabled us to study the acceleration of the rates of intramolecular ligand reorganization on pentacoordinated phosphorus. It allowed us to determine whether the enhancement of the reorganization rates was brought about by accelerated pseudorotation due to the conformational transmission effect or by the involvement of hexacoordinated zwitterionic phosphorus intermediates. The results of the study further substantiate the findings that the involvement of such hexacoordinated intermediates is of no importance in the type of oxyphosphoranes studied.

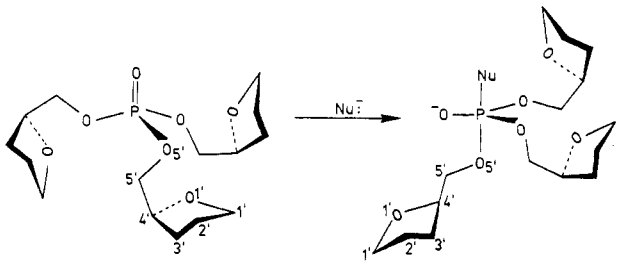
The concept of conformational transmission in pentacoordinated (P(V)) trigonal-bipyramidal (TBP) phosphorus compounds has received considerable attention during the past few years.[1] In these studies it has been shown that phosphorus compounds possessing the common P–O–C–C–O fragment are subject to a conformational rearrangement around the central C–C linkage of this fragment if the coordination state of phosphorus is increased from four (P(IV)) to five (P(V)-TBP).

The incorporation of an additional ligand in a P(IV) geometry causes a considerable change in the intrinsic chemical bonding properties around the central phosphorus atom,[2] resulting in an enhanced electron density on the axially located oxygens linked directly to phosphorus. In its turn, this effect is transmitted into a conformational change around the central C–C linkage of the axially located O–C–C–O fragment. The actual conformation of the O–C–C–O linkage is changed from the well-known gauche orientation in the P(IV) state to a pronounced anti orientation of the two vicinally orientated oxygen atoms in the P(V)-TBP state (Scheme I).

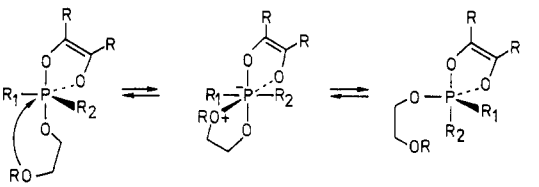
It has been emphasized regularly[1a,b,h] that this concept of conformational transmission forms an effective mechanism by which the conformation of phosphorylated biomolecules possessing the P–O–C–C–O atomic sequence, e.g. RNA, DNA and phospholipids, can be changed.

In a previous paper,[3] we reported a variable-temperature ^{13}C NMR study on a series of monocyclic oxyphosphoranes in order to determine the influence of this conformational transmission effect on the barriers to pseudorotation. It was demonstrated, by examining compounds **1** and **2**, that the pseudorotation rate of monocyclic oxyphosphoranes **1b**, **1d**, **2b**, and **2d**, which exhibit the conformational

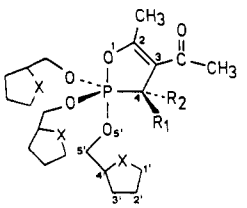
Scheme I

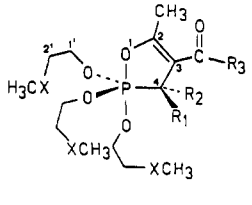


Scheme II



transmission effect, is 2–4 times faster as compared to that of their counterparts **1a**, **1c**, **2a**, and **2c** in which no conformational transmission occurs. A straightforward explanation for the lowering of the pseudorotation barriers in the compounds with X = O presented. It was shown that the interconversion of the ground-state TBP in the pseudorotation process proceeds via one TBP and two square-pyramidal (SP) transition states. Furthermore, it was demonstrated that in these SP structures, which determine the magnitude of the activation barriers in the ligand exchange process, a net stabilization due to the conformational transmission effect occurs. As a result, a lowering of the activation barrier by 2–3 kJ mol^{-1} was found.





1a : X=CH_2, R_1=H, R_2=C_6H_5
1b : X=O, R_1=H, R_2=C_6H_5
1c : X=CH_2, R_1=R_2=CH_3
1d : X=O, R_1=R_2=CH_3

2a : X=CH_2, R_1=H, R_2=C_6H_5, R_3=CH_3
2b : X=O, R_1=H, R_2=C_6H_5, R_3=CH_3
2c : X=CH_2, R_1=R_2=CH_3, R_3=OC_2H_5
2d : X=O, R_1=R_2=CH_3, R_3=OC_2H_5

In addition it was briefly noted that an alternative mechanism, in which a hexacoordinated zwitterionic

(1) (a) Koole, L. H.; Lanters, E. J.; Buck, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5451. (b) Koole, L. H.; van Kooyk, R. J. L.; Buck, H. M. *J. Am. Chem. Soc.* **1985**, *107*, 4032. (c) De Vries, N. K.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1986**, *106*, 150. (d) De Vries, N. K.; Buck, H. M. *Phosphorus Sulfur* **1987**, *31*, 267. (e) Van Genderen, M. H. P.; Koole, L. H.; Olde Scheper, B. G. C. M.; van de Ven, L. J. M.; Buck, H. M. *Phosphorus Sulfur* **1987**, *32*, 73. (f) Van Genderen, M. H. P.; Buck, H. M. *Recl. Trav. Chim. Pays-Bas* **1987**, *106*, 449. (g) Van Genderen, M. H. P., Buck, H. M. *Magn. Reson. Chem.* **1987**, *25*, 872. (h) Meulendijks, G. H. W. M.; van Es, W.; de Haan, J. W.; Buck, H. M. *Eur. J. Biochem.* **1986**, *157*, 421.

(2) (a) Holmes, R. R. *Pentacoordinated Phosphorus*; American Chemical Society: Washington, DC, 1980; Vol. 1 and 2 (ACS Monograph no. 175 and 176). (b) Luckenbach, R. *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*: George Thieme Verlag: Stuttgart, 1973.

(3) De Keijzer, A. E. H.; Koole, L. H.; Buck, H. M. *J. Am. Chem. Soc.*, in press.

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Table I. Calculated Proton-Proton Coupling Constants (Hz) for the Rotamers in Compounds 5-8

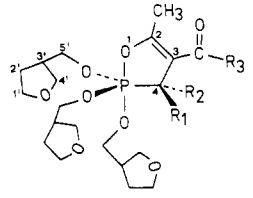
	g^+			g^t			g^-		
	$J_{3'5'}$	$J_{1'2'}$	$J_{3'5''}$	$J_{3'5'}$	$J_{1'2'}$	$J_{3'5''}$	$J_{3'5'}$	$J_{1'2'}$	$J_{3'5''}$
5a,b	1.76		1.74	3.95		12.61	12.61		3.97
6a,b		4.82			4.82			7.92	
7a,b		4.11			4.11			7.50	
8a,b		4.93			4.93			8.12	

phosphorus transition state might account for the more rapid ligand reorganization rates, as was proposed earlier by Eisenhut et al.[4] in case of the solvent-induced acceleration of pseudorotation in $(CH_3)_2NPF_4$, is most unlikely.

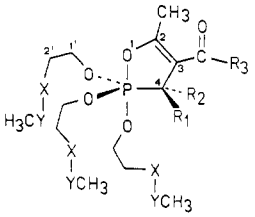
We now present a detailed study on the synthesis, conformational analysis, and ^{13}C NMR variable-temperature experiments of several new monocyclic oxyphosphoranes. A careful examination of the selected compounds will enable us to discriminate between the two mechanisms, conformational transmission or hexacoordinated zwitterionic phosphorus transition states, concerned.

The invocation of a mechanism that involves hexacoordinated intermediates would require the addition of one of the additional ligand oxygens to the central phosphorus atom to form a bicyclic zwitterionic hexacoordinated intermediate. A subsequent ring opening, accompanied with a slight movement of the ligands to form a new trigonal plane, then results in a Berry permutation[5] as is generalized in Scheme II. The most straightforward mechanism is presented, a number of other mechanisms can be drawn that would have the same permutational result as the one presented.

In order to investigate the possibility of the acceleration of pseudorotation by means of such a hexacoordinated intermediate, in contrast to the mechanism involving conformational transmission, a number of new compounds have been synthesized. Of special interest are compounds **3a**, **3b**, **4c**, and **4f**, which show *no* conformational transmission but possess additional oxygen atoms in the ligands, thus permitting a zwitterionic transition state to accelerate the pseudorotation rate.



3a : R_1=H,R_2=C_6H_5,R_3=CH_3
3b : R_1=R_2=CH_3,R_3=OC_2H_5

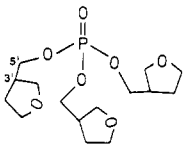


4a : X=Y=CH_2,R_1=H,R_2=C_6H_5,R_3=CH_3
4b : X=O,Y=CH_2,R_1=H,R_2=C_6H_5,R_3=CH_3
4c : X=CH_2,Y=O,R_1=H,R_2=C_6H_5,R_3=CH_3
4d : X=Y=CH_2,R_1=R_2=CH_3,R_3=OC_2H_5
4e : X=O,Y=CH_2,R_1=R_2=CH_3,R_3=OC_2H_5
4f : X=CH_2,Y=O,R_1=R_2=CH_3,R_3=OC_2H_5

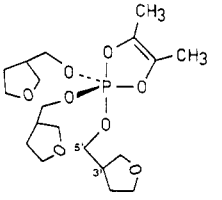
The isomerization processes of these new compounds were followed by variable-temperature ^{13}C NMR studies, and the activation barriers of the pseudorotation processes were determined. Comparing these barriers with those of the phosphoranes in which conformational transmission is present (**4b**, **4e**) or absent (**4a**, **4d**), respectively, allows us to draw some conclusions about the possible involvement of a hexacoordinated phosphorus intermediate.

Results and Discussion

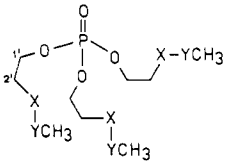
Conformational Analysis. The accurate determination of the $C_{3'}$–$C_{5'}$ conformation in compounds **3a** and **3b** and the $C_{1'}$–$C_{2'}$ conformation in compounds **4a–f** was hampered by decoalescence phenomena. We therefore selected the closely related model compounds **5a–8b**, upon which the conformational analysis was performed. The $C_{3'}$–$C_{5'}$ and $C_{1'}$–$C_{2'}$ conformations of compounds **5a**, **5b** and **6a–8b**, respectively, are based on the modified Karplus relationship as developed by Haasnoot et al.[6] This Karplus[7] equation relates the vicinal coupling constants of an ethane fragment to the torsion angle between the coupling protons.



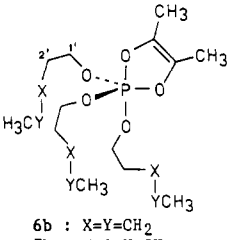
5a



5b



6a : X=Y=CH_2
7a : X=O,Y=CH_2
8a : X=CH_2,Y=O



6b : X=Y=CH_2
7b : X=O,Y=CH_2
8b : X=CH_2,Y=O

This standard equation was extended with a correction term that accounts for the influence of electronegative substituents on J_{HH}:

$$J(\mathrm{HH}) = P_1 \cos^2 \phi + P_2 \cos \phi + P_3 + \sum_i \Delta X_i [P_4 + P_5 \cos^2 (\xi_i \phi + P_6 |\Delta X_i|)]$$

$$\Delta X_i = \Delta X_i^{\alpha} - P_7 \sum_j \Delta X_j^{\beta}$$

In this equation, ϕ is the proton–proton torsion angle, ΔX_i is the difference in electronegativity between the α-substituents and hydrogen according to the electronegativity scale of Huggins,[8] corrected for β-substituents, and ξ_i is a substituent orientation parameter. Values of P_1–P_7 used for both cyclic and acyclic (in parentheses) systems are: P_1 = 13.22 (13.89), P_2 = –0.99 (–0.98), P_3 = 0 (0), P_4 = 0.87 (1.02), P_5 = –2.46 (–3.40), P_6 = 19.9 (14.9), P_7 = 0 (0.24).

The theoretical values of $J_{3'5'}$ and $J_{3'5''}$ of compounds **5a** and **5b**, as well as the values of $J_{1'2'}$ for compounds **6a**, **6b**, **7a**, **7b**, **8a**, and **8b** have been calculated for each staggered rotamer[9] and are collected in Table I.

(4) Eisenhut, M.; Mitchell, H. L.; Traficante, D. D.; Kaufman, R. J.; Deutch, J. M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 5385.
(5) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(6) Haasnoot, C. A. G.; de Leeuw, F. A. A. M.; Altona, C. *Tetrahedron* **1980**, *36*, 2783.
(7) Karplus, M. *J. Chem. Phys.* **1959**, *30*, 11.
(8) Huggins, M. J. *J. Am. Chem. Soc.* **1953**, *75*, 4123.

Table II. Measured Proton–Proton Coupling Constants and Calculated Rotamer Populations in Compounds 5–8[a]

	$J_{HH'}$	J_{HH}	$J_{HH''}$	x_{g^+}	x_{g^t}	x_{g^-}
5a	6.6		7.6	0.35	0.47	0.18
5b	6.7		7.7	0.36	0.47	0.17
6a		6.6		0.42		0.58
6b		6.7		0.40		0.60
7a		4.9		0.78		0.22
7b		5.5		0.60		0.40
8a		6.4		0.55		0.45
8b		6.4		0.55		0.45

[a] The rotamer populations are uncorrected for phosphorus pseudorotation.

Table III. Activation Parameters for the Exchange Processes in Phosphoranes 1, 3, and 4

	R_1	R_2	R_3	R_4[a]	T_c[b]	$\Delta\nu$[c]	$\Delta G_c^{\ddagger}$[d]	
1a	H	C_6H_5	CH_3	CP	288[e]	325[e]	54.6	
1b	H	C_6H_5	CH_3	THFF	270[e]	295[e]	51.2	A
3a	H	C_6H_5	CH_3	THFM	294[f]	408[f]	55.3	
4a	H	C_6H_5	CH_3	C_5H_{11}	269	222	51.7	
4b	H	C_6H_5	CH_3	$C_2H_4OC_2H_5$	260	199	50.1	B
4c	H	C_6H_5	CH_3	$C_3H_6OCH_3$	271	215	52.0	
1c	CH_3	CH_3	CH_3	CP	371[e]	285[e]	71.5	
1d	CH_3	CH_3	CH_3	THFF	358[e]	216[e]	69.7	C
3b	CH_3	CH_3	OC_2H_5	THFM	365	165	71.9	
4d	CH_3	CH_3	OC_2H_5	C_5H_{11}	325	205	63.2	
4e	CH_3	CH_3	OC_2H_5	$C_2H_4OC_2H_5$	316	186	61.6	D
4f	CH_3	CH_3	OC_2H_5	$C_3H_6OCH_3$	323	196	62.9	

[a] CP = cyclopentanemethyl, THFF = tetrahydrofurfuryl, THFM = 3-tetrahydrofuranylmethyl. Solvents: group A and B, $C_6D_5CD_3$; group C and D, C_6D_5Br. [b] The coalescence temperatures, T_c (K) refer to the temperatures of maximum broadening of the NMR signals studied and were determined with an accuracy of ±2 K. [c] Differences in chemical shifts (Hz) between the equatorial and axial sites in the absence of exchange, measured with an accuracy of ±2 Hz. [d] $\Delta G_c^{\ddagger}$ values (kJ mol^{-1}) calculated from the equation $\Delta G^{\ddagger} = (1.91 \times 10^{-2})T_c(9.973 + \log(T_c/\Delta\nu))$. Estimated uncertainty ±0.4 kJ mol^{-1}. [e] T_c and $\Delta\nu$ of compounds **1a–d** have been taken from ref 3. [f] T_c and $\Delta\nu$ of compound **3a** have been determined from the low-temperature 100-MHz ^{13}C NMR spectrum of this compound.

The population densities for the individual rotamers can now be obtained by using the experimental parameters J_{HH} and the theoretical values of J_{g^+}, J_{g^t} and J_{g^-} in the equation:

$$J_{HH} = x_{g^+}J_{g^+} + x_{g^t}J_{g^t} + x_{g^-}J_{g^-}$$

with the normalization equation:

$$x_{g^+} + x_{g^t} + x_{g^-} = 1$$

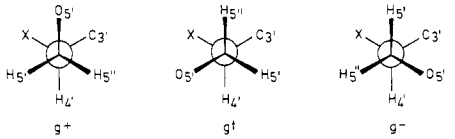
The spectral parameters for compounds **5a** and **5b** were taken from the 300-MHz expansion plots of the $H_{5'5''}$ patterns and iteratively analyzed with the PANIC program.[10] The coupling constants $J_{1'2'}$ of compounds **6a**, **6b**, **7a**, **7b**, **8a**, and **8b** were determined from the 200-MHz expansion plots by employing the same standard computer simulation–iteration procedure. The correct assignment of the $H_{5'5''}$ patterns in the expansion plots of the rather complex $H_{1'1''}/H_{4'4''}/H_{5'5''}$ region was determined from the two-dimensional *J*-resolved 300-MHz ^1H NMR spectrum of both the P(IV) and P(V) compounds **5a** and **5b** and the precursor alcohol. The individual assignment of $H_{5'}$ and $H_{5''}$ was arbitrarily chosen in line with the one used by Koole et al.[1a] for the tetrahydrofurfuryl and cyclopentylmethyl compounds. A reverse assignment would only affect the g^- and g^t populations. The g^+ population remains unchanged, the g^t and g^- populations interchange. Both assignments result in the same conclusion, i.e. *no* change in rotamer populations upon going from a P(IV) to a P(V) coordination. The spectral parameters determined for the P(IV) and P(V) compounds **5a–8b**, along with the resulting rotamer populations, are listed in Table II.

From these data we may now conclude that *no* conformational transmission occurs in compounds **5b**, **6b**, and **8b**. Applying these results to the compounds **3** and **4** means that conformational transmission is present in **4b** and **4e** and that *no* conformational transmission occurs in **3a**, **3b**, **4a**, **4c**, **4d**, and **4f**.

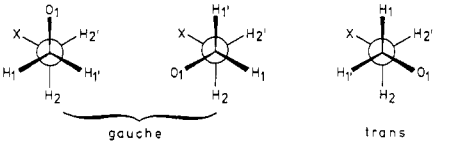
Exchange Process Studies. The $POCH_2$ moieties of compounds **3** and **4** exhibit an exchange process that can be readily followed by variable-temperature ^{13}C NMR analysis and allows the determination of the pseudorotation barriers. The activation parameters of the exchange process have been evaluated according to the method described previously.[3] The results of the ^{13}C NMR variable-temperature studies on the compounds **1**, **3**, and **4** have been summarized in Table III.

From these data, and the data regarding the conformational transmission effect, we are now able to draw some conclusions concerning the possible involvement of hexacoordinated intermediates. Comparing the data of compound sets A (**1a**, **1b**, and **3a**), B (**4a**, **4b**, and **4c**), C (**1c**, **1d**, and **3b**), and D (**4d**, **4e**, and **4f**), respectively, it is clear that, in all cases, the compounds exhibiting the confor-

(9) In solution a rapid interconversion between the three staggered conformations g^+, g^t, and g^- yields weighted time-averaged coupling constants $J_{3'5'}$ and $J_{3'5''}$, which are related to the individual rotamers and their populations.



In case of the acyclic compounds, two of these rotamers (g^+, g^t) are mirror images and have identical populations, therefore a two-state description with a gauche and a trans state is used.



(10) PANIC program, copyright Bruker Spectrospin AG, Switzerland.

Table IV. ^1H and ^{31}P NMR Data for the Phosphoranes 3 and 4 at 25 °C

^1H	3a	3b	4a	4b	4c	4d	4e	4f
CH_3	1.68	2.10	1.69	1.63	1.68	2.11	2.05	2.09
$COCH_3$	2.46		2.48	2.49	2.42			
$POCH_2$[a]	3.23–3.78	3.30–3.82	3.70	3.84	3.83	3.63	3.78	3.73
H_4	4.15		4.15	4.15	4.13			
$H_{1'}/H_{4'}$	3.23–3.78	3.30–3.82						
$H_{2'}$	1.24	1.24	1.34	3.27	1.59	1.38	3.28	1.63
$H_{2''}$	1.59	1.60						
$H_{3'}$	2.16	2.16						
$C(CH_3)_2$		1.46				1.48	1.42	1.40
$COCH_2$		3.93				3.93	3.93	3.93
OCH_2CH_3		0.99				1.00	0.91	1.01
C_6H_5	6.94–7.24		6.93–7.23	6.94–7.28	6.95–7.22			
X			1.15		3.18	1.15		3.21
Y			1.15	3.20		1.15	3.18	
YCH_3			0.77	0.97	3.08	0.71	0.89	3.02
^{31}P	−30.3	−27.0	−29.0	−28.9	−29.0	−26.0	−25.9	−26.0

[a] The $POCH_2$ signals of compounds 3 and 4 were broadened by slow exchange at room temperature.

mational transmission effect show a lowering of the pseudorotation barrier as compared to their counterparts in which the conformational transmission effect is absent, as could be expected on the basis of our previous investigations.

Interestingly, however, the compounds **3a**, **3b**, **4c**, and **4f** in which no conformational transmission occurs, but which still possess additional oxygen atoms in the ligands thus allowing hexacoordinated zwitterionic intermediates to be formed, show virtually identical activation energies as those of the compounds in which no additional oxygen atoms are present.

On the basis of these experimental results and the theoretical considerations presented in the previous paper,[3] it is now justifiable to conclude that *no* hexacoordinated zwitterionic intermediates are formed in the monocyclic oxyphosphoranes studied. Therefore, the lowering of the pseudorotation barriers is entirely brought about by the presence of the conformational transmission effect.

Conclusion

This study clearly demonstrates the impact of the conformational transmission effect on the barriers to pseudorotation in monocyclic oxyphosphoranes. It clearly shows that the lowering of the activation energies is entirely based on the presence of the conformational transmission effect and that there is *no* involvement of a hexacoordinated zwitterionic intermediate in this type of monocyclic oxyphosphoranes.

Experimental Section

Spectroscopy. ^1H NMR spectra of compounds 6–8 were run in the FT mode on a Bruker AC-200 instrument at 200.1 MHz. For compound **5** as well as the 3-tetrahydrofuranmethanol, the one- and two-dimensional spectra were run on a Bruker CXP-300 spectrometer at 300.1 MHz. Proton chemical shifts are referenced against TMS as internal standard (δ 0). ^{31}P NMR spectra were recorded in the FT mode at 80.9 MHz on a Bruker AC-200 instrument. Chemical shifts are related to 85% H_3PO_4 as external standard and are designated positive if downfield with respect to the reference. ^{13}C NMR spectra were run in the FT mode at 50.3 MHz on a Bruker AC-200 spectrometer (compounds **3b** and **4**) or at 100.3 MHz on a Bruker AM-400 instrument (compound **3a**). Chemical shifts are referenced against internal TMS. The variable temperature experiments were performed and analyzed as described previously.[3] All spectra were recorded in $CDCl_3$ unless stated otherwise.

Synthesis. All solvents and commercial reagents were reagent grade and were dried prior to use with the appropriate drying agents. All moisture-sensitive compounds were handled under a dry nitrogen atmosphere. The general instability of the phosphites and oxyphosphoranes has precluded the obtention of correct standard analytical data. The identification of these compounds rests therefore on ^1H, ^{13}C, and ^{31}P spectroscopy, methods of preparation, and comparison of the obtained physical data with those presented for well-defined P(III) and P(V) compounds.[11]

3-Tetrahydrofuranmethanol. This compound was prepared form triethyl 1,1,2-ethanetricarboxylate according to literature procedures.[12] Bp: 76–77 °C (4 mm). Yield: 37%. ^1H NMR: δ 1.65 (m, 1 H, $H_{2'}$), 2.04 (m, 1 H, $H_{2''}$), 2.48 (m, 1 H, $H_{3'}$), 3.40–3.70 (m, 3 H, $H_{4''}/H_{5'}/H_{5''}$), 3.70–3.93 (m, 3 H, $H_{4'}/H_{1'}/H_{1''}$), 4.48 (s, 1 H, OH). ^{13}C NMR: δ 28.3 ($C_{2'}$), 41.1 ($C_{3'}$), 63.9 ($C_{4'}$), 67.4 ($C_{1'}$), 70.2 ($C_{5'}$). Anal. Calcd for $C_5H_{10}O_2$: C, 58.80; H, 9.87. Found: C, 58.62; H, 9.59. MS calcd for $C_5H_{10}O_2$ *m/e* 102.13, measured 102.15.

3-Methoxy-1-propanol. This compound was prepared from 1,3-propanediol according to a literature procedure.[13] Bp: 160–168 °C. Yield: 69%. ^1H NMR: δ 1.70 (m, 2 H, CH_2), 3.23 (s, 3 H, OCH_3), 3.40 (t, 2 H, CH_2O), 3.55 (s, 1 H, OH), 3.57 (t, 2 H, OCH_2). ^{13}C NMR: δ 31.8 (CH_2), 58.2 (CH_2OH), 59.8 (OCH_3), 70.2 (CH_2O). Anal. Calcd for $C_4H_{10}O_2$: C, 53.31; H, 11.18. Found: C, 53.49; H, 11.09.

Phosphites. All phosphites were prepared from the corresponding alcohols and PCl_3 according to the procedure described for the preparation of tris(cyclopentylmethyl)phosphite.[3]

Tripentyl Phosphite. Bp: 83 °C (0.04 mm). Yield: 60%. ^1H NMR: δ 0.91 (t, 9 H, CH_3), 1.36 (m, 12 H, CH_2CH_2), 1.62 (m, 6 H, OCH_2CH_2), 3.80 (dt, 6 H, $POCH_2$). ^{13}C NMR: δ 13.8 (CH_3), 22.2 (CH_2CH_3), 27.9 (CH_2), 30.8 (OCH_2CH_2), 62.1 ($POCH_2$). ^{31}P NMR: δ 139.8.

Tris(2-ethoxyethyl) Phosphite. Bp: 102 °C (0.07 mm). Yield: 74%. ^1H NMR: δ 1.20 (t, 9 H, CH_3), 3.52 (t, 6 H, OCH_2CH_3), 3.58 (t, 6 H, CH_2CH_2O), 3.97 (dt, 6 H, $POCH_2$). ^{13}C NMR: δ 14.8 (CH_3), 61.1 ($POCH_2$), 66.1 (OCH_2CH_3), 69.9 (CH_2CH_2O). ^{31}P NMR: δ 140.1.

Tris(3-methoxypropyl) Phosphite. Bp: 101 °C (0.01 mm). Yield: 44%. ^1H NMR: δ 1.89 (m, 6 H, CH_2), 3.32 (s, 9 H, OCH_3), 3.47 (t, 6 H, CH_2O), 3.90 (dt, 6 H, $POCH_2$). ^{13}C NMR: δ 30.9 (CH_2), 58.1 (OCH_3), 58.7 ($POCH_2$), 68.6 (CH_2O). ^{31}P NMR: δ 139.5.

Tris(3-tetrahydrofuranylmethyl) Phosphite. Bp: 154–156 °C (0.005 mm). Yield: 47%. ^1H NMR: δ 1.24 (m, 3 H, $H_{2'}$), 1.54 (m, 3 H, $H_{2''}$), 2.16 (m, 3 H, $H_{3'}$), 3.27–3.72 (m, 18 H, $H_{1'/1''}$, $H_{4'/4''}$, $POCH_2$). ^{13}C NMR: δ 30.0 ($C_{2'}$), 41.7 ($C_{3'}$), 65.1 ($C_{5'}$), 68.5 ($C_{1'}$), 71.4 ($C_{4'}$). ^{31}P NMR: δ 139.0.

Phosphates. All phosphates were obtained by oxidation of the corresponding phosphites. An ozone oxygen stream was passed through a solution of the phosphite in dry dichloromethane at

(11) (a) Ramirez, F.; Madan, O. P.; Heller, S. R. *J. Am. Chem. Soc.* **1965**, *87*, 73. (b) Gorenstein, D.; Westheimer, F. H. *J. Am. Chem. Soc.* **1970**, *92*, 634. (c) Buono, G.; Llinas, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 4532. (d) Aganov, A. V.; Polezhaeva, N. A.; Khayanov, A. I.; Arbuzov, B. A. *Phosphorus Sulfur* **1985**, *22*, 303.

(12) Bogner, J.; Duplan, J.-C.; Infarnet, Y.; Delmau, J.; Huet, J. *Bull. Soc. Chim. Fr.* **1972**, *9*, 3616.

(13) Smith, L. I.; Sprung, J. A. *J. Am. Chem. Soc.* **1943**, *65*, 1276.

Table V. ^{13}C NMR Data for the Phosphoranes 3 and 4 at 25 °C

^{13}C	3a	3b	4a	4b	4c	4d	4e	4f
CH_3	17.9	17.0	18.1	18.0	18.0	17.4	17.4	17.4
$COCH_3$	30.5		30.3	30.3	30.5			
$C_{1'}$	68.8	67.8						
$C_{2'}$	29.8	29.0	31.9	71.2	32.5	30.9	70.5	31.7
$C_{3'}$	41.3	40.9						
$C_{4'}$	71.4	70.2						
$POCH_2$[a]	70.2	66.9 (a)	68.4	67.7	65.6	64.2 (a)	63.9 (a)	61.0 (a)
		70.2 (e)				68.2 (e)	67.6 (e)	64.9 (e)
C_2	166.2	163.0	166.8	166.5	166.9	163.8	163.2	163.4
C_3	114.4	116.0	113.9	113.9	114.2	108.3	108.4	108.4
C_4	50.2	45.5	50.2	49.9	50.5	42.0	42.5	42.0
OCH_2CH_3		14.5				14.7	14.7	14.7
$COCH_2$		60.5				58.6	58.9	59.0
$C(CH_3)_2$		23.0				23.1	23.2	23.3
C_6H_5	127.9–130.5		127.6–130.3	127.6–130.4	127.6–130.4			
ipso	139.0		139.9	139.2	139.8			
C=O	194.6	165.8	194.2	194.2	194.2	165.9	166.0	165.8
X			29.4		70.6	28.5		69.0
Y			23.7	67.3		22.7	66.5	
YCH_3			15.1	16.4	59.0	14.3	15.9	58.7

[a] Compounds **3b** and **4d–f** show no pseudorotation at 25 °C, signal intensities are approximately (a)/(e) = 1:2; (a) axial, (e) equatorial.

0 °C. After 1 h the solution was sparged with oxygen and allowed to warm to room temperature. Evaporation of the solvent yielded the desired phosphates as was confirmed by ^{31}P NMR.

Tripentyl Phosphate (6a). ^1H NMR: δ 0.90 (t, 9 H, CH_3), 1.37 (m, 12 H, CH_2CH_2), 1.70 (m, 6 H, OCH_2CH_2), 4.04 (dt, 6 H, $POCH_2$). ^{13}C NMR: δ 13.7 (CH_3), 22.0 (CH_2CH_3), 27.4 (CH_2), 29.8 (OCH_2CH_2), 67.5 ($POCH_2$). ^{31}P NMR: δ −0.2. Anal. Calcd for $C_{15}H_{33}O_4P$: C, 58.44; H, 10.71. Found: C, 58.53; H, 10.64.

Tris(ethoxyethyl) Phosphate (7a). ^1H NMR: δ 1.21 (t, 9 H, CH_3), 3.56 (q, 6 H, OCH_2CH_3), 3.64 (m, 6 H, CH_2CH_2O), 4.22 (m, 6 H, $POCH_2$). ^{13}C NMR: δ 14.7 (CH_3), 66.2 (OCH_2CH_3), 66.4 ($POCH_2$), 68.8 (CH_2CH_2O). ^{31}P NMR: δ −0.5. Anal. Calcd for $C_{12}H_{27}O_7P$: C, 45.86; H, 8.60. Found: C, 45.67; H, 8.73.

Tris(3-methoxypropyl) Phosphate (8a). ^1H NMR: δ 1.94 (m, 6 H, CH_2), 3.36 (s, 9 H, OCH_3), 3.48 (t, 6 H, CH_2O), 4.14 (dt, 6 H, $POCH_2$). ^{13}C NMR: δ 30.0 (CH_2), 58.2 (OCH_3), 64.5 ($POCH_2$), 68.0 (CH_2O). ^{31}P NMR: δ −0.5. Anal. Calcd for $C_{12}H_{27}O_7P$: C, 45.86; H, 8.60. Found: C, 45.83; H, 8.49.

Tris(3-tetrahydrofuranylmethyl) Phosphate (5a). ^1H NMR: δ 1.23 (m, 3 H, $H_{2'}$), 1.55 (m, 3 H, $H_{2''}$), 2.21 (m, 3 H, $H_{3'}$), 3.40 (m, 12 H, $H_{1'/1''}$, $H_{4'/4''}$), 3.68 (m, 6 H, $POCH_2$). ^{13}C NMR: δ 28.7 ($C_{2'}$), 40.1 ($C_{3'}$), 67.7 ($C_{1'}$), 69.4 ($POCH_2$), 70.2 ($C_{4'}$). ^{31}P NMR: δ 0.0. Anal. Calcd for $C_{15}H_{27}O_7P$: C, 51.42; H, 7.77. Found: C, 51.83; H, 7.83.

Phosphoranes. All phosphoranes used for the conformational analysis study were obtained by adding an equimolar amount of 2,3-butanedione at 0 °C to a solution of the corresponding phosphite in a deuteriated solvent. ^{31}P NMR showed the reactions to be complete after 30 min at room temperature.

2,2,2-Tripentoxy-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (6b). ^1H NMR: δ 0.91 (t, 9 H, CH_3), 1.38 (m, 12 H, CH_2CH_2), 1.59 (m, 6 H, OCH_2CH_2), 1.91 (s, 6 H, 2 CH_3), 3.85 (m, 6 H, $POCH_2$). ^{13}C NMR: δ 10.2 (CH_3), 13.7 (CH_2CH_3), 22.2 (CH_2CH_3), 27.8 (CH_2), 30.3 (OCH_2CH_2), 67.1 ($POCH_2$), 128.3 (C=C). ^{31}P NMR: δ −50.4.

2,2,2-Tris(ethoxyethoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (7b). ^1H NMR: δ 1.20 (t, 9 H, OCH_2CH_3), 1.83 (s, 6 H, 2 CH_3), 3.53 (t, 6 H, OCH_2CH_3), 3.57 (t, 6 H, CH_2CH_2O), 4.02 (m, 6 H, $POCH_2$). ^{13}C NMR: δ 10.0 (CH_3), 14.7 (OCH_2CH_3), 65.8 (OCH_2CH_3), 66.0 ($POCH_2$), 69.6 (CH_2CH_2O), 128.2 (C=C). ^{31}P NMR: δ −50.4.

2,2,2-Tris(3′-methoxypropoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (8b). ^1H NMR: δ 1.82 (s, 6 H, 2 CH_3), 1.85 (m, 6 H, CH_2), 3.31 (s, 9 H, OCH_3), 3.48 (t, 6 H, CH_2O), 3.94 (m, 6 H, $POCH_2$). ^{13}C NMR: δ 10.2 (CH_3), 30.5 (CH_2), 57.8 (OCH_3), 63.8 ($POCH_2$), 68.9 (OCH_2), 128.3 (C=C). ^{31}P NMR: δ −50.4.

2,2,2-Tris(3′-tetrahydrofuranylmethoxy)-4,5-dimethyl-1,3,2-dioxaphosphol-4-ene (5b). ^1H NMR ($C_6D_5CD_3$): δ 1.66 (m, 3 H, $H_{2'}$), 1.90 (s, 6 H, 2 CH_3), 2.05 (m, 3 H, $H_{2''}$), 2.55 (m, 3 H, $H_{3'}$), 3.65–4.20 (m, 18 H, $H_{1'/1''}$, $H_{4'/4''}$, $POCH_2$). ^{13}C NMR ($C_6D_5CD_3$): δ 11.4 (CH_3), 29.7 ($C_{2'}$), 41.5 ($C_{3'}$), 68.6 ($C_{1'}$), 70.3 ($POCH_2$), 71.6 ($C_{4'}$), 130.2 (C=C). ^{31}P NMR ($C_6D_5CD_3$): δ −51.0.

In order to avoid decomposition during handling and purification of the phosphoranes used for the variable temperature studies, they were prepared in situ in the NMR tubes by adding equivalent amounts of freshly distilled phosphite and the appropriate precursor pentadiones[3] to the deuteriated solvents. The tubes were flushed with argon and sealed. After leaving them at room temparure for 10–14 days, the reactions were complete as was confirmed by ^{31}P NMR spectroscopy. ^1H, ^{13}C, and ^{31}P NMR spectra were then recorded and are listed in Table IV and V.

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