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^{13}C AND ^{31}P SPECTRA AND THE GEOMETRIES OF CIS - AND TRANS -2-Z-4-Me-1,3,2-DIOXAPHOSPHOLANES

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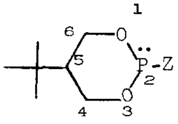
Carbon-13 nmr spectroscopy has shown itself to be a most powerful tool in the investigation of conformations of cyclic systems, e g. 1,3-dioxanes[1] and cyclohexanes[2] Recently[3] ^{13}C nmr has been combined with ^{31}P nmr and pmr results in the determination of the conformations of the trivalent six-membered ring heterocycles most closely related to 1,3-dioxanes, the 1,3,2-dioxaphosphorinanes (1) By contrast to what is known about the 1,3-dioxanes,[1] the



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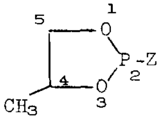
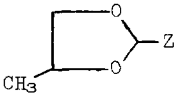


2 a, Z = MeO
b, Z = Ph
c, Z = Me_2N
d, Z = $PhCH_2$
e, Z = t-Bu
f, Z = t-BuO



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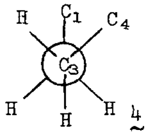
5-t-butyl-2-Z-1,3,2-dioxaphosphorinanes (1) were found[3] to be more stable in the cis form with the substituent Z axial (Z = Cl, CH_3O, CH_3, i-Pr, and Ph)

Because of the unusual effects of the phosphorus heteroatom on 1, we desired to determine the consequences of having trivalent phosphorus in a five-membered ring, the 1,3,2-dioxaphospholane system (2) The conformational stabilities and relative energies of cis and trans isomers of the 2-Z-4-methyl-1,3-dioxolanes[4] (3) have been well studied For 3 the cis isomer is the more stable form, and no single conformer is greatly favored energetically for either the cis or trans isomer By contrast for the series of 2, the trans isomer is the more stable form with the ratio trans/cis about 2[5] A full account of the rather difficult ^{1}H nmr studies of these $AMKX_3Y$ systems by which we have determined the conformations and cis or trans geometrie of various 2 will be published elsewhere.[5] What we wish to emphasize here is the ease of assignment of cis and trans geometries to the isomers of 2 on the basis of ^{13}C and ^{31}P nmr spectra alone Furthermore, some unusual effects of geometry on both ^{13}C and ^{31}P chemical shifts resulting from the δ relation of Z and Me will be noted

In Table I are recorded the ^{13}C and ^{31}P chemical shifts of 1,3,2-dioxaphospholanes 2a-2f. Several trends are noteworthy. In all cases for 4-Me and Z cis $\delta^{31}P$ is downfield of what it is in the trans isomer. This trend is reversed from that found in the cis and trans 5-*t*-butyl-2-Z-1,3,2-dioxaphosphorinanes[3] (1). In that ring system it can be proposed that the upfield $\delta^{31}P$ shift noted for Z axial is a consequence of a type of γ-effect.[2,6] Thus, in carbon systems the ^{13}C shift of the carbon (C_2 and C_3 in 4) α to those whose hydrogens are involved in steric interactions (C_1 and C_4) are upfield shifted. The types of substitution effects on chemical shift in ^{13}C, ^{15}N, and ^{31}P systems are generally similar.[7] In cis-2, however, any steric interactions are of the δ type (5a)[8] which have the opposite chemical shift consequences to those found for the γ-effect. E.g., $\delta^{13}C$ for C-3 in 7, is downfield of that for C-1.[9] The system 2 then provides a clear demonstration of the δ-effect on the chemical shift of an α phosphorus atom which is part of a ring. These results also show the danger of extrapolating correlations of $\delta^{31}P$ and cis/trans geometry from one ring system to another.



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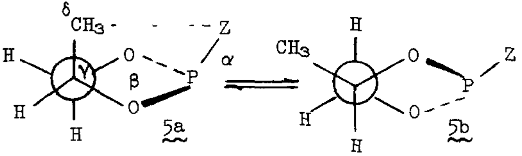

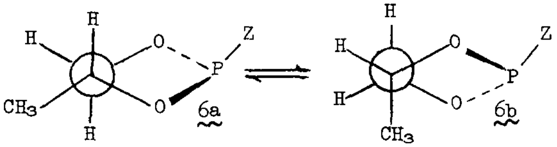

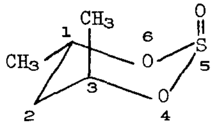

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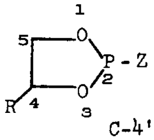
As predicted by the δ-effect, $\delta^{13}C$ for C-4 of cis-2a-f is found downfield by 0.5-2.6 ppm of that for trans-2a-f, an effect seen in 7. This phenomenon is also operative for C-2α in 2-d ($Z=PhCH_2$) in that $\delta^{13}C$ for C-2α of the cis-isomer is found 1.45 ppm downfield from that for the trans-isomer.

The chemical shifts of C'-4 of 2a-2f are most interesting. The δ-effect predicts that $\delta^{13}C$ for C-4' for the cis isomer should be downfield from that of the trans isomer. This is exactly opposite to what is noted in Table I except for 2f. However, it has been shown that the $\delta^{13}C$ values for axial 5-methyl groups in trans-2-methoxy-5-methyl-1,3,2-dioxaphosphorinane[3e] and cis-5-methyl-2-R-dioxanes[1c] are at lower field than are those for their equatorial counterparts. Furthermore, pmr analysis shows[5] that the trans 2a-2f exist in more than one conformation as expressed by the equilibrium 6a ⇌ 6b (pseudoxial methyl in 6b) whereas the

Table I. ^{13}C and ^{31}P Spectral Parameters for 2[a]



R	Z	$\delta^{31}P$[b]	C-4	C-4'	C-5	C-2α	C-2β
cis-Me	CH_3O	-139.62	74.23[c] (9.8)[d]	18.99 (< 3)	70.01 (7.6)	49.17 (9.1)	
trans-Me	CH_3O	-135.25	72.84 (9.4)	19.97 (4.2)	70.82 (8.3)	49.17 (9.1)	
H	CH_3O	-132.56	64.44 (8.9)		64.44 (8.9)	49.08 (9.0)	
cis-Me	Ph	-169.00	75.08 (9.5)	18.45 (< 3)	70.19 (8.6)		
trans-Me	Ph	-165.19	72.52 (8.9)	19.36 (3.7)	70.52 (7.9)		
H	Ph	-161.42	64.15 (9.5)		64.15 (9.5)		
cis-Me	Me_2N	-147.34	72.78 (7.5)	17.41 (3.0)	69.80 (7.5)	34.98 (19.8)	
trans-Me	Me_2N	-142.51	71.78 (8.1)	20.14 (4.1)	70.74 (9.5)	34.98 (19.8)	
H	Me_2N	-140.55	64.37 (8.8)		64.37 (8.8)	34.84 (19.7)	
cis-Me	$PhCH_2$	-190.36	74.44 (9.7)	18.79 (< 3)	69.89 (8.4)	46.10 (49.2)	
trans-Me	$PhCH_2$	-185.44	72.45 (9.8)	19.77 (3.7)	70.61 (8.0)	44.65 (47.6)	
cis-Me	t-Bu	-207.37	74.07 (6.4)	17.03 (3.4)	70.95 (6.6)	37.06 (43.7)	23.99 (19.9)
trans-Me	t-Bu	-201.48	73.58 (8.8)	20.09 (4.5)	71.96 (7.6)	37.79 (44.9)	23.35 (18.6)
cis-Me	t-BuO	-140.22	73.82 (9.0)	20.64 (< 3)	68.98 (7.6)	75.44 (7.5)	31.27 (9.1)
trans-Me	t-BuO	-137.84	71.21 (7.8)	19.64 (4.5)	69.58 (7.6)	75.44 (7.5)	31.27 (9.1)

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[a] Measured in benzene at 30°. ^{13}C nmr spectra were obtained using a Varian XL-100-15 spectrometer equipped with a Varian 620-F computer and operating in the Fourier transform mode. ^{31}P nmr spectra were obtained using a Varian XL-100-15 spectrometer operating in the continuous wave mode. [b] In ppm downfield from external 85 % H_3PO_4. [c] In ppm downfield from internal TMS.
[d] $|J_{CP}|$ in Hz.

cis **2a**-**2f** populate essentially only **5b**. If the downfield shift effect of an axial methyl is the dominant one, the apparent anomaly regarding the C-4' shifts of Table I is readily explained

On careful examination of Table I, one notes that $\delta^{13}C$ for C-4' for the trans isomers is not affected much by changing substituent Z (C-4' = 19 36-20.14 ppm), whereas the chemical shifts for C-4' of the cis-isomers range from 17.03 to 20 64 ppm. This is reasonable, since in the cis isomers the 4-methyl group and the substituent Z are on the same side of the ring. One would expect the variation of the interaction between the cis 4-methyl group and the substituent Z would lead to a relatively large change in $\delta^{13}C$ for C-4'. Another noteworthy feature for the 4-methyl group is that the coupling J_{CP} for the 4-methyl of the trans isomer is always larger than that of the cis isomer This probably demonstrates the dihedral angular dependence of $^3J_{CP}$ and appears to be useful in the assignment of geometries to cis and trans isomers of 2-Z-4-methyl-1,3,2-dioxaphospholanes

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