

Conformations of Six-Membered Ring Phosphorus Heterocycles.

I. The Ring Conformations and Phosphorus Configurations of Isomeric Six-Membered Ring Phosphites

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Abstract: A six-membered ring phosphorochloridite (5-*tert*-butyl-2-chloro-1,3,2-dioxaphosphorinane) and a geometrically isomeric pair of six-membered ring phosphites (*cis*- and *trans*-5-*tert*-butyl-2-methoxy-1,3,2-dioxaphosphorinane) have been synthesized, and their conformational and configurational properties have been investigated. The *cis*-phosphite is shown to be the more stable isomer by about 1.4 kcal/mol at 25° and by nmr analysis to be a chair-form conformer with the *tert*-butyl equatorial and the methoxy axial. The predominate conformer of the *trans* isomer is the chair form with both substituents axial. The axial preference of the methoxy substituent in the phosphite series, as in the corresponding cyclic sulfites, is found to be greater than for the 5-*tert*-butyl-2-methoxy-1,3-dioxanes. A true boat form for the other conformer(s) of the *trans*-phosphite is ruled out, but present data indicate both chair and twist conformers to be worthy of further consideration.

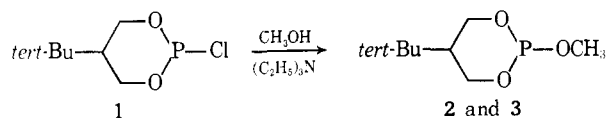
The conformations of cyclic six-membered ring phosphites, 1,3,2-dioxaphosphorinanes, and the conformational preferences of substituents on such rings have not been thoroughly studied. This is in marked contrast to the considerable attention given the corresponding six-membered dioxanes and sulfites. All three systems are related to the cyclohexanes. Although the sulfites, dioxanes, and phosphites are related in the sense that all have oxygen heteroatoms at the 1 and 3 positions of a six-membered ring, the different atoms, carbon, sulfur, and phosphorus, at the 2 position, and the different bond angles and bond lengths peculiar to each atom would make any attempt to extrapolate findings from one system to another very hazardous. Marked differences between the conformational requirements of groups at the 2 position in 1,3-dioxanes and those of substituents on cyclohexane rings have already been noted.² The question of the preferred configuration at phosphorus in a cyclic phosphite (axial *vs.* equatorial orientation of the substituent) involves, among other things, the consideration of the "size" of an electron pair compared to that of other substituents, a topic of current interest in other systems.³ In this respect the phosphites are rather like the sulfites which also have a lone pair and oxygen on the ring atom at the 2 position. However, in that they possess an alkoxy group at atom 2, the phosphites also resemble the 2-alkoxy-1,3-dioxanes.

This paper reports a study of ring conformations and configuration at phosphorus of the *cis*- and *trans*-5-*tert*-butyl-2-methoxy-1,3,2-dioxaphosphorinanes **2** and **3**. Like the sulfites and 1,3-dioxanes this system is

amenable to nmr analysis. The spectra of the phosphites are complicated, however, by the strong spin-spin interactions of the phosphorus nucleus which results in an AA'BB'XY spin system. But when the spectra are fully analyzed, the phosphorus-hydrogen coupling constants, $^3J_{HP}$, for the methylene protons become a valuable aid not present in the other systems in assigning the ring conformation at the phosphorus end of the ring.

Results

Synthesis. Phosphites **2** and **3** were readily formed from the phosphorochloridite, 5-*tert*-butyl-2-chloro-1,3,2-dioxaphosphorinane (**1**). With extreme care, a ratio



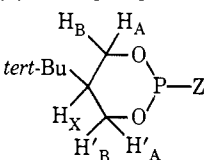
of **3**, the thermodynamically less stable form, to **2** as high as 9:1 could be realized. The ratio was unchanged by distillation under reduced pressure. The isomer ratio was easily determined by integration of the *tert*-butyl hydrogen nmr signals which were separated by about 10 Hz in the two isomers (Table I). Vpc analysis was not a useful analytical tool in this case because the isomers were sometimes equilibrated in the instrument and because the peaks were not well separated. Equilibration of the isomers **2** and **3** was also effected on a neat sample or in solution by addition of traces of trifluoroacetic acid, by heating the sample above 80° for several hours, or by allowing the sample to stand several days at room temperature. A near-equilibrium mixture of **2** and **3** nearly always resulted whenever any of the apparatus used in the preparation was not previously washed thoroughly with triethylamine and oven dried. The equilibrated mixture (CDCl₃) contained **2** and **3** in ratio 1:11 corresponding to ΔG_{25}° of 1.4 kcal/mol. The equilibration of **2** and **3** is slow enough to allow its determination to be made by nmr. Spectra taken over a considerable range of temperatures showed the expected shift in the **2** and **3** ratio, but the data were not considered accurate enough to allow determination of ΔH° .

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(1) National Aeronautics and Space Administration Fellow, 1966–1968. Taken from the Ph.D. Thesis of J. H. Hargis, University of Utah, 1969; published in part in preliminary form, J. H. Hargis and W. G. Bentrude, *Tetrahedron Lett.*, 5365 (1968).

(2) (a) E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.*, 90, 3444 (1968); (b) K. Pihlaja and J. Heikkilä, *Acta Chem. Scand.*, 21, 2390, 2430 (1967); (c) F. G. Riddell and M. J. T. Robinson, *Tetrahedron*, 23, 3417 (1967).

(3) For examples concerning the hydrogen *vs.* an electron pair on nitrogen in pyrimidines see: H. Booth, *Chem. Commun.*, 803 (1968); T. Masamune, *ibid.*, 244 (1968); R. W. Bablock and H. R. Katritzky, *Tetrahedron Lett.*, 1159 (1969); M. J. T. Robinson, *ibid.*, 1153 (1968); J. B. Lambert, R. G. Keske, R. E. Carhart, and A. P. Jovanovich, *J. Amer. Chem. Soc.*, 89, 3761 (1967).

Table I. Nmr Parameters^c for 2-Substituted 5-*tert*-Butyl-1,3,2-dioxaphosphorinanes


Compd	Temp, °C	$J_{AB} = J_{A'B'}$	$J_{AX} = J_{A'X}$	$J_{BX} = J_{B'X}$	$J_{AP} = J_{A'P}$	$J_{BP} = J_{B'P}$	ν_X	ν_A	ν_B	$\nu_{tert-Bu}$
1 ^a	37	-10.8	11.7	3.83	5.28	11.3	130.0	273.8	255.0	56
1 ^d	37	-11.0			4.43	12.1		274.0	255.0	56
2 ^{a,d}	37	-10.6 (0.049)	11.9 (0.039)	3.71 (0.035)	2.89 (0.072)	11.0 (0.066)	119.8	254.3 (0.041)	232.1 (0.034)	51
3 ^a	37	-11.6	4.65	4.91	5.03	8.40	90.0	263.6	235.0	61
3 ^b	-62	-11.5	4.10	3.10	3.90	9.40	79.8	262.8	229.2	62

^a Approximate 20% solutions in CDCl₃. ^b Approximately 20% solution in CS₂; determined at 100-MHz shifts reported at 60 MHz; spectra in CDCl₃ and CS₂ identical at 37°. ^c Values in hertz; absolute values of J given except for J_{AB} assumed to be negative; chemical shifts (ν) in hertz downfield from TMS at 60 MHz. ^d Numbers in parentheses are calculated probable errors from LAOCN3 program. RMS error calculated line positions, 0.220. Maximum deviation of calculated from assigned line position, 0.50 Hz.

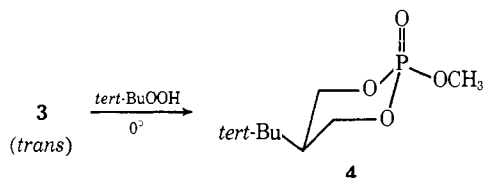
Assignment of *cis* or *trans* Geometry to Phosphites 2 and 3. When various mixtures of the phosphites 2 and 3 were treated with *tert*-butyl hydroperoxide at 0°, the corresponding phosphate mixtures resulted. As shown in Table II, the ratio of phosphates determined

Table II. Reactions of Mixtures of Phosphites 2 and 3

Reactant	Ratio 3/2	Ratio of products ^a	
		Phosphates	Phosphonates
(CH ₃) ₂ COOH	80/20	76/24	
	10/90	11/89	
CH ₃ I	77/23		71/29
	11/89		9/91

^a Ratios determined by vpc analysis, not corrected for possible sensitivity differences.

by vpc analysis corresponded quite closely to the phosphite ratio suggesting a high degree of stereoselectivity. Since the temperature was well below that required for inversion at phosphorus, and since the *tert*-butyl hydroperoxide oxidation of optically active phosphines gives highly pure optically active phosphine oxides with retention of configuration at phosphorus,⁴ the phosphorus configuration in the phosphites can be inferred if that of the product phosphates is known. The predominate isomer (4) from *tert*-butyl hydroperoxide oxidation of material containing largely 3 was isolated and subjected to an X-ray crystallographic study which showed the *tert*-butyl and methoxy groups to be *trans* and equatorial in a chair-form molecule.^{5a} Thus isomer 3 is the *trans* isomer.

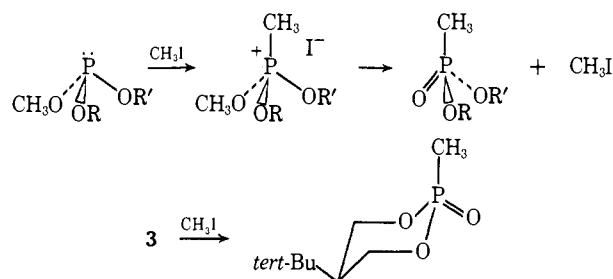


Confirmation of this finding resulted from reaction of a phosphite mixture at room temperature with

(4) D. B. Denney and W. H. Hanifin, Jr., *Tetrahedron Lett.*, 2177 (1963).

(5) (a) The X-ray crystallographic studies were carried out by Dr. C. N. Caughlan and M. U. Haque, Montana State University (unpublished); (b) M. U. Haque, C. N. Caughlan, J. H. Hargis, and W. G. Bentrude, *J. Chem. Soc. A*, 1786 (1970).

methyl iodide. As seen in Table II high stereoselectivity is also noted in this reaction which should proceed⁶ as shown in Scheme I. Since inversion at phosphorus

Scheme I

is slow at the temperatures used, reaction (attack by phosphorus) should occur where the nonbonded pair is most exposed. Regardless of the amount of s or p character of the pair this should be the axial direction if the methoxy is equatorial, or the equatorial direction in the event the methoxy is axial. An X-ray study^{5b} also established the structure of the methylphosphonate (Scheme I) from phosphite 3 as a chair form molecule with the *tert*-butyl and methyl substituents in the equatorial and axial positions, respectively. From both the *tert*-butyl hydroperoxide and methyl iodide reactions, the conclusion is the same. The *tert*-butyl and the methoxy in phosphite 3 are *trans*. Thus the more stable isomer (2) is the *cis* compound.

Analysis of Proton Nmr Spectra. Since it was possible to obtain isomer mixtures of the pure phosphites containing at least 90% of either isomer, analysis of the complex ¹H nmr splitting patterns could be carried out even though neither isomer could be isolated completely free of the other. Because neither ³¹P decoupling facilities nor adequate ¹H decoupling was available, the spectra were first approximated as being ABXY with the X and Y designations assigned to the methine hydrogen and phosphorus, respectively. The methylene portion of the spectrum was then inspected, and transition energies and intensities were calculated by hand using the appropriate quantum mechanically derived relationships. Parameters J and ν thus derived were used as starting values for calculation of refined parameters

(6) A. J. Kirby and S. G. Warren, "The Organic Chemistry of Phosphorus," Elsevier, Amsterdam, 1967, pp 37-45.

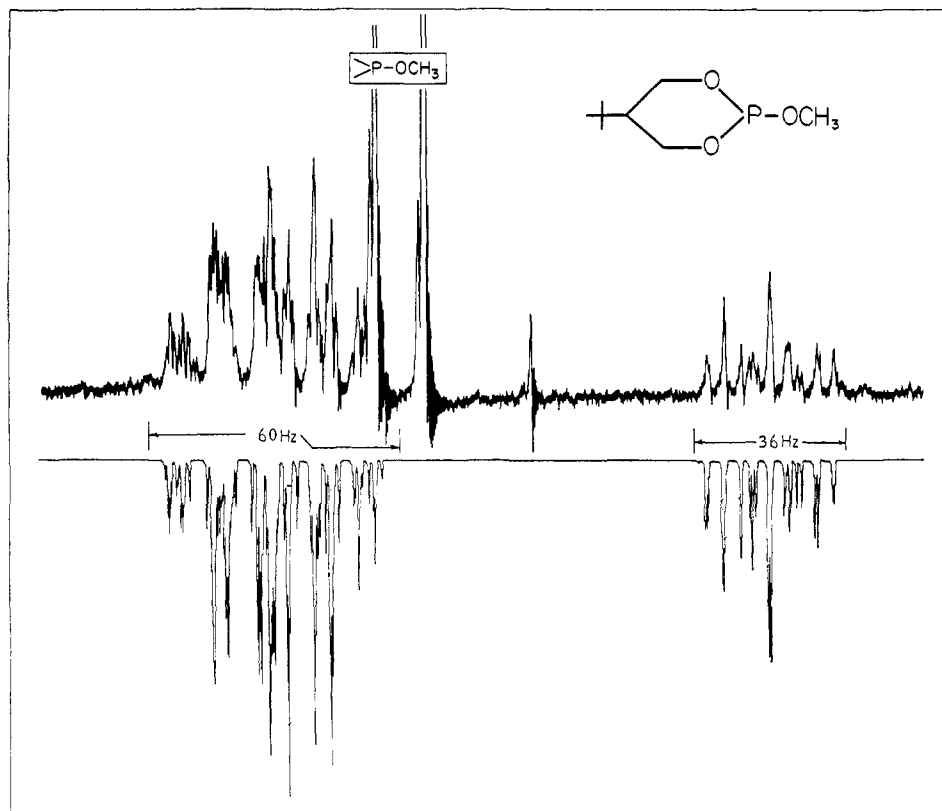


Figure 1. Experimental and calculated nmr spectra for *cis*-5-*tert*-butyl-2-methoxy-1,3,2-dioxaphosphorinane (**2**) at 60 MHz.

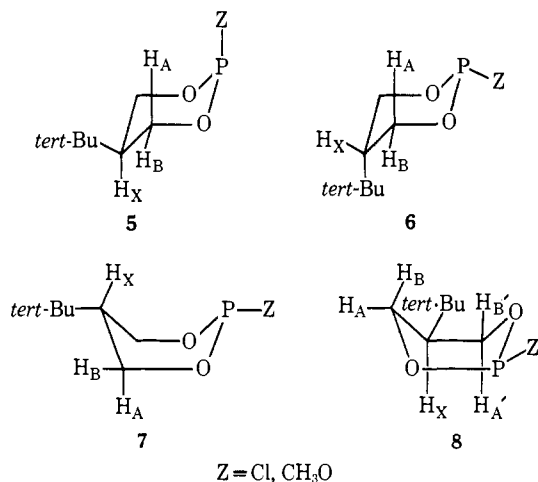
using the LAOCN3 iterative computer program.⁷ The resolution of a given proton spectrum which contained over a hundred calculated transitions did not allow unambiguous assignment of calculated lines to their counterparts in the observed spectrum. Under a single broad peak one might have to assign six or seven groups of lines. This was especially true of the methylene spectrum for which major peaks were further broadened by cross-ring couplings. We therefore used the LAOCN3 program to slightly change the positions of groups of lines until the most satisfactory fit of calculated plot to the superimposed experimental spectrum was obtained. Errors in coupling constants resulting from this procedure are estimated to be about 0.2 Hz. Changes larger than this in any one parameter led to appreciable discrepancies between computed and experimental spectra. The errors in parameters calculated by LAOCN3 are much smaller but cannot be regarded as accurate estimates. These are included in Table I for **2** and are representative of those found for the other compounds. In this instance, the spectrum was especially well resolved and 85 lines were used (though not all were observed) in matching the 131 calculated lines. For the phosphorochloridite, the experimental spectrum merited use of only 56 of 133 lines. After each iteration the experimental spectra were reexamined and reassignment of experimental lines was made until the best possible fit was obtained. On occasion more than one set of parameters gave acceptable fits for the AB protons. Only one set, however, generated the observed X proton (methine H) pattern of the observed spectrum. This provided a useful cross-check in each case.

(7) We thank Professor A. A. Bothner-By for sending us this program.

Results of this analysis are shown in Table I for the phosphites **2** and **3** and phosphorochloridite **1**. A calculated spectrum for each case was produced using a plotter in conjunction with the computer for comparison with the experimental spectrum. Fine splittings, <2 Hz, from cross-ring, long-range interactions between the AB and A'B' methylene protons were noted in each instance. However, usually no effort to determine precise values of these coupling constants was made, because the resolution did not justify it and since the primary goal of the nmr analysis was the determination of the conformations of **1**, **2**, and **3** by examination of the values of J_{AX} , J_{BX} , J_{AP} , and J_{BP} . A comparison of an especially well-resolved experimental spectrum of **2** with the calculated one using a Lorentian curve function, line width at half-height of 0.5 Hz and assuming $J_{AA'} = 1.05$ Hz, $J_{AB'} = 0.36$ Hz, and $J_{BB'} = 1.82$ Hz is shown in Figure 1. The latter couplings are not necessarily unique.

J_{AX} , J_{BX} and J_{AY} , J_{BY} sets were distinguished and assigned to interaction with the appropriate nucleus (H or P) by deuterium substitution for the methine hydrogen at carbon-5. This also aided the initial ABXY analysis. From Table I it is seen that in the chloridite (**1**) the lower field proton (A) is coupled to one nucleus with a large coupling constant, approximately 11 Hz, and to the other with J about 5 Hz. On deuterium substitution, the large coupling disappears. This suggests a trans-diaxial relationship for H_A and H_X . For the upfield methylene hydrogen (H_B) deuterium substitution removes the smaller coupling, a fact consistent with an equatorial-axial or equatorial-equatorial relationship for H_B and H_X . The B proton shows a larger (~ 11 Hz) coupling to phosphorus than that of

H_A (~ 5 Hz). These coupling patterns and the nearly identical ones for **2** are those predicted for a chair form ring with the 5-*tert*-butyl group equatorial and A and B methylene hydrogens axial and equatorial, respectively (structure **5**). The relative values of J_{AP} and J_{BP} for the methylene protons are reasonable if anything like a Karplus-like relationship holds for the variation of J_{HP} with the HCOP dihedral angle. Evidence for such a relationship has resulted from several studies⁸ al-



though the effect is not so well established as is that for vicinal proton interactions. The relatively large J_{BP} would result from the near 180° HCOP dihedral angle.

The alternate chair structure (**6**) is ruled out by the values of J_{AX} and J_{BX} . In the same way the corresponding boat form with the *tert*-butyl and Z substituents pseudoaxial resulting from ring inversion at phosphorus is excluded. Boat form **7** or a rapidly equilibrating mixture of twist forms corresponding to **7** would be expected to give more nearly equal values of J_{AP} and J_{BP} . The same can be said for J_{AX} and J_{BX} with equilibrating twist forms. Boat form **8** would give different chemical-shift values of the A and A' protons as well as nonequivalent B protons.

The methylene-methine coupling constants for **1** and **2** may be compared to those for a series of corresponding *trans*-2-alkyl-5-*tert*-butyl-1,3-dioxanes which have the *tert*-butyl equatorial. Values of J_{4e5a} 4.5–5.6 Hz were reported^{2a} along with J_{4a5a} of 10.6–12.2 Hz. The slightly smaller values of J_{4e5a} in the compounds **1** and **2** are to be expected if the *tert*-butyl end of the molecule in those cases is slightly more puckered than in the dioxanes. The longer P–O bonds⁹ (1.59 Å) compared to C–O bonds¹⁰ (1.41 Å) may cause a flattening of the

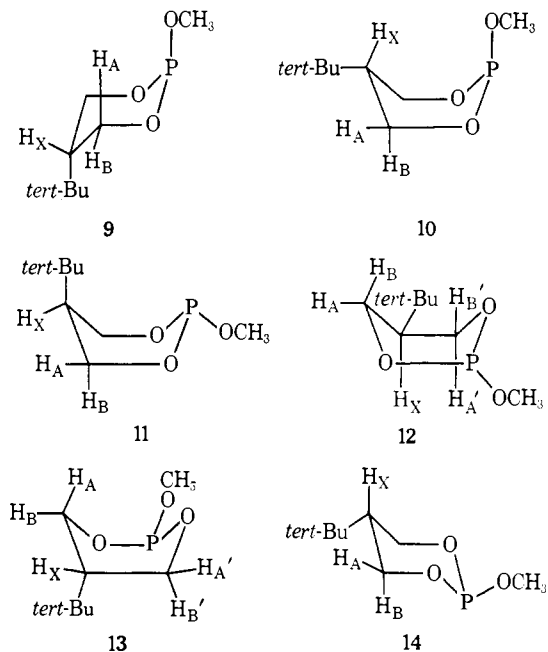
(8) For cases in which the HCCP or HCOP angular relation is known with reasonable certainty see: (a) M. Tsuboi, F. Kuriyagawa, K. Matsuo, and Y. Kyogoku, *Bull. Chem. Soc. Jap.*, **40**, 1813 (1967); (b) J. G. Verkade and R. W. King, *Inorg. Chem.*, **1**, 948 (1962); (c) J. G. Verkade, R. W. King, and C. W. Heitsch, *ibid.*, **3**, 884 (1966); (d) E. J. Boros, K. J. Coskran, R. W. King, and J. G. Verkade, *J. Amer. Chem. Soc.*, **88**, 1140 (1966); (e) C. Benzera and G. Ourisson, *Bull. Soc. Chim. Fr.*, 1825 (1966); (f) C. Benzera, *Tetrahedron Lett.*, 4471 (1969); (g) M. Kainosho and A. Nakamura, *Tetrahedron*, **25**, 4071 (1969). For examples of $^3J_{HP}$ which clearly show an angular dependence but for which the geometry is less certain see: (h) C. Bodkin and P. Simpson, *Chem. Commun.*, 829 (1969); (i) K. D. Bartle, R. S. Edmundson, and D. W. Jones, *Tetrahedron*, **23**, 1701 (1967); (j) M. Mikolajczyk, *Chem. Commun.*, 1221 (1969); (k) D. Gagnaire and J. B. Robert, *Bull. Chem. Soc. Fr.*, 2240 (1967); (l) D. Gagnaire, J. B. Robert, and J. Verrier, *ibid.*, 2392 (1968). This topic is discussed as part of a review by M. J. Gallagher and I. D. Jenkins, *Top. Stereochem.*, **3**, 1 (1968).

(9) Mean value, see D. E. C. Corbridge, *Top. Phosphorus Chem.*, **3**, 57 (1966).

phosphorus end of the ring and a consequent increased puckering at the other end. However, such puckering is not observed in similar tetracoordinate phosphorus compounds which are strongly flattened about phosphorus.^{5,11}

The conformation of **3** is not so readily deduced. The temperature dependence of the chemical shifts and coupling constants for **3**, which may be noted in Table I, suggest that **3** consists of a mixture of at least two conformers in mobile equilibrium. At -62° the values of J_{AP} and J_{BP} are within 1 Hz of those noted for **1** and **2** and suggest that in the predominate form at that temperature the HCOP dihedral angles are about 60° and 180° . The methylene-methine proton couplings are approaching those expected for axial-equatorial and equatorial-equatorial couplings. For the corresponding *cis*-2-alkyl-5-*tert*-butyl-1,3-dioxanes ranges of J_{4e5e} 1.1–2.0 Hz and J_{4a5e} 3.9–4.3 Hz were reported.^{2a} The observed values are consistent with the chair-form structure of **9** for the predominant conformer at -62° . The small differences in the values we find and the ranges reported for the dioxanes are probably the result of the presence of other conformer(s). Structures **10** and **11** or similar equilibrating twist forms are excluded for the conformer of **3** predominant at -62° on the basis of J_{AP} and J_{BP} values as they were for **2**. Forms in which the two A protons or two B protons are nonequivalent (**12** and **13**) also need not be considered.

It is worthwhile to note that the *tert*-butyl shift for the axial *tert*-butyl of **3** at -62° is about 10 Hz downfield from that of the equatorial *tert*-butyl, as is observed^{2a} in the corresponding dioxanes. The relative shifts of the methine hydrogens in the two forms are



also the same as in the dioxanes. However, a difference in anisotropy effects in the two ring systems is seen in the fact that the order of chemical shift of the methylene protons is reversed, the axial hydrogen being downfield

(10) Value of dimethyl ether, U. Blukis, P. H. Kasai, and R. J. Myers, *J. Chem. Phys.*, **38**, 2753 (1963); K. Kimura and M. Kubo, *ibid.*, **30**, 151 (1959).

(11) T. A. Beineke, *Acta Crystallogr., Sect. B*, **25**, 413 (1969); H. J. Geise, *Recl. Trav. Chim. Pays-Bas*, **86**, 362 (1967); M. U. Haque, C. N. Caughlan, and W. L. Moats *J. Org. Chem.*, **35**, 1446 (1970).

Table III. Predicted Averaged Coupling Constants

Trial	Conformers	Mol %	Assumed couplings				Calcd av couplings				T, °C
			J _{AX}	J _{BX}	J _{AP}	J _{BP}	J _{AX}	J _{BX}	J _{AP}	J _{BP}	
1	14	30	3.70	11.9	11.0	2.90	3.98	4.69	5.33	8.57	37
	9	70	4.10	1.60	2.90	11.0					
2	14	15	Same	Same	Same	Same	4.05	3.15	4.12	9.79	-62
	9	85									
3	14	30	3.70	11.9	11.0	2.90	3.42	5.25	5.33	8.57	37
	9	70	3.30	2.40	2.90	11.0					
4	14	15	Same	Same	Same	Same	3.36	3.83	4.12	9.79	-62
	9	85									
5	14	30	6.00	11.9	11.0	2.90	4.67	4.69	5.33	8.57	37
	9	70	4.10	1.60	2.90	11.0					
6	14	15	Same	Same	Same	Same	4.39	3.15	4.12	9.79	-62
	9	85									
7	10	35	3.70	11.9	3.50	3.50	3.96	5.20	3.10	8.40	37
	9	65	4.10	1.60	2.90	11.0					
8	15	58	5.12	7.00	6.50	6.50	4.65	4.90	4.99	8.39	37
	9	42	4.00	2.00	2.90	11.0					
9	15	28	Same	Same	Same	Same	4.31	3.40	3.91	9.74	-62
	9	72									
Exptl values							4.65	4.90	5.03	8.40	37
							4.10	3.10	3.90	9.40	-62

of the equatorial one in the phosphites but upfield of the equatorial one in the dioxanes. Also, hydrogen-phosphorus couplings of the order seen here for **1** and **2** and at -62° for **3** have been noted by previous workers^{8g,k,l} for trivalent 1,3,2-dioxaphosphorinanes for which chair conformations seem likely.

To attempt to answer the question of the structure of the other conformer or conformers of **3**, the predicted effects on the measured coupling constants of mixing **9** with other forms can be compared to the observed couplings recorded in Table I. The measured value of J_{AX} is seen to undergo a small increase in response to temperature increase (Table I). While we would not want to attach importance to the absolute magnitude of the increase, the direction of the change in J_{AX} is quite certain. At the same time the value of J_{BX} is raised by over 1.5 Hz. The parameters J_{AP} and J_{BP} are increased and decreased, respectively, by about 1 Hz. The observed changes in J_{AX} and J_{BX} immediately exclude structure **11** for which the hydrogen-hydrogen couplings would be essentially the same as in **9**.

In Table III are recorded results of attempts to calculate values of the observed time-averaged coupling constants assuming reasonable coupling constants for the possible conformers which are considered. Although we must interpret the calculated J values in Table III with caution, we believe that a conservative assessment of the trends seen allows us to say that a rigid boat form (**10**) may be excluded from further consideration as an important conformer in equilibrium with form **9**. Also, we believe that rapidly interconverting twist forms of **10** (structures **15a** and **15b**) deserve at least as important consideration as does **14**. The following arguments lead to these conclusions.

In trials 1-6 consideration is made of **14** as the second conformer. In each trial it is assumed that the hydrogen-phosphorus couplings for **14** are the same as those for **2** and that J_{AP} and J_{BP} are exactly reversed in **9** and **14**. The latter will be true if the two forms are equivalent chairs, since the position of the A and B hydrogens

and consequently their HCOP dihedral angles will be interchanged. For trials 1-6 the mole percentages of **14** and **9** were adjusted using the assumed values of J_{AP} and J_{BP} until the calculated averaged hydrogen-phosphorus couplings most nearly duplicated the experimental values of 37 and -62° . Then the averaged values of J_{AX} and J_{BX} were calculated. In trials 1-4 the coupling constants, J_{AX} and J_{BX} for **14** are taken to be the same as those measured for **2** in which the *tert*-butyl group is almost certainly equatorial. In trial 1 the values of J_{AX} and J_{BX} used for **9** are the average of the range of constants J_{4a5e} and J_{4e5a} reported by Eliel and Knoeber^{2a} for the series of 2-alkyl-5-*tert*-butyl-1,3-dioxanes. From Table III it is seen that except for J_{AX} , which is a little low in the 37° case, all values are predicted within 0.3 Hz of those measured. As the temperature is lowered (trial 2), an increase in mole fraction of the more stable isomer **9** is accompanied by a proper change in the averaged coupling constants with the exception of J_{AX} . The change in calculated J_{AX} is very small and in the wrong direction, but in view of the small change in measured J_{AX} and increased error in measurement of the parameters at -62° , we hesitate to base any important conclusions on this possibly anomalous behavior.

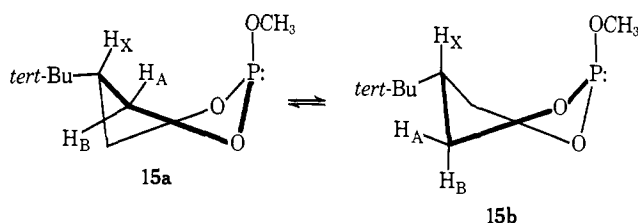
In trials 3 and 4, account is taken in the selected J_{AX} and J_{BX} values of **9** of the possibility that the *tert*-butyl end of the ring may be slightly more puckered in the phosphites than in the dioxanes (*vide supra*). This is seen by comparing the measured value J_{BX} for **2** of 3.71 Hz to the range of J_{4e5a} measured^{2a} for the corresponding 5-*tert*-butyl-1,3-dioxanes of 4.4-5.6 Hz. The low value of J_{BX} is consistent with an increase in the $H_{4e}H_{5a}$ dihedral angle. Ring puckering would also move the values of J_{AX} and J_{BX} in **9** toward each other. This effect is reflected in the values of J_{AX} and J_{BX} chosen for trials 3 and 4. The resulting averaged J_{AX} calculated is much too low for the 37° comparison (trial 3).

The low values of J_{AX} in trials 1-4 can be remedied by using a relatively large value for J_{AX} in **14** as shown

in trials 5 and 6. Values for J_{4e5a} as high as 6.6 Hz have been reported.¹² However, it is not clear to us what combination of effects on ring geometry would result in a coupling constant J_{AX} in **14** nearly twice that for similarly situated protons in **2**.

Trial 7 shows that the rigid boat form **10** is an unsuitable alternative. Assuming equal J_{AP} and J_{BP} for **10** with an assumed value for $J(\text{POCH}_{120^\circ})$ slightly larger than that for $J(\text{POCH}_{60^\circ})$ observed in **2** and values of the hydrogen-hydrogen couplings equal to those of **2**, the calculated averaged coupling J_{AP} is seen to be much too low.

In trials 8 and 9 the assumption that **9** is in equilibrium with rapidly interconverting twist forms of **10** (structures **15a** and **15b**) leads to excellent agreement of calculated averaged coupling constants with measured values. The following considerations show the values



of J_{AX} and J_{BX} chosen for **15** to be reasonable ones. The hydrogen-phosphorus couplings of **2** would be expected to average to something close to 7 Hz if HCOP dihedral angles for H_A and H_B are approximately 60° and 180° in one form and are interchanged in the other. For H_A in the two twist forms the $H_A\text{CCH}_X$ dihedral angles would be approximately 0° and 60° . If a strict Karplus dihedral angular relation¹³ were applied, the observed couplings at 0° and 60° would be about 8 and 2 Hz for an average of 5 Hz. Similarly for H_B an averaging of coupling constants of approximately 4 and 12 Hz corresponding to $H_B\text{CCH}_X$ dihedral angles of 120° and 180° would yield an average J_{BX} of 8 Hz. Considering the possible but unevaluated ring distortion and electronegativity effects on J values, the values for **15** taken in trials 7 and 8 seem reasonable. It is obvious from trials 8 and 9 that a twist form of **11** similar to **15** need not be considered. In **11** (twist) the values of J_{AX} and J_{BX} would be reversed leading to large errors in predicted averaged J_{AX} and J_{BX} .

We conclude from the above considerations that a twist boat form for the less stable conformer of phosphite **3** is worthy of serious consideration, although we certainly are not prepared to say that our results establish the presence of such a species. Forms such as **12** and **13** might also be important even though they are themselves asymmetric and have five nonequivalent protons. The form of **12** and **13** shown is only one of a *dl* pair each of which is formed with equal probability from **9**. Interconversion of the two forms through **8** effectively makes the A and A' protons equivalent and has the same effect on the B protons. More work is needed relative to the importance of twist forms in these systems.

Configuration at Phosphorus. The phosphite isomer **3**, as shown by reaction with *tert*-butyl hydroperoxide

(12) J. E. Anderson, F. G. Riddell, and M. J. T. Robinson, *Tetrahedron Lett.*, 2017 (1967).

(13) M. Karplus, *J. Chem. Phys.*, **30**, 11 (1959); *J. Amer. Chem. Soc.*, **85**, 2870 (1963).

and methyl iodide, is the *trans* species. Nmr analysis indicates that the *tert*-butyl axial in the chair form conformation predominant at -62° . Thus the methoxy is axial in the predominant conformer of the *trans* isomer (structure **9**). The same types of evidence show that the *cis* isomer (**2**) is a chair conformer (structure **5**, $Z = \text{CH}_3\text{O}$) with the methoxy also assigned an axial orientation and the *tert*-butyl equatorial.

These assignments, of course, depend on a correct interpretation of the stereochemistry of the nearly stereospecific reactions with hydroperoxide and methyl iodide. It might be argued that the stereochemistry of these reactions is indeed opposite to that assumed. This could result in one of two ways. The first would involve some type of simultaneous inversion-displacement process. This seems unlikely in that it would require rehybridization at phosphorus in concert with nucleophilic attack by phosphorus. It is, perhaps, not inconceivable that this could occur if the direction of attack toward the most exposed portion of the electron pair, as described above, were very highly hindered or product development control were governing. This would mean that the methoxy in **3** is really equatorial and that attack takes place from the equatorial direction with simultaneous inversion. This seems very unlikely and further would be contrary to the preferential axial attack noted¹⁴ in *N*-alkyl piperidines, species in which attack is slow with respect to nitrogen inversion and in which product control by the Hammett-Curtin principle obtains. The transition state for the phosphite reactions probably would not be unlike those of *N*-alkyl piperidines. Also isomer **3**, because of its apparent conformational mobility, would likely not have the same steric restrictions as **2**. Yet the same stereospecificity is observed.

Second, it is possible that the alkyl iodide or hydroperoxide reaction intermediate might be in equilibrium with a pentacovalent species which could undergo pseudorotation to give product of opposite configuration to that expected. Careful inspection of this possibility for methyl iodide reveals that reaction of the intermediate with iodide to give a pentacovalent species would result in inversion only by subsequent pseudorotation steps through intermediates in which methyl occupies the energetically unfavorable¹⁵ axial position. Also, if pentacovalent intermediates are important and have sufficient lifetime for pseudorotation through energetically unfavorable forms, it seems quite likely that reactions **2** and **3** would pass through intermediates (perhaps common) at some stage which would lead to greatly reduced stereospecificity with one isomer or the other. Very recent work by Denney and Finley¹⁶ establishes that one of the isomers of 2-methoxy-4-methyl-1,3,2-dioxaphosphorinane reacts stereospecifically with neopentyl hypochlorite to give product neopentyl phosphate of inverted configuration whereas the other phosphite isomer gives both retention and inversion in amounts depending on reaction temperature.

(14) H. O. House and T. M. Bare, *J. Org. Chem.*, **33**, 943 (1968); H. O. House, B. A. Tefertiller, and C. G. Pitt., *ibid.*, **31**, 1073 (1966); D. R. Brown, B. G. Hutley, J. McKenna, and J. M. McKenna, *Chem. Commun.*, 719 (1966); D. R. Brown, J. McKenna, J. M. McKenna, and J. M. Stuart, *ibid.*, 380 (1967).

(15) For references see F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(16) J. H. Finley and D. B. Denney, *J. Amer. Chem. Soc.*, **92**, 362 (1970).

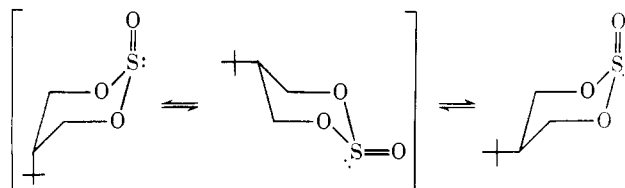
The results are reasonably interpreted by assuming that *one* isomer gives a relatively stable pentacovalent intermediate while that formed from the other undergoes pseudorotation with loss of reaction stereospecificity. The argument based on observed stereospecificity also applies to the *tert*-butyl hydroperoxide oxidation, a reaction for which a pentacovalent species at first seems more likely in that it would involve five oxygens covalently bonded to phosphorus. In this case we believe that stereospecificity results from the extremely rapid reaction of *tert*-butoxide with the proton of the hydroxyl in the initially formed $[(RO)_3POH]^+ [OH]^-$ which precludes formation of a pentacovalent species.

Discussion

This represents the first complete analysis of both conformation and configuration of isomeric trivalent 1,3,2-dioxaphosphorinanes monosubstituted at a ring carbon. The existence of geometrical isomers of mono- and disubstituted analogs was previously established,¹⁷ and hydrogen-phosphorus couplings and axial and equatorial methylene hydrogen shifts had been assigned.^{8g,h,k,l} But *cis* or *trans* structure of isomers and preferred configuration of phosphorus has been unclear. Verkade, *et al.*,^{17c} have suggested an axial methoxy preference for both isomers of 5-methyl-5-chloromethyl-2-methoxy-1,3,2-dioxaphosphorinane, whereas Gagnaire and coworkers^{8k,l} have argued for an equatorial methoxy in analogous compounds. Our results appear to establish firmly the axial preference for methoxy on phosphorus in six-membered ring phosphites.¹⁸ Verkade and coworkers have reaffirmed their findings in a paper which also appears in this issue.^{17d}

Apparently, unfavorable nonbonded 1,3-steric interactions are overcome in the phosphites by the anomeric effect¹⁹ so that the *cis* isomer is the more stable. We estimate (Table III) that if conformer **14** is the species in equilibrium with **9** and **2**, then the *trans* isomer at 25° is roughly 30% in the chair form **14**. With the ratio **2/14** equal to 37, the axial preference is about 2 kcal/mol. A similar figure is obtained if the ratio of **9** to **14** is about 2 (ΔG°_{25} ca. 0.5 cal/mol), and the axial-equatorial conformational energy difference for the 5-*tert*-butyl is about 1.5 kcal/mol.^{2a,c,20} Very recent work by Eliel and Nodes shows that at 25° only 16% of the less stable *trans*-2-methoxy-5-*tert*-butyl-1,3-dioxane [ΔG°_{25} (*cis* \rightarrow *trans*) = 0.5 kcal/mol] exists in the chair form with substituents diaxial. The methoxyl preference for the axial position is only 0.60 kcal/mol. That the methoxy axial bias is greater in the phosphite than the dioxane also is obvious if **15** rather than **14** is present. However, a striking similarity between the

phosphite system and the analogous sulfites is seen in the relatively great stability of the *cis*-2-*tert*-butyl-1,3-trimethylene sulfite, ΔG°_{40} for the equilibrium *cis* \rightleftharpoons *trans* being 1.50 kcal/mol.²⁰ From the data of Van Woerden, *et al.*,^{20a} it can be calculated that ΔG°_{40} for the equatorial to axial conversion of the S=O bond is favorable by 2.1 kcal/mol.



It seems likely that the principle structural differences between the phosphites, sulfites, and dioxanes are in changed bond lengths and angles about the phosphorus, sulfur, and carbon atoms. For example, the difference in equatorial-axial conformational free energy of the *tert*-butyl group in the three types of compounds is closely similar. For the cyclic sulfites a value of 1.8 kcal/mol has been reported (40°)²⁰ which is not very different from that in the 1,3-dioxane system^{2a,c} (1.4, 1.7 kcal/mol, 25°). It is quite certain that at 25°, 40-70% of phosphite **3** is in the form **9** (Table III). This combined with the 11:1 ratio of **2** to total *trans* isomer gives ΔG for the equilibrium **2** \rightleftharpoons **9** of 1.5-1.9 kcal/mol, a range closely comparable to the values determined in the dioxane and sulfite series. Thus the relatively high percentage of *trans* isomer with substituents axial noted in the phosphite (40-70%) and sulfite (~70%, 40°) systems probably results from a greater preference of the oxy substituents for the axial position in those molecules compared to the 1,3-dioxanes.

In this regard, longer bonds to oxygen in the sulfite and phosphite cases, as mentioned previously, could potentially cause a flattening of the ring at this end. In the sulfites, this effect is slight²¹ apparently because of the relatively small (100°) O-S-O internal bond angle. It appears then that the geometry of the phosphorus end of the ring will depend on the angles imposed on the ring by the phosphorus atom. If flattening results (as it does in pentavalent compounds,^{5,11} O-P-O angle about 104°), then the axial methoxyl will be moved away from the axial methylene hydrogens thus reducing the nonbonded interactions. It is also possible that the syn-axial 1,3 interactions may be minimized to some degree for a substituent on phosphorus by an increase in the *s* character of the P-O bonds. These factors are very hard to evaluate in the absence of accurate data concerning bond angles in such systems. Evaluation of the magnitude of the anomeric effect in the phosphite systems awaits an estimation of the size of the syn-axial 1,3 interactions between oxygen and hydrogen.

A further difference between the phosphites and dioxanes may be seen in structures **16-19**. The unshared pair on phosphorus makes the phosphites more like the sulfites. The competitive conformational requirements of an electron pair and a methoxy may be quite different than those of a methoxy and a hydrogen. The relative energies of these forms will depend on a balance

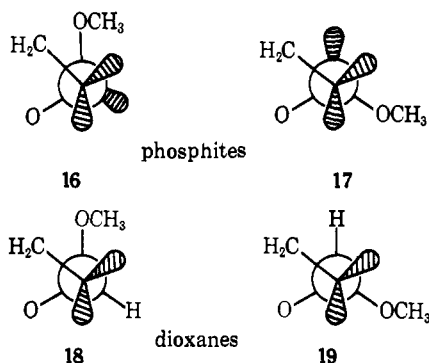
(17) (a) D. Z. Denney and D. B. Denney, *J. Amer. Chem. Soc.*, **88**, 1830 (1966); (b) G. Aksnes, R. Eriksen, and K. Mellingen, *Acta Chem. Scand.*, **21**, 1028 (1967); (c) D. W. White, G. K. McEwen, and J. G. Verkade, *Tetrahedron Lett.*, 5369 (1968); (d) D. W. White, R. D. Bertrand, G. K. McEwen, and J. G. Verkade, *J. Amer. Chem. Soc.*, **92**, 7125 (1970).

(18) After this work was completed a preliminary account of results with which we are in agreement appeared^{8b} for the 4-methyl-2-ethoxy-1,3,2-dioxaphosphoranes. The *trans* isomer was found to be the more stable with the ethoxy axial. The less stable isomer is a mobile equilibrium mixture of conformers.

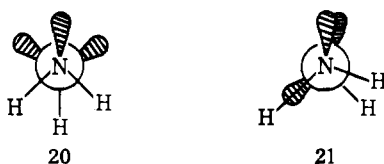
(19) For anomeric effects on 2-alkoxy substituents in 1,3-dioxanes and references to the effect in other systems see: (a) E. L. Eliel and C. A. Giza, *J. Org. Chem.*, **33**, 3754 (1968); (b) F. W. Nader and E. L. Eliel, *J. Amer. Chem. Soc.*, **92**, 3050 (1970).

(20) (a) H. F. Van Woerden, H. Cerfontain, C. H. Green, and R. J. Reijerkerk, *Tetrahedron Lett.*, 6107 (1968); (b) H. F. Van Woerden and E. Havinga, *Recl. Trav. Chim. Pays-Bas*, **86**, 341 (1967).

(21) C. Altona, H. J. Geise, and C. Romers, *ibid.*, **85**, 1197 (1966); J. W. L. Van Oyen, R. C. D. E. Hasekamp, G. C. Verschoor, and C. Romers, *Acta Crystallogr., Sect. B*, **24**, 1471 (1968).



of nuclear–nuclear and electron–electron repulsive terms and nuclear–electron attractive terms as demonstrated by *ab initio* calculations²² of rotational barriers in molecules such as HOOH, NH₂OH, H₂NNH₂, and (CH₂S(O)H)[−], all having vicinal electron pairs. At first glance repulsive interactions between adjacent electron pairs might be expected to make **16** less stable than **17** (assuming considerable p character in the lone pair on phosphorus). However, *ab initio* calculations on NH₂OH,^{22d} e.g., suggest that the conformation for which all electron–electron repulsive interactions (not just the nonbonded ones) are a minimum is the form **20**. That **21** is the most stable conformer results^{22d} from



the other interaction terms. Prediction of the most stable form cannot be made simply by consideration of vicinal lone pair interactions.

The presence of twist boat conformers similar to **15** has recently been postulated for dithianes,²³ dioxanes,¹⁹ and certain substituted six-membered sulfites—*dl*-1,3-dimethyltrimethylene sulfite²⁴ and *dl*-1,3-diisopropyl-2,2-dimethyltrimethylene sulfite.²⁵ In the dithianes boat forms appear to be accessible because of lesser nonbonded interactions (larger ring) and reduced torsional strain with a resultant ΔH° of 3.4 kcal/mol for the chair–boat interconversion²³ compared to 6.8 and 5.9 kcal/mol for the same process in 1,3-dioxane and cyclohexane, respectively.²⁶ The lower chair–boat ΔH° for the dithianes is predicted by consideration of the rotational barrier of dimethyl sulfide, 2.13 kcal/mol^{27a} compared to 3.3 kcal/mol for propane^{27b} and 2.72 kcal/mol for dimethyl ether.¹⁰ Rotational

(22) For recent examples of such calculations see: (a) A. Rauk, S. Wolfe, and I. G. Csizmadia, *Can. J. Chem.*, **47**, 113 (1969); (b) W. H. Fink and L. C. Allen, *J. Chem. Phys.*, **46**, 2261 (1967); (c) W. H. Fink and L. C. Allen, *ibid.*, **46**, 2276 (1967); (d) W. H. Fink, D. C. Pan, and L. C. Allen, *ibid.*, **47**, 895 (1967). For a discussion of the complexities of predicting conformational and rotational energies see J. P. Lowe, *Progr. Phys. Org. Chem.*, **6**, 1 (1968).

(23) E. L. Eliel and R. O. Hutchins, *J. Amer. Chem. Soc.*, **91**, 2703 (1969).

(24) G. Wood and M. H. Miskow, *Tetrahedron Lett.*, 1109 (1969).

(25) L. Cazaux and P. Maroni, *ibid.*, 3667 (1969).

(26) Experimental values of ΔH° (kcal/mol) and ΔS° (eu) for chair–boat interconversions are, respectively: (a) 5.9 and 3.5 for cyclohexane (N. L. Allinger and L. A. Freiberg, *J. Amer. Chem. Soc.*, **82**, 2393 (1969)); (b) for 1,3-dioxane, 6.8 and 3.9 (K. Pihlaja, *Acta Chem. Scand.*, **22**, 716 (1968)); (c) for 1,3-dithiane, 3.4 and 5.3 (ref 23).

(27) (a) L. Pierce and M. Hayashi, *J. Chem. Phys.*, **35**, 479 (1961); (b) K. S. Pitzer, *ibid.*, **12**, 310 (1944).

barriers for dimethyl phosphite and dimethyl sulfite apparently have not been measured. The above sulfites are molecules which in assuming the twist form have escaped 1,3-syn-axial interactions between the sulfuryl oxygen and an axial methyl or isopropyl group. However, Miskow and Wood have recently suggested²⁴ that even *trans*-2-*tert*-butyl-1,3-trimethylene sulfite, studied by Van Woerden, *et al.*,²⁰ is really in the twist form. This question is yet unresolved.

It therefore seems likely that twist forms (**15**) are worthy of important consideration in the cyclic phosphite systems. On the assumption that rotamers **9** and **15** are in equilibrium and using the mole percentages calculated in trials 8 and 9 of Table III, the chair–boat (twist) transformation of *trans*-5-*tert*-butyl-2-methoxy-1,3,2-dioxaphosphorinane, values of 1.8 kcal/mol for ΔH and +6.3 eu for ΔS are obtained. This gives, perhaps fortuitously, a very reasonable ΔS and predicts, as expected,²⁶ a relatively low ΔH value. A choice between chair–chair and chair–twist equilibria for the *trans*-phosphite will require extensive careful temperature and substituent variation studies.

In such considerations, it should be remembered that chair–chair conversions in the sulfites and phosphites may be influenced by vicinal-pair electron repulsions called into play on rotation about the O–P or O–S bond. Sizable experimental barriers for rotation about one bond in trivalent phosphorus amides (P–N bond)²⁸ and in sulfenamides (S–N bond)²⁹ have been reported.

Experimental Section

Proton nmr spectra were taken on either a Varian A-60 or A-56/60 spectrometer. Chemical shifts are reported in parts per million downfield from tetramethylsilane as internal standard. The 100-MHz spectra was obtained by Mr. R. Thrift of the University of Illinois, Department of Chemistry. Melting points are uncorrected. Analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and by M-H-W Laboratories, Garden City, Mich. Vapor phase chromatography was performed on F and M Model 810 and Aerograph A-90 P-3 instruments. The columns were 1/4 in. \times 6 ft 20% SE 30 on 60–80 mesh Chromosorb W. Ratios of products were not corrected for possible sensitivity differences of isomers pairs (thermal conductivity detector).

The simulated nmr spectra were obtained using the iterative computer program LAOCN3, furnished by Bothner-By and Castellano,³⁰ in conjunction with a Univac 1108 computer. Spectra were plotted with a CalComp digital plotter and a plot routing adapted from that of Swalen and Reilly.³¹

Preparation of Deuterium-Labeled Diethyl *tert*-Butylmalonate. To a mechanically stirred suspension of sodium methoxide (95.0 g, 1.86 mol) in 100 ml of benzene was added deuterium oxide (34.0 g, 1.70 mol). This was distilled to give the 60–40 benzene–methanol-*d*₁ azeotrope. A solution of diethyl *tert*-butylmalonate³² (84.5 g, 0.389 mol) and 25.1 g of the above azeotropic mixture (ca. 0.3 mol of methanol-*d*₁) was prepared and to this was added about 0.2 g of metallic sodium. The mixture was refluxed for 3 days and the resulting ethanol, methanol, and benzene were distilled off and replaced with more of the azeotropic mixture. This procedure was repeated five times followed by removal of the volatile materials on a rotary evaporator. The remaining liquid was washed with two 10-ml portions of deuterium oxide and distilled to give 58.9 g of an approximately 2:1 mixture of diethyl and dimethyl *tert*-butylmalonate.

(28) A. H. Cowley, M. J. Dewar, and W. R. Jackson, and W. B. Jennings, *J. Amer. Chem. Soc.*, **92**, 5206 (1970).

(29) M. Raban, G. W. J. Kenney, Jr., and F. B. Jones, Jr., *ibid.*, **91**, 6677 (1969).

(30) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964); LAOCN3, Mellon Institute, Pittsburgh, Pa., 1966.

(31) J. D. Swalen and C. A. Reilly, *J. Chem. Phys.*, **37**, 21 (1962).

(32) P. Boldt and L. Schultz, *Naturwissenschaften*, **51**, 288 (1964).

nate, bp 81° (7 mm). A pmr spectrum indicated complete deuteration.

Synthesis of 5-*tert*-Butyl-2-chloro-1,3,2-dioxaphosphorinane (1). A solution of 2-*tert*-butyl-1,3-propanediol (21.8 g, 0.165 mol), prepared by NaBH₄ reduction of *tert*-butyl diethylmalonate,³² and triethylamine (33.3 g, 0.330 mol) in enough ether to make 100 ml of solution was added dropwise to 200 ml of vigorously stirred anhydrous ether which had been previously chilled to 0° in a dry, nitrogen-flushed flask. Simultaneously, a solution of PCl₃ (22.7 g, 0.165 mol) in 100 ml of anhydrous ether was added. The additions were complete in 1.5 hr. After the reaction was stirred for an additional 40 min at 0°, the triethylamine hydrochloride was filtered away, and the solvent was removed by a nitrogen stream. The remaining liquid was distilled to give product **1**, a white solid, in 65% yield (21.2 g, 0.108 mol): bp 60° (0.75 mm); mp 59–60°; ir (film) 2930, 1460, 1360, 1275, 1042, 1010, 955, and 840 cm⁻¹; pmr (CDCl₃) 0.93 (9 H singlet), 2.17 (1 H multiplet), and 4.25 ppm (4 H multiplet).

Conversion of (1) to 5-*tert*-Butyl-2-methoxy-1,3,2-dioxaphosphorinane (2 and 3). A solution of **1** (33.2 g, 0.168 mol) in 500 ml of anhydrous ether was placed in a clean, nitrogen-flushed flask which had been rinsed with triethylamine and then dried overnight at 110°. To this stirred solution at 0° was added, dropwise, over a 4-hr period a 250-ml ether solution of triethylamine (18.7 g, 0.185 mol) and anhydrous methanol (5.60 g, 0.175 mol). After removal of the amine hydrochloride and ether, distillation of the residue yielded a mixture of two isomers of the phosphite (**2** and **3**) in 93% yield (29.9 g, 0.156 mol), bp 32° (0.075 mm). The ratio of **3/2**, as determined from the integrated intensity of the *tert*-butyl protons in the pmr spectrum was 77/23. This ratio varied with the reaction but was as high as 89/11; ir of **3** (film) 2950, 1750, 1725, 1490, 1400, 1370, 1300, 1235, 1140, 1120, 1052, 1033, 1000, 895, 843, and 730 cm⁻¹; pmr (CDCl₃) 1.01 (9 H singlet), 1.50 (1 H multiplet), 3.46 (3 H doublet, *J* = 12 Hz), and 4.10 ppm (4 H multiplet).

Upon heating (>80°), standing several days at room temperature, or addition of a trace of trichloroacetic acid, the ratio **3/2** reaches an apparent equilibrium value of 8/92 at 25°: ir of **2** (film) 2925, 1470, 1360, 1237, 1135, 1030, 1000, 965, 887, 795, and 725 cm⁻¹; pmr (CDCl₃) 0.85 (9 H singlet), 1.98 (1 H multiplet), 3.45 (3 H doublet, *J* = 12 Hz), and 4.0 ppm (4 H multiplet).

Anal. Calcd for C₈H₁₇O₃P (mixture of **2** and **3**): C, 49.99; H, 8.93; P, 16.11. Found: C, 50.12; H, 8.85; P, 16.00.

Reaction of 2 and 3 with Methyl Iodide. A 77/23 mixture of **3/2** (5.29 g, 0.028 mol) was placed in a triethylamine washed flask under a nitrogen atmosphere and to this was added methyl iodide (9.52 g, 0.067 mol). After standing for 4 hr at room temperature and then overnight at -15°, the contents of the flask were dissolved in chloroform. Gas chromatography showed the ratio of product methylphosphonates, the 5-*tert*-butyl-2-methyl-2-oxo-1,3,2-dioxaphosphorinanes, to be 71/29. The solvent was removed, and the remaining white solid was recrystallized from chloroform-hexane to give 3.40 g (65%) of product. Repeated recrystallization from hexane yielded 3.05 g (58%) of crystalline solid (needles, mp 127–128°), shown to be a single isomer by vpc. A crystal of this material was chosen for X-ray study: ir (Nujol) 1320, 1260, 1050, 1012, 910, 903, 830, and 803 cm⁻¹; pmr (CDCl₃) 0.95 (9 H singlet), 1.54 (3

H doublet, *J*_{HP} = 16 Hz), 2.15 (1 H multiplet), and 4.28 ppm (4 H multiplet).

Anal. Calcd for C₈H₂₇O₃P: C, 49.99; H, 8.93; P, 16.11. Found: C, 50.03; H, 9.12; P, 16.27.

By the same procedure a mixture of phosphites in which the ratio of **3/2** was 11/89 was converted to a 9/91 ratio of the corresponding methylphosphonate as determined by vpc. The major phosphonate isomer in this instance was the minor one in the previous reaction. The resulting oil was crystallized from hexane to yield 61% of a white solid, mp 64–65°, which after repeated recrystallization had mp 69–71°; ir (Nujol) 1250, 1120, 1048, 1005, 910, 888, 843, and 800 cm⁻¹; pmr (CDCl₃) 0.97 (9 H singlet), 1.5 (3 H, doublet *J* = 18 Hz), 2.04 (1 H, multiplet), and 4.33 ppm (4 H, multiplet).

Anal. Calcd for C₈H₁₇O₃P: C, 49.99; H, 8.93; P, 16.11. Found: C, 49.87; H, 8.90; P, 16.06.

Oxidations of 2 and 3 with *tert*-Butyl Hydroperoxide. The phosphite mixture was dissolved in benzene and contained in a triethylamine washed flask. The solution was flushed with nitrogen, chilled to 0°, and to it was slowly added distilled *tert*-butyl hydroperoxide. The ratios of product phosphates was determined by vpc. From a 80/20 ratio mixture of **3/2**, a 76/24 ratio of phosphates resulted. The major isomer, pure by vpc, was obtained on repeated crystallizations from hexane, mp 76–77°; ir (Nujol) 1300, 1265, 1240, 1190, 1118, 1040, 1002, 975, 860, 830, and 813 cm⁻¹; pmr (CDCl₃) 1.01 (9 H singlet), 1.90 (1 H, multiplet), 3.81 (3 H doublet, *J* = 11 Hz), and 4.45 ppm (4 H, doublet of doublets, deceptively simple case, apparent *J* = 5.9, 11.7 Hz). A crystal was taken for X-ray study.

Anal. Calcd for C₈H₁₇O₄P: C, 46.15; H, 8.23; P, 14.87. Found: C, 46.20; H, 8.22; P, 15.05.

A 10/90 ratio mixture of **3/2** gave two phosphates in 11/89 ratio by vpc. The major phosphate isomer formed in this instance was the minor product in the previous reaction. Repeated recrystallization gave material, mp 90–91°, pure by vpc; ir (Nujol) 1285, 1140, 1060, 1045, 1010, 990, 855, 840 cm⁻¹; pmr (CDCl₃) 0.95 (9 H singlet), 2.07 (1 H multiplet), 3.78 (3 H doublet, *J* = 11 Hz), and 4.30 ppm (4 H multiplet).

Anal. Calcd for C₈H₁₇O₄P: C, 46.15; H, 8.23; P, 14.87. Found: C, 45.92; H, 8.17; P, 15.02.

Acknowledgments. We wish to thank: Drs. J. D. Swalen and C. A. Reilly for the computer program from which the spectrum plotting routine was adapted; Dr. A. K. MacKnight for assistance with the derivation of the quantum mechanics for treatment of the ABXY spin system and in adaption of plotting routine; and Mr. R. Thrift for the 100-MHz spectra. Stimulating discussions with Professors E. L. Eliel, R. O. Hutchens, J. G. Verkade, and D. B. Denney are acknowledged. This work was supported by grants from the National Science Foundation (GP-8363) and the Petroleum Research Fund, administered by the American Chemical Society (PRF 2439-A4).