(1956).
(3) (a) S. Bank and B. Bockrath, *J. Amer. Chem. Soc.*, **93**, 430 (1971); (b) *ibid.*, **94**, 6076 (1972).
(4) E. R. Minnich, L. D. Long, J. M. Ceraso, and J. L. Dye, *J. Amer. Chem. Soc.*, **95**, 1061 (1973).
(5) G. Levin, C. Sutphen, and M. Szwarc, *J. Amer. Chem. Soc.*, **94**, 2652 (1972).
(6) S. Bank and W. D. Closson, *Tetrahedron Lett.*, 1349 (1965).
(7) A. Rainis, R. Tung, and M. Szwarc, *J. Amer. Chem. Soc.*, **95**, 659 (1973), and references cited therein.
(8) (a) K. S. Chen, S. W. Mao, K. Nakamura, and N. Hirota, *J. Amer. Chem. Soc.*, **93**, 6004 (1971); (b) N. Hirota, *ibid.*, **90**, 3603 (1968); (c) A. Crowley, N. Hirota, and R. Kreilick, *J. Chem. Phys.*, **46**, 4815 (1967).
(9) R. L. Ward and S. I. Weissman, *J. Amer. Chem. Soc.*, **79**, 2086 (1957).
(10) R. Chang and C. S. Johnson, Jr., *J. Amer. Chem. Soc.*, **88**, 2338 (1966).
(11) (a) J. F. Garst and F. E. Barton, II, *Tetrahedron Lett.*, 587 (1969); (b) J. F. Garst, *Accounts Chem. Res.*, **4**, 400 (1971).
(12) (a) J. F. Garst, F. E. Barton, II, and J. I. Morris, *J. Amer. Chem. Soc.*, **93**, 4310 (1971); (b) J. F. Garst and J. T. Barbas, *Tetrahedron Lett.*, 3125 (1969); (c) *J. Amer. Chem. Soc.*, **91**, 3385 (1969); (d) J. F. Garst, J. T. Barbas, and F. E. Barton, II, *ibid.*, **90**, 7159 (1968); (e) J. F. Garst, P. W. Ayers, and R. C. Lamb, *ibid.*, **88**, 4260 (1966).
(13) G. D. Sargent, J. N. Cron, and S. Bank, *J. Amer. Chem. Soc.*, **88**, 5363 (1966).
(14) G. D. Sargent and G. A. Lux, *J. Amer. Chem. Soc.*, **90**, 7160 (1968).
(15) S. Bank and J. F. Bank, *Tetrahedron Lett.*, 4533 (1969).
(16) B. Bockrath and L. M. Dorfman, *J. Phys. Chem.*, **77**, 2618 (1973).
(17) E. Warhurst and R. Whittaker, *Trans. Faraday Soc.*, **62**, 707 (1966), and previous papers in this series.
(18) J. F. Garst and F. E. Barton, II, *J. Amer. Chem. Soc.*, **96**, 523 (1974).
(19) J. K. Kochi and J. W. Powers, *J. Amer. Chem. Soc.*, **92**, 137 (1970).
(20) F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966).
(21) (a) M. von Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949); (b) M. M. Baizer, "Organic Electrochemistry," Marcel Dekker, New York, N.Y., 1973, p 282.
(22) E. Warhurst, *Quart. Rev., Chem. Soc.*, **5**, 44 (1951).
(23) A. J. Frey, "Synthetic Organic Electrochemistry," Harper & Row, New York, N.Y., 1972, p 48.
(24) (a) E. deBoer, *Advan. Organometal. Chem.*, **2**, 115 (1964), and references therein; (b) J. Jagur-Grodzinski, M. Feld, and M. Szwarc, *J. Phys. Chem.*, **69**, 628 (1965).
(25) "When the explanation of substituent or medium effects is given in terms of similar effects in a model reaction, the quantities compared are thermodynamic, ... The simple relationships often found among such quantities are not, however, part of the formal structure of thermodynamics. Hence they are called *extrathermodynamic relationships*." This definition and an excellent discussion can be found in J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N.Y., 1963, p 128 ff.
(26) M. Szwarc, Ed., "Ions and Ion Pairs in Organic Reactions," Wiley-Interscience, New York, N.Y., 1973.
(27) (a) J. G. Pacifici, J. Garst, and E. G. Janzen, *J. Amer. Chem. Soc.*, **87**, 3014 (1965); (b) J. F. Garst in "Solute-Solvent Interactions," J. F. Coetzee and C. D. Ritchie, Ed., Marcel Dekker, New York, N.Y., 1969, p 570 ff.

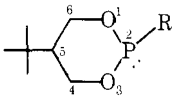
Conformations of Saturated Six-Membered Ring Phosphorus Heterocycles. III.[1] Pmr Studies of 2-Alkyl- and 2-Phenyl-5-*tert*-butyl-1,3,2-dioxaphosphorinanes

Wesley G. Bentrude,* Han-Wan Tan, and K. C. Yee

Contribution from the Department of Chemistry, University of Utah, Salt Lake City, Utah 84112. *Received May 20, 1974*

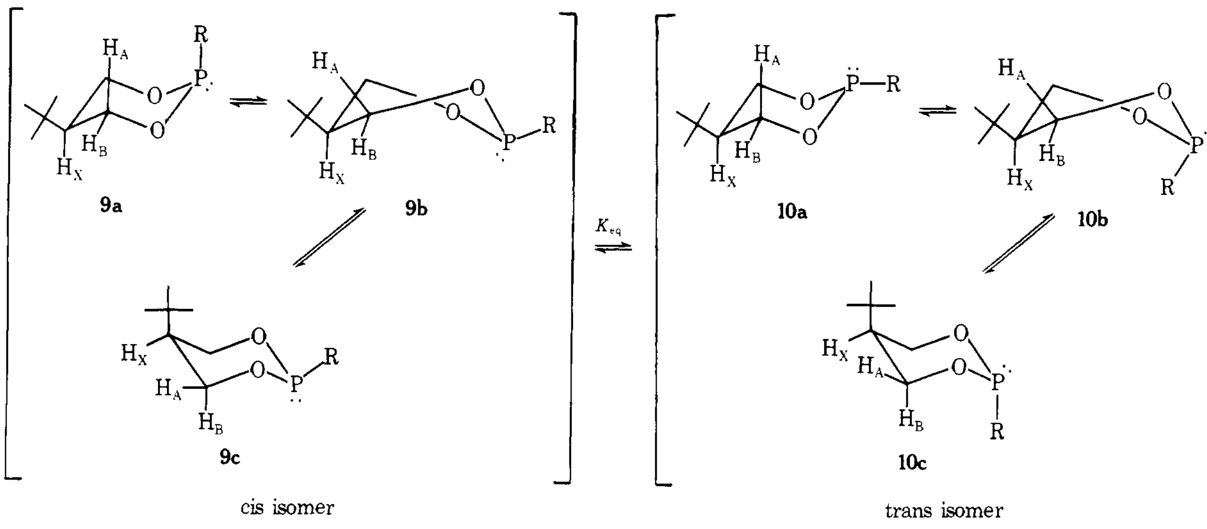
Abstract: Four 2-R-5-*tert*-butyl-1,3,2-dioxaphosphorinanes were studied largely by pmr methods [R = Me (**3**), *i*-Pr (**4**), *t*-Bu (**5**), and Ph (**6**)]. Equilibration studies in solution showed that for **3**, **4**, and **6**, the cis isomer is thermodynamically more stable than the trans isomer. The ratio cis/trans *decreases* with *increasing* temperature. For **5**, the opposite is true, the trans form exceeds the cis isomer in thermodynamic stability. By far the most stable conformation for *cis*-**3**, **4**, and **6** is the chair form **9a** with 2-R axial and 5-*tert*-butyl equatorial. The axial R preference is explained in terms of optimization of vicinal interactions about the P–O bonds of the rings which are more important than repulsive 1,3-syn-axial interactions except for R = *t*-Bu (**5**). Normal steric effects are seen to be present but of secondary importance. For **5** the trans form with both ring substituents equatorial (**10a**) is the most stable. Trans-**3**, **4**, and **6** exist in chair conformers with substituents diequatorial (**10a**) but also populate conformer **10c** with substituents diaxial. These results are compared with those from earlier investigations of the corresponding 2-R-5-*tert*-butyl-1,3,2-dioxaphosphorinanes with R = Cl (**1**), MeO (**2**), Me$_2$N (**7**), and MeNH (**8**). Conformational free energy changes (approximate values given in text) for the conversion of R axial to R equatorial were found to be in the order CH$_3$O > Ph > CH$_3$ > *i*-Pr > MeNH > Me$_2$N > *t*-Bu. The first four have an axial preference. The values of J_{HP} for the equatorial 4- and 6-hydrogens of *trans*-**5** in which the phosphorus lone pair is axial show couplings to phosphorus (19.8–21.6 Hz) about twice those seen for the corresponding compounds with phosphorus lone pair equatorial. This useful configurational effect applied to *trans*-**2** rules out the population of more than 5% of form **10a** by *trans*-**2**. As much as 58% of *trans*-**2** exists in the twist conformation **10b**. Contrary to our earlier report, both cis and trans isomers of 5-*tert*-butyl-2-chloro-1,3,2-dioxaphosphorinane (**1**) are found under proper conditions of equilibration in cis/trans ratio 93/7. Findings in the 1,3,2-dioxaphosphorinanes are related to anomeric effects noted in other ring systems. Results are interpreted in terms of recent ideas concerning back bonding donations of electron lone pairs to adjacent antibonding orbitals.

That substituents CH$_3$O and Cl on trivalent phosphorus in 1,3,2-dioxaphosphorinanes show a preference for the axial rather than the equatorial position is well established.[2] For example, for **2** the more stable isomer is the cis chair with MeO axial and *t*-Bu equatorial, **9a**.[2a] The trans isomer exists to a large extent in a chair conformation with both substituents axial, **10c**. Phosphorochlorodite[2a] **1** also appears to be largely one isomer with *t*-Bu equatorial and Cl presumably axial, **9a**. Although such a preference is predicted by the anomeric effect[3] for electronegative substituents and noted for those substituents at the 2 position of 1,3-dioxanes,[4] the axial preference is considerably greater in the 1,3,2-dioxaphosphorinanes. For this reason, we have now studied the conformations of such rings in which phenyl and various alkyl substituents are attached to trivalent phosphorus (compounds **3**–**6**). These substituents are less



1, R = Cl **5**, R = *t*-Bu
2, R = OMe **6**, R = Ph
3, R = CH$_3$ **7**, R = Me$_2$N
4, R = *i*-Pr **8**, R = MeNH

Scheme I



electronegative and also sterically somewhat more bulky than Cl or MeO. The 1,3,2-dioxaphosphorinanes, though superficially analogous to the 1,3-dioxanes, differ significantly from them. Perhaps most important is the fact that in the phosphorus system the conformational competition at the 2 position is between a substituent, R, and an electron lone pair rather than between R and hydrogen as in 2-R-1,3-dioxanes. Clearly, bond length and bond angles about C-2 and phosphorus will be different as well.

The 1,3,2-dioxaphosphorinanes are in this respect like the trimethylene sulfites[5] in which the oxygen and lone pair on sulfur are oriented preferentially axial and equatorial, respectively, but offer two distinct advantages over the cyclic sulfites for conformational study. First, three-bond phosphorus-hydrogen couplings involving the methylene hydrogens at C-4 and C-6 allow conformational changes about phosphorus to be probed by pmr methods. Second, a variety of phosphorus substituents may be studied. 1,3,2-Dioxaphosphorinanes are then ideal compounds for the investigation of steric and electronic effects on conformation.

Results

Syntheses. Compounds **3–6** were readily prepared by reaction of 2-*tert*-butyl-1,3-propanediol with the corresponding dichlorophosphine, $RPCl_2$, in the presence of Et_3N. Vacuum distillation gave nonequilibrium cis–trans mixtures of pure **3–6.** Ratios of isomers were determined by integration of the 5-*t*-Bu pmr resonances and by ^{31}P spectroscopy. Stereospecific, retentive[6] N_2O_4 oxidation of each of **3–6** gave the corresponding isomeric oxide pairs in 90–100% yields. The cis and trans oxides proved to be readily separated by vpc, and the cis/trans ratio thus determined served as a further check of that ratio in the trivalent precursors. Oxidation by S_8, also generally assumed to be retentive in stereochemistry,[7] was also effective for this purpose. Equilibration of each pair of isomers occurred within a few hours in solvent at room temperature. (In the case of **5,** a trace of CF_3CO_2H was added to catalyze isomerization.) On heating to higher temperatures, a new equilibrium ratio was observed which, however, relaxed to the former ratio when the original temperature was reestablished. Results of equilibration and oxidation experiments appear in Table I. In ensuing portions of this paper, it is shown that the cis isomer is the thermodynamically favored form for **3, 4,** and **6,** while the *opposite* is true for **5.**

Polymer Formation. Phosphonites **3–6** all showed a tendency to form polymeric materials, especially when neat. Depolymerization occurred on heating under vacuum. Thus the monomers **3–6** could be easily re-formed simply by vacuum distillation. This phenomenon was especially notable for **3.** Solutions of **3** 10–80% v/v in *o*-dichlorobenzene (ODCB) were transformed in a few days to equilibrium mixtures of cis and trans isomers along with polymer. Evidence for the presence of polymer was seen in pmr spectra taken which showed the formation of a third *t*-Bu resonance at δ 0.935 (ODCB) and a third CH_3-P doublet at δ 1.23 (ODCB). The ^{31}P spectrum showed five new peaks about midway between the resonances displayed at -161.6 and -185.2 ppm downfield from external 85% H_3PO_4 by the cis and trans isomers, respectively. That a polymer rather than a third monomeric form was present was indicated by: (1) the multiplicity of ^{31}P peaks; (2) the slightly broad and nonringing character of the *t*-Bu and CH_3-P pmr resonances of the new material; (3) the decrease in concentration of polymer as benzene solutions are heated (a monomeric less stable material should increase in concentration); and (4) the increase in equilibrium concentration of polymer as the initial concentration of monomer is increased.

Polymer formation with 2,5,5-trimethyl-1,3,2-dioxaphosphorinane has been reported.[8] We mention this phenomena for **3–6** since from the pmr spectra alone it is easy to mistake the polymeric material(s) for a third room-temperature stable, monomeric species, which if present would be of considerable interest. In view of the similarity of the ^{31}P chemical shifts of the polymeric form of **3** to those of monomeric **3,** it is likely that 12- or 18-membered ring di- or trimeric forms are present as was demonstrated for 2,5,5-trimethyl-1,3,2-dioxaphosphorinane.[8b]

Assignment of Cis and Trans Geometries to Isomers of 3–6. (a) Phosphonite 3. The major oxide from N_2O_4 oxidation of equilibrated **3** is that which has been shown by X-ray crystallography[9a] to be the cis isomer. The retentive stereochemical nature of this oxidation is well established,[6] hence the more stable stereoisomer of **3** is the cis form **3a.**

(b) Phosphonite 4. Equilibrated isopropyl compound **4** gives as major oxide on N_2O_4 reaction a material with properties analogous to those of **3a** oxide. This includes conformational mobility evidenced by changes in proton couplings on temperature change and on addition of lanthanide shift reagents. Further, the chemical shifts for the methylene protons of **4a** oxide fall in the order (*i.e.*, $\delta H_A < \delta H_B$) found for the cis oxides of **2** and **3** and sulfides of **5** and **6,** all of whose cis or trans geometries are known by X-ray crystallography,[9] and for the cis sulfides of **2** and **3** and oxides of **5** and **6** as well. The latter geometries can safely be assumed

Table I. Isomer Ratios and Equilibration Studies

Compd	T, °C[a]	Isomer ratio by pmr, cis/trans	Solvent	Corresponding oxide or sulfide ratio[b] (% yield)
3		65/35 (initial[c])	C_6D_6	
	Ambient	84/16 (6 hr)	C_6D_6	85/15 (oxide, >90)
	145	72/28 (45 min)	ODCB[e]	72/28 (oxide, 92)
	120–140	73/27 (36 hr)	CH_2Cl_2[g]	72/28 (sulfide, *f*)
4		48/52 (initial[c])	C_6H_6	
	Ambient	74/26 (3 hr)	C_6H_6	
	Ambient	75/25 (17 hr)	C_6H_6	74/26 (oxide, 100)
		81/19 (initial[c])	CH_2Cl_2	84/16 (sulfide, *f*)
5		67/33 (initial[c])	C_6H_6	66/34 (oxide, 92)
	Ambient	47/53 (326 hr)	C_6H_6	
	Ambient	7/93[d] (1 hr)	C_6H_6	8/92 (oxide, *f*)
	Ambient	7/93[d] (1 hr)	C_6H_6	4/96 (sulfide, *f*)
6		94/6 (initial[c])	C_6H_6	
	Ambient	90/10 (1 day)	C_6H_6	90/10 (oxide, 100)
	Ambient	91/9 (1 day)	$CDCl_3$	
	135–140	80/20 (68 hr)	$CDCl_3$[g]	78/22 (oxide, *f*)
	Ambient	91/9 (2 hr)	CH_2Cl_2	90/10 (sulfide, 95)

[a] Indicates temperature at which sample was equilibrated. [b] Ratios are cis/trans in each case. [c] Immediately following distillation. [d] CF_3CO_2H added. [e] *o*-Dichlorobenzene. [f] Yield not determined. Only products seen in vpc. [g] Heated as neat sample. Oxidized in solvent listed.

from those of their oxide or sulfide counterparts. Use of LIS effects[6c,10] and proton chemical shifts[11] to assign geometries to pentavalent 5-*tert*-butyl-2-R-2-oxo-1,3,2-dioxaphosphorinanes will be covered in detail in a full paper. Preliminary accounts have been published.[10,11] Further evidence for assignment of the cis geometry to **4a**, the more stable isomer of **4**, by comparison to **3a** will be presented below in consideration of the pmr spectra of these compounds and in a subsequent paper[12] on ^{13}C and ^{31}P nmr properties of 2-R-5-*tert*-butyl-1,3,2-dioxaphosphorinanes.

(c) **Phosphonites 5 and 6.** The sulfides from the minor isomer of equilibrated **5** and major isomer of **6** both were found by X-ray crystallography to be of cis geometry.[9] Sulfur oxidation of phosphines and 1,3,2-dioxaphosphorinanes is presumed generally[7] to proceed with retention of configuration about phosphorus; *hence for* **5** *the thermodynamically more stable form is the trans isomer, while for* **6** *it is the cis compound.* Again the pmr properties of the oxides of **5** and **6** when compared with those from **2** and **3** confirm the above assignment. That the di-*tert*-butyl compound **5** should be more stable as the trans isomer is reasonable in view of the size of the ring substituents. The assignments of geometries to the isomers of **5** and **6** are further confirmed below and in the ^{13}C and ^{31}P studies.[12]

Pmr Data and the Conformations of 3–6. In Table II are recorded pmr data for phosphonites **3–6**. For comparison purposes the same data are included for phosphorochloridite **1**,[2a] phosphite **2**,[2a] and phosphoramidites **7** and **8**.[1a] (See Experimental Section for method of determination of parameters.) In each instance the cis isomer is designated as the **a** isomer, *i.e.*, **1a**, **2a**, etc.

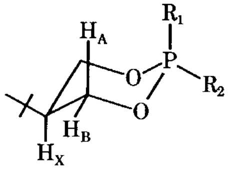
(a) **Cis Isomers.** For cis phosphonites **3a**, **4a**, and **6a**, values of J_{AX} in the range 11.0 to 11.5 Hz and J_{BX}, 3.50 to 3.91 Hz, are found which are consistent with an equatorially positioned *t*-Bu group. Further, the ranges of J_{AP}, 1.50 to 2.92 Hz, and J_{BP}, 10.3 to 11.0 Hz, are quite analogous to those found for **1a**,[2a] **2a**,[2a] and other trivalent 1,3,2-dioxaphosphorinanes[2b-d] for which chair-form ring conformations with phosphorus substituents axial have been postulated. We assign, therefore, the conformation **9a** (Scheme I) to the cis phosphonites **3a**, **4a**, and **6a**.

For phosphonite **5a**, the cis isomer is the minor form, and it was not possible to obtain any coupling constant information for this species. An interesting observation is that with **5a**, the pmr chemical shift for the 5-*t*-Bu is downfield of that for 5-*t*-Bu in **5b**. This is opposite to the order noted with **2**, **3**, **4**, and **6** and for the cis and trans oxides and sulfides of these compounds and at least suggests that **5a** has an unusual conformation. Axial alkyl groups at the 5 position of 1,3-dioxanes[14] and corresponding 2 position of trimethylene sulfites[5] tend to appear at lower field in the pmr than do their equatorial counterparts. This is suggestive of the presence of **9c** as one of the conformers of **5a**, and this idea is confirmed by ^{13}C shift data.[12] However, much caution is needed in making such a deduction based on pmr shifts alone since **7a** and **8a** also show the same relation of the 5-*t*-Bu pmr chemical shifts, yet ^{13}C shifts give no evidence for an axial positioning of the 5-*t*-Bu in **7a**.[12] This ordering for **7** and **8** more likely results from lack of population of conformers of *trans*-**7** and **8** with *tert*-butyl axial. We assign conformations **9b** and **9c** to **5a** on the basis of ^{13}C and ^{31}P data[12] and the expected severity of 1,3-steric interactions accompanying an axial 2-*t*-Bu which serve to make the trans isomer **5b** more stable than its cis counterpart.

(b) **Trans Isomers.** The values of J_{AX} and J_{BX} clearly show the *tert*-butyl to be equatorial in **5b** which is the more stable isomer of **5** and the only trans form of **3–6** for which a full pmr analysis was possible. Most notable is the large value of $^3J_{BP}$ found for **5b**, $J_{BP} = 21.6$ Hz (iterative analysis in *o*-dichlorobenzene as solvent). Because of the size of the *t*-Bu groups, the only reasonable conformation for **5b** is **10a** (Scheme I). (If this is so, the cis/trans ratio becomes a limiting one independent of R and determined by the relative conformational energies of the equatorial and axial trans 5-*t*-Bu and of twist- and chair-ring conformations, *i.e.*, forms **9b**, **9c**, and **10a**.) A similarly large value of J_{BP} was noted[1a] for **7b** and **8b** (Table II) and was used as evidence for the equatorial position of the Me_2N and MeNH in the trans isomers of those compounds.

The values of J_{BP} for **3b** and **4b** are intermediate between those for cis isomers with phosphorus substituent axial and those of the trans isomers, **5b**, **7b**, and **8b**, whose conformations are represented by the single conformer **10a**. This shows that for **3b** and **4b**, conformer **10a** is not the only conformer populated among several which are in rapid equilibrium on the pmr time scale. Conformers **10b** and **10c** both would be expected to have J_{BP} values much lower than **10a**. If only conformers **10a** and **10c** are populated, and one assigns to them values of J_{BP} of 19.5–21.5 and 2.92 Hz, respectively [values for J_{BP} ($J_{H_{eq}P}$) for **5b** in C_6H_6 and OCDB and J_{AP} ($J_{H_{ax}P}$) for **3a** in OCDB], then a **10a**/**10c** ratio

Table II. Pmr Spectral Parameters for 2-R-5-*tert*-Butyl-1,3,2-dioxaphosphorinanes[a]



Compd	R^1	R^2	Solvent	J_{AB}[b]	J_{AX}	J_{BX}	J_{AP}	J_{BP}	J_{XP}	δ_A[c]	δ_B	δ_X	$\delta_{5\text{-}t\text{-Bu}}$	δ_{R_1} or δ_{R_2}
1a[e]	Cl	Lone pair	$CDCl_3$	−10.8	11.7	3.83	5.28	11.3		4.56	4.25	2.17	0.933	
2a[e]	CH_3O	Lone pair	$CDCl_3$	−10.6 (0.049)[d]	11.9 (0.039)	3.71 (0.035)	2.89 (0.072)	11.0 (0.066)		4.24 (0.041)	3.87 (0.034)	2.00	0.850	3.45 (12)[k]
2b[e]	Lone pair	CH_3O	$CDCl_3$	−11.6	4.91	4.65	8.40	5.03		3.92	4.39	1.50	1.02	3.46 (12)[k]
3a[g]	CH_3	Lone pair	ODCB	−11.13 (0.042)	11.49 (0.034)	3.91 (0.034)	2.92 (0.059)	10.37 (0.065)	1.0	3.89 (0.032)	3.83 (0.033)	1.80	0.717	1.27 (9.6)[k]
3b[j]	Lone pair	CH_3	ODCB	−11.5		4.0		15.3			4.23		0.833	1.27 (7.8)[k]
3a	CH_3	Lone pair	C_6H_6										0.575	1.19 (9.6)[k]
3b	Lone pair	CH_3	C_6H_6										0.725	1.26 (7.7)[k]
4a[g]	*i*-Pr	Lone pair	C_6H_6	−11.07 (0.025)	11.73 (0.039)	3.76 (0.041)	2.48 (0.037)	10.47 (0.041)	1.1	3.70 (0.020)	3.79 (0.022)	1.81	0.575	1.00[l] (14.0)[k]
4b[j]	Lone pair	*i*-Pr	C_6H_6	−11.5		4.0		16.0			4.16		0.690	1.12[l] (14.0)[k]
5a	*t*-Bu	Lone pair	C_6D_6										0.775	1.05 (12.1)[k]
5b[j]	Lone pair	*t*-Bu	C_6D_6	−11.44	11.18	3.84	2.50	19.75	1.3	3.87	4.15	1.68	0.600	1.10 (12.2)[k]
5a	*t*-Bu	Lone pair	ODCB										0.858	0.992 (12.0)[k]
5b[i]	Lone pair	*t*-Bu	ODCB	−11.31 (0.042)	10.81 (0.074)	3.75 (0.065)	2.39 (0.090)	21.56 (0.073)	1.2	3.82 (0.045)	4.12 (0.040)	1.68	0.767	1.01 (12.0)[k]
6a[i]	Ph	Lone pair	$CDCl_3$	−11.0	11.0	3.50	1.50	11.0	1.0	3.90	4.10	2.04	0.725	7.4
6b	Lone pair	Ph	$CDCl_3$										1.08	
6a	Ph	Lone pair	C_6H_6										0.458	
6b	Lone pair	Ph	C_6H_6										0.983	
6a[h]	Ph	Lone pair	ODCB	−10.77 (0.037)	11.37 (0.058)	3.71 (0.051)	2.89 (0.051)	10.25 (0.060)	0.9	$\delta_B - \delta_A = 0.14$[m]		*m*	*m*	*m*
7a[f]	Me_2N	Lone pair	C_6D_6									1.65	0.690	2.49 (8.4)[k]
7b[f]	Lone pair	Me_2N	C_6D_6	−11.36 (0.042)	10.68 (0.063)	4.08 (0.072)	2.50 (0.069)	19.62 (0.094)	1.1	3.94 (0.038)	4.09 (0.046)	1.72	0.635	2.63 (8.7)[k]
8a	MeNH	Lone pair	C_6D_6										0.667	*n*
8b	Lone pair	MeNH	C_2D_6	−11.36 (0.036)	10.24 (0.058)	4.58 (0.055)	2.32 (0.11)	20.24 (0.11)	0.8	3.92 (0.057)	4.08 (0.059)	1.70	0.650	2.55 (*n*)

[a] 15–20% v/v solutions at ambient probe temperatures. [b] Coupling constants in hertz. Absolute values given except for J_{AB}, assumed negative, and J_{XP} (see Experimental Section). [c] Chemical shifts in parts per million downfield from internal TMS. [d] Numbers in parentheses associated with *J*'s and δ's are probable error (in hertz) of parameter determined from LAOCN3 iterative analysis of methylene spectrum, ABXY approximation. RMS errors of line positions: **3a**, 0.177; **4a**, 0.098; **5b**, 0.135; **6a**, 0.096. [e] Data from ref 2a. [f] Data from ref 1a. [g] Data from iterative analysis of second-order 220-MHz spectrum. [h] Data from iterative analysis of second-order 100-MHz spectrum. [i] Data from iterative analysis of second-order 60-MHz spectrum. [j] Data from first-order analysis of 220-MHz spectrum. [k] Coupling constant J_{HP} to CH_3 of R_1 or R_2. [l] $\delta(CH_3)_2CH$. [m] No TMS was added to this sample, thus chemical shifts relative to TMS are not available. [n] Obscured by overlap of CH_3NH and CH_3NH.

Table III. Conformer and Isomer Distributions for **1–8**

Compd	Calculated isomer distribution **9a**	 **9b** ⇌ **9c**	 **10a**	 ⇌	 **10b**	 **10c**	$\Delta G°_{25}$(**9** → **10**), kcal/mol	Solvent
1	93			1.5		5.5	1.5	C_6H_6, ODCB[a]
2	92		0.4		3.6	4.0	1.4	$CDCl_3$
3	84		10.5–12.0			4.0–5.5	0.99	C_6D_6
4	74		18.0–21.0			8.0–5.0	0.63	C_6H_6
5		7	93				−1.5	C_6H_6
6	90			4.7		5.3	1.3	C_6H_6, $CDCl_3$
7	11	6	83				−0.94	C_6H_6, $CDCl_3$
8	42	3	55				−0.12	C_6H_6, $CDCl_3$

[a] *o*-Dichlorobenzene.

range of 66/34 to 75/25 results. This leads to the distribution for **3** among **9a, 10a,** and **10c** given in Table III. The same treatment of phosphonite **4** gives a similar distribution range of **10a/10c,** 70/30 to 80/20, but with a small decrease in proportion of **10c** as is consistent with the expected larger size of the *i*-Pr. This effect is noted as well on the ratio of **9a/10a.** (See Table III.)

By use of the **9a/10c** ratios estimated above, it can be calculated that $\Delta G°_{25}$ for equatorial to axial *t*-butyl interconversion in **3** is 1.6 to 1.8 kcal/mol. For **4,** a range of 1.3 to 1.6 kcal/mol is derived. These ranges are quite consistent with 1.4 and 1.7 kcal/mol found[4] for the 5-*t*-Bu in the 1,3-dioxane system and 1.8 kcal/mol measured for the 2-*t*-butyl in the corresponding trimethylene sulfites.[5] Thus the range of $\Delta G°_{25}$ *t*-Bu (eq → ax) values determined *supports the validity of the above treatment* based on **10a** ⇌ **10c.**

Twist form **10b,** rapidly equilibrating between two equivalent skew boat structures, would have a value of J_{BP} of ~7 Hz and would require 57/43 to 66/34 ratios of **10a/10b** to predict for **3b** the experimental pmr couplings. Thus *at least* 57% of **3b** is in form **10a.** This would only reduce the **10a** population of **3b** in Table III to 9.1%. But as noted below, the populations of **10b** and **10c** are about equal with the small substituent R = CH_3O. Surely with the increased steric bulk of R, the population of **10b** must be reduced such that it contributes only a minor amount to the equilibrium **10a** ⇌ **10b** ⇌ **10c.** The X proton coupling most sensitive to the presence of **10b,** J_{AX}, is not obtainable. *What is clear is that* **10a** *is the conformer present in largest amounts for both* **3b** *and* **4b.**

On the basis of proton couplings for **2b,** we were unable earlier[2a] to choose between 42/58 **10c/10b** and 70/30 **10c/10a** ratios, although the former gave a somewhat better fit to the experimental pmr data taken at ambient probe temperatures and especially at −62°. If one assumes that J_{BP} for conformer **10a** of **2b** is 20 Hz, then the ratio **10c/10a** of 70/30 predicts J_{BP} to be 8.0, whereas the experimental value is 5.03. (In ref 2a, H_A of structure **10** is H_B and vice versa.) This allows us to rule out the 70/30 ratio of **10c/10a.** By use of the parameters assigned in ref 2a for **10a, 10b,** and **10c,** except for J_{BP} for **10a** (20 Hz), satisfactory agreement is obtained between estimated and experimental coupling constants for a **10a/10b/10c** ratio of 5/45/50. The calculated and experimental values are (experimental numbers in parentheses): J_{AX} = 4.8 (4.9); J_{BX} = 4.6 (4.7); J_{AP} = 8.6 (8.4); J_{BP} = 5.4 (5.0). Excluding conformer **10a,** a 42/58 ratio of **10c/10b** (see above) gives *J* values of: J_{AX} = 4.9 (4.9); J_{BX} = 4.7 (4.7); J_{AP} = 8.4 (8.4); J_{BP} = 5.0 (5.0). The **10a, 10b,** and **10c** populations based on the above ratio appear in Table III. The corresponding $\Delta G°_{25}$ for **9a** ⇌ **10c** is 2.0 kcal/mol, a value only slightly outside of the range (1.3 to 1.8 kcal/mol) estimated on the basis of this equilibrium for **3** and **4.**

Application of an average value (based on **9a** ⇌ **10c** for **2–4**) of 1.7 kcal/mol for $\Delta G°_{25}$ (eq–ax) for the 5-*t*-butyl to the phenylphosphonite system (**6**) gives the isomer and conformer distribution shown in Table III. Since Ph like CH_3O [$\Delta G°_{25}$ (cis → trans) = 1.3, 1.4 kcal/mol] has a greater axial preference than Me or *i*-Pr [$\Delta G°_{25}$ (cis → trans) = 0.99, 0.63 kcal/mol], there is a strong possibility that **6b** populates **10b.** This is indicated in Table III. Regardless of the exact percentage of **10b** present, *it is obvious that with* **2** *and* **6** *a lower fraction of the trans isomer exists in the conformation* **10a** *with substituents diequatorial than is the case with either* **3b** *or* **4b.** [This must be so also if any given value (such as 1.7 kcal/mol) for $\Delta G°_{25}$ (ax → eq) for the 5-*t*-butyl is applied to all four compounds, **2, 3, 4,** and **6.**] Clearly the axial preferences of CH_3O and Ph are much greater than those of Me and *i*-Pr.

We earlier reported[2a] that only the cis isomer **1a** of **1** had been detected. Purification of crude **1** by sublimation did lead indeed to isolation of pure **1a.** (The configurational stability of phosphorus in five-membered ring phosphorochlorodites also is known to be very dependent on purity.)[15] However, pmr analysis of freshly distilled, vpc-pure **1** in *o*-dichlorobenzene, to which a drop of CF_3COOH was added at ambient probe temperatures (31°), showed a **1a/1b** ratio of 93/7. This ratio was lowered to 85/15 at 121° and restored to 93/7 when the sample was cooled to 31°. The 31° ratio was confirmed by ^{31}P nmr measurements[12] in C_6H_6 and by ^{13}C nmr.[12] A $\Delta G°_{25}$ (eq → ax) of 1.7 kcal/mol for the 5-*t*-Bu of **1** gives the isomer distributions recorded in Table III. Of course these numbers are quite sensitive to the value of $\Delta G°_{25}$ assumed for the 5-*t*-Bu. Nonetheless applying the *same* value to **1** and **6** shows clearly the greater contribution of the diaxial substituted isomer (**10c**) for **1b** (like **2b**) as a result of the smaller size[16] and greater electronegativity of Cl (see discussion below).

Moreover, given the cis-trans distributions of Table III and the assumption that $\Delta G°_{25}$ (eq–ax) for the 5-*t*-Bu is constant, it also must follow that for **1b–4b** and **6b** the fraction **10c** populated is in the decreasing order **1b** > **2b** > **6b** > **3b** > **4b.**

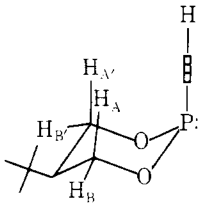
Since for the Me_2N and MeNH compounds **7** and **8** the trans isomer has a J_{BP} value about the same as that for **5,** it is unlikely that forms **10b** or **10c** are populated to more than a few per cent. The ratio of [**10a**]/[**9b** ⇌ **9c**] should remain constant regardless of R, and based on that ratio for **5,** it is easy to calculate the percentage of **9b** ⇌ **9c** for **7** and **8** from the percentages of their trans isomers. The remainder must then be conformer **9a.** Table III shows that this method assigns the major population of the cis isomer of both the Me_2N and MeNH compounds the conformation **9a,** in agreement with our earlier paper[1a] in which ^{31}P and ^{13}C data were used.

(c) **Chemical Shift Correlations.** Several correlations between chemical shift, $^2J_{HP}$, and conformation are evident in Table II. Only two will be pointed out. First, for the 2-Me substituent, $^2J_{HP}$ is greater in absolute magnitude for the cis compound than for the trans. In cases where the sign of

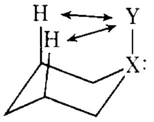
$^2J_{HP}$ has been determined for trivalent alkyl-substituted phosphorus,[17] the sign has been found to be *positive*.

Second, the relative chemical shifts, δ_A and δ_B, for the A and B methylene protons are dependent on the orientations of the substituent and lone pair on phosphorus. With the strongly polar P-O and P-Cl bonds of substituents CH_3O and Cl, spectra in $CDCl_3$ show that δ_A (axial) is 0.3 to 0.4 ppm downfield of δ_B (equatorial) for the cis isomer in which the substituent is axial. The same is true for **2b** with a high proportion of axial CH_3O. In this case, $\delta_B > \delta_A$ since conformer **10c** is predominant. But again the axial proton is downfield with respect to its equatorial counterpart. Isomer **3a** in ODCB with axial Me shows the same relationship for δ_A and δ_B as **2a,** $\delta_A > \delta_B$. The two resonances for **4a,** R′ = *i*-Pr, are closely similar in benzene with δ_B greater now than δ_A but by only 0.09 ppm. For **5b,** with conformer **10a** dominant, it is observed that $\delta_B > \delta_A$ by a rather large amount (about 0.30 ppm). The axial proton appears upfield of the equatorial one when the lone pair is axial in **7b** and **8b** as well.

Phosphonite **6a** represents an exception in that $\delta_B > \delta_A$ even though the Ph is axially oriented. This result is to be expected if the Ph is oriented as shown in **11.** Comparison of δ_B-δ_A in C_6H_6 and ODCB (**5b**) and $CDCl_3$ and ODCB (**6a**) suggests that the relative shifts of protons A and B are not greatly affected by this sort of solvent change, and that data for **1** and **2** taken in $CDCl_3$ may be compared with those for **3-8** in aromatic solvents.



11



12

Estimation of $\Delta G°_{25}$ (Ax → Eq) for Various R. From the data of Table III, it is possible to make *rough estimates* for 1,3,2-dioxaphosphorinanes of the preferences of substituents on trivalent phosphorus studied for the axial or equatorial position. These are given in Table IV in terms of the free energy required to convert an axial phosphorus substituent to an equatorial one, *i.e.*, to convert **9a** to **10a.**

The values of $\Delta G°_{25}$ (ax → eq) for MeO and Ph are *minimum* values based on the estimated maximum percentage of **10a** (0.4% and 4.7%). Our data give us no basis for estimating the population of **10a** for **1a.** Since **9a** is populated to about the same extent in **1** and **2,** and Cl and MeO should have offsetting size and electronegativity differences, $\Delta G°_{25}$ (ax → eq) for Cl probably is also of the order 3.2 kcal/mol or greater. For the remainder of the compounds, $\Delta G°_{25}$ (ax → eq) for R was derived in straightforward fashion from **9a/10a** of Table III, with the exception of **5.** For **5,** we have no way of detecting a small amount of **9a** since **5a** is the minor isomer and was not amenable to pmr analysis. In a later paper,[12] we will cite ^{31}P evidence suggesting that no more than 5% of **5a** could be in conformation **9a.** This leads to a $\Delta G°_{25}$ (ax → eq) value for the 2-*t*-Bu of −3.2 as a maximum (most positive) estimate. Thus the relative "size" of a substituent on trivalent phosphorus in these 1,3,2-dioxaphosphorinane systems is *t*-Bu > Me_2N > *i*-Pr > CH_3 > Ph > $CH_3O \cong$ Cl.

Because of the assumptions involved in obtaining the estimates of **9a/10a** in Table III, too much significance should not be attached to the values of $\Delta G°_{25}$ (ax → eq) for R in Table IV, but the relative ordering is certainly correct.

Table IV. Estimated $\Delta G°_{25}$ for the Conversion **9a** → **10a**

R	*K*	$\Delta G°_{25}$ (ax → eq), kcal/mol
CH_3O	≥23.0	≥3.2
Ph	≥19	≥1.8
CH_3	7.0–8.0	1.1–1.2
i-Pr	3.5–4.1	0.75–0.84
MeNH	0.77	−0.16
Me_2N	0.13	−1.2
t-Bu	≥0.004	<−3.2[a]

[a] Actual value may be more negative.

Discussion

Substituent Orientations. Undoubtedly the most striking aspect of the results of this study is the axial preference found for the relatively nonelectronegative groups CH_3, *i*-Pr, and Ph on phosphorus in 1,3,2-dioxaphosphorinanes. It may be concluded that *configuration about phosphorus in these rings is not determined primarily by repulsive 1,3-syn-axial interactions* as are the orientations of alkyl and phenyl substituents at the 2 position in 1,3-dioxanes.[4] Furthermore, classical anomeric effects[3] do not appear operative since not only CH_3O and Cl but also relatively electropositive phosphorus substituents express axial preferences. Only when the alkyl substituent is sterically very large (*t*-Bu) is it thermodynamically more stable in the equatorial orientation.

Axial preferences for substituents on heteroatoms in six-membered rings have also been noted for rings in which the substituted heteroatom is not flanked by oxygens. Examples are the phosphorinanes[18] (**12,** X = P; Y = H), thiane 1-oxide[19] (**12,** X = S; Y = O), selenanes[20] (**12,** X = Se; Y = H, CH_3, O), and protonated thiane[21] (**12,** X = S; Y = H). It has been argued[20] that the axial preferences in these rings result from *attractive* 1,3-syn-axial interactions which have replaced the more normal *repulsive* 1,3-syn-axial interactions which account for the observed equatorial preferences of substituents on cyclohexane rings and electropositive groups at the 2 position of 1,3-dioxanes.

Significantly with 1-methylphosphorinane,[22] the small axial preference of the relatively large methyl at room temperature has recently been shown to be the results of *entropy* effects. *Enthalpy actually favors the equatorial orientation of the methyl.* This is *opposite* to the effect of temperature we have noted for several members of **1-8.** When R is sterically of small bulk (**1-4** and **6**), then the cis isomer with R axial is *favored* by the enthalpy of the cis-trans equilibrium.

We interpret the difference between the 1-methylphosphorinane and 1,3,2-dioxaphosphorinane systems to be a *direct result of the presence of the ring oxygens in our compounds* and as explained below to be consistent with recent theoretical views. Vicinal interactions involving the lone pairs and substituents on phosphorus and on the ring oxygen are the dominant factors that favor axial R orientation. Normal steric effects derived from 1,3-repulsive syn-axial interactions do contribute, though they are of *secondary* importance. This is indicated by the steric order Me > *i*-Pr > *t*-Bu noted in Table IV for $\Delta G°_{25}$ (ax → eq). With very bulky R groups (MeNH, Me_2N, *t*-Bu in **8, 7,** and **5**), the magnitude of the repulsive 1,3-syn-axial interactions is increased in magnitude such that they become of controlling importance. Thus **9** ⇌ **10** for **5, 7,** and **8** is shifted to the left by increased temperature.

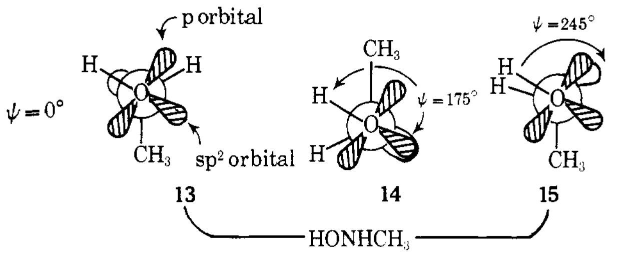
Axial Preferences and Rotational Barriers. Consideration of configuration about phosphorus in 1,3,2-dioxaphosphorinanes in terms of P-O vicinal interactions is quite analogous to the assessment of relative energies of conformations available to a system by rotation about a single bond. It has become apparent in recent years that the potential barrier diagrams for a bond undergoing rotation which bears substituents having electron lone pairs on them do not resemble the familiar threefold barrier function displayed by molecules such as ethane or methanol.[23o]

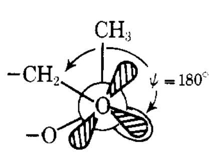
An empirical rule, termed the *gauche effect*,[24] has been stated and has been useful in prediction of the relative stabilities of rotational isomers containing adjacent electron pairs and polar bonds. Perhaps the clearest theoretical treatment of internal rotation potential functions is that of Radom, Hehre, and Pople.[23o] In this treatment, changes in potential energy, V, with dihedral angle, φ, are described for symmetric molecules by an equation (1) involving three

$$V(\varphi) = \tfrac{1}{2}V_1(1 - \cos\varphi) + \tfrac{1}{2}V_2(1 - \cos 2\varphi) + \tfrac{1}{2}V_3(1 - \cos 3\varphi) \quad (1)$$

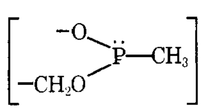
contributing terms. V_3 is the threefold barrier energy, and the term with which it is associated is the sole function needed to describe rotation in ethane, methylamine, etc. V_2 and the second term of (1) reflect the effects of rotation on a stabilizing interaction involving nonbonded electron donation to an adjacent, partially vacant p orbital (a type of π bonding). Dipole-dipole interactions are accounted for by the term in (1) which includes V_1. The shape of the overall potential energy diagram, $V(\varphi)$, depends on the signs and relative magnitudes of V_1, V_2, and V_3.

Of the molecules whose rotational potential energy functions have been described in this way,[23o] CH_3NHOH is the one most nearly related to molecules with whose configuration about phosphorus we are concerned. For CH_3NHOH, the calculations[23o] predict that the two stable conformations are **13** (ψ = 0°) and **14** (ψ = 175°). These correspond to the cis and trans conformations of H_2NOH which both theory and experiment[25] indicate are the stable ones. Rotamer **15** (ψ = 245°), it is calculated, represents one of two potential energy maxima. (Structure **15** as drawn is the mirror image of conformer derived by 245° bond rotation of **13**.) The calculated energy difference between **14** and **15** is 4.0 kcal/mol.[23o]

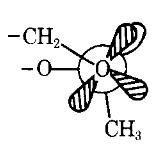




16

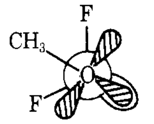


$\left[\begin{matrix}-O\\ -CH_2O\end{matrix} > P{-}CH_3\right]$



17

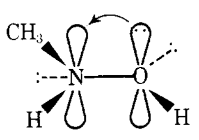
For 2-methyl-1,3,2-dioxaphosphorinane, the structures **16** (ψ = 180°) and **17** depict the configurations about phosphorus for Me axial and equatorial, respectively, gained from inspection of Dreiding models. (Bond lengths and angles appear in a later paragraph.) The similarities of **14** and **16** and of **15** and **17** are obvious. Thus results of theory and experiment for CH_3NHOH and NH_2OH, applied by analogy to 2-substituted 1,3,2-dioxaphosphorinanes, correctly predict the observed axial preference for a substituent on trivalent phosphorus in such rings. [The potential energy curve for *N*-methylhydroxylamine indicates that the difference in energy between conformations **16** and **17** is about 3.5 kcal/mol.] Conformation **16** is also favored by the *gauche effect*[24] rules in that gauche arrangements of polar bonds and of lone pairs are maximized in **16.** The structure of $MeOPF_2$, as determined by molecular rotational spectroscopy, corresponds to **18**[26] and is clearly analogous to **16.**



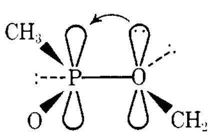
18

The COP bond angle of 123.5° is consistent with the hybridization about oxygen depicted in **13–17.**

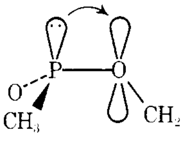
The theoretical rationale for the preferred rotational isomers for CH_3NHOH and NH_2OH, **13** and **14**, is based on the response of the individual potential functions containing V_1, V_2, and V_3 of eq 1 to changes in :NOH dihedral angle φ. The minimum at φ = 175° (structure **14**) stems from the twofold barrier V_2 function which has minima at 0 and 180° (and maxima at 90 and 270°). The latter overcomes an opposing V_1 maximum at 180°. The bonding stabilization in the V_2 term proposed by Radom, Hehre, and Pople[23o] is shown for CH_3NHOH in **19** in which electron density from the highest energy lone pair orbital on oxygen is donated to a partially vacant 2p orbital on nitrogen, a type of back bonding which is optimized by the conformation **19** (**14**) or its 180° rotamer **13.** A similar donation of the nitrogen pair into the OH bond, which is maximized by conformation **14** (**19**), is also invoked.[23o] Oxygen to phosphorus bonding like that in **19** is depicted for **16** (axial methyl) in **20.** In **17** (equatorial methyl), *neither phosphorus lone pair to O-CH*$_2$ (**21**) *or oxygen lone pair donation to the P-O or P-C bonds* (**20**) *can be effective.* Calculations show[23o] that the stabilization of **19** is enhanced by substitution of a more electronegative group in place of Me of H on nitrogen, and this provides one theoretical rationale for the anomeric effect operative in molecules containing an electron-withdrawing polar bond adjacent to lone pairs.



19



20



21

It appears that for 2-substituted 1,3-dioxanes this sort of lone pair donation is not strong enough to overcome repulsive 1,3-steric interactions, except when X is an electronegative substituent such as MeO[4] or halogen. (A difference in hybridization at oxygen in the two systems may importantly affect back bonding.) By contrast with 1,3,2-dioxaphosphorinanes, forces favoring axial orientation prevail even for alkyls. If the above model is accepted, then in 1,3,2-dioxaphosphorinanes, the axial preferences with Me, *i*-Pr, and Ph may stem from reduced repulsive 1,3-syn-axial interactions in the phosphorus compounds. Although P-O bonds clearly are longer than C-O bonds, XPX bond angles in PX_3 compounds are normally[27] around 100° compared with the near 109° OCX angles expected for dioxane, and this difference would increase 1,3 interactions. The balance between these effects is difficult to evaluate in the absence of structural data on the 2-substituted 5-*tert*-butyl-1,3,2-dioxaphosphorinanes. Comparison can be made using Dreiding models of 2-methyl-1,3,2-dioxaphosphorinane (bond angles about phosphorus, ∠OPR, 100°; ∠COP, 120°; P-O bond length, 1.74 Å; P-CH_3 bond length, 1.87 Å) and 2-axial methyl-1,3-dioxane (∠COC, 110°; ∠OCR, 109°; C–O bond length, 1.41 Å; C–CH_3 bond length, 1.54 Å), both with methyl axial. These models show that when the methyl hydrogen is placed equidistant between the hydrogen centers at C-4 and C-6, the distance between methyl and axial hydrogen centers is 2.05 Å for 1,3,2-dioxaphosphorinane, 1.90 Å for cyclohexane, and 1.75 Å for 2-axial methyl-1,3-dioxane. This suggests that repulsive 1,3-syn-axial interactions may be reduced somewhat relative to the other two rings. However, it should be pointed out that the size of ∠COP is most critical. For example, when ∠COP = 110°, the critical distance is only 1.60 Å. The sizable range (>4 kcal/mol) of ΔG°_{25} (ax → eq) values for alkyl substituents in Table IV strongly indicates that 1,3 interactions are not trivial in magnitude and shows that the vicinal effects which overcome them must also be energetically large.

Alternately, the axial preference in 1,3,2-dioxaphosphorinanes may reflect an increased importance of lone-pair orbital donation of the sort illustrated in **20** compared with that available to 1,3-dioxanes. Furthermore, a phosphorus lone pair to CH_2–O bond donation (**21**) is a potential source of axial substituent stabilization *not available to 1,3-dioxanes*. This alone could account for the differences in these systems. A combination of all three effects may be important.

A closely similar theoretical view of interactions in systems containing adjacent polar bonds and electron pairs has been proposed by David, Eisenstein, Hehre, Salem, and Hoffmann.[31] This treatment also pictures the stabilization of conformations like **13, 14, 16,** and **18** as resulting from donation of the adjacent lone pair into the neighboring σ-antibonding orbital (*superjacent* level). This donation has the same stereochemical requirements as does that pictured by **19** and **20.** Similarly, the stabilization is increased when the σ^* orbital is of relatively low energy as for a polar bond. Overlap of the higher energy p lone pair with the σ^* P–CH_3 orbital (structure **16**) is considered to be more effective than that of the sp^2 lone pair (structure **17**). Repulsive destabilizing (*subjacent* level effects) influences in **16** and **17** also may be important. Assuming dominance of the n to σ^* donation in **16,** the axial substituent preference is predicted.

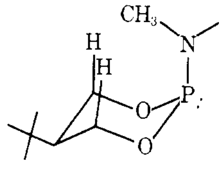
This general conception of the anomeric effect was first suggested by Altona[32] and applied in more general terms by Baddeley.[33] It has recently been applied to carbohydrates[34] and in its valence bond equivalent (double-bond no-bond resonance) to 2-substituted 1,3-dioxanes.[3]

Steric Size of R in 1–8. As mentioned earlier, the order of ΔG°_{25} (ax → eq) of Table IV, Me > *i*-Pr > *t*-Bu, is that expected for a normal repulsive steric effect superimposed on electronic effects which favor axial orientation. The latter should be reasonably constant in the alkyl series. MeO and Cl are not only sterically smaller[16] (cyclohexane conformational energies) than alkyl groups but also more electronegative.[35] These factors account for the greatly decreased "size" of MeO and Cl compared with methyl since back bonding (structure **20**) is predicted[23o] to increase with increase in electronegativity.

The phenyl group (**6**) is somewhat unusual in that it is "smaller" than methyl (**3**). This order has also been noted for 4,6-dimethyl-, 2-phenyl-, and 2-methyl-1,3-dioxanes[4b] where ΔG°_{25} (eq → ax) for the 2-methyl and 2-phenyl (ether solution) are 4.0 and 3.1 kcal/mol, respectively. Both the 1,3,2-dioxaphosphorinanes and 1,3-dioxanes are in direct contrast to cyclohexane for which ΔG°_{25} (eq → ax) values are[16] for Me, 1.7 kcal/mol, and for Ph, 3.0 kcal/mol.

Eliel and Bailey have proposed[36] that in cyclohexanes an axial phenyl in the preferred perpendicular conformation analogous to **11** experiences a destabilizing steric compression involving the ortho hydrogen of the phenyl ring and the equatorial hydrogens at C-2 and C-6 in the cyclohexane chair. This interaction is absent in 2-phenyl-1,3-dioxanes, and it is proposed[36] that this difference accounts for the apparent smaller size of phenyl relative to methyl in the 1,3-dioxanes series. A similar rationale could be applied to the 2-phenyl- and 2-methyl-substituted 1,3,2-dioxaphosphorinanes; but the expected greater *electronegativity* of Ph also could be a factor.

The unusually large steric "size" of Me_2N and MeNH we interpreted previously[1a] as resulting from conformational preferences imposed on these groups by virtue of the P–N vicinal interactions present in such a system. (See also ref 6c.) As a consequence, the amino group tries to assume a conformation which, when the group is axial, brings a methyl in close proximity to axial hydrogens at C-4 and C-6, structure **22.** This interaction overcomes the effects of the relatively electronegative Me_2N.[35]



22

Effects of Lone-Pair Orientation on $^3J_{HCOP}$. The very large value of $^3J_{HP}$ for H_B of trans **5** (**5b**), which on steric grounds is expected to have both *tert*-butyl substituents equatorial, indicates that $^3J_{HCOP}$ values are subject to both a Karplus-like dihedral angular dependence and an effect of phosphorus lone-pair orientation. The latter effect also is noted for **7b** and **8b** which, like **5b,** have the lone pair on phosphorus axial. Analogous effects of lone-pair orientation on $^3J_{HCCP}$ have been noted.[37] When the hydrogen-substituted carbon β to trivalent phosphorus is cis to the phosphorus lone pair, $|J_{HP}|$ is increased. It was suggested[38] very early in the conformational study of 1,3,2-dioxaphosphorinanes that phosphorus lone-pair orientation could influence J_{HCOP}. This effect is clearly a very useful one for the study of conformations of trivalent 1,3,2-dioxaphosphorinanes.

Nonchair Conformations. Table III suggests that for the trans methyl phosphite, **2b,** conformers **10b** and **10c** are about equally populated. Since ΔG for the conversion of **10c** to **10b** is the sum of $\Delta G_{t\text{-Bu}}$ (ax → eq) + ΔG [chair (MeO axial) → twist (MeO axial)], it appears that the ΔG (chair → twist) for R = MeO is of the order 1.5–2.0 kcal/mol. This compares with 8.3 ± 0.5 kcal/mol[39] for 1,3-dioxane and 1.9 kcal/mol for 1,3-dithiane.[40] We have also found evidence for an unusually low ΔG value for the chair → twist interconversion of certain 2-oxo-1,3,2-dioxaphosphorinanes.[1a,41] Perhaps, flattening of the 1,3,2-dioxaphosphorinane rings about phosphorus and the rather lengthy P–O ring bonds results in reduced nonbonded interactions in the twist conformation as was proposed[40] for the 1,3-dithianes boat forms. Torsional repulsions also may be reduced in twist form 1,3,2-dioxaphosphorinanes.

Experimental Section

Pmr Analysis. Spectra were taken on Varian A-60, A-56/60, or XL-100-12 spectrometers. Spectra at 220 MHz were courtesy of Professor J. C. Martin, University of Illinois. Analysis of the AA′BB′XY spectra of **3–6** by hand calculation on the basis of an ABXY approximation followed by iterative AA′BB′XY analysis using the LAOCN3 program was described previously.[1a] In cases where a first-order analysis was done at 220 MHz, the parameters were cross checked by computer simulation of the spectrum at 60 or 100 MHz. The parameters in Table II for **3b** and **4b** were obtained from first-order analysis of the presumed B portion of the

Table V

			Elemental analyses[a]			
Compd	Mp, °C	Ir, cm^{-1}	% C	% H	% P	Formula
3a oxide	127–128	1320, 1260, 1050, 1012, 903, 910, 830, 803 (Nujol)	49.99 (50.03)	8.93 (9.12)	16.11 (16.27)	$C_8H_{17}O_3P$
3b oxide	69–71	1250, 1120, 1048, 1005, 910, 888, 842, 800 (Nujol)	49.99 (49.87)	8.93 (8.90)	16.11 (16.06)	$C_8H_{17}O_3P$
4a,b oxides (mixture)			54.53 (54.38)	9.61 (9.85)	14.06 (14.47)	$C_{10}H_{21}O_3P$
5a oxide	147–148	2950, 2900, 1800, 1470, 1390, 1370, 1310, 1250, 1220, 1130, 1060, 1015, 980, 940, 900, 835, 815, 790, 760, 650 (KBr)	56.40 (56.34)	9.90 (9.81)	13.22 (12.46)	$C_{11}H_{23}O_3P$
5b oxide	165–166	2950, 2900, 1800, 1470, 1390, 1320, 1250, 1220, 1140, 1050, 1010, 980, 945, 890, 830, 800, 770, 663 (KBr)	56.40 (56.45)	9.90 (9.94)	13.22 (13.05)	$C_{11}H_{23}O_3P$
6a oxide	106–107	3030, 2900, 2700, 1830, 1580, 1480, 1440, 1370, 1310, 1270, 1240, 1180, 1130, 1050, 1010, 990, 955, 895, 840, 805, 775, 760, 705 (KBr)	61.41 (61.34)	7.53 (7.56)	12.18 (11.98)	$C_{13}H_{19}O_3P$
6b oxide	89.0–89.5	3030, 2850, 2700, 1760, 1580, 1480, 1440, 1400, 1360, 1310, 1270, 1240, 1135, 1110, 1040, 1000, 960, 935, 905, 893, 833, 810, 765, 757, 745, 710, 702, 690 (KBr)	61.41 (61.23)	7.53 (7.43)	12.18 (12.23)	$C_{13}H_{19}O_3P$

[a] Experimental values found are in parentheses.

220-MHz methylene spectrum which showed in each case multiplets of minor intensity downfield from the much more intense methylene absorptions of the cis isomers. A complete ABXY analysis was not possible for these isomers, because the A portion was buried under the absorption of the cis isomers. The chemical shift of H_B for **3b** and **4b** is consistent with that found for **5b** in which the phosphorus lone pair is axial. The assignment of these minor intensity multiplets to H_B of **3b** and **4b** is confirmed by the methyl proton decoupled ^{31}P spectrum of **3b** which showed a phosphorus–hydrogen coupling at lowest effective decoupler amplifier power about 1 Hz lower than J_{BP} determined as described above.

Gas chromatography was performed on either a Hewlett-Packard Model 700 (flame ionization detector) of F & M Model 810 (thermal conductivity detector) gas chromatograph. Ratios of products were not corrected for possible differences in sensitivities of cis and trans isomers since such differences have generally been found to be negligible. **Infrared spectra** were taken on a Beckman IR5A instrument.

All melting points are uncorrected. Analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and Galbraith Laboratories, Inc., Knoxville, Tenn.

Alkylphosphorus dichlorides, $RPCl_2$, were synthesized according to the method of Perry, *et al.*,[42] with slight modification in 60–80% yields. Commercial $C_6H_5PCl_2$ was distilled before use.

Synthesis of 2-Alkyl- and 2-Phenyl-5-*tert*-butyl-1,3,2-dioxaphosphorinanes. The procedure for 2-methyl-5-*tert*-butyl-1,3,2-dioxaphosphorinane is typical.

To 140 ml of anhydrous ether cooled in an ice–water bath were added simultaneously and dropwise over a 1.5-hr period solutions of 2-*tert*-butyl-1,3-propanediol (10 g, 0.077 mol) and triethylamine (19 g, 0.19 mol) in 150 ml of anhydrous ether and CH_3PCl_2 (10 g, 0.085 mol) in 130 ml of anhydrous ether. The reaction was stirred vigorously during the addition and then for an additional 2 hr at ice temperature. A nitrogen atmosphere was maintained at all times. The solution was then filtered under nitrogen pressure through glass wool (to remove the product amine salt). Short path distillation removed most of the ether, and the remaining volatile materials were removed at room temperature (0.03 mm). Fractional distillation through a 6-in. Vigreux column yielded three fractions, bp 30–39° (0.05–0.15 mm), with **3a**/**3b** ratios 78/22, 65/35, and 83/17 as indicated by pmr analysis of freshly prepared ODCB solutions. Overall yield was 42%. The third fraction showed the presence of about 5% of polymeric impurity [*tert*-butyl peak at δ 0.935 (ODCB)].

Phosphonites **4**, **5**, and **6** were prepared similarly in 21, 30, and 48% yields with bp 45–50° (0.025 mm), 54–55° (0.3 mm), and 82–84° (0.05 mm). Phosphonite mixture **3** is a colorless liquid; **4** and **5** are semisolids; and **6** is a low-melting solid. Vpc analysis showed the product phosphonites to be >99% pure. Most of the pmr data for **3–6** appear in Table II. In addition for **4a** unreported in Table II, there is observed a multiplet (1 H) at δ 2.48 [$C\mathit{H}(CH_3)_2$] in C_6H_6 and for **6a** a 5 H multiplet at δ 7.41 (C_6H_5P) in $CDCl_3$.

2-Alkyl- and 2-Phenyl-5-*tert*-butyl-2-oxo- and 2-Thio-1,3,2-dioxaphosphorinanes. The phosphonites **3–6** were oxidized to the corresponding phosphonates for vpc analysis as well as elemental analysis in routine fashion. For example, to **5** (0.16 g, 0.74 mmol) and 0.36 g of A.R. grade benzene cooled in an ice bath was added 400 μl. of N_2O_4 saturated CH_2Cl_2 over a 10-min period. Phosphonate ratios were determined by vpc (see Table I), and the percentage yield of phosphonates was determined by addition of an appropriate internal standard.

Near-quantitative conversions of **3–6** to the thiophosphonates were effected by reactions at 0–5° of **3–6** either neat or in benzene with excess powdered S_8. Separations of the isomeric phosphonates and thiophosphonates were accomplished by column chromatography of larger scale reactions of Florisil 100–200 H mesh and eluted with ether–ligroin (60–90°). Quantitative elemental analyses and melting points and infrared data for the oxides are listed in Table V. Nmr parameters for these derivatives and the corresponding thio compounds will appear in a full paper on their conformations.

Acknowledgment. This work was supported by grants from the National Science Foundation (GP-8363, 22885, and 36637X) and the National Cancer Institute of the Public Health Service (CA-11045).

References and Notes

(1) (a) For paper II in this series, see W. G. Bentrude and H.-W. Tan, *J. Amer. Chem. Soc.*, **95**, 4666 (1973). A portion of the present work was published in preliminary form: (b) W. G. Bentrude and K. C. Yee, *Tetrahedron Lett.*, 3999 (1970); (c) W. G. Bentrude, K. C. Yee, R. D. Bertrand, and D. M. Grant, *J. Amer. Chem. Soc.*, **93**, 797 (1971).

(2) (a) W. G. Bentrude and J. H. Hargis, *J. Amer. Chem. Soc.*, **92**, 7136 (1970); (b) D. W. White, R. D. Bertrand, G. K. McEwen, and J. G. Verkade, *ibid.*, **92**, 7125 (1970); (c) C. L. Bodkin and P. Simpson, *J. Chem. Soc. B*, 1136 (1971); (d) M. Haemers, R. Ottinger, J. Reisse, and D. Zimmermann, *Tetrahedron Lett.*, 461 (1971); (e) K. Bergesen and P. Albriktsen, *Acta Chem. Scand.*, **26**, 1680 (1972); (f) M. Haemers, R. Ottinger, D. Zimmermann, and J. Reisse, *Tetrahedron Lett.*, 2241 (1973); (g) M. Haemers, R. Ottinger, D. Zimmermann, and J. Reisse *Tetrahedron*, **29**, 3539 (1973).

(3) For a very extensively referenced recent paper on the anomeric effect, see W. F. Bailey and E. L. Eliel, *J. Amer. Chem. Soc.*, **96**, 1798 (1974).

(4) (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).

(5) (a) C. Altona, H. J. Geise, and C. Romers, *Recl. Trav. Chim. Pays-Bas*, **85**, 1197 (1966); (b) H. F. van Woerden and E. Havinga, *ibid.*, **86**, 341, 353 (1967); (c) J. W. L. van Oyen, R. C. D. E. Hasekamp, G. C. Ver-

schoor, and C. Romers, *Acta Crystallogr., Sect. B,* **24,** 1471 (1968); (d) H. F. van Woerden, H. Cerfontain, C. H. Green, and R. J. Reijerkerk, *Tetrahedron Lett.,* 6107 (1968); (e) W. Wucherpfennig, *Justus Liebigs Ann. Chem.,* **737,** 144 (1970); (f) R. F. M. White, *J. Mol. Struct.,* **6,** 75 (1970); (g) G. Wood, J. M. McIntosh, and M. H. Miskow, *Can. J. Chem.,* **49,** 1202 (1971); (h) P. Albriktsen, *Acta Chem. Scand.,* **25, 478** (1971); (i) G. Wood, G. W. Buchanan, and M. H. Miskow, *Can. J. Chem.,* **50,** 521 (1972); (j) C. H. Green and D. G. Hellier, *J. Chem. Soc., Perkin Trans. 2,* 458 (1972); (k) M.-C. Vertut, J.-P. Fayet, G. Chassaing, and L. Cazaux, *C. R. Acad. Sci., Ser. C,* **276,** 843 (1973).

(6) (a) D. Z. Denney, G. Y. Chen, and D. B. Denney, *J. Amer. Chem. Soc.,* **91,** 6838 (1969); (b) J. Michalski, A. Okruszek, and W. Stec, *J. Chem Soc. D,* 1495 (1970); (c) J. A. Mosbo and J. G. Verkade, *J. Amer. Chem. Soc.,* **95,** 4659 (1973).

(7) D. P. Young, W. E. McEwen, D. C. Velez, J. W. Johnson, and C. A. VanderWerf, *Tetrahedron Lett.,* 359 (1964); L. Horner and H. Winkler, *ibid.,* 175 (1964).

(8) (a) D. W. White, *Phosphorus,* **1,** 33 (1971); (b) J. P. Albrand, J. P. Dutasta, and J. B. Robert, *J. Amer. Chem. Soc.,* **96,** 4584 (1974).

(9) (a) M. Haque, C. N. Caughlan, J. H. Hargis, and W. G. Bentrude, *J. Chem. Soc. A,* 1786 (1970), report the X-ray crystallographic study of *cis*-**3** oxide. (b) The structures of the oxide of *cis*-**2** and the cis sulfides of **5** and **6** have been determined by C. N. Caughlan and coworkers, Department of Chemistry, Montana State University, Bozeman, Mont.

(10) (a) K. C. Yee and W. G. Bentrude, *Tetrahedron Lett.,* 2775 (1971); (b) W. G. Bentrude, H.-W. Tan, and K. C. Yee, *J. Amer. Chem. Soc.,* **94,** 3264 (1972); (c) A. J. Dale, *Acta Chem. Scand.,* **26,** 2985 (1972).

(11) Essentially the observed phenomenon that for a cis oxide or sulfide (phosphoryl oxygen equatorial) δH_A (axial) $<$ δH_B (equatorial). With the corresponding trans isomers, δH_A (axial) $>$ δH_B (equatorial).

(12) A full paper on ^{31}P and ^{13}C nmr correlations useful in assigning geometries in trivalent 5-*tert*-butyl-2-substituted 1,3,2-dioxaphosphorinanes is in preparation. Part of these findings have appeared in ref 1a and 1c. In general, it is found that those cis isomers of **1–8** with phosphorus substituent axial display a notable γ effect,[13] and it is consistently found the $\delta_{^{31}P}$ for a cis isomer with phosphorus substituent axial is *upfield* of that for the trans isomer.

(13) See, *e.g.,* G. W. Buchanan, D. A. Ross, and J. B. Stothers, *J. Amer. Chem. Soc.,* **88,** 4301 (1966); (b) D. K. Dalling and D. M. Grant, *ibid.,* **89,** 6612 (1967); (c) J. D. Roberts, F. J. Weigert, J. I. Kroschwitz, and H. J. Reich, *ibid.,* **92,** 1338 (1970).

(14) See, *e.g.,* E. L. Eliel and M. C. Knoeber, *J. Amer. Chem. Soc.,* **90,** 3444 (1968).

(15) R. H. Cox, M. G. Newton, and B. S. Campbell, *J. Amer. Chem. Soc.,* **93,** 528 (1971). Carefully purified neat 4,4-dimethyl-2-chloro-1,3,2-dioxaphospholane showed an unchanged, noncoalesced pmr spectrum over the temperature range −40 to +150°.

(16) J. A. Hirsch, *Top. Stereochem.,* **1,** 199 (1967), quotes best values of conformational energies of 0.43 kcal/mol for Cl and 0.60 for MeO.

(17) For example, in Me_3P [W. McFarlane, *Proc. Roy. Soc., Ser. A,* **306,** 185 (1968)] and $MePCl_2$ [J. P. Albrand and D. Gagnaire, *Chem. Commun.,* 874 (1970)].

(18) J. B. Lambert and W. L. Oliver, Jr., *Tetrahedron,* **27,** 4245 (1971). An axial phenyl is found in the solid state for 1-phenyl-4-phosphorinanone: A. T. McPhail, J. J. Breen, and L. D. Quin, *J. Amer. Chem. Soc.,* **93,** 2574 (1971).

(19) (a) J. B. Lambert and R. G. Keske, *J. Org. Chem.,* **31,** 3429 (1966); (b) C. R. Johnson and D. B. McCants, Jr., *J. Amer. Chem. Soc.,* **87,** 1109 (1965); (c) J. C. Martin and J. J. Uebel, *ibid.,* **86,** 2936 (1964).

(20) J. B. Lambert, C. E. Mixan, and D. H. Johnson, *Tetrahedron Lett.,* 4335 (1972).

(21) (a) J. B. Lambert, D. S. Bailey, and C. E. Mixan, *J. Org. Chem.,* **37,** 377 (1972); (b) J. B. Lambert, R. G. Keske, and D. K. Weary, *J. Amer. Chem. Soc.,* **89,** 5921 (1967).

(22) S. I. Featherman and L. D. Quin, *J. Amer. Chem. Soc.,* **95,** 1699 (1973).

(23) (a) A. Veillard, *Theor. Chim. Acta,* **5,** 413 (1966); (b) E. Clementi and D. R. Davis, *J. Chem. Phys.,* **45,** 2539 (1966); (c) W. H. Fink and L. C. Allen, *ibid.,* **46,** 2261, 2276 (1967); (d) L. Pedersen and K. Morokuma, *ibid.,* **46,** 3941 (1967); (e) U. Kaldor and I. Shavitt, *ibid.,* **44,** 1823 (1966); (f) W. E. Palke and R. M. Pitzer, *ibid.,* **46,** 3948 (1967); (g) W. H. Fink, D. C. Pan, and L. C. Allen, *ibid.,* **47,** 895 (1967); (h) R. M. Stevens, *ibid.,* **52,** 1397 (1970); (i) M. D. Newton, W. A. Lathan, W. J. Hehre, and J. A. Pople, *ibid.,* **52,** 4064 (1970); (j) A. Veillard, *Theor. Chem. Acta,* **18,** 21 (1970); (k) I. H. Hillier, V. R. Saunders, and J. F. Wyatt, *Trans. Faraday Soc.,* **66,** 2665 (1970); (l) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.,* **93,** 289 (1971); (m) R. B. Davidson and L. C. Allen, *J. Chem. Phys.,* **55,** 519 (1971); (n) S. Wolfe, A. Rauk, L. M. Tel, and I. G. Csizmadia, *J. Chem. Soc. B,* 136 (1971); (o) L. Radom, W. J. Hehre, and J. A. Pople, *J. Amer. Chem. Soc.,* **94,** 2371 (1972).

(24) S. Wolfe, *Accounts Chem. Res.,* **5,** 102 (1972).

(25) P. A. Giguere and I. D. Liu, *Can. J. Chem.,* **30,** 948 (1952).

(26) E. G. Codding, Ph.D. Thesis, Michigan State University, East Lansing, Mich., 1971.

(27) For PX_3 (XPX angle): Me_3P[28] (98.6°); Ph_3P[29] (103°); PCl_3[30] (100°).

(28) L. S. Bartell and L. O Brockway, *J. Chem. Phys.,* **32,** 512 (1960).

(29) J. J. Daly, *J. Chem. Soc.,* 3799 (1964).

(30) P. Kisliuk and C. H. Townes, *J. Chem. Phys.,* **18,** 1109 (1950).

(31) S. David, O. Eisenstein, W. J. Hehre, L. Salem, and R. Hoffmann, *J. Amer. Chem. Soc.,* **95,** 3806 (1973).

(32) C. Romers, C. Altona, H. R. Buys, and E. Havinga, *Top. Stereochem.,* **4,** 73 (1969).

(33) G. Baddeley, *Tetrahedron Lett.,* 1645 (1973).

(34) G. A. Jeffrey, J. A. Pople, and L. Radon, *Carbohyd. Res.,* **20, 440** (1972).

(35) Pauling electronegativities for O, N, and Cl are 3.5, 3.0, and 3.0, respectively (L. Pauling, "Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithàca, N.Y., 1960, p 90). The Allred atomic electronegativities for these atoms are 3.44, 3.04, and 3.16 [A. L. Allred, *J. Inorg. Nucl. Chem.,* **17,** 215 (1961)]. Huheey group electronegativities for MeO and Me_2N are 2.68 and 2.40, respectively [J. E. Huheey, *J. Phys. Chem.,* **69,** 3284 (1965)].

(36) See W. F. Bailey, Ph.D. Dissertation, University of Notre Dame, Notre Dame, Ind., 1973.

(37) (a) S. E. Cremer and R. J. Chorvat, *J. Org. Chem.,* **32,** 4066 (1967); (b) W. McFarlane, *Chem. Commun.,* 229 (1968); (c) L. D. Quin and T. P. Barket, *J. Amer. Chem. Soc.,* **92,** 4303 (1970); (d) J. P. Albrand, D. Gagnaire, M. Picard, and J. B. Robert, *Tetrahedron Lett.,* 4593 (1970); (e) C. H. Bushweller, J. A. Brunelle, W. G. Anderson, and H. S. Bilofsky, *ibid.,* 3261 (1972); (f) J. B. Robert and J. D. Roberts, *J. Amer. Chem. Soc.,* **94,** 4902 (1972); (g) C. H. Bushweller and J. A. Brunelle, *J. Amer. Chem. Soc.,* **95,** 5949 (1973).

(38) (a) D. Gagnaire and J. B. Robert, *Bull. Soc. Chim. Fr.,* 2240 (1967); (b) D. Gagnaire, J. B. Robert, and J. Verrier, *ibid.,* 2392 (1968); (c) J. P. Albrand, A. Cogne, D. Gagnaire, and J. B. Robert, *Tetrahedron,* **28,** 819 (1972).

(39) R. M. Clay, G. M. Kellie, and F. G. Riddell, *J. Amer. Chem. Soc.,* **95,** 4632 (1973).

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

(41) W. G. Bentrude and K. C. Yee, *J. Chem. Soc. D,* 169 (1972).

(42) (a) B. J. Perry, J. B. Ressor, and J. L. Ferron, *Can. J. Chem.,* **41,** 2299 (1963); (b) J. B. Reesor, B. J. Perry, and E. Sherlock, *ibid.,* **38,** 1416 (1960).