S–C–P Anomeric Interactions. 9. Effect of the Coordination at Phosphorus in the Conformational Equilibria of 2-*P*-Substituted-1,3-dithianes[1]

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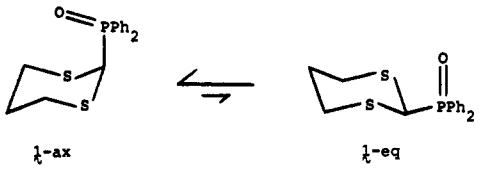
The conformational energies (*A* values) of the (diphenylphosphinyl)borane and diphenylphosphinyl groups were determined by multinuclear (^1H, ^{13}C, ^{31}P) NMR analysis of mobile (*cis*-4-phenylcyclohexyl)diphenylphosphine–borane, as well as the corresponding phosphine, and conformationally fixed models. The equatorial preferences observed are $-\Delta G°(P(BH_3)Ph_2)$ = 3.3 kcal/mol and $-\Delta G°(PPh_2)$ = 1.8 kcal/mol. The conformational preference of these groups in the 1,3-dithian-2-yl ring were also determined by NMR analysis: −0.1 and −0.3 kcal/mol, respectively. The slight predominance of the equatorial isomers reflects nonetheless the influence of substantial S–C–P(BH_3) and S–C–P: anomeric interactions, worth 1.8 and 1.0 kcal/mol, respectively. Evaluation of these values, together with previous data obtained for S–C–P(O) and S–C–P(S) systems, supports the participation of endo and exo hyperconjugative interactions, although the participation of 3p–3d electron donation among the sulfur and phosphorus atoms could also account for the results. Alternative rationalizations that have been considered to account for the strong S–C–P(O) anomeric effect appear now to play a minor role in the conformational equilibria of 2-P-substituted 1,3-dithianes.

Introduction

Proton NMR spectroscopy and X-ray crystallographic studies demonstrated the predominance of the axial conformer of 2-(diphenylphosphinoyl)-1,3-dithiane (1, eq 1).[2]

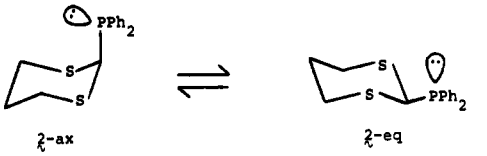


1-ax 1-eq (1)

Chemical equilibration of anancomeric models allowed quantitative determination of the conformational free energy in 1, 1.0 kcal/mol,[3] which corresponds to an anomeric effect of 2.6 kcal/mol,[4] one of the largest yet recorded.[5]

This observation, together with other published work,[1,6] provides experimental evidence in support of a significant anomeric interaction in S–C–P segments and seems to argue against the suggestion of Schleyer et al.[7] that such stabilizing interactions should be negligibly small. Nevertheless, the theoretical studies carried out in ref 7a refer to a $HSCH_2PH_2$ species, whereas a closer model to 1 would be the corresponding phosphine oxide.

An alternative way to examine the pertinence of the calculations could be through the determination of the conformational free energy in eq 2, which involves the



2-ax 2-eq (2)

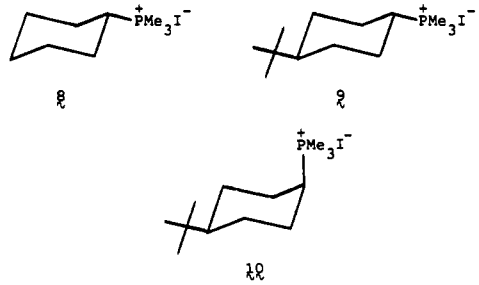
analogous phosphines 2-ax ⇌ 2-eq, in order to establish the existence (or lack) of an anomeric effect in S–C–P: segments.

This paper describes the conformational behavior of **2**, as well as that for the precursor phosphine–borane **3** (eq 3). Evaluation of the anomeric effect, if any, in **2** and **3** required estimation of the *A* values for the (diphenylphosphinyl)borane and diphenylphosphinyl groups in cyclohexane.

3-ax 3-eq (3)

Results and Discussion

A. Conformational Preference (*A* Value) of the (Diphenylphosphinyl)borane Group in Cyclohexane. Mobile and conformationally fixed compounds **4–7** were prepared as outlined in Schemes I and II. Table I contains the chemical shifts for the carbon atoms at 37 °C in $CDCl_3$. The assignments were based on reported carbon-13 NMR data for related phosphorus compounds.[8-12] The similarity of cyclohexyl chemical shifts in **4–7** and the analogous $-P^+Me_3$ derivatives **8–10**[8] suggests comparable inductive and field effects for the trimethylphosphonium and phosphine–borane substituents; in particular, the steric



8 9 10

(1) For part 8, see: Juaristi, E. *Het. Chem.* **1990**, 1, 267–276.
(2) Juaristi, E.; Valle, L.; Mora-Uzeta, C.; Valenzuela, B. A.; Joseph-Nathan, P.; Fredrich, M. F. *J. Org. Chem.* **1982**, *47*, 5038–5039.
(3) Juaristi, E.; Valle, L.; Valenzuela, B. A.; Aguilar, M. A. *J. Am. Chem. Soc.* **1986**, *108*, 2000–2005.
(4) Juaristi, E. *Acc. Chem. Res.* **1989**, *22*, 357–364.
(5) Kirby, A. J. *The Anomeric Effect and Related Stereoelectronic Effects at Oxygen*; Springer-Verlag: Berlin, 1983.
(6) Mikolajczyk, M. *Pure Appl. Chem.* **1987**, *59*, 983–988 and references cited therein.
(7) (a) Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* **1985**, *107*, 6393–6394. (b) See also: Kumar, P. N. V. P.; Wang, D. X.; Lam, B.; Albright, T. A.; Jemmis, E. D. *J. Mol. Struct.* **1989**, *194*, 183–190.
(8) Gordon, M. D.; Quin, L. D. *J. Org. Chem.* **1976**, *41*, 1690–1694.
(9) Buchanan, G. W.; Bowen, J. H. *Can. J. Chem.* **1977**, *55*, 604–611.
(10) Modro, T. A. *Can. J. Chem.* **1977**, *55*, 3681–3685.
(11) Juaristi, E.; López-Núñez, N. A.; Glass, R. S.; Petsom, A.; Hutchins, R. O.; Stercho, J. P. *J. Org. Chem.* **1986**, *51*, 1357–1360.
(12) Juaristi, E.; López-Núñez, N. A.; Valenzuela, B. A.; Valle, L.; Toscano, R. A.; Soriano-Garcia, M. *J. Org. Chem.* **1987**, *52*, 5185–5189.

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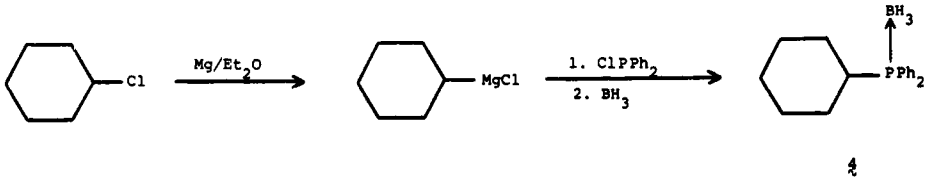
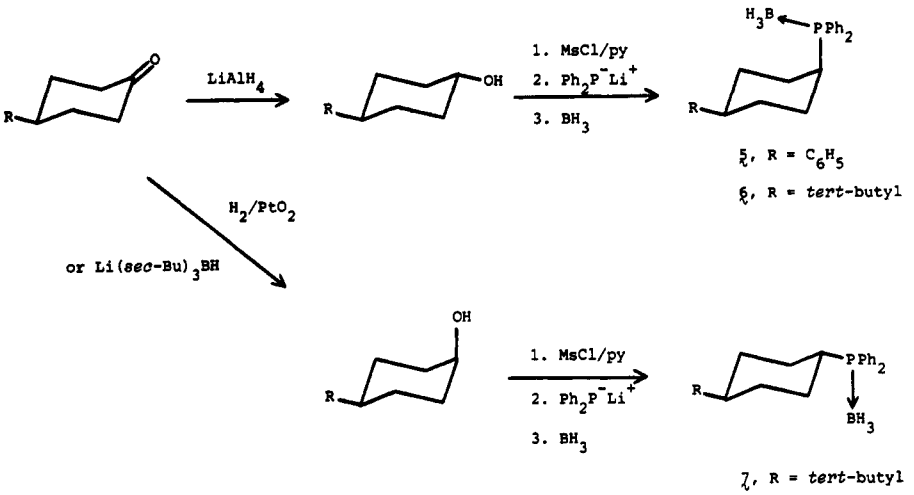
Scheme I



Scheme II



Scheme III

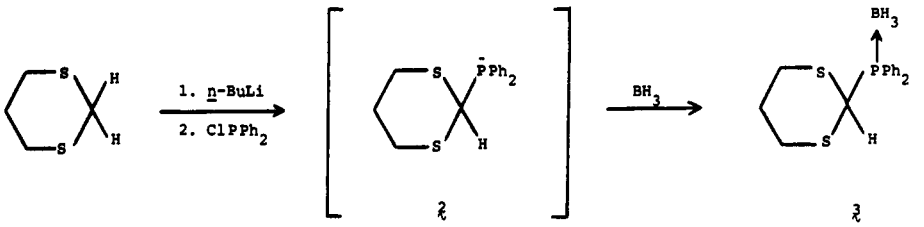


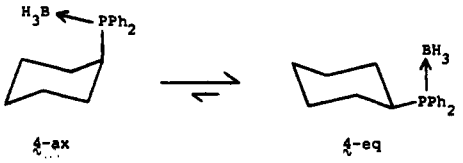
Table I. Ambient-Temperature ^{13}C NMR Signal Assignments in Cyclohexane Derivatives 4–10 (ppm from Me_4Si, $CDCl_3$). C/P Coupling Constants in Parentheses

compd	C(1)	C(2,6)	C(3,5)	C(4)	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	other
4	33.90 (36)	26.64 (1)	26.77 (12)	25.86 (2)	128.67 (53)	132.69 (9)	128.67 (10)	130.97 (3)	
5	31.70 (34)	23.84	30.14 (7)	39.57	128.98 (53)	132.60 (9)	128.72 (10)	131.02 (2)	*a*
6	29.10 (32)	25.68 (3)	23.12 (3)	46.20	129.85 (53)	132.55 (9)	128.63 (10)	130.86 (3)	*b*
7	33.61 (36)	26.96	27.54 (13)	47.28	128.61 (54)	132.62 (8)	128.65 (9)	130.95 (3)	*c*
8[d]	32.0 (52)	25.1	25.5 (~15)	25.1					*e*
9[d]	32.1 (51)	25.8 (3)	26.5 (15)	47.2					*f*
10[d]	29.2 (48)	24.2 (2)	23.8 (4)	45.6					*g*

[a] Phenyl at C(4): ipso, 145.49; ortho, 127.38; meta, 128.33; para, 125.73. [b] $(CH_3)_3C$, 27.56; $(CH_3)_3C$, 32.72. [c] $(CH_3)_3C$, 27.39; $(CH_3)_3C$, 32.41. [d] Taken from ref 8. [e] P–CH_3, 7.5(52). [f] P–CH_3, 7.8(55); $(CH_3)_3C$, 27.6; $(CH_3)_3C$, 32.6. [g] P–CH_3, 10.0(52), $(CH_3)_3C$, 27.4; $(CH_3)_3C$, 32.7.

sizes of CH_3 and BH_3 attached to phosphorus must be about equal.

Spectroscopic comparison of **4** with anancomeric **6** and **7** by means of Eliel's equation[13] ($K = (\delta_{eq} - \delta_{mobile})/(\delta_{mobile} - \delta_{ax})$) indicated the equilibrium 4-ax ⇌ 4-eq to be too highly biased, with a large predominance of the equatorial conformer (eq 4). However, equilibrium constants closer

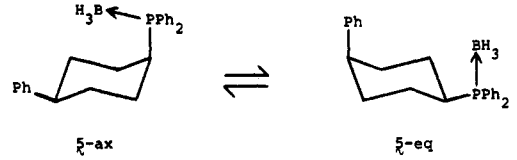


(4)

4-ax 4-eq

to unity were observed for **5**, which incorporate the phenyl group as a counterpoise substituent,[14] and permitted a more precise calculation of $\Delta G°$.

With **5**, the chemical shift for C(1) offered the best signal spread and was convenient for incorporation into Eliel's equation,[15] $K = 1/[(33.61 - 32.0)/(32.0 - 29.1)] = 1/0.56 = 1.8$, and then $\Delta G° = -RT \ln K = -0.4$ kcal/mol (eq 5).



(5)

5-ax 5-eq

(13) Eliel, E. L. *Chem. Ind. (London)* **1959**, 568.

(14) Eliel, E. L.; Della, E. W.; Williams, T. H. *Tetrahedron Lett.* **1963**, 831–835. See, also: Juaristi, E. *Introduction to Stereochemistry and Conformational Analysis*; Wiley: New York, in press.

(15) The chemical shift for C(1) in the mobile isomer has been slightly corrected (δ 0.3) because of the upshielding effect of similar magnitude observed at C(4) in phenylcyclohexane relative to cyclohexane.[12,16]

(16) Juaristi, E. Ph.D. Dissertation, University of North Carolina at Chapel Hill, 1977, pp 230–231.

Table II. Ambient-Temperature ^{13}C NMR Signal Assignments in 1,3-Dithiane Derivatives 2, 3, and 11–14. C/P Coupling Constants in Parentheses.

compd	C(2)	C(4,6)	C(5)	C_{ipso}	C_{ortho}	C_{meta}	C_{para}	other
2	42.02 (30)	29.36 (9)	25.40	135.44 (14)	133.77 (21)	128.62 (9)	128.11	
3	38.88 (27)	29.32 (3)	24.70	127.64 (53)	133.20 (9)	128.59 (10)	131.62 (2)	
11	44.73 (27)	41.74 (6)	43.25	126.27 (56)	133.57 (10)	128.52 (11)	131.77 (3)	*a*
12	37.42 (26)	35.54	42.73	129.78 (52)	132.71 (8)	128.59 (10)	131.28 (2)	*b*
13	45.57 (30)	41.26 (8)	43.43	134.46 (15)	133.90 (21)	128.57 (9)	128.03	*c*
14	42.06 (36)	34.52 (9)	44.03	137.93 (15)	133.49 (20)	128.48 (6)	128.11	*d*

[a] CH_3, 21.50. [b] CH_3, 21.50. [c] CH_3, 21.58. [d] CH_3, 21.58.

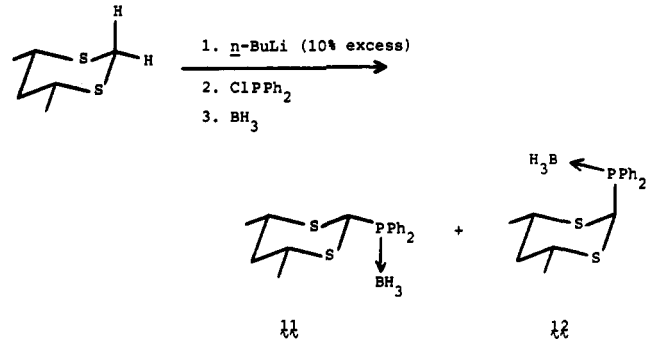
The prevalence of the equatorial phosphorus-containing group over equatorial phenyl ($-\Delta G°(C_6H_5)$ = 2.9 kcal/mol)[17] indicates that the conformational preference of the (diphenylphosphinyl)borane substituent in cyclohexane is $-\Delta G°_{310K}(P(BH_3)Ph_2)$ = 2.9 + 0.4 = 3.3 kcal/mol, intermediate between those found for the diphenylphosphinoyl, $-\Delta G°_{298K}(P(O)Ph_2)$ = 2.7 kcal/mol,[11] and the diphenylphosphinothioyl group, $-\Delta G°_{300K}(P(S)Ph_2)$ = 3.6 kcal/mol.[12]

Direct observation of the two conformers of **5** (eq 5) was possible at low temperature (171 K, THF-d_8) by ^{31}P NMR spectroscopy. The equilibrium constant K(**5**-ax ⇌ **5**-eq) = 61/39 = 1.56 was readily obtained by measurement of the signal intensities at δ 17.96 (**5**-eq) and 14.12 (**5**-ax). In this way, $-\Delta G°_{171K}$ (**5**-ax ⇌ **5**-eq) = 0.15 kcal/mol; assuming additivity, this implies $-\Delta G°_{171K}(P(BH_3)Ph_2)$ = 3.0 kcal/mol. From the conformational free energy difference at 310 and 171 K, a $\Delta S°$ = +1.5 cal/K·mol and $-\Delta H°$ = 2.8 kcal/mol are obtained. Although the accuracy of this measurement of $\Delta H°$ and $\Delta S°$ from two points can be of some concern, it is worth mentioning that roughly similar values have been recorded for the $P(O)Ph_2$ ($-\Delta H°$ = 2.0 kcal/mol; $\Delta S°$ = 2.6 cal/K·mol)[11] and $P(S)Ph_2$ ($-\Delta H°$ = 2.5 kcal/mol; $\Delta S°$ = 3.7 cal/K·mol)[12] substituents. The substantial entropy term, as well as the observation of Dreiding models, suggest that the axial (diphenylphosphinyl)borane group is conformationally constrained to rotamers with the P–BH_3 bond above the cyclohexane ring, whereas an equatorial $P(BH_3)Ph_2$ substituent is apparently free to fully rotate around the C(1)–P bond.

The conformational energies (*A* values) for the (diphenylphosphinyl)borane and diphenylphosphinothioyl[12] groups of 3.3 and 3.6 kcal/mol, respectively, are remarkably large and fall in the scarcely represented range between phenyl ($-\Delta G°$ = 2.9 kcal/mol)[17] and *tert*-butyl ($-\Delta G°$ = 4.9 kcal/mol).[18] The smaller conformational energy of the diphenylphosphinoyl group, $-\Delta G°(P(O)Ph_2)$ = 2.7 kcal/mol,[11] reflects the different steric demand of the P=O vs P → BH_3 and P=S groups, since rotamers with the phenyl rings above the cyclohexane must be too high in energy.[19]

B. Conformational Preference of the (Diphenylphosphinyl)borane Group in the 1,3-Dithiane Ring. (1,3-Dithian-2-yl)(diphenylphosphine–borane) (**3**) was prepared from 1,3-dithiane, *n*-butyllithium, and chlorodiphenylphosphine; the phosphine intermediate was then treated with 1 M borane solution in THF[20] (Scheme III). The anancomeric models **11** and **12** were prepared in similar fashion from *cis*-4,6-dimethyl-1,3-dithiane[21,22] (Scheme IV). These isomers were then separated chromatographically. Table II incorporates the ^{13}C NMR data for **3**, **11**, and **12**.

Scheme IV



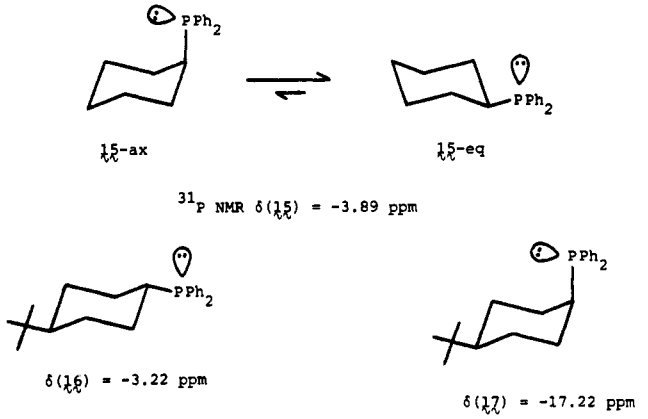
11 **12**

Most useful for the determination of $\Delta G°$ in eq 3 is the ^{13}C NMR chemical shift for the ipso carbons: 126.27 and 129.78 ppm in the cis (equatorial phosphorus) and trans (axial phosphorus) isomers, respectively. By comparison, $\delta(C_{ipso})$ = 127.64 ppm in the mobile dithiane (**3**, Table II). Application of Eliel's equation provided K = 1/0.64 = 1.56, and $\Delta G°_{310K}$ = −0.3 kcal/mol (eq 3). In addition, C(4,6) present also an adequate spread of chemical shifts ($\delta_{eq} - \delta_{ax}$) so as to make the calculations reliable. Nevertheless, before incorporation into Eliel's equation δ C(4,6) in **3** must be corrected for the introduction of the methyl groups: δ 9.35.[23] Accordingly, K = 1/[(41.74 − 38.67)/(38.67 − 35.54)] = 1/0.98 = 1.02, and $\Delta G°_{310K}$ = 0.0 kcal/mol. Therefore, average $\Delta G°_{310K}$ = −0.15 ± 0.1 kcal/mol; i.e., the equatorial isomer predominates slightly at equilibrium.

C. Is There an S–C–P(BH_3) Anomeric Effect? The anomeric effect is usually defined as the *tendency* of an electronegative substituent to assume the axial rather than the equatorial orientation at anomeric carbons.[24] Manifestation of an anomeric effect in **3** would require that the magnitude of such an effect overcomes the steric hindrance experienced by axial 2-substituents. In this respect, the steric requirement of a group at the 2-position in 1,3-dithiane is expected to be generally smaller (because of the long C–S bonds) than the steric requirement in a cyclohexane. For example, the equatorial preference of a *tert*-butyl group in cyclohexane amounts to 4.9 kcal/mol,[18] whereas it decreases (by a factor of 0.6) to 2.7 kcal/mol in 2-*tert*-butyl-1,3-dithiane.[21a] Thus, the expected size of the diphenylphosphinylborane group in **3** is ca. 0.6 times

(17) Eliel, E. L.; Manoharan, M. *J. Org. Chem.* **1981**, *46*, 1959–1962.
(18) Manoharan, M.; Eliel, E. L. *Tetrahedron Lett.* **1984**, *25*, 3267–3268.
(19) Nevertheless, variable temperature NMR, $Eu(fod)_3$ experiments, and single-crystal X-ray diffraction studies showed that the axial phosphinothioyl substituent in cyclohexane does not engender a palpable equilibrium between chair and flexible (boat, twist) conformations.[12]
(20) Zweifel, G.; Brown, H. C. *Org. React.* **1963**, *13*, 1–54.
(21) (a) Eliel, E. L.; Hutchins, R. O. *J. Am. Chem. Soc.* **1969**, *91*, 2703–2715. (b) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807–1816.
(22) We anticipated the exclusive formation of the equatorial isomer.[20b] Partial epimerization was probably facilitated by the high acidity of H(2) in the initial product **11**.
(23) Eliel, E. L.; Rao, V. S.; Ridell, F. G. *J. Am. Chem. Soc.* **1976**, *98*, 3583–3590.
(24) Lemieux, R. U.; Chü, N. J. *Abstracts of Papers*; 133rd National Meeting of the American Chemical Society; American Chemical Society: Washington, DC, 1958; N-31.

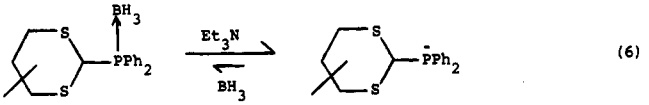
Scheme V



its *A* value, ca. 0.6 × 3.3 kcal/mol (see section A) = 2.0 kcal/mol. The difference between this value and the one experimentally obtained (−0.15 kcal/mol, see section B) affords an anomeric effect equal to −0.15 + 2.0 = 1.8 kcal/mol.

This procedure applies Franck's methodology to calculate the purely steric preference of the phosphorus substituent.[25] Because of the structural differences between the alkyl and P-containing substituent, the resulting values for the anomeric effect are only approximate as a consequence. However, it is a reasonable expectation that the factor will be greatest for the largest group, so the method can only *underestimate* the anomeric effect.[26]

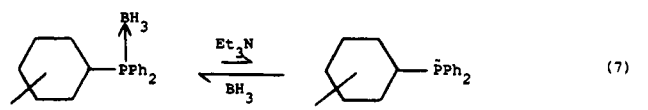
D. Conformational Preference of the Diphenylphosphinyl Group in the 1,3-Dithiane Ring. The mobile phosphine, (1,3-dithian-2-yl)diphenylphosphine (**2**), and the equatorial and axial conformationally fixed models **13** and **14** were prepared by treatment of the corresponding phosphine–boranes **3**, **11**, and **12** with an excess of triethylamine[27] (eq 6).



(6)

Table II includes the ^{13}C NMR data for these phosphines. Here again, C_{ipso} proved a most convenient signal for use in Eliel's equation because it provides an adequate signal spread and because it should be little affected by the presence of the anchoring methyl groups at C(4,6). In this way, $K = 2.54$ and $\Delta G°_{310K} = -0.6$ kcal/mol are obtained (eq 2).

E. Conformational Preference of the Diphenylphosphinyl Group in Cyclohexane. Removal of the boronato group of phosphine–boranes **4**, **6**, and **7** proved much more difficult than the similar reaction in the dithiane analogues (see section D). Nevertheless, small amounts (ca. 5%) of the desired phosphines could be detected by ^{31}P NMR spectroscopy, when the phosphine–boranes were treated with an excess of triethylamine at 50 °C for 48 h[27] (eq 7).



(7)

The ^{31}P NMR data were convenient for use in the determination of the *A* value for the diphenylphosphinyl group (Scheme V). Indeed, $K = [\delta(16) - \delta(15)/\delta(15) - \delta(17)] = [-3.22 - (-3.89)/-3.89 - (-17.22)] = 0.05$, and $\Delta G°_{310K} = -1.8$ kcal/mol.

F. Is There an S–C–P: Anomeric Effect? As determined in part E, the diphenylphosphinyl group is considerably smaller than *t*-Bu, and its *A* value is actually closer to that of an isopropyl group (2.15 kcal/mol). This equatorial preference decreases (by a factor of 0.9) to 1.95 kcal/mol in 2-isopropyl-1,3-dithiane.[21a] Thus, the expected size of the diphenylphosphinyl group in **2** is ca. 0.9 times its *A* value, ca. 0.9 × 1.8 kcal/mol (section E) = 1.6 kcal/mol. The difference between this value and the one experimentally obtained (ca. −0.6 kcal/mol, see section D) affords an anomeric effect to −0.6 + 1.6 = 1.0 kcal/mol. This is a substantial conformational effect and it is in disagreement with the theoretical prediction,[7] as discussed above.

Summary and Conclusions

A. Concerning the *A* Values of Phosphorus-Containing Groups in Cyclohexane. The general paucity of conformational information for phosphorus substituents in a cyclohexane system is now less critical thanks to the availability of the following semi- or quantitative data: $-\Delta G°(PMe_2) \sim 1.7$ kcal/mol,[8] $-\Delta G°(PPh_2) = 1.8$ kcal/mol (this work), $-\Delta G°[P(O)Ph_2] = 2.7$ kcal/mol,[11] $-\Delta G°[P(S)Me_2] > 3.0$ kcal/mol,[8] $-\Delta G°(PMe_3) > 3.0$ kcal/mol,[8] $-\Delta G°[P(BH_3)Ph_2] = 3.3$ kcal/mol (this work), and $-\Delta G°[P(S)Ph_2] = 3.6$ kcal/mol.[12]

The smaller *A* values for the tervalent phosphines relative to the tetravalent derivatives reflects the larger steric requirements of oxygen in the phosphinoyl substituent, BH_3 in the phosphinylborane group, and sulfur in the phosphinothioyl substituent. On the other hand, the smaller *A* value for dimethyl- and diphenylphosphine relative to an isopropyl group ($\Delta G° = -2.15$ kcal/mol)[28] is probably determined by the longer C–P bond (ca. 1.8 Å) relative to a C–C bond (ca. 1.5 Å).

B. Concerning the Relative Magnitude of S–C–P Anomeric Interactions. A generally observed trend in six-membered heterocycles presenting anomeric interactions is that the contribution of the axial isomer increases with growing electron-withdrawing properties of the substituent.[29-32] It is therefore relevant that the relative magnitude of the S–C–P anomeric effects in our 2-substituted 1,3-dithianes increases in the same order as the inductive electron-withdrawing properties of the organophosphorus groups studied.[10,33] Indeed, S–C–P(O), 2.6 kcal/mol > S–C–P(S), 2.2 kcal/mol > S–C–P(BH_3), 1.8 kcal/mol > S–C–P:, 1.0 kcal/mol.

This trend is adequately explained in terms of endo and exo hyperconjugative interactions.[34] Indeed, the antiperiplanar orientation of the p-type lone-pair orbital on the endocyclic sulfurs and the axial C(2)–P bond allows for a significant endo anomeric interaction in axial **2** (A, Scheme VI). However, exo anomeric interactions also stabilize the equatorial conformers B and C (Scheme VI), and a relatively weak anomeric effect is therefore observed.

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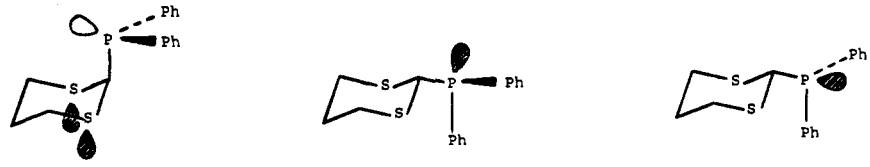
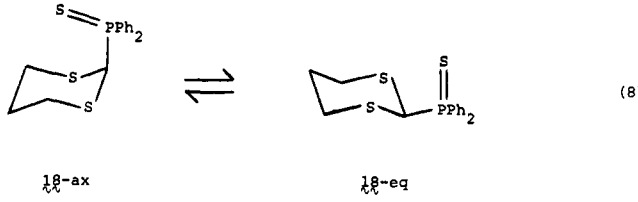
Scheme VI



A B C

Coordination of the phosphorus atom to oxygen in 1 [$\bar{P}Ph_2 \rightarrow P(O)Ph_2$] to borane in 3 [$\bar{P}Ph_2 \rightarrow P(BH_3)Ph_2$] and to sulfur in 18 [$\bar{P}Ph_2 \rightarrow P(S)Ph_2$] leads to an increased axial preference because the endo anomeric effect is stronger in axial 1, 3, and 18 (lower energy of the σ^*_{C-P} orbital; greater stabilization through the $n_s \rightarrow \sigma^*_{C-P}$ interaction),[35] but the exo anomeric interactions are not possible because of the unavailability of an antiperiplanar n_P orbital.



(8)

18-ax 18-eq

Nevertheless, through-space 3p–3d electron donation from sulfur to axial phosphorus[3] could also account for the results, especially since the precise structural data available[36] are not in line with the double bond–no bond picture expected from the $n_s \rightarrow \sigma^*_{C-P}$ hyperconjugation mechanism.[37]

In this context, it is important to notice that electron transfer from sulfur to the axial phosphorus is supported by the observation of significant upfield ^{13}C chemical shifts for the ortho and para carbons in the axial phosphinoyl,[3,4] phosphinothioyl,[4,12] phosphinylborane (Table II), and phosphinyl (Table II) groups.

Alternative rationalizations that have been considered to account for the strong S–C–P(O) anomeric effect, such as (a) electrostatic, attractive interaction between the phosphoryl oxygen and the syn-axial hydrogens,[3,6] and (b) repulsive interaction between the lone pairs on sulfur and on the equatorial phosphoryl oxygen,[38] appear, under the new evidence, to play a minor role in the conformational equilibria of 1–3 and 18.

Experimental Section

General Information. Proton NMR spectra were recorded on Varian EM-360 (60-MHz) or Varian EM-390 (90-MHz) spectrometers. ^{13}C, ^{31}P, and ^{11}B NMR spectra were recorded on a JEOL FX-90Q (22.49-, 36.23- and 28.69-MHz, respectively) instrument operated in pulsed Fourier transform mode and locked on solvent deuterium. ^{13}C NMR data are reported in δ from internal TMS; ^{31}P NMR data are reported in δ from external phosphoric acid; ^{11}B NMR data are reported in δ from external $BF_3 \cdot Et_2O$.

Flasks, stirring bars, and hypodermic needles used for the generation of organometallic compounds were dried for ca. 12 h at 120 °C and allowed to cool in a desiccator over anhydrous calcium sulfate. Anhydrous solvents (ethers) were obtained by distillation from benzophenone ketyl.[39] The BuLi employed was titrated according to the method of Juaristi et al.[40]

Melting points, determined with a Mel-Temp or an Electrothermal apparatus, are uncorrected.

Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

(1,3-Dithian-2-yl)diphenylphosphine–Borane (3). 1,3-Dithiane (1 g, 8.33 mmol, freshly sublimed) was placed in a 50-mL round-bottom flask provided with a rubber septum before the addition of 30 mL of THF under nitrogen. The flask was immersed in a carbon tetrachloride/dry ice bath (ca. −20 °C), and then 3.78 mL of 2.2 M *n*-BuLi in hexane was added. The reaction mixture was stirred at −20 °C for 2 h and then transferred to another flask containing 1.84 g (8.3 mmol) of chlorodiphenylphosphine. The reaction mixture was stirred at −20 °C for 1 h and then treated with 8.5 mL of 1 M borane–THF solution. Stirring was continued at −20 °C for 2 h at room temperature, and the reaction mixture was then concentrated at low pressure. The residue was quenched by careful addition of 30 mL of water. Extraction with ethyl ether and the usual workup procedure yielded a yellowish solid, which was recrystallized from acetone–hexane to afford 1.17 g (44.4% yield) of **3** as white crystals: mp 146–147 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 2.07 (m, 2 H), 2.5–3.53 (m, 4 H), 4.70 (d, J = 12 Hz, 1 H), 7.6 (m, 6 H), 7.95 (m, 4 H); ^{13}C NMR in Table II; ^{31}P NMR (36.23 MHz, $CDCl_3$) δ 28.19; ^{11}B NMR (28.69 MHz, $CDCl_3$) δ −38.31. Anal. Calcd for $C_{16}H_{20}BPS_2$: C, 60.38; H, 6.33. Found: C, 60.42; H, 6.04.

Cyclohexyldiphenylphosphine–Borane (4). Magnesium (0.23 g, 9.3 mmol), a crystal of iodine, and 30 mL of diethyl ether were placed in a 100-mL round-bottom flask provided with a condenser, addition funnel, and a stirring bar. The cyclohexyl chloride (1 g, 8.5 mmol) dissolved in 5 mL of dry diethyl ether was added at such a rate as to maintain gentle reflux. A solution of chlorodiphenylphosphine (1.5 mL, 8.5 mmol) in 10 mL of dry ether was then added dropwise, and the reaction mixture was stirred at ambient temperature overnight. The resulting whitish solution was then treated with 9 mL of 1 M borane THF solution, and stirring was continued for an additional 6 h at ambient temperature. The reaction mixture was then concentrated at reduced pressure, redissolved in a small amount of acetone, and purified by flash chromatography (hexane–ethyl acetate (9:1)). The eluted product was recrystallized from hexane–chloroform to afford 0.51 g (21.4% yield) of the pure product: mp 95–96.5 °C; ^1H NMR (60 MHz, $CDCl_3$) δ 1.0–1.95 (m, 10 H), 2.35 (m, 1 H), 7.4–8.0 (m, 10 H); ^{13}C NMR in Table I; ^{31}P NMR (36.23 MHz, $CDCl_3$) δ 21.38; ^{11}B NMR (28.69 MHz, $CDCl_3$) δ −41.52. Anal. Calcd for $C_{18}H_{24}BP$: C, 76.61; H, 8.57. Found: C, 76.99; H, 8.65.

(*cis*-4-Phenylcyclohexyl)diphenylphosphine–Borane (5). Lithium metal (0.32 g, 4.5 mmol) and 30 mL of dry THF were placed in a 500-mL round-bottom flask provided with condenser, addition funnel, and a magnetic bar, and the mixture was heated to reflux before the dropwise addition of 1.0 g (0.81 mL, 4.5 mmol) of chlorodiphenylphosphine in 80 mL of dry THF. The orange-red mixture was refluxed for 3 h, and then the solution was transferred via cannula, under positive pressure of nitrogen, to another flask capped with a rubber septum and submerged in a water-ice bath. *trans*-4-Phenylcyclohexyl methanesulfonate (1.0 g, 3.9 mmol; prepared from *trans*-4-phenylcyclohexanol[41] according to the usual procedure)[42] in 80 mL of dry THF was then added, and when the

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addition was completed, the cooling bath was removed and the reaction mixture refluxed for 2.5 h. Treatment with 1M borane-THF solution (4.5 mL, 4.5 mmol) was followed by stirring of the reaction mixture at ambient temperature for 24 h, and then solvent removal at reduced pressure. The residue was purified by flash chromatography (hexane) and then by recrystallization from hexane-acetone (2:1) to afford 264 mg (18.7% yield) of the pure product: mp 158-159 °C; ^{1}H (90 MHz, $CDCl_3$) δ 1.2-3.0 (m, 10 H), 7.3 (m, 5 H), 7.5 (m, 6 H), 7.8 (m, 4 H); ^{13}C NMR in Table I; ^{31}P NMR (36.23 MHz $CDCl_3$) δ 20.31; ^{11}B NMR (28.69 MHz, $CDCl_3$) δ -39.53. Anal. Calcd for $C_{24}H_{28}BP$: C, 80.45; H, 7.87. Found: C, 80.66; H, 7.72.

(*cis*-4-*tert*-Butylcyclohexyl)diphenylphosphine-borane (6) was similarly prepared from *trans*-4-*tert*-butylcyclohexyl methanesulfonate (1.0 g, 4.2 mmol; prepared from *trans*-4-*tert*-butylcyclohexanol[43] according to the usual procedure).[42] The desired product was purified by flash chromatography (ethyl acetate/hexane (90:10)) and recrystallization from methylene chloride-hexane to furnish 260 mg (15.8% yield) of pure **6**: mp 124-125 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.83 (s, 9 H), 1.0-3.15 (m, 10 H), 7.3-8.1 (m, 10 H); ^{13}C NMR in Table I; ^{31}P NMR (36.23 MHz, $CDCl_3$) δ 20.06; ^{11}B NMR (28.69 MHz, $CDCl_3$) δ -38.87. Anal. Calcd for $C_{22}H_{32}BP$: C, 78.11; H, 9.53. Found: C, 77.78; H, 9.47.

(*trans*-4-*tert*-Butylcyclohexyl)diphenylphosphine-borane (7) was similarly prepared from *cis*-4-*tert*-butylcyclohexyl methanesulfonate (0.65 g, 2.7 mmol; prepared from *cis*-4-*tert*-butylcyclohexanol[44] according to the usual procedure).[42] The crude product was purified by flash chromatography (hexane) and recrystallization from hexane-chloroform to afford 288 mg (17.5% yield) of pure **7**: mp 143-144 °C; ^{1}H NMR (60 MHz, $CDCl_3$) δ 0.84 (s, 9 H), 0.9-3.0 (m, 10 H), 7.5 (m, 6 H), 7.8 (m, 4 H); ^{13}C NMR in Table I; ^{31}P NMR (36.23 MHz, $CDCl_3$), δ 21.11; ^{11}B NMR (28.69 MHz, $CDCl_3$) δ -41.72. Anal. Calcd for $C_{22}H_{32}BP$: C, 78.11; H, 9.53. Found: C, 77.92; H, 9.75.

(*cis*-4,*cis*-6-Dimethyl-1,3-dithian-2-yl)- and (*trans*-4,-*trans*-6-Dimethyl-1,3-dithian-2-yl)-*rel*-2-(diphenylphosphine-Borane) (11 and 12). *cis*-4,6-Dimethyl-1,3-dithiane[21] (0.8 g, 5.4 mmol) was placed in a dry round-bottom flask provided with a magnetic stirring bar and capped with a rubber septum. The flask was flushed with nitrogen prior to the addition of 50 mL of dry THF via a cannula, after which the solution was cooled to -20 °C and *n*-butyllithium (2.6 mL of a 2.3 M hexane solution, 6.0 mmol, 10% excess) was syringed into it dropwise. The resulting solution was stirred for 90 min at -20 °C, following which it was added to a THF solution (ca. 40 mL) of chlorodiphenylphoshine (1.2 g, 5.4 mmol) also at -20 °C. The reaction mixture was stirred at this temperature for 90 min and then treated with 8.0 mL of 1 M borane-THF solution. The reaction mixture was then left standing in the refrigerator for 24 h, and concentrated at reduced pressure. The desired products were purified by flash chromatography (hexane) and then recrystallized from hexane-acetone to afford 161 mg (8.6% yield) of **11** and 506 mg (27.1% yield) of **12**.

11: mp 167-169 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.26 (d, J = 7 Hz, 6 H), 1.35 (m, 1 H), 2.1 (dm, J = 11 Hz, 1 H), 2.9 (m, 2 H), 4.9 (d, J = 12 Hz, 1 H), 7.5 (m, 6 H), 7.95 (m, 4 H); ^{13}C NMR in Table II; ^{31}P NMR (36.23 MHz, $CDCl_3$) δ 27.59; ^{11}B NMR (28.69 MHz, $CDCl_3$) δ -38.46. Anal. Calcd for $C_{18}H_{24}BPS_2$: C, 62.43; H, 6.98. Found: C, 62.96; H, 7.02.

14: mp 193-195 °C; ^{1}H NMR (90 MHz, $CDCl_3$) δ 1.16 (d, $J \approx$ 6 Hz, 6 H), ca. 1.2 (m, 1 H), 2.1 (dm, J = 11 Hz, 1 H), 3.7 (m, 2 H), 4.56 (d, J = 14.4, 1 H), 7.58 (m, 6 H), 7.9 (m, 4 H); ^{31}P NMR (36.23 MHz, $CDCl_3$) δ 27.79; ^{11}B NMR (28.69 MHz, $CDCl_3$) δ -38.19. Anal. Calcd for $C_{18}H_{24}BPS_2$: C, 62.43; H, 6.98. Found: C, 62.03; H, 6.82.

Reaction of Phosphine-Boranes with Triethylamine. A solution of the phosphine-borane (50-100 mg) in 1-2 mL of triethylamine was kept under nitrogen at 50 °C for 48 h. Excess triethylamine was removed in vacuo, and the residual, air-sensitive phosphine was redissolved in deuterated solvent and transferred via a cannula to the NMR tube for analysis.

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Selective Oxidation of Alcohols and Aldehydes with Hydrogen Peroxide Catalyzed by Methyltrioctylammonium Tetrakis(oxodiperoxotungsto)phosphate(3-) under Two-Phase Conditions

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The use of methyltrioctylammonium tetrakis(oxodiperoxotungsto)phosphate(3-) (**1c**) in combination with hydrogen peroxide as the primary oxidant in an aqueous/organic biphase system provides a cheap, efficient, and versatile catalytic method for alcohol and aldehyde oxidation. By this method, a variety of water-insoluble primary and secondary alcohols and aldehydes were oxidized to carboxylic acids and ketones in good yields under mild conditions and after relatively short reaction times.

The oxidation of organic substrates by aqueous hydrogen peroxide is very attractive from a synthetic and industrial viewpoint since this reagent is relatively inexpensive, of low equivalent weight, environmentally clean, and easy to handle. The help of a metal catalyst is often required, and in recent years a considerable effort has been devoted to the search for new efficient metal derivatives suited to this purpose.[1]

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