

Conformational Analysis of 1,3-Dithian-2-yltrimethylphosphonium Chloride. Origin of the S-C-P Anomeric Effect¹

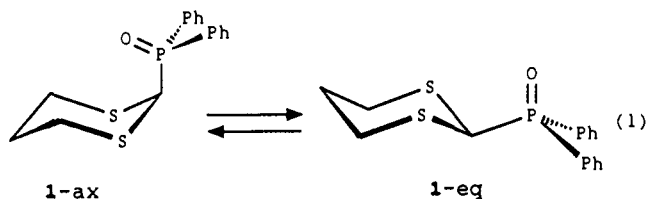
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Abstract: The conformational energy of the trimethylphosphonium group in the 1,3-dithian-2-yl system was determined by multinuclear (¹H, ¹³C, ³¹P) NMR analysis of the mobile title compound as well as the corresponding conformationally fixed models. A definite preference for the axial conformation, $\Delta G^{\circ}_{300K} = 0.36 \pm 0.10$ kcal/mol, reflects a substantial S-C-PMe₃ anomeric effect in this system, with a value at least equal to 2.2 kcal/mol. This result is compared with thermodynamic data obtained from the systematic study of other 2-P-substituted 1,3-dithianes, in order to gain insight into the nature of the S-C-P anomeric effect. In particular, the trimethylphosphonium group lacks unshared electrons; therefore, this result is not in line with interpretations of the S-C-P anomeric effect invoking a dominant repulsion between electrons at sulfur and the P-substituents in the equatorial conformation. Analysis of the NMR spectroscopic data lends support to a two-electron/two-orbital stereoelectronic interaction that stabilizes the axial isomer. Furthermore, the substantial anomeric effect observed in the title system clearly violates expectations in terms of the so-called "reverse anomeric effect".

Introduction

The ¹H NMR spectroscopic study of 1,3-dithian-2-ylidiphosphine oxide (1), a useful precursor of ketene dithioketals,² provided evidence for a predominant axial conformation (eq 1) and led to the discovery of the S-C-P(O) anomeric effect.³

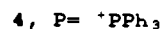
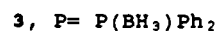
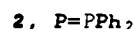
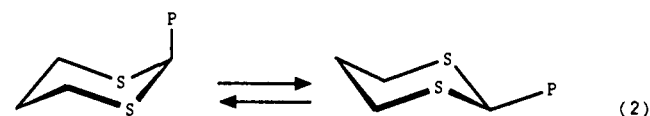


Quantitative evaluation of this conformational equilibrium was achieved by chemical equilibration of ananomeric (conformationally fixed⁴) models and afforded the conformational free energy difference $\Delta G^{\circ}_{312K} = 1.0$ kcal/mol.⁵ Comparison of this result with the *A* value for the diphenylphosphinoyl group (i.e., its conformational preference in cyclohexane, $\Delta G^{\circ}_{300K} = -2.74$ kcal/mol⁶) and consideration of the relative effective sizes of the substituent in cyclohexane and in the 1,3-dithian-2-yl system afforded the magnitude of the anomeric effect present in 1: 2.64 kcal/mol, which is one of the largest yet recorded.⁷ This finding

has provided a driving force for numerous recent studies of anomeric interactions involving second- and lower-row elements.⁸

In contrast with the ample experimental corroboration of the S-C-P(O) anomeric effect (vide supra), no definitive interpretation of its origin has been produced. Five distinct mechanisms have been examined,^{7b} but the discussion has mostly centered on whether a two-orbital/two-electron interaction stabilizes the axial conformer 1-ax (either $n_S \rightarrow \sigma^*_{C-P}$ or $3p \rightarrow 3d$)^{5a,9} or a repulsive interaction between the lone electron pairs on sulfur and on the equatorial phosphoryl oxygen destabilizes 1-eq^{10,11} (Scheme I).

In this regard, substantial S-C-P anomeric effects have recently been observed for the analogous 2-P-substituted 1,3-dithianes 2-4 (eq 2),^{9,12} which lack the phosphoryl group required for the



electronic repulsion in the Mikolajczyk postulate.^{10,11} Nevertheless, in the opinion of these researchers,¹² the equatorial triphenylphosphonium group is now destabilized by repulsive interactions between the lone pairs on the endocyclic sulfur atoms and the π -electrons of the phenyl ring.

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(2) Juaristi, E.; Gordillo, B.; Valle, L. *Tetrahedron* 1986, 42, 1963. For an excellent review on the use of ketene dithioketals in synthesis, see: Kolb, M. *Synthesis* 1990, 171.

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(4) Anteunis, M. J. O. *Conformational Analysis, Scope and Present Limitations*; Academic Press: New York, 1971; p 32. See also: Juaristi, E. *Introduction to Stereochemistry and Conformational Analysis*; Wiley: New York, 1991; Chapter 3.

(5) (a) Juaristi, E.; Valle, L.; Valenzuela, B. A.; Aguilar, M. A. *J. Am. Chem. Soc.* 1986, 108, 2000. (b) A comparable value, $\Delta G^{\circ}_{298K} = 0.81$ kcal/mol, was obtained from the chemical equilibration of 5-*tert*-butyl-2-(diphenylphosphinoyl)-1,3-dithiane: Mikolajczyk, M.; Graczyk, P.; Balczewski, P. *Tetrahedron Lett.* 1987, 28, 573.

(6) Juaristi, E.; López-Núñez, N. A.; Glass, R. S.; Petsom, A.; Hutchins, R. O.; Stercho, J. P. *J. Org. Chem.* 1986, 51, 1357.

(7) (a) Juaristi, E. *Acc. Chem. Res.* 1989, 22, 357. (b) For a detailed discussion, see: Juaristi, E. *Heteroat. Chem.* 1990, 1, 267.

(8) See, for example: (a) Mikolajczyk, M. *Pure Appl. Chem.* 1987, 59, 983. (b) Pinto, B. M.; Johnson, B. D.; Sandoval-Ramirez, J.; Sharma, R. D. *J. Org. Chem.* 1988, 53, 3766. (c) Tschierske, C.; Köhler, H.; Zaszke, H.; Kleinpeter, E. *Tetrahedron* 1989, 45, 6987. (d) Schleyer, P. v. R.; Jemmis, E. D.; Spitznagel, G. W. *J. Am. Chem. Soc.* 1985, 107, 6393. (e) Pericas, M. A.; Rivera, A.; Guiler, J. *Tetrahedron* 1986, 42, 2717. (f) Anet, F. A. L.; Kopelevich, M. *J. Chem. Soc., Chem. Commun.* 1987, 595. (g) Caserio, M. C.; Shih, P.; Fisher, C. L. *J. Org. Chem.* 1991, 56, 5517.

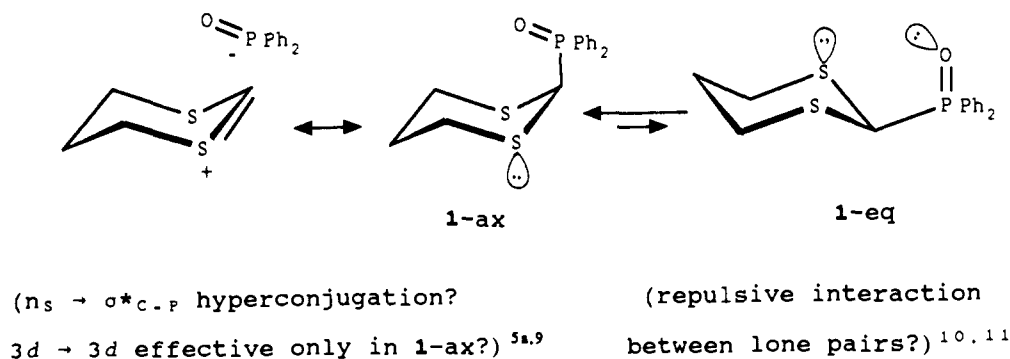
(9) Juaristi, E.; Aguilar, M. A. *J. Org. Chem.* 1991, 56, 5919.

(10) Mikolajczyk, M.; Gracyk, P.; Kabachnik, M. I.; Baranov, A. P. *J. Org. Chem.* 1989, 54, 2859.

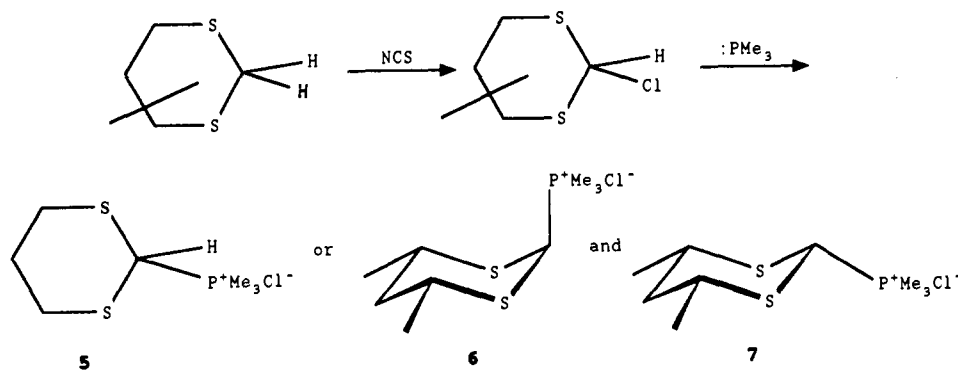
(11) A recent review article favors this hypothesis: Zamojski, A. *Chemtracts: Org. Chem.* 1990, 3, 396.

(12) Mikolajczyk, M.; Gracyk, P.; Wiczorek, M. W.; Bujacz, G. *Angew. Chem., Int. Ed. Engl.* 1991, 30, 578.

Scheme I



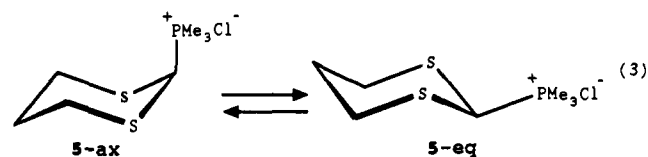
Scheme II

Table I. Ambient-Temperature 270-MHz ¹H NMR Signal Assignments in Dithiane Derivatives **5**–**7** (ppm from Me₄Si, CDCl₃)^a

compd	H(2)	H(4,6ax)	H(4,6eq)	H(5ax)	H(5eq)	⁺ P(CH ₃) ₃
5	6.21 (14.5)	2.96	3.08	2.12	2.12	2.35 (14.5)
6	5.81 (13.2)	2.98	<i>b</i>	≈1.3	2.19	2.33 (13.9)
7	6.30 (16.5)	3.33	<i>c</i>	≈1.3	2.17	2.31 (15.4)

^aH/P coupling constants in parentheses. ^bCH₃–C(4,6): 1.27. ^cCH₃–C(4,6): 1.29.

We report in this paper that 2-(trimethylphosphonio)-1,3-dithiane **5** also presents a large anomeric effect (eq 3). The



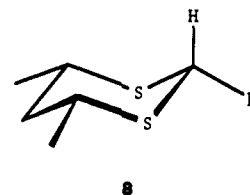
substituent in this case does not incorporate any unshared electrons, so electronic repulsion in the equatorial isomer is not possible.

In addition, the existence of an anomeric effect in **5** is contrary to expectations based on our present knowledge of the so-called "reverse anomeric effect".¹³

Results and Discussion

A. Preparation of the Desired Compounds and Relevant Spectroscopic Observations. 1,3-Dithian-2-yltrimethylphosphonium chloride (**5**) was prepared in 85% yield by the addition of 2-chloro-1,3-dithiane¹⁴ to trimethylphosphine in dry THF. The anancomeric models **6** and **7** were prepared from *cis*-4,6-dimethyl-1,3-dithiane¹⁵ according to the same procedure (Scheme II). Assignment of configuration to diastereomeric **6** and **7** was possible from inspection of the proton and carbon NMR spectra (Tables I and II, respectively). In particular, the shielding γ -

gauche effect in the axial model **6** causes an upfield shift for C(4,6).¹⁶ Interestingly, the equatorial H(2) in **6** resonates at *higher* field than does the axial H(2) in **7**. This anomalous chemical shift behavior for the hydrogens at C(2) in 1,3-dithiane was first pointed out by Eliel et al.¹⁷ and may be the result of a stereoelectronic $\sigma_{C-S} \rightarrow \sigma^*_{C-H}$ two-electron-two-orbital interaction. Indeed, Bailey et al.¹⁸ reported recently that, in contrast with the normal situation in which the magnitude of the one-bond coupling constants for an axial C–H bond in a six-membered ring is 8–10 Hz smaller than ¹J for the corresponding C–H equatorial bonds (i.e., ¹J_{C–H_{eq} > ¹J_{C–H_{ax}), *cis*-4,6-dimethyl-1,3-dithiane (**8**) exhibits the opposite behavior; that is ¹J_{C(2)–H_{ax} = 154.1 Hz > ¹J_{C(2)–H_{eq} = 144.9 Hz.}}}}



This reversal of the relative magnitudes of the coupling constants at C(2) was explained by Wolfe et al.¹⁹ as originating from a reversal in C–H bond lengths²⁰ as a result of $\sigma_{C-H} \rightarrow \sigma^*_{C-S}$ or $\sigma_{C-S} \rightarrow \sigma^*_{C-H}$ stereoelectronic (antiperiplanar) orbital interactions.

(13) Lemieux, R. U. *Pure Appl. Chem.* **1971**, *25*, 527. See also: Lemieux, R. U. *Exploration with Sugars—How Sweet It Was*. In *Profiles, Pathways and Dreams*; Seeman, J. I., Ed.; American Chemical Society: Washington, DC, 1990; pp 100–102.

(14) See, for example: Arai, K.; Oki, M. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 553.

(15) (a) Eliel, E. L.; Hutchins, R. O. *J. Am. Chem. Soc.* **1969**, *91*, 2703. (b) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807.

(16) Grant, D. M.; Cheney, B. V. *J. Am. Chem. Soc.* **1967**, *89*, 5315. Wilson, N. K.; Stothers, J. B. *Top. Stereochem.* **1973**, *8*, 1.

(17) Eliel, E. L.; Rao, V. S.; Vierhapper, F. W.; Juaristi, G. Z. *Tetrahedron Lett.* **1975**, 4339.

(18) Bailey, W. F.; Rivera, A. D.; Rossi, K. *Tetrahedron Lett.* **1988**, *29*, 5621.

(19) Wolfe, S.; Pinto, B. M.; Varma, V.; Leung, R. Y. N. *Can. J. Chem.* **1990**, *68*, 1051. Wolfe, S.; Kim, C.-K. *Can. J. Chem.* **1991**, *69*, 1408.

Table II. Ambient-Temperature 67.8-MHz ^{13}C NMR Signal Assignments in Dithiane Derivatives **5-7** (ppm from Me_4Si , CDCl_3)^a

compd	C(2)	C(4,6)	C(5)	$^+\text{P}(\text{CH}_3)_3$	$\text{CH}_3\text{-C-}$ (4,6)
5	35.02 (52.8)	28.80 (5.6)	24.44	8.14 (54.0)	
6	34.70 (51.8)	36.26	41.84	9.49 (52.8)	21.78
7	39.93 (55.1)	41.12 (7.8)	43.17	7.33 (54.0)	21.51

^aC/P coupling constants in parentheses.

Furthermore, the finding by Juaristi and Cuevas^{21a} that all equatorial bonds in 1,3-dithiane, which are antiperiplanar to C-S bonds, do exhibit smaller $^1J_{\text{C-H}_{\text{eq}}}$ coupling constants, together with the anomalous chemical shifts for the axial and equatorial protons at C(2), C(4), and C(5) in 1,3-oxathiane^{21b} (Scheme III), could be explained as the result of relevant stereoelectronic contributions by $\sigma_{\text{C-S}} \rightarrow \sigma_{\text{C-H}}^*$ two-electron/two-orbital interactions. This stereoelectronic effect causes an upfield shift for the antiperiplanar, equatorial hydrogens, as well as causing a concomitant decrease in the C-H_{eq} coupling constants, which is nearly balanced by the normal Perlin effect.^{22,23}

B. Conformational Preference of the Trimethylphosphonium Group in the 1,3-Dithiane Ring. Spectroscopic comparison of **5** with ananomer **6** and **7** by means of Eliel's equation²⁴ [$K = (\delta_{\text{eq}} - \delta_{\text{mobile}})/(\delta_{\text{mobile}} - \delta_{\text{ax}})$] was most convenient with incorporation of ^{31}P and ^{13}C NMR data, since these nuclei offer the best signal spread. Indeed, the ^{31}P NMR spectra of **5**, **6**, and **7** afforded $\delta = 39.99$, 42.46, and 35.69, respectively. Therefore, K (eq 3) = 0.57, and $\Delta G^\circ_{300\text{K}} = 0.33$ kcal/mol.

Most useful for the determination of ΔG° by means of ^{13}C NMR data are carbons C(2) and C(4,6), provided that the values for mobile **5** are corrected for the shifting effect introduced by the methyl groups at C(4,6).^{25,26} In this fashion, incorporation of the chemical shifts for C(2) into Eliel's equation affords $K = 1/[(39.93 - 36.41)/(36.41 - 34.70)] = 0.49$, and $\Delta G^\circ_{300\text{K}} = 0.43$ kcal/mol. On the other hand, use of C(4,6) gives $K = 1/[(41.12 - 38.15)/(38.15 - 36.26)] = 0.64$, and $\Delta G^\circ_{300\text{K}} = 0.27$ kcal/mol.

An important advantage of the use of coupling constants,³ rather than chemical shifts, in Eliel's equation is that these parameters should be little affected by the anchoring substituents. Most useful for the determination of ΔG° in eq 3 are $^2J_{\text{H(2)/P}}$ and $^1J_{\text{C(2)/P}}$. Accordingly, $K = 1/[(16.5 - 14.5)/(14.5 - 13.2)] = 0.65$ and $K = 1/[(55.1 - 52.8)/(52.8 - 51.8)] = 0.44$, respectively. Therefore, the estimated $\Delta G^\circ_{300\text{K}}$ values are 0.26 and 0.50 kcal/mol, respectively.

In summary, an average $\Delta G^\circ_{300\text{K}}$ (eq 3) = 0.36 ± 0.10 kcal/mol is obtained, which corresponds to a 65:35 **5-ax**:**5-eq** ratio. That is, there is a sizable predominance of the axial conformer, in spite of the stringent steric requirements of the trimethylphosphonium group.

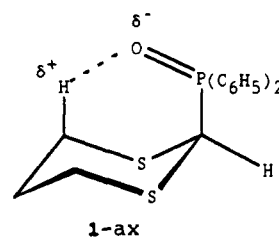
C. Magnitude of the S-C- $^+\text{PMe}_3$ Anomeric Effect in **5.** The predominance of the axial conformer in the **5-ax** \rightleftharpoons **5-eq** equilibrium (eq 3) indicates that the magnitude of the S-C-P anomeric effect in this system overcomes the substantial steric hindrance experienced by the axial trimethylphosphonium group, whose A value exceeds 3 kcal/mol.²⁷ Nevertheless, 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,²⁸ whereas it decreases (by a factor of 0.6) to 2.7

(20) Shorter, stronger bonds give rise to larger 1J coupling constants.(21) (a) Juaristi, E.; Cuevas, G. *Tetrahedron Lett.* **1992**, *33*, 1847. (b) Juaristi, E.; Cuevas, G.; Flores-Vela, A. *Tetrahedron Lett.* **1992**, *33*, 6927.(22) It has been recently proposed¹⁹ that stereoelectronic effects upon one-bond coupling constants be termed "Perlin effects".(23) On the "oxygen part" of the 1,3-oxathiane molecule, however, the well-accepted $n_{\text{O}} \rightarrow \sigma_{\text{C-H}}^*$ interaction appears to be dominant.(24) Eliel, E. J. *Chem. Ind. (London)* **1959**, 568.(25) C(2) is shifted 1.39 ppm downfield, and C(4,6) is shifted 9.35 ppm downfield, in going from the parent dithiane to *cis*-4,6-dimethyl-1,3-dithiane.²⁶(26) Eliel, E. L.; Rao, V. S.; Ridell, F. G. *J. Am. Chem. Soc.* **1976**, *98*, 3583.(27) Gordon, M. D.; Quin, L. D. *J. Org. Chem.* **1976**, *41*, 1690.(28) Monoharan, M.; Eliel, E. L. *Tetrahedron Lett.* **1984**, *25*, 3267.**Table III.** Temperature-Dependent Variation in the Coupling Constant of H(2) to Phosphorus in **1**, and Estimated Free Energy Differences (Eq 1)

temp (K)	$^2J_{\text{H(2)/P}}$	K	ΔG° (kcal/mol)
323	6.60	0.29	0.80
300	5.94	0.19	0.98
273	5.71	0.16	0.99
258	5.28	0.11	1.33

kcal/mol in 2-*tert*-butyl-1,3-dithiane.^{15a} Thus, by application of Franck's methodology,²⁹ the effective size of the trimethylphosphonium group in **5** must be ca. 0.6 times its A value, 0.6×3.0 kcal/mol = >1.8 kcal/mol. The difference between this value and the one obtained experimentally (0.36 kcal/mol; see section B) affords an anomeric effect at least equal to $0.36 + 1.8 = 2.16$ kcal/mol.

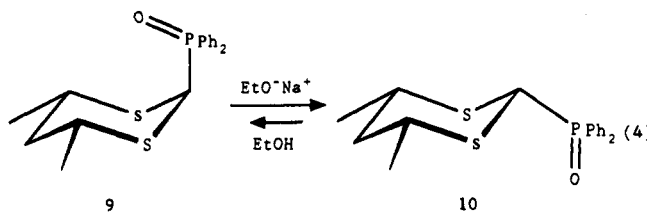
The trimethylphosphonium group lacks unshared electrons; therefore, it is clear that interpretations of the S-C-P anomeric effect based on dominant repulsion between unshared electrons in the equatorial isomer¹⁰⁻¹² cannot be correct. The substantial anomeric stabilization in **5-ax** seems also to rule out the argument^{5a,8a,30} that electrostatic, attractive interactions between the phosphoryl oxygen and the axial hydrogens in **1-ax** are responsible for its stability.



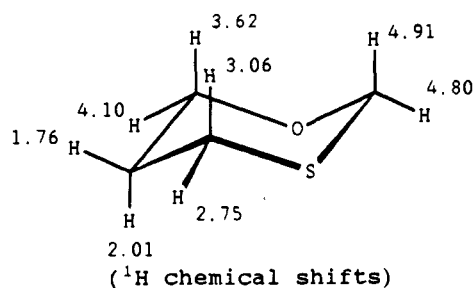
On the other hand, the significant upfield ^{13}C chemical shifts for ortho and para carbons in axial phosphinoyl,^{5a,7} phosphinothioyl,^{7,31} phosphinylborane,⁹ and phosphinyl groups⁹ seem to support a mechanism in which electron transfer ($n_{\text{S}} \rightarrow \sigma_{\text{C-P}}^*$ or $3p \rightarrow 3d$) stabilizes the axial isomer. The former mechanism should result in a lower $^1J_{\text{P-C}}$ for an axial P-group than for an equatorial P-group, due to lower bond order in the former.²⁰ This expectation is fulfilled in the case of **6** and **7**, but not for the corresponding 2-diphenylphosphinoyl analogues,^{5a} so a distinction here is not yet possible.

D. Enthalpic and Entropic Contributions to the S-C-P(O) and S-C- $^+\text{PMe}_3$ Anomeric Effects. Lately, Booth et al.³² have stressed that in studies of the anomeric effect it is the ΔH° values (rather than the $T\Delta S^\circ$ -dependent ΔG° values) that correlate with the steric, polar, and stereoelectronic interactions of interest. We therefore deemed it necessary to evaluate the enthalpic and entropic contributions to the anomeric interaction involved in **1** and **5**.

2-(Diphenylphosphinoyl)-1,3-dithiane (**1**) and its conformationally fixed models (**9** and **10**, eq 4) were prepared according to the described procedure.^{5a}

(29) Franck, R. W. *Tetrahedron* **1983**, *39*, 3251.(30) Mikolajczyk, M.; Balczewski, P.; Wroblewski, K.; Karolak-Wojciechowska, J.; Miller, A.; Wieczorek, M. N.; Antipin, M. Y.; Struchkov, Y. T. *Tetrahedron* **1984**, *40*, 4885.(31) Juaristi, E.; López-Núñez, N. A.; Valenzuela, B. A.; Valle, L.; Toscano, R. A.; Soriano-García, M. *J. Org. Chem.* **1987**, *52*, 5185.(32) (a) Cf.: Booth, H.; Dixon, J. M.; Khedhair, K. A.; Readshaw, S. A. *Tetrahedron* **1990**, *46*, 1625 and references therein. (b) See also: Juaristi, E.; Cuevas, G. *Tetrahedron* **1992**, *48*, 5019.

Scheme III

Table IV. Chemical Equilibrations of Ananameric **9** and **10** with Ethanolic Sodium Ethoxide at Various Temperatures (Eq 4)

temp (K)	<i>K</i> (10 / 9)	ΔG° (kcal/mol)
323	0.31	0.75
313	0.26	0.84
203	0.22	0.91
298	0.19	0.98
283	0.17	1.00
273	0.16	0.99

As previously reported,^{3,5a} comparison of the proton NMR of **9** and **10** with that of **1** (all three in CDCl₃) revealed a most interesting variation in the coupling constants of H(2) to phosphorus: 4.2, 15.0, and 6 Hz, respectively. While ²J_{H(2)/P} for the ananameric models remains unchanged at various temperatures, that for the mobile compound (**1**) shows a systematic change (Table III). On the assumption that ²J_{H(2)/P} in the mobile dithiane is the weighted average of those for the model diastereomers **9** and **10**,³³ $K = (J_{eq} - J) / (J - J_{ax})$, which yields the free energy differences at the temperatures of measurement.

This temperature-dependent behavior clearly reflects a substantial entropy effect. Indeed, a plot of ln *K* versus 1/*T* was linear (*r* = 0.978) and allowed for the derivation of ΔH° and ΔS° . The resulting values are $\Delta H^\circ = 2.21 \pm 0.17$ kcal/mol and $\Delta S^\circ = 4.27 \pm 0.59$ cal/K·mol (eq 1).

By comparison, ΔH° (POP₃) in cyclohexane is -1.96 kcal/mol, and $\Delta S^\circ = 2.6$ cal/K·mol (eq 2).⁶ Therefore, the present results confirm the existence of a large enthalpic S-C-P(O) anomeric effect in **1**: $2.21 + (0.6 \times 1.96) = 3.39$ kcal/mol. In fact, this favorable enthalpy term overcomes the entropic contribution, the equatorial conformer being of higher entropy.³⁴

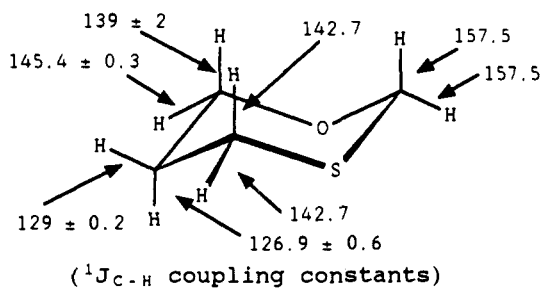
Essentially identical ΔH° and ΔS° values for equilibrium **9-ax** \rightleftharpoons **10-eq** were derived from a ln *K* versus 1/*T* plot (*r* = 0.964) obtained by chemical equilibration (EtO⁻Na⁺/EtOH) of these diastereomers at various temperatures (Table IV). The equilibrium data were derived by direct integration of the ³¹P NMR signals after equilibration from both sides. The resulting values are $\Delta H^\circ = 2.29 \pm 0.26$ kcal/mol and $\Delta S^\circ = 4.59 \pm 0.9$ cal/K·mol.

The similarity of the thermodynamic data obtained in ethanol and chloroform is striking, but is in agreement with previous observations,^{5a} which suggested that less polar media do not necessarily give rise to a stronger S-C-P(O) anomeric effect.

In contrast with 1,3-dithian-2-yl-diphenylphosphine oxide (**1**), where a substantial entropic contribution favors the equatorial isomer ($\Delta S^\circ = 4.27 \pm 0.59$ cal/K·mol; eq 1), the spectroscopic behavior of **5** in the 258–318 K temperature range shows essentially invariable ²J_{H/P} coupling constants (Table V). Upon incorporation into Eliel's equation, this affords, of course, constant values for the equilibrium constant at various temperatures, indicating that ΔH° (eq 3) is ≈ 0 . From the comparison of $\Delta G^\circ_{300K} = 0.36$ and $\Delta G^\circ_{258K} = 0.31$ kcal/mol, a value for the entropy

(33) Also, it has to be assumed that the methyl substituents at C(4,6) have a negligible effect on the value of the coupling constant between the nuclei at C(2).

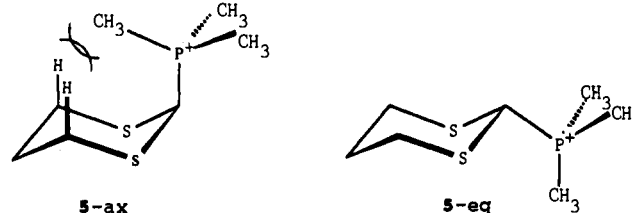
(34) Observation of Dreiding models suggests that an axial diphenylphosphinoyl group is conformationally constrained to rotamers with the P-O bonds above the cyclohexane ring, whereas an equatorial diphenylphosphinoyl substituent is apparently free to fully rotate around the C-P bond.

Table V. Temperature Effect on the ²J_{H/P} and ¹J_{C/P} Coupling Constants in **5** (in CD₂Cl₂)

temp (K)	² J _{H/P}	¹ J _{C/P}
318	15.2	52.8
303	14.5	52.9
288	14.5	52.9
273	15.2	52.9
258	15.2	54.0

change in eq 3 is derived as $\Delta S^\circ = -1.19$ cal/K·mol.

For a "sphere-like" group such as the trimethylphosphonium group we had anticipated a similar number of populated rotamers (presumably three isoenergetic staggered conformers) in **5-ax** and **5-eq** and that ΔS° for eq 3 would therefore be near 0. However, the relatively small but definite negative ΔS° value (eq 3) indicates a greater entropy for **5-ax** than for **5-eq**. The interpretation we give to this result is as follows: the steric congestion of the methyl pointing inside the ring in **5-ax** is much greater than that experienced by any of the *P*-Me groups in the equatorial conformer. This brings the ground state in **5-ax** closer in energy to the transition state for rotation and renders the PMe₃ group more mobile (i.e., the group rotates more rapidly around the C(2)-P bond) than in **5-eq**.



Experimental Section

General. For a description of general experimental data, see ref 9.

1,3-Dithian-2-yltrimethylphosphonium Chloride (5). A 50-mL dry flask provided with a magnetic stirrer and a septum and containing 1 g (8.3 mmol) of recently sublimed 1,3-dithiane was flushed with nitrogen before the addition of 10 mL of dry benzene. A suspension of finely divided *N*-chlorosuccinimide in 10 mL of dry benzene was then added dropwise. The resulting mixture was stirred for 5 min, and the supernatant solution was transferred to another flask containing 8.75 mL of 1 M trimethylphosphine in THF (Aldrich). A white, hygroscopic precipitate formed immediately. The solvent was eliminated via a cannula, and the phosphonium salt was washed three times with dry diethyl ether. The excess ether was removed under a stream of dry nitrogen to afford 1.63 g (85% yield) of the desired product as a white, extremely hygroscopic solid, mp 276–281 °C. ¹H NMR: see Table I. ¹³C NMR: see Table II. ³¹P NMR (36.23 MHz, CDCl₃): δ 39.99.

(trans-4,trans-6-Dimethyl-1,3-dithian-2-yl)- and (cis-4,cis-6-Dimethyl-1,3-dithian-2-yl)-rel-2-trimethylphosphonium Chloride (6 and 7). One gram (6.7 mmol) of *cis*-4,6-dimethyl-1,3-dithiane¹⁷ was treated with NCS and trimethylphosphine according to the procedure described for **5**. A 58:42 mixture of the expected products **6** and **7** was obtained in 83% yield (1.45 g), mp 280–283 °C. ¹H NMR spectra: see Table I. ¹³C NMR spectra: see Table II. ³¹P NMR (36.23 MHz, CDCl₃): **6** δ 42.46; **7** δ 35.69.

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