# Conformational Preference in 1,3-Dithianes Containing 2-Phosphoryl, -(thiophosphoryl), and -(selenophosphoryl) groups. Chemical and Crystallographic Implications of the Nature of the Anomeric Effect

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The operation of the anomeric effect in all the title compounds studied was found. The magnitude of the anomeric effect was found to be larger than 10 kJ/mol. Crystallographic, spectroscopic, and thermodynamic data suggest that the $n_S$–$\sigma^*_{C-P}$ hyperconjugative interaction is one of the factors responsible for the anomeric effect. The second interaction stabilizing the axial position of phosphorus can be P=Y···H(4 or 6) hydrogen bond formation. Some other interactions are also possible, namely $\sigma_{C(4,6)-S}$–$\sigma^*_{C(2)-P}$ (preferring the equatorial position of phosphorus) and $\sigma_{C(4,6)-S}$–$\pi^*_{P=Y}$ hyperconjugations and the $n_S$–$n_Y$ repulsions. The latter interaction was also proposed as MO counterpart of lone pair–lone pair repulsions suggested by molecular mechanics calculations. It was proved that various conformation probes can afford different equilibrium constants, if weighted average method and conformationally fixed models are applied. Most of the physical quantities are dependent on the alkyl substitution in the 1,3-dithiane ring. Thus, the relevant procedure for the selection of conformational probe was presented. Since the γ-effect value in $^{13}C$ NMR spectra was found to be very sensitive to the position of a substituent connected with the anomeric carbon atom of 1,3-dithianes, it was applied as a conformational probe. A long range $^4J_{C-P}$ coupling constant in the $^{13}C$ NMR spectra and $^{31}P$ spin-lattice $T_1^{DD}$ relaxation times suggest the existence of close contact(s) between a heteroatom Y (Y = O, S, Se) connected with the axial phosphorus P=Y and axial protons H(4,6) in the 1,3-dithiane ring. Crystallographic data show that the distance from Y to one of these protons is usually much smaller than to the other one and smaller than the sum of H,Y van der Waals radii. The possibility of H···Y hydrogen bond formation is discussed.

## Introduction

The anomeric effect[1,2] in heteroanes containing various substituents connected with the anomeric carbon atom has usually been interpreted (at least in part) in terms of negative hyperconjugation, and such a point of view is still receiving experimental support.[3-9]

In 1982, Juaristi *et al.*[10] found that 2-(diphenylphosphinoyl)-1,3-dithiane exists in the axial form both in a solution and in the solid state. This finding was significant not only because it constituted the first account of the existence of an anomeric interaction between sulfur and phosphorus (the anomeric effect of the dimethoxyphosphoryl group in a pyranose ring had already been established by Thiem *et al.*[11]) but also because geometrical parameters in the crystal did not come up to expectations based on $n_S$–$\sigma^*_{C-P}$ negative hyperconjugation.[12,13] Contrary to expectations, the equatorial C–P bond was even longer (by 0.015 Å) than the axial one (see Figure 1). Thus, the bond length changes in this system suggested to Juaristi *et al.*[12,13] that $n_S$–$\sigma^*_{C-P}$ interaction is rather negligible.

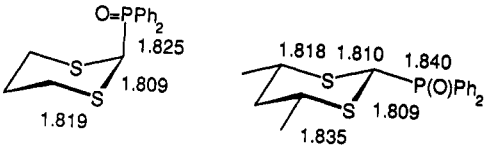


**Figure 1.** Selected bond lengths in 2-(diphenylphosphinoyl)-1,3-dithianes (in angstroms; taken from refs 12 and 13).

Such opinion seemed to be supported by the lack of the anomeric H/D isotope effect on the conformational equilibrium in the 1,3-dithiane ring ($\Delta G° = 0 \pm 5$ J/mol).[14] Moreover, Anet and Kopelevich[14] found identical stretching frequencies for the axial and equatorial C–D bonds. However, as was found in *ab initio* studies by Wolfe *et al.*[15,16] the observed differences in stretching frequencies between 1,3-dioxane, 1,3-dithiane, and stretching frequencies between 1,3-dioxane, 1,3-dithiane, and cyclohexane systems result from an interplay of several factors, with $n_Y$–$\sigma^*_{C-D(H)}$ and $\sigma_{C(4)-Y}$–$\sigma^*_{C-D(H)}$ hyperconjugations in 1,3-dioxane and 1,3-dithiane (Y = O, S) and $\sigma_{C-H}$–

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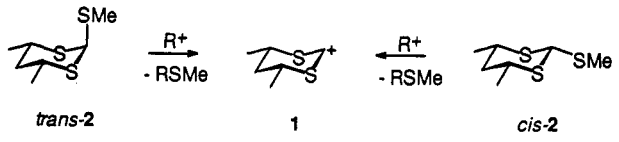
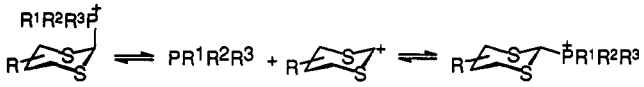
**Scheme 1**




*trans*-2 1 *cis*-2

**Scheme 2**




3-ax 4 5 3-eq

$\sigma^*_{C-D(H)}$ and $\sigma_{C-C}-\sigma^*_{C-D(H)}$ hyperconjugations in cyclohexane among the most important interactions. As far as the H/D isotope effect on the conformational equilibrium in 2-deuterio-1,3-dithiane is concerned, Wolfe and Kim showed[16] than an analysis which emphasizes C–H (C–D) stretching would not account for the observations. It must be noted that the importance of $\sigma_{C(4)-Y}-\sigma^*_{C-D(H)}$ hyperconjugation in the 1,3-dithiane ring has recently been confirmed by Juaristi and Cuevas on the basis of the reverse Perlin effect observed for all $^1J_{C-H}$ coupling constants.[17]

It might be expected that protic solvents would influence the difference in magnitude of $^1J_{C-H(2)}$ coupling constants in 1,3-dithiane by lowering the energy of the lone electrons of sulfur and thereby decrease the effectiveness of the $n-\sigma^*_{C-H}$ interaction.[18] However, Bailey *et al.*[18] found that protic solvents do not attenuate the difference in magnitude of $^1J_{C-H(2)}$ coupling constants in 1,3-dithiane. This observation led Bailey *et al.*[18] to the conclusion that factors other than those based on $n-\sigma^*$ interactions are responsible for the difference in magnitude of $^1J_{C-H(2)}$ for the axial and equatorial C–H(2) bonds.

Recently, Caserio *et al.*[19] found an almost equal rate of formation of *cis*-4,6-dimethyl-1,3-dithian-2-yl cation (1) from the appropriate 2-methylthio derivatives *trans*-2 and *cis*-2 under FT-ICR conditions in the gas phase (Scheme 1). This finding might be interpreted as contrary to expectations based on the $n_S-\sigma^*_{C-S}$ hyperconjugation.[20] It must be stressed, however, that applicability of the antiperiplanar lone pair hypothesis[21] should be assumed at first. Our studies on the S–C–P$^+$ systems have shown[22] that both the C–P bond breaking in 2-[(methylthio)-phosphonio]-1,3-dithianes **3**, ($R^1$ = SMe, $R^2$, $R^3$ = Ph; Scheme 2) and formation in 2-phosphonio-1,3-dithianes **3** ($R^1$, $R^2$, $R^3$ = Ph, Me, SMe), from phosphine **4** and cation **5**, in solution, do not fulfill the requirements of the antiperiplanar lone pair hypothesis.[21] Therefore, a comparable rate of heterolysis of the exocyclic axial and equatorial bonds cannot be *a priori* treated as evidence against the $n_S-\sigma^*_{C-P}$ (or $n_S-\sigma^*_{C-S}$ in Caserio systems) negative hyperconjugation in the transition state, without considering a nature of the transition state. Since the relevant transition states in the CSCP system are late,[22] the above kinetic results *are not against* the $n_S-\sigma^*_{C-P}$ hyperconjugation and may be best interpreted in terms of conformational adjustment.[2b,22]

The energy $\Delta E_{IS}$ of the bond separation reaction[23] is considered to be a measure of the magnitude of the anomeric effect[2a,23-25] and/or negative hyperconjugation,[26,27] and a low $\Delta E_{IS}$ for second-row atoms (e.g., Cl, S, and P)[23] has usually been interpreted in terms of the negligible participation of hyperconjugative mechanisms in the origin of the observed anomeric effects. However, *ab initio* molecular orbital calculations[28] show that the total energy difference between the *sc* and *ap* conformers of, e.g., $ClCH_2SH$ (11.1 kJ/mol) is close to the difference in magnitudes of *stabilizing* (negative hyperconjugation) orbital interactions, i.e., 11.7 kJ/mol. Therefore, though $\Delta E°_{IS}$ is negative ($\Delta E°_{IS}$ = 5.4 kJ/mol and −14.6 kJ/mol in *sc* and *ap* conformations of $ClCH_2SH$, respectively[23]), we really deal with the anomeric effect and negative hyperconjugation as an origin of this effect in $ClCH_2SH$. The only reason for the misunderstanding mentioned above may be the predilection of most workers to use $\Delta E_{IS}$ values as a measure of anomeric interactions. Since initial molecular orbital calculations were (for obvious reasons) devoted to interactions between first-row elements, for which $\Delta E_{IS}$ is strongly positive, the importance of *destabilizing* interactions has been underestimated.

Since acyclic and cyclic *S,S*-dithioacetals of formylphosphonates had just been studied[29-32] in our laboratory, it soon became clear that the dimethoxyphosphoryl group, $(MeO)_2P{=}O$, just like the $Ph_2P{=}O$ one, tends to be situated axially, when attached to the anomeric carbon atom of 1,3,5-trithiane[33] and 1,3-dithiane[34] rings. This prompted us to study a larger set of SCP-containing derivatives in the hope that this larger set of organophosphorus substituents, which differ in "size", electron-withdrawing, and other special properties, e.g., the presence of $\pi$-electrons, would provide us with the possibility to reveal the factors responsible for the preferred conformation of the title compounds.

In 1987, we presented our preliminary results on $(MeO)_2P{=}O$-, $Ph_2P{=}O$-, $Ph_2P{-}S$-,[35] and $Ph_2P{=}Se$[36]-substituted 1,3-dithianes, which indicated an anomeric effect in the CSCP systems studied. The same year Juaristi *et al.* in their independent studies[37] estimated the magnitude of the anomeric effect involving the $Ph_2P{=}S$ group in 1,3-dithiane as ca. 16 kJmol$^{-1}$. Interestingly, the anomeric effect in the CSCP system has also been found

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for the $Ph_2P{=}S$ group at the C(2) atom of the 1,3,5-trithiane ring[38] and for some other phosphorus-containing substituents at the C(2) atom of 1,3-dithiane[39-43] and oxathiane[39,44,45] ring. It should be noted that the anomeric effect involving sulfur has also been found in variously 2-X-substituted thianes,[1a,46,47] 1,3-oxathianes,[48,49] 1,3-dithianes,[4,5,48,50-55] and 5-methyl-5-aza-1,3-dithiacyclohexanes[56] and interpreted (at least in part) in terms of $n_S$–$\sigma^*_{C-X}$ negative hyperconjugation by Pinto *et al.*,[57,58] Tschierske *et al.*,[5] and Juaristi *et al.*[42,43,56] Such an interpretation has been based on the dependence of axial preference on electron-withdrawing properties of the 2-X substituent. However, the problem of the nature of the anomeric effect in the SCP system is still a matter of controversy (*vide infra*).

In this paper, we would like to present full results of our studies on various 1,3-dithianes **6–13** containing $R^1R^2P{=}Y$ ($R^1$, $R^2$ = Ph, Me) groups at the C(2) atom and

| Ring | Substituent: P(OMe)$_2$ | P(OEt)$_2$ | P(OCH$_2$CF$_3$)$_2$ | PPh$_2$ | PPh$_2$ | PPhMe | PMe$_2$ | PPh$_2$ |
|---|---|---|---|---|---|---|---|---|
| | 6a | 7a | 8a | 9a | 10a | 11a | 12a | 13a |
| | 6b | 7b | 8b | 9b | 10b | 11b | 12b | 13b |
| | 6c | 7c | 8c | 9c | 10c | 11c | 12c | 13c |
| | 6d | 7d | 8d | 9d | 10d | 11d | 12d | 13d |
| | 6e | 7e | 8e | 9e | 10e | 11e | 12e | 13e |
| | 6f | 7f | 8f | 9f | 10f | 11f | 12f | 13f |

our interpretation of the anomeric effect involved. Both conformationally "stiff" (**c–f**) and labile (**a, b**) compounds

**Scheme 3**

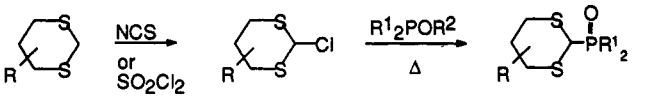
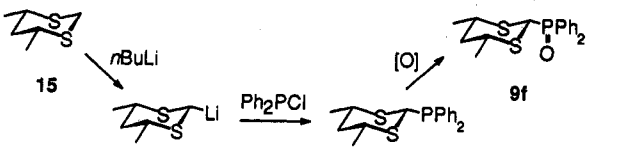



**Table 1. Results of the Synthesis of 6–9 *via* the Arbuzov Reaction (Scheme 3)**

| | yield (%) | | | | |
|---|---|---|---|---|---|
| | **6** | **7** | **8**[a] | **8**[b] | **9** |
| **a** | | | | | 85.4 |
| **b** | 55.0 | 45.9 | 41.4 | | 60.1 |
| **c** | 79.3 | 65.2 | 50.7 | 58.5 | 53.2 |
| **d** | 12.6 | 15.3 | 10.4 | 16.6 | 34.7 |
| **e** | 58.9 | 58.7 | | 28.7 | |
| **f** | 13.0 | 10.5 | | 8.5 | |

[a] $R^1 = CF_3CH_2O$, $R^2 = CF_3CH_2$. [b] $R^1 = CF_3CH_2O$, $R^2 = SiMe_3$.

**Scheme 4**




were obtained, and they were studied by means of chemical methods, NMR and IR spectroscopy, and X-ray crystallography.

## Results and Discussion

**1. Synthesis of Model Compounds.** The synthesis of the phosphonates **6b–f**, **7b–f**, and **8b–f** was accomplished by the method described earlier,[30] which involves the reaction of appropriate 2-chloro-1,3-dithiane with trivalent phosphorus compound (Scheme 3). In the case of 5-*tert*-butyl-1,3-dithiane (**14**) and *cis*-4,6-dimethyl-1,3-dithiane (**15**), two diastereomeric products are formed, the more stable isomers with axial phosphoryl groups (**c** and **e**, respectively) being formed in excess (Table 1). Interestingly, it makes almost no difference whether we use tris(2,2,2-trifluoroethyl) phosphite (**16**) or bis(2,2,2-trifluoroethyl) trimethylsilyl phosphite (**17**) to synthesize **8c,d**, presumably owing to high reactivity of $\alpha$-chlorosulfides[59] towards nucleophilic reagents.

The preparation of 2-(diphenylphosphinoyl)-1,3-dithianes *via* the reaction between 2-lithio-1,3-dithiane and chlorodiphenylphosphine and subsequent spontaneous oxidation of the resultant phosphine (Scheme 4) was described by Juaristi *et al.*[12,13] This reaction occurs highly stereoselectively and affords only **9f**, if **15** is used as a substrate. Nevertheless, the overall yield of this reaction is low (40% for **9a**[12] and 21% for **9f**[13]), and in each case chromatographic purification is necessary. Since the Arbuzov reaction involving 2-chloro-1,3-dithianes and trialkyl phosphites has been known to proceed in a good yield (*vide supra*), we decided to prepare the compounds **8a–d** following the procedure applied for **6c,d**, using isopropyl diphenylphosphinite (**18**) as a P(III) reaction partner (Scheme 3, $R^1$ = Ph, $R^2$ = *i*-Pr). The results are collected in Table 1. It is evident that the yields are much better than those reported by Juaristi *et al.* Moreover,

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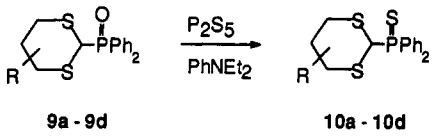
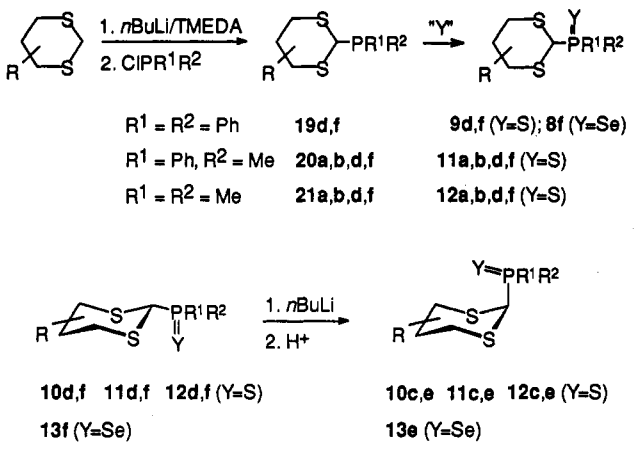
**Scheme 5**




**Scheme 6**



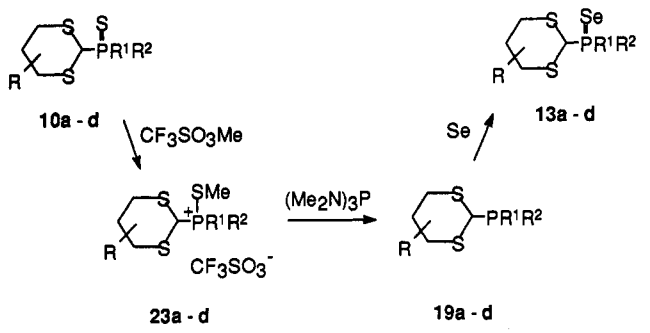

for **9a** and **9b** ordinary crystallization is sufficient to obtain the desired compounds of analytical purity. Though chromatographic resolution is necessary for **9c,d**, it can be easily performed using a chloroform–ethyl acetate mixture as an eluent.

The conversion of the phosphine oxides **9a–d** into the corresponding sulfides **10–d** was achieved with the use of phosphorus pentasulfide in refluxing benzene (Scheme 5) in 68.5, 56.4, 71.5, and 72.2% isolated yield, respectively. It should be emphasized that for **9c** and **9d** this reaction occurs highly stereoselectively (epimerization at C(2) was not observed). This method has also the virtue of simplicity because chromatographic purification can be avoided.

Since other phosphine oxides were not available, the synthesis of **10f, 11a,b,d,f** and **12a,b,d,f** was accomplished following the procedure of Juaristi *et al.*[37] (Scheme 6). An appropriate 2-lithio-1,3-dithiane was reacted with chlorophosphine to give the relevant phosphine **19–21** in a highly stereoselective manner. In the case of the conformationally fixed dithianes **14** and **15** only the phosphine-containing equatorial phosphino group is formed. The addition of sulfur to it results in the formation of the desired sulfide. In order to convert *all*-equatorial sulfides **10d,f, 11d,f,** and **12d,f** into their epimers **10c,e, 11c,e,** and **12c,e**, respectively, we followed the deprotonation–protonation methodology of Eliel *et al.*[60] (applied to convert **9e** into **9f** by Juaristi *et al.*[12]), as is pictured in Scheme 6. It must be noted that the protonation with aqueous ammonium chloride, to obtain **11c,e** and **12c,e** (unlike **10e**), should be done not later than 10 min after the addition of *n*-butyllithium; otherwise, considerable decomposition of the anion occurs.

Phosphine selenides **13a–f** were obtained by the addition of selenium to the appropriate phosphines **19a–f**. In the case of **13f** we followed the method applied for the synthesis of the sulfide **10f** (Scheme 6), and the product was isolated in almost 70% yield. However, its conversion into **13e** using the deprotonation–protonation procedure (Scheme 6) is plagued by very low yield (18.4%), and considerable

**Scheme 7**




amount (23.8%) of the substrate was recovered. Therefore, we focused our attention on a reaction that could afford phosphines containing an axial phosphino group. We assumed that the addition of selenium would occur stereoselectively to give **13c,e** in a high yield. Such a method of synthesis of phosphines has been developed in our group[61] and is based on the conversion of (methylthio)-phosphonium salts into phosphines in the reaction with tris(*N,N*-dimethylamino)phosphine (**22**) (Scheme 7). Methylthiophosphonium salts are accessible *via* alkylation of the appropriate sulfides with methyl trifluoromethanesulfonate (methyl triflate). Following this method, selenides **13a,b** were obtained in 65.4 and 74.6% yield, respectively (Scheme 7). However, conformationally fixed **10c,d** always gave a mixture of selenides **13c,d**. Since the ratio of diastereomeric selenides **13c,d** was found to be practically equal to the ratio of the related phosphines **19c,d** (9:44 and 9:44 in experiment 1; 40:9 and 45:10 in experiment 2), it might be concluded that the addition of selenium occurs highly stereoselectively. Hence, the low selectivity of the method, as a whole, is entirely due to spontaneous epimerization[62] of diphenyl(methylthio)-phosphonium salts **23**. Nevertheless, since the overall yield of **13c,d** is high (30.5 + 50.2 = 80.7%) and the products are easily separable, this method seems to constitute a good way both to conformationally labile and fixed **13a–d** (and perhaps **13e,f**).

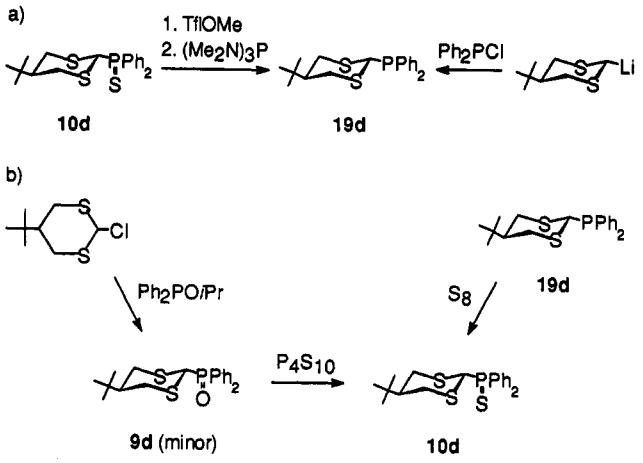
**Configurational Assignments.** The problem of stereochemical relations between diastereomeric products under scrutiny was solved using three methods: chemical correlation, X-ray structure determination, and NMR spectroscopy. It should be noted that for all compounds **6–13** with phosphorus located axially (groups **c** and **e**) larger $R_f$ values on TLC chromatograms on silica gel were always observed than for compounds **d** and **f** in all eluents applied (various mixtures of benzene, chloroform, dichloromethane, ethyl acetate, methanol, 2-propanol, *n*-heptane, and *n*-hexane).

**Chemical Correlation.** The reaction between 2-lithio-1,3-dithianes and chlorodiphenylphosphine and subsequent addition of oxygen or sulfur is known[12,13,37] to proceed stereoselectively to afford, in the case of conformationally fixed models, compounds containing phosphorus in the equatorial position. Hence, all phosphines, thus obtained, contain the phosphino group in the equatorial position. Consequently, the thio- or selenophosphoryl group in each diastereomeric compound obtained from 2-lithio-1,3-dithiane, the appropriate chlorophosphine, and sulfur (or selenium) is located equatorially. This conclusion is supported by the fact that the deprotonation–protonation sequence, when applied to such

(60) Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807.

(61) Omelańczuk, J.; Mikołajczyk, M. *Tetrahedron Lett.* **1984**, *25*, 2493.
(62) Graczyk, P.; Mikołajczyk, M. *Tetrahedron Lett.* **1991**, *32*, 7329.

**Scheme 8**




a compound, affords its isomer (they are mutually interconvertible by epimerization), which should[60] possess the thiophosphoryl group in an axial position (group **c**, or **e**).

The alkylation–desulfurization sequence applied to **10d** gives, as a main product, the phosphine identical (with regard to NMR spectra) with the phosphine **19d** derived from the appropriate 2-lithio-1,3-dithiane and chlorophosphine (Scheme 8a). Therefore, this sequence preserves the configuration at C(2). Hence, diastereomeric salts **23** (Scheme 7) and the related phosphines **19** have the same configuration as the starting 2-thiophosphoryl derivatives **10**.

The configuration of **9c,d** can be related to their thiophosphoryl analogs **10c,d** under the reasonable assumption that the reaction of phosphine oxide with phosphorus pentasulfide does not influence the configuration at C(2). Since a minor product of the Arbuzov reaction between 5-*tert*-butyl-2-chloro-1,3-dithiane and $Ph_2POiPr$ (**18**), upon treatment with phosphorus pentasulfide, affords product indistinguishable from the one obtained from **19d** (Scheme 8b), its configuration is *trans* (**9d**). Consequently, the major product can be identified as **9c**.

**X-ray Structure Determination.** In order to confirm configurational assignments obtained by other methods (including NMR) and to study structural features that may be connected with a mechanism responsible for conformational behavior of the compounds under investigation, single-crystal X-ray structure determination was performed for **6c,d,e**, **8c,d**, **9c,d**, **10c,d,f**, and **13c,d**.[63] It must be noted that X-ray structural data for **9a**[10] and **9f**[13] have been reported by Juaristi *et al.* (see Figure 1).

All the conclusions drawn on the basis of chemical correlation were confirmed. In addition, the configuration of diastereomeric phosphonates **6c,d,e,f** and **8c,d** was established. Thus, the main product of the Arbuzov reaction has, in all cases, the phosphoryl group oriented axially.

**NMR Spectroscopy. $^{13}C$ NMR.** The usefulness of carbon $^{13}C$ NMR spectroscopy in the structure determination of various heteroanes is now well established.[64] We found[35] that the $^3J_{C-P}$ coupling constant and γ-effect[65–67] values (the latter calculated on the basis of chemical shifts

(63) Experimental details of X-ray analyses will be published elsewhere.
(64) Eliel, E. L.; Pietrusiewicz, K. M. In *Topics in Carbon-13 NMR Spectroscopy*; Levy, G. C., Ed.; Wiley-Interscience: New York, 1979; Vol. 3, p 171.

**Table 4. γ-Effect (ppm) in $^{13}C$ NMR[a] Spectra of 6–13 and the Related $^3J_{C-P}$ (Hz) Values**

| | 6 | 7 | 8 | 9 | 10 | 11[b,c] | 12[b] | 13 |
|---|---|---|---|---|---|---|---|---|
| | | | | γ-Effect | | | | |
| **a** | −4.15[d] | | | −2.94 | −1.51 | −1.68 | −0.30 | −0.96 |
| **b** | −3.96 | −3.78 | −4.63 | −2.94 | −1.57 | −1.95 | −1.25 | −1.16 |
| **c** | −4.18 | −4.20 | −4.14 | −3.65 | −4.56 | −4.80 | −4.73 | −4.80 |
| **d** | 0.68 | 0.77 | −1.04 | 1.24 | 1.58 | 1.12 | 1.10 | 1.70 |
| **e** | −4.30 | −4.37 | −4.04 | −3.94[e] | −4.69 | −4.79 | −4.84 | −4.96 |
| **f** | 1.49 | 1.49 | 1.59 | 2.04[e] | 2.21 | 1.80 | 1.69 | 2.29 |
| | | | | $J_{C-P}$ Values | | | | |
| **a** | 0[d] | | | 0 | 3.5 | 3.1 | 4.4 | 4.2 |
| **b** | 0 | 0 | 0 | 0 | 3.4 | 4.4 | 4.6 | 3.7 |
| **c** | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **d** | 8.7 | 8.7 | 7.0 | 6.5 | 7.3 | 7.6 | 7.6 | 7.2 |
| **e** | 0 | 0 | 0 | 0[e] | 0 | 0 | 0 | 0 |
| **f** | 9.2 | 9.3 | 9.8 | 7.3[e] | 7.5 | 7.4 | 7.4 | 7.4 |

[a] SF = 75.47 MHz, *T* 296 K, in $CDCl_3$ unless otherwise stated. [b] In $CD_2Cl_2$. [c] Mean value if C(4) and C(6) are anisochronous. [d] Based on data in ref 34. [e] Based on data in ref 12.

in **6–13** and the parent 1,3-dithianes, which are collected in Tables 2 and 3, respectively; supplementary material) are the most informative physical quantities for this class of compounds. It should be pointed out that the γ-gauche upshielding effect in $^{13}C$ NMR spectra has also been used extensively by other researchers for the assignment of the configuration at C(2) in these and analogous systems.[37,55,56]

For all 1,3-dithiane derivatives of established configuration (e.g., on the basis of X-ray structure determination), with phosphorus located axially, the γ-effect value is negative, about −3 to −4 ppm (Table 4). If phosphorus occupies the equatorial position, the γ-effect value is positive (except for **8d**) and equals 1–2 ppm. As will be shown below, **8d** is not conformationally homogeneous in solution, and the observed γ-effect contains contributions from other conformers (e.g., twist-boat). The coupling constant $^3J_{C-P}$ (its absolute value, Table 4) in the former case is zero but equals about 7–8 Hz when phosphorus is situated equatorially, in good agreement with expectations based on the *anti* arrangement of the CSCP system.

Since the structural dependence of $^3J_{C-P}$ and γ-effect values has been confirmed, the configuration for the remaining diastereomeric compounds **7c,d,e,f** and **8e,f** can be proposed on the basis of their $^{13}C$ NMR spectra.

A long-range $^5J_{C-P}$ coupling constant of about 2 Hz, between the quaternary carbon of the *tert*-butyl group and phosphorus in 5-*tert*-butyl-1,3-dithiane derivatives (Table 5; supplementary material) can be regarded as an additional proof of the equatorial positioning of both *tert*-butyl and phosphorus (zig–zag-type coupling, Figure 2a). This coupling can be observed for all compounds belonging to the group **d**. It should be mentioned, however, that for **8d** its magnitude is smaller (1.2 Hz) for the reasons quoted above.

For diasteromeric compounds **6–13**, containing phosphorus located axially (groups **c** and **e**), one can observe another long-range $^4J_{C-P}$ coupling constant of 1.7–3.3 Hz between the carbon C(5) and phosphorus atom (Table 5, (supplementary material), Figure 2b). Such coupling is interesting, since the arrangement of the CCSCP system is not a zig–zag type. One may guess that the key role is

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(66) Pandia Rajan, K.; Manimekalai, A. *Magn. Reson. Chem.* **1991**, *29*, 904.
(67) Clemans, G. B.; Alemayehu, M. *Tetrahedron Lett.* **1993**, *34*, 1563.

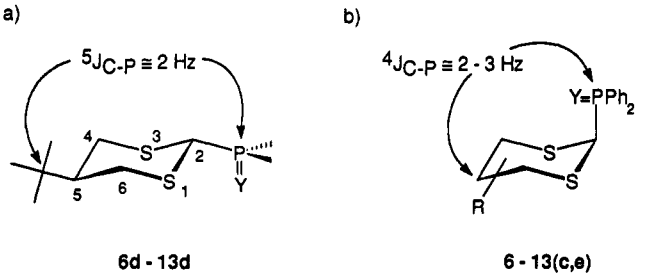



**Figure 2.** Long-range $J_{C-P}$ coupling constants in (a) 2-P-substituted 1,3-dithianes **6d-13d** and (b) axial 2-P-substituted 1,3-dithianes **6-13(c,e)**.

played by a heteroatom connected to phosphorus.[68] Taking into account that all the relevant X-ray structures contain a heteroatom placed over the heteroane ring and the distance between this heteroatom and the axial H(4) and H(6) protons is comparable with the sum of van der Waals radii, one may conclude that the spin information is also transmitted *via* heteroatom and the axial H(4) and H(6) hydrogens.

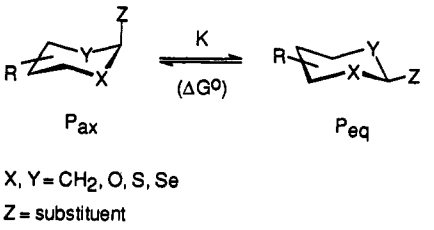
One can find a larger number of coupling constants and chemical shifts in $^{13}C$ NMR spectra which are dependent on the position of phosphorus with regard to the 1,3-dithiane ring. They are collected in Table 6 (the chemical shifts of anomeric carbons and coupling constant between anomeric carbons and phosphorus; supplementary material), Table 7 (the chemical shifts of aromatic carbons; supplementary material), and Table 8 (coupling constants between aromatic carbons and phosphorus; supplementary material), and some of them will be discussed later as possible conformational probes.

**$^1$H NMR.** Let us consider *cis*-4,6-dimethyl-1,3-dithiane derivatives (**e** and **f**). In the upfield part of the $^1H$ NMR (300.13 MHz, $CDCl_3$ or $CD_2Cl_2$) spectra one can observe a doublet, due to methyl groups ($\delta$ 1.1–1.3 ppm, cf. Table 9; supplementary material), and a doublet of triplets ($\delta$ 1.2–1.3 ppm, Table 10; supplementary material), which can be attributed to the $H(5)_{ax}$ proton. If phosphorus is located equatorially, $H(5)_{eq}$ appears as a ddt, and the relatively large coupling constant of about 2–4 Hz (Table 11; supplementary material) can be ascribed to a long-range coupling $^5J_{H-P}$ with phosphorus (cf. $^5J_{C-P}$ in the $^{13}C$ NMR spectra of dithianes **d**). When phosphorus occupies the axial position such a coupling is not observed, and $H(5)_{eq}$ gives rise to a doublet of triplets. It should be noted that since the chemical shift difference between $H(5)_{ax}$ and $H(5)_{eq}$ is always above 0.6 ppm, and between $H(5)_{eq}$ and $H(4)_{ax}$ above 0.8 ppm at SF = 300.13 MHz (weak coupling; $\Delta\nu > 180$ Hz, maximum $J \cong 14$ Hz), a first-order approximation, for the analysis of the spectra, can be applied.

Axial attachment of phosphorus is responsible for the well-known,[10,12,34] considerable deshielding of axial $H(4,6)_{ax}$ protons, which resonate at $\delta$ about 3.5–4.2 ppm (Table 9; $\delta$ 2.83 ppm in unsubstituted **15**). Long-range coupling $^4J_{H-P}$ = 1–2 Hz (Table 12; supplementary material) between $H(4,6)_{ax}$ and P may serve as an additional probe for the axial position of phosphorus.

In the $^1H$ NMR spectra of 5-*tert*-butyl-1,3-dithiane derivatives having *cis* configuration (**c**), the observed coupling constants for the H(5) proton, $^3J_{anti} \cong 11.6$ Hz and $^3J_{gauche} \cong 2.4$ Hz (Table 11; supplementary material), strongly support the equatorial position of the *tert*-butyl group and allow one to make an unambiguous assignment of $H(4,6)_{ax}$ and $H(4,6)_{eq}$ resonances, with axial protons shifted downfield. Obviously, nonequivalence of H(4) and H(6) can be anticipated for **11**, and it is really observed (0.02–0.03 ppm for axial and 0.13 ppm for equatorial protons, cf. Table 9; supplementary material). As in group **e**, the axial protons in **c** are coupled with phosphorus with a small coupling constant of about 1–2 Hz (Table 12; supplementary material). If phosphorus is located equatorially the chemical shift difference $\Delta\delta$ between $H(4,6)_{ax}$ and $H(4,6)_{eq}$ is much smaller (0.2–0.4 ppm; Table 9; supplementary material) and the equatorial protons, which resonate at lower field, are coupled with phosphorus with a larger constant $^4J_{H-P}$ = 2.7–5.0 Hz (Table 12; supplementary material), which additional supports the *trans* arrangement of the whole system.

**Scheme 9**




The problem of magnitude of *anti* and *gauche* coupling constants is very important when conformational homogeneity of 2,5-disubstituted 1,3-dithianes is discussed.[69] Now, it can be mentioned that for **8d** the coupling constants $^3J_{anti}$ = 10.34 Hz and $^3J_{gauche}$ = 3.57 Hz strongly support the view (based on $\gamma$-effect value in $^{13}C$ NMR) that this compound is, in fact, not conformationally homogeneous.

The chemical shifts of the anomeric proton $\delta_{H(2)}$ and the coupling constants between H(2) and phosphorus in **6–13** are collected in Table 13 (supplementary material).

**$^{31}$P NMR.** We found that the separation of dipole–dipole from the total spin-lattice relaxation of $^{31}P$ nuclei can be applied for unambiguous assignment of configuration of the compounds under investigation. In particular, the relaxation times $T_1^{DD}$ stemming from dipolar interactions are smaller for compounds with phosphorus located axially.[70]

It should be mentioned that $^{31}P$ NMR spectra can be expected to reflect the ratio of isomers quantitatively, owing to close rates of relaxation of isomers **c** and **d**. The latter problem is especially important as far as the results of equilibration, followed by $^{31}P$ NMR spectra, are concerned.

The chemical shifts for the compounds studied are collected in Table 14 (supplementary material).

**Conformation of 1,3-Dithiane and 5,5-Dimethyl-1,3-dithiane Derivatives in a Solution.** The position of conformational equilibrium of the conformationally labile compound (Scheme 9) may be estimated in several ways using NMR methods. A direct and usually most reliable[71,72] method is based on integration of low-temperature

(68) If it is absent, as in **19–21**[40] and 2-phosphonio-1,3-dithianes,[40,41] the coupling is not observed.

(69) Graczyk, P. P.; Mikołajczyk, M. *Magn. Reson. Chem.* **1992**, *30*, 1261.

(70) Mikołajczyk, M.; Wróblewski, K.; Graczyk, P. P. *Magn. Reson. Chem.* **1992**, *30*, 883.

(71) Booth, H.; Griffiths, D. V. *J. Chem. Soc., Perkin Trans. 2* **1975**, 111.

(72) Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278.

**Table 15. Conformational Equilibrium Constants $K$ for 1,3-Dithiane Derivatives a and b Calculated *via* the Weighted Average Method (See Text)**

| | ref pair | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| compd | c,d | e,f | c,d | e,f | c,d | e,f | c,d | e,f | c,d | e,f | c,d | e,f |
| **6a** | *a* | *b* | 0.25 | *a* | 0.025 | 0.026 | *b* | *b* | 0.24 | *a* | *a* | *a* |
| **6b** | *b* | *a* | 0.14 | *a* | 0.059 | 0.063 | *b* | *b* | 0.14 | *a* | *a* | *a* |
| **7b** | *a* | *a* | 0.17 | *a* | 0.092 | 0.122 | *b* | *b* | 0.19 | *a* | *a* | 3.00 |
| **8b** | *a* | *a* | 0.022 | *a* | *a* | *a* | *b* | *b* | 0.006 | *a* | *a* | *a* |
| **9a** | 0.34 | 0.19 | 0.32 | *a* | 0.17 | 0.20 | *b* | *b* | 0.37 | *a* | 0.17 | *a* |
| **9b** | 0.27 | 0.14 | 0.24 | *a* | 0.17 | 0.20 | *b* | *b* | 0.30 | *a* | 0.44 | 0.18 |
| **10a**[c] | 1.73 | 0.90 | 1.99 | 0.26 | 1.07 | 0.89 | 0.88 | 0.88 | 1.28 | 0.23 | 0.56 | 0.93 |
| **10b**[c] | 0.79 | 0.44 | 0.92 | *a* | 0.96 | 0.81 | 0.70 | 0.70 | 1.24 | 0.21 | 1.21 | 1.64 |
| **10a** | 1.70 | 0.83 | 1.43 | 0.26 | 1.00 | 0.83 | 0.91 | 0.91 | 1.19 | 0.20 | 2.69 | 0.73 |
| **10b** | 0.77 | 0.40 | 1.03 | 0.06 | 0.91 | 0.83 | 0.91 | 0.83 | 1.22 | 0.21 | 9.52 | 1.28 |
| **11a** | 1.48 | 0.98 | 1.44 | 0.43 | 1.11 | 0.89 | 0.69 | 0.72 | 1.35 | 0.14 | 0.71 | 0.97 |
| **11b** | 0.63 | 0.49 | 0.98 | 0.20 | 0.93 | 0.76 | 1.38 | 1.47 | 1.24 | 0.11 | 1.15 | 1.42 |
| **12a** | 2.44 | 1.44 | 2.15 | 1.00 | 3.16 | 2.28 | 1.38 | 1.47 | 2.08 | 0.28 | 1.21 | 1.32 |
| **12b** | 1.48 | 0.94 | 1.43 | 0.61 | 1.48 | 1.22 | 1.53 | 1.64 | 2.04 | 0.27 | 1.41 | 1.50 |
| **13a** | 2.80 | 1.10 | 2.69 | 0.35 | 1.40 | 1.20 | 1.40 | 1.30 | 1.70 | 0.40 | 0.39 | 1.04 |
| **13b** | 0.83 | 0.37 | 1.27 | *a* | 1.30 | 1.10 | 1.10 | 1.00 | 1.68 | 0.39 | 1.27 | 1.94 |
| spec | $^1$H NMR | | | | | | $^{13}$C NMR | | | | $^{31}$P NMR | |
| probe | $^2J_{H-P}$ | | $\delta_{H(2)}$ | | $\gamma$-effect | | $^3J_{C-P}$ | | $\delta_{C(2)}$ | | $\delta$ | |

[a] Data $P$ for labile compound is out of range of the data for reference systems. [b] Quantity $P$ measured with too small accuracy. [c] In $CD_2Cl_2$.

$^{13}$C,[72-78] $^1$H,[4,76,77] $^{19}$F,[79] $^{31}$P,[35,37,38,41a,42] and $^{77}$Se NMR[4] spectra, when ring inversion is slow, and separate signals due to both conformers may be observed. Variable-temperature $^{13}$C[3,56,80-82] and $^1$H NMR[56,83] studies under the conditions of slow ring inversion have been used to derive the relevant $\Delta H°$ and $\Delta S°$ values. At intermediate temperatures line-shape analysis of NMR signals has been applied.[79-81] Nevertheless, these methods are not applicable at higher (room) temperatures.

In 1959, Eliel introduced a weighted average method[84] for studying conformational equilibria of conformationally labile compounds. This method is extremely useful for equilibria at higher temperatures. As far as the NMR spectra are concerned, each observed spectral parameter $P$ in a solution of conformationally labile compound (Scheme 9) is a weighted average of the values $P_{ax}$ and $P_{eq}$ characteristic for the axial and equatorial conformers, respectively, provided that the rate of interconversion is high enough. Such a situation occurs at room temperature since the ring inversion barrier for six-membered rings is relatively low. Therefore, this method has been widely applied in quantitative conformational analysis of variously substituted six-membered derivatives. As conformational probes, e.g., $^3J_{H-H}$,[9,85,86] $^3J_{H-D}$,[85] $^3J_{H-P}$,[87] chemical shift differences of geminal $Me_2C$ groups in $^1$H NMR,[14] $^{13}$C NMR chemical shifts,[4,88] "absolute" $^{13}$C NMR chemical shifts,[85] and NOE enhancement coefficients[85] have been applied. The values characteristic for individual conformers have been taken from low-temperature measurements or from model systems, which were intended to "imitate" particular conformers.

The weighted average method for the estimation of the conformational equilibria of mobile 2-P-substituted 1,3-diheteroanes was introduced in 1982 by Juaristi *et al.*[10] (for **9a**; reference systems **9e** and **9f**) with $^2J_{H(2)-P}$ as conformational probe. Since then they also used this[12,37,43] and other NMR parameters, which offered the necessary spread, namely chemical shift of the *ipso* carbon of the Ph group,[42] $\delta_{C(2)}$,[43] $\delta_{C(4,6)}$,[42,43] $\delta_{Me(4)}$ in $^{13}$C NMR,[44] $\delta_{31P}$,[43] and $^1J_{C(2)-P}$.[43] Usually, 2-P-substituted *cis*-4,6-dimethyl-1,3-dithiane derivatives served as reference systems. An analogous approach based on $\delta_{C(1)}$,[37,42,74] $\delta_{Me(4)}$ in $^{13}$C NMR,[74] and $\delta_{31P}$[42] has been applied by this group for 1-P-substituted cyclohexanes (with 4-*tert*-butylcyclohexane derivatives as reference).

The preferred conformation of 2-P-substituted 1,3-diheteroanes in a solution has been estimated quantitatively by us using $\gamma$-effect values in $^{13}$C NMR spectra,[40,41,73] a $^2J_{H(2)-P}$ coupling constant,[89] and a wide variety of other NMR parameters.[39] The results based on various quantities in $^1$H, $^{13}$C, and $^{31}$P NMR spectra as conformational probes $P$ for the title systems are collected in Table 15. It can be easily noticed that one may obtain very different equilibrium constants for a given compound which depend on the conformational probe P and reference system applied (**cd** *vs* **ef**). Interestingly, in most cases just the **ef** reference pair provides such an interval of $P_{ax}$ and $P_{eq}$ values that does not contain the observed $P$ for **a** or **b** derivatives (this situation is marked as footnote a in the Table 15). Compounds from this pair (**ef**) are really conformationally homogeneous, and hence the reason for such a situation can be ascribed only to the influence of the 4,6-methyl groups on the spectral properties of interest. In other words, conformationally fixed *cis*-4,6-dimethyl-1,3-dithiane derivatives imitate conformers of 1,3-dithiane and 5,5-dimethyl-1,3-dithiane derivatives rather imper-

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fectly, at least as far as $^2J_{H-H}$ and $\delta_{H(2)}$ in $^1H$ NMR and $\delta_{C(2)}$ in $^{13}C$ NMR spectra are concerned. It must be noted that the influence of 4,6-methyl groups in the 1,3-dithiane ring on $\delta_{C(2)}$[43] and $\delta_{C(4,6)}$[42,43] chemical shifts has been recognized by Juaristi *et al.*, and the relevant corrections have been employed.[90] Nevertheless, these corrections have been derived from chemical shift differences between 2-unsubstituted 1,3-dithiane and *cis*-4,6-dimethyl-1,3-dithiane, and their assumption is of doubtful validity.[92] It should also be noted that our results indicate a strong dependence between substitution at C(4,6) and the magnitude of the $^2J_{H(2)-P}$ coupling constant (e.g., $^2J_{H(2)-P}$ equal to 11.52 Hz in **10d**, 13.32 Hz in **10f**; 11.73 Hz in **13d**, 13.48 Hz in **13f**), in contrast to what has been assumed by Juaristi *et al.* (footnote 12 in ref 10 and footnote 17 in ref 12). Unfortunately, they have not checked the reliability of the probes using other methods, e.g., low variable-temperature measurements. The room-temperature weighted-average data have been applied by this group *in connection* with low single-temperature NMR data to derive thermodynamic parameters ($\Delta H°$ and $\Delta S°$) for conformational equilibria.[37,42,74] It should also be stressed that the agreement between equilibrium constants $K$ obtained by equilibration of diastereomeric models and $K$ for conformationally labile systems derived from the weighted average method (e.g., for **10a**, **10e**, and **10f**[37]) may be misleading. These values may differ markedly.[93]

In our opinion, 5-*tert*-butyl-1,3-dithianes (**cd**), though conformationally impure, are better reference systems than *cis*-4,6-dimethyl-1,3-dithianes (**ef**), presumably due to the very small influence of the 5-*tert*-butyl group on the discussed NMR spectral properties.[90,92] The fact that a given conformational probe $P$ really depends on alkyl substituents connected with the ring can be easily recognized if **cd** and **ef** systems give very diverse $K$ values. In such a situation this conformational probe must be rejected, and the desired values $P_{ax}$ and $P_{eq}$ should be taken from low-temperature spectra of the studied conformationally labile compound (assuming that spectral parameters do not depend on temperature).

The closest $K$ values were calculated using the $\gamma$-effect value and $^3J_{C(4,6)-P}$ coupling constant in $^{13}C$ NMR spectra and—to a much smaller extent—the chemical shift in the $^{31}P$ NMR spectra. The use of other conformational probes, e.g., $^2J_{H-P}$ or $\delta_{C(2)}$ may lead, in our opinion, to erroneous results (*vide supra*). On the other hand, the accuracy of determination of $^3J_{C(4,6)-P}$ is so small (about 0.4 Hz, based on digital resolution) that this constant can only be applied if the equilibrium constant $K$ is close to 1. Otherwise (as, e.g., for **6–9**), it implies $K = 0$.

**Table 16. $\gamma$-Effect Values in $^{13}C$ NMR (75.47 MHz, $CD_2Cl_2$, 180 K) Spectra of 1,3-Dithiane Derivatives 10a,b and 13a,b and Calculated Equilibrium Constants $K$ for the Solutions in $CD_2Cl_2$ at 296 K**

| compd | $\gamma$-effect in conformer: axial (ppm) | $\gamma$-effect in conformer: equatorial (ppm) | $K$ |
|---|---|---|---|
| **10a** | −4.825 | 1.500 | 1.19 |
| **10b** | −5.025 | 1.468 | 1.16 |
| **13a** | −4.924 | 1.571 | 1.57[a] |
| **13b** | −5.476 | 1.504 | 1.57 |

[a] $K$ based on $\gamma$-effect value for **13a** at 296 K in $CDCl_3$.

The only probe, which is practically alkyl-substitution-independent and measurable with high accuracy, is the $\gamma$-effect value in the $^{13}C$ NMR spectra. This conclusion is strongly supported by low-temperature $^{13}C$ NMR studies of the conformationally labile **10a**, **10b**, **13a**, and **13b**. The relevant $\gamma$-effects for individual conformers at 180 K and equilibrium constants $K$ derived from them (for equilibrium at 296 K) are collected in Table 16. When these data are compared with the those listed in Table 15, one can find striking agreement between $K$ values derived from low-temperature $\gamma$-effects and $K$'s based on the $\gamma$-effect values and $^3J_{C-P}$ coupling constants in reference systems (e.g., for **10a** $K = 1.19$ and $K = 0.88$–$1.07$, respectively). On the other hand, the probes $^2J_{H-P}$, $\delta_{H(2)}$, and $\delta_{C(2)}$ applied to the systems **cd** and **ef** in each and every case do not provide $K$ values comparable to those presented in Table 16. The use of $\delta_P$ in $^{31}P$ NMR spectra leads to results in moderate accord with the $K$'s in Table 15. However, it should be noted that $\gamma$-effects estimated at 180 K for individual conformers may not correspond exactly to the $\gamma$-effect values at 296 K. The chemical shifts of carbons C(4,6) in $^{13}C$ NMR spectra of 1,3-dithiane are known[4] to be temperature dependent and increase by 1.3 ppm with the increase of temprature by 116 K.

All the results presented above prompted us to apply in further discussion the $\gamma$-effect-derived conformational equilibrium constants and the related $\Delta G°$ values. Since 5-*tert*-butyl-1,3-dithiane derivatives seem to better imitate conformers of **a** and **b** derivatives they were used as reference systems.

**Equilibration of Diastereomeric Compounds.** The preference of a given substituent to occupy the axial position can also be determined by the equilibration of diastereomeric compounds. It was known[12,35] that the epimerization at C(2) of 2-P-substituted 1,3-dithianes may occur in the presence of sodium methoxide. This method, however, in the case of **8c,d** and **8e,f** resulted in the formation of only epimerized products of transesterification, and the epimerization had to be performed in other solvent (tetrahydrofuran).

The ratio of products was determined either as the ratio of integrals of H(5) signals in the $^1H$ NMR spectra (compounds **9–13**) or as the ratio of the appropriate signals in $^{31}P$ NMR spectra (other compounds).

All equilibrium constants determined in benzene: methanol = 6:4 (v/v), in dichloromethane-$d_2$, or in chloroform-$d$ and the related $\Delta G°$ values are collected in

(90) While the introduction of the 5-*tert*-butyl group also influences the chemical shifts of C(4,6) (cf. Table 3 and see also Eliel *et al.*[91]), it does not influence markedly $\gamma$-effect values (compare e.g., $\gamma$-effects in Table 16 for **10a**: −4.825 and 1.500 ppm with $\gamma$-effects in Table 4, for **10c**: −4.56 and for **10d** 1.58 ppm; analogously for **13a** −4.924 and 1.571, for **13c** −4.80, **13d** 1.70 ppm.

(91) Eliel, E. L.; Rao, V. S.; Riddell, F. G. *J. Am. Chem. Soc.* **1976**, *98*, 3583.

(92) This assumption is incorrect and may lead to erroneous results. The relevant corrections should be based on the relationship between the chemical shifts in 2-P-substituted derivatives. Therefore, the corrections for $\delta_{C(4,6)}$ do not correspond to the use of $\gamma$-effect values. A possible error due to this correction is expected to be larger in *cis*-4,6-dimethyl-1,3-dithiane derivatives (**e,f**) than in 5-*tert*-butyl-1,3-dithiane derivatives (**c,d**) because C(4,6) chemical shifts in the former system are much more influenced by the presence of anchoring substituent(s) than those in the latter (9.44 *vs* 1.26 ppm, *vide infra*). Interestingly, we found that the approach of Juaristi *et al.* may be used with sufficient accuracy for axial derivatives of the compounds studied here. For instance, the correction of chemical shifts of C(4,6) in diastereomeric **10c** and **10e** (by 31.22–29.96 = 1.26 and 39.40–29.96 = 9.44 ppm; corrections calculated based on the change in chemical shifts on passing from unsubstituted to the parent 1,3-dithianes **14** and **15**, respectively; Table 3, supplementary material) gives very close values: $\delta$ 25.40 and 25.27 ppm, respectively. However, this approach fails to correct the chemical shifts in equatorial derivatives; the analogous correction for **10d** and **10f** leads to diverse values $\delta$ 31.54 and 32.17 ppm. Maximum diversity (up to ca. 0.8 ppm) occurs for **6d** and **6f** (30.64 and 31.45 ppm, respectively).

(93) A dependence of $\Delta G°_{ax-eq}$ on alkyl substitution of the heteroane ring has been observed by Tschierske *et al.* (up to 1.0 kJmol$^{-1}$)[48] and us (up to 3.1 kJmol$^{-1}$).[41a] This seems to be due to a solvent effect on equilibria.[48] The relevant diversity for **10** may reach 1.8 kJmol$^{-1}$ (cf. data for **10c,d** *vs* **10e,f** in Table 20).

**Table 17. Equilibrium Constants $K$ and Free Energy Differences $\Delta G^\circ$ for 1,3-Dithiane Derivatives a, b, c,d, and e,f**

| | a | b | c,d | | e,f | |
|---|---|---|---|---|---|---|
| compd | $\Delta G^\circ_{296}$[a] (kJ/mol) | $\Delta G^\circ_{296}$[a] (kJ/mol) | $K_{exp}$ | $\Delta G^\circ_{exp}$[b] (kJ/mol) | $K_{exp}$ | $\Delta G^\circ_{exp}$[b] (kJ/mol) |
| 6 | 9.08[c] | 6.96[c] | 0.168[d] | 4.35 ± 0.12 | 0.119[d] | 5.19 ± 0.29 |
| 7 | | 5.87[c] | 0.142[d] | 4.76 ± 0.28 | 0.174[d] | 4.26 ± 0.22 |
| 8[e] | | | | | | |
| 9 | 4.36[c] | 4.36[c] | 0.187[d] | 4.09 ± 0.25 | | |
| 10 | −0.17 | 0.10 | 0.425[d] | 2.08 ± 0.17 | 0.500[d] | 1.69 ± 0.15 |
| 10 | 0.00[c] | 0.23[c] | | | | |
| 11 | −0.26 | 0.18 | 0.345[d] | 2.59 ± 0.13 | 0.519[d] | 1.60 ± 0.14 |
| 12 | −2.83 | −0.96 | 0.593[d] | 1.27 ± 0.15 | 0.731[d] | 0.76 ± 0.14 |
| 13 | −0.83[c] | −0.65 | 0.499[d] | 1.69 ± 0.14 | 0.729[d] | 0.77 ± 0.14 |

[a] At 296 K in $CD_2Cl_2$, unless otherwise stated. [b] At 293 K. [c] In $CDCl_3$. [d] In PhH:MeOH = 6:4 (v/v). [e] In PhH/MeOH mixture other reaction occurs.

Table 17 together with the $\Delta G^\circ$ values for conformationally labile compounds calculated based on the $\gamma$-effect value and **cd** derivatives as reference systems. These data will be discussed below.

**Influence of Solvent on the Relative Stability of Isomers of 1,3-Dithiane Derivatives.** In the studies on the anomeric effect the influence of solvent on the conformational preference is usually connected with the origin of this preference.[1,2] Thus, the insensibility of chemical shift difference between axial and equatorial H(4,6) protons, $\Delta\delta_{H(4,6)}$, to solvent variation in **9a** has been noted by Juaristi *et al.*[10] and interpreted in such a way that the contribution of the equatorial conformer of **9a** does not increase with the increasing dielectric constant of the medium (stronger anomeric effect is not observed in less polar media[12]),[94] in contrast to what may be expected if dipole–dipole interactions were operative. They concluded[12] that dipole–dipole interaction is not the sole operative mechanism causing the strong anomeric effect in the CSCP=O system.

In the studies on the conformational preference free energy differences $\Delta G^\circ$ for the equilibria between conformers (diastereomers) of various derivatives are sometimes compared with each other. Since they may refer to different solvents (see, e.g., ref 37, footnote 22) it is necessary to learn the strength of the influence of solvent on the $\Delta G^\circ$ value.

As far as the NMR studies on the conformation of derivatives **10a** and **10b** are concerned, it is of crucial importance to establish which spectral parameters, which may serve as conformational probes, are influenced by a solvent and which are independent of the medium. Therefore, $^1H$ and $^{13}C$ NMR spectra of diastereomeric **10c** and **10d** were recorded in seven different solvents, and the selected data are presented in Table 18. It is clear that the observed invariability of all the coupling constants and $\gamma$-effects indicates the absence of important changes in conformational equilibrium. On the other hand, $\Delta\delta$ value for **10c** decreases almost twice on going from benzene-$d_6$ to acetonitrile-$d_3$. For **10d** the relative change is dramatic: from $\Delta\delta$ = 0.36 ppm in benzene-$d_6$ to a change in the sequence of signals in dimethyl sulfoxide-$d_6$. Therefore, it must be emphasized that the changes in $\Delta\delta$ for conformationally labile compounds observed with the change of solvent need not arise only from the shift in the conformational equilibrium but, to a certain degree, may be due to the influence of solvent on the chemical shifts of axial and equatorial protons H(4,6) in both conformations. Moreover, the direction of this influence is exactly the same as it should be expected on the basis of solvent polarity—large $\Delta\delta$ is nonpolar and small $\Delta\delta$ in polar solvents.

In order the evaluate the relation between the properties of a solvent and the magnitude of axial preference of the $Ph_2P$=S group, $\gamma$-effects in $^{13}C$ NMR spectra of **10a** and **10b** in various solvents were used as conformational probes. The appropriate data from Table 18 served as reference. The calculated equilibrium constants and free energy differences, $\Delta G^\circ_{296}$, are collected in Table 19. As expected on the basis of the least polarity the greatest axial preference is observed in benzene-$d_6$. Surprisingly, the largest amount of the equatorial conformer can be found in dichloromethane-$d_2$ and chloroform-$d$ (cf. Table 17). Solvents which are usually considered as "polar" ($CD_3CN$ and DMSO-$d_6$) unexpectedly stabilize axial conformers of **10a** and **10b**. This effect is especially pronounced for dimethyl sulfoxide solutions and can be rationalized by taking into account the oligomeric structure of liquid DMSO which causes it to behave like an ether. However, it is clearly seen that the conformational preference is strongly dependent on solvent, and this dependence does not stem from "polarity" but, perhaps, is due to specific interactions between solvent and solute.

The conclusions presented above are strongly supported by the data from equilibration of diastereomeric **10c, 10d, 10e,** and **10f** in various solvents. The appropriate equilibrium constants and free energy differences $\Delta G^\circ_{exp}$ are presented in Table 20 (in benzene:methanol = 6:4, v/v, in Table 17). The most striking finding is that the replacement of a benzene:methanol = 6:4 (v/v) solution by anhydrous ethanol results in the *increase* of $\Delta G^\circ_{exp}$ for **10c,d** from 2.08 to 2.66 kJ/mol and the *decrease* of $\Delta G^\circ_{exp}$ from 1.69 to 1.22 kJ/mol in the case of **10e,f**. Thus, the influence of solvent must not be considered solely in terms of "polarity", which is very imprecise.[96,97] It is clear that specific interactions between solvent and solute should be taken into account, more so because they are not the same for very similar **10c,d** and **10e,f**. Obviously, the nature of the axial preference is, perhaps, almost the same for **10c,d** and **10e,f**, and hence, solvent studies should not be expected to indicate the nature of the anomeric effect observed. It must be pointed out that the $\Delta G^\circ_{exp}$ values for **10c,d** and **10e,f** can differ by more than 1.5 kJ/mol. Such differences seem to arise from different solvent effects on the equilibria under scrutiny. This point of view is strongly supported by the studies[48] on the equilibria in other derivatives of 1,3-diheteroanes.

Finally, it should be mentioned that the equilibration of diastereomeric pairs **6c,d, 6e,f, 8c,d,** and **8e,f** was performed in tetrahydrofuran in the presence of a catalytic amount of *n*-butyllithium. The equilibrium constants and $\Delta G^\circ_{exp}$ values are shown in Table 21. They indicate a larger axial preference of the $(CF_3CH_2O)_2P$=O group than of the $(MeO)_2P$=O one (by about 3 kJ/mol), and they will be discussed below.

**Temperature Dependence of the $\Delta G^\circ_{exp}$ Value.** The use of 5-*tert*-butyl-1,3-dithiane derivatives as conforma-

(94) The changes in $\Delta\delta$ value with solvent polarity were used by us[95] and Juaristi *et al.*[10,12] to estimate the position of conformational equilibrium. This might be correct if variable solvent studies on conformationally fixed models were performed.

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(96) Mayer, U. *Pure Appl. Chem.* **1979**, *51*, 1697.

(97) Reichardt, C. In *Molecular Interactions*; Ratajczak, H., Orville-Thomas, W. J., Eds.; John Wiley & Sons: New York, 1982; Vol. 3, p 241.

**Table 18. Selected $^1H$ and $^{13}C$ NMR Data for 10c and 10d in Seven Various Solvents at 296 K**

| | $^1H$ NMR[a] | | | | | | | | | | $^{13}C$ NMR[b] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | $\Delta\delta$ (ppm) | | $^3J_{gauche}$[c] (Hz) | | $^3J_{anti}$[c] (Hz) | | $^4J_{H-P}$[d] (Hz) | | $^2J_{H-P}$ (Hz) | | $^3J_{C-P}$[e] (Hz) | | $\gamma$-effect (ppm) | |
| solvent | 10c | 10d | 10c | 10d | 10c | 10d | 10c | 10d | 10c | 10d | 10c | 10d | 10c | 10d |
| $C_6D_6$ | 2.03 | 0.36 | 2.54 | 2.77 | 11.63 | 10.85 | 1.6 | 3.29 | 5.42 | 11.50 | 0 | 7.0 | −4.44 | 1.17 |
| $C_6H_6/CD_3OD$[f] | 1.79 | 0.24 | 2.64 | 2.55 | 11.59 | 10.99 | 1.6 | 2.70 | 5.38 | 11.20 | 0 | 7.4 | −4.46 | 1.23 |
| $CDCl_3$ | 1.41 | 0.23 | 2.76 | 2.57 | 11.49 | 11.19 | 1.7 | 3.20 | 5.36 | 11.52 | 0 | 7.3 | −4.56 | 1.58 |
| $CD_2Cl_2$ | 1.40 | 0.20 | 2.74 | 2.59 | 11.50 | 11.17 | 1.8 | 3.67 | 5.35 | 11.19 | 0 | 7.5 | −4.53 | 1.58 |
| DMSO-$d_6$ | 1.37 | 0.04[g] | 2.2 | *h* | 11.67 | *h* | 1.5 | *h* | 5.23 | 10.26 | 0 | 7.6 | −4.55 | 1.02 |
| $CD_3OD$ | 1.50 | 0.06 | 2.60 | 2.46 | 11.52 | 10.93 | 2.2 | 3.62 | *i* | 10.38 | *j* | *j* | *j* | *j* |
| $CD_3CN$ | 1.37 | 0.07 | 2.65 | 2.41 | 11.54 | 11.37 | 1.6 | 3.46 | 5.26 | 10.68 | 0 | 7.7 | −4.42 | 1.26 |

[a] SF = 300.13 MHz. [b] SF = 75.47 MHz. [c] Between H(5) and H(4,6). [d] Between H(4,6) and P. [e] Between C(4,6) and P. [f] 6:4 (v/v). [g] Axial protons resonate at lower field than equatorial ones. [h] Not determined due to complexity of H(4,6) region. [i] Not determined due to signal overlap. [j] Spectrum not recorded due to low solubility of the substance.

**Table 19. $\gamma$-Effect Values, the Related Equilibrium Constants $K$, and Free Energy Difference $\Delta G°_{296}$ for Solutions of 10a and 10b in Various Solvents**

| | $\gamma$-effect[a] (ppm) | | $K$ | | $\Delta G°_{296}$ (kJ/mol) | |
|---|---|---|---|---|---|---|
| solvent | 10a | 10b | 10a | 10b | 10a | 10b |
| $C_6D_6$ | −3.29 | −3.14 | 0.26 | 0.30 | 3.31 | 2.96 |
| $C_6D_6$:$CD_3OD$ = 6:4 (v/v) | −2.34 | −2.28 | 0.60 | 0.62 | 1.26 | 1.18 |
| $CD_3CN$ | −1.30 | −1.37 | 0.82 | 0.86 | 0.49 | 0.37 |
| DMSO-$d_6$ | −2.39 | −2.49 | 0.63 | 0.59 | 1.14 | 1.30 |

[a] In $^{13}C$ NMR spectra at 75.47 MHz; the C(4,6) chemical shifts in the parent 1,3-dithianes were determined in appropriate solvent.

**Table 20. Results of Equilibration of 10c–10f in Various Solvents at 293 K**

| | $K$ | | $\Delta G°_{exp}$ (kJ/mol) | |
|---|---|---|---|---|
| solvent | 10c,d | 10e,f | 10c,d | 10e,f |
| *i*-PrOH | 0.339 | *a* | 2.64 ± 0.19 | *a* |
| EtOH 100% | 0.336 | 0.606 | 2.66 ± 0.24 | 1.22 ● 0.14 |
| EtOH 95% | 0.379 | 0.806 | 2.36 ± 0.17 | 0.52 ± 0.40 |
| DMSO-$d_6$ | 0.370 | *a* | 2.42 ± 0.19 | *a* |
| MeOH | 0.498 | 0.990 | 1.70 ± 0.17 | 0.02 ± 0.15 |

[a] Not determined.

**Table 21. Results of Equilibration of 6c–6f and 8c–8f in Tetrahydrofuran at 293 K**

| | $K \times 10^3$ | | $\Delta G°_{exp}$ (kJ/mol) | |
|---|---|---|---|---|
| compd | c,d | e,f | c,d | e,f |
| 6 | 64.9 | 34.2 | 6.66 ± 0.66 | 8.23 ± 0.50 |
| 8 | 10.6 | 9.70 | 11.06 ± 0.60 | 11.29 ± 0.60 |

tionally fixed models was questioned by Juaristi *et al.*[37] Since the presence of flexible forms is usually[98] reflected in the differences in entropy $\Delta S°$, we determined thermodynamic parameters for the equilibria between **10c** and **10d**, as well as for **10e** and **10f**. Following the usual procedure,[99] we carried out equilibrations of **10c,d** and **10e,f** at six temperatures in benzene:methanol = 6:4 (v/v) solutions. The results are collected in Table 22. For the equilibrium between **10c** and **10d** the appropriate corrections $\Delta\Delta G°$ for conformational nonhomogeneity[69] and the resulting $\Delta G° = \Delta G°_{exp} + \Delta\Delta G°$ values are also presented. It was reasonably assumed that $\Delta H°$ is independent of temperature within the range from 281 to 334 K, and hence $\Delta G°$ should be a linear function of temperature ($\Delta G° = \Delta H° - T\delta S°$). The relevant plot of $\Delta G°_{exp}$ values as a function of temperature is shown in Figure 3. A least-squares method applied to these data provides for **10c,d** $\Delta H° = 5.19 \pm 0.23$ kJ/mol, $\Delta S° = 10.6 \pm 0.7$ J mol$^{-1}$ deg$^{-1}$ (correlation coefficient $r = 0.988$), and for **10e,f** $\Delta H° = 5.71 \pm 0.12$ kJ/mol, $\Delta S° = 13.8 \pm 0.4$ J mol$^{-1}$ deg$^{-1}$ (correlation coefficient $r = 0.998$). The large $\Delta S°$ for **10e,f** which can be regarded as conformationally stiff implies that the axial $Ph_2P{=}S$ group has much smaller rotational possibilities than the equatorial one, in good agreement with the results based on phosphorus spin-lattice relaxation times.[70]

**Table 22. Results of Equilibration of 10c,d and 10e,f in Benzene:Methanol = 6:4 (v/v) at Various Temperatures**

| | 10c,d | | | | 10e,f | |
|---|---|---|---|---|---|---|
| $T$ (K) | $K$ | $\Delta G°_{exp}$ (kJ/mol) | $\Delta\Delta G°$[a] (kJ/mol) | $\Delta G°$ (kJ/mol) | $K$ | $\Delta G°_{exp}$ (kJ/mol) |
| 281 | 0.386 | 2.22 ± 0.21 | 0.10 | 2.32 ± 0.21 | 0.456 | 1.83 ± 0.14 |
| 293 | 0.425 | 2.08 ± 0.17 | 0.14 | 2.22 ± 0.17 | 0.500 | 1.69 ± 0.15 |
| 303 | 0.465 | 1.93 ± 0.27 | 0.18 | 2.11 ± 0.27 | 0.537 | 1.57 ± 0.17 |
| 312 | 0.478 | 1.91 ± 0.18 | 0.19 | 2.10 ± 0.18 | 0.584 | 1.40 ± 0.13 |
| 325 | 0.518 | 1.78 ± 0.19 | 0.24 | 2.02 ± 0.19 | 0.635 | 1.23 ± 0.15 |
| 334 | 0.558 | 1.62 ± 0.15 | 0.22 | 1.84 ± 0.15 | 0.668 | 1.12 ± 0.14 |

[a] Correction for conformational nonhomogeneity of **10c,d**;[69] $\Delta G° = \Delta G°_{exp} + \Delta\Delta G°$.

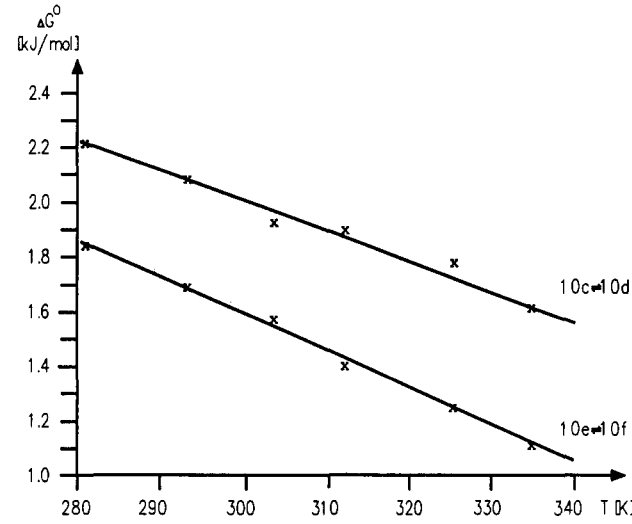



**Figure 3.** Plot of $\Delta G°_{exp}$ values as a function of temperature for the equilibration of **10c,d** and **10e,f**.

The consideration of $^3J_{anti}$ and $^3J_{gauche}$ coupling constants in the $^1H$ NMR spectra of **10c,d** suggests that the amount of high-entropy twist-boat forms should be larger for the *trans* isomer[69] (**d**) more so because it is the less thermodynamically stable isomer. This, in turn, should result in a further increase in the $\Delta S°$ value. However, the $\Delta S°$ value for **10c,d** is smaller than that for **10e,f**. This observation additionally supports the negligible influence of conformational nonhomogeneity of **10c,d** on the $\Delta G°_{exp}$ value.

It is interesting that the relation between $\Delta H°$ for **10c,d** and **10e,f** is opposite to that of $\Delta G°_{exp}$ values because of

(98) Eliel, E. L.; Hutchins, R. O. *J. Am. Chem. Soc.* **1969**, *91*, 2703.
(99) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic & Organometallic Compounds*; Academic Press: London, 1970; p 26–27.

the difference in entropy terms $\Delta S°$. It would be very interesting to compare $\Delta G°$, $\Delta H°$, and $\Delta S°$ for **10c,d** and **10e,f** in the vapor phase. If the appropriate parameters were equal, the observed differences in thermodynamic parameters of **10c,d** and **10e,f** would arise from different solvent effects on the equilibria.

Finally, it should be noted that the temperature dependence of the $\Delta G°_{exp}$ value for **9e,f** (and for **9a**; $\Delta G°$ obtained by weighted average method) has been used by Juaristi *et al.*[100] to derive the relevant $\Delta H°$ and $\Delta S°$ values, which were then applied to estimate enthalpic and entropic contributions to the SCP=O anomeric effect (see below).

**Magnitude of the Anomeric Effect.** The application of Franck's methodology[101] to estimate the magnitude of the anomeric effect $\Delta G°_{AE} = \Delta G°_{H} - F\Delta G°_{C}$ in 2-P-substituted 1,3-diheteroanes was introduced for OCP=O anomeric interactions by Juaristi *et al.*[44] It can be performed only for such substituents for which free energy differences $\Delta G°_{C}$ for conformational equilibria in monosubstituted cyclohexanes are known ($\Delta G°_{H}$ means free energy difference for ax ⇌ eq conformational equilibrium in monosubstituted heteroane). Thus, for the $(MeO)_2P$=O group (compounds **6**) $\Delta G°_{6(C)} = -8.34 \pm 0.46$ kJ/mol,[11] for the $Ph_2P$=O group (compounds **9**) $\Delta G°_{9(C)} = -11.46 \pm 0.38$ kJ/mol,[74] and for the $Ph_2P$=S group (compounds **10**) $\Delta G°_{10(C)} = -15.10$ kJ/mol.[37] When a substituent is transferred from cyclohexane to the anomeric carbon atom of a heteroane the steric interactions increase $F$ times. Then, let us calculate the magnitude of the $F$ factor for the above substituents. It is not constant for 1,3-dithiane derivatives and depends on a substituent.[2b,102] Thus, $F_{Me}$ for 1,3-dithiane based on the methyl group is equal to

$$F_{Me(D)} = -7.42/-7.28 = 1.019$$

where $\Delta G°_{C} = -7.28$ kJ/mol[72] and $\Delta G°_{D} = -7.42$ kJ/mol[98] mean free energy differences for the methyl group in cyclohexane and at C(2) of 1,3-dithiane, respectively. When the *tert*-butyl group, for which $\Delta G°_{C} = -20.5$ kJ/mol and $\Delta G°_{D} = -11.4$ kJ/mol,[98] is taken as a reference

$$F_{t\text{-}Bu(D)} = -11.4/-20.5 = 0.556$$

Let us assume that $F$ is a linear function of $\Delta G°_{C}$.[103] The linear interpolation between the $F$ values for the methyl and *tert*-butyl group gives for the $(MeO)_2P$=O group $F_6 = 0.98$, for the $Ph_2P$=O group $F_9 = 0.87$, and for the $Ph_2P$=S group $F_{10} = 0.75$.

Let us calculate the magnitude of the anomeric effect for 5-*tert*-butyl-1,3-dithiane derivatives based on the data in Table 17. For the $(MeO)_2P$=O group

$$\Delta G°_{AE} = 4.35 + 0.23 - 0.98(-8.34) = 12.8 \text{ kJ/mol}$$

(assuming $\Delta\Delta G° = 0.23$ kJ/mol[69]). By the same token for the $Ph_2P$=O group

$$\Delta G°_{AE} = 4.09 + 0.24 - 0.87(-11.46) = 11.6 \text{ kJ/mol}$$

and for the $Ph_2P$=S group

$$\Delta G°_{AE} = 2.08 + 0.14 - 0.75(-15.10) = 13.5 \text{ kJ/mol}$$

The results presented above are in good agreement with the magnitudes of the anomeric effects determined by Juaristi *et al.* for the $Ph_2P$=O and $Ph_2P$=S groups in the 1,3-dithiane ring (15.6 kJ/mol[12] and 15.7 kJ/mol,[37] respectively, or following Franck's methodology 11.0 kJ/mol[44] and 9.7 kJ/mol,[104] respectively). As was pointed out by Juaristi *et al.*,[12,104] the magnitude of these effects is the largest yet recorded. In our[39] and Juaristi's[42] opinion, it is due to the one-directionality[2b,85] of the interactions involved. It must be noted, however, that Tschierske *et al.*[48] suggested that the magnitude of the anomeric effect in 1,3-dithiane derivatives should be divided by two owing to the presence of two sulfur atoms in the ring. It seems to us that this point of view would be correct if *both* sulfur atoms equally participated in the interactions responsible for the anomeric effect, which seems to be not true (see below). As discussed by Juaristi *et al.*[104] the results on tetrahydropyran/1,3-dioxane series suggest rather a "saturation" of the effect.

Since free energy differences $\Delta G°_{C}$ for conformational equilibria in monosubstituted cyclohexanes are negative for almost all substitutents, practically it is enough to find $\Delta G° > 0$ in a heteroane in order to say that the anomeric effect is observed. On this basis, the operation of the anomeric effect for **7**, **8**, **11**, **12**, and **13** is unquestionable. Nevertheless, the exact magnitude of the effect is not known.

Finally, it should be mentioned that our $\Delta H°$ and $\Delta S°$ data for **10** containing the SCP=S system (*vide supra*) are qualitatively consistent with Juaristi's interpretation[100] of the anomeric effect in SCP=O system **9**, i.e., that the enthalpic anomeric effect operates in **10**, and that equatorial isomers are entropy-favored.

**The Nature of the Anomeric Effect in Light of X-ray Data.** Since appropriate bond lengths and angles are usually indicative of the mechanism responsible for the anomeric effect,[1,2] the solid-state structure of the compounds under investigation was studied by means of X-ray crystallography. The selected data are collected in Table 23. They will be discussed assuming that they sufficiently correspond to minima of potential energy of isolated molecules; i.e., crystal packing forces are not so important as intramolecular interactions.

While the data for 2-(diphenylphosphinoyl)-1,3-dioxanes[89] and 2-(dimethoxyphosphoryl)-1,3-diselenanes[73] are rather consistent with the expectations based on the $n_O$–$\sigma^*_{C-P}$ and $n_{Se}$–$\sigma^*_{C-P}$ negative hyperconjugations, respectively, the appropriate bond lengths for the relevant 1,3-dithianes do not give such an answer. Firstly, the relative C(2)–P bond lengths in diastereomers are not characteristic for the position of phosphorus, e.g., in **6c,d** and **10c,d** (see also Figure 1) the equatorial C(2)–P bonds are longer than the axial ones (contrary to $n_S$–$\sigma^*_{C-P}$-based anticipation), while in **9c,d** and **13c,d** they are shorter, in agreement with the concept of the $n_S$–$\sigma^*_{C-P}$ negative hyperconjugation. In **8c,d** the axial C(2)–P bond is of the same length as the equatorial one. Secondly, the *endo* S–C(2) bonds

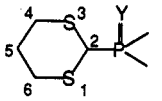
(100) Juaristi, E.; Cuevas, G. *Tetrahedron Lett.* **1992**, *33*, 2271.
(101) Franck, R. W. *Tetrahedron* **1983**, *39*, 3251.

(102) It should be noted that the dependence of F on the size of substituent has been appreciated by Juaristi *et al.*[42,44] In particular, factor $F = 0.9$ based on interactions of the isopropyl group in cyclohexane and 1,3-dithiane rings was applied to estimate the magnitude of the anomeric effect of the $Ph_2P$(:) group. However, because of structural differences between alkyl- and phosphorus-containing groups,[44] both our and Juaristi's estimates of the magnitude of the anomeric effect should be treated as only approximate.

(103) In fact, the relationship between $F$ and $\Delta G°_{C}$ is not linear. However, we believe that this assumption is justified within the other errors inherent in estimation of the magnitude of the anomeric effect (e.g., comparison of $\Delta G°$ values obtained for derivatives having different alkyl substituents at the ring, at different temperatures, in different solvents, *etc.*).

(104) Juaristi, E. *Heteroatom. Chem.* **1990**, *1*, 267.

**Table 23. Selected Bond Lengths and Distances for 1,3-Dithiane Derivatives[a]**



| compd | C(2)–P (Å) | S(1)–C(2) (Å) | S(3)–C(2) (Å) | H(4)–Y (Å) | H(6)–Y (Å) | C(4)–S(3) (Å) | C(6)–S(1) (Å) |
|---|---|---|---|---|---|---|---|
| **6c** | 1.782(5) | 1.811(6) | 1.812(5) | 2.57 | 2.49 | 1.819(5) | 1.812(5) |
| **6d** | 1.798(4) | 1.796(4) | 1.791(5) | | | 1.805(5) | 1.809(4) |
| **6e** | 1.809(4) | 1.811(4) | 1.804(4) | 2.54 | 2.66 | 1.822(4) | 1.827(4) |
| **8c** | 1.794(3) | 1.796(4) | 1.814(4) | 2.82 | 2.72 | 1.802(4) | 1.802(4) |
| **8d** | 1.794(3) | 1.806(3) | 1.815(3) | | | 1.821(3) | 1.815(4) |
| **9c** | 1.834(4) | 1.805(5) | 1.803(5) | 2.76 | 2.54 | 1.824(5) | 1.810(6) |
| **9d** | 1.821(2) | 1.807(3) | 1.799(2) | | | 1.816(3) | 1.815(3) |
| **9f**[b] | 1.840(4) | 1.810(4) | 1.808(4) | | | 1.818(5) | 1.835(5) |
| **10c** | 1.817(5) | 1.803(4) | 1.817(5) | 2.96 | 2.88 | 1.822(5) | 1.815(6) |
| **10d** | 1.831(3) | 1.809(4) | 1.814(5) | | | 1.811(4) | 1.820(4) |
| **10f** | 1.817 | 1.806(6) | 1.823(6) | | | 1.822(9) | 1.832(8) |
| **13c** | 1.855(4) | 1.801(5) | 1.807(5) | 3.13 | 2.96 | 1.790(5) | 1.807(5) |
| **13d** | 1.841(3) | 1.804(3) | 1.810(3) | | | 1.820(3) | 1.815(4) |

[a] For compounds with phosphorus located axially appropriate distances between Y and axial hydrogens $H(4,6)_{ax}$ are given as H(4)–Y and H(6)–Y [b] From refs 12 and 13.

which should be shortened, when involved in $n_S$–$\sigma^*_{C-P}$ negative hyperconjugation, are longer in **6c** than in **6d**. For other compounds S–C(2) bond lengths practically do not depend on the configuration. Thirdly, C(4)–S and C(6)–S bonds are almost of the same length regardless of the position of phosphorus (except for in **8c,d** and **13c,d**). Nevertheless, a comparison of the structural data between **6c** and **8c** supports $n_S$–$\sigma^*_{C-P}$ negative hyperconjugation as a source of the anomeric effect in the SCP=O system. In the latter compound, which contains the more electron-withdrawing $(CF_3CH_2O)_2P(O)$ group, the C(2)–P bond is longer than that in the former one containing the $(MeO)_2P$=O group (1.794 *vs* 1.782 Å, respectively), as expected based on more effective negative hyperconjugation in **8c**. This conclusion is additionally supported by a more definitive difference between the two C(2)–S bond distances of 0.018 Å in **8c**, while in **6c** they are equal. If hyperconjugative interactions were weak (or absent) both C(2)–S bonds should be of the same length (no reason for differentiation, neglecting crystal packing forces). It is, however, known that the presence of two possible donors (bonds) may lead to thermodynamical (and in consequence structural) differentiation of chemical species which differ only in a donor involved in hyperconjugation.[105] In other words, if two possible donors are present (e.g., two $\pi$-lone pairs of endocyclic sulfur atoms), hyperconjugation may not involve both of them equally. One of them may be involved more, the more the stronger hyperconjugation, as found by us for **6c** *vs* **8c**.[106] This effect is also consistent with the "saturation" of the anomeric effect in diheteroanes as compared with monoheteroanes (*vide supra*).

The distances between axial hydrogens $H(4,6)_{ax}$ and the heteroatom Y connected with axially located phosphorus are not equal. Interestingly, the shorter H···Y=P distance for **6c**, **9c**, and **10c** is much shorter than the sum of H and Y van der Waals radii which suggest the formation of a H···Y hydrogen bond.[107,108] Though the relevant d parameter[107] for **6c**, **9c**, and **10c** (0.21, 0.16, and 0.12 Å, respectively) is smaller than that given by Taylor and Kennard (0.3 Å),[107] in the opinion of Desiraju[108] even long separations may have to be considered seriously. This is because "the C–H···O contact is not really a van der Waals interaction but is primarily electrostatic, falling off much more slowly with distance".[108] Our hypothesis is strongly supported by the fact that the second, longer H···Y distance is for **9c**, and **10c** larger than or equal to the sum of van der Waals radii (H = 1.20 Å, O = 1.50 Å, and S = 1.80 Å[107]), thus indicating an attractive character of the H··Y interaction.

A comparison of the appropriate shortest distances in **6c** (2.49 Å) and **8c** (2.72 Å) is very valuable since the steric requirements of the phosphoryl oxygens in the $(MeO)_2$-P=O and $(CF_3CH_2O)_2P$=O groups should be very similar (the P=O bond lengths in **6c** and **8c** are almost the same: 1.455(3) and 1.457(3) Å, respectively). The longer (by 0.23Å!) distance for **8c** can be easily explained on the basis of decreased electron density at the P=O oxygen in **8c** and hence a much smaller tendency to form the hydrogen bond in **8c** when compared to **6c**.

In our opinion, the observed bond lengths do not allow us to exclude $n_S$–$\sigma^*_{C-P}$ negative hyperconjugation as one of the factors responsible for the anomeric effect observed and bond length changes involved. The variation in bond lengths can be the result of some other possible factors. Besides the $n_S$–$\sigma^*_{C-P}$ hyperconjugation, one should take into acount the following interactions:

$\sigma_{C(4,6)-S}$–$\sigma^*_{C(2)-P}$. This hyperconjugative interaction, analogous to the one operating in equatorial $\beta$-glucosides,[109] tends to lengthen the C(4,6)–S and equatorial C(2)–P bonds and to shorten the C(2)–S ones. The first bonds are really longer in **13d** than in **13c** and in **8d** than in **8c**. The differences in **9c,d** and **10c,d** are not so distinct because of the opposite influence of $\sigma_{C(4,6)-S}$–$\pi^*_{P-Y}$ interaction in **c** isomers, which is more effective for P=O and P—S than for P=Se (see below). The phosphoryl group in **8c** is, perhaps, not able to participate in the $\sigma_{C(4,6)-S}$–$\pi^*_{P-O}$ interaction, as a result of a greater distance from the axial H(4,6) hydrogens and, hence, from C(4,6) carbons (overlap control). Interestingly, the C(4,6)–S bonds in **8d** are long, even if compared with other compounds from group **d**, as it should be expected on the basis of a high electronegativity of the $(CF_3CH_2O)_2P$=O group. Presumably, $\sigma_{C(4,6)-S}$–$\sigma^*_{C(2)-P}$ interaction is responsible, in part, for the lack of differences in axial and equatorial C–P bond lengths as well as for the lack of correlation between the position of phosphorus and C(2)–S

(105) Saunders, M.; Jimenez-Vazquez, H. A. *Chem. Rev.* **1991**, *91*, 375; part 5.
(106) The relevant differences in C(2)–Se bond lengths in 1,3-diselenane systems are even more pronounced: 1.903(8) and 1.973(6) Å.[73]
(107) Taylor, R.; Kennard, O. *J. Am. Chem. Soc.* **1982**, *104*, 5063.
(108) Desiraju, G. *Acc. Chem. Res.* **1991**, *24*, 290.
(109) Briggs, A. J.; Glenn, R.; Jones, P. G.; Kirby, A. J.; Ramaswamy, P. *J. Am. Chem. Soc.* **1984**, *106*, 6200.

bonds length in 1,3-dithiane derivatives, as a whole. It must be noted that the unexpected structural pattern of 2-P-substituted 1,3-dithianes as compared with 1,3-dioxanes and 1,3-diselenanes (where features characteristic of the hyperconjugative mechanism may easily be recognized) may be due to variation in the magnitude of the $\sigma_{C(4,6)-Y}-\sigma^*_{C(2)-P}$ interaction. This interaction in 1,3-dioxanes is weak because of low donor ability of the $\sigma_{C-O}$ orbital. In 1,3-diselenanes, the $\sigma_{C(4,6)-Se}-\sigma^*_{C(2)-P}$ interaction may be unimportant because of overlap reasons. This is, perhaps, why 1,3-dioxanes and 1,3-diselenanes, unlike 1,3-dithianes, exhibit "normal" structures.

$\sigma_{C(4,6)-S}-\pi^*_{P=Y}$. This type of interaction, which is possible only if the P=Y (Y = O, S, Se) group is located axially and *endo* over the 1,3-dithiane ring (cf. RSCC=O system[110]) is expected to stabilize the axial position of phosphorus and to lengthen C(4,6)–S bonds. Since the energy of $\pi^*_{P=Se}$ orbital is high due to the low electronegativity of selenium, this interaction should be negligible for **13**. Such is the case because the C(4,6)–S bond length differences between **13c** and **13d** imply that these bonds are involved only in $\sigma_{C(4,6)-S}-\sigma^*_{C(2)-P}$ interaction (*vide supra*). The importance of the $\sigma_{C(4,6)-S}-\pi^*_{P=Y}$ interaction seems to be not so large for **8c**, since C(4)–S and C(6)–S bond lengths are smaller than the appropriate bond lengths in other compounds **c** containing the axial P=O group.

$n_S-n_Y$. This interaction, which is the molecular orbital counterpart of lone electron pair–lone pair repulsions proposed by us on the basis of molecular mechanics calculations,[111] destabilizes the equatorial position of phosphorus and enhances the observed anomeric effect. One could expect it to be more effective for large selenium (Y = Se) than for oxygen or sulfur. Since repulsive interactions are known[112] to be accompanied by bond lengthening, the relevant bond lengths should provide the appropriate evidence. The equatorial C(2)–P bond lengths increase in the order **9d** [1.821(2) Å], **10d** [1.831(3) Å], and **13d** [1.841(3) Å] which agrees with the increasing $n_S-n_Y$ repulsions. The $\sigma_{C(4,6)-S}-\sigma^*_{C(2)-P}$ hyperconjugative interaction which could lengthen the C(2)–P bond must not be considered as reponsible for this observation. The positive charges at phosphorus, which could increase the acceptor ability of the $\sigma^*_{C(2)-P}$ orbital, decrease on going from **9d** to **10d** to **13d**, in contrast to what is needed to explain the increasing bond length (in $H_3P$=O, $H_3P$=S, and $H_3P$=Se these charges are equal to 0.805, 0.403, and 0.378, respectively[113]). Increasing dipole moments[113] on going from $H_3P$=O to $H_3P$=S to $H_3P$=Se are also consistent with this interpretation.

While in **9d** the phosphoryl oxygen, in the solid state, is located between two endocyclic sulfur atoms (the H–C–P–O angle equal to 170.4°), in **10d** and **13d** the system H–C(2)–P–Y (Y = S, Se) is in the *gauche* conformation. This finding agrees very well with the increasing $n_S-n_Y$ repulsions on going from Y = O to Y = S to Y = Se. It must be noted, however, that C(2)–P bond length changes could also be the result of other interactions, i.e., $\sigma_{C(2)-S}-\sigma^*_{P-Y}$ or $\sigma_{C(2)-H}-\sigma^*_{P-Y}$, or "electrostatic attraction" which are expected to shorten the C(2)–P bond most effectively for Y = O. Nevertheless, the preferred *ap* conformation around the C(2)–P bond in **9d** excludes both $\sigma_{C(2)-S}-\sigma^*_{P-O}$ and $\sigma_{C(2)-H}-\sigma^*_{P-O}$ hyperconjugations, if it is not due to crystal packing forces and the interaction is energy gap-controlled (since the donor ability of the C–S bond should be greater than that of the C–H one).

In our opinion, the relative energy of the interactions presented above depends on a substituent. Moreover, crystal packing forces cannot be neglected as one of the factors responsible for the solid-state structure. Thus, further study is needed to establish the relative importance of the proposed interactions.

**Spectroscopic Properties of Molecules and the Nature of the Anomeric Effect.** As far as the direct one-bond spin coupling constants through the C–H bond in RCHXY systems are concerned, one can find a considerable body of experimental data[17,114,115] showing lower coupling constants $^1J_{C-H}$ for those bonds that possess *ap* orientation to a lone electron pair (for first-row atoms X and Y) or for donor bond (when both X and Y are atoms below the first row), as would be expected based on hyperconjugation. This regularity has been reviewed, reproduced by the relevant *ab initio* calculations, and termed "Perlin effect" by Wolfe *et al.*[114]

The relationship analogous to the Perlin effect can also be found for other coupling constants, namely $^{13}C-^{199}Hg$ in alkylmercurials,[116] $^{13}C-^{31}P$ in glycosylphosphonates,[11] 2-(diphenylphosphinoyl)-1,3-dioxanes,[89] and cyclohexylphosphonates.[117] In 1,3-dithianes studied here the $^1J_{C-P}$ coupling constant through the axial bond is always larger than that through the equatorial one (cf. Table 6; supplementary material), in disagreement with the expectation based on the $n_S-\sigma^*_{C(2)-P}$ interaction. The difference between these constants is rather small, from 0.6–2.6 Hz for $Ph_2P$=Se to 11.4–13.3 Hz for $(MeO)_2P$=O derivatives.

In the 1,3-dithiane system $^1J_{C-H}$ coupling constants through the equatorial bonds were found[17] to be smaller than through the axial ones, in contrast to what has been observed for 1,3-dioxane[18,118] and cyclohexane.[119] This finding has been rationalized[17] in terms of the dominant $\sigma_{C(4,6)-S}-\sigma^*_{C(2)-H}$ over $n_s-\sigma^*_{C(2)-H}$ hyperconjugative interactions, which are responsible for the weakening of the equatorial C(2)–H bond in the 1,3-dithiane system. We found that the introduction of the diphenylphosphinoyl group, $Ph_2P(O)$, at C(2) of a 1,3-dithiane ring does not alter this regularity. In particular, one-bond coupling constant $^1J_{H-C(2)}$ between the anomeric carbon and proton was determined in the $^{13}C$ NMR (75.47 MHz, $CDCl_3$) spectra of **9c** and **9d** using the gated decoupling method as 136 and 148 Hz, respectively.

The chemical shifts for aromatic carbons are sensitive probe in studies of the polar and resonance effects of substituents.[120] Thus, significant upfield $^{13}C$ chemical shifts for the *ortho* and *para* carbons in the axial phosphinoyl $Ph_2P(O)$,[12] thiophosphinoyl $Ph_2P(S)$,[37] phosphinyl $Ph_2P(:)$,[42] and phosphinylborane $Ph_2P-BH_3$[42] groups attached to a 1,3-dithiane ring were interpreted by

(110) Olivato, P. R.; Guerrero, S. A.; Hase, Y.; Rittner, R. *J. Chem. Soc., Perkin Trans. 2* **1990**, 465.
(111) Mikołajczyk, M.; Graczyk, P.; Kabachnik, M. I.; Baranov, A. P. *J. Org. Chem.* **1989**, *54*, 2859.
(112) Palenik, G. J.; Koziol, A. E.; Katritzky, A. R.; Fan, W.-Q. *J. Chem. Soc., Chem. Commun.* **1990**, 715.
(113) Yang, C.; Goldstein, E.; Breffle, S.; Jin, S. *THEOCHEM* **1992**, *259*, 345.
(114) Wolfe, S.; Mario Pinto, B.; Varma, V.; Leung, R. Y. N. *Can. J. Chem.* **1990**, *68*, 1051 and references cited therein.
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(118) Bock, K.; Wiebe, L. *Acta Chem. Scand.* **1973**, *27*, 2676.
(119) Kalinowski, H.-O. In *Carbon-13 NMR Spectroscopy*; Berger, S., Braun, S., Eds.; John Wiley: New York, 1988, p 495.
(120) Levy, G. C.; Nelson, G. L. *Carbon-13 NMR for Organic Chemists*; Wiley-Interscience: New York, 1972; Chapter 4.

Juaristi *et al.* to prove that some form of electron transfer occurs to the axially located substituent. They proposed[2a,12,104,121] 3p–3d donation from sulfur to axial phosphorus as being responsible for this effect, due to the unexpected structural data for $Ph_2P$=O-substituted 1,3-dithianes (*vide supra*, Figure 1). In our opinion, the increased electron density at axial phosphorus may be due (among other factors) to the $n_S$–$\sigma^*_{C-P}$ and $\sigma_{C(4,6)-S}$–$\pi^*_{P=Y}$ hyperconjugations (here Y = O). It must be noted that the importance of p–d bonding with d orbitals of second-row atoms has been questioned on theoretical grounds.[25]

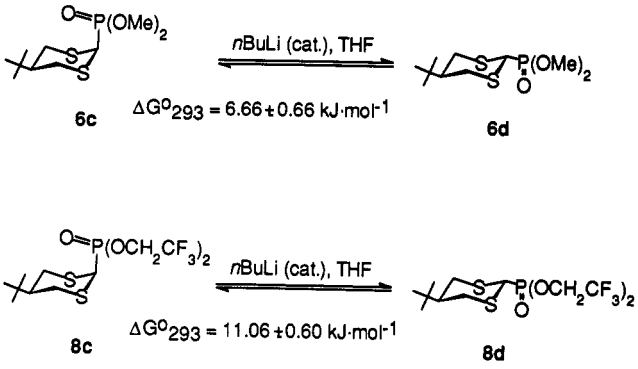
In 1,3-dithiane derivatives both *ortho* and *para* carbons resonate at higher field in the axial $Ph_2P$=O (**9**), $Ph_2P$=S (**10**), PhMeP=S (**11**), and $Ph_2P$=Se (**13**) groups (cf. Table 7; supplementary material). However, it must be noted that the results on 2-phosphonio-1,3-dithiane derivatives suggest that the changes in chemical shifts of aromatic carbons should be interpreted with caution.[2b] They result, perhaps, from much larger number of factors than those considered here.

The operation of $n_S$–$n_{Se}$ repulsions in **13d** is strongly supported by $T_1^{DD}$ relaxation time measurements.[70] Such repulsions should result in a decreased freedom of rotation about the equatorial C(2)–P bond and shortening of $T_1^{DD}$. Indeed, while for a wide variety of 2-P-substituted 1,3-dithianes the $T_1^{DD}$ relaxation times for axial isomers are much shorter than those for the equatorial ones (equatorial substituents rotate much more freely than the axial groups), for **13c** and **13d** they are almost the same: 28.92 and 30.98 s, respectively.[70] It should be added that the $T_1^{DD}$ relaxation time for **13d** is the shortest from all compounds **d** studied here,[70] which additionally supports the importance of $n_S$–$n_{Se}$ interactions in **13d**.

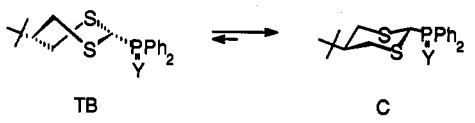
The infrared spectra in the solid state (KBr) of the compounds containing the phosphoryl group are very interesting with regard to the P=O stretching frequency. The decrease of the stretching frequency for the axially situated P=O group occurs for **6c** *vs* **6d** (1222 *vs* 1248 $cm^{-1}$, respectively); it may stem from the hydrogen bond formation and/or $\sigma_{C(4,6)-S}$–$\pi^*_{P=O}$ hyperconjugation. Interestingly, for **8c** and **8d**, where, as suggested by X-ray data, the hydrogen bond is not formed, the appropriate stretching frequencies are close ($\nu_{P=O}$ = 1256 and 1260 $cm^{-1}$, respectively), similar to **8e** and **8f** (1262 and 1256 $cm^{-1}$, respectively).

**Thermodynamic Implications for the Nature of the Anomeric Effect.** The energy of two orbital–two electron hyperconjugative interaction depends on the energy of orbitals involved and the overlap integral.[122] If one assumes that the latter is constant, the stabilization will increase with the decreasing energy gap between orbitals. Thus, in 1,3-dithiane derivatives the energy of lone electron pairs of sulfur can reasonably be assumed to be independent of configuration at the anomeric carbon atom, and the axial preference owing to $n_S$–$\sigma^*_{C-P}$ interaction would increase with the increasing electronegativity of a substituent. Since the $\Delta G°_{exp}$ values for derivatives containing the $(MeO)_2P$=O (**6**) group are about 3 kJ/mol smaller than $\Delta G°_{exp}$ for those with the more electronegative (and undoubtedly larger) $(CF_3CH_2O)_2P$=O (**8**) group (Scheme 10), the occurrence of the $n_S$–$\sigma^*_{C-P}$ mechanism in these compounds seems to be supported. This mechanism is, perhaps, responsible for a larger amount of a twist boat conformer in **8d** than in **6d**[69] since such conformer can be stabilized *via* the $n_S$–$\sigma^*_{C-P}$ interaction.

**Scheme 10**




**Scheme 11**




The reasoning presented above, which supports the operation of the $n_S$–$\sigma^*_{C-P}$ negative hyperconjugation, completely fails when the relative amount of twist boat conformers in **6d**, **9d**, **10d**, and **13d** is to be explained. Regardless of the temperature, the largest amount of flexible conformers TB (Scheme 11) is found for **13d**.[69] One should not expect the $Ph_2P$=Se group to provide the antibonding $\sigma^*_{C-P}$ orbital of the lowest energy since the positive charges at phosphorus, which could increase the acceptor ability of the $\sigma^*_{C(2)-P}$ orbital, decrease on going from **9d** to **10d** to **13d** (*vide supra*). However, the above observation can be accounted for in terms of a predominant role of $n_S$–$n_{Se}$ repulsions in **13d** as compared with $n_S$–$n_Y$ (Y = O, S) in **9d** and **10d**. Such repulsions, which destabilize the equatorial position of the P=Se group, can be reduced in the TB conformer, as an examination of the appropriate Dreiding models suggests. The relative amount of the TB conformers in **9d** and **10d** is, presumably, the result of a larger number of factors, and it cannot be interpreted in so straightforward manner.

## Summary

The operation of the anomeric effect in all the compounds studied was found. For example, the magnitude of the anomeric effect for the $Ph_2P$=O group in the 1,3-dithiane ring was found to be 11.6 kJ/mol. Interactions which could be responsible for the anomeric effect are summarized in Figure 4.

Crystallographic, spectroscopic, and thermodynamic data support the importance of the $n_S$–$\sigma^*_{C(2)-P}$ hyperconjugative interaction for the anomeric effect. The second stabilizing interaction may be P=Y···H(4 or 6) hydrogen bond formation. X-ray data imply that in the $n_S$–$\sigma^*_{C(2)-P}$ interaction one endocyclic sulfur atom is more involved than the other. Some other interactions are also possible, namely $\sigma_{C(4,6)-S}$–$\sigma^*_{C(2)-P}$ (preferring the equatorial position of phosphorus) and $\sigma_{C(4,6)-S}$–$\pi^*_{P=Y}$ hyperconjugations and the $n_S$–$n_Y$ repulsions. The latter interaction was proposed as MO counterpart of lone pair–lone pair repulsions suggested by molecular mechanics calculations. The relative participation of the interactions responsible for the anomeric effect in 1,3-dithianes was shown to be

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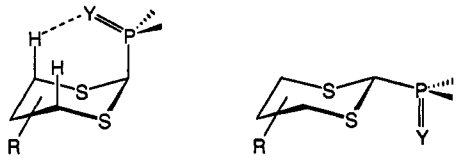
(122) Epiotis, N. D.; Cherry, W. R.; Shaik, S.; Yates, R. L.; Bernardi, F. *Top. Curr. Chem.* **1977**, *70*, 1.



| | | |
|---|---|---|
| Stabilizing interactions | $n_S$ - $\sigma^*_{C(2)-P}$ | $\sigma_{C(4,6)-S}$ - $\sigma^*_{C(2)-P}$ |
| | $\sigma_{C(4,6)-S}$ - $\pi^*_{P=Y}$ | |
| | H···Y=P | |
| Destabilizing interactions | 1,3-*syn*-diaxial | $n_Y$-$n_X$ |

**Figure 4.** Stabilizing and destablizing interactions in 2-P-substituted 1,3-dithianes **6–13**.

dependent on the P substituent. However, the anomeric effect in 1,3-dithiane derivatives seems to be weaker than that in analogous 1,3-dioxanes[89] and 1,3-oxathianes.[2b,39]

It was proved that various conformational probes may afford different equilibrium constants, if weighted average method and conformationally fixed models are applied. Most of physical quantities are dependent on the alkyl substitution at C(4), C(5), and C(6) of the 1,3-dithiane ring. Thus, the relevant procedure for the selection of conformational probe was presented. The $\gamma$-effect value in $^{13}C$ NMR spectra was found to be very sensitive to the position of a substituent connected with the anomeric carbon atom of 1,3-dithianes, and it was applied as a conformational probe.

The chemical shift difference $\Delta\delta$ between axial and equatorial H(4,6) protons in **10c,d** was proved to be strongly dependent on the nature of solvent. Therefore, the changes in the magnitude of $\Delta\delta$ with the change of the solvent cannot be connected with the shift in the conformational equilibrium. The conformational equilibrium in 2-(diphenylthiophosphinoyl)-1,3-dithianes **10** was found to be dependent on solvent, but the dependence cannot be anticipated on the basis of the relative "polarity" of medium. The interactions involved are so specific that the direction of changes in $\Delta G°$ with the change of a solvent can even be reversed for the solutes of very close structure.

A long range $^4J_{C-P}$ coupling constant in the $^{13}C$ NMR spectra and $^{31}P$ spin-lattice $T_1^{DD}$ relaxation times suggest the existence of close contact(s) between a heteroatom Y (Y = O, S, Se) connected with the axial phosphorus and axial protons H(4,6) in 1,3-dithiane ring. Crystallographic data show that the distance from Y to one of these protons is usually much smaller than that to the other one and smaller than the sum of H,Y van der Waals radii, thus strongly suggesting a possibility of the H···Y hydrogen bond formation.

## Experimental Section

$^1H$ NMR spectra of 0.5–0.8% solutions in an appropriate deuterated solvent containing 0.1% of tetramethylsilane were recorded at SF (sweep frequency) 200.13, 250.13, or 300.13 MHz on Bruker AC 200, Bruker WP 250, and Bruker MSL 300 spectrometers, respectively. The $^{13}C$ NMR spectra of about 4% solutions in the appropriate deuterated solvent containing 0.4% of tetramethylsilane were measured at 50.32, 62.89, or 75.47 MHz on the Bruker instruments or at 25.16 MHz on a Tesla BS 567A spectrometer. The $^{31}P$ NMR spectra were measured on Jeol JNM-FX 60, Bruker HFX90, Bruker AC 200, and Bruker MSL 300 instruments at 24.3, 36.4, 81.0, and 121.49 MHz, respectively, with 85% $H_3PO_4$ as an external reference. The $^{77}Se$ NMR spectra were measured at 57.22 MHz on Bruker MSL 300 with diphenyl diselenide as an external reference. The $^{31}P$–$^{77}Se$ coupling constants were evaluated from the $^{77}Se$ NMR spectra. Solutions were not degassed.

The following instrumental parameters for $^1H$ NMR spectra are typical: flip angle, 60–75°; SW (sweep width), 9 ppm; number of scans, 100–400; TD (data size), 16K, AQ (acquisition time), 2.3–3.1 s. The sign of the coupling constants was not determined.

Typical parameters for $^{13}C$ NMR spectra: flip angle, 60–75°; SW, 160 ppm; number of scans, 100–1000; TD, 16K, AQ, 0.67 s. The assignment of signals, if not straightforward, was based on DEPT technique.

All standard 16K FID's in the $^1H$ and $^{13}C$ NMR spectra were zero filled to 64K prior to the Fourier transformation. The accuracy of coupling constants in $^1H$ NMR (300 MHz) spectra, based on digital resolution, has been estimated to be equal to about ±0.08 Hz.

In $^{31}P$ NMR spectra used for quantitative determination of the ratio of diastereoisomers after equilibration, the flip angle was 30–35° and the relaxation delay 5 s.

The following abbreviations are employed in description of NMR spectra: s (single); bs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); *etc.*; m (multiplet).

Mass spectra were recorded with an LKB 2091 spectrometer.

Infrared spectra were taken on a SPECORD 71IR or SPECORD M80. The following abbreviations are employed in description of IR spectra: m (medium), s (strong), vs (very strong).

Melting points were measured using Boëtius apparatus and are uncorrected.

Anhydrous hydrocarbons, diethyl ether, and tetrahydrofuran were distilled from $LiALH_4$. Dichloromethane and chloroform were distilled from $P_2O_5$. Other compounds, if not described below, were commercially available.

Tris(2,2,2-trifluoroethyl) phosphite (**16**),[123a] bis(2,2,2-trifluoroethyl) trimethylsilyl phosphite (**17**),[124] isopropyl diphenylphosphinite (**18**),[125a] tris(dimethylamino)phosphine (hexamethylphosphorus triamide, **22**),[126a] chlorodimethylphosphine (**24**),[127] 2-*tert*-butyl-1,3-propanedithiol (**25**),[98,128] dimethoxymethane (**26**),[129] *meso*-2,4-pentanedithiol (**27**),[98,128,130] 2,2-dimethyl-1,3-propanedithiol (**28**),[91,128,131] methylphenylthiophosphinic chloride (**29**),[123b] dimethylthiophosphinic chloride (**30**),[123b] and tri-*n*-butylphosphine (**31**)[123c] were prepared according to known procedures.

Column chromatographic separations were achieved using Kieselgel 60, 230–400 mesh. Preparative thin-layer chromatograms were obtained with precoated plates (silica gel 60F-254, layer thickness 2 mm). Analytical thin-layer chromatography (TLC) was conducted on precoated plates (silica gel 60F-254, layer thickness 0.25 mm). All chromatographic materials were purchased from Merck.

A cooling bath temperature of −20 °C was maintained using carbon tetrachloride and solid carbon dioxide.

**2-(Dimethoxyphosphoryl)-5,5-dimethyl-1,3-dithiane (6b).** *N*-Chlorosuccinimide (10.5 g, 79.0 mmol) was added, under nitrogen, in small portions, during 20 min to a magnetically stirred solution of 5,5-dimethyl-1,3-dithiane (**32**, 10.5 g, 71.0 mmol) in benzene (166 mL). The reaction mixture was stirred for an additional 20 min, and then a solution of trimethyl phosphite (9.15 g, 73.8 mmol) in benzene (70 mL) was added dropwise and with sirring. When the addition was completed (ca. 10 min) the mixture was refluxed for 6 h. After cooling, it was filtered, the

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filtrate was evaporated under reduced pressure, and the residue was purified by column chromatography to give chromatographically pure **6b** (10.0 g, 55.0%), a colorless oil which crystallizes on long standing: mp 34.0–37.5 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.11 (s, 3H, $CH_3$), 1.28 (s, 3H, $CH_3$), 2.20 (d, $^2J_{H-H}$ = 13.8 Hz, 2H, H(4,6)$_{eq}$), 3.39 (dd, $^2J_{H-H}$ = 13.8 Hz, $^4J_{H-P}$ = 2.7 Hz, 2H, H(4,6)$_{ax}$), 3.55 (d, $^2J_{H-P}$ = 18.2 Hz, 1H, HCP), 3.89 (d, $^3J_{H-P}$ = 10.6 Hz, 6H, $CH_3O$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 20.4; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 24.01 (s, $CH_3C$), 25.95 (s, $CMe_2$), 30.64 (s, $CH_3C$), 32.89 (d, $^1J_{C-P}$ = 157.4 Hz, CHP), 38.13 (s, $CH_2$), 54.46 (d, $^2J_{C-P}$ = 7.3 Hz, $CH_3O$); IR ($CCl_4$, film) 1036 (vs), 1060 (s), 1247 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 256 (22, M$^{\bullet+}$), 233 (11), 149 (11), 147 (100), 79 (14), 69 (41), 41 (20). Anal. Calcd for $C_8H_{17}O_3PS_2$: C, 37.49; H, 6.69. Found: C, 37.48; H, 6.66.

**5-*tert*-Butyl-2-(dimethoxyphosphoryl)-1,3-dithiane (6c,d), Mixture of Diastereomers.** To a solution of **14** (3.0 g, 17.0 mmol) in benzene (40 mL), stirred under nitrogen atmosphere, was added *N*-chlorosuccinimide (2.5 g, 18.7 mmol) in small portions during 20 min. The mixture was stirred for an additional 20 min and filtered under nitrogen. The filtrate was added dropwise to a stirred 70 °C solution of trimethyl phosphite (2.03 mL, 17.2 mmol) in benzene (15 mL). After the addition was completed (ca. 20 min) the mixture was refluxed for 12 h, cooled, and evaporated under reduced pressure. Pure isomers were isolated by column chromatography with chloroform–ethyl acetate as an eluent.

***cis*-5-*tert*-Butyl-2-(dimethoxyphosphoryl)-1,3-dithiane (6c).** Colorless solid (3.84 g, 79.3%). Crystallization from *n*-hexane gave analytically pure sample as needles: mp 103.4–104.2 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.92 (s, 9H, $CH_3C$), 1.69 (tt, $^3J_{H-H}$ = 11.54 Hz, $^3J_{H-H}$ = 2.37 Hz, 1H, *t*-BuC*H*), 2.59 (dd, $^2J_{H-H}$ = 13.77 Hz, $^3J_{H-H}$ = 2.37 Hz, 2H, H(4,6)$_{eq}$), 3.38 (ddd, $^2J_{H-H}$ = 13.77 Hz, $^3J_{H-H}$ = 11.54 Hz, $^4J_{H-P}$ = 1.65 Hz, 2H, H(4,6)$_{ax}$), 3.42 (d, $^2J_{H-P}$ = 18.0 Hz, 1H, HCP), 3.90 (d, $^3J_{H-P}$ = 10.56 Hz, 6H, $CH_3O$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 21.3; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 27.04 (s, $CH_2$), 27.13 (s, $CH_3C$), 31.76 (d, $^1J_{C-P}$ = 159.5 Hz, CHP), 34.12 (s, $CMe_3$), 46.44 (d, $^4J_{C-P}$ = 1.8 Hz, *C*H-*t*-Bu), 54.51 (d, $^2J_{C-P}$ = 7.4 Hz, $CH_3O$); IR (KBr) 1020 (vs), 1059 (vs), 1222 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 284 (20, M$^{\bullet+}$), 175 (100), 147 (16), 57 (34), 45 (17), 41 (28). Anal. Calcd for $C_{10}H_{21}O_3PS_2$: C, 42.23; H, 7.44. Found: C, 41.98; H, 7.50.

***trans*-5-*tert*-Butyl-2-(dimethoxyphosphoryl)-1,3-dithiane (6d).** Colorless solid (0.61 g, 12.6%). Crystallization from *n*-hexane afforded analytically pure sample as colorless plates: mp 83.8–85.4 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.91 (s, 9H, $CH_3C$), 1.76 (tt, $^3J_{H-H}$ = 11.06 Hz, $^3J_{H-H}$ = 2.61 Hz, 1H, *t*-BuC*H*), 2.68 (dd, $^2J_{H-H}$ = 14.08 Hz, $^3J_{H-H}$ = 11.06 Hz, 2H, H(4,6)$_{ax}$), 2.96 (ddd, $^2J_{H-H}$ = 14.08 Hz, $^4J_{H-P}$ = 4.81 Hz, $^3J_{H-H}$ = 2.61 Hz, 2H, H(4,6)$_{eq}$), 3.86 (d, $^3J_{H-P}$ = 10.98 Hz, 6H, $CH_3O$), 4.48 (d, $^2J_{H-P}$ = 18.54 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 21.6; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 27.08 (s, $CH_3C$), 31.90 (d, $^3J_{C-P}$ = 8.7 Hz, $CH_2$), 34.09 (d, $^5J_{C-P}$ = 1.7 Hz, $CMe_3$), 40.81 (d, $^1J_{C-P}$ = 148.1 Hz, CHP), 46.10 (s, *C*H-*t*-Bu), 54.15 (d, $^2J_{C-P}$ = 6.6 Hz, $CH_3O$); IR (KBr) 830 (vs), 1030 (vs), 1243 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 284 (13, M$^{\bullet+}$), 175 (100), 117 (15), 109 (21), 79 (23), 57 (68), 45 (31), 41 (72), 29 (35). Anal. Calcd for $C_{10}H_{21}O_3PS_2$: C, 42.23; H, 7.44. Found: C, 42.46; H, 7.38.

**2-(Dimethoxyphosphoryl)-*cis*-4,6-dimethyl-1,3-dithiane (6e,f), Mixture of Diastereomers.** The procedure for the synthesis of **6c,d** was followed to transform **15** (3.0 g, 20.3 mmol) into a mixture of **6e** and **6f**. The mixture was separated by column chromatography with *n*-hexane–diethyl ether as an eluent to give chromatographically pure **6e** and **6f**.

***r*-2-(Dimethoxyphosphoryl)-*t*-4,*t*-6-dimethyl-1,3-dithiane (6e).** Colorless solid (3.06 g, 58.9%). Crystallization from *n*-hexane gave colorless needles: mp 84.5–85.8 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.18 (d, $^3J_{H-H}$ = 6.90 Hz, 6H, $CH_3C$), 1.22 (dt, $^2J_{H-H}$ = 13.82 Hz, $^3J_{H-H}$ = 11.81 Hz, 1H, H(5)$_{ax}$), 2.07 (dt, $^2J_{H-H}$ = 13.82 Hz, $^3J_{H-H}$ = 2.20 Hz, 1H, H(5)$_{eq}$), 3.56 (dqdd, $^3J_{H-H}$ = 11.81 Hz, $^3J_{H-H}$ = 6.90 Hz, $^3J_{H-H}$ = 2.20 Hz, $^4J_{H-P}$ = 1.85 Hz, 2H, C*H*CH$_3$), 3.71 (d, $^2J_{H-P}$ = 18.99 Hz, 1H, HCP), 3.86 (d, $^3J_{H-P}$ = 10.56 Hz, 6H, $CH_3O$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 21.1; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.58 (s, $CH_3$), 35.10 (s, $CHCH_3$), 36.87 (d, $^1J_{C-P}$ = 160.3 Hz, CHP), 43.40 (d, $^4J_{C-P}$ = 1.7 Hz, $CH_2$), 54.52 (d, $^2J_{C-P}$ = 7.4 Hz, $CH_3O$); IR (KBr) 840 (s), 1048 (vs), 1232 (s), 1256 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 256 (29, M$^{\bullet+}$), 156 (33), 147 (100), 109 (15), 79 (21), 69 (43), 45 (28), 41 (32). Anal. Calcd for $C_8H_{17}O_3PS_2$: C, 37.49; H, 6.69. Found: C, 37.66; H, 6.68.

***r*-2-(Dimethoxyphosphoryl)-*c*-4,*c*-6-dimethyl-1,3-dithiane (6f).** Colorless oil (0.67 g, 13.0%) which crystallized on standing: mp 45.0–48.0 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.27 (d, $^3J_{H-H}$ = 6.84 Hz, 6H, $CH_3C$), 1.37 (dt, $^2J_{H-H}$ = 14.11 Hz, $^3J_{H-H}$ = 11.58 Hz, 1H, H(5)$_{ax}$), 2.13 (dtd, $^2J_{H-H}$ = 14.11 Hz, $^3J_{H-H}$ = 2.20 Hz, $^5J_{H-P}$ = 2.20 Hz, 1H, H(5)$_{eq}$), 2.89 (dqdd, $^3J_{H-H}$ = 11.58 Hz, $^3J_{H-H}$ = 6.84 Hz, $^3J_{H-H}$ = 2.20 Hz, $^4J_{H-P}$ = 0.7 Hz, 2H, C*H*CH$_3$), 3.88 (d, $^3J_{H-P}$ = 11.03 Hz, 6H, $CH_3O$), 4.61 (d, $^2J_{H-P}$ = 20.04 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 20.9; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.47 (d, $^4J_{C-P}$ = 1.9 Hz, $CH_3C$), 40.89 (d, $^3J_{C-P}$ = 9.2 Hz, $CHCH_3$), 43.35 (s, $CH_2$), 43.87 (d, $^1J_{C-P}$ = 147.0 Hz, CHP), 54.16 (d, $^2J_{C-P}$ = 6.5 Hz, $CH_3O$); IR (KBr) 832 (s), 864 (s), 1044 (vs), 1248 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 256 (15, M$^{\bullet+}$), 149 (11), 147 (100), 69 (27), 41 (14). Anal. Calcd for $C_8H_{17}O_3PS_2$: C, 37.49; H, 6.69. Found: C, 37.82; H, 6.66.

**2-(Diethoxyphosphoryl)-5,5-dimethyl-1,3-dithiane (7b).** The procedure used for **6b** was applied to transform **32** (1.687 g, 11.4 mmol) and triethyl phosphite (2.01 g, 12.1 mmol) into **7b**. Column chromatography with *n*-heptane–diethyl ether as an eluent afforded chromatographically pure **7b** (1.488 g, 45.9%), colorless oil: $n^{22}_D$ = 1.5141; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.09 (s, 3H, $CH_3C$), 1.35 (t, $^3J_{H-H}$ = 7.1 Hz, 6H, $CH_3CH_2$), 1.60 (s, 3H, $CH_3C$), 2.19 (d, $^2J_{H-H}$ = 13.8 Hz, 2H, H(4,6)$_{eq}$), 3.33 (dd, $^2J_{H-H}$ = 13.8 Hz, $^4J_{H-P}$ = 3.0 Hz, 2H, H(4,6)$_{ax}$), 3.51 (d, $^2J_{H-P}$ = 18.2 Hz, 1H, HCP), 4.24 (dq, $^3J_{H-P}$ = 7.8 Hz, $^3J_{H-H}$ = 7.1 Hz, 4H, $CH_2CH_3$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 18.8; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 16.53 (d, $^3J_{C-P}$ = 5.8 Hz, $CH_3CH_2$), 24.28 (s, $CH_3C$), 25.96 (s, $CMe_2$), 30.40 (s, $CH_3C$), 33.55 (d, $^1J_{C-P}$ = 156.5 Hz, CHP), 38.30 (s, $CH_2S$), 63.76 (d, $^2J_{C-P}$ = 7.2 Hz, $CH_2O$); IR (film) 968 (s), 1024 (vs), 1039 (vs), 1244 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 284 (12, M$^{\bullet+}$), 251 (8), 147 (100), 69 (25), 41 (12). Anal. Calcd for $C_{10}H_{21}O_3PS_2$: C, 42.24; H, 7.44. Found: C, 42.60; H, 7.49.

**5-*tert*-Butyl-2-(diethoxyphosphoryl)-1,3-dithiane (7c,d), Mixture of Diastereomers.** The procedure for the synthesis of **6c,d** was followed to transform **14** (2.0 g, 11.4 mmol) and triethyl phosphite (2.01 g, 12.1 mmol) into a mixture of **7c** and **7d**. The mixture was separated by column chromatography with *n*-heptane–diethyl ether as an eluent to give chromatographically pure **7c** and **7d**.

***cis*-5-*tert*-Butyl-2-(diethoxyphosphoryl)-1,3-dithiane (7c).** Colorless solid (2.315 g, 65.2%). Crystallization from *n*-hexane afforded an analytically pure sample of **7c**, colorless prisms: mp 68.2–70.1 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.90 (s, 9H, $CH_3C$), 1.36 (td, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-P}$ = 0.6 Hz, 6H, $CH_3CH_2$), 1.67 (tt, $^3J_{H-H}$ = 11.6 Hz, $^3J_{H-H}$ = 2.4 Hz, 1H, *t*-BuC*H*), 2.56 (ddd, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 2.4 Hz, $^4J_{H-H}$ = 0.6 Hz, 2H, H(4,6)$_{eq}$), 3.35 (d, $^2J_{H-P}$ = 18.0 Hz, 1H, HCP), 3.36 (dddd, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 11.6 Hz, $^4J_{H-P}$ = 2.2 Hz, $^4J_{H-H}$ = 0.5 Hz, 2H, H(4,6)$_{ax}$), 4.25 (dq, $^3J_{H-P}$ = 7.7 Hz, $^3J_{H-H}$ = 7.1 Hz, 4H, $CH_2O$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 19.6; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 16.56 (d, $^3J_{C-P}$ = 5.9 Hz, $CH_3CH_2$), 27.01 (s, $CH_2S$), 27.14 (s, $CH_3C$), 32.09 (d, $^1J_{C-P}$ = 158.4 Hz, CHP), 34.11 (s, $CMe_3$), 46.53 (d, $^4J_{C-P}$ = 1.8 Hz, *C*H-*t*-Bu), 63.75 (d, $^2J_{C-P}$ = 7.3 Hz, $CH_2O$); IR (KBr) 960 (vs), 972 (vs), 1024 (vs), 1042 (vs), 1232 (s), 1240 (s), 2968 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 312 (11, M$^{\bullet+}$), 279 (10), 175 (100), 57 (20), 41 (13). Anal. Calcd for $C_{12}H_{25}O_3PS_2$: C, 46.13; H, 8.07. Found: C, 46.21; H, 8.05.

***trans*-5-*tert*-Butyl-2-(diethoxyphosphoryl)-1,3-dithiane (7d).** Colorless solid (0.542 g, 15.3%). Crystallization from *n*-hexane afforded an analytically pure sample of **7d**, colorless crystals: mp 78.5–82.2 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.91 (s, 9H, $CH_3C$), 1.37 (td, $^3J_{H-H}$ = 7.1 Hz, $^4J_{H-P}$ = 0.6 Hz, 6H, $CH_3CH_2$), 1.75 (tt, $^3J_{H-H}$ = 11.09 Hz, $^3J_{H-H}$ = 2.63 Hz, 1H, *t*BuC*H*), 2.66 (dd, $^2J_{H-H}$ = 14.1 Hz, $^3J_{H-H}$ = 11.09 Hz, 2H, H(4,6)$_{ax}$), 2.94 (ddd, $^2J_{H-H}$ = 14.1 Hz, $^4J_{H-P}$ = 5.0 Hz, $^3J_{H-H}$ = 2.63 Hz, 2H, H(4,6)$_{eq}$), 4.23 (dq, $^3J_{H-P}$ = 8.1 Hz, $^3J_{H-H}$ = 7.1 Hz, 4H, $CH_2O$), 4.46 (d, $^2J_{H-P}$ = 18.6 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 18.8; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 16.40 (d, $^3J_{C-P}$ = 6.0 Hz, $CH_3CH_2$), 27.11 (s, $CH_3C$), 31.98 (d, $^3J_{C-P}$ = 8.7 Hz, $CH_2S$), 34.08 (d, $^5J_{C-P}$ = 1.7 Hz, $CMe_3$), 41.44 (d, $^1J_{C-P}$ = 147.4 Hz, CHP), 46.17 (s, *C*H-*t*-Bu), 63.72 (d, $^2J_{C-P}$ = 6.6 Hz, $CH_2O$); IR (KBr) 976 (s), 1020 (vs), 1052 (s), 1246 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 312 (20, M$^{\bullet+}$), 279 (26), 175 (100), 57 (84), 45 (20), 41

(55), 29 (45). Anal. Calcd for $C_{12}H_{25}O_3PS_2$: C, 46.13; H, 8.07. Found: C, 46.25; H, 8.07.

**2-(Diethoxyphosphoryl)-*cis*-4,6-dimethyl-1,3-dithiane (7e,f), Mixture of Diastereomers.** The procedure for the synthesis of **6c,d** was followed to transform **15** (1.0 g, 6.8 mmol) and triethyl phosphite (1.2 g, 7.2 mmol) into a mixture of **7e** and **7f**. The mixture was separated by column chromatography with *n*-heptane–diethyl ether as eluent to give chromatographically pure **7e** and **7f**.

***r*-2-(Diethoxyphosphoryl)-*t*-4,*t*-6-dimethyl-1,3-dithiane (7e).** Colorless solid (1.128 g, 58.7%). Crystallization from *n*-hexane gave colorless prisms: mp 75.0–76.8 °C; $^1$H NMR (200.13 MHz, $CDCl_3$) $\delta$ 1.19 (d, $^3J_{H-H}$ = 6.90 Hz, 6H, $CH_3CH$), 1.23 (dt, $^2J_{H-H}$ = 13.80 Hz, $^3J_{H-H}$ = 11.62 Hz, 1H, H(5)$_{ax}$), 1.36 (td, $^3J_{H-H}$ = 7.07 Hz, $^4J_{H-P}$ = 0.61 Hz, 6H, $CH_3CH_2$), 2.08 (dt, $^2J_{H-H}$ = 13.80 Hz, $^3J_{H-H}$ = 2.22 Hz, 1H, H(5)$_{eq}$), 3.57 (dqdd, $^3J_{H-H}$ = 11.62 Hz, $^3J_{H-H}$ = 6.90 Hz, $^3J_{H-H}$ = 2.22 Hz, $^4J_{H-P}$ = 2.17 Hz, 2H, $CHCH_3$), 3.71 (d, $^2J_{H-P}$ = 18.44 Hz, 1H, HCP), 4.24 (dq, $^3J_{H-P}$ = 7.60 Hz, $^3J_{H-H}$ = 7.07 Hz, 4H, $CH_2O$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 19.4; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 16.52 (d, $^3J_{C-P}$ = 5.9 Hz, $CH_3CH_2$), 21.61 (s, $CH_3CH$), 35.03 (s, $CHCH_3$), 37.24 (d, $^1J_{C-P}$ = 159.6 Hz, CHP), 43.49 (d, $^4J_{C-P}$ = 1.8 Hz, $CCH_2C$), 63.81 (d, $^2J_{C-P}$ = 7.3 Hz, $CH_2O$); IR (KBr) 972 (s), 1028 (vs), 1055 (s), 1260 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 284 (15, M$^{\cdot+}$), 251 (14), 147 (100), 69 (25), 41 (19). Anal. Calcd for $C_{10}H_{21}O_3PS_2$: C, 42.24; H, 7.44. Found: C, 42.51; H, 7.44.

***r*-2-(Diethoxyphosphoryl)-*c*-4,*c*-6-dimethyl-1,3-dithiane (7f).** Colorless oil (201 mg, 10.5%): $n^{22}_D$ = 1.5077; $^1$H NMR (200.13 MHz, $CDCl_3$) $\delta$ 1.27 (dd, $^3J_{H-H}$ = 6.84 Hz, $^5J_{H-P}$ = 0.54 Hz, 6H, $CH_3CH$), 1.36 (dt, $^2J_{H-H}$ = 14.01 Hz, $^3J_{H-H}$ = 11.44 Hz, 1H, H(5)$_{ax}$), 1.36 (td, $^3J_{H-H}$ = 7.06 Hz, $^4J_{H-P}$ = 0.60 Hz, 6H, $CH_3CH_2$), 2.10 (dtd, $^2J_{H-H}$ = 14.01 Hz, $^3J_{H-H}$ = 2.31 Hz, $^5J_{H-P}$ = 2.31 Hz, 1H, H(5)$_{eq}$), 2.89 (dqdd, $^3J_{H-H}$ = 11.44 Hz, $^3J_{H-H}$ = 6.87 Hz, $^3J_{H-H}$ = 2.31 Hz, $^4J_{H-P}$ = 0.78 Hz, 2H, $CHCH_3$), 4.25 (dq, $^3J_{H-P}$ = 8.30 Hz, $^3J_{H-H}$ = 7.06 Hz, 4H, $CH_2O$), 4.57 (d, $^2J_{H-P}$ = 19.97 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 18.6; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 16.40 (d, $^3J_{C-P}$ = 5.8 Hz, $CH_3CH_2$), 21.49 (d, $^4J_{C-P}$ = 1.9 Hz, $CH_3CH$), 40.89 (d, $^3J_{C-P}$ = 9.3 Hz, $CHCH_3$), 43.50 (s, $CCH_2C$), 44.50 (d, $^1J_{C-P}$ = 146.7 Hz, CHP), 63.74 (d, $^2J_{C-P}$ = 6.5 Hz, $CH_2O$); IR (film) 972 (s), 1020 (vs), 1035 (vs), 1256 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 284 (10, M$^{\cdot+}$), 147 (100), 81 (11), 69 (24), 41 (16), 29 (17). Anal. Calcd for $C_{10}H_{21}O_3PS_2$: C, 42.24; H, 7.44. Found: C, 42.57; H, 7.64.

**2-[Bis(2,2,2-trifluoroethoxy)phosphoryl]-5,5-dimethyl-1,3-dithiane (8b).** The procedure used for **6b** was applied to transform **24** (1.687 g, 11.4 mmol) and **16** (3.74 g, 11.4 mmol) into **8b**. Column chromatography with benzene–diethyl ether as an eluent afforded chromatographically pure **8b** (1.853 g, 41.4%), colorless oil: $n^{22}_D$ = 1.4512; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.09 (s, 3H, $CH_3$), 1.30 (s, 3H, $CH_3$), 2.14 (d, $^2J_{H-H}$ = 14.0 Hz, 2H, H(4,6)$_{eq}$), 3.38 (dd, $^2J_{H-H}$ = 14.0 Hz, $^4J_{H-P}$ = 3.2 Hz, 2H, H(4,6)$_{ax}$), 3.58 (d, $^2J_{H-P}$ = 18.9 Hz, 1H, HCP), 4.46 (dqd, $^2J_{H-H}$ = 12.1, $^3J_{H-F}$ = 8.1 Hz, $^3J_{H-P}$ = 8.1 Hz, 2H, $CHHCF_3$), 4.56 (dqd, $^2J_{H-H}$ = 12.1, $^3J_{H-F}$ = 8.1 Hz, $^3J_{H-P}$ = 8.1 Hz, 2H, $CHHCF_3$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 19.4; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 22.98 (s, $CH_3$), 25.78 (s, $CMe_2$), 31.45 (s, $CH_3C$), 31.73 (d, $^1J_{C-P}$ = 160.5 Hz, CHP), 37.45 (s, $CH_2S$), 63.74 (qd, $^2J_{C-F}$ = 38.1 Hz, $^2J_{C-P}$ = 6.7 Hz, $CH_2O$), 122.51 (qd, $^1J_{C-F}$ = 277.6 Hz, $^3J_{C-P}$ = 7.7 Hz, $CF_3$); IR (film) 856 (s), 964 (vs), 1068 (vs), 1104 (vs), 1164 (vs), 1252 (vs), 1292 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 392 (13, M$^{\cdot+}$), 149 (15), 148 (14), 147 (100), 69 (62), 55 (15), 45 (57), 41 (42). Anal. Calcd for $C_{10}H_{15}F_6O_3PS_2$: C, 30.61; H, 3.85. Found: C, 30.54; H, 3.89.

**2-[Bis(2,2,2-trifluoroethoxy)phosphoryl]-5-*tert*-butyl-1,3-dithiane (8c,d), Mixture of Diastereomers.** The procedure for the synthesis of **6c,d** was followed to transform **14** (2.0 g, 11.4 mmol) and **16** (3.74 g, 11.4 mmol; method A) or **17** (5.3 g, ca 11.4 mmol; method B) into mixtures of **8c** and **8d**. The mixtures obtained *via* methods A and B were separated by column chromatography with benzene–diethyl ether as eluent to give chromatographically pure **8c** and **8d**.

***cis*-2-[Bis(2,2,2-trifluoroethoxy)phosphoryl]-5-*tert*-butyl-1,3-dithiane (8c).** Method A: 2.424 g (50.7%) of colorless solid. Method B: 2.794 g (58.5%) of colorless solid. Crystallization from *n*-hexane afforded an analytically pure sample **8c**, colorless needles: mp 55.3–57.1 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.92 (s, 9H, $CH_3$), 1.69 (tt, $^3J_{H-H}$ = 11.6 Hz, $^3J_{H-H}$ = 2.3 Hz, 1H, *t*-Bu*CH*), 2.60 (dd, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 2.3 Hz, 2H, H(4,6)$_{eq}$), 3.27 (ddd, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 11.6 Hz, $^4J_{H-P}$ = 2.6 Hz, 2H, H(4,6)$_{ax}$), 3.56 (d, $^2J_{H-P}$ = 19.0 Hz, 1H, HCP), 4.47 (dqd, $^2J_{H-H}$ = 12.1 Hz, $^3J_{H-F}$ = 8.1 Hz, $^3J_{H-P}$ = 8.1 Hz, 4H, $CH_2O$), 4.57 (dqd, $^2J_{H-H}$ = 12.1 Hz, $^3J_{H-F}$ = 8.1 Hz, $^3J_{H-P}$ = 8.1 Hz, 4H, $CH_2O$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 20.2; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 27.08 (s, $CH_3$, $CH_2S$), 31.70 (d, $^1J_{C-P}$ = 161.4 Hz, CHP), 34.16 (s, $CMe_3$), 46.10 (d, $^4J_{C-P}$ = 1.8 Hz, *CH*-*t*-Bu), 63.75 (qd, $^2J_{C-F}$ = 38.1 Hz, $^2J_{C-P}$ = 6.7 Hz, $CH_2O$), 122.53 (qd, $^1J_{C-F}$ = 277.7 Hz, $^3J_{C-P}$ = 7.8 Hz, $CF_3$); IR (KBr) 962 (s), 1088 (vs), 1112 (s), 1164 (vs), 1178 (vs), 1256 (vs), 1290 (s), 1304 (s), 2896 (s), 2968 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 420 (9, M$^{\cdot+}$), 175 (100), 117 (10), 57 (34), 45 (15), 41 (25). Anal. Calcd for $C_{12}H_{19}F_6O_3PS_2$: C, 34.29; H, 4.56. Found: C, 34.48; H, 4.54.

***trans*-2-[Bis(2,2,2-trifluoroethoxy)phosphoryl]-5-*tert*-butyl-1,3-dithiane (8d).** Method A: 0.499 g (10.4%) of colorless solid. Method B: 0.793 g (16.6%) of colorless solid. Crystallization from *n*-hexane afforded an analytically pure sample of **8d**, colorless crystals: mp 87.0–88.5 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.92 (s, 9H, $CH_3$), 1.83 (tt, $^3J_{H-H}$ = 10.34 Hz, $^3J_{H-H}$ = 3.57 Hz, 1H, *t*-Bu*CH*), 2.72 (dd, $^2J_{H-H}$ = 13.6 Hz, $^3J_{H-H}$ = 10.34 Hz, 2H, H(4,6)$_{ax}$), 3.00 (ddd, $^2J_{H-H}$ = 13.6 Hz, $^4J_{H-P}$ = 4.7 Hz, $^3J_{H-H}$ = 3.57 Hz, 2H, H(4,6)$_{eq}$), 4.43 (dqd, $^2J_{H-H}$ = 11.8 Hz, $^3J_{H-F}$ = 8.0 Hz, $^3J_{H-P}$ = 8.0 Hz, 2H, $CH_2O$), 4.48 (d, $^2J_{H-P}$ = 17.1 Hz, 1H, HCP), 4.51 (dqd, $^2J_{H-H}$ = 11.8 Hz, $^3J_{H-F}$ = 8.0 Hz, $^3J_{H-P}$ = 8.0 Hz, 2H, $CH_2O$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 22.2; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 27.05 (s, $CH_3$), 30.17 (d, $^3J_{C-P}$ = 7.0 Hz, $CH_2S$), 34.28 (d, $^5J_{C-P}$ = 1.2 Hz, $CMe_3$), 38.79 (d, $^1J_{C-P}$ = 156.4 Hz, CHP), 45.20 (s, *CH*-*t*-Bu), 63.44 (qd, $^2J_{C-F}$ = 38.1 Hz, $^2J_{C-P}$ = 6.2 Hz, $CH_2O$), 122.37 (qd, $^1J_{C-F}$ = 277.7 Hz, $^3J_{C-P}$ = 8.1 Hz, $CF_3$); IR (KBr) 958 (s), 1076 (vs), 1092 (s), 1168 (vs), 1193 (s), 1260 (vs), 1294 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 420 (7, M$^{\cdot+}$), 175 (100), 57 (33), 55 (11), 45 (11), 41 (22), 18 (14). Anal. Calcd for $C_{12}H_{19}F_6O_3PS_2$: C, 34.29; H, 4.56. Found: C, 34.57; H, 4.70.

**2-[Bis(2,2,2-trifluoroethoxy)phosphoryl]-*cis*-4,6-dimethyl-1,3-dithiane (8e,f), Mixture of Diastereomers.** The procedure for the synthesis of **6c,d** was followed to transform **15** (1.0 g, 6.8 mmol) and **17** (3.2 g, ca 6.8 mmol) into a mixture of **8e** and **8f**. The mixture was separated by column chromatography with *n*-heptane–diethyl ether as eluent to give chromatographically pure **8e** and **8f**.

***r*-2-[Bis(2,2,2-trifluoroethoxy)phosphoryl]-*t*-4,*t*-6-dimethyl-1,3-dithiane (8e).** Colorless solid (760 mg, 28.7%). Crystallization from *n*-hexane gave colorless needles: mp 80.2–81.8 °C; $^1$H NMR (200.13 MHz, $CDCl_3$) $\delta$ 1.21 (d, $^3J_{H-H}$ = 6.89 Hz, 6H, $CH_3$), 1.26 (dt, $^2J_{H-H}$ = 13.95 Hz, $^3J_{H-H}$ = 11.61 Hz, 1H, H(5)$_{ax}$), 2.09 (dt, $^2J_{H-H}$ = 13.95 Hz, $^3J_{H-H}$ = 2.14 Hz, 1H, H(5)$_{eq}$), 3.48 (dqdd, $^3J_{H-H}$ = 11.61 Hz, $^3J_{H-H}$ = 6.89 Hz, $^3J_{H-H}$ = 2.14 Hz, $^4J_{H-P}$ = 2.0 Hz, 2H, CH), 3.88 (d, $^2J_{H-P}$ = 19.72 Hz, 1H, HCP), 4.45 (dqd, $^2J_{H-H}$ = 12.02 Hz, $^3J_{H-F}$ = 8.1 Hz, $^3J_{H-P}$ = 8.1 Hz, 2H, $CHHO$), 4.54 (dqd, $^2J_{H-H}$ = 12.02 Hz, $^3J_{H-F}$ = 8.1 Hz, $^3J_{H-P}$ = 8.1 Hz, 2H, $CHHO$); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 20.4; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.49 (s, $CH_3$) 35.36 (s, $CHCH_3$), 36.91 (d, $^1J_{C-P}$ = 162.9 Hz, CHP), 42.98 (d, $^4J_{C-P}$ = 1.7 Hz, $CCH_2C$), 63.78 (qd, $^2J_{C-F}$ = 38.1 Hz, $^2J_{C-P}$ = 7.3 Hz, $CH_2O$), 122.53 (qd, $^1J_{C-F}$ = 277.3 Hz, $^3J_{C-P}$ = 8.0 Hz, $CF_3$); IR (KBr) 960 (s), 1080 (vs), 1107 (s), 1162 (vs), 1262 (vs), 1292 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 392 (9, M$^{\cdot+}$), 147 (100), 101 (26), 69 (25), 45 (13), 41 (13). Anal. Calcd for $C_{10}H_{15}F_6O_3PS_2$: C, 30.61; H, 3.85. Found: C, 30.63; H, 3.83.

***r*-2-[Bis(2,2,2-trifluoroethoxy)phosphoryl]-*c*-4,*c*-6-dimethyl-1,3-dithiane (8f).** Colorless crystals (226 mg, 8.5%): mp 70.5–73.0 °C; $^1$H NMR (200.13 MHz, $CDCl_3$) $\delta$ 1.30 (dd, $^3J_{H-H}$ = 6.85 Hz, $^5J_{H-P}$ = 0.60 Hz, 6H, $CH_3$), 1.39 (dt, $^2J_{H-H}$ = 14.15 Hz, $^3J_{H-H}$ = 11.47 Hz, 1H, H(5)$_{ax}$), 2.13 (dtd, $^2J_{H-H}$ = 14.15 Hz, $^3J_{H-H}$ = 2.34 Hz, $^5J_{H-P}$ = 2.34 Hz, 1H, H(5)$_{eq}$), 2.89 (dqdd, $^3J_{H-H}$ = 11.47 Hz, $^3J_{H-H}$ = 6.85 Hz, $^3J_{H-H}$ = 2.34 Hz, $^4J_{H-P}$ = 0.84 Hz, 2H, $CHCH_3$), 4.45 (dqd, $^2J_{H-H}$ = 11.99 Hz, $^3J_{H-F}$ = 8.80 Hz, $^3J_{H-P}$ = 8.0 Hz, 2H, $CHHO$), 4.54 (dqd, $^2J_{H-H}$ = 11.99 Hz, $^3J_{H-F}$ = 8.80 Hz, $^3J_{H-P}$ = 8.0 Hz, 2H, $CHHO$), 4.70 (d, $^2J_{H-P}$ = 20.86 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 21.4; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.45 (d, $^4J_{C-P}$ = 1.9 Hz, $CH_3$), 40.99 (d, $^3J_{C-P}$ = 9.8 Hz, $CHCH_3$), 43.06 (s, $CCH_2C$), 43.97 (d, $^1J_{C-P}$ = 152.0 Hz, CHP), 63.35 (qd, $^2J_{C-F}$ = 38.6 Hz, $^2J_{C-P}$ = 5.9 Hz, $CH_2O$), 122.31 (qd, $^1J_{C-F}$ = 277.5 Hz, $^3J_{C-P}$ = 8.2 Hz, $CF_3$); IR (KBr) 964 (s), 1064 (vs), 1104 (s), 1168 (vs), 1256 (s), 1302 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative

intensity) 392 (8, $M^{\bullet+}$), 147 (100), 69 (27), 45 (16), 41 (18). Anal. Calcd for $C_{10}H_{15}F_6O_3PS_2$: C, 30.61; H, 3.85. Found: C, 30.53; H, 3.89.

**2-(Diphenylphosphinoyl)-1,3-dithiane (9a).** The procedure for the synthesis of **6c,d** was applied to transform 1,3-dithiane (11.4 g, 94.8 mmol) and **18** (23.2 g, 94.8 mmol) into **9a**. After the addition of 2-chloro-1,3-dithiane solution to **18** a white precipitate soon appeared. After the solution cooled to room temperature, *n*-pentane (250 mL) was added, and the mixture was left to stand overnight in a refrigerator (−15 °C). Colorless crystals were filtered off, washed with *n*-pentane, and dried in vacuum to give **9a** (25.8 g, 85.4%), needles: mp 246.0–248.0 °C (lit.[12] mp 242–243 °C); $^1$H NMR (300.13 MHz, $CDCl_3$) δ 2.01 (dtt, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 2.9 Hz, 1H, $H(5)_{ax}$), 2.14 (dtt, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 5.7 Hz, $^3J_{H-H}$ = 2.5 Hz, 1H, $H(5)_{eq}$), 2.56 (ddd, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 5.7 Hz, $^3J_{H-H}$ = 2.9 Hz, 2H, $H(4,6)_{eq}$), 3.72 (dddd, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 11.1 Hz, $^3J_{H-H}$ = 2.5, $^4J_{H-P}$ = 2.5 Hz, Hz, 2H, $H(4,6)_{ax}$), 4.07 (d, $^2J_{H-P}$ = 5.9 Hz, 1H, HCP), 7.45–7.90 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 34.8 (lit.[12] δ 34.1); $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 24.96 (s, $CCH_2C$), 27.02 (s, $CH_2S$), 37.22 (d, $^1J_{C-P}$ = 69.4 Hz, CHP), 128.50 (d, $^3J_{C-P}$ = 11.7, $C_{Ar(meta)}$), 131.28 (d, $^2J_{C-P}$ = 8.7 Hz, $C_{Ar(ortho)}$), 131.90 (d, $^4J_{C-P}$ = 2.6 Hz, $C_{Ar(para)}$); IR (KBr) 693 (vs), 717 (s), 741 (s), 1152 (s), 1178 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 320 (3, $M^{\bullet+}$), 183 (12), 175 (100), 119 (46), 77 (12), 69 (21), 57 (40), 55 (22), 43 (22), 41 (25), 18 (18). Anal. Calcd for $C_{16}H_{17}OPS_2$: C, 59.98; H, 5.35. Found: C, 59.96; H, 5.48.

**5,5-Dimethyl-2-(diphenylphosphinoyl)-1,3-dithiane (9b).** The procedure for the synthesis of **6c,d** was applied to transform **32** (1.617 g, 10.9 mmol) and **18** (2.66 g, 10.9 mmol) into **9b**. After the addition of the relevant 2-chloro-1,3-dithiane solution to **18**, a white precipitate soon appeared. After the solution cooled to room temperature, *n*-pentane (30 mL) was added, and the mixture was left to stand overnight in a refrigerator (−15 °C). Colorless crystals were filtered off, washed with *n*-pentane, and dried in vacuum to give **9b** (2.283 g, 60.1%), very thin needles mp 256.0–259.7 °C. Sublimation in vacuum afforded analytically pure sample: mp 263.2–263.4 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 1.12 (s, 3H, $CH_3$), 1.25 (s, 3H, $CH_3$), 2.23 (d, $^2J_{H-H}$ = 13.8 Hz, 2H, $H(4,6)_{eq}$), 3.49 (dd, $^2J_{H-H}$ = 13.8 Hz, $^4J_{H-P}$ = 2.2 Hz, 2H, $H(4,6)_{ax}$), 4.02 (d, $^2J_{H-P}$ = 5.5 Hz, 1H, HCP), 7.40–7.90 (M, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 33.9; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 24.84 (s, $CH_3$), 25.99 (d, $^4J_{C-P}$ = 1.6 Hz, $CMe_2$), 29.75 (s, $CH_3$), 36.80 (d, $^1J_{C-P}$ = 70.0 Hz, CHP), 39.14 (s, $CH_2$), 128.50 (d, $^3J_{C-P}$ = 11.5 Hz, $C_{Ar(meta)}$), 131.32 (d, $^2J_{C-P}$ = 7.5 Hz, $C_{Ar(ortho)}$), 131.92 (d, $^4J_{C-P}$ = 1.8 Hz, $C_{Ar(para)}$); IR (KBr) 688 (vs), 710 (s), 740 (s), 1109 (s), 1160 (s), 1175 (vs), 1423 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 348 (5, $M^{\bullet+}$), 149 (10), 147 (100), 77 (12), 69 (19). Anal. Calcd for $C_{18}H_{21}OPS_2$: C, 62.04; H, 6.08. Found: C, 62.10; H, 6.20.

**5-*tert*-Butyl-2-(diphenylphosphinoyl)-1,3-dithianes (9c,d), Mixture of Diastereomers.** The procedure for the synthesis of **6c,d** was applied to transform **14** (17.6 g, 100 mmol) and **18** (24.4 g, 100 mmol) into a mixture of **9c** and **9d**. After the addition of the relevant 2-chloro-1,3-dithiane solution to **18**, a white precipitate soon appeared. Separation of the crude mixture into individual isomers was easily achieved by column chromatography with dichloromethane–ethyl acetate as eluent to afford chromatographically pure **9c** and **9d**.

***cis*-5-*tert*-Butyl-2-(diphenylphosphinoyl)-1,3-dithiane (9c).** Colorless solid (20.5 g, 53.2%). Crystallization from methanol gave analytically pure sample as colorless needles, mp 262.0–262.9 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 0.91 (s, 9H, $CH_3$), 1.73 (tt, $^3J_{H-H}$ = 11.58 Hz, $^3J_{H-H}$ = 2.41 Hz, 1H, *t*-BuC*H*), 2.55 (dd, $^2J_{H-H}$ = 11.58 Hz, $^3J_{H-H}$ = 2.41 Hz, 2H, $H(4,6)_{eq}$), 3.65 (ddd, $^2J_{H-H}$ = 11.58 Hz, $^3J_{H-H}$ = 11.58 Hz, $^4J_{H-P}$ = 0.96 Hz, 2H, $H(4,6)_{ax}$), 3.80 (d, $^2J_{H-P}$ = 3.61 Hz, 1H, HCP), 7.44–7.84 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 35.6; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 27.20 (s, $CH_3$), 27.56 (s, $CH_2$), 34.10 (d, $^1J_{C-P}$ = 71.3 Hz, CHP), 34.15 (S, $CMe_3$), 46.38 (d, $^4J_{C-P}$ = 2.2 Hz, $CHtBu$), 128.54 (d, $^3J_{C-P}$ = 10.9 Hz, $C_{Ar(meta)}$), 131.13 (d, $^2J_{C-P}$ = 8.6 Hz, $C_{Ar(ortho)}$), 131.76 (s, $C_{Ar(para)}$); IR (KBr) 690 (vs), 712 (vs), 1105 (s), 1162 (vs), 1178 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 376 (3, $M^{\bullet+}$), 343 (9), 177 (9), 176 (10), 175 (100), 57 (15). Anal. Calcd for $C_{20}H_{25}OPS_2$: C, 63.82; H, 6.70. Found: C, 63.76; H, 6.81.

***trans*-5-*tert*-Butyl-2-(diphenylphosphinoyl)-1,3-dithiane (9d).** Colorless solid (13.5 g, 34.7%). Crystallization from methanol afforded analytically pure sample: mp 227.0–227.8 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 0.90 (s, 9H, $CH_3$), 1.76 (tt, $^3J_{H-H}$ = 11.07 Hz, $^3J_{H-H}$ = 2.65 Hz, 1H, *t*-BuC*H*), 2.70 (dd, $^2J_{H-H}$ = 13.70 Hz, $^3J_{H-H}$ = 11.07 Hz, 2H, $H(4,6)_{ax}$), 2.96 (ddd, $^2J_{H-H}$ = 13.70 Hz, $^4J_{H-P}$ = 3.07 Hz, $^3J_{H-H}$ = 2.65 Hz, 2H, $H(4,6)_{eq}$), 4.92 (d, $^2J_{H-P}$ = 13.05 Hz, 1H, HCP), 7.48–7.98 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 30.0; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 27.07 (s, $CH_3$), 32.46 (d, $^3J_{C-P}$ = 6.5 Hz, $CH_2$), 34.08 (d, $^5J_{C-P}$ = 1.7 Hz, $CMe_3$), 45.65 (d, $^1J_{C-P}$ = 65.2 Hz, CHP), 45.96 (s, *C*H-*t*-Bu), 128.40 (d, $^3J_{C-P}$ = 12.1 Hz, $C_{Ar(meta)}$), 129.95 (d, $^1J_{C-P}$ = 104.7 Hz, $C_{Ar(ipso)}$), 132.04 (d, $^2J_{C-P}$ = 9.5 Hz, $C_{Ar(ortho)}$), 132.53 (d, $^4J_{C-P}$ = 1.8 Hz, $C_{Ar(para)}$); IR (KBr) 688 (vs), 710 (s), 745 (s), 1108 (s), 1170 (vs), 1189 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 376 (2, $M^{\bullet+}$), 177 (9), 176 (12), 175 (100), 57 (17), 41 (9). Anal. Calcd for $C_{20}H_{25}OPS_2$: C, 63.82; H, 6.70. Found: C, 63.72; H, 6.72.

**2-[Diphenyl(thiophosphinoyl)]-1,3-dithiane (10a).** A solution of *N,N*-diethylaniline (11.4 g, 76.4 mmol) in benzene (110 mL) was added dropwise during 20 min to a stirred suspension of **9a** (22.5 g, 70.3 mmol) and phosphorus pentasulfide (31.6 g, 71.1 mmol) in benzene (740 mL). After the addition was completed, the mixture was stirred under reflux for 6 h and cooled, and then 10% aqueous potassium carbonate solution (600 mL) was added. Stirring was continued until solid phase was completely dissolved. The water phase was discarded. The organic layer was washed with 10% hydrochloric acid (100 mL) and water (150 mL) and dried over anhydrous magnesium sulfate. The solution was filtered through silica gel (50 g) and evaporated under reduced pressure. The solid residue was crystallized from chloroform–diethyl ether to give chromatographically pure **10a** (16.2 g, 68.5%). Subsequent recrystallization from ethyl acetate afforded an analytically pure sample of **10a** as colorless needles: mp 179.0–180.5 °C (lit.[37] mp 177–178 °C); $^1$H NMR (300.13 MHz, $CDCl_3$) δ 2.0–2.1 (m, 2H), 2.60–2.75 (m, 2H), 3.45–3.60 (m, 2H), 4.69 (d, $^2J_{H-P}$ = 9.23 Hz, 1H, HCP), 7.4–8.1 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 49.4 (lit.[37] δ 48.8); $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 24.67 (s, $CCH_2C$), 28.45 (d, $^3J_{C-P}$ = 3.5 Hz, $CH_2S$), 42.36 (d, $^1J_{C-P}$ = 51.8 Hz, CHP), 128.41 (d, $^3J_{C-P}$ = 12.1, $C_{Ar(meta)}$), 131.49 (d, $^1J_{C-P}$ = 80.5 Hz, $C_{Ar(ipso)}$), 131.81 (d, $^4J_{C-P}$ = 2.9 Hz, $C_{Ar(para)}$), 132.03 (d, $^2J_{C-P}$ = 9.7 Hz, $C_{Ar(ortho)}$); IR (KBr) 672 (s), 692 (s), 720 (vs), 748 (s), 1096 (s), 1432 (m) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 336 (4, $M^{\bullet+}$), 183 (14), 139 (13), 121 (10), 119 (100). Anal. Calcd for $C_{16}H_{17}PS_3$: C, 57.11; H, 5.09. Found: C, 57.14; H, 5.08.

**5,5-Dimethyl-2-[diphenyl(thiophosphinoyl)]-1,3-dithiane (10b).** The preparation was carried out following the same procedure as for **10a** and starting from **9b** (17.6 g, 47.3 mmol). Crystallization of the product from chloroform–diethyl ether gave **9b** (13.3 g, 71.5%) as colorless crystals: mp 174.2–176.5 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 1.13 (s, 3H, $CH_3$), 1.15 (s, 3H, $CH_3$), 2.43 (d, $^2J_{H-H}$ = 13.8 Hz, 2H, C*H*H), 3.16 (dd, $^2J_{H-H}$ = 13.8 Hz, $^4J_{H-P}$ = 3.4 Hz, 2H, CH*H*), 4.63 (d, $^2J_{H-P}$ = 8.0 Hz, 1H, HCP), 7.4–8.1 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 48.7; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 25.99 (s, $CMe_2$), 26.99 (d, $^5J_{C-P}$ = 1.4 Hz, $CH_3$), 27.25 (s, $CH_3$), 40.51 (d, $^3J_{C-P}$ = 3.4 Hz, $CH_2$), 42.44 (d, $^1J_{C-P}$ = 51.6 Hz, CHP), 128.40 (d, $^3J_{C-P}$ = 12.1 Hz, $C_{Ar(meta)}$), 131.45 (d, $^1J_{C-P}$ = 80.5 Hz, $C_{Ar(ipso)}$), 131.82 (d, $^4J_{C-P}$ = 2.7 Hz, $C_{Ar(para)}$), 132.10 (d, $^2J_{C-P}$ = 9.7 Hz, $C_{Ar(ortho)}$); IR (KBr) 661 (s), 683 (vs), 702 (vs), 712 (vs), 741 (s), 1091 (vs), 1430 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 364 (2, $M^{\bullet+}$), 183 (14), 147 (100), 139 (13), 69 (18). Anal. Calcd for $C_{18}H_{21}PS_3$: C, 59.31; H, 5.81. Found: C, 59.11; H, 5.86.

***cis*-5-*tert*-Butyl-2-[diphenyl(thiophosphinoyl)]-1,3-dithiane (10c).** The procedure for the synthesis of **10a** was accommodated to transform **9c** (17.8 g, 47.3 mmol) into **10c**. Crystallization of the crude product from chloroform–diethyl ether afforded **10c** (13.3 g, 71.5%), colorless crystals: mp 190–192 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 0.88 (s, 9H, $CH_3$), 1.73 (tt, $^3J_{H-H}$ = 11.49 Hz, $^3J_{H-H}$ = 2.76 Hz, 1H, *t*-BuC*H*), 2.48 (dd, $^2J_{H-H}$ = 13.69 Hz, $^3J_{H-H}$ = 2.76 Hz, 2H, $H(4,6)_{eq}$), 3.89 (ddd, $^2J_{H-H}$ = 13.69 Hz, $^3J_{H-H}$ = 11.49 Hz, $^4J_{H-P}$ = 1.70 Hz, 2H, $H(4,6)_{ax}$), 4.25 (d, $^2J_{H-P}$ = 5.36 Hz, 1H, HCP), 7.4–8.0 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 52.5; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 26.66 (s, $CH_2$), 27.10 (s, $CH_3$), 34.10 (s, $CMe_3$), 34.74 (d, $^1J_{C-P}$ = 52.4 Hz, CHP), 45.62 (d, $^4J_{C-P}$ = 2.2 Hz, *C*H-*t*-Bu), 128.45 (d, $^3J_{C-P}$ = 11.7 Hz, $C_{Ar(meta)}$), 131.55 (d, $^4J_{C-P}$ = 2.6 Hz, $C_{Ar(para)}$), 131.75 (d, $^2J_{C-P}$ = 9.2 Hz, $C_{Ar(ortho)}$), 132.76 (d, $^1J_{C-P}$ = 77.0 Hz, $C_{Ar(ipso)}$); IR (KBr) 704 (vs), 720 (s), 728 (s), 1090 (s), 1427 (s) cm$^{-1}$;

MS (70 eV) *m/e* (relative intensity) 392 (1, $M^{\bullet+}$), 183 (9), 177 (8), 176 (9), 175 (100), 119 (36), 77 (8), 57 (17). Anal. Calcd for $C_{20}H_{25}PS_3$: C, 61.19; H, 6.42. Found: C, 61.22; H, 6.58.

***trans*-5-*tert*-Butyl-2-[diphenyl(thiophosphinoyl)]-1,3-dithiane (10d). Method A.** The procedure for the synthesis of **10a** was applied to transform **9d** (3.91 g, 10.4 mmol) into **10d**. Crystallization of the crude product from ethyl acetate afforded **10d** (2.94 g, 72.2%), colorless crystals: mp 188.0–190.0 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.88 (s, 9H, $CH_3$), 1.73 (tt, $^3J_{H-H}$ = 11.19 Hz, $^3J_{H-H}$ = 2.57 Hz, 1H, *t*-BuC*H*), 2.71 (dd, $^2J_{H-H}$ = 13.78 Hz, $^3J_{H-H}$ = 11.19 Hz, 2H, H(4,6)$_{ax}$), 2.94 (ddd, $^2J_{H-H}$ = 13.78 Hz, $^4J_{H-P}$ = 3.20 Hz, $^3J_{H-H}$ = 2.57 Hz, 2H, H(4,6)$_{eq}$), 5.00 (d, $^2J_{H-P}$ = 11.52 Hz, 1H, HCP), 7.45–8.03 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 48.3; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 27.11 (s, $CH_3$), 32.80 (d, $^3J_{C-P}$ = 7.3 Hz, $CH_2$), 33.99 (d, $^5J_{C-P}$ = 2.0 Hz, *C*Me$_3$), 45.74 (s, *C*H-*t*-Bu), 48.74 (d, $^1J_{C-P}$ = 50.0 Hz, CHP), 128.34 (d, $^3J_{C-P}$ = 12.6 Hz, $C_{Ar(meta)}$), 130.35 (d, $^1J_{C-P}$ = 83.6 Hz, $C_{Ar(ipso)}$), 132.09 (d, $^4J_{C-P}$ = 2.9 Hz, $C_{Ar(para)}$), 132.35 (d, $^2J_{C-P}$ = 10.2 Hz $C_{Ar(ortho)}$); IR (KBr) 632 (s), 656 (s), 696 (vs), 712 (vs), 752 (vs), 1100 (s), 1368 (s), 1432 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 392 (1, $M^{\bullet+}$), 177 (8), 176 (8), 175 (100), 57 (14). Anal. Calcd for $C_{20}H_{25}PS_3$: C, 61.19; H, 6.42. Found: C, 61.31; H, 6.46.

**Method B.** Following the general procedure of Juaristi *et al.*,[37] dithiane **14** (10.0 g, 56.7 mmol) and chlorodiphenylphosphine (13.8 g, 62.6 mmol) were converted into **10d** (13.0 g, 58.3%), indistinguishable (TLC, $^1$H NMR, $^{31}$P NMR) from the product obtained *via* method A.

***r*-2-[Diphenyl(thiophosphinoyl)]-*t*-4,*t*-6-dimethyl-1,3-dithiane (10e).** The published[37] method was modified as follows. The solution of **10f** (2.476 g, 6.79 mmol) in tetrahydrofuran (70 mL) was stirred at −20 °C under nitrogen when a 1.50 M solution of *n*-butyllithium in *n*-hexane (5.0 mL, 7.50 mmol) was added. After the mixture was stirred for 15 min, concentrated hydrochloric acid (2.0 mL, ca. 20 mmol) was added, and the mixture was evaporated under reduced pressure. The residue was extracted with benzene (3 × 10 mL). Combined benzene solutions were filtered through silica gel (5 g) and evaporated under reduced pressure. The remaining solid was crystallized from ethyl acetate to furnish **10e** (2.149 g, 86.8%), colorless prisms: mp 191.8–193.8 °C (lit.[37] mp 185–186 °C); $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.13 (d, $^3J_{H-H}$ = 6.87 Hz, 6H, $CH_3$), 1.24 (dt, $^2J_{H-H}$ = 13.77 Hz, $^3J_{H-H}$ = 11.83 Hz, 1H, H(5)$_{ax}$), 2.11 (dt, $^2J_{H-H}$ = 13.77 Hz, $^3J_{H-H}$ = 2.06 Hz, 1H, H(5)$_{eq}$), 4.23 (dqdd, $^3J_{H-H}$ = 11.83 Hz, $^3J_{H-H}$ = 6.87 Hz, $^3J_{H-H}$ = 2.06 Hz, $^4J_{H-P}$ = 1.75 Hz, 2H, C*H*CH$_3$), 4.60 (d, $^2J_{H-P}$ = 5.83 Hz, 1H, HCP), 7.43–7.96 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 51.6 (lit.[37] $\delta$ 51.3); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.78 (s, $CH_3$), 34.71 (s, *C*HCH$_3$), 40.57 (d, $^1J_{C-P}$ = 54.2 Hz, CHP), 42.96 (d, $^4J_{C-P}$ = 2.8 Hz, $CH_2$), 128.40 (d, $^3J_{C-P}$ = 11.6 Hz, $C_{Ar(meta)}$), 131.43 (d, $^4J_{C-P}$ = 2.8 Hz, $C_{Ar(para)}$), 131.69 (d, $^2J_{C-P}$ = 9.0 Hz, $C_{Ar(ortho)}$), 133.02 (d, $^1J_{C-P}$ = 77.3 Hz, $C_{Ar(ipso)}$); IR (KBr) 688 (vs), 720 (vs), 752 (s), 1100 (vs), 1432 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 364 (3, $M^{\bullet+}$), 183 (11), 149 (10), 148 (10), 147 (100), 139 (13), 69 (15). Anal. Calcd for $C_{18}H_{21}PS_3$: C, 59.31; H, 5.81. Found: C, 59.39; H, 5.81.

***r*-2-[Diphenyl(thiophosphinoyl)]-*c*-4,*c*-6-dimethyl-1,3-dithiane (10f).** The procedure of Juaristi *et al.*[37] with a small modification (see below) was followed to convert **15** (4.0 g, 27.0 mmol) into **10f**. After the reaction mixture was quenched with saturated aqueous ammonium chloride solution (50 mL), organic solvents were evaporated under reduced pressure, and the residue was extracted with benzene (3 × 60 mL). Combined benzene solutions were washed with water (30 mL), dried over anhydrous magnesium sulfate, and filtered through silica gel (15 g). The filtrate was evaporated, and the solid residue was crystallized from ethyl acetate to afford **10f** (4.8 g, 49%), colorless needles: mp 217.0–219.0 °C (lit.[37] mp 213–215 °C); $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.24 (d, $^3J_{H-H}$ = 6.82 Hz, 6H, $CH_3$), 1.34 (dt, $^2J_{H-H}$ = 13.98 Hz, $^3J_{H-H}$ = 11.66 Hz, 1H, H(5)$_{ax}$), 2.07 (ddt, $^2J_{H-H}$ = 13.98 Hz, $^5J_{H-P}$ = 4.13 Hz, $^3J_{H-H}$ = 2.23 Hz, 1H, H(5)$_{eq}$), 2.91 (dqd, $^3J_{H-H}$ = 11.66 Hz, $^3J_{H-H}$ = 6.82 Hz, $^3J_{H-H}$ = 2.23 Hz, 2H, C*H*CH$_3$), 5.04 (d, $^2J_{H-P}$ = 13.32 Hz, 1H, HCP), 7.43–8.05 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 46.3 (lit.[37] $\delta$ 46.0); $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.51 (s, $CH_3$), 41.61 (d, $^3J_{C-P}$ = 7.5 Hz, *C*HCH$_3$), 43.24 (s, $CH_2$), 51.43 (d, $^1J_{C-P}$ = 49.5 Hz, CHP), 128.36 (d, $^3J_{C-P}$ = 12.6 Hz, $C_{Ar(meta)}$), 130.41 (d, $^1J_{C-P}$ = 84.1 Hz, $C_{Ar(ipso)}$), 132.02 (d, $^4J_{C-P}$ = 3.1 Hz, $C_{Ar(para)}$), 132.43 (d, $^2J_{C-P}$ = 10.2 Hz, $C_{Ar(ortho)}$); IR (KBr) 648 (vs), 688 (m), 720 (vs), 1100 (m), 1432 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 364 (1, $M^{\bullet+}$), 183 (11), 149 (11), 147 (100), 69 (19). Anal. Calcd for $C_{18}H_{21}PS_3$: C, 59.31; H, 5.81. Found: C, 59.12; H, 5.70.

**2-[Methylphenyl(thiophosphinoyl)]-1,3-dithiane (11a).** Following the general procedure of Juaristi *et al.*,[37] 1,3-dithiane (1.20 g, 10.0 mmol) and chloromethylphenylphosphine (**33**, 1.90 g, 12.0 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as eluent, afforded **11a** (1.05 g, 38.3%), colorless solid: mp 89.5–91.2 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 1.93–2.05 (m, 2H), 2.16 (d, $^2J_{H-P}$ = 12.7 Hz, 3H, $CH_3P$), 2.59–2.75 (m, 2H), 3.34–3.47 (m, 2H), 4.21 (d, $^2J_{H-P}$ = 4.2 Hz, 1H, HCP), 7.49–8.05 (m, 5H, Ph); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 46.7; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 19.96 (d, $^1J_{C-P}$ = 58.7 Hz, $CH_3P$), 25.20 (s, C$CH_2$C), 28.57 (d, $^3J_{C-P}$ = 3.3 Hz, C′$H_2$S), 28.61 (d, $^3J_{C-P}$ = 3.3 Hz, C″$H_2$S), 44.75 (d, $^1J_{C-P}$ = 49.2 Hz, CHP), 128.79 (d, $^3J_{C-P}$ = 12.9, $C_{Ar(meta)}$), 131.69 (d, $^2J_{C-P}$ = 8.9 Hz, $C_{Ar(ortho)}$) 132.31 (s, $C_{Ar(para)}$); IR (KBr) 610 (vs), 690 (s), 708 (vs), 746 (vs), 892 (vs), 912 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 274 (4, $M^{\bullet+}$), 155 (9), 121 (18), 119 (100), 45 (14). Anal. Calcd for $C_{11}H_{15}PS_3$: C, 48.15; H, 5.51. Found: C, 47.79; H, 5.54.

**5,5-Dimethyl-2-[methylphenyl(thiophosphinoyl)]-1,3-dithiane (11b).** Following the general procedure of Juaristi et al.,[37] dithiane **32** (2.96 g, 20.0 mmol) and chlorophosphine **33** (3.80 g, 24.0 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as an eluent and subsequent crystallization from ethyl acetate, afforded **11b** (3.19 g, 52.7%), colorless crystals: mp 126.2–128.0 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 1.09 (s, 3H, $CH_3$C), 1.14 (s, 3H, $CH_3$C), 2.17 (d, $^2J_{H-P}$ = 12.7 Hz, 3H, $CH_3P$), 2.37 (d, $^2J_{H-H}$ = 13.8 Hz, 1H, C′*H*H), 2.45 (d, $^2J_{H-H}$ = 13.8 Hz, 1H, C″*H*H), 3.04 (dd, $^2J_{H-H}$ = 13.8 Hz, $^4J_{H-P}$ = 3.0 Hz, 2H, C′H*H*), 3.10 (dd, $^2J_{H-H}$ = 13.8 Hz, $^4J_{H-P}$ = 3.0 Hz, 2H, C″H*H*), 4.12 (d, $^2J_{H-P}$ = 8.2 Hz, 1H, HCP), 7.5–8.0 (m, 5H, Ph); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 46.0; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 19.57 (d, $^1J_{C-P}$ = 58.5 Hz, $CH_3P$), 26.64 (s, *C*Me$_2$), 27.14 (s, *C*H$_3$C), 40.39 (d, $^3J_{C-P}$ = 4.4 Hz, C′$H_2$), 40.45 (d, $^3J_{C-P}$ = 4.4 Hz, C″$H_2$), 44.51 (d, $^1J_{C-P}$ = 48.7 Hz, CHP), 128.77 (d, $^3J_{C-P}$ = 11.2 Hz, $C_{Ar(meta)}$), 131.78 (d, $^2J_{C-P}$ = 9.7 Hz, $C_{Ar(ortho)}$), 132.33 (s, $C_{Ar(para)}$); IR (KBr) 644 (s), 740 (vs), 890 (s), 904 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 302 (2, $M^{\bullet+}$), 155 (8), 149 (9), 148 (8), 147 (100), 69 (29). Anal. Calcd for $C_{13}H_{19}PS_3$: C, 51.62; H, 6.33. Found: C, 51.72; H, 5.43.

***cis*-5-*tert*-Butyl-2-[methylphenyl(thiophosphinoyl)]-1,3-dithiane (11c).** The reaction was carried out in an atmosphere of dry nitrogen. To a magnetically stirred, cooled (−20 °C) suspension of **11d** (0.992 g, 3.00 mmol) in tetrahydrofuran (40 mL) was added a 1.4 M solution of *n*-butyllithium in *n*-hexane (2.5 mL, 3.5 mmol). The suspension turned into a yellow solution (3 min), and after 5 min of additional stirring, the mixture was quenched with saturated aqueous ammonium chloride solution (1.0 mL). The mixture was concentrated under reduced pressure, water (10 mL) was added, and the whole was extracted with chloroform (3 × 10 mL). Combined organic solutions were washed with water (5 mL) and dried over anhydrous magnesium sulfate. The solvent was evaporated under reduced pressure, and the residue was crystallized from ethyl acetate to afford **11c** (0.819 g, 82.6%), small, colorless needles: mp 138.2–141.0 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 0.86 (s, 9H, $CH_3$C), 1.69 (tt, $^3J_{H-H}$ = 11.48 Hz, $^3J_{H-H}$ = 2.75 Hz, 1H, *t*-BuC*H*), 2.18 (d, $^2J_{H-P}$ = 12.3 Hz, 3H, $CH_3P$), 2.40 (ddd, $^2J_{H-H}$ = 13.6 Hz, $^3J_{H-H}$ = 2.75 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, H(4)$_{eq}$), 2.53 (ddd, $^2J_{H-H}$ = 13.6 Hz, $^3J_{H-H}$ = 2.75 Hz, $^4J_{H-H}$ = 1.8 Hz, 1H, H(6)$_{eq}$), 3.63 (ddd, $^2J_{H-H}$ = 13.6 Hz, $^3J_{H-H}$ = 11.48 Hz, $^4J_{H-P}$ = 1.9 Hz, 1H, H(4)$_{ax}$), 3.65 (d, $^2J_{H-P}$ = 6.2 Hz, 1H, HCP), 3.67 (ddd, $^2J_{H-H}$ = 13.6 Hz, $^3J_{H-H}$ = 11.48 Hz, $^4J_{H-P}$ = 1.9 Hz, 1H, H(6)$_{ax}$), 7.50–8.00 (m, 5H, Ph); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 49.1; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 21.31 (d, $^1J_{C-P}$ = 57.5 Hz, $CH_3P$), 26.69 (s, C′$H_2$), 26.78 (s, C″$H_2$), 27.16 (s, *C*H$_3$C), 34.34 (s, *C*Me$_3$), 34.92 (d, $^1J_{C-P}$ = 50.6 Hz, CHP), 46.15 (d, $^4J_{C-P}$ = 2.4 Hz, *C*H-*t*-Bu), 128.85 (d, $^3J_{C-P}$ = 11.1 Hz, $C_{Ar(meta)}$), 131.70 (d, $^2J_{C-P}$ = 10.3 Hz, $C_{Ar(ortho)}$), 132.13 (s, $C_{Ar(para)}$); IR (KBr) 692 (s), 708 (s), 744 (vs), 764 (s), 884 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 330 (1, $M^{\bullet+}$), 177 (9), 176 (10), 175 (100), 155 (9), 57 (18). Anal. Calcd for $C_{15}H_{23}PS_3$: C, 54.51; H, 7.01. Found: C, 54.86; H, 7.20.

***trans*-5-*tert*-Butyl-2-[methylphenyl(thiophosphinoyl)]-1,3-dithiane (11d).** Following the general procedure of Juaristi *et al.*,[37] dithiane **14** (3.52 g, 20.0 mmol) and chlorophosphine **33**

(3.80 g, 24.0 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as an eluent and subsequent crystallization from chloroform–diethyl ether, afforded **11d** (2.681 g, 40.6%), colorless needles: mp 160.4–163.0 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 0.89 (s, 9H, $CH_3C$), 1.63 (ttd, $^3J_{H-H}$ = 11.18 Hz, $^3J_{H-H}$ = 2.66 Hz, $J$ = 0.6 Hz, 1H, *t*-BuC*H*), 2.16 (d, $^2J_{H-P}$ = 13.1 Hz, 3H, $CH_3P$), 2.66 (ddd, $^2J_{H-H}$ = 13.85 Hz, $^3J_{H-H}$ = 11.18 Hz, $^4J_{H-P}$ = 1.0 Hz, 1H, H(4)$_{ax}$), 2.69 (ddd, $^2J_{H-H}$ = 13.85 Hz, $^3J_{H-H}$ = 11.18 Hz, $^4J_{H-P}$ = 0.9 Hz, 1H, H(6)$_{ax}$), 2.91 (dddd, $^2J_{H-H}$ = 13.85 Hz, $^4J_{H-P}$ = 2.9 Hz, $^3J_{H-H}$ = 2.66 Hz, $^4J_{H-H}$ = 2.4 Hz, 1H, H(4)$_{eq}$), 2.96 (dddd, $^2J_{H-H}$ = 13.85 Hz, $^4J_{H-P}$ = 2.9 Hz, $^3J_{H-H}$ = 2.66 Hz, $^4J_{H-H}$ = 2.4 Hz, 1H, H(6)$_{eq}$), 4.60 (d, $^2J_{H-P}$ = 11.40 Hz, 1H, HCP), 7.5–8.0 (m, 5H, Ph); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 43.3; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 18.51 (d, $^1J_{C-P}$ = 59.9 Hz, $CH_3P$), 27.23 (s, $CH_3C$), 32.66 (d, $^3J_{C-P}$ = 7.6 Hz, $CH_2$), 34.27 (d, $^5J_{C-P}$ = 2.1 Hz, $CMe_3$), 46.39 (s, *C*H-*t*-Bu), 49.82 (d, $^1J_{C-P}$ = 48.0 Hz, CHP), 128.74 (d, $^3J_{C-P}$ = 12.2 Hz, $C_{Ar(meta)}$), 131.81 (d, $^2J_{C-P}$ = 10.8 Hz, $C_{Ar(ortho)}$), 132.54 (s, $C_{Ar(para)}$); IR (KBr) 614 (m), 688 (m), 708 (m), 744 (m), 764 (m), 892 (vs), 1432 (m), 2960 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 330 (1, M$^{\bullet+}$), 177 (8), 176 (9), 175 (100), 155 (10), 57 (24), 41 (11). Anal. Calcd for $C_{15}H_{23}PS_3$: C, 54.51; H, 7.01. Found: C, 54.72; H, 6.97.

***r*-2-[Methylphenyl(thiophosphinoyl)]-*t*-4,6-dimethyl-1,3-dithiane (11e).** The procedure for the synthesis of **11c** was applied to transform **11f** (0.907 g, 3.00 mmol) into **11e**. Crystallization of the crude product from ethyl acetate afforded **11e** (0.746 g, 82.2%), colorless crystals: mp 124.0–125.5 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 1.07 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH_3C'$), 1.20 (d, $^3J_{H-H}$ = 6.9 Hz, 3H, $CH_3C''$), 1.20 (dt, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 11.80 Hz, 1H, H(5)$_{ax}$), 2.06 (d, $^2J_{H-P}$ = 12.2 Hz, 3H, $CH_3P$), 2.09 (dt, $^2J_{H-H}$ = 13.9 Hz, $^3J_{H-H}$ = 2.27 Hz, 1H, H(5)$_{eq}$), 4.01 (d, $^2J_{H-P}$ = 6.1 Hz, 1H, HCP), 4.07 (dqdd, $^3J_{H-H}$ = 11.80 Hz, $^3J_{H-H}$ = 6.9 Hz, $^3J_{H-H}$ = 2.27 Hz, $^4J_{H-P}$ = 1.0 Hz, 1H, C*H*′CH$_3$), 4.09 (dqdd, $^3J_{H-H}$ = 11.80 Hz, $^3J_{H-H}$ = 6.9 Hz, $^3J_{H-H}$ = 2.27 Hz, $^4J_{H-P}$ = 1.0 Hz, 1H, C*H*″CH$_3$), 7.5–8.0 (m, 5H, Ph); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 50.4; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 21.80 (d, $^1J_{C-P}$ = 57.5 Hz, $CH_3P$), 21.90 (s, *C*′H$_3$C), 21.96 (s, *C*″H$_3$C), 34.71 (s, *C*′HCH$_3$), 34.95 (s, *C*″HCH$_3$), 43.41 (d, $^4J_{C-P}$ = 2.4 Hz, $CH_2$), 43.66 (d, $^1J_{C-P}$ = 52.0 Hz, CHP), 128.80 (d, $^3J_{C-P}$ = 11.6 Hz, $C_{Ar(meta)}$), 131.56 (d, $^2J_{C-P}$ = 8.2 Hz, $C_{Ar(ortho)}$), 132.03 (s, $C_{Ar(para)}$); IR (KBr) 692 (s), 708 (s), 744 (vs), 882 (s), 892 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 302 (2, M$^{\bullet+}$), 149 (8), 148 (7), 147 (100), 69 (20). Anal. Calcd for $C_{13}H_{19}PS_3$: C, 51.62; H, 6.33. Found: C, 51.79; H, 6.49.

***r*-2-[Methylphenyl(thiophosphinoyl)]-*c*-4,*c*-6-dimethyl-1,3-dithiane (11f).** Following the general procedure of Juaristi *et al.*,[37] dithiane **15** (2.96 g, 20.0 mmol) and chlorophosphine **33** (3.80 g, 24.0 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as an eluent and subsequent crystallization from chloroform–diethyl ether, afforded **11f** (2.647 g, 43.8%), colorless crystals: mp 124.5–130.0 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 1.23 (dd, $^3J_{H-H}$ = 6.8 Hz, $^5J_{H-P}$ = 0.4 Hz, 3H, $CH_3C'$), 1.23 (dt, $^2J_{H-H}$ = 14.0 Hz, $^3J_{H-H}$ = 11.50 Hz, 1H, H(5)$_{ax}$), 1.25 (dd, $^3J_{H-H}$ = 6.8 Hz, $^5J_{H-P}$ = 0.4 Hz, 3H, $CH_3C''$), 2.08 (ddt, $^2J_{H-H}$ = 14.0 Hz, $^5J_{H-P}$ = 4.2 Hz, $^3J_{H-H}$ = 2.29 Hz, 1H, H(5)$_{eq}$), 2.18 (d, $^2J_{H-P}$ = 13.1 Hz, 3H, $CH_3P$), 2.88 (dqdd, $^3J_{H-H}$ = 11.50 Hz, $^3J_{H-H}$ = 6.8 Hz, $^3J_{H-H}$ = 2.29 Hz, $^4J_{H-P}$ = 1.0 Hz, 1H, C*H*′CH$_3$), 2.91 (dqdd, $^3J_{H-H}$ = 11.50 Hz, $^3J_{H-H}$ = 6.8 Hz, $^3J_{H-H}$ = 2.29 Hz, $^4J_{H-P}$ = 1.0 Hz, 1H, C*H*″CH$_3$), 4.68 (d, $^2J_{H-P}$ = 12.6 Hz, 1H, HCP, 7.5–8.0 (m, 5H, Ph); $^{31}$P NMR (121.49 MHz $CD_2Cl_2$) $\delta$ 42.9; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 18.86 (d, $^1J_{C-P}$ = 59.9 Hz, $CH_3P$), 21.74 (s, $CH_3C$), 41.39 (d, $^3J_{C-P}$ = 7.0 Hz, *C*′HCH$_3$), 41.45 (d, $^3J_{C-P}$ = 7.8 Hz, *C*″HCH$_3$), 43.60 (s, $CH_2$), 52.46 (d, $^1J_{C-P}$ = 47.4 Hz, CHP), 128.76 (d, $^3J_{C-P}$ = 12.3 Hz, $C_{Ar(meta)}$), 131.81 (d, $^2J_{C-P}$ = 10.3 Hz, $C_{Ar(ortho)}$), 132.49 (s, $C_{Ar(para)}$); IR (KBr) 602 (s), 708 (s), 750 (s), 886 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 302 (1, M$^{\bullet+}$), 155 (10), 149 (8), 147 (100), 69 (22), 41 (9). Anal. Calcd for $C_{13}H_{19}PS_3$: C, 51.62; H, 6.33. Found: C, 51.64; H, 6.48.

**2-[Dimethyl(thiophosphinoyl)]-1,3-dithiane (12a).** Following the general procedure of Juaristi *et al.*,[37] 1,3-dithiane (2.40 g, 20.0 mmol) and **24** (2.4 mL, ca 24.0 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as an eluent and subsequent crystallization from ethyl acetate, afforded **12a** (1.151 g, 27.1%), colorless crystals: mp 114–116 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 1.85 (d, $^2J_{H-P}$ = 12.7 Hz, 6H, $CH_3P$), 1.90–2.17 (m, 2H), 2.73–2.82 (m, 2H), 3.34–3.44 (m, 2H), 4.11 (d, $^2J_{H-P}$ = 10.2 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 45.3; $^{13}$C NMR (75.47 MHz, $CD_2Cl32$) $\delta$ 20.45 (d, $^1J_{C-P}$ = 55.8 Hz, $CH_3P$), 25.35 (s, $CCH_2C$), 29.97 (d, $^3J_{C-P}$ = 4.4 Hz, $CH_2S$), 44.78 (d, $^1J_{C-P}$ = 48.6 Hz, CHP); IR (KBr) 730 (s), 908 (s), 918 (vs), 940 (s), 1276 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 212 (5, M$^{\bullet+}$), 121 (6), 119 (100), 93 (7), 45 (11). Anal. Calcd for $C_6H_{13}PS_3$: C, 33.94; H, 6.17. Found: C, 33.87; H, 6.12.

**5,5-Dimethyl-2-[dimethyl(thiophosphinoyl)]-1,3-dithiane (12b).** Following the general procedure of Juaristi *et al.*,[37] dithiane **32** (2.96 g, 20.0 mmol) and chlorophosphine **24** (2.4 mL, ca. 24.0 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as an eluent and subsequent crystallization from ethyl acetate, afforded **12b** (2.50 g, 52.1%), colorless crystals: mp 156.0–157.0 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 1.16 (s, 3H, $CH_3C$), 1.17 (s, 3H, $CH_3C$), 1.85 (d, $^2J_{H-P}$ = 12.7 Hz, 6H, $CH_3P$), 2.57 (d, $^2J_{H-H}$ = 13.9 Hz, 2H, C*H*H), 3.04 (dd, $^2J_{H-H}$ = 13.9 Hz, $^4J_{H-P}$ = 3.1 Hz, 2H, CH*H*), 4.01 (d, $^2J_{H-P}$ = 9.4 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 45.1; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 20.20 (d, $^1J_{C-P}$ = 55.9 Hz, $CH_3P$), 26.19 (s, $CH_3C$), 26.71 (s, $CMe_2$), 28.12 (d, $^5J_{C-P}$ = 2.0 Hz, $CH_3C$), 41.11 (d, $^3J_{C-P}$ = 4.6 Hz, $CH_2$), 44.74 (d, $^1J_{C-P}$ = 48.2 Hz, CHP); IR (KBr) 730 (vs), 924 (vs), 936 (vs), 2824 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 240 (3, M$^{\bullet+}$), 149 (9), 148 (8), 147 (100), 93 (11), 69 (44), 45 (9), 41 (11). Anal. Calcd for $C_8H_{17}PS_3$: C, 39.97; H, 7.13. Found: C, 40.32; H, 7.30.

***cis*-5-*tert*-Butyl-2-[dimethyl(thiophosphinoyl)]-1,3-dithiane (12c).** The procedure for the synthesis of **11c** was applied to transform **12d** (300 mg, 1.12 mmol) into **12c**. Crystallization of the crude product from ethyl acetate afforded **12c** (266 mg, 88.7%), colorless crystals: mp 193.5–195.0 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 0.90 (s, 9H, $CH_3C$), 1.76 (tt, $^3J_{H-H}$ = 11.42 Hz, $^3J_{H-H}$ = 2.82 Hz, 1H, *t*-BuC*H*), 1.87 (d, $^2J_{H-P}$ = 12.1 Hz, 6H, $CH_3P$), 2.53 (dddd, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 2.82 Hz, $^4J_{H-H}$ = 0.7 Hz, $^4J_{H-P}$ = 0.4 Hz, 2H, H(4,6)$_{eq}$), 3.38 (d, $^2J_{H-P}$ = 5.4 Hz, 1H, HCP), 3.90 (dddd, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 11.42 Hz, $^4J_{H-P}$ = 1.7 Hz, $^4J_{H-H}$ = 0.7 Hz, 2H, H(4,6)$_{ax}$); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 48.2; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 21.87 (d, $^1J_{C-P}$ = 54.6 Hz, $CH_3P$), 26.81 (s, $CH_2$), 27.19 (s, $CH_3C$), 34.45 (s, $CMe_3$), 37.14 (d, $^1J_{C-P}$ = 51.0 Hz, CHP), 46.39 (d, $^4J_{C-P}$ = 2.3 Hz, *C*H*t*Bu); IR (KBr) 730 (s), 926 (vs), 946 (s), 2828 (vs), 2960 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 268 (2, M$^{\bullet+}$), 177 (8), 176 (9), 175 (100), 93 (10), 41 (11). Anal. Calcd for $C_{10}H_{21}PS_3$: C, 44.74; H, 7.89. Found: C, 44.75; H, 7.89.

***trans*-5-*tert*-Butyl-2-[dimethyl(thiophosphinoyl)]-1,3-dithiane (12d).** Following the general procedure of Juaristi *et al.*,[37] dithiane **14** (1.76 g, 10.0 mmol) and chlorophosphine **24** (1.0 mL, ca 12 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as an eluent and subsequent crystallization from ethyl acetate, afforded **12d** (1.161 g, 43.3%), colorless crystals: mp 219.0–220.3 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 0.93 (s, 9H, $CH_3C$), 1.68 (ttd, $^3J_{H-H}$ = 11.26 Hz, $^3J_{H-H}$ = 2.56 Hz, $J$ = 0.6 Hz, 1H, *t*-BuC*H*), 1.83 (d, $^2J_{H-P}$ = 13.0 Hz, 6H, $CH_3P$), 2.74 (ddd, $^2J_{H-H}$ = 13.86 Hz, $^3J_{H-H}$ = 11.26 Hz, $^4J_{H-H}$ = 1.1 Hz, 2H, H(4,6)$_{ax}$), 3.01 (dddd, $^2J_{H-H}$ = 13.86 Hz, $^4J_{H-P}$ = 2.7 Hz, $^3J_{H-H}$ = 2.56 Hz, $^4J_{H-H}$ = 1.1 Hz, 2H, H(4,6)$_{eq}$), 4.45 (d, $^2J_{H-P}$ = 12.2 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 42.9; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) $\delta$ 19.54 (d, $^1J_{C-P}$ = 56.7 Hz, $CH_3P$), 27.29 (s, $CH_3C$), 32.64 (d, $^3J_{C-P}$ = 7.6 Hz, $CH_2$), 34.32 (d, $^5J_{C-P}$ = 2.0 Hz, $CMe_3$), 46.64 (s, *C*H-*t*-Bu), 48.46 (d, $^1J_{C-P}$ = 47.1 Hz, CHP); IR (KBr) 572 (s), 732 (vs), 932 (vs), 948 (vs), 1288 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 268 (1, M$^{\bullet+}$), 177 (9), 176 (9), 175 (100), 57 (27), 41 (11). Anal. Calcd for $C_{10}H_{21}PS_3$: C, 44.74; H, 7.89. Found: C, 44.90; H, 7.90.

***r*-2-[Dimethyl(thiophosphinoyl)]-*t*-4,*t*-6-dimethyl-1,3-dithiane (12e).** The procedure for the synthesis of **11c** was used to transform **12f** (300 mg, 1.25 mmol) into **12e**. Crystallization of the crude product from ethyl acetate afforded **12e** (229 mg, 76.3%), colorless crystals: mp 176.0–177.0 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) $\delta$ 1.16 (d, $^3J_{H-H}$ = 6.88 Hz, 6H, $CH_3C$), 1.24 (dt, $^2J_{H-H}$ = 13.7 Hz, $^3J_{H-H}$ = 11.72 Hz, 1H, H(5)$_{ax}$), 1.87 (d, $^2J_{H-P}$ = 12.0 Hz, 6H, $CH_3P$), 2.12 (dtd, $^2J_{H-H}$ = 13.7 Hz, $^3J_{H-H}$ = 2.27 Hz, $^5J_{H-H}$ = 0.9 Hz, 1H, H(5)$_{eq}$), 3.70 (ddt, $^2J_{H-P}$ = 6.0 Hz, $^5J_{H-H}$ = 0.9 Hz, $^4J_{H-H}$ = 0.6 Hz, 1H, HCP), 4.18 (dqddd, $^3J_{H-H}$ = 11.72 Hz, $^3J_{H-H}$ = 6.88 Hz, $^3J_{H-H}$ = 2.27 Hz, $^4J_{H-P}$ = 1.1 Hz, $^4J_{H-H}$ = 0.6 Hz, 2H, C*H*CH$_3$); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) $\delta$ 49.0; $^{13}$C NMR

(75.47 MHz, $CD_2Cl_2$) δ 21.97 (s, $CH_3C$), 22.12 (d, $^1J_{C-P}$ = 54.6 Hz, $CH_3P$), 34.79 (s, $CHCH_3$), 43.03 (d, $^1J_{C-P}$ = 52.2 Hz, CHP), 43.55 (d, $^4J_{C-P}$ = 2.6 Hz, $CH_2$); IR (KBr) 604 (s), 728 (vs), 926 (vs), 944 (vs), 1248 (m), 1286 (m) $cm^{-1}$; MS (70 eV) *m/e* (relative intensity) 240 (4, $M^{\bullet+}$), 149 (10), 147 (100), 93 (14), 69 (42), 41 (15). Anal. Calcd for $C_8H_{17}PS_3$: C, 39.97; H, 7.13. Found: C, 39.75; H, 7.05.

***r*-2-[Dimethyl(thiophosphinoyl)]-*c*-4,*c*-6-dimethyl-1,3-dithiane (12f).** Following the general procedure of Juaristi *et al.*,[37] dithiane **15** (1.48 g, 10.0 mmol) and chlorophosphine **24** (1.0 mL, ca. 12 mmol) were converted into a mixture which, after chromatographic separation on silica gel with benzene–acetone as an eluent and subsequent crystallization from ethyl acetate, afforded **12f** (1.532 g, 63.7%), colorless crystals: mp 127.6–130.1 °C; $^1$H NMR (300.13 MHz, $CD_2Cl_2$) δ 1.26 (dt, $^2J_{H-H}$ = 14.12 Hz, $^3J_{H-H}$ = 11.49 Hz, 1H, $H(5)_{ax}$), 1.29 (d, $^3J_{H-H}$ = 6.85 Hz, 6H, $CH_3C$), 1.85 (d, $^2J_{H-P}$ = 13.0 Hz, 6H, $CH_3P$), 2.12 (ddt, $^2J_{H-H}$ = 14.12 Hz, $^5J_{H-P}$ = 4.16 Hz, $^3J_{H-H}$ = 2.26 Hz, 1H, $H(5)_{eq}$), 2.95 (dqdd, $^3J_{H-H}$ = 11.49 Hz, $^3J_{H-H}$ = 6.85 Hz, $^3J_{H-H}$ = 2.26 Hz, $^4J_{H-P}$ = 1.0 Hz, 2H, $CHCH_3$), 4.52 (d, $^2J_{H-P}$ = 13.2 Hz, 1H, HCP); $^{31}$P NMR (121.49 MHz, $CD_2Cl_2$) δ 42.5; $^{13}$C NMR (75.47 MHz, $CD_2Cl_2$) δ 19.76 (d, $^1J_{C-P}$ = 56.6 Hz, $CH_3P$), 21.76 (s, $CH_3C$), 41.31 (d, $^3J_{C-P}$ = 7.4 Hz, $CHCH_3$), 43.69 (s, $CH_2$), 53.14 (d, $^1J_{C-P}$ = 46.5 Hz, CHP); IR (KBr) 728 (s), 856 (s), 920 (vs), 948 (s), 1288 (m), 2848 (s) $cm^{-1}$; MS (70 eV) *m/e* (relative intensity) 240 (2, $M^{\bullet+}$), 149 (7), 147 (100), 103 (51), 69 (31), 47 (10), 41 (22). Anal. Calcd for $C_8H_{17}PS_3$: C, 39.97; H, 7.13. Found: C, 40.33; H, 7.14.

**2-[Diphenyl(selenophosphinoyl)]-1,3-dithiane (13a).** The reaction was carried out under nitrogen. To a stirred solution of **10a** (3.201 g, 9.51 mmol) in dichloromethane (40 mL) was added methyl trifluoromethanesulfonate (highly toxic; 1.12 mL, 10.2 mmol). The solution was stirred for 15 min and refluxed for 1 h. After the solution was cooled to 0 °C, tris(dimethylamino)-phosphine (**22**, 1.85 mL, 10.2 mmol) was added, and the solution was stirred for an additional 5 min. Then, selenium powder (0.85 g, 10.7 mmol) was added, and the mixture was stirred for 3h. The reaction mixture was washed with water (2 × 20 mL), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residual solid was extracted with benzene (5 × 20 mL), and the extract was filtered through silica gel (10 g). The filtrate was evaporated under reduced pressure and the residue crystallized from chloroform–*n*-pentane to afford **13a** (2.387 g, 65.4%) as colorless prisms: mp 156.5–158.0 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 2.00–2.15 (m, 2H), 2.70–2.83 (m, 2H), 3.37–3.50 (m, 2H), 4.91 (d, $^2J_{H-P}$ = 10.20 Hz, 1H, HCP), 7.4–8.1 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 41.5; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 24.60 (s, C-$CH_2$-C), 29.00 (d, $^3J_{C-P}$ = 4.2 Hz, $CH_2S$), 43.08 (d, $^1J_{C-P}$ = 43.0 Hz, CHP), 128.40 (d, $^3J_{C-P}$ = 12.2, $C_{Ar(meta)}$), 129.97 (d, $^1J_{C-P}$ = 72.4 Hz, $C_{Ar(ipso)}$), 131.94 (d, $^4J_{C-P}$ = 2.9 Hz, $C_{Ar(para)}$), 132.66 (d, $^2J_{C-P}$ = 10.0 Hz, $C_{Ar(ortho)}$); $^{77}$Se NMR (57.20 MHz, $CDCl_3$) δ −783.79 (d, $^1J_{Se-P}$ = 755.8 Hz); IR (KBr) 624 (s), 692 (vs), 748 (s), 1096 (vs), 1432 (s) $cm^{-1}$; MS (70 eV) *m/e* (relative intensity) 384 (3, $M^{\bullet+}$ + 1), 382 (3, $M^{\bullet+}$ − 1), 183 (9), 121 (11), 119 (100). Anal. Calcd for $C_{16}H_{17}PS_2Se$: C, 50.12; H, 4.47. Found: C, 49.72; H, 4.42.

**5,5-Dimethyl-2-[diphenyl(selenophosphinoyl)]-1,3-dithiane (13b).** The preparation was carried out following the same procedure as for **13a** and starting from **10b** (1.956 g, 5.37 mmol). Crystallization of the product from ethyl acetate gave **13b** (1.648 g, 74.6%) as colorless needles: mp 177.0–178.6 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 1.13 (s, 6H, $CH_3$), 2.48 (d, $^2J_{H-H}$ = 13.88 Hz, 2H, C*H*H), 3.02 (dd, $^2J_{H-H}$ = 13.88 Hz, $^4J_{H-P}$ = 3.54 Hz, 2H, CH*H*), 4.81 (d, $^2J_{H-P}$ = 8.51 Hz, 1H, HCP), 7.45–8.05 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 40.8; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 26.56 (s, $CH_3$), 26.73 (s, $CMe_2$), 27.55 (d, $^5J_{C-P}$ = 1.5 Hz, $CH_3$), 40.92 (d, $^3J_{C-P}$ = 3.7 Hz, $CH_2$), 43.04 (d, $^1J_{C-P}$ = 43.0 Hz, CHP), 128.38 (d, $^3J_{C-P}$ = 12.2 Hz, $C_{Ar(meta)}$), 130.02 (d, $^1J_{C-P}$ = 72.2 Hz, $C_{Ar(ipso)}$), 131.93 (d, $^4J_{C-P}$ = 3.1 Hz, $C_{Ar(para)}$), 132.72 (d, $^2J_{C-P}$ = 9.9 Hz, $C_{Ar(ortho)}$); $^{77}$Se NMR (57.20 MHz, $CDCl_3$) δ −780.02 (d, $^1J_{Se-P}$ = 755.0 Hz); IR (KBr) 688 (vs), 1092 (vs), 1360 (s), 1432 (vs) $cm^{-1}$; MS (70 eV) *m/e* (relative intensity) 412 (3, $M^{\bullet+}$ + 1), 410 (1, $M^{\bullet+}$ − 1), 183 (13), 149 (10), 147 (100), 69 (21). Anal. Calcd for $C_{18}H_{21}PS_2Se$: C, 52.55; H, 5.15. Found: C, 52.20; H, 5.06.

**Studies on the Stereochemistry of Addition of Selenium to 2-Phosphino-1,3-dithianes. Experiment A.** Selenium powder (47 mg, 0.59 mmol) was added to a solution of **19c** prepared from **10c** (230 mg, 0.59 mmol) *via* desulfurization (see below). In the $^{31}$P NMR (36.43 MHz) spectrum of the phosphine, the relative intensity of signals δ −19.2 and −2.7 ppm was 81:19, respectively. In the spectrum of the resultant mixture, the relative intensity of signals at δ 38.9 and 41.6 was 18:82, respectively, while the signals at δ −19.2 and −2.7 were absent.

**Experiment B.** Selenium powder (47 mg, 0.59 mmol) was added to a solution of **19d** prepared from **10d** (230 mg, 0.59 mmol) *via* desulfurization (see below). In the $^{31}$P NMR (36.43 MHz) spectrum of the phosphine, the relative intensity of signals δ −19.2 and −2.7 ppm was 17:83, respectively. In the spectrum of the resultant mixture, the relative intensity of signals at δ 38.9 and 41.6 was 83:17, respectively, while the signals at δ −19.2 and −2.7 were absent.

**5-*tert*-Butyl-2-[diphenyl(selenophosphinoyl)]-1,3-dithianes (13c,d), Mixture of Diastereomers.** The preparation was carried out following the same procedure as for **13a** and starting from **10d** (3.487 g, 8.88 mmol; **10c** may also be applied). The crude product was separated by column chromatography with *n*-hexane–benzene as an eluent to afford chromatographically pure **13c** and **13d**.

***cis*-5-*tert*-Butyl-2-[diphenyl(selenophosphinoyl)]-1,3-dithiane (13c)** (1.191 g, 30.5%). Crystallization from acetone–*n*-pentane afforded analytically pure sample, colorless crystals: mp 158.5–159.5 °C. $^1$H NMR (300.13 MHz, $CDCl_3$) δ 0.87 (*s*, 9H, $CH_3$), 1.76 (tt, $^3J_{H-H}$ = 11.33 Hz, $^3J_{H-H}$ = 2.90 Hz, 1H, *t*-BuC*H*), 2.47 (dd, $^2J_{H-H}$ = 13.77 Hz, $^3J_{H-H}$ = 2.90 Hz, 2H, $H(4,6)_{eq}$), 3.89 (ddd, $^2J_{H-H}$ = 13.77 Hz, $^3J_{H-H}$ = 11.33 Hz, $^4J_{H-P}$ = 1.99 Hz, 2H, $H(4,6)_{ax}$), 4.48 (d, $^2J_{H-P}$ = 5.92 Hz, 1H, HCP), 7.44–8.01 (*m*, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 42.2; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 26.41 (s, $CH_2$), 27.10 (s, $CH_3$), 34.12 (s, $CMe_3$), 34.45 (d, $^1J_{C-P}$ = 43.0 Hz, CHP), 45.46 (d, $^4J_{C-P}$ = 2.6 Hz, *C*H-*t*-Bu), 128.46 (d, $^3J_{C-P}$ = 11.6 Hz, $C_{Ar(meta)}$), 131.55 (d, $^1J_{C-P}$ = 68.1 Hz, $C_{Ar(ipso)}$), 131.67 (d, $^4J_{C-P}$ = 2.7 Hz, $C_{Ar(para)}$), 132.43 (d, $^2J_{C-P}$ = 9.2 Hz, $C_{Ar(ortho)}$);; $^{77}$Se NMR (57.20 MHz, $CDCl_3$) δ −791.67 (d, $^1J_{Se-P}$ = 755.9 Hz); IR (KBr) 648 (vs), 688 (vs), 752 (s), 1096 (vs), 1368 (s), 1408 (s), 1432 (s), 1480 (m) $cm^{-1}$; MS (70 eV) *m/e* (relative intensity) 440 (3, $M^{\bullet+}$ + 1), 438 (2, $M^{\bullet+}$ − 1), 183 (14), 177 (14), 176 (15), 175 (100), 57 (18). Anal. Calcd for $C_{20}H_{25}PS_2Se$: C, 54.66; H, 5.73. Found: C, 55.05; H, 5.76.

***trans*-5-*tert*-Butyl-2-[diphenyl(selenophosphinoyl)]-1,3-dithiane (13d).** Colorless solid (1.952 g, 50.2%), which after crystallization from dichloromethane–*n*-pentane gave thin needles. On standing they turned into large prisms: mp 178.5–180.7 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 0.88 (s, 9H, $CH_3$), 1.73 (tt, $^3J_{H-H}$ = 11.09 Hz, $^3J_{H-H}$ = 2.58 Hz, 1H, *t*-BuC*H*), 2.73 (dd, $^2J_{H-H}$ = 13.86 Hz, $^3J_{H-H}$ = 11.09 Hz, 2H, $H(4,6)_{ax}$), 2.94 (ddd, $^2J_{H-H}$ = 13.86 Hz, $^4J_{H-P}$ = 3.60 Hz, $^3J_{H-H}$ = 2.58 Hz, 2H, $H(4,6)_{eq}$), 5.07 (d, $^2J_{H-P}$ = 11.73 Hz, 1H, HCP), 7.44–8.08 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) δ 39.7; $^{13}$C NMR (75.47 MHz, $CDCl_3$) δ 27.14 (s, $CH_3$), 32.91 (d, $^3J_{C-P}$ = 7.2 Hz, $CH_2$), 33.97 (d, $^5J_{C-P}$ = 2.1 Hz, $CMe_3$), 45.66 (s, *C*H-*t*-Bu), 48.16 (d, $^1J_{C-P}$ = 42.4 Hz, CHP), 128.38 (d, $^3J_{C-P}$ = 12.5 Hz, $C_{Ar(meta)}$), 129.21 (d, $^1J_{C-P}$ = 74.3 Hz, $C_{Ar(ipso)}$), 132.14 (d, $^4J_{C-P}$ = 2.6 Hz, $C_{Ar(para)}$), 132.89 (d, $^2J_{C-P}$ = 10.3 Hz, $C_{Ar(ortho)}$); $^{77}$Se NMR (57.20 MHz, $CDCl_3$) δ −791.7 (d, $^1J_{Se-P}$ = 751.0 Hz); IR (KBr) 688 (vs), 744 (s), 1096 (s), 1368 (s), 1432 (s), 1480 (s) $cm^{-1}$; MS (70 eV) *m/e* (relative intensity) 440 (3, $M^{\bullet+}$ + 1), 438 (1, $M^{\bullet+}$ − 1), 183 (18), 177 (10), 176 (10), 175 (100), 57 (23). Anal. Calcd for $C_{20}H_{25}PS_2Se$: C, 54.66; H, 5.73. Found: C, 54.94; H, 5.68.

***r*-2-[Diphenyl(selenophosphinoyl)]-*t*-4,6-dimethyl-1,3-dithiane (13e).** The published[37] method for phosphine sulfides was accommodated for the synthesis of **13e** as follows. The suspension of **13f** (808 mg, 1.96 mmol) in tetrahydrofuran (20 mL) was stirred at −20 °C under nitrogen when a 1.50 M solution of *n*-butyllithium in *n*-hexane (1.4 mL, 2.10 mmol) was added. The resulting solution was stirred for an additional 1 h and quenched with saturated aqueous ammonium chloride (0.5 mL). After being stirred for 0.5 h, the mixture was evaporated under reduced pressure. The residue was extracted with benzene (3 × 10 mL). Combined benzene solutions were washed with water (20 mL), dried over anhydrous magnesium sulfate, and evaporated under reduced pressure. The residue was separated by column chromatography to give chromatographically pure **13e** (149 mg, 18.4%) and substrate **13f** (192 mg, 23.8%). Crystallization of **13e** from ethyl acetate afforded analytically pure sample as colorless prisms: mp 177–183 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) δ 1.14 (d, $^3J_{H-H}$ = 6.86 Hz, 6H, $CH_3$), 1.27 (dt, $^2J_{H-H}$ = 13.82 Hz, $^3J_{H-H}$ = 11.80 Hz, 1H, $H(5)_{ax}$), 2.11 (dt, $^2J_{H-H}$ = 13.82 Hz, $^3J_{H-H}$

= 1.91 Hz, 1H, H(5)$_{eq}$), 4.32 (dqdd, $^3J_{H-H}$ = 11.80 Hz, $^3J_{H-H}$ = 6.86 Hz, $^3J_{H-H}$ = 1.91 Hz, $^4J_{H-P}$ = 1.84 Hz, 2H, C*H*CH$_3$), 4.84 (d, $^2J_{H-P}$ = 6.64 Hz, 1H, HCP), 7.40–8.00 (*m*, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 43.9; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.69 (s, $CH_3$), 34.44 (s, *C*HCH$_3$), 40.05 (d, $^1J_{C-P}$ = 44.8 Hz, CHP), 42.86 (d, $^4J_{C-P}$ = 2.9 Hz, $CH_2$), 128.38 (d, $^3J_{C-P}$ = 11.5 Hz, $C_{Ar(meta)}$), 131.50 (d, $^4J_{C-P}$ = 2.7 Hz, $C_{Ar(para)}$), 132.34 (d, $^2J_{C-P}$ = 9.2 Hz, $C_{Ar(ortho)}$); $^{77}$Se NMR (57.20 MHz, $CDCl_3$) $\delta$ −806.90 (d, $^1J_{Se-P}$ = 755.9 Hz); IR (KBr) 688 (vs), 744 (s), 1096 (vs), 1432 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 412 (6, M$^{\cdot+}$ + 1), 410 (6, M$^{\cdot+}$ − 1), 183 (7), 147 (100), 69 (14). Anal. Calcd for $C_{18}H_{21}PS_2Se$: C, 52.55; H, 5.15. Found: C, 52.42; H, 5.27.

***r*-2-[Diphenyl(selenophosphinoyl)]-*c*-4,*c*-6-dimethyl-1,3-dithiane (13f).** The procedure of Juaristi *et al.*[37] for the preparation of **10f** was modified to convert **15** (1.954 g, 13.2 mmol) and selenium (1.1 g, 13.9 mmol) into **13f**. After the reaction mixture was quenched with saturated aqueous ammonium chloride solution (25 mL), organic solvents were evaporated under reduced pressure, and the residue was extracted with chloroform (3 × 60 mL). Collected chloroform solutions were filtered through silica gel (5 g) and concentrated to about 25 mL. Diethyl ether (25 mL) was added, and the mixture was left to crystallize in a refrigerator overnight to afford **13f** (3.784 g, 69.8%), colorless crystals: mp 199.0–200.7 °C; $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.24 (d, $^3J_{H-H}$ = 6.83 Hz, 6H, $CH_3$), 1.34 (dt, $^2J_{H-H}$ = 14.02 Hz, $^3J_{H-H}$ = 11.61 Hz, 1H, H(5)$_{ax}$), 2.06 (ddt, $^2J_{H-H}$ = 14.02 Hz, $^5J_{H-P}$ = 4.46 Hz, $^3J_{H-H}$ = 2.23 Hz, 1H, H(5)$_{eq}$), 2.93 (dqd, $^3J_{H-H}$ = 11.61 Hz, $^3J_{H-H}$ = 6.83 Hz, $^3J_{H-H}$ = 2.23 Hz, 2H, C*H*CH$_3$), 5.11 (d, $^2J_{H-P}$ = 13.48 Hz, 1H, HCP), 7.4–8.1 (m, 10H, Ph); $^{31}$P NMR (121.49 MHz, $CDCl_3$) $\delta$ 39.2; $^{13}$C NMR (75.47 MHz, $CDCl_3$) $\delta$ 21.45 (s, $CH_3$), 41.69 (d, $^3J_{C-P}$ = 7.4 Hz, *C*HCH$_3$), 43.19 (s, $CH_2$), 50.73 (d, $^1J_{C-P}$ = 42.2 Hz, CHP), 128.34 (d, $^3J_{C-P}$ = 12.6 Hz, $C_{Ar(meta)}$), 129.28 (d, $^1J_{C-P}$ = 75.2 Hz, $C_{Ar(ipso)}$), 132.04 (d, $^4J_{C-P}$ = 3.0 Hz, $C_{Ar(para)}$), 132.95 (d, $^2J_{C-P}$ = 10.4 Hz, $C_{Ar(ortho)}$); $^{77}$Se NMR (57.20 MHz, $CDCl_3$) $\delta$ −764.91 (d, $^1J_{Se-P}$ = 753.9 Hz); IR (KBr) 688 (vs), 708 (s), 744 (s), 1096 (vs), 1248 (s), 1432 (s) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity) 412 (3, M$^{\cdot+}$ + 1), 410 (1, M$^{\cdot+}$ − 1), 183 (13), 147 (100), 69 (17). Anal. Calcd for $C_{18}H_{21}PS_2Se$: C, 52.55; H, 5.15. Found: C, 52.30; H, 5.22.

**5-*tert*-Butyl-1,3-dithiane (14).** The standard procedure of Corey and Seebach[132] was applied to convert **25** (40.0 g, 0.243 mol) and **26** (23.6 mL, 0.269 mol) into **14** (38.8 g, 90.4%), colorless needles: mp 51.0–52.8 °C (from methanol); $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 0.92 (s, 9H, $CH_3$), 1.74 (tt, $^3J_{H-H}$ = 11.11 Hz, $^3J_{H-H}$ = 2.26 Hz, 1H, *t*-BuC*H*), 2.63 (dd, $^2J_{H-H}$ = 14.16 Hz, $^3J_{H-H}$ = 11.11 Hz, 2H, H(4,6)$_{ax}$), 2.85 (dd, $^2J_{H-H}$ = 14.16 Hz, $^3J_{H-H}$ = 2.26 Hz, 2H, H(4,6)$_{eq}$), 3.36 (d, $^2J_{H-H}$ = 13.81 Hz, 1H, H(2)$_{eq}$), 3.36 (d, $^2J_{H-H}$ = 13.81 Hz, 1H, H(2)$_{ax}$); $^{13}$C NMR (75.47 MHz, $CDCl_3$) see Table 3 (supplementary material) and cf. ref 91; IR (KBr) 718 (vs), 1180 (m), 1220 (s), 1360 (vs), 1425 (m), 2858 (vs) cm$^{-1}$; MS (70 eV) *m/e* (relative intensity (176 (68, M$^{\cdot+}$), 119 (100), 73 (93), 57 (57), 45 (28), 41 (56), 39 (22). Anal. Calcd for $C_8H_{16}S_2$: C, 54.49; H, 9.15; S, 36.36. Found: C, 54.68; H, 9.18; S, 36.24.

***cis*-4,6-Dimethyl-1,3-dithiane (15).** The standard method of Corey and Seebach[132] was applied to convert **26** (13.0 mL, 0.148 mol) and **27** (18.3 g, 0.134 mol) into **15** (18.3 g, 92.3%), colorless needles: mp 85.0–85.5 °C (lit.[60] mp 81–82.5 °C); $^1$H NMR (300.13 MHz, $CDCl_3$) $\delta$ 1.23 (d, $^3J_{H-H}$ = 6.86 Hz, 6H, $CH_3$), 1.35 (dt, $^2J_{H-H}$ = 13.91 Hz, $^3J_{H-H}$ = 11.44 Hz, 1H, H(5)$_{ax}$), 2.10 (dt, $^2J_{H-H}$ = 13.91 Hz, $^3J_{H-H}$ = 2.20 Hz, 1H, H(5)$_{eq}$), 2.84 (dqd, $^3J_{H-H}$ = 11.44 Hz, $^3J_{H-H}$ = 6.86 Hz, $^3J_{H-H}$ = 2.20 Hz, 2H, C*H*CH$_3$), 3.55 (d, $^2J_{H-H}$ = 14.10 Hz, 1H, H(2)$_{eq}$), 4.92 (d, $^2J_{H-H}$ = 14.10 Hz, 1H, H(2)$_{ax}$); $^{13}$C NMR (75.47 MHz, $CDCl_3$) see Table 3 (supplementary material) and cf. ref 91.

**5,5-Dimethyl-1,3-dithiane (32).** The general procedure of Corey and Seebach[132] was used to transform **26** (8.1 mL, 92.2 mmol) and **28** (11.4 g, 83.7 mmol) into **32** (11.0 g, 88.7%), colorless liquid: bp 90–91 °C/14 mmHg, $n^{20}_D$ = 1.5473 (lit.[133] bp 93–94 °C/12 mmHg, $n^{25}_D$ = 1.5473); purity ca. 97% (GLC); $^1$H NMR (80 MHz, $CDCl_3$) $\delta$ 1.65 (s, 6H, $CH_3$), 3.04 (s, 4H, $CCH_2$), 4.12 (s, 2H, $SCH_2S$); $^{13}$C NMR (75.47 MHz) data are collected in Table 3 (supplementary material).

**Chloromethylphenylphosphine (33).** All operations were carried out in a nitrogen atmosphere. A mixture of **29** (110.0 g, 0.577 mol) and triphenyl phosphite (212.4 g, 0.685 mol) was heated under reflux in an apparatus provided with a 100-cm Vigreux column and variable reflux distillation head. The pure reaction product **33** (67.0 g, 73.2%) was collected as a colorless liquid, bp 95–96 °C/13 mmHg (lit.[125b] 66–67 °C/2 mmHg).

**Procedure of Equilibration of Diastereomeric 1,3-Dithiane Derivatives.** The reactions were carried out in solutions containing 0.15–0.20 mmol of isomer in 5.0 mL of appropriate solvent (if solubility was insufficient, saturated solutions were applied). Sodium methoxide was used as a catalyst, and its concentration was 0.007 M (it corresponds to ca. 0.2 equiv with regard to the substrate). Equilibrium was always reached from both sides, at constant temperature. Quenching was effected with the addition of saturated aqueous ammonium chloride solution (0.2 mL). The mixture was then evaporated, dried in vacuum, and extracted with chloroform-*d* (or benzene-$d_6$). The extract was filtered and transferred into an NMR sample tube for analysis by means of NMR spectroscopy. The results are collected in Tables 17 and 20–22.

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**Supplementary Material Available:** Tables 2, 3, and 5–14 (12 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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