Synthesis and Conformational Behavior of 2-Phosphonio- and 2-Phosphinyl-1,3-dithianes. Operation of the Generalized Anomeric Effect in the S–C–P$^+$ System

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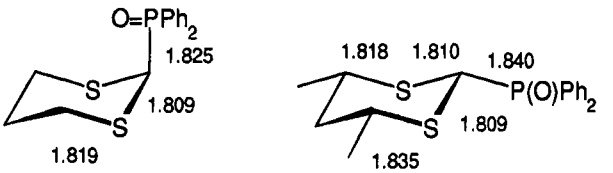
Received October 21, 1994 (Revised Manuscript Received May 17, 1995®)

A stereoselective preparation of various 2-phosphinyl- and 2-phosphonio-1,3-dithianes by desulfurization of the appropriate 2-thiophosphoryl-1,3-dithianes was described. The structure of the title compounds was studied by means of ^{1}H, ^{13}C, and ^{31}P NMR methods. Configurational assignments were also based on chemical correlation and X-ray structure determination. Both the NMR studies of conformationally labile models and equilibration of diastereomeric compounds showed an increased preference of the phosphinyl and phosphonium groups for the axial orientation. Magnitude of the anomeric effect found varies in the range from ca. 6 kJ/mol in phosphines to more than 10 kJ/mol in phosphonium salts. The anomeric effect could stem from the $n_s-\sigma^*_{C-P}$ hyperconjugative interaction. If phenyl groups are connected with phosphorus, overlap repulsion involving lone electron pairs of the endocyclic sulfur atoms and π-electrons of phenyl rings should also be taken into account. The reverse anomeric effect was not observed. No manifestation of the exo anomeric effect in 2-phosphinyl-1,3-dithianes was found.

Introduction

Conformational behavior of 1,3-diheteroanes containing second- and third-row elements has been subjected to extensive investigations during the past decade.[1–4] It is now generally accepted that the preferred conformation of noncharged species reflects the anomeric effect.[1–6] Nevertheless, the nature of this effect still seems to be a subject of intensive debate.

In 1982, Juaristi *et al.*[7] found that the anomeric effect is exhibited in the 2-(diphenylphosphinoyl)-1,3-dithiane system. The geometrical parameters of **1** and **2** in the solid state were interpreted by Juaristi *et al.*[8,9] as contrary to expectations if an $n_S-\sigma^*_{C-P}$ interaction makes the relevant contribution to the stabilization of the preferred axial conformation of **1**. The equatorial C–P bond in **2** is even longer (by 0.015 Å) than the axial one in **1** (see Figure 1). Some other results reported by Schleyer *et al.*,[10] Anet and Kopelevich,[11] and Caserio *et al.*[12] for various sulfur derivatives might also lead to the same conclusion, which has recently been discussed by us in detail.[3,4] Juaristi *et al.* have proposed[1,13,14] 3p–3d

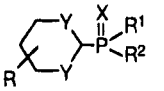


1 2

Figure 1. Selected bond lengths in 2-(diphenylphosphinoyl)-1,3-dithianes **1** and **2** (data from refs 8 and 9).

donation from endocyclic sulfur to phosphorus as being responsible (at least in part) for the anomeric effect observed in the S–C–P system.

A detailed analysis of our crystallographic, spectroscopic, and thermodynamic data for a wide variety of 2-substituted 1,3-dioxanes **3**,[15–17] 1,3-diselenanes **4**,[18] and 1,3-dithianes **5**[4,16,19] has recently suggested to us that the



R = none; 5,5-Me$_2$; 5-*t*-Bu; *cis*-4,6-Me$_2$

3: Y=O; X=O; $R^1=R^2$=Ph

4: Y=Se; X=O; $R^1=R^2$=OMe

5: Y=S; X=O, Se; R^1, R^2=Me, Ph, OMe, OEt, OCH_2CF_3

$n_Y-\sigma^*_{C(2)-P}$ negative hyperconjugation is one of the fac-

® Abstract published in *Advance ACS Abstracts,* July 1, 1995.

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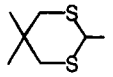
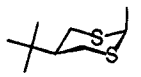
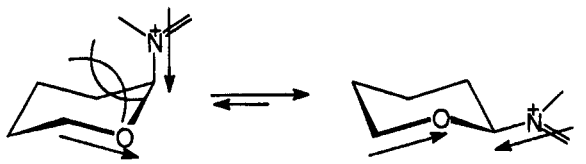
Chart 1

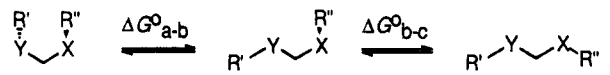
Ring	S ‖ PPh$_2$	S ‖ PPhMe	S ‖ PMe$_2$	SMe | $^+$PPh$_2$	SMe | $^+$PPhMe	SMe | $^+$PMe$_2$	$^{..}$PPh$_2$	$^{..}$PPhMe	$^{..}$PMe$_2$	$^+$PPh$_3$	$^+$PPh$_2$Me	$^+$PPhMe$_2$	$^+$PMe$_3$
	6a	7a	8a	9a	10a	11a	12a	13a	14a	15a	16a	17a	18a
	6b	7b	8b	9b	10b	11b	12b	13b	14b	15b	16b	17b	18b
	6c	7c	8c	9c	10c	11c	12c	13c	14c	15c	16c	17c	18c
	6d	7d	8d	9d	10d	11d	12d	13d	14d	15d	16d	17d	18d
	6e	7e	8e	9e	10e	11e	12e	13e	14e	15e	16e	17e	18e
	6f	7f	8f	9f	10f	11f	12f	13f	14f	15f	16f	17f	18f



22a 22e

Figure 2. Electrostatic interactions in 2-ammoniotetrahydropyrans **22a** and **22e** as a source of the reverse anomeric effect (from ref 25).

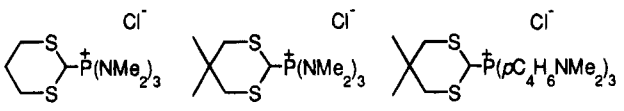
Scheme 1



24(sc,sc) 24(ap,sc) 24(ap,ap)

tors responsible for the anomeric effect in C−Y−C−P=X systems. Some other interactions are also possible, for instance, $\sigma_{C(4,6)-Y}-\sigma^*_{C(2)-P}$, $\sigma_{C(2)-P}-\sigma^*_{C(4,6)-Y}$ (preferring the equatorial position of phosphorus), and $\sigma_{C(4,6)-Y}-\pi^*_{P=X}$ hyperconjugations and the n_Y-n_X repulsions.

Since the anomeric effect is very often rationalized in terms of electrostatic interactions[1,3,20-22] we decided to study the conformational behavior of 2-phosphonio-1,3-dithianes **9**−**11** (Chart 1), and **15**−**21**, containing the



19 20 21

S−C−P$^+$ fragment, which are related to O−C−N$^+$ systems for which the *reverse anomeric effect*,[3,5a,23,24] i.e., increased equatorial preference, has been postulated (see Figure 2). We expected that the latter effect could also be operative, though weaker, for second-row atoms, if the electrostatic explanation[25] is correct. It should be noted that recent results of Perrin and Armstrong[26] on glycopyranosylammonium ions suggest that the reverse anomeric effect does not operate in the C−O−C−N$^+$ system. Moreover, a small anomeric effect has been observed and attributed to $n_O-\sigma^*_{C-N}$ overlap.[26] Therefore, the comparison of the phosphonium salts with phosphines **12**−**14** would reveal the importance of negative hyperconjugation as a source of the possible effect, since in the salts only one-directional hyperconjugative interactions can occur. Moreover, phosphines **12**−**14** offer a good opportunity of studying the *exo* anomeric effect, usually defined[1,3,5b] as the preference for the *gauche* conformation around the exocyclic C−XR bond in 2-substituted heteroanes containing the C−Y−C−XR system (i.e., **23** (*sc,sc*) and **23** (*ap,sc*) are the energetically preferred

23(sc,sc) 23(ap,sc)

species). The nature of this effect is still a matter of a debate,[3] which emphasizes either its hyperconjugative[27] or steric[28,29] origin. It must be added that the second definition, which emphasizes energetic consequences of the anomeric interactions and their directionality, was presented by Praly and Lemieux.[30] For equilibria in the R′−Y−CH$_2$−X−R″ system **24** (Scheme 1) one has two possible partial anomeric effects: one concerning the preference for the *sc* arrangement of the X−C bond and the second dealing with the conformation around the C−Y bond. The observed anomeric effect for the molecule as a whole is dependent on the relative strength of these partial anomeric effects, which could compete with each other. When the C−Y bond is a part of a ring, then the

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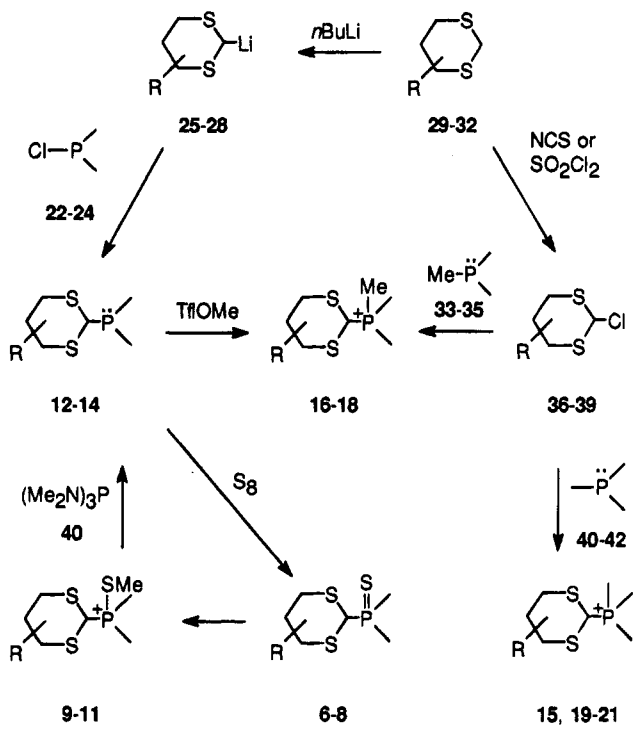
Scheme 2



magnitude of the anomeric effect about the C–X bond describes the *exo*-anomeric effect.

Recently, we reported preliminary results of our studies on the conformational behavior of 2-phosphinyl- **12–14**[16,31] and 2-phosphino-1,3-dithianes **15–18**[16,32–34] which suggested operation of the generalized anomeric effect in C–S–C–P(:) and C–S–C–P^+ systems, respectively. An analogous conclusion has been presented by Juaristi and Aguilar[35] on the basis of PPh_2 and $^+PPh_2$–BH_3, and by Juaristi and Cuevas[36] on the basis of $^+PMe_3$ derivatives of 1,3-dithiane. This research group has interpreted their results as stemming from n_S–σ^*_{C-P} and/or 3p–3d interactions.

In this paper we would like to present the full results of our studies on both conformationally labile (**a** and **b**) and diastereomeric (**c–f**) salts in the form of chlorides (e.g., **15b**-Cl) and/or triflates (e.g., **16d**-TfIO) and/or iodides (e.g, **16d**-I). Additionally, three conformationally labile nitrogen-containing phosphonium salts **19**, **20**, and **21** have been obtained. Interpretation of the results will be based on spectroscopic, thermodynamic, kinetic, and theoretical approaches.

Results and Discussion

Synthesis of Model Compounds. A general view at the synthetic methodology is outlined in Scheme 2. Phosphonium salts **9–11** were obtained from sulfides **6–8**, while salts **16–18** were accessible either by the alkylation of the appropriate 2-phosphinyl-1,3-dithianes **12–14** or by the reaction between the relevant 2-chloro-1,3-dithianes **36–39** and phosphines **33–35**. The latter method was also applied for the synthesis of salts **15** and **19–21**.

As far as the diastereomeric purity of substances **c–f** was concerned, the main problem was connected with assuring sufficient stereoselectivity of the applied reactions. It should be added that the synthesis of diastereomeric **6–8** has already been described by us.[2,4,16,37]

Synthesis of 2-[(Methylthio)phosphonio]-1,3-dithianes 9–11. The alkylation of the thiophosphoryl group with methyl triflate is well known[38] to give the appropriate (methylthio)phosphonium salts in a very good yield. We carried out this reaction in NMR sample tubes. After the addition of methyl triflate to a solution of the appropriate thiophosphoryl derivatives **6–8c–f** one could observe new signals of increasing intensity in ^{31}P NMR spectra, shifted downfield from the signal of the substrate. New signals were attributed to the relevant (methylthio)phosphonium salts **9–11c–f** on the basis of ^1H and ^{13}C NMR spectra (see below) and chemical correlation. Some examples of the total degree of conversion of substrates into products, found on the basis of integration in ^{31}P NMR spectra, are given in Table 1. As expected, the rate of the reaction depends on the substituents connected with phosphorus and on the position of the thiophosphoryl group with respect to the 1,3-dithiane ring. In general, the degree of conversion increases on going from **6** to **8**. However, the most striking difference is observed between compounds containing the axial and equatorial thiophosphoryl group. While conformationally fixed models with the equatorial P=S group (series **d** and **f**) are alkylated at almost the same rate as conformationally labile compounds (cf. **6a** and **6f** or **7a** and **7d**), the axial thiophosphoryl group (series **c** and **e**) is alkylated much slower. This is perhaps due to the fact that the thiophosphoryl sulfur atom in the axial position is located over the 1,3-dithiane ring, very close to the axial hydrogen atoms H(4) and H(6).[16] Thus, the axial P=S group is not as easily accessible as the equatorial one.

However, in the case of 2-thiophosphoryl-1,3-dithianes **6–7c–f** this reaction was accompanied by epimerization[39] of the resulting diastereomeric (methylthio)phosphonium salts **9–10c–f**. Therefore, we optimized their synthesis to ensure high conversion of a substrate **6–7c–f** and high diastereomeric purity of **9–10c–f**. The results are collected in Table 2. We chose time $t \cong 40$ min for **6c,e** and $t \cong 20$ min for **6d,f**. It corresponds to about 90% conversion of **6c,d,e,f** and to the 15, 7, 8, and 0% content of the undesired diastereomer, respectively. For compounds **7c–f** containing the methylphenylthiophosphinoyl group, PhMeP=S, the epimerization was much slower. Therefore, it was possible to convert **7c–f** quantitatively into triflates **9c–f**, exhibiting almost 100% diastereomeric purity, if the alkylation was carried out for no longer than 1 h. When the reaction was carried out for a sufficiently long time (2–7 days for **6c–f**, 45 days for **7c–f**), an equilibrium between isomeric methylthiophosphonium salts (**9** and **10**, respectively) was reached. The composition of the resultant mixtures is given in the last column of Table 2 (to be discussed later).

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Table 1. Degree of Conversion of 2-Thiophosphoryl-1,3-dithianes 6–9(a-f) in the Reaction with Methyl Triflate

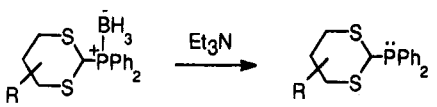
substrate	time (min)	conversn (%)	substrate	time (min)	conversn (%)	substrate	time (min)	conversn (%)
6a	17	88	**7a**	14	78	**8a**	6	90
6b	34	89	**7b**	26	92	**8b**	5	71
							11	95
6c	14	54	**7c**	13	83	**8c**	14	88
	38	88		39	100			
6d	20	93	**7d**	13	71	**8d**	9	79
				40	96			
6e	8	44	**7e**	22	92	**8e**	26	96
	18	58						
6f	16	87	**7f**	18	100	**8f**	20	96

Table 2. Ratio of Products in the Alkylation of 2-Thiophosphoryl-1,3-dithianes 6–7(c-f)

substrate	time (min)	ratio[a]	time (min)	ratio[a]	time (days)	ratio[a]
6c	14	94:6	39	85:15[b]	7	49:51[c,d]
6d	23	93:7[b]	64	55:45	7	53:47[c,d]
6e	8	92:8	38	92:8[d,e]	2	17:83[d,f]
6f	16	100:0	35	93:7[d,e]	2	83:17[d,f]
7c	39	100:0	$1.0\cdot10^5$	71:29[c,d]	45	79:21[d]
7d	40	100:0	$1.0\cdot10^5$	54:46[c,d]	45	25:75[c,d]
7e	22	100:0	$1.0\cdot10^5$	70:30	45	59:41[c,d]
7f	18	100:0	$1.0\cdot10^5$	81:19[c,d]	45	40:60[c,d]

[a] The first product:the second product; in CD_2Cl_2; based on the intensity in ^{31}P NMR spectra, unless otherwise stated. [b] Based on the intensity of the *tert*-butyl group signals in the ^1H NMR spectra. [c] Based on integration in the ^{31}P NMR spectra. [d] Reaction carried out in $CDCl_3$. [e] Based on the intensity of the CH_3-C(4,6) signals in ^1H NMR spectra. [f] Based on integration of the H(2) doublet in the ^1H NMR spectra.

Scheme 3



12a,e,f

Finally, it should be mentioned that dimethyl(methylthio)phosphonium salts **11c–f** did not epimerize to a noticeable degree even after 2 months.

Synthesis of 2-Phosphinyl-1,3-dithianes 12–14. The key substances in the preparation of phosphonium salts **16–18** of defined configuration (**c–f**) were diastereomeric 2-phosphinyl-1,3-dithianes **12–14**. 2-(Diphenylphosphinyl)-1,3-dithianes **12a,e,f** have been prepared by Juaristi and Aguilar[35] by treatment of the relevant 2-(diphenylphosphinyl)borane-1,3-dithianes with triethylamine at 50 °C for 48 h (Scheme 3). However, 2-phosphinyl-1,3-dithianes **12–14a,b,d,f** were conformationally labile, and the equatorial diastereomers could have also been prepared by highly stereoselective reaction of the apporpriate 2-lithio-1,3-dithianes with chlorophosphines developed by Juaristi *et al.*[40] Following this idea, we prepared **12d** of about 90% purity in almost 93% yield. Unfortunately, all attempts to efficiently convert **12d** into **12c** *via* a deprotonation–protonation sequence failed. It must be noted that **12c** was undoubtedly formed, though in a low yield, as one could guess from the results of alkylation of the crude deprotonation–protonation product with methyl iodide, which was carried out by us to obtain **16c**-I. Thus, we focused our attention on a method of the synthesis of phosphines that was worked out in our group[41] and which consists in the conversion of (methylthio)phosphonium salts into phosphines in the reaction with tris(*N,N*-dimethylamino)phosphine (**40**) (Scheme 2).

For all (methylthio)phosphonium salts, except for **11c** and **11e**, we found this reaction to occur with a high stereoselectivity. In particular, the relative ratio of diastereomeric diphenyl(methylthio)phosphonium salts **9c:9d** and **9e:9f** was transferred almost unchanged into the ratio of appropriate phosphines (see Table 3). As far as methyl(methylthio)phenylphosphonium salts **10c–f** are concerned, the stereoselectivity of desulfurization seemed to be dependent on temperature (e.g., for **10c**) and was higher at 273 K than at room temperature. The importance of the temperature at which the desulfurization was carried out is evident for dimethyl(methylthio)-phosphonium salts **11c–f**. While the reaction with compounds containing the equatorial phosphonium group (**d** and **f**) occurred, as before, with a high stereoselectivity, a considerable epimerization (up to 72%) took place at room temperature if the axial Me_2P^+SMe group in **11c**

Table 3. Ratio of Products in the Desulfurization of 9–11(c-f)

		ratio	
substrate	T (K)	salt[a]	phosphine[b]
9c	293	85:15	88:12[c]
9d	293	93:7	85:15,[c] 94:6[c,d]
9e	293	92:8	91:9,[c] 9:1[c,d]
9f	293	93:7	100:0,[c] 96:4[c,d]
9c	298	100:0	74:26[e]
	273	100:0	9:1[d,e]
10d	298	100:0	100:0,[e] 97:3[d,f]
	273	100:0	100:0,[c] 97:3[c,d]
10e	298	100:0	91:9,[e] 91:9[d,f]
	273	100:0	9:1[c,d]
10f	298	100:0	100:0[e]
	273	100:0	100:0,[c] 100:0[c,d]
11c	293	100:0	28:72[e]
	273	100:0	37:63[c]
	213	100:0	86:14[d,f]
11d	293	100:0	100:0[e]
11e	298	100:0	52:48[e]
	273	100:0	83:17[c,d]
	213	100:0	93:7[c,d]
11f	293	100:0	100:0[e]

[a] As in Table 2. [b] With respect to *a*. [c] Based on the intensity of the CH_3-C signals in ^1H NMR spectra. [d] Measured after the alkylation of phosphines as ratio of appropriate salts. [e] Based on the intensity in the ^{31}P NMR spectra. [f] Based on the integration in the ^{31}P NMR spectra.

(40) Juaristi, E.; López-Núñez, N. A.; Valenzuela, B. A.; Valle, L.; Toscano, R. A.; Soriano-Garcia, M. *J. Org. Chem.* **1987**, *52*, 5185.
(41) Omelańczuk, J.; Mikołajczyk, M. *Tetrahedron Lett.* **1984**, *25*, 2493.

Table 4. Results of the Reaction between 2-Chloro-1,3-dithianes 38 and 39 and Phosphines 33–35 and –41

salt	T (K)	yield[a] (%)	ratio[b] c:d	T (K)	yield[a] (%)	ratio[b] e:f
15	293	89.3	89:11	293	78.3	90:10
16	293	73.8	69:31	293	82.1	67:33
17	293	95.8	56:44	293	94.6	52:48
	273	87.6	58:42			
18	273	95.2	70:30	293	82.2	67:33

[a] Isolated. [b] Based on integration in the ^{31}P NMR spectra.

and **11e** was involved. This epimerization was shown to be dependent on temperature, and at 216 K (−60 °C) its extent decreased to 14 and 7%, respectively.

Synthesis of 2-Phosphonio-1,3-dithianes 15–18. Phosphonium salts, in general, could be prepared *via* the alkylation of phosphines according to Scheme 2. In the case of 2-phosphonio-1,3-dithianes **15–18**, such an approach can be realized (barring stereochemistry of products) in two ways. The first one consists of the reaction between 2-chloro-1,3-dithianes **36–39** and phosphines **33–35** and **41**. The second one is based on the alkylation of 2-phosphinyl-1,3-dithianes **12–14** with methyl triflate or iodomethane. It should be noted that 2-(triphenylphosphonio)-1,3-dithianes **15** could only be prepared by the former method.

Reaction between 2-Chloro-1,3-dithianes 36–39 and Phosphines 33–35 and 41. Preparation of 2-(Triphenylphosphonio)-1,3-dithianes 15. This method was successfully applied for the preparation of **15a** by Kruse[42] and recently by Juaristi and Cuevas[36] to synthesize **18a,e,f**. Following this methodology, conformationally labile **15a,b** and **19–21** were prepared in 89.4, 72.5, 53.4, 52.7, and 60.2% yields, respectively. However, applicability of this reaction to the synthesis of anancomeric salts (especially **15c–f**) was not so obvious. In fact, Juaristi and Cuevas[36] observed almost no selectivity in the synthesis of **18e,f** (58:42, respectively).

In order to synthesize salts **15–18c–f**-Cl, triphenylphosphine (**41**), diphenylmethylphosphine (**33**), dimethylphenylphosphine (**34**), and trimethylphosphine (**35**), respectively, were reacted with the appropriate 2-chloro-1,3-dithianes **38** and **39** in benzene solutions. Solid products were analyzed by means of NMR spectroscopy, and two diastereomeric products were always obtained. Their relative ratio and overall yield of the reaction are collected in Table 4. In each case, the products containing axial phosphonium groups are preferred, but the preference largely depends on the number of the phenyl groups in a phosphine. It is interesting that very bulky triphenylphosphine (**41**) has the greatest preference for the axial approach to 1,3-dithiane ring.[43] If the number of phenyl substituents decreases, the stereoselectivity tends to diminish, and is very low for dimethylphenylphosphonium derivatives **17**, both at 293 and 273 K. Stereoselectivity increases again for trimethylphosphonium salts **18**. A possible explanation of this observation has already been presented by us.[3,44] It should also be noted that this reaction for **18e,f** occurred somewhat more stereoselectively (67:33, respectively) than that reported by Juaristi and Cuevas[36] (58:42, respectively), presumably due to solvent effects.[45]

In order to obtain pure **15c**-Cl we attempted, unsuccessfully, to improve the diastereomeric ratio of the crude product using a deprotonation–protonation sequence. Eventually, pure **15c**-Cl, as a 1:1 complex with dimethylformamide, was obtained in 42.5% yield by crystallization of the curde reaction mixture from dimethylformamide–diethyl ether.

When a concentrated dimethylformamide solution of the crude **15c**-Cl was heated for a few minutes, the diastereomeric ratio was changed in favor of **15d**-Cl, indicating that the latter is the thermodynamically more stable isomer. By crystallization of this new mixture from dimethylformamide–diethyl ether we were able to obtain **15d**-Cl of about 94% diastereomeric purity. An analogous approach to the crude **15e,f** afforded a product containing 94% of **15f**-Cl.

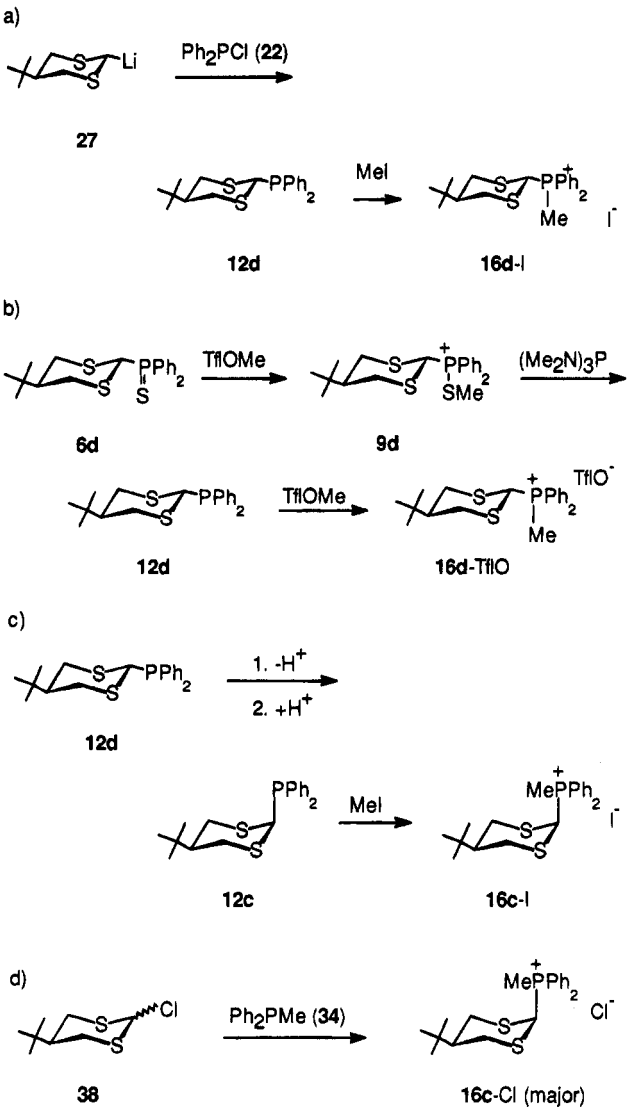
Alkylation of 2-Phosphinyl-1,3-dithianes 12–14. The alkylation of 2-phosphinyl-1,3-dithianes **12–14**, derived from the desulfurization of salts **9–11**, was accomplished in NMR sample tubes with the use of methyl triflate. This reaction was found to occur highly stereoselectively affording the corresponding phosphonium triflates **16–18** in a quantitative yield. Hence, the relative ratio of phosphines, which are unstable and tend to oxidize spontaneously, can be determined as the ratio of the appropriate alkylated products (cf. Table 3, footnote d).

Phosphonium triflates, thus obtained, were characterized by means of NMR spectroscopy. It should be noted, however, that the spectral parameters could be influenced by the presence of tris(*N,N*-dimethylamino)(methylthio)phosphonium triflate [$(Me_2N)_3P^+SMe$ $TflO^-$] in the reaction mixture. This impurity was not present when pure 2-phosphinyl-1,3-dithianes, accessible by the reaction between 2-lithio-1,3-dithianes **25–28** and chlorophosphines **22–24**, were alkylated. Unfortunately, the latter method is limited to sufficiently stable phosphines containing the equatorial phosphino group, namely **12d** and **12f**. Thus, the alkylation of **12d** with methyl iodide was performed in 66.6% yield. The solid product contained **16c** and **16d**, in the relative ratio of about 1:99, as it was found on the basis of intensities of the corresponding signals in ^{31}P NMR spectrum. The **16c**-enriched (up to 65%) product was obtained in a low yield (13.7%) by the alkylation of the crude product of the deprotonation–protonation of **12d**.

Structural Assignments. Chemical Correlation. The reaction between 2-lithio-1,3-dithianes and chlorodiphenylphosphine (**22**) and subsequent addition of oxygen, sulfur,[8,9,40] or selenium[4,16] is known to proceed stereoselectively to afford, in the case of conformationally fixed models, compounds containing a P=O, P=S, or P=Se group in the equatorial position. Hence, all

(42) Kruse, C. G. Ph.D. Thesis, University of Leiden, 1978.
(43) The largest preference for the axial approach to 1,3-dithiane ring has been observed for Ph_2P-SMe.[44]
(44) Graczyk, P. P.; Mikołajczyk, M. Manuscript in preparation.
(45) It is known that stereoelectronic interactions responsible for the anomeric effect and for the kinetic anomeric effect are solvent dependent and are generally less important in more polar media.[3] Juaristi and Cuevas carried out the reaction in a mixture benzene: THF = 2:1 (v/v), which is a more polar medium than benzene itself. Therefore, the stereoselectivity in pure benzene should be higher, as observed.

Scheme 4



phosphines, thus obtained, also contain the equatorial phosphinyl group. In particular, 5-*tert*-butyl-2-(diphenylphosphinyl)-1,3-dithiane with δ −2.0 (^{31}P NMR) has the *trans* configuration (**12d**) (see Scheme 4a) and, therefore, the upfield isomer with δ −18.5 *cis* configuration (**12c**).

The alkylation−desulfurization sequence applied to **6d** (see Scheme 4b) gives as the main product the phosphine spectroscopically identical with the phosphine **12d** derived from the appropriate 2-lithio-1,3-dithiane **27** and chlorophosphine $ClPPh_2$ (**22**) (Scheme 4a). Hence, diastereomeric 2-[(methylthio)phosphonio]-1,3-dithianes **9**−**11c**−**f** and the related phosphines **12**−**14c**−**f** have the same configuration as the starting 2-thiophosphoryl derivatives **6**−**8c**−**f**. The alkylation of **12d**, thus prepared, with methyl triflate led to **16d**-TfIO (Scheme 4b) almost identical (in NMR) with **16d**-I (Scheme 4a). These salts are isomeric (as far as the cations are concerned) with the main product of methylation of a phosphine resulting from the deprotonation−protonation reaction of **12d** (Scheme 4c). Therefore, the latter product should possess the phosphonium group located axially (configuration *cis*), **16c**-I. Consequently, the relevant configuration to both diastereomeric products of the reaction between diphenylmethylphosphine (**34**) and 5-*tert*-butyl-2-chloro-1,3-dithiane (**38**) (Scheme 4d) can be ascribed on the basis of chemical shifts and coupling pattern in NMR spectra, with the main product having configuration *cis*, namely **16c**-Cl.

X-ray Structure Determination. In order to confirm the configurational assignments discussed above and based on NMR data, a single crystal X-ray structure determination was performed for **15c**-Cl·DMF[33] and **16d**-I.[46] The most valuable finding was that the main product of the reaction between chlorodithiane **38** and triphenylphosphine (**41**) has the *cis* configuration (**15c**). As expected, the alkylation of **12d** (Scheme 4a) leads to the product of *trans* configuration (**16d**).

NMR Spectroscopy. ^{13}C NMR. Structural determination of various heteroane systems by means of ^{13}C NMR spectroscopy is a common practice now.[47] On the basis of C(4,6) chemical shifts (Table 5; supporting information) the relevant γ-effect[48−50] values were calculated (Table 6). Alike in noncharged C−S−C−P=X (X = O, S, Se) systems,[4] the γ-effects and $^3J_{C(4,6)-P}$ coupling constants (Table 6) are the most informative spectral parameters. It should be noted that the γ-gauche upshielding effect in ^{13}C NMR spectra has also been extensively used by other researchers for assignment of the configuration at C(2) in these and analogous systems.[36,40,51,52]

The γ-effect value is negative and amounts about −3 to −4 ppm (Table 6) for all 1,3-dithiane derivatives with phosphorus located axially (configuration established, e.g., on the basis of X-ray structure determination). For the equatorial phosphorus the γ-effect value is positive and equals to about 1−2 ppm. Coupling constant $^3J_{C-P}$ (its absolute value, Table 6) in the former case is zero (except for **12c**), but equals about 7−8 Hz when phosphorus is situated equatorially, which is in good agreement with the expectation based on the *anti* arrangement of the C−S−C−P system. The situation is more complicated if we deal with 2-phosphinyl-1,3-dithianes **12c** and **12d**, whose configuration was established *via* chemical correlation. Though the γ-effect values differ substantially (−4.44 and +1.95 ppm in **12c** and **12d**, respectively), the coupling constant $^3J_{C-P}$ is almost the same in both isomers (7.2 and 7.9 Hz, respectively). The large coupling constant in **12c** is not so surprising, as it might be expected on the basis of the *gauche* arrangement of the C−S−C−P system, and this stems from the orientational effect of the phosphorus lone pair on C−P coupling. It was demonstrated both experimentally[53] and theoretically[54,55] that the phosphorus lone pair is an efficient spin information transmitter. Thus, because of the spatial proximity of the P and C(4,6) atoms in **12c**, the magnitude of the coupling seems to be governed by through-space interaction, which should be at a maximum for a lone pair lying over the 1,3-dithiane ring

(46) Experimental details of the X-ray analysis of **16d**-I will be reported elsewhere.

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Table 6. γ-Effect (ppm) in the ^{13}C NMR spectra[a] of 9–18 and the Related $^{3}J_{C-P}$ (Hz) Values

	γ-effect									
	9[b]	10[b,c]	11[b]	12[d]	13[c,d]	14[d]	15[e]	16[b]	17[b]	18[b]
a	−1.21	−2.01	−1.43	−0.47	−0.38	−0.60	0.11	−0.49	−2.32	−1.03
b	−1.68	−2.36	−1.51	−0.81	−0.75	−0.75	−0.26	−1.01	−2.67	−1.08
c	−4.39	−4.38	−3.52	−4.44	−4.64	−4.60	−4.48	−4.42	−4.39	−3.48
d	1.00	0.90	1.07	1.95	1.71	1.50	1.09	1.16	0.67	0.78
e	−3.12	−3.10	−2.78	−4.63	−4.83	−4.85	−3.55	−3.36	−3.62	−2.94
f	2.42	2.42	2.42	2.04	1.72	1.53	1.14	2.36	2.10	1.95
	$^{3}J_{C-P}$ values									
	9[b]	10[b,c]	11[b]	12[d]	13[c,d]	14[d]	15[e]	16[b]	17[b]	18[b]
a	3.2	1.8	3.4	7.7	6.8	7.3	7.0	4.9	0	4.8
b	3.4	3.7	3.5	6.4	7.0	8.2	5.7	5.0	0	5.4
c	0	0	0	7.2	7.0	7.9	0	0	0	0
d	7.2	7.5	7.8	7.9	7.1	6.3	7.5	7.1	7.3	7.4
e	0	0	0	8.7	8.1	8.6	0	0	0	0
f	7.7	7.2	7.6	7.4	6.4	6.4	7.4	6.7	7.5	7.8

[a] SF = 75.47 MHz, temperature 296 K, in CD_2Cl_2 unless otherwise stated. [b] Triflates. [c] Mean value if C(4) and C(6) are anisochronous. [d] Obtained by desulfurization of sulfides. [e] Chlorides.

(this effect will be discussed below in context of the exo anomeric effect in **12–14**).

On the basis of the structural dependence of $^{3}J_{C-P}$ and γ-effect values in ^{13}C NMR spectra the configuration for the remaining diastereomeric compounds, i.e., **13–14c–f** and **17–18c–f**, can be ascribed. A long range $^{5}J_{C-P}$ coupling constant of about 2 Hz (Table 7, supporting information), between the quaternary carbon of the *tert*-butyl group and phosphorus in 5-*tert*-butyl-1,3-dithiane derivatives, can be regarded as an additional support to the equatorial positioning of both *tert*-butyl and phosphorus (zig–zag-type coupling). It can be observed for almost all (except for **14d**, probably owing to unfavorable orientation of a lone pair of phosphorus) compounds belonging to group **d**.

For diastereomeric compounds containing the P=X (X = O, S, Se) group located axially one can observe[2,4,16] another long range $^{4}J_{C-P}$ coupling constant of magnitude 1.7–3.3 Hz between carbon C(5) and phosphorus, which is indicative of the close contact between X and axial hydrogens H(4) and H(6). Though a sulfur atom is also present in **9–11**, the only effect in **9** and **10** is a broadening of the C(5) singlet; i.e., the coupling constant is very small. In **11c,e** it is equal to about 3 Hz (Table 7, supporting information). This observation can be easily explained if one assumes that the phenyl group has a larger tendency to be placed over the 1,3-dithiane ring than the methylthio group as well as an *exo* arrangement of the MeS moiety. As will be shown on the basis of ^{1}H NMR data this seems to be the case.

Several other ^{13}C NMR parameters are collected in Tables 8–13 (supporting information; Table 8, Chemical Shifts of C(2) and the Related Coupling constant $^{1}J_{C-P}$; Table 9, Chemical shifts of the Methyl Me–C–C Carbons and Quaternary Carbon of the 5-*tert*-Butyl Group; Table 10, Chemical Shifts of Aromatic Carbons C_{Ar} *Ortho*, *Meta*, and *Para*; Table 11, Coupling constants $^{2}J_{C-P}$, $^{3}J_{C-P}$, and $^{4}J_{C-P}$ with C_{Ar} *Ortho*, *Meta*, and *Para*, Respectively; Table 12, Chemical Shifts of Me–P Carbons and the Related Coupling Constant $^{1}J_{C-P}$; Table 13, Chemical Shifts of the Me–S–P Carbons and the Related Coupling Constant $^{2}J_{C-P}$).

^{1}H NMR. The ^{1}H NMR data for **9–18** are collected in Tables 14–20 (supporting information; Table 14, Chemical Shift of Axial $H(4,6)_{ax}$ and Equatorial R(4,6); Table 15, Chemical Shift of Axial $R(5)_{ax}$ and Equatorial $R(5)_{eq}$; Table 16, Coupling Constants *Anti* $^{3}J_{H(4,6)-H(5)}$, *Gauche* $^{3}J_{H(4,6)-H(5)}$, and Long Range $^{5}J_{H(5)-P}$; Table 17, Chemical Shift of H(2) and the Related Coupling Constant $^{2}J_{H-P}$; Table 18, Coupling Constants $^{4}J_{H(4,6)-P}$ and Geminal $^{2}J_{H-H}$; Table 19, Chemical shifts of Me–P Protons; Table 20, Chemical Shifts of Me–S–P Protons and the Related Coupling Constant $^{3}J_{H-P}$). Whereas the ^{1}H NMR spectra of phosphines **12–14** resemble those of their oxides, sulfides, and selenides,[4,16,19] the sequence of signals in the spectra of phosphonium salts is rather unexpected. The coupling between H(4,6) protons and phosphorus in phosphonium salts **b**, **c**, and **d** is observed in the *upfield* part of the CH_2 resonance, in contrast to the spectra of noncharged species. If groups **c** and **e** are considered and compared with the parent 1,3-dithianes **31** and **32**, one can easily find that the axial $H(4,6)_{ax}$ protons are slightly (by about 0.3 ppm) deshielded by the axial C–P bond in **11c** and **11e**, practically not deshielded in **18c** and **18e**, and shielded in all other salts (by up to 1.0 ppm in **15c,e**). Such a large shielding can be attributed to the shielding effect of the phenyl ring(s) connected with phosphorus and lying over the 1,3-dithiane ring. X-ray analyses of a single crystal of **10c**-Cl·DMF[33] and **15b**-Cl[46] revealed that one of the phenyl rings of the axial phosphonium group is almost parallel to the plane formed by the endocyclic sulfur atoms and methylene carbons. Thus, the influence of the phenyl ring(s) should not only be limited to $H(4,6)_{ax}$ resonances but it ought to be extended over all protons of C(4)–C(5)–C(6) region. This conclusion is strongly supported by the shielding of the equatorial $H(4,6)_{eq}$ protons (by about 0.4 ppm) and the *tert*-butyl group (by about 0.3 ppm) in **9c**, **10c**, **15c**, **16c**, and **17c**, as well as the shielding of the methyl Me–C(4,6) protons (by more than 0.1 ppm) and the equatorial $H(5)_{eq}$ proton (by 0.2–0.5 ppm) in **9e**, **10e**, **15e**, **16e**, and **17e** (this effect will be discussed below in context of the exo anomeric effect in **12–14**). In each case, when axial phosphonium group contains phenyl ring(s), the axial $H(5)_{ax}$ proton is shielded by more than 0.1 ppm. This observation may

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Table 22. Conformational Equilibrium Constants for 1,3-Dithiane Derivatives 9–18a Calculated *via* the Weighted Average Method (See Text)

spectrum probe compd	^{1}H NMR				^{13}C NMR						^{31}P NMR	
	$^2J_{H-P}$		$\delta_{H(2)}$		γ-effect		$^3J_{C-P}$		$\delta_{C(2)}$		δ	
	c,d	**e,f**	**c,d**	**e,f**	**c,d**	**e,f**	**c,d**	**e,f**	**c,d**	**e,f**	**c,d**	**e,f**
9a	5.75	0.78	1.37	0.73	1.44	0.53	0.80	0.71	2.38	*a*	*b*	*b*
10a	2.09	0.55	0.91	0.36	0.82	0.25	0.32	0.33	1.18	*a*	*a*	0.67
11a	2.26	0.82	1.09	0.44	0.84	0.35	0.77	0.81	1.32	*a*	1.14	0.86
12a	1.23	9.93	4.50	1.12	1.65	1.60	*b*	*b*	*c*	0.04	2.59	1.47
13a	*b*	*b*	3.71	1.58	2.04	2.13	*b*	*b*	7.11	*a*	4.23	2.09
14a	*c*	*c*	*c*	*c*	1.92	2.00	*b*	*b*	*a*	*a*	3.82	1.85
15a	40.2	4.09	*a*	*a*	4.68	3.55	14.0	17.5	8.64	0.85	6.54	*a*
16a	7.00	1.63	4.59	2.11	2.38	1.01	2.23	2.72	3.43	0.31	*b*	*b*
17a	2.00	0.51	1.08	0.28	0.69	0.30	*b*	*b*	1.21	*a*	*b*	*b*
18a	14.7	1.04	*a*	1.36	1.35	0.64	1.85	1.60	2.26	0.11	1.50	1.13

[a] Data *P* for labile compound are out of range of the data for reference systems. [b] Quantity *P* measured with too small accuracy. [c] Not determined.

serve as a piece of evidence for the tendency of the phenyl group to be located over the 1,3-dithiane ring plane, even in such cases when other substituents connected with axial phosphorus are relatively "small", e.g., two methyl groups in **17c,e**. The situation in **9c,e** and **10c,e** is not so clear since the $^4J_{C-P}$ coupling constant is non-zero (see Table 7, supporting information) and suggests that the *endo* arrangement of the methylthio group cannot be neglected. Interestingly, in the relevant phosphine sulfides **6c,e** and **7c,e** such shielding effects are not observed, in agreement with the exclusive *exo* position of the phenyl ring(s).[4,16,19]

The unexpected order of the CH_2 resonances in the ^{1}H NMR spectra of phosphonium salts **b–d** is not due only to the shielding effect of the phenyl group connected with the axial phosphorus. While the axial H(4,6) protons in **31** and **32** resonate at δ 2.63 and 2.83 ppm, respectively,[11,15] they are shifted *downfield* in all salts containing the phosphonium group in the equatorial position; e.g., $\delta_{H(4,6)ax}$ in **15d** and **15f** is equal to 3.81 and 4.08 ppm, respectively (see Table 14, supporting information). But even if the aromatic substituents are absent, as in **11d**, **11f**, **18d**, and **18f**, the axial $H(4,6)_{ax}$ protons are deshielded by more than 0.4 ppm. Hence, phenyl rings are not necessary for the observed effect, although the deshielding of axial protons increases with the increasing number of phenyl rings. This behavior can be perhaps attributed to the increasing electron-withdrawing properties of the phosphonium group (cf. the increase of the chemical shift of anomeric proton, Table 17, supporting information). It should be noted, however, that the equatorial $H(4,6)_{eq}$ protons are also deshielded but to a much smaller extent (0.05–0.26 ppm in salts from group **c**). The origin of this phenomenon is not clear, especially as far as the deshielding of the axial protons is concerned. Analogous reversal of the CH_2–S resonances was reported in the literature[56] for 2-(trimethylplumbyl)-1,3-dithiane, but the scope and limitations of this effect seem to require further studies.

^{31}P NMR. The ^{31}P NMR chemical shifts of all the compounds under investigation are collected in Table 21 (supporting information). They cannot be applied for *a priori* assignment of configuration. Nevertheless, relaxation times T_1^{DD} of ^{31}P nuclei corresponding to the dipolar mechanism of relaxation can be applied as an efficient structural probe for these compounds, as has recently been demonstrated by us.[57] In particular, T_1^{DD} values for compounds containing phosphorus located axially are always shorter than those for their diastereomers. This methodology has been applied by us to confirm stereochemical assignments for **9c,d**, **12c,d**, **15c,d**, **16c,d**,[57] and **18c,d**. Relaxation times T_1^{DD} for **18c,d** will be discussed below in connection with the $\Delta S°$ value for conformational equilibrium in **18b**.

Conformation of 1,3-Dithiane and 5,5-Dimethyl-1,3-dithiane Derivatives in a Solution. The ring inversion barrier for six-membered rings is relatively low.[58] Therefore, in the case of conformationally labile compounds each observed NMR parameter *P* in a solution of a conformationally labile compound is at room temperature a weighted average[59] of the values P_{ax} and P_{eq} characteristic for axial and equatorial conformer, respectively (eq 1).

$$P = xP_{ax} + (1 - x)P_{eq} \quad (1)$$

$$K = \frac{1 - x}{x} \quad (2)$$

where *x* is the molar fraction of the axial conformer and *K* is the conformational equilibrium constant. Thus, the conformational equilibrium constant *K* may be estimated quantitatively using eq 2, provided P_{ax} and P_{eq} are known. This approach has been extensively applied in conformational studies of heteroanes and has recently been summarized by us.[4]

The preferred conformation of the title compounds in a solution was estimated quantitatively using various physical quantities in ^{1}H, ^{13}C, and ^{31}P NMR spectra (from the appropriate tables) as conformational probes P. The results are collected in Tables 22 (1,3-dithiane derivatives; **a**) and 23 (5,5-dimethyl-1,3-dithiane derivatives; **b**). As for the C–S–C–P=X (X = O, S, Se) systems[4] one may obtain very different equilibrium constants for a given compound which depend on the conformational probe *P* and applied reference system (**c,d** *vs* **e,f**). Usually, only the **e,f** reference pair provides such an interval of P_{ax} and P_{eq} values which does not contain the observed *P* for **a** or **b** derivatives (this situation is marked as footnote a in Tables 22 and 23). Compounds from this pair (**e,f**) are conformationally homogeneous, and hence the reason for such a situation can be ascribed only to the influence of the methyl groups at C(4) and C(6) of

(56) Drew, M. G.; Kitching, W. *J. Org. Chem.* **1981**, *46*, 558.
(57) Mikołajczyk, M.; Wróblewski, K.; Graczyk, P. P. *Magn. Reson. Chem.* **1992**, *30*, 883.
(58) Friebolin, H.; Schmid, H. G.; Kabuss, S.; Faisst, W. *Org. Magn. Reson.* **1969**, *1*, 67.
(59) Eliel, E. L. *Chem. Ind.* **1959**, 568.

Table 23. Conformational Equilibrium Constants for 1,3-Dithiane Derivatives 9–18b Calculated *via* the Weighted Average Method (See Text)

spectrum probe compd	^{1}H NMR $^2J_{H-P}$ c,d	^{1}H NMR $^2J_{H-P}$ e,f	^{1}H NMR $\delta_{H(2)}$ c,d	^{1}H NMR $\delta_{H(2)}$ e,f	^{13}C NMR γ-effect c,d	^{13}C NMR γ-effect e,f	^{13}C NMR $^3J_{C-P}$ c,d	^{13}C NMR $^3J_{C-P}$ e,f	^{13}C NMR $\delta_{C(2)}$ c,d	^{13}C NMR $\delta_{C(2)}$ e,f	^{31}P NMR δ c,d	^{31}P NMR δ e,f
9b	0.42	0.01	1.15	0.56	1.01	0.35	0.90	0.79	2.44	*a*	*b*	*b*
10b	0.24	0.03	0.75	0.26	0.62	0.15	0.97	1.06	1.19	*a*	0.79	1.78
11b	0.84	0.30	0.93	0.35	0.78	0.32	0.81	0.85	1.54	*a*	1.57	1.16
12b	*b*	*b*	0.90	*a*	1.32	1.34	*b*	*b*	*c*	*a*	1.06	0.53
13b	*b*	*b*	1.35	0.51	1.58	1.65	*b*	*b*	3.09	*a*	1.30	0.57
14b	*c*	*c*	*c*	*c*	1.72	1.80	*b*	*b*	9.35	*a*	1.37	0.54
15b	2.95	1.38	*a*	*a*	3.14	2.35	3.17	3.35	12.5	1.03	8.05	*a*
16b	1.24	0.46	1.49	0.41	1.57	0.70	2.38	2.94	3.08	0.26	*b*	*b*
17b	0.42	0.04	0.73	0.09	0.52	0.20	*b*	*b*	1.14	*a*	*b*	*b*
18b	0.16	0.02	*a*	0.62	1.29	0.62	2.70	2.25	2.78	0.19	1.90	1.37

[a] Data for the labile compound are out of range of the data for reference systems. [b] Quantity *P* measured with too small accuracy. [c] Not determined.

the 1,3-dithiane ring on the spectral properties of interest. It must be noted that the influence of 4,6-methyl groups in the 1,3-dithiane ring on $\delta_{C(2)}$[36] and $\delta_{C(4,6)}$[35,36] chemical shifts has been recognized by Juaristi *et al.*, and the relevant corrections have been employed. However, because of the possible error[4] involved in the latter approach we selected 5-*tert*-butyl-1,3-dithiane derivatives as the reference systems. Though conformationally impure,[60,61] they provide more reliable results than *cis*-4,6-dimethyl-1,3-dithiane derivatives, presumably due to a very small influence of 5-*tert*-butyl group on the discussed NMR spectral properties.

Methodology of the selection of the conformational probe has recently been discussed by us.[4] On the basis of this approach the conformational equilibrium constants were calculated using the γ-effect value and the $^3J_{C(4,6)-P}$ coupling constant in ^{13}C NMR spectra and the chemical shift δ in the ^{31}P NMR spectra. However, the only probe, which is practically substitution-independent and measurable with high accuracy, is the γ-effect value in the ^{13}C NMR spectra. This conclusion is supported by the low-temperature ^{13}C NMR studies of conformationally labile **15b**-Cl (and **18b**-Cl, *vide infra*). The relevant γ-effects in the ^{13}C NMR (75.47 MHz, CD_2Cl_2) spectra for the axial and equatorial conformers of **15b**-Cl at 180 K are equal to −4.045 and 2.025 ppm, respectively. Equilibrium constant *K* derived from these values (for equilibrium present at 296 K) is equal to 1.66 and is slightly smaller than that derived from P_{ax} and P_{eq} from anancomeric models **c,d** and **e,f** (cf. Table 23). In our opinion this can be due to the dependence of γ-effect values on temperature. Thus, γ-effects measured at 180 K for individual conformers may not correspond exactly to γ-effect values at 296 K. The chemical shifts of carbons C(4,6) in ^{13}C NMR spectra of 1,3-dithiane are known[62] to be temperature dependent and increase by 1.3 ppm with the increase of temperature by 116 K. If the increase in $\delta_{C(4,6)}$ in the case of both conformers of **15b** was more significant than that for the parent dithiane **30**, this would lead to the relative increase in γ-effects at 180 K and to a slight underestimation of the *K* value derived from them, as observed.

It must be noted that Juaristi and Cuevas[36] recently estimated conformational equilibrium constant *K* for **18a**-Cl at 300 K in $CDCl_3$ solution using as conformational probes $^2J_{H-P}$, $^1J_{C(2)-P}$, the chemical shift in the ^{31}P NMR spectra, and the corrected[63] chemical shifts of C(2) and C(4,6) as $K = 0.65$, 0.44, 0.57, 0.49, and 0.64, respectively. They concluded that the axial conformer of **18a**-Cl is preferred in free energy terms. This result is somewhat different from our findings. The equilibrium constants for **18a**-TflO, **18b**-Cl, and **18b**-TflO calculated by us on the basis of the γ-effect value as a conformational probe and 5-*tert*-butyl-1,3-dithiane derivatives as reference systems are as follows: $K = 1.35$ (CD_2Cl_2), 1.39 ($CDCl_3$), and 1.29 (CD_2Cl_2), respectively. Therefore, our results suggest that the equatorial disposition of the PMe_3 group in the 1,3-dithiane ring is preferred in free energy terms. Nevertheless, the difference between our and Juaristi's[36] results is not very large and corresponds to about $\Delta\Delta G^\circ = 2$ kJ·mol^{-1} at room temperature.

Table 24. Results of ^{31}P NMR Low-Temperature Measurements for 18b-Cl in CD_2Cl_2:CS_2 = 4:1 (v/v)

T (K)	equil. const. *K*	ΔG° (J·mol^{-1})
166	1.056	−74.84
169	1.055	−75.44
172	1.085	−116.35
175	1.112	−154.11
178	1.109	−153.69
181	1.136	−192.03
184	1.179	−252.18
187	1.150	−217.41
190	1.194	−280.08
193	1.210	−305.79

Interestingly, **18a**-TflO and **18b**-TflO possess practically identical spectral characteristics (e.g., in CD_2Cl_2 at 296 K: γ-effects −1.03 and −1.08 ppm, $^3J_{C(2)-P}$ = 4.8 and 5.4 Hz, $\delta_{C(2)}$ 35.47 and 35.80 ppm, δ_{Me-P} in ^{13}C NMR 7.49 and 7.39 ppm, $\delta_{H(2)}$ 5.20 and 5.09 ppm; δ_{31P} 37.4 and 37.1 ppm, respectively). This suggests that the conformational behavior of **18a** and **18b** should also be very close. Our low-temperature ^{31}P NMR studies of **18b**-Cl in a CD_2Cl_2:CS_2 = 4:1 (v/v) solution have shown that the equatorial conformer predominates ($K > 1$, $\Delta G^\circ < 0$) above 160 K (see Table 24 and Figure 3). The relevant ΔH° and ΔS° values are equal to 1.40 ± 0.12 kJ·mol^{-1} and 8.79 ± 0.67 J·mol^{-1}·K^{-1}, respectively, which afford $K = 1.64$ for 298 K. This value is different from that reported by Juaristi and Cuevas[36] for **18a**-Cl ($K = 0.54$). Our low-

(60) Eliel, E. L.; Hutchins, R. O. *J. Am. Chem. Soc.* **1969**, *91*, 2703.
(61) Graczyk, P. P.; Mikołajczyk, M. *Magn. Reson. Chem.* **1992**, *30*, 1261.
(62) Pinto, B. M.; Johnston, B. D.; Sandoval-Ramirez, J.; Dev Sharma, R. *J. Org. Chem.* **1988**, *53*, 3766.

(63) Chemical shifts of C(2) and C(4,6) have been corrected by Juaristi and Cuevas[36] in order to subtract the deshielding effect of the methyl groups at C(4,6) on going from **18a** to the reference system **18e,f**. This correction has been based on comparison of chemical shifts in parent (2-unsubstituted) 1,3-dithianes. Therefore, it must be stressed that such a correction of C(4,6) chemical shifts does not correspond to the use of γ-effect values.

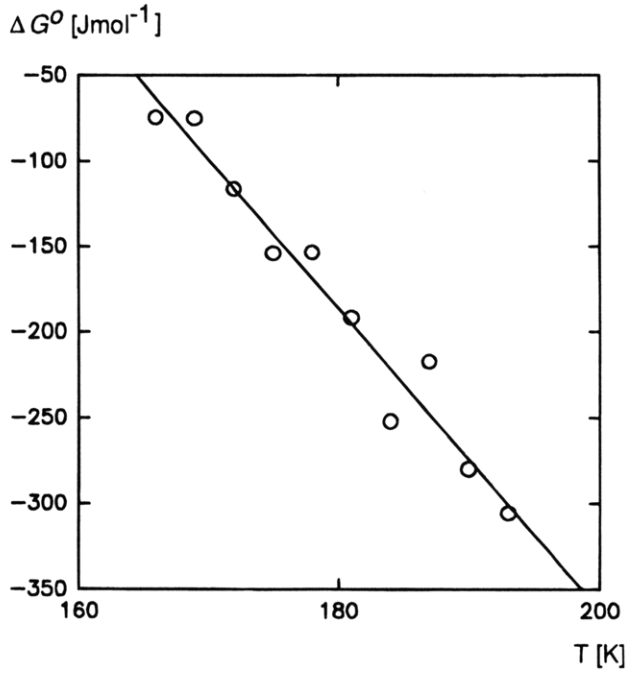

Figure 3. Plot of $\Delta G°$ as a function of temperature T for **18b**-Cl in CD_2Cl_2:CS_2 = 4:1 (v/v) solution.

temperature studies, however, agree well with the data derived from the γ-effect value as a conformational probe and 5-*tert*-butyl-1,3-dithiane derivatives as reference systems (K = 1.29 for **18b**-TflO and K = 1.39 for **18b**-Cl).

Juaristi and Cuevas[36] determined thermodynamic parameters for conformational equilibrium in **18a**-Cl in $CDCl_3$ solution using temperature dependence of the $^2J_{H(2)-P}$ and $^1J_{C(2)-P}$ values. They obtained $\Delta H°$ = 0 kJ·mol^{-1} and $\Delta S°$ = −4.98 J·mol^{-1}·K^{-1}. While these data and our set of values ($\Delta H°$ = 1.40 ± 0.12 kJ·mol^{-1} and $\Delta S°$ = 8.79 ± 0.67 J·mol^{-1}·K^{-1} for **18b**-Cl in a CD_2Cl_2:CS_2 = 4:1 (v/v) solution) indicate operation of the enthalpic anomeric effect[1,3,64] in the C−S−C−$^+$PMe$_3$ system, they differ as far as entropic contributions $\Delta S°$ are concerned. This difference might arise from solvent and/or aggregation effects.

In order to account for their negative $\Delta S°$ value Juaristi and Cuevas[36] proposed an explanation based on much faster rotation of the axial PMe_3 group than that of the equatorial one. This faster rotation is due, in their opinion,[36] to the steric congestion of the methyl group pointing inside the 1,3-dithiane ring in the axial conformer **18a**(ax). This would bring the ground state in **18a**(ax) closer in energy to the transition state for rotation and render the axial PMe_3 group more mobile than the equatorial one. Such reasoning, though seductive, would seem to be misleading. The assumption of invariability of energy of the transition state for the rotation about the C(2)−P bond may, in our opinion, be invalid.[65]

Let us consider the energies of each of the two rotamers for the axial and equatorial conformers of **18a**, namely corresponding to the ground state, **18a**(ax)$_0$ and **18a**(eq)$_0$, respectively, and the transition state for rotation about the C(2)−P bond, i.e., **18a**(ax)$_{ts}$ and **18a**(eq)$_{ts}$, respectively (Figure 4). Relative enthalpies of formation of these

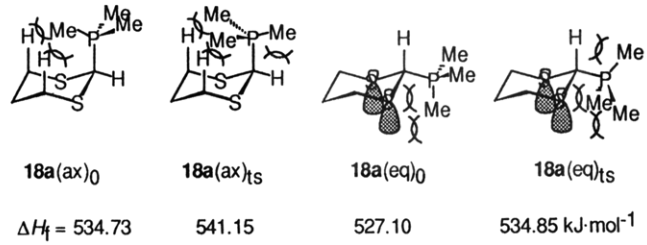

Figure 4. Rotamers **18a**(ax)$_0$ and **18a**(eq)$_0$ corresponding to the ground state and **18a**(ax)$_{ts}$ and **18a**(eq)$_{ts}$ corresponding to the transition state for rotation about the C(2)−P bond.

species were calculated[67] using a semiempirical molecular orbital approach (PM3) and are also shown in Figure 4. It is clear that enthalpy of activation due to the rotation about the axial C−P bond (6.4 kJ·mol^{-1}) does not differ markedly from that for the rotation about the equatorial C−P bond (7.8 kJ·mol^{-1}). This is because the H···Me destabilizing interactions increase the energy of the the ground state as well as the transition state. In addition, for the equatorial PMe_3 group the increased rotational and vibrational possibilities of the Me group *gauche* to both the C(2)−S bonds in **18a**(eq)$_0$ as compared with those of the endo methyl of the axial PMe_3 in **18a**(ax)$_0$ may contribute to positive $\Delta S°$ for the **18a**(ax) ⇌ **18a**(eq) conformational equilibrium. Finally, some differences (difficult to estimate) between **18a**(ax)$_0$ and **18a**(eq)$_0$ stemming from solvent effects and ion-pairing phenomena should also be taken into account.

The positive $\Delta S°$ value for the **18a**(ax) ⇌ **18a**(eq) conformational equilibrium is in line with the results of spin-lattice ^{31}P relaxation time measurements. Separation of dipole−dipole relaxation time T_1^{DD} from the total spin-lattice relaxation time T_1 has shown that various phosphorus-containing axial substituents always have shorter T_1^{DD}.[57] This may be interpreted in terms of slower rotation about the axial than the equatorial C−P bond.[57] For **18c**-Cl and **18d**-Cl [which are good models of **18a**(ax)$_0$ and **18a**(eq)$_0$] we found T_1 = 2.11 and 9.76 s and T_1^{DD} = 3.57 and 8.42 s, respectively. As expected on the basis of slower rotation about the axial C−P bond the relaxation time T_1^{DD} for **18c**-Cl is almost 5 s (!) shorter than that for **18d**-Cl.

It must be noted that very recent reinvestigation results from Juaristi's group[68] show $\Delta H° \cong 0$ kJ·mol^{-1} and $\Delta S°$ = 3.06 J·mol^{-1}·K^{-1} for **18a**-Cl in CD_2Cl_2 (note the positive entropy change). They obtained $\Delta G°_{318}$ = −0.84 kJ·mol^{-1}, which compares favorably with $\Delta G°_{318}$ = −1.40 kJ·mol^{-1} obtained by extrapolation using our low-temperature $\Delta H°$ and $\Delta S°$ data for **18b**-Cl. The differences between $\Delta H°$ and $\Delta S°$ values are not significant and may be due to solvent effects (our measurements were conducted in CD_2Cl_2/CS_2 mixture), structural differences between **18a**-Cl and **18b**-Cl, and aggregation phenomena, most probably inherent in low-temperature studies. Presumably, solvent effects might also account for the negative $\Delta S°$ value ($\Delta S°$ = −4.98 J·mol^{-1}·K^{-1}) found by Juaristi *et al.*[36] for **18a**-Cl in $CDCl_3$ solution.

(64) Booth, H.; Khedhair, K. A. *J. Chem. Soc., Chem. Commun.* **1985**, 467.

(65) This is in contrast to the effect on ring inversion barriers.[3] In the course of ring inversion interactions that destabilize the ground state (usually 1,3-diaxial) decrease in the transition state.[3,66] In contrast, H···Me destabilizing interactions in **18a**(ax)$_{ts}$ do not.

(66) Eliel, E. L.; Knoeber, Sr. M. C. *J. Am. Chem. Soc.* **1968**, *90*, 3444.

(67) Details of semiempirical MO calculations (MNDO, AM1, and PM3) for 2-phosphonio- and 2-phosphinyl-1,3-dithianes will be reported elsewhere.

(68) Juaristi, E. Private communication.

Table 25. Equilibrium Constants K and Free Energy Differences ΔG° for 1,3-Dithiane Derivatives 9–18

	a	b	c,d		e,f	
compd	G°_{296}[a] (kJ/mol)	ΔG°_{296}[a] [kJ/mol]	K_{exp}	ΔG°_{exp}[b] (kJ/mol)	K_{exp}	ΔG°_{exp}[b] (kJ/mol)
9	−0.90	−0.02	1.08[c]	−0.18 ± 0.22	4.86[c]	−3.85 ± 0.14
10	0.49	1.18	0.299[c]	2.94 ± 0.37	0.681[c]	0.94 ± 0.17
11	0.43	0.61	*d*	*d*	*d*	*d*
12	−1.23	−0.68	*d*	*d*	*d*	*d*
13	−1.75	−1.13	*d*	*d*	*d*	*d*
14	−1.61	−1.33	*d*	*d*	*d*	*d*
15	−3.80	−2.82	1.74	−1.35 ± 0.23	6.10	−4.40 ± 0.14
16	−2.13	−1.11	0.831	0.45 ± 0.26	2.12	−1.83 ± 0.14
17	0.91	1.61	0.340	2.65 ± 0.14	0.579	1.34 ± 0.22
18	−0.74	−0.63	*d*	*d*	*d*	*d*

[a] At 296 K in CD_2Cl_2, unless otherwise stated. [b] At 293 K. [c] In $CDCl_3$. [d] Epimerization does not occur.

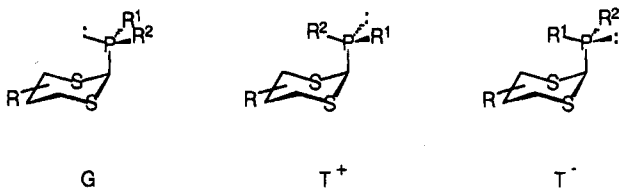

Figure 5. Rotamers G, T^+, and T^- in axial 2-phosphinyl-1,3-dithianes.

Equilibration of Diastereomeric Compounds. The equilibration of diastereomeric 2-phosphonio-1,3-dithianes **9** and **10** occurred spontaneously (*vide supra*, cf. Table 2). On the other hand, the isomerization of **15**–**17** was found to proceed smoothly in the presence of a tertiary amine (triethylamine or diisopropylethylamine). Unfortunately, salts **11** and **18** and phosphines **12**–**14** remained unchanged under all the conditions applied (including a solution of sodium methoxide).

The ratio of products was determined as the ratio of integrals of the appropriate signals in ^{31}P NMR spectra. It should be noted that since ^{31}P spin-lattice relaxation times of isomers are very close,[57] the ratio of integrals in ^{31}P NMR spectrum can be treated as a quantitative measure of the relative amount of isomers.

All equilibrium constants and the related ΔG° values are collected in Table 25 together with the ΔG° values for conformationally labile compounds based on the γ-effect value and **c,d** derivatives as reference systems. These data will be discussed below.

The Exo Anomeric Effect in 2-Phosphinyl-1,3-dithianes.[31] In the axial 2-phosphinyl-1,3-dithianes three rotamers should be taken into account: G, T^+, and T^- (Figure 5). We expected that if *exo* anomeric interactions in the S–C–P(:) system were strong, the preferred rotamers should be T^+ and T^- having R^2 or R^1 (R^1, R^2 = Ph, Me) located over the 1,3-dithiane ring. Surprisingly, analysis of the ^1H NMR spectrum of **12c** revealed that the shielding effect of the phenyl group is not observed (see Table 15, supporting information, and discussion concerning structural assignments based on ^1H NMR spectra). Therefore, both phenyl substituents in **12c** should be located *exo*, which means that it has the G-conformation. On the other hand, in all salts **15**–**17c** containing at least one phenyl group connected with the axial phosphorus, such a shielding by 0.3 ppm is indeed observed (*vide supra*; cf. Table 15, supporting information). Therefore, it is reasonable to assume that the effective "size" of the phenyl group attached to the axial phosphorus is smaller than that of the methyl group. For this reason the structure T^+ for **13c** with the methyl group located over the 1,3-dithiane ring must be excluded. Hence, lack of the shielding effect of the phenyl group in **13c** is consistent only with the rotamer G-**13c**.

An analogous relationship can also be observed for other nuclei of the C(4)–C(5)–C(6) region (*vide supra*).

A very strong support to the conclusions presented above and based on the shielding effect of the phenyl rings is provided by coupling constant $^3J_{C(4,6)-P}$ in the ^{13}C NMR spectra of 2-phosphinyl-1,3-dithianes **12**–**14** (see Table 6 and discussion of ^{13}C NMR spectra). The large (*ca.* 7–8 Hz) constant for the relevant axial 2-phosphinyl-1,3-dithianes has been attributed by us to the presence of a lone electron pair located *endo*, as in the *G* rotamer.

Therefore, the *exo*-anomeric effect is not manifested in the S–C–P(:) system, although it cannot be excluded for derivatives containing the equatorial phosphino group.[35] Our findings have their consequences as far as the origin of the anomeric effect in this system is concerned (*vide infra*).

Finally, it should be noted that 2-phosphino-1,3-dithianes provide an interesting example where competition between hyperconjugative anomeric interactions, in a system where both heteroatoms Y and X possess lone electron pairs, does not influence the overall conformational equilibrium. In the equatorial conformer the *endo*-interactions cannot operate. The axial conformers exist mainly (if not exclusively) as the G rotamer, in which the *exo*-anomeric interactions are impossible.

The Anomeric Effect in the S–C–P System. The application of Franck's methodology[69] to estimate the magnitude of the anomeric effect in 2-P-substituted 1,3-dithiane systems was introduced by Juaristi *et al.*[70] and applied by us recently[4,16] for various C–S–C–P=X (X = O, S, Se) systems. The magnitude of the anomeric effect ΔG°_{AE} is given by

$$\Delta G^\circ_{AE} = \Delta G^\circ - F\Delta G^\circ_C \qquad (3)$$

where ΔG° is the free energy difference in 2-substituted 1,3-dithiane (collected in Table 25), ΔG°_C is the free energy difference in substituted cyclohexane, and F is the Franck factor reflecting the decrease of steric interactions on going from cyclohexane to the 1,3-dithiane ring. It can be based on the methyl group (ΔG°_C = −7.28 kJ/mol,[71] in dithiane ΔG° = −7.42 kJ/mol;[60] hence, F = 1.019) or the *tert*-butyl group (ΔG°_C = −20.5 kJ/mol,[60] in dithiane ΔG° = −11.4 kJ/mol;[60] hence, F = 0.556).

Thus, for the PPh_2 group (compounds **12**) $\Delta G^\circ_{12(C)}$ = −7.5 kJ/mol,[35] for the PMe_2 group (compounds **14**)

(69) Franck, R. W. *Tetrahedron* **1983**, *39*, 3521.
(70) Juaristi, E.; Flores-Vela, A.; Labastida, V. *J. Org. Chem.* **1989**, *54*, 5191.
(71) Booth, H.; Everett, J. R. *J. Chem. Soc., Chem. Commun.* **1976**, 278.

$\Delta G°_{14(C)} \cong -7.1$ kJ/mol,[72] and for the $^+PMe_3$ group (compounds **18**) $\Delta G°_{18(C)} \geq -12.5$ kJ/mol.[72] Since the magnitude of F is not constant and depends on the size of a substituent, let us assume that F is a linear function of $\Delta G°_C$.[73] The linear interpolation between the F values for the methyl and *tert*-butyl group gives $F_{12} = 1.01$ for the PPh_2 group, $F_{14} = 1.02$ for the PMe_2 group, and $F_{18} \leq 0.836$ for the $^+PMe_3$ group. Thus, the magntidue of the anomeric effect $\Delta G°_{AE}$ for 5,5-dimethyl-1,3-dithiane derivatives **b**, based on the data in Table 25, is equal to $\Delta G°_{AE(12)} = 6.9$ kJ/mol, $\Delta G°_{AE(14)} = 5.9$ kJ/mol, and $\Delta G°_{AE(18)} \geq 9.8$ kJ/mol for **12b**, **14b**, and **18b**, respectively. Though the $\Delta G°_{AE}$ values can be treated only as an approximate measure of the anomeric effect,[1,3] they undoubtedly indicate relatively strong anomeric interactions in S−C−P^+ and S−C−P(:) systems. Moreover, our variable temperature NMR study of **18b**-Cl indicates that the axial conformer is enthalpy-preferred, which is equivalent with operation of the enthalpic anomeric effect in the C−S−C−$^+PMe_3$ system. It should be noted that the Juaristi's group found the anomeric effect of the PPh_2 (**12**) and $^+PMe_3$ (**18**) groups in the 1,3-dithiane ring to be slightly smaller, i.e., 4.2[35] and >9.0 kJ/mol,[36] respectively. The results presented above show that the anomeric effect involving phosphonium salts is stronger than that for the appropriate phosphines. This finding can be easily accounted for in terms of one-directionality[30] of the anomeric interactions in salts, which are expected to amplify the preference for the axial arrangement of the C−S−C−P system. The second reason for a much stronger anomeric effect in the salts stems from the positive charge at phosphorus, which should result in a decrease of the energy of $\sigma^*_{C-P^+}$ orbital and stronger $n_S-\sigma^*_{C-P^+}$ hyperconjugative interaction.

A stronger anomeric effect for the PPh_2: group (6.9 kJ/mol) than for PMe_2 (5.9 kJ/mol) is consistent with the participation of π-electrons of the phenyl ring in repulsive interactions with lone electron pairs of endocyclic sulfur atoms. These interactions are expected to destabilize the equatorial arrangement of phosphorus and to increase the anomeric effect of the PPh_2 group, as it is observed. Nevertheless, the difference in electron-withdrawing properties of the phenyl *vs* methyl groups, resulting in lower energy of the σ^*_{C-P} orbital, must also be taken into account. These factors are also, most probably, responsible for our observation that **15b**-Cl exists in the axial conformation in the solid state while **18b**-Cl exists in the equatorial one.[46]

Since the free energy differences $\Delta G°_C$ for conformational equilibria in monosubstituted cyclohexanes are negative for almost all substituents, practically it is enough to find $\Delta G° \geq 0$ in a heteroane in order to say that the *generalized anomeric effect* is observed. On this basis, the operation of the anomeric effect for **10**, **11**, **16**, and **17** is unquestionable (cf. Table 25), in contrast to the expectations based on electrostatic view on the nature of the reverse anomeric effect.[3,5,23,24,34]

Interestingly, the equatorial preference of the triphenylphosphonium group (**15**) does not exclude at first sight the operation of the anomeric effect. It should be expected that the triphenylphosphonium group Ph_3P^+ is "larger" as compared with Ph_2P=S. Such a point of view is strongly supported by the fact that in the axial Ph_2P=S group the phenyl rings tend to be situated *exo* both in 1,3-dithiane[16] and cyclohexane rings.[40] Thus, the magnitude of the anomeric effect $\Delta G°_{AE}$ in **15b**-Cl, according to Franck's methodology, is equal to at least

$$\Delta G°_{AE} \geq -2.82 - 0.75(-15.10) \geq 8.5 \text{ kJ/mol}$$

assuming $\Delta G°_C = -15.10$ kJ/mol[40] and $F = 0.75$ for the Ph_2P=S group.

Therefore, the anomeric effect in **15b**-Cl is large, even though the equatorial preference predominates. It must, however, be noted that **15b**-Cl in the solid state exists in the axial conformation. This may suggest that the equatorial preference in a solution is due to a solvent effect.

Spectroscopic Properties of Molecules and the Nature of the Anomeric Effect. The negative hyperconjugation usually results in the decrease of the one-bond coupling constant through the acceptor bond in the NMR spectra of anomeric molecules. This behavior has been termed[74] the "Perlin effect". In particular, $^1J_{C-P}$ coupling constants through the axial C−P bond in cyclohexyl[75] (vicinal axial C−H bond as a donor), tetrahydropyran-2-yl,[76] and 1,3-dioxan-2-yl[17] derivatives have been reported to be smaller than those through the equatorial one.

In 1,3-dithiane derivatives the situation is not so clear. In the 1,3-dithiane system itself the *anti*-Perlin effect was found.[77] In contrast, in all diastereomeric phosphonium salts **9**−**11** and **15**−**18**, the $^1J_{C-P}$ coupling constant for compounds with phosphorus located equatorially is larger than that for their isomers (see Table 8, supporting information). The difference between coupling constants is not so large as in 2-phosphinoyl-1,3-dioxanes (more than 24 Hz)[17] and varies in the range from 3.3 to 11.6 Hz. Nevertheless, this finding strongly supports the hyperconjugative $n_S-\sigma^*_{C-P}$ origin of the anomeric effect in S−C−P^+ system.

The chemical shifts for aromatic carbons are sensitive probe in studies of the polar and resonance effects of substituents.[78] Thus, significant upfield ^{13}C chemical shifts for the *ortho* and *para* carbons in the axial phosphinoyl $Ph_2P(O)$,[9] thiophosphinoyl $Ph_2P(S)$,[40] phosphinyl $Ph_2P(:)$,[35] and phosphinylborane Ph_2P-BH_3[35] groups attached to a 1,3-dithiane ring were interpreted by Juaristi *et al.* to prove that some form of electron transfer occurs to the axially located substituent. They proposed[1,9,13,14] 3p−3d donation from sulfur to axial phosphorus as being responsible for this effect, more so because of the unexpected structural data for 2-(diphenylphosphinoyl)-substituted 1,3-dithianes (*vide supra*, Figure 1).[79]

In 1,3-dithiane derivatives both *ortho* and *para* carbons resonate at higher field in the axial Ph_2P: (**12**) group (see Table 10, supporting information). However, the opposite occurs for Ph_2P^+SMe (**9**) and PhMeP: (**13**) substituents. A more complicated situation exists in Ph_2P^+-Me (**16**) derivatives since *para* carbons appear at higher

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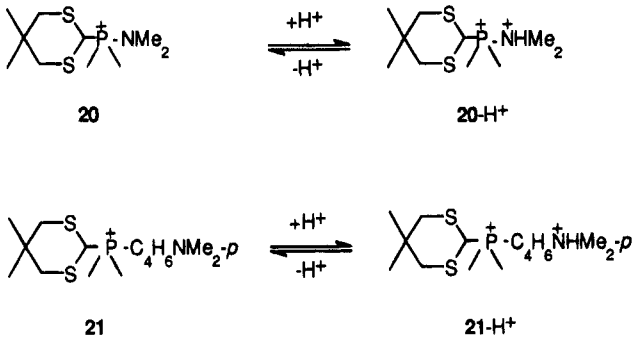
(79) It should be noted that the increased electron density at the axial phosphorus may be due (among other factors) to $n_S-\sigma^*_{C-P}$ negative hyperconjugation.

Scheme 5



field and *ortho* ones at lower field if the phosphonium group is located axially. Interestingly, the relationship between the chemical shift of the *para* carbon of the $PhP^{+}Me_2$ (**17**) group in two diastereomeric pairs **c,d** and **e,f** is reversed. Thus, the chemical shift increases by 0.26 ppm on going from **17d** to **17c** but it decreases by 0.40 ppm on passing from **17f** to **17e**. Analogous inconsistency can be found for **10** and **15** as far as the chemical shift of *ortho* carbons is concerned. Therefore, the changes in chemical shifts should be treated with caution. They result, perhaps, from a larger number of factors than those considered here.

Thermodynamic Implications for the Nature of the Anomeric Effect in 1,3-Dithiane Derivatives. Lack of manifestation of the exo anomeric effect in the axial **12**–**14** suggests that the $n_P-\sigma^*_{C-S}$ negative hyperconjugation is weak as compared with steric interactions involved. This is in contrast to $X-CH_2-H_2P(:)$ systems, for which the antiperiplanar arrangement of the C–X (X = F,[80] Cl[10]) bond and phosphorus lone electron pair is preferred, perhaps due to much more effective $n_P-\sigma^*_{C-X}$ hyperconjugation. The rotational behavior of axial phosphinyl groups seems to be governed by destabilizing interactions and can be sufficiently explained on the grounds of classical steric effects.

The energy of the two-orbital two-electron hyperconjugative interaction depends on the energy of involved orbitals and the overlap integral.[81] 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 endocyclic sulfur can be reasonably assumed to be constant and the axial preference owing to $n_S-\sigma^*_{C-P}$ interaction would increase with the increasing electronegativity of a substituent (if steric requirements are also constant).

In order to gain an insight into the nature of the anomeric effect of the phosphonium group, it would be reasonable to change the electronegativity of substituents connected with phosphorus and to observe the changes in the conformational preference. We decided to accomplish this idea by using the salts **20** and **21** and assuming that their protonation (Scheme 5) will occur at nitrogen, thus increasing the electron-withdrawing properties of the phosphonium group as a whole. Moreover, in the case of **21** the protonation could decrease the density of π-electrons of aryl rings and, in contrast to $n_S-\sigma^*_{C-P}$ interaction, enhance the equatorial preference due to weaker repulsive interactions between lone electron pairs n_s of endocyclic sulfur atoms and π-electrons of phenyl rings.

The conformational equilibria in **20** and **21**, to which the increasing amount of trifluoroacetic acid was added, were studied by means of ^{13}C and ^{1}H NMR spectroscopy, and the results are collected in Table 26. These data suggest that the addition of trifluoroacetic acid to **20** practically does not influence the conformational equilibrium since all coupling constants and $\Delta\delta_{Me}$ values remain unchanged. Rather large changes in γ-effect values are, presumably, due to the influence of the medium on the chemical shifts of C(4,6) carbons in conformers. On the other hand, the conformation of **21** is affected. After the addition of 1–2 equiv of acid both the γ-effect (in ^{13}C NMR spectrum) and $\Delta\delta_{Me}$ (only, however, in ^{1}H NMR spectrum) values increase, as if the equilibrium was shifted toward the equatorial conformer. If more acid is added, all the NMR data ($^3J_{C-P}$, γ-effect and $\Delta\delta_{Me}$) imply an increasing amount of the axial conformer of **21**. In order to ascertain that the changes in the spectra of **21** are due to the presence of amino groups, the conformation of **15b** was also studied. Interestingly, the addition of trifluoroacetic acid to **15b** causes an increase of the γ-effect value, in contrast to **21**. This observation can be, perhaps, attributed to the influence of the medium on C(4,6) chemical shifts in conformers of **15b**. Other values as $^3J_{C-P}$, $\Delta\delta_{Me}$ (in ^{13}C NMR), and $^4J_{H-P}$ imply that the amount of the axial form increases with the addition of acid. Nevertheless, the changes observed for **15b** are much smaller than those for **21**. Hence, the conformational behavior of **21** upon the protonation is indeed due to the presence of dimethylamino groups.

The behavior of **21** may be accounted for in terms of $n_S-\pi$ repulsions and $n_S-\sigma^*_{C-P}$ negative hyperconjugation. A possible explanation is as follows. Before the protonation, the conformation of **21** is mainly determined by $n_S-\pi$ repulsions since the electron-withdrawing properties of the phosphonium group as a whole are too small to afford a σ^*_{C-P} orbital of sufficiently low energy. The first portions of acid begin to protonate nitrogen. The electron density at phosphorus decreases, but more significant is the decrease in π-electron density. The $n_S-\pi$ repulsions in the equatorial conformer of **21** become weaker and the equatorial preference increases (or at least does not decrease), as has been observed. With the increasing degree of protonation, the electron-withdrawing properties of the phosphonium group increase and the energy of the σ^*_{C-P} orbital becomes low enough to ensure the domination of the $n_S-\sigma^*_{C-P}$ negative hyperconjugation. This is why the addition of a larger amount of acid enhances the axial preference. It should be noted that the alkylation of a solution of **21** in $CDCl_3$ with methyl triflate with 1, 2, and 3 equiv of methyl trifluoromethanesulfonate affords products in which γ-effects are equal to 0.878, 0.816, and 0.757 ppm (however, the reaction is not clean). These results are very close to those obtained *via* protonation. In **20** the protonation of nitrogen is, perhaps, very difficult, and therefore, the conformation is not affected.

Crystallographic Implications of the Nature of the Anomeric Effect in 2-Phosphonio-1,3-dithianes. Although a direct comparison between $C-PPh_3$ grouping in **15b**-Cl and $C-PMe_3$ grouping in **18b**-Cl cannot be performed, it is interesting that in the crystal the axial C(2)–P bond [1.830(3) Å in **15b**-Cl] is longer than the

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Table 26. Selected Data from ^{13}C and ^{1}H NMR Spectra for 15b, 20, and 21 Protonated with Trifluoroacetic Acid

	^{13}C NMR[a]									^{1}H NMR[b]			
	$^{3}J_{C-P}$[c] (Hz)			γ-effect (ppm)			$\Delta\delta_{Me}$[d] (ppm)			$^{4}J_{H-P}$[e] (Hz)		$\Delta\delta_{Me}$[d] (ppm)	
equiv of acid	**15b**	**20**	**21**	**15b**	**20**	**21**	**15b**	**20**	**21**	**20**	**21**	**20**	**21**
0	5.8	8.1	6.2	0.10	0.67	0.70	5.15	7.46	5.76	6.14	4.18	0.14	0.08
1	6.2	8.1	6.2	0.31	0.88	0.81	4.86	7.40	5.58	5.96	4.16	0.14	0.09
2	5.7	8.1	5.9	0.43	1.01	0.82	4.60	7.40	5.50	5.90	4.15	0.15	0.09
5	5.4	8.3	5.7	0.59	1.42	0.74	4.26	7.32	5.03	5.44	4.23	0.16	0.06
8	5.4	8.2	5.1	0.57	1.56	0.55	4.19	7.39	4.55	5.73	4.13	0.16	0.03

[a] SF = 50.32 MHz, in $CDCl_3$. [b] SF = 200.13 MHz, in $CDCl_3$. [c] Between C(4,6) and P. [d] The difference between the chemical shifts of methyl groups at C(5). [e] Between H(4,6) and P.

equatorial one [1.810(3) Å in **18b**-Cl].[16,46] Such an elongation of the axial bond agrees with the $n_S-\sigma_{C-P}$ negative hyperconjugation as a source of the anomeric effect in the C−S−C−P$^+$ system. However, it would be more appropriate to consider C(2)−P bonds in a pair of diastereomeric compounds.

Summary and Conclusions

Stereoselective preparation of various 2-phosphinyl- and 2-phosphonio-1,3-dithianes was described and their structure was studied by means of ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy. Both the studies on conformationally labile models and equilibration of diastereomeric compounds show an increased preference of phosphino and phosphonium groups to the axial orientation. Magnitude of this anomeric effect varies in the range from ca. 6 kJ/mol in phosphines to more than 10 kJ/mol in phosphonium salts.

It is widely accepted in the chemical literature[17,82,83] that there is only a quantitative difference between first- and second-row atoms in the magnitude of anomeric interactions. Though the importance of electrostatic interactions for second-row atoms should be smaller owing to a decrease in electronegativity, it seems improbable that completely different effects operate in C−S−C−P$^+$ and C−O−C−N$^+$ systems. The anomeric effect in the former system could stem from the $n_S-\sigma^*_{C-P}$ hyperconjugative interaction. This concept has been strongly supported on the basis of the observed Perlin effect in phosphonium salts, elongation of the axial C(2)−P bond in **15b**-Cl *vs* the equatorial one in **18b**-Cl, and influence of protonation on conformation of **21**. Overlap repulsion involving lone electron pairs of endocyclic sulfur atoms and π-electrons of phenyl rings may also be valuable to account for changes in conformational behavior of **21** upon protonation, as well as some observations concerning reactivity of phosphines toward 2-chloro-1,3-dithianes.[44]

Operation of the hyperconjugative mechanism in the C−S−C−P$^+$ system is in line with the results of recent experimental studies on C−O−C−N$^+$ systems performed by Perrin and Armstrong,[26] where operation of the anomeric effect was found. The relevant *ab initio* calculations for the C−O−C−N$^+$ system published by Cramer[84] suggest that the anomeric effect exhibited in the C−O−C−N$^+$ system is due to $n_O-\sigma^*_{C-N}$ negative hyperconjugation. However, this effect may be opposed by steric effects, by local dipole−diple effects, and by solvation.[84] Perhaps a lack of such solvent effects is responsible for the axial conformation of **15b**-Cl in the solid state.

In the case of 2-phosphinyl-1,3-dithianes another factor must also be taken into account. In the opinion of Box[85-88] and Tvaroška and Bleha[89] a source of ground-state preferences in the C−O−C−O system can be found rather in destabilizing interactions in the antiperiplanar conformation. Box[85-87] claims that the predominant role of destabilizing interactions, with a minor contribution from the $n-\sigma^*$ interactions, is a better model for rationalizing the chemistry of simple acetals. In 2-phosphinyl-1,3-dithianes **12**−**14** such interactions may occur between lone electron pairs on endocyclic sulfur atoms and a lone pair of phosphorus. However, this possibility has not been supported by our data.

Experimental Section

General experimental procedures are the same as those described previously.[4]

The ^{31}P spin-lattice relaxation time and NOE procedure was as follows. The samples were examined as 0.002 M solutions in chloroform-*d*. Dissolved oxygen was removed by four freeze−pump−thaw cycles, and the tubes were filled with nitrogen. Phosphorus ^{31}P spin-lattice relaxation times were determined at 121.49 MHz at 305 K, using the standard Bruker microprogram with a time delay between sequences equal to at least $5T_1$. The NOE enhancement coefficients η were determined using the gated decoupling technique. The acquisition time used for the NOE measurements was less than 2.5 s in order to avoid radiofrequency heating when the decoupler was gated on. Delays between the cycles were adjusted so as to be equal to $10T_1$. The error in determination of T_1 does not exceed 5% whereas the values of η, obtained as the average of some 3−5 measurements, had an accuracy of ca. 10%.

2-Thiophosphoryl-1,3-dithianes **6**−**8**,[4,16,19,37] chloromethylphenylphosphine (**23**),[16,4] chlorodimethylphosphine (**24**),[90] 5-dimethyl-1,3-dithiane (**30**),[4,58,91] 5-*tert*-butyl-1,3-dithiane (**31**),[4,91,92] *cis*-4,6-dimethyl-1,3-dithiane (**32**),[4,91,92] *tris*(dimethylamino)-phosphine (hexamethylphosphorous triamide, **40**),[93a] tris[4-(dimethylamino)phenyl]phosphine (**42**),[94,95] and trimethylphos-

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phine–silver iodide complex (**43**)[96,97] were prepared according to known procedures. Other compounds, if not described below, were commercially available.

Reaction of Methyl Triflate with 2-Thiophosphoryl-1,3-dithianes 6–8. Synthesis of 2-[(Methylthio)phosphonio]-1,3-dithianes 9–11. The synthesis of 2-[(methylthio)-phosphonio]-1,3-dithianes was carried out in NMR sample tubes. If 10 mm o.d. tube were applied, it contained appropriate 2-thiophosphoryl-1,3-dithiane (0.25 mmol) dissolved in CD_2Cl_2 (2.0 mL). For a 5 mm o.d. NMR tube, the relevant quantities were 0.10 mmol and 0.8 mL, respectively. Prior to the addition of $CF_3SO_3CH_3$ the tubes were flushed with N_2.

General Procedure. To a solution of 2-thiophosphoryl-1,3-dithiane (1.0 equiv) in CD_2Cl_2 was added $CF_3SO_3CH_3$ (1.1 equiv) in one portion. The course of the reaction was followed by ^1H, ^{31}P, and ^{13}C NMR. The degree of conversion as a function of time is presented in Table 1. The proportion of products is shown in Table 2. NMR spectral parameters for all (methylthio)phosphonium salts are collected in Tables 5–13 (^{13}C NMR data) (Tables 5 and 7–13 are in the supporting information), Tables 14–20 (^1H NMR data) (supporting information), and Table 21 (^{31}P NMR data) (supporting information).

***trans*-5-*tert*-Butyl-2-(diphenylphosphinyl)-1,3-dithiane (12d).** All operations are conducted under nitrogen atmosphere. To a −20 °C stirred solution of **31** (1.0 g, 5.7 mmol) in tetrahydrofuran (THF, 25 mL) was added a 1.25 M solution of *n*-BuLi in *n*-hexane (4.9 mL, 6.1 mmol). After the solution was stirred for 1.5 h, with the temperature maintained at −20 °C, *N,N,N',N'*-tetramethylethylenediamine (0.66 g, 5.7 mmol) and **22** (1.2 mL, 6.5 mmol) were added. The mixture was stirred at −20 °C for 1.5 h, and then it was quenched with saturated aqueous NH_4Cl solution (2 mL). Organic solvents were evaporated in vacuum. The residue was dissolved in a benzene (30 mL)–water (10 mL) mixture. The water phase was discarded, and the organic layer was washed with a 20% aqueous solution of acetic acid (3 × 25 mL) and water (50 mL) and dried over $MgSO_4$. The solvent was removed in vacuum to give **12d** (1.90 g, 92.8%) as colorless oil of about 90% purity (on the basis of intensity of the *t*-Bu proton singlets in the ^1H NMR spectrum): ^1H NMR (300.13 MHz, C_6D_6) δ 0.50 (s, 9H), 1.54 (tt, $^3J_{H-H}$ = 11.25 Hz, $^3J_{H-H}$ = 2.23 Hz, 1H), 2.27 (dd, $^2J_{H-H}$ = 13.70 Hz, $^3J_{H-H}$ = 11.25 Hz, 2H), 2.50 (ddd, $^2J_{H-H}$ = 13.70 Hz, $^3J_{H-H}$ = 2.23 Hz, $^4J_{H-P}$ = 1 Hz, 2H), 4.59 (s, 1H), 7.0–8.2 (m, 10H); ^{31}P NMR (121.49 MHz, CD_2Cl_2) δ −2.0; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 27.24 (s), 33.47 (d, $^3J_{C-P}$ = 7.9 Hz), 34.24 (d, $^5J_{C-P}$ = 1.9 Hz), 43.80 (d, $^1J_{C-P}$ = 27.6 Hz), 46.71 (s), 132.58 (d, $^2J_{C-P}$ = 7.3 Hz), 129.74 (s), 134.24 (d, $^3J_{C-P}$ = 20.5 Hz). This compound was not further analyzed due to its unstability and the ease of oxidation in air.

Desulfurization of 2-[(Methylthio)phosphonio]-1,3-dithianes 9–11. Synthesis of 2-Phosphinyl-1,3-dithianes 12–14. The synthesis of all phosphines **12–14** was carried out in NMR sample tubes with the use of solutions of appropriate 2-[(methylthio)phosphonio]-1,3-dithianes **9–11** in CD_2Cl_2.

General Procedure. The temperature of a solution of relevant 2-[(methylthio)phosphonio]-1,3-dithiane, which was obtained *via* the alkylation of 2-thiophosphoryl-1,3-dithiane (1.0 equiv, see above), in CD_2Cl_2, was maintained at *T* (K) when **40** (1.1 equiv) was added in one portion. The course of the reaction was followed by ^1H, ^{31}P, and ^{13}C NMR. The reaction was completed just after the addition of **40**. The ratio of products as a function of temperature is shown in Table 3. NMR spectral parameters for all 2-phosphinyl-1,3-dithianes are collected in Tables 5–13 (^{13}C NMR data) (Tables 5 and 7–13 in supporting information), Tables 14–20 (^1H NMR data) (supporting information), and Table 21 (^{31}P NMR data) (supporting information).

(1,3-Dithian-2-yl)triphenylphosphonium Chloride (15a-Cl). Following the literature,[42] 1,3-dithiane (1.80 g, 15.0 mmol) and **41** (4.10 g, 15.6 mmol) were converted into **15a**-Cl (5.59 g, 89.4%): white powder, mp 178–181 °C (lit.[42] mp 182–184 °C); ^1H NMR (300.13 MHz, CD_2Cl_2 δ 1.80–2.25 (*m*, 2H), 2.55–2.70 (*m*, 2H), 3.80–3.95 (m, 2H), 7.60–8.15 (m, 15H), 8.99 (d, $^2J_{H-P}$ = 14.7 Hz, 1H); ^{31}P NMR (121.49 MHz, CD_2Cl_2) δ 26.5; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 25.34 (s), 30.38 (d, $^3J_{C-P}$ = 7.0 Hz), 36.62 (d, $^1J_{C-P}$ = 50.0 Hz), 117.47 (d, $^1J_{C-P}$ = 86.2 Hz), 130.29 (d, $^3J_{CP}$ = 13.1), 135.44 (d, $^2J_{C-P}$ = 10.1 Hz), 131.94 (s); IR (KBr) 528 (vs), 692 (vs), 724 (s), 752 (s), 1108 (vs), 1440 (s), 2660 (s), 2720 (s) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 263(16), 262 (100), 261 (14), 183 (63), 119 (30), 108 (34), 107 (13), 45 (15). Anal. Calcd for $C_{22}H_{22}ClPS_2$: C, 63.37; H, 5.32. Found: C, 63.11; H, 5.52.

(5,5-Dimethyl-1,3-dithian-2-yl)triphenylphosphonium Chloride (15b-Cl). The procedure of Kruse[42] for **15a**-Cl was applied to transform **30** (1.607 g, 10.8 mmol) and **41** (2.843 g, 10.8 mmol) into **15b**-Cl (3.499 g, 72.5%): white powder; mp 155–161 °C. Crystallization of the product from dimethylformamide (DMF)–diethyl ether afforded an analytically pure sample of **15b**-Cl: large prisms; mp 168.0–173.3 °C; ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.08 (s, 3H), 1.13 (s, 3H), 2.27 (dd, $^2J_{H-H}$ = 14.3 Hz, $^4J_{H-P}$ = 5.0 Hz, 2H), 3.58 (d, $^2J_{H-H}$ = 14.3 Hz, 2H), 7.60–8.10 (*m*, 15H), 8.52 (d, $^2J_{H-P}$ = 13.0 Hz, 1H); ^{31}P NMR (121.49 MHz, CD_2Cl_2) δ 26.6; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 24.64 (s), 26.95 (s), 29.40 (s), 36.86 (d, $^1J_{C-P}$ = 53.8 Hz), 42.11 (d, $^3J_{C-P}$ = 5.7 Hz), 117.37 (d, $^1J_{C-P}$ = 86.9 Hz), 130.41 (d, $^3J_{C-P}$ = 12.8 Hz), 135.34 (d, $^2J_{C-P}$ = 9.7 Hz), 135.70 (d, $^4J_{C-P}$ = 2.7 Hz); IR (KBr) 520 (vs), 688 (s), 722 (s), 748 (s), 1110 (vs), 1440 (s) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 268 (18), 262 (100), 261 (15), 183 (54), 147 (37), 108 (23), 69 (18). Anal. Calcd for $C_{24}H_{26}ClPS_2$: C, 64.77; H, 5.89. Found: C, 64.39; H, 6.14.

(5-*tert*-Butyl-1,3-dithian-2-yl)triphenylphosphonium Chloride (15c,d-Cl), Mixture of Diastereomers. Dithiane **31** (5.26 g, 30.0 mmol) and **41** (7.9 g, 30 mmol) were converted by the reported[42] method into a mixture of **15c**-Cl and **15d-Cl** (12.6 g, 89.3%) as a white powder. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets at δ 23.9 and 27.0 ppm of relative integration 89:11, which were attributed to **15c**-Cl and **15d**-Cl, respectively. Anal. Calcd for $C_{26}H_{30}ClPS_2$: C, 66.01; H, 6.39. Found: C, 66.49; H, 6.38. Spectroscopic data for **15c**-Cl, based on the spectra of this mixture, are given below.

(*cis*-5-*tert*-Butyl-1,3-dithian-2-yl)triphenylphosphonium chloride (15c-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.59 (s, 9H), 1.64 (m, 3H), 2.38–2.42 (m, 2H), 7.6–8.3 (m, 15H), 8.85 (d, $^2J_{H-P}$ = 7.46 Hz, 1H); ^{31}P NMR (121.49 MHz, CD_2Cl_2) δ 23.4; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 26.85 (s), 27.06 (s), 29.07 (d, $^1J_{C-P}$ = 42.2 Hz), 34.04 (s), 43.95 (s), 119.80 (d, $^1J_{C-P}$ = 83.7 Hz), 130.56 (d, $^3J_{C-P}$ = 12.2 Hz), 135.16 (s), 135.23 (d, $^2J_{C-P}$ = 9.4 Hz).

(*cis*-5-*tert*-Butyl-1,3-dithian-2-yl)triphenylphosphonium Chloride (15c-Cl)·DMF, Solvate of 15c-Cl with DMF. The crude **15c,d**-Cl (0.935 g, 1.98 mmol) was dissolved with minimal heating in DMF (2.5 mL), and the mixture was left to crystallize in an atmosphere of diethyl ether vapors. After 3 days crystals were separated, washed with diethyl ether, and dried in vacuum to afford analytically pure **15c**-Cl·DMF (460 mg, 42.5%): colorless needless; mp 195–200 °C. The ^{31}P NMR (121.49 MHz, CD_2Cl_2) spectrum of the freshly prepared solution of **15c**-Cl·DMF shows only one signal at δ 23.3 ppm. After 8 h, the spectrum of this solution consists of two signals at δ 23.3 and 26.9 of relative intensity 87:13, respectively. In the ^1H NMR (300.13 MHz, CD_2Cl_2) spectrum of **15c**-Cl·DMF, measured 45 min after the preparation of the solution, the relative intensity of singlets δ 0.60 and 0.92 was 96:4, respectively. Apart from the signals characteristic for **15c**-Cl, of practically identical chemical shifts and coupling constants with those in the spectrum of crude **15c,d**-Cl, one could observe the following signals: δ 2.88 (d, $^4J_{H-H}$ = 0.4 Hz, 3H), 2.96 (s, 3H), 8.02 (bs, 1H), characteristic of DMF; IR (KBr) 520 (vs), 696 (s), 720 (s), 1106 (s), 1442 (s), 1672 (vs) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 348 (37), 262 (73), 218 (27), 183 (54), 175 (100), 162 (22), 108 (26), 73 (20), 57 (97), 55 (34), 41 (67), 36 (23). Anal. Calcd for $C_{29}H_{37}ClNOPS_2$: C, 63.77; H, 6.83. Found: C, 63.55; H, 6.68.

(*cis*-5-*tert*-Butyl-1,3-dithian-2-yl)triphenylphosphonium Chloride (15c-Cl): Attempted Preparation *via* a Deprotonation–Protonation Sequence. To a suspension of crude **15c,d**-Cl (4.70 g, 10.0 mmol) in THF (80 mL) stirred

Table 27. Relative Intensity in ^{31}P NMR Spectra of 15c,d-Cl–DMF Mixtures (See Text)

	relative intensity in spectra no.				
δ (ppm)	1	2	3	4	5
−4.6	0	7	9	30	21
22.5	0	0	0	5	8
22.8	0	0	0	11	18
23.0	70	65	47	18	14
26.5	0	0	0	4	5
26.9	30	28	44	24	21
43.4	0	0	0	8	13

at −60 °C under N_2 was added a 1.4 M solution of *n*-BuLi in *n*-hexane (8.0 mL, 11.2 mmol). The suspension turned into a yellow solution, which was stirred at −60 °C for 15 min before a solution of acetic acid (0.72 g, 12 mmol) in THF (10.0 mL) was added rapidly. A white precipitate was formed, and the mixture became colorless. The suspension was concentrated under reduced pressure. Water (20 mL) was added, and the whole was extracted with $CHCl_3$ (3 × 30 mL). The combined organic solutions were washed with water (50 mL), evaporated under reduced pressure, and dried in vacuum to give 4.0 g of a colorless oil. Its ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum showed three singlets at δ 22.2, 23.8, and 27.1 ppm of relative integration 42:10:48, respectively.

(*trans*-5-*tert*-Butyl-1,3-dithian-2-yl)triphenylphosphonium Chloride (15d-Cl). Crude **15c,d**-Cl (1.60 g, 3.38 mmol) was dissolved in DMF (5.0 mL), and the mixture was boiled for 2 min. After being cooled to 32 °C the solution was left to crystallize in an atmosphere of diethyl ether vapors. After 7 days the crystals were separated, washed with acetone and diethyl ether, and dried in vacuum to afford **15d**-Cl (0.595 g, 37.2%), as colorless crystals, mp 190–195 °C. In the ^1H NMR (300.13 MHz, CD_2Cl_2) spectrum of this product the relative integration of singlets δ 0.60 and 0.92 ppm was 3:97 and did not change in time. The spectral parameters for **15d**-Cl were determined based on this mixture: ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.92 (s, 9H), 1.67 (tt, $^3J_{H-H}$ = 11.34 Hz, $^3J_{H-H}$ = 2.23 Hz, 1H), 2.87 (ddd, $^2J_{H-H}$ = 14.00 Hz, $^4J_{H-P}$ = 5.0 Hz, $^3J_{H-H}$ = 2.23 Hz, 2H), 2.81 (dd, $^2J_{H-H}$ = 14.00 Hz, $^3J_{H-H}$ = 11.34 Hz, 2H), 7.60–8.10 (m, 10H), 8.57 (d, $^2J_{H-P}$ = 14.0 Hz, 1H); ^{31}P NMR (121.49 MHz, CD_2Cl_2) δ 27.0; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 27.39 (s), 32.63 (d, $^3J_{C-P}$ = 7.5 Hz), 34.63 (d, $^5J_{C-P}$ = 2.1 Hz), 37.49 (d, $^1J_{C-P}$ = 53.8 Hz), 46.73 (s), 117.14 (d, $^1J_{C-P}$ = 87.6 Hz), 130.30 (d, $^3J_{C-P}$ = 13.0 Hz), 135.38 (d, $^2J_{C-P}$ = 10.2 Hz), 135.67 (d, $^4J_{C-P}$ = 2.7 Hz); IR (KBr) 516 (vs), 524 (s), 688 (s), 720 (s), 1104 (s), 1434 (s) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 263 (16), 262 (100), 261 (14), 183 (57), 175 (24), 108 (30), 36 (20). Anal. Calcd for $C_{26}H_{30}ClPS_2$: C, 66.01; H, 6.39. Found: C, 66.00; H, 6.37.

Studies on the Influence of Heating on 15c,d-Cl–DMF Solution. A capillary containing C_6D_6 was placed into a 10 mm o.d. NMR sample tube containing a suspension of crude **15c,d**-Cl (700 mg, 1.48 mmol) in DMF (2.0 mL), and the ^{31}P NMR (121.49 MHz) spectrum no. 1 of the mixture was recorded. The suspension was gently heated until the solid was dissolved, and spectrum no. 2 was taken. Then, the solution was boiled and the next spectra (nos. 3–5) were recorded after 15, 60, and 120 s of boiling, respectively. The relative intensity of signals is shown in Table 27.

(*cis*-4,6-Dimethyl-1,3-dithian-2-yl)triphenylphosphonium Chloride (15e,f-Cl): Mixture of Diastereomers. The procedure of Kruse[42] for **15a**-Cl was applied to transform **32** (2.473 g, 16.7 mmol) and **41** (4.51 g, 17.2 mmol) into **15e,f**-Cl (5.817 g, 78.3%), white powder. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets at δ 23.4 and 26.5 ppm of relative integration 90:10, which were attributed to **15e**-Cl and **15f**-Cl, respectively. Anal. Calcd for $C_{24}H_{26}ClPS_2$: C, 64.77; H, 5.89. Found: C, 64.67; H, 5.98. Spectroscopic data for **15e**-Cl, based on the spectra of this mixture, are given below.

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*t*-2-yl)triphenylphosphonium chloride (15e-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.02 (d, $^3J_{H-H}$ = 6.73 Hz, 6H), 1.13 (dt, $^2J_{H-H}$ = 14.12 Hz, $^3J_{H-H}$ = 12.03 Hz, 1H), 1.63 (dt, $^2J_{H-H}$ = 14.12 Hz, $^3J_{H-H}$ = 2.00 Hz, 1H), 1.79 (dqdd, $^3J_{H-H}$ = 12.03 Hz, $^3J_{H-H}$ = 6.73 Hz, $^3J_{H-H}$ = 2.00 Hz, $^4J_{H-P}$ = 2.0 Hz, 2H), 7.60–8.20 (*m*, 15H), 8.84 (d, $^2J_{H-P}$ = 8.57 Hz, 1H); ^{31}P NMR (121.49 MHz, CD_2Cl_2) δ 23.5; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 21.48 (s), 34.25 (d, $^1J_{C-P}$ = 50.5 Hz), 36.07 (s), 41.08 (s), 120.12 (d, $^1J_{C-P}$ = 83.6 Hz), 130.60 (d, $^3J_{C-P}$ = 12.1 Hz), 135.17 (s), 135.43 (d, $^2J_{C-P}$ = 10.1 Hz).

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*c*-2-yl)triphenylphosphonium Chloride (15f-Cl). The procedure for **15d**-Cl was applied to convert the crude **15e,f**-Cl (1.64 g, 3.69 mmol) into **15f**-Cl (581 mg, 35.4%): colorless crystals; mp 196–202 °C. The ^{31}P NMR (121.49 MHz, CD_2Cl_2) spectrum of this product showed the presence of two signals at δ 23.6 and 26.4 ppm of relative integration 6:94. The spectral parameters for **15f**-Cl were determined based on this mixture: ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.18 (d, $^3J_{H-H}$ = 6.89 Hz, 6H), 1.27 (dt, $^2J_{H-H}$ = 14.11 Hz, $^3J_{H-H}$ = 11.70 Hz, 1H), 2.20 (ddt, $^2J_{H-H}$ = 14.11 Hz, $^5J_{H-P}$ = 4.10 Hz, $^3J_{H-H}$ = 2.16 Hz, 1H), 4.08 (dqdd, $^3J_{H-H}$ = 11.70 Hz, $^3J_{H-H}$ = 6.89 Hz, $^3J_{H-H}$ = 2.16 Hz, $^4J_{H-P}$ = 0.8 Hz, 2H), 7.40–8.10 (*m*, 15H), 8.99 (d, $^2J_{H-P}$ = 16.20 Hz, 1H); ^{31}P NMR (121.49 MHz, CD_2Cl_2) δ 26.4; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 21.77 (d, $^4J_{C-P}$ = 1.6 Hz), 39.40 (d, $^1J_{C-P}$ = 53.8 Hz), 40.77 (d, $^3J_{C-P}$ = 7.4 Hz), 43.99 (s), 117.37 (d, $^1J_{C-P}$ = 87.7 Hz), 130.20 (d, $^3J_{C-P}$ = 13.0 Hz), 135.10 (d, $^2J_{C-P}$ = 9.2 Hz), 135.50 (s); IR (KBr) 518 (vs), 692 (m), 722 (s), 732 (m), 1112 (s), 1440 (m) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 278 (30), 277 (67), 262 (21), 183 (28), 147 (19), 86 (65), 84 (100), 49 (16), 47 (25). Anal. Calcd for $C_{24}H_{26}ClPS_2$: C, 64.77; H, 5.89. Found: C, 64.55; H, 5.94.

(5-*tert*-Butyl-1,3-dithian-2-yl)diphenylmethylphosphonium Chloride (16c,d-Cl): Mixture of Diastereomers. Dithiane **31** (5.26 g, 30.0 mmol) and phosphine **33** (931 g, 5.29 mmol) were converted by the reported[42] method into a mixture of **16c**-Cl and **16d**-Cl (1.605 g, 73.8%), white powder. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets at δ 25.7 and 28.0 ppm of relative integration 69:31, which were attributed to **16c**-Cl and **16d**-Cl, respectively. Anal. Calcd for $C_{21}H_{28}ClPS_2$: C, 61.37; H, 6.87. Found: C, 61.56; H, 6.84. Spectroscopic data for **16c**-Cl and **16d**-Cl, based on the spectra of this mixture, are given below.

(*cis*-5-*tert*-Butyl-1,3-dithian-2-yl)diphenylmethylphosphonium chloride (16c-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.60 (s, 9H), 1.57 (tt, $^3J_{H-H}$ = 11.20 Hz, $^3J_{H-H}$ = 2.52 Hz, 1H), 1.78 (ddd, $^2J_{H-H}$ = 13.90 Hz, $^3J_{H-H}$ = 11.20 Hz, $^4J_{H-P}$ = 1.7 Hz, 2H), 2.40 (dd, $^2J_{H-H}$ = 13.90 Hz, $^3J_{H-H}$ = 2.52 Hz, 2H), 2.82 (d, $^2J_{H-P}$ = 13.28 Hz, 3H), 7.48 (d, $^2J_{H-P}$ = 10.4 Hz, 1H), 7.65–8.14 (m, 10H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 25.7; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 10.24 (d, $^1J_{C-P}$ = 56.1 Hz), 26.54 (s), 26.74 (s), 29.96 (d, $^1J_{C-P}$ = 46.9 Hz), 33.80 (s), 43.75 (s), 119.02 (d, $^1J_{C-P}$ = 81.1 Hz), 130.19 (d, $^3J_{C-P}$ = 11.8 Hz), 134.30 (d, $^2J_{C-P}$ = 9.2 Hz), 135.05 (s).

(*trans*-5-*tert*-Butyl-1,3-dithian-2-yl)diphenylmethylphosphonium chloride (16d-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.91 (s, 9H), 1.71 (tt, $^3J_{H-H}$ = 11.30 Hz, $^3J_{H-H}$ = 2.38 Hz, 1H), 2.87 (d, $^2J_{H-P}$ = 13.72 Hz, 3H), 2.93 (m, 2H), 3.44 (dd, $^2J_{H-H}$ = 13.22 Hz, $^3J_{H-H}$ = 11.30 Hz, 2H), 7.65–8.14 (m, 11H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 28.0; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 8.23 (d, $^1J_{C-P}$ = 56.8 Hz), 27.30 (s), 32.68 (d, $^3J_{C-P}$ = 8.0 Hz), 34.36 (d, $^5J_{C-P}$ = 2.3 Hz), 38.16 (d, $^1J_{C-P}$ = 55.4 Hz), 46.73 (s), 117.35 (d, $^1J_{C-P}$ = 85.9 Hz), 130.04 (d, $^3J_{C-P}$ = 11.1 Hz), 133.79 (d, $^2J_{C-P}$ = 10.4 Hz), 135.05 (s).

(5-*tert*-Butyl-1,3-dithian-2-yl)diphenylmethylphosphonium Iodide (16c,d-I): Mixture of Diastereomers. The reaction was carried out under N_2. To a magnetically stirred, cooled (−20 °C) solution of **31** (1.00 g, 5.68 mmol) in THF (25.0 mL) was added a 1.25 M solution of *n*-BuLi in *n*-hexane (4.9 mL, 6.1 mmol). After 1.5 h of stirring at −20 °C, *N,N,N',N'*-tetramethylethylenediamine (0.66 g, 5.7 mmol) and **22** (1.4 g, 6.5 mmol) were added. The mixture was additionally stirred for 1.5 h before the next portion of a 1.25 M solution of *n*-BuLi in *n*-hexane (4.9 mL, 6.1 mmol) was added. After 0.5 h of stirring at −20 °C, the mixture was quenched with saturated aqueous NH_4Cl solution (5.0 mL). The cooling bath was removed, and organic solvents were evaporated in vacuum. The residue was dissolved in a benzene (30 mL)–water (10 mL) mixture. The water phase was discarded, and organic layer was washed with 20% aqueous acetic acid solution (3 ×

25 mL) and water (50 mL). The organic phase was dried with anhydrous $MgSO_4$ and filtered. Then, CH_3I (0.84 g, 6.0 mmol) was added and the mixture was stirred for 12 h. The precipitate was filtered off, washed with benzene (40 mL), and dried in vacuum to give 0.392 g (13.7%) of colorless powder. The ^{31}P NMR (121 MHz, $CDCl_3$) spectrum of the product consisted of two singlets at δ 24.8 and 25.5 of similar integration. The ^1H NMR (300.13 MHz, $CDCl_3$) spectrum revealed that the spectral characteristic of the main product (which constitutes 65% of the mixture, on the basis of integration of all signals in the range from δ 0.5 to δ 1.0 ppm) is practically identical with that of **16c**-Cl (*vide supra*).

***(trans*-5-*tert*-Butyl-1,3-dithian-2-yl)diphenylmethylphosphonium Iodide (16d-I).** To a solution of **12d** (1.9 g, 5.3 mmol) in benzene (25.0 mL) was added CH_3I (0.84 g, 5.9 mmol), and the mixture was stirred in the dark for 20 h. A white precipitate was filtered off, washed with benzene (3 × 20 mL), and dried in vacuum to afford 1.90 g (66.6%) of **16d**-I: white powder; mp 197−202 °C dec. The ^{31}P NMR (81.02 MHz, $CDCl_3$) spectrum of the product showed the presence of two signals at δ 25.3 and 27.9 ppm of relative intensity 1.1:98.9, which were attributed to **16c**-I and **16d**-I, respectively. The ^1H and ^{13}C NMR spectra of the main product are very close to the spectra of **16d**-Cl and **16d**-TflO: ^1H NMR (200.13 MHz, CD_2Cl_2) δ 0.92 (s, 9H), 1.78 (tt, $^3J_{H-H}$ = 11.36 Hz, $^3J_{H-H}$ = 2.38 Hz, 1H), 2.82 (d, $^2J_{H-P}$ = 13.43 Hz, 3H), 2.90 (ddd, $^2J_{H-H}$ = 13.87 Hz, $^4J_{H-P}$ = 5.0 Hz, $^3J_{H-H}$ = 2.38 Hz, 2H), 3.64 (dd, $^2J_{H-H}$ = 13.87 Hz, $^3J_{H-H}$ = 11.36 Hz, 2H), 7.65−8.15 (m, 11H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 27.9; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 8.47 (d, $^1J_{C-P}$ = 57.1 Hz), 27.38 (s), 32.09 (d, $^3J_{C-P}$ = 8.1 Hz), 34.76 (d, $^5J_{C-P}$ = 2.1 Hz), 37.52 (d, $^1J_{C-P}$ = 52.8 Hz), 46.85 (s), 117.35 (d, $^1J_{C-P}$ = 87.9 Hz), 130.41 (d, $^3J_{C-P}$ = 12.8 Hz), 134.23 (d, $^2J_{C-P}$ = 9.6 Hz), 135.82 (d, $^4J_{C-P}$ = 2.2 Hz); IR (KBr) 896 (vs), 1112 (s), 1440 (s) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 221 (30), 201 (22), 200 (100), 199 (23), 185 (49), 183 (79), 175 (57), 78 (39), 77 (23), 73 (48), 57 (52), 55 (31), 43 (25), 41 (38), 28 (80). Anal. Calcd for $C_{21}H_{28}IPS_2$: C, 50.20; H, 5.62. Found: C, 50.34; H, 5.80.

***cis*-4,6-Dimethyl-1,3-dithian-2-yl)diphenylmethylphosphonium Chloride (16e,f-Cl): Mixture of Diastereomers.** The procedure of Kruse[42] for **15a**-Cl was applied to transform **32** (1.00 g, 6.76 mmol) and **33** (1.49 g, 7.45 mmol) into **16e,f**-Cl (2.123 g, 82.1%) as a yellowish oil that crystallized on standing. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets at δ 26.3 and 27.6 ppm of relative integration 67:33, which were attributed to **16e**-Cl and **16f**-Cl, respectively. Anal. Calcd for $C_{19}H_{24}ClPS_2$: C, 59.59; H, 6.32. Found: C, 59.24; H, 6.36. Spectroscopic data for **16e**-Cl and **16f**-Cl, based on the spectra of this mixture, are given below.

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*t*-2-yl)diphenylmethylphosphonium chloride (16e-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.06 (d, $^3J_{H-H}$ = 6.75 Hz, 6H), 1.12 (dt, $^2J_{H-H}$ = 14.10 Hz, $^3J_{H-H}$ = 1.94 Hz, 1H), 2.02 (dqdd, $^3J_{H-H}$ = 11.75 Hz, $^3J_{H-H}$ = 6.75 Hz, $^3J_{H-H}$ = 1.94 Hz, $^4J_{H-P}$ = 1.5 Hz, 2H), 2.79 (d, $^2J_{H-P}$ = 13.13 Hz, 3H), 7.53 (d, $^2J_{H-P}$ = 11.14 Hz, 1H), 7.60−8.10 (m, 10H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 26.3; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 10.40 (d, $^1J_{C-P}$ = 56.0 Hz), 21.42 (s), 35.18 (d, $^1J_{C-P}$ = 47.7 Hz), 35.61 (s), 41.23 (s), 119.27 (d, $^1J_{C-P}$ = 81.0 Hz), 130.19 (d, $^3J_{C-P}$ = 11.8 Hz), 134.03 (d, $^2J_{C-P}$ = 9.1 Hz), 135.17 (d, $^4J_{C-P}$ = 2.0 Hz).

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*c*-2-yl)diphenylmethylphosphonium chloride (16f-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.21 (d, $^3J_{H-H}$ = 6.88 Hz, 6H), 1.33 (dt, $^2J_{H-H}$ = 14.15 Hz, $^3J_{H-H}$ = 11.53 Hz, 1H), 2.20 (ddt, $^2J_{H-H}$ = 14.15 Hz, $^5J_{H-P}$ = 4.18 Hz, $^3J_{H-H}$ = 2.18 Hz, 1H), 2.84 (d, $^2J_{H-P}$ = 13.62 Hz, 3H), 3.66 (dqd, $^3J_{H-H}$ = 11.53 Hz, $^3J_{H-H}$ = 6.88 Hz, $^3J_{H-H}$ = 2.18 Hz, 2H), 7.6−8.1 (m, 11H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 27.6; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 8.25 (d, $^1J_{C-P}$ = 57.4 Hz), 21.52 (d, $^4J_{C-P}$ = 1.8 Hz), 40.15 (d, $^1J_{C-P}$ = 54.8 Hz), 41.28 (d, $^3J_{C-P}$ = 7.4 Hz), 43.79 (s), 117.40 (d, $^1J_{C-P}$ = 85.6 Hz), 130.06 (d, $^3J_{C-P}$ = 12.8 Hz), 133.71 (d, $^2J_{C-P}$ = 10.3 Hz), 135.08 (d, $^4J_{C-P}$ = 2.0 Hz).

(5-*tert*-Butyl-1,3-dithian-2-yl)dimethylphenylphosphonium Chloride (17c,d-Cl): Mixture of Diastereomers. Method A. Dithiane **31** (1.055 g, 5.99 mmol) and phosphine **34** (0.86 g, 6.6 mmol) were converted by the reported[42] method, at room temperature, into a mixture of **17c**-Cl and **17d**-Cl (2.001 g, 95.8%) as white powder. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets at δ 28.4 and 30.1 ppm of relative integration 56:44, which were attributed to **17c**-Cl and **17d**-Cl, respectively. Anal. Calcd for $C_{16}H_{26}ClPS_2$: C, 55.07; H, 7.51. Found: C, 55.28; H, 7.62. Spectroscopic data for **17c**-Cl and **17d**-Cl, based on the spectra of this mixture, are given below.

(*cis*-5-*tert*-Butyl-1,3-dithian-2-yl)dimethylphenylphosphonium chloride (17c-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.59 (s, 9H), 1.51 (tt, $^3J_{H-H}$ = 11.43 Hz, $^3J_{H-H}$ = 2.39 Hz, 1H), 1.77 (ddd, $^2J_{H-H}$ = 14.03 Hz, $^3J_{H-H}$ = 11.43 Hz, $^4J_{H-P}$ = 1.4 Hz, 2H), 2.37 (dd, $^2J_{H-H}$ = 14.03 Hz, $^3J_{H-H}$ = 2.39 Hz, 2H), 2.68 (d, $^2J_{H-P}$ = 13.55 Hz, 6H), 6.37 (d, $^2J_{H-P}$ = 10.88 Hz, 1H), 7.5−8.1 (m, 5H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 28.4; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 7.93 (d, $^1J_{C-P}$ = 55.5 Hz), 26.23 (s), 26.67 (s), 30.43 (d, $^1J_{C-P}$ = 48.7 Hz), 33.77 (s), 43.95 (s), 120.65 (d, $^1J_{C-P}$ = 78.3 Hz), 130.44 (d, $^3J_{C-P}$ = 11.1 Hz), 132.80 (d, $^2J_{C-P}$ = 9.4 Hz), 135.35 (s).

(*trans*-5-*tert*-Butyl-1,3-dithian-2-yl)dimethylphenylphosphonium chloride (17d-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 0.89 (s, 9H), 1.63 (tt, $^3J_{H-H}$ = 11.09 Hz, $^3J_{H-H}$ = 2.60 Hz, 1H), 2.60 (d, $^2J_{H-P}$ = 14.01 Hz, 6H), 2.92 (ddd, $^2J_{H-H}$ = 13.90 Hz, $^4J_{H-P}$ = 4.13, $^3J_{H-H}$ = 2.60, 2H), 3.10 (dd, $^2J_{H-H}$ = 13.90 Hz, $^3J_{H-H}$ = 11.09 Hz, 2H), 6.90 (d, $^2J_{H-P}$ = 14.10 Hz, 1H), 7.5−8.1 (m, 5H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 30.1; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 7.39 (d, $^1J_{C-P}$ = 55.5 Hz), 27.19 (s), 32.14 (d, $^3J_{C-P}$ = 7.4 Hz), 34.31 (d, $^5J_{C-P}$ = 2.0 Hz), 38.36 (d, $^1J_{C-P}$ = 54.8 Hz), 46.27 (s), 120.65 (d, $^1J_{C-P}$ = 78.3 Hz), 129.90 (d, $^3J_{C-P}$ = 12.5 Hz), 132.56 (d, $^2J_{C-P}$ = 9.4 Hz), 134.98 (s).

Method B. The synthesis of **17c,d**-Cl was carried out as in method A, but the phosphine **34** was added at 0 °C instead of at room temperature. A mixture of **17c**-Cl and **17d**-Cl was obtained as a white powder (1.830 g, 87.6%). The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets at δ 28.4 and 30.1 ppm of relative integration 58:42, respectively.

(*cis*-4,6-Dimethyl-1,3-dithian-2-yl)dimethylphenylphosphonium Chloride (17e,f-Cl): Mixture of Diastereomers. The procedure of Kruse[42] for **15a**-Cl was applied to transform **32** (1.00 g, 6.76 mmol) and **34** (1.04 g, 7.45 mmol) into **17e,f**-Cl (2.051 g, 94.6%) as a white powder. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets as δ 29.4 and 29.5 ppm of relative integration 52:48, which were attributed to **17e**-Cl and **17f**-Cl, respectively. Anal. Calcd for $C_{14}H_{22}ClPS_2$: C, 52.40; H, 6.91. Found: C, 52.03; H, 6.64. Spectroscopic data for **17e**-Cl and **17f**-Cl, based on the spectra of this mixture, are given below.

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*t*-2-yl)dimethylphenylphosphonium chloride (17e-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.07 (d, $^3J_{H-H}$ = 6.76 Hz, 6H), 1.10 (dt, $^2J_{H-H}$ = 14.13 Hz, $^3J_{H-H}$ = 11.80 Hz, 1H), 1.71 (dt, $^2J_{H-H}$ = 14.13 Hz, $^3J_{H-H}$ = 11.80 Hz, 1H), 1.71 (dt, $^2J_{H-H}$ = 14.13 Hz, $^3J_{H-H}$ = 2.0 Hz, 1H), 2.00 (dqdd, $^3J_{H-H}$ = 11.80 Hz, $^3J_{H-H}$ = 6.76 Hz, $^3J_{H-H}$ = 2.0 Hz, $^4J_{H-P}$ = 1.9 Hz, 2H), 2.65 (d, $^2J_{H-P}$ = 13.50 Hz, 6H), 6.79 (d, $^2J_{H-P}$ = 13.09 Hz, 1H), 7.60−8.05 (m, 5H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 29.4; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 8.21 (d, $^1J_{C-P}$ = 55.7 Hz), 21.43 (s), 35.46 (s), 36.32 (d, $^1J_{C-P}$ = 49.9 Hz), 41.47 (s), 120.56 (d, $^1J_{C-P}$ = 78.8 Hz), 130.31 (d, $^3J_{C-P}$ = 11.4 Hz), 132.50 (d, $^2J_{C-P}$ = 9.2 Hz), 135.32 (d, $^4J_{C-P}$ = 2.6 Hz).

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*c*-2-yl)dimethylphenylphosphonium chloride (17f-Cl): ^1H NMR (300.13 MHz, CD_2Cl_2) δ 1.24 (d, $^3J_{H-H}$ = 6.93 Hz, 6H), 1.29 (dt, $^2J_{H-H}$ = 14.34 Hz, $^3J_{H-H}$ = 11.65 Hz, 1H), 2.17 (ddt, $^2J_{H-H}$ = 14.34 Hz, $^5J_{H-P}$ = 4.04 Hz, $^3J_{H-H}$ = 2.10 Hz, 1H), 2.56 (d, $^2J_{H-P}$ = 13.97 Hz, 6H), 3.43 (dqdd, $^3J_{H-H}$ = 11.65 Hz, $^3J_{H-H}$ = 6.93 Hz, $^3J_{H-H}$ = 2.10 Hz, $^4J_{H-P}$ = 1.0 Hz, 2H), 7.32 (d, $^2J_{H-P} \cong$ 15 Hz, 1H), 7.60−8.05 (m, 5H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 29.5; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 7.65 (d, $^1J_{C-P}$ = 55.9 Hz), 21.50 (d, $^4J_{C-P}$ = 1.6 Hz), 40.70 (d, $^1J_{C-P}$ = 55.5 Hz), 41.52 (d, $^3J_{C-P}$ = 7.2 Hz), 43.59 (s), 118.13 (d, $^1J_{C-P}$ = 84.6 Hz), 129.97 (d, $^3J_{C-P}$ = 12.7 Hz), 132.37 (d, $^2J_{C-P}$ = 10.2 Hz), 134.93 (d, $^4J_{C-P}$ = 2.6 Hz).

(5,5-Dimethyl-1,3-dithian-2-yl)trimethylphosphonium Chloride (18b-Cl). The procedure of Kruse[42] for **15a**-Cl was modified as follows. All operations were carried out under a N_2 atmosphere. To a magnetically stirred solution of **30** (1.48 g, 10.0 mmol) in benzene (24 mL) was added *N*-chlorosuccinimide (NCS, 1.40 g, 10.5 mmol) in small portions over a period of 15 min. After 20 min of additional stirring, the suspension was filtered and the residue was washed with benzene (5.0 mL). Combined organic solutions were cooled in liquid N_2, and $(CH_3)_3P$ (**35**), obtained *via* thermal decomposition[96,98] of **43** (3.50 g, 11.3 mmol), was distilled in vacuo. The cooling bath was removed, and the mixture was stirred for 12 h. Then, the precipitate was filtered off, washed with benzene (3 × 30 mL), and dried in vacuum to afford **18b**-Cl (1.304 g, 50.4%) as a white powder. Crystallization of this product from DMF gave **18b**-Cl (1.00 g, 38.7%): colorless crystals; mp 267–269 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 1.16 (s, 3H), 1.21 (s, 3H), 2.34 (d, $^2J_{H-P}$ = 14.3 Hz, 9H), 2.58 (dd, $^2J_{H-H}$ = 13.9 Hz, $^4J_{H-P}$ = 3.8 Hz, 2H), 2.89 (d, $^2J_{H-H}$ = 13.9 Hz, 2H), 5.88 (d, $^2J_{H-P}$ = 13.5 Hz, 1H); ^{31}P NMR (81.02 MHz, $CDCl_3$) δ 37.9; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 7.82 (d, $^1J_{C-P}$ = 53.9 Hz), 25.67 (s), 26.79 (s), 28.23 (d, $^5J_{C-P}$ = 2.0 Hz), 35.53 (d, $^1J_{C-P}$ = 53.2 Hz), 41.04 (d, $^3J_{C-P}$ = 5.3 Hz); IR (KBr) 974 (vs), 1288 (s), 2816 (s), 2980 (s) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 149 (8), 147 (100), 93 (8), 69 (30), 41 (9), 28 (9), 18 (30). Anal. Calcd for $C_9H_{20}ClPS_2$: C, 41.77; H, 7.79. Found: C, 41.72; H, 7.84.

(5-*tert*-Butyl-1,3-dithian-2-yl)trimethylphosphonium Chloride (18c,d-Cl): Mixture of Diastereomers. Dithiane **31** (1.00 g, 5.68 mmol) and **43** (2.11 g, 6.82 mmol) were converted by the method applied for **18b**-Cl into a mixture of **18c**-Cl and **18d**-Cl (1.550 g, 95.2%) as a white powder. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the product consisted of two singlets at δ 35.8 and 41.5 ppm of relative integration 30:70, which were attributed to **18d**-Cl and **18c**-Cl, respectively. Anal. Calcd for $C_{11}H_{24}ClPS_2$: C, 46.06; H, 8.43. Found: C, 46.03; H, 8.57. Spectroscopic data for **18c**-Cl and **18d**-Cl, based on the spectra of this mixture, are given below.

(*cis*-5-*tert*-Butyl-1,3-dithian-2-yl)trimethylphosphonium chloride (18c-Cl): ^{1}H NMR (300.13 MHz, CD_2Cl_2) δ 0.92 (s, 9H), 1.78 (tt, $^3J_{H-H}$ = 11.12 Hz, $^3J_{H-H}$ = 2.76 Hz, 1H), 2.31 (d, $^2J_{H-P}$ = 13.90 Hz, 9H), 2.64 (ddd, $^2J_{H-H}$ = 14.28 Hz, $^3J_{H-H}$ = 11.12 Hz, $^4J_{H-P}$ = 1.9 Hz, 2H), 2.79 (dd, $^2J_{H-H}$ = 14.28 Hz, $^3J_{H-H}$ = 2.76, 2H), 5.87 (d, $^2J_{H-P}$ = 12.7 Hz, 1H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 41.5; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 9.05 (d, $^1J_{C-P}$ = 53.0 Hz), 26.98 (s), 27.67 (s), 30.03 (d, $^1J_{C-P}$ = 52.4 Hz), 34.19 (s), 44.85 (s).

(*trans*-5-*tert*-Butyl-1,3-dithian-2-yl)trimethylphosphonium chloride (18d-Cl): ^{1}H NMR (300.13 MHz, CD_2Cl_2) δ 0.94 (s, 9H), 1.70 (m, 1H), 2.28 (d, $^2J_{H-P}$ = 14.46 Hz, 9H), 2.95–3.01 (m, 2H), 3.03–3.10 (m, 2H), 6.11 (d, $^2J_{H-P}$ = 14.64 Hz, 1H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 35.8; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 7.30 (d, $^1J_{C-P}$ = 54.4 Hz), 27.17 (s), 31.98 (d, $^3J_{C-P}$ = 8.1 Hz), 34.30 (d, $^5J_{C-P}$ = 2.0 Hz), 37.51 (d, $^1J_{C-P}$ = 54.8 Hz), 46.18 (s).

(*cis*-4,6-Dimethyl-1,3-dithian-2-yl)trimethylphosphonium Chloride (18e,f-Cl): Mixture of Diastereomers. The procedure of Kruse[42] for **15a**-Cl was applied to transform **32** (1.00 g, 6.76 mmol) and a benzene solution of **35** (ca. 0.62 g, 8.1 mmol; obtained by thermal decomposition of 2.51 g of **43**), at room temperature, into **18e,f**-Cl (1.437 g, 82.2%) as a white powder. The ^{31}P NMR (121.49 MHz, $CDCl_3$) spectrum of the mixture consisted of two singlets at δ 34.9 and 41.6 ppm of relative integration 33:67, which were attributed to **18f**-Cl and **18e**-Cl, respectively. Anal. Calcd for $C_9H_{20}ClPS_2$: C, 41.77; H, 7.79. Found: C, 42.00; H, 7.96. Spectroscopic data for **18e**-Cl and **18f**-Cl, based on the spectra of this mixture, are given below (see also ref 34).

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*t*-2-yl)trimethylphosphonium chloride (18e-Cl): ^{1}H NMR (300.13 MHz, CD_2Cl_2) δ 1.26 (d, $^3J_{H-H}$ = 6.70 Hz, 6H), 1.30 (dt, $^2J_{H-H}$ = 14.21 Hz, $^3J_{H-H}$ = 11.73 Hz, 1H), 2.16 (dt, $^2J_{H-H}$ = 14.21 Hz, $^3J_{H-H}$ = 2.33 Hz, 1H), 2.26 (d, $^2J_{H-P}$ = 13.77 Hz, 9H), 2.92 (dqdd, $^3J_{H-H}$ = 11.73 Hz, $^3J_{H-H}$ = 6.70 Hz, $^3J_{H-H}$ = 2.33 Hz, $^4J_{H-P}$ = 1.7 Hz, 2H), 6.05 (d, $^2J_{H-P}$ = 14.02 Hz, 1H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 41.46; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 9.54 (d, $^1J_{C-P}$ = 52.8 Hz), 21.81 (s), 34.71 (d, $^1J_{C-P}$ = 52.1 Hz), 36.29 (s), 41.98 (s).

(*r*-4,*c*-6-Dimethyl-1,3-dithian-*c*-2-yl)trimethylphosphonium chloride (18f-Cl): ^{1}H NMR (300.13 MHz, CD_2Cl_2) δ 1.30 (d, $^3J_{H-H}$ = 6.88 Hz, 6H), 1.34 (dt, $^2J_{H-H}$ = 14.1 Hz, $^3J_{H-H}$ = 11.5 Hz, 1H), 2.20 (ddt, $^2J_{H-H}$ = 14.1 Hz, $^5J_{H-P}$ = 4.5 Hz, $^3J_{H-H}$ = 2.10 Hz, 1H), 2.26 (d, $^2J_{H-P}$ = 14.40 Hz, 9H), 3.29 (dqdd, $^3J_{H-H}$ = 11.5 Hz, $^3J_{H-H}$ = 6.88 Hz, $^3J_{H-H}$ = 2.10 Hz, $^4J_{H-P}$ = 1.0 Hz, 2H), 6.34 (d, $^2J_{H-P}$ = 16.54 Hz, 1H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 34.9; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 7.37 (d, $^1J_{C-P}$ = 54.7 Hz), 21.54 (s), 40.00 (d, $^1J_{C-P}$ = 54.7 Hz), 41.11 (d, $^3J_{C-P}$ = 7.6 Hz, 43.29 (s).

Alkylation of Phosphines 12–14 with $CF_3SO_3CH_3$. Synthesis of Phosphonium Triflates 16–18-TflO. The synthesis of all phosphonium salts **16–18**-TflO was carried out in NMR sample tubes with the use of solutions of the appropriate 2-phosphinyl-1,3-dithianes **12–14** in CD_2Cl_2.

General Procedure. To a solution of the relevant 2-phosphinyl-1,3-dithiane **12–14**, which was obtained *via* the desulfurization of 2-[(methylthio)phosphonio]-1,3-dithiane **9–11** (1.0 equiv, see above), in CD_2Cl_2, was added $CF_3SO_3CH_3$ (1.1 equiv) in one portion. The course of the reaction was followed by ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy. The reaction was completed just after the addition of $CF_3SO_3CH_3$. NMR spectral parameters for all phosphonium salts **16–18** are collected in Tables 5–13 (^{13}C NMR data) (Tables 5 and 7–13 are in the supporting information), Tables 14–20 (^{1}H NMR data) (supporting information), and Table 21 (^{31}P NMR data) (supporting information).

Tris(*N*,*N*-dimethylamino)(1,3-dithian-2-yl)phosphonium Chloride (19): Following the method[42] for **15a**-Cl, 1,3-dithiane (1.363 g, 11.4 mmol) and **40** (1.86 g, 11.4 mmol) were converted into **19** (1.929 g, 53.4%), white powder, which are crystallization from DMF–diethyl ether afforded an analytically pure sample: colorless, very hygroscopic crystals, mp 202.0–206.8 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 2.0–4.0 (m, 6H), 2.92 (d, $^3J_{H-P}$ = 10.1 Hz, 18H), 7.41 (d, $^2J_{H-P}$ = 18.1 Hz, 1H); ^{31}P NMR (24.3 MHz, CH_2Cl_2) δ 53.5; ^{13}C NMR (22.63 MHz, $CDCl_3$) δ 25.74 (s), 30.78 (d, $^3J_{C-P}$ = 7.4 Hz), 38.00 (d, $^2J_{C-P}$ = 4.4 Hz), 41.83 (d, $^1J_{C-P}$ = 113.2 Hz); IR (KBr) 982 (vs), 1052 (m), 1160 (s), 1287 (s), 1296 (s) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 281(32), 163(11), 119(100), 76(35), 60(13). Anal. Calcd for $C_{10}H_{25}ClN_3PS_2$: C, 37.78; H, 7.93. Found: C, 37.40; H, 8.54. Poor microanalysis results are due to hygroscopicity of **19**.

Tris(dimethylamino)(5,5-dimethyl-1,3-dithian-2-yl)-phosphonium Chloride (20). The procedure of Kruse[42] for **15a**-Cl was applied to transform **30** (1.617 g, 10.9 mmol) and **40** (1.78 g, 10.9 mmol) into **20** (1.988 g, 52.7%): white powder, mp 155–165 °C. Crystallization of the product from DMF–diethyl ether afforded an analytically pure sample of **20**: hygroscopic crystals; mp 181–185 °C; ^{1}H NMR (300.13 MHz, $CDCl_3$) δ 1.12 (s, 3H), 1.26 (s, 3H), 2.36 (dd, $^2J_{H-H}$ = 14.01 Hz, $^4J_{H-P}$ = 6.14 Hz, 2H), 2.93 (d, $^3J_{H-P}$ = 10.0 Hz, 18H), 3.63 (d, $^2J_{H-H}$ = 14.01 Hz, 2H), 6.85 (d, $^2J_{H-P}$ = 16.8 Hz, 1H); ^{31}P NMR (24.3 MHz, $CDCl_3$) δ 54.0; ^{13}C NMR (75.47 MHz, CD_2Cl_2) δ 23.53 (s), 26.95 (s), 29.40 (s), 38.06 (d, $^2J_{C-P}$ = 4.4 Hz), 41.76 (d, $^1J_{C-P}$ = 113.2 Hz), 42.68 (d, $^3J_{C-P}$ = 7.4 Hz); IR (KBr) 971 (vs), 1004 (vs), 1059 (m), 1150 (s), 1288 (s), 1300 (s) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 309 (37), 163 (21), 119 (100), 76 (30), 28 (16). Anal. Calcd for $C_{12}H_{29}ClN_3PS_2$: C, 41.66; H, 8.43. Found: C, 41.56; H, 8.84. Poor results of microanalysis (H) are due to hygroscopicity of **20**.

Tris[4-(dimethylamino)phenyl](5,5-dimethyl-1,3-dithian-2-yl)phosphonium chloride (21). The procedure of Kruse[42] for **15a**-Cl was accommodated to transform **30** (900 mg, 6.08 mmol) and **42** (3.841 g, 6.69 mmol) into a mixture, from which **21** (2.102 g, 60.2%), yellowish solid, was isolated by column chromatography with chloroform–methanol as an eluent. Crystallization of the product from dichloromethane–diethyl ether afforded an analytically pure sample of **21**: colorless crystals; mp 245–250 °C; ^{1}H NMR (200.13 MHz, CD_2Cl_2) δ 1.10 (s, 3H), 1.17 (s, 3H), 2.39 (dd, $^2J_{H-H}$ = 14.00 Hz, $^4J_{H-P}$ = 4.30 Hz, 2H), 3.08 (s), 3.26 (d, $^2J_{H-H}$ = 14.00 Hz, 2H),

(98) Evans, J. G.; Goggin, P. L.; Goodfellow, R. J.; Smith, J. G. *J. Chem. Soc. A* **1968**, 464.

6.34 (d, $^2J_{H-P}$ = 12.4 Hz, 1H), 6.75–7.70 (m, 12H); ^{31}P NMR (121.49 MHz, $CDCl_3$) δ 23.9; ^{13}C NMR (75.47 MHz, $CDCl_3$) δ 24.14 (s), 26.77 (s), 30.16 (d, $^5J_{C-P}$ = 2.6 Hz), 39.90 (s), 41.23 (d, $^1J_{C-P}$ = 56.2 Hz), 42.84 (d, $^3J_{C-P}$ = 6.5 Hz), 100.48 (d, $^1J_{C-P}$ = 101.6 Hz), 112.04 (d, $^3J_{C-P}$ = 13.6 Hz), 135.73 (d, $^2J_{C-P}$ = 11.4 Hz), 153.95 (d, $^4J_{C-P}$ = 2.3 Hz); IR (KBr) 808 (m), 1108 (vs), 1376 (s), 1524 (s), 1596 (vs) cm^{-1}; MS (70 eV) *m/e* (relative intensity) 392 (24), 391 (100), 271 (37), 240 (62), 151 (60), 147 (40), 69 (20), 41 (16). Anal. Calcd for $C_{30}H_{41}ClN_3PS_2$: C, 62.75; H, 7.20. Found: C, 63.12; H, 7.06.

Diphenylmethylphosphine (33). Using the reported method,[99a] Ph_2PCl (29.8 g, 0.135 mol) and CH_3MgI, which was prepared from Mg (4.4 g, 0.183 mol) and CH_3I (25.7 g, 0.183 mol), were converted into **33** (23.4 g, 86.7%): colorless liquid; bp 91 °C/0.2 mmHg (lit.[99b] bp 160 °C/15 mmHg), n^{21}_D = 1.6261; ^{31}P NMR (121.49 MHz, C_6D_6) δ −26.4.

Dimethylphenylphosphine (34). The reported method[99c] was applied to convert **23** (23.4 g, 0.148 mol) and CH_3MgI, which was obtained from Mg (4.80 g, 0.20 mol) and CH_3I (28.5 g, 0.20 mol), into **34** (14.5 g, 71.2%): colorless liquid; bp 69 °C/8 mmHg (lit.[99c] bp 84–85 °C/13.5 mmHg); n^{21}_D = 1.5643; ^{31}P NMR (121.49 MHz, C_6D_6) δ −38.8.

Equilibration of Diastereomeric 1,3-Dithiane Derivatives. Compounds containing the (methylthio)phosphonium group **9–10**: The equilibrations occured spontaneously in NMR sample tubes. The results are collected in Tables 2 and 25.

(99) Houben-Weyl *Methoden der organischen Chemie*; G. Thieme: Stuttgart, 1958; Vol. 12, (a) Part 1, p 34; (b) Part 1, p 54; (c) Part 1, p 36.

Other compounds containing phosphonium groups **15–17**: Equilibrations were carried out in NMR sample tubes using solutions, which contained 0.25 mmol of a substance in 2.0 mL of CD_2Cl_2 (tube 10 mm o.d.) or 0.10 mmol of a substance in 0.8 mL of CD_2Cl_2 (tube 5 mm o.d.). All salts (except for **15**) were obtained *via* alkylation of phosphines **12–14** with $CF_3SO_3CH_3$ and were of sufficient diastereomeric purity to assure the equilibrium could be reached from both sides. As a catalyst, 0.2 equiv (with respect to the isomer) of Et_3N or *i*-Pr_2NEt was applied. The equilibration course was followed by ^{31}P NMR spectra. The results are collected in Table 25.

The Influence of CF_3COOH on the Conformation of 15b, 20, and 21. The reactions were carried out in 5 mm o.d. NMR sample tubes.

General Procedure. To a solution of the appropriate salt (0.25 mmol) in $CDCl_3$ (1.0 mL) was added relevant quantity of CF_3COOH (1 equiv = 19 μL), and the ^{1}H and ^{13}C NMR spectra of the mixture were recorded. The results are collected in Table 26.

Supporting Information Available: Tables 5 and 7–21 (16 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.

JO941772E