Preparation of 2-Pyrrolidinones 6a-f. The *N*-(carbomethoxy)-2-pyrrolidinones **5a-f** (5 mmol) in 10 mL of ethanol-free chloroform and 6 mmol of distilled trimethylsilyl iodide were stirred at 60 °C for 15 h. At this point, the solvent was evaporated and the residue dissolved in 20 mL of a 1:1 ether-water mixture. The ether was removed to yield the crude lactams **6a-f** which were purified by sublimation (0.1 mm) or recrystallization.

6a: mp 107 °C (lit. mp 103-105 °C); 96%; IR (KBr) 3180, 1685 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.05-7.35 (m, 5 H), 7.50-7.80 (br s, 1 H), 4.67 (m, 1 H), 2.27-2.68 (m, 3 H), 1.75-2.13 (m, 1 H); high-resolution mass spectrum, *m/e* 161.083 (calcd 161.084). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.50; H, 6.88. Found: C, 74.42; H, 6.88.

6b: mp 194 °C; 92%; IR (KBr) 3160, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.64-7.84 (br s, 1 H), 7.20 (s, 10 H), 2.62-2.86 (m, 2 H), 2.29-2.52 (m, 2 H); high-resolution mass spectrum, *m/e* 237.115 (calcd 237.115). Anal. Calcd for $C_{16}H_{15}NO$: C, 80.98; H, 6.37. Found: C, 80.64; H, 6.24.

6c: mp 114 °C; 98%; IR (KBr) 3170, 1695 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.35-7.60 (br s, 1 H), 7.00-7.35 (m, 5 H), 2.07-2.50 (m, 4 H), 1.61 (s, 3 H); high-resolution mass spectrum, *m/e* 175.101 (calcd 175.100).

6d (cis):[12] mp 113 °C; 86%; IR (KBr) 3205, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.17 (br s, 5 H), 6.47 (br s, 1 H), 4.64 (t, J = 6 Hz, 1 H), 2.42-2.72 (m, 1 H), 1.05-1.30 (m, 2 H), 1.22 (d, J = 7 Hz, 3 H); high-resolution mass spectrum, *m/e* 175.101 (calcd 175.100). Anal. Calcd for $C_{11}H_{13}NO$: C, 75.40; H, 7.48. Found: C, 75.50; H, 7.37.

6d (trans):[12] mp 127 °C; 85%; IR (KBr) 3200, 1690 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.16 (br s, 5 H), 6.04 (br s, 1 H), 4.50 (m, 1 H), 2.30-2.80 (m, 2 H), 1.35-1.70 (m, 1 H), 1.18 (d, J = 6 Hz, 3 H); high-resolution mass spectrum, *m/e* 175.100 (calcd 175.100).

6e: mp 127 °C (lit.[13] mp 132 °C); 90%; IR (KBr) 3190, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.50-7.90 (br s, 1 H), 2.24-2.49 (m, 2 H), 1.70-1.95 (m, 2 H), 1.20-1.70 (m, 10 H); high-resolution mass spectrum, *m/e* 153.116 (calcd 153.115). Anal. Calcd for $C_9H_{15}NO$: C, 70.55; H, 9.87. Found: C, 70.60; H, 9.02.

6f: mp 92 °C; 90%; IR (KBr) 3190, 1700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.40-6.90 (br s, 1 H), 5.32-5.68 (m, 2 H), 1.52-2.54 (m, 10 H); high-resolution mass spectrum, *m/e* 151.102 (calcd 151.100).

Registry No. 1a, 103-82-2; **1b**, 117-34-0; **1c**, 492-37-5; **1e**, 98-89-5; **1f**, 4771-80-6; **2a**, 1575-70-8; **2a** acid chloride, 76403-12-8; **2a** acid azide, 76403-13-9; **2a** isocyanate, 76403-14-0; **2b**, 6966-03-6; **2b** acid chloride, 50790-27-7; **2b** acid azide, 76403-15-1; **2b** isocyanate, 76403-16-2; **2c**, 76403-17-3; **2c** acid chloride, 76403-18-4; **2c** acid azide, 76403-19-5; **2c** isocyanate, 76403-20-8; **2d**, 76403-21-9; **2d** acid chloride, 76403-22-0; **2d** acid azide, 76403-23-1; **2d** isocyanate, 76403-24-2; **2e**, 72335-50-3; **2e** acid chloride, 72335-83-2; **2e** acid azide, 76403-25-3; **2e** isocyanate, 76403-26-4; **2f**, 76403-27-5; **2f** acid chloride, 76403-28-6; **2f** acid azide, 76403-29-7; **2f** isocyanate, 76403-30-0; **3a**, 76403-31-1; **3b**, 76403-32-2; **3c**, 76403-33-3; **3d**, 76403-34-4; **3e**, 76403-35-5; **3f**, 76403-36-6; **4a**, 76403-37-7; **4b**, 76403-38-8; **4c**, 76403-39-9; **4d**, 76403-40-2; **4e**, 76403-41-3; **4f**, 76403-41-3; **5a**, 76403-42-4; **5b**, 76403-43-5; **5c**, 76403-44-6; *cis*-**5d**, 76403-45-7; *trans*-**5d**, 76403-46-8; **5e**, 76403-47-9; **5f**, 76403-48-0; **6a**, 22050-10-8; **6b**, 40052-79-7; **6c**, 5578-98-3; *cis*-**6d**, 76403-49-1; *trans*-**6d**, 76403-50-4; **6e**, 5498-74-8; **6f**, 76403-51-5; allyl bromide, 106-95-6; 2-methylallyl bromide, 1458-98-6.

(13) K. W. Rosenmund, and P. Engel, *Arch. Pharm.*, **284**, 209 (1951).
(14) R. D. Moffet, *J. Am. Chem. Soc.*, **79**, 3186 (1957).

Thiono-Thiolo Rearrangement and Solvolysis of the Secondary Alkyl Phosphorothionates. 3[1a]

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The protic acid catalyzed thiono-thiolo (O→S) migration of secondary alkyl groups in trialkyl phosphorothionates **1** occurs in a complex fashion. Analysis of product distribution, stereochemistry, and deuterium incorporation experiments supports an ion-pair-type intermediate, **7**, as being responsible for the entire process. Nucleophilic attack by **1** on **7** initiates the chain reaction leading to **2**. In trifluoroacetic acid medium inversion of configuration (96%) at the carbon atom of the migration *sec*-butyl group was observed. A high concentration of **1** promotes this mode of rearrangement. However, the overall stereospecificity of *sec*-butyl migration is much lower due to an elimination process leading to the dialkyl hydrogen phosphorothioate **3** and an intermediate olefin which after protonation in acidic medium returns to the ion pair **7**. The latter process is responsible for the non-stereospecific formation of part of the rearrangement product **2** and contributes to the lower stereospecificity of the trifluoroacetolysis process. The role of reaction-medium acidity is discussed.

An attempt to apply the protic acid catalyzed thiono-thiolo rearrangement of O-alkyl esters of phosphorothioic acids to the stereospecific conversion of the alcohols into alkanethiols[1a] demonstrated that the mechanism of this rearrangement is complex. It has been shown that this process depends on the nature of the migrating alkyl group R, the chemical environment of the phosphorus atom, and the solvating properties of the reaction medium.[1] The stereochemical results of the rearrangement of optically active 2-[(α-methylbenzyl)oxy]-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (**1f**) in CF_3COOH and $(CF_3)_2CHOH$ (comparable ionizing powers[2] but different dielectric constants) are very similar while a large difference occurs in the stereochemical course between TFA and AcOH solutions (different ionizing powers, comparable dielectric constants, and a strongly emphasized difference in their acidities[3]). These differences have been discussed in terms of a dissociative mechanism involving ion-pair intermediates. Recombination within the internal ion pair (low acidity and low ionizing power, e.g., AcOH) affords the *S*-alkyl product with retention at the α-carbon atom in the

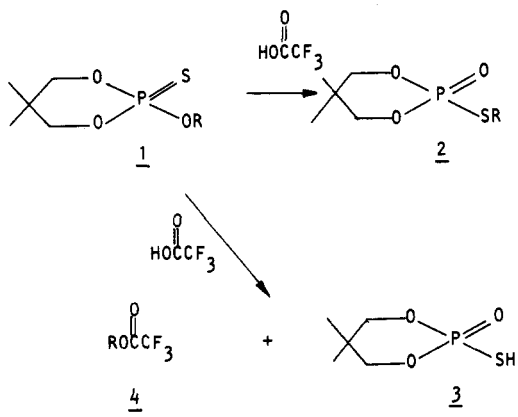
(1) (a) Part 2: Bruzik, K.; Stec, W. J. *J. Org. Chem.* **1979**, *44*, 4488. (b) Stec, W. J.; Uznański, B.; Bruzik, K.; Michalski, J. *Ibid.* **1976**, *41*, 1291.

(2) Schadt, F. L.; Bentley, T. W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1976**, *98*, 7667.

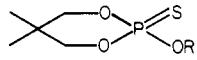
(3) For a review of the acidity of the carboxylic acids in inert solvents see: Popov, A. J. "The Chemistry of Nonaqueous Solvents"; Lagovski, J. J., Ed.; Academic Press: New York 1970; Vol. 3, p 366; Joesten, M. D.; Schaad, L. J. "Hydrogen Bonding"; Marcel Dekker: New York, 1974.

0022-3263/81/1946-1618$01.25/0

Scheme I



migrating alkyl group. Competition of this process with nucleophilic attack of the neutral phosphorothionate (high acidity, e.g., TFA) on the internal ion pair results in predominant inversion or substantial racemization. In this paper we present further evidence of the complexity of this reaction. As model compounds, 2-RO-substituted 2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinanes (1) were applied.



1a, R = 2-propyl
b, R = 2-butyl
c, R = 2-buten-1-yl
d, R = 3-buten-2-yl
e, R = benzyl
f, R = α-methylbenzyl
g, R = diphenylmethyl
h, R = methyl

Studies of the thiono–thiolo rearrangement of **1a–g** in protic media revealed the substantial solvolytic character of this rearrangement. This observation was of interest because the mechanisms of solvolytic reractions at the carbon atom of organophosphorus compounds are still very obscure.[4] Particularly interesting is the trifluoroacetolysis of our model compounds due to the absence of nucleophilic assistance in this solvent[5] during the departure of the leaving group. This trifluoroacetolysis of the derivatives of strong acids (i.e., tosylates) is close in character to the typical "limiting" S_N1 process.

Depending on the reaction conditions, the formation of 2-hydroxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (3) and the corresponding alkyl trifluoroacetate (4) can be observed in addition to the 2-(alkylthio)-2-oxo-5,5-dimethyl-1,3,2-dioxaphosphorinane (Scheme I).

The results of product-distribution studies are collected in Table I. Inspection of Table I reveals that in acidic medium, decreasing the concentration of 1 causes (with the exception of **1f–h**) an increase in the yield of 3. The presence of alkyl trifluoroacetates 4 was also confirmed by means of gas chromatography/mass spectroscopy. In the case of **1f** solvolysis occurred in more nucleophilic media like trifluoroethanol and acetic acid.[6] The behavior of **1f** in trifluoroethanol requires special comments. The ^{31}P NMR spectrum recorded for a sample of **1f** dissolved in trifluoroethanol (0.2 M) at 23 °C showed after 1.5 h that

Table I. Participation of the Solvolysis Process in the Thiono–Thiolo Rearrangement of 2-(2-Alkoxy)-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (1) at 23 °C[d]

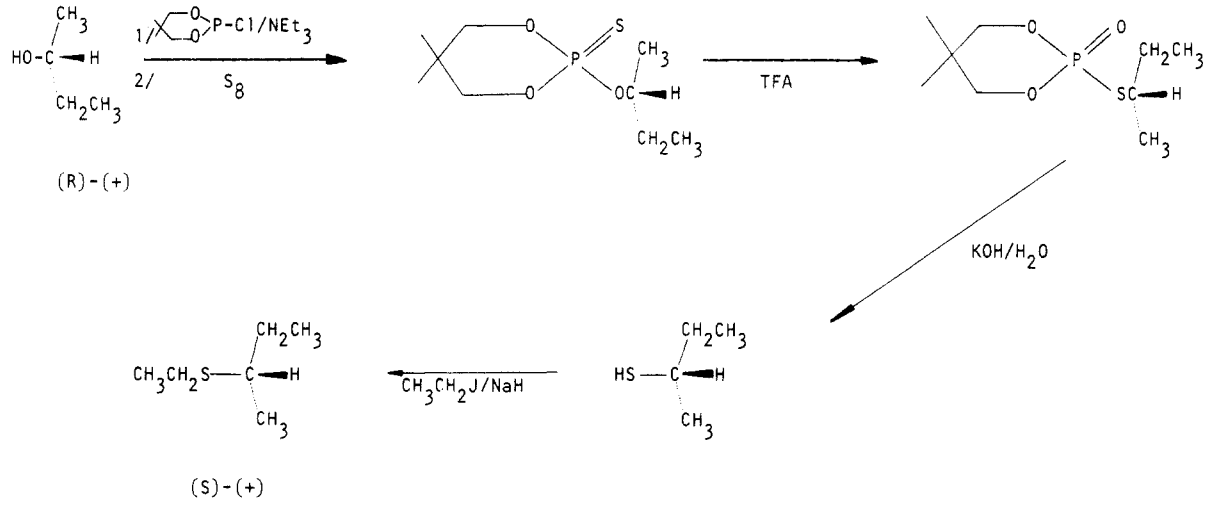
substrate 1	reaction conditions [solvent, acid (concn, M), concn of 1, M]	% solvolysis[a]	% reaction[b]
a	CH_2Cl_2, TFA (3), 1.0	16	38
	TFA, 1.0	28	60
	TFA, 0.05	87	75
b	CH_2Cl_2, TFA (1:1 v/v), 1.5	12	68
	TFA, 1.0	25	95
	TFA, 0.05	81	>98
c	CH_2Cl_2, TFA (0.2), 0.2	<2	
	CH_2Cl_2, TFA (2.0), 0.2	31	>98
d	CH_2Cl_2, TFA (2.0), 0.2	20	95
	TFA, 0.2	37	>98
e	CH_2Cl_2, TFA (3.0), 1.0	10	63
	TFA, 1.0	28	
	TFA, 0.05	55	>98
f	TFA[c]	<2	>98
	$(CF_3)_2CHOH$, 0.2	<2	>98
	CF_3CH_2OH, 0.2	8	>98
	CH_3COOH, 0.1	32	82

[a] Estimated on the basis of the integrated intensity of the signals for 3 in relation with that one for 2 in the ^{31}P NMR spectrum. [b] Measured by means of ^{31}P NMR as the ratio of the sum of signal intensities for products 2 and 3 in relation to the sum of the intensities of signals for 1–3. [c] In the whole range of the studied concentration (0.1–1 mol/L) trifluoroacetolysis was not observed. [d] Trifluoroacetolysis was not observed in the rearrangement of methyl ester **1h**. Rearrangement of **1g** in more nucleophilic media like acetic acid and trifluoroethanol was also not assisted by solvolysis.

the signal of 3 was more intense than that of **2f**. The same sample after 2 days at 23 °C showed a decrease in the concentration of 3 and an increase in the amount of **2f**. After 2 weeks the concentration of 3 became constant and was established as indicated in Table I. The above observation suggested the intermediacy of alkenes, which under the reaction conditions would react with acids, giving products indistinguishable from those formed during rearrangement and solvolysis. Indeed, in independent experiments the presence of styrene (maximum concentration after 90 min) and α-methylbenzyl 2,2,2-trifluoroethyl ether in the CF_3CH_2OH solution of **1f** was established by means of gas chromatography/mass spectroscopy. It has been previously shown by Streitwieser and Walsh[7] that elimination–addition reactions take place during the acetolysis of 2-octyl derivatives. The question arose to what extent the elimination–addition process[8] contributes to the rearrangement and solvolysis of 1. To answer this question, we carried out experiments using deuterated TFA as the reaction medium.[9] Analysis of deuterium incorporation in the product mixture serves as a probe which determines the extent to which the elimination process contributes to the overall reaction scheme.[10] The results

(4) Cox, J. R.; Newton, M. G. *J. Org. Chem.* **1969**, *34*, 2600.
(5) Fry, J. L.; Harris, J. M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1970**, *92*, 2540. Bentley, T. W.; Schleyer, P. v. R. *Ibid.* **1976**, *98*, 7658. Schadt, F. L.; Lancelot, C. J.; Schleyer, P. v. R. *Ibid.* **1978**, *100*, 228.
(6) Nucleophilicities of these solvents toward model tosylates were recently determined by Schleyer et al.[2] in comparison with 80% aqueous ethanol.
(7) Streitwieser, A.; Walsh, T. D. *J. Am. Chem. Soc.* **1965**, *87*, 1686.
(8) Mueller, W. H.; Oswald, A. A. *J. Org. Chem.* **1966**, *31*, 1894.
(9) This type of test with tritiated acetic acid was applied by Streiwieser et al.[7]
(10) The addition of protic acid to olefin proceeds with transient formation of the carbonium ion pairs, which rapidly recombine to give corrsponding alkyl esters.[11,12] The large excess of deuterated acid must be used to avoid isotope dilution during the reaction.

Scheme II



of this analysis are shown in Table II. Surprisingly, the extent of elimination in this reaction is quite high. It is lowered by increasing the concentration of the nucleophilic substrate (entries 3 and 5) and by the presence of an "external" nucleophile like anisole. For a better insight into the process of thiono–thiolo rearrangement of **1**, a stereochemical approach was applied. If **1** is optically active, the product **2** and the alkyl trifluoroacetate (**4**) formed in the series of the consecutive elimination–addition reactions should be fully racemized. Thus, the overall stereospecificity observed in the rearrangement (solvolysis) of optically active C-chiral substrates is lowered by the participation of the parallel process of elimination–addition. The extent of this side process will be reflected in the degree of racemization observed regardless of the stereospecific path of the rearrangement and solvolysis. Most of the work on the stereochemistry of the solvolysis of simple secondary alkyl derivatives showed that these reactions proceed with essentially complete inversion of configuration at carbon.[14a] In other "exceptional" cases it was shown that partially racemized compounds are formed in competing side processes. However, there are only very few examples in the literature concerning the stereochemistry of trifluoroacetolysis.[15] It has been found that that derivatives with bidentate leaving groups (e.g., sulfinic esters, isothiocyanates) rearrange with predominant retention at carbon.[14b,c] Recently we have shown[1a] that this is not the case in the thiono–thiolo rearrangement of benzyl phosphorothionates catalyzed by TFA.

Optically active **1b** was prepared via the condensation of 2-butanol (of known optically purity[16] and known absolute configuration[17]) with 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane in the presence of triethylamine and an excess of elemental sulfur. After dissolution of (*R*)-(−)-**1b** ($[\alpha]^{20}_D$ −2.68° (*c* 8.7, acetone); 38.2% ee)[18] in TFA–CH_2Cl_2 (1:1 v/v) at 23 °C, the reaction progress was monitored by means of ^{31}P NMR. When the concentration of **1b** was lowered to 8% of its initial concentration, TFA was neutralized and (+)-**2b** ($[\alpha]^{25}_D$ +6.02° (neat)) isolated. This product was treated with aqueous KOH, and the liberated 2-butanethiol was condensed with alkyl iodide to give (*S*)-(+)-2-butyl ethyl sulfide ($[\alpha]^{25}_D$ +7.12° (neat); 22.3% ee Scheme II). Because the optical purity and absolute configuration of 2-butyl ethyl sulfide[20] were known, the stereospecificity of the **1b** → **2b** conversion was determined as proceeding with 58% inversion. Since the

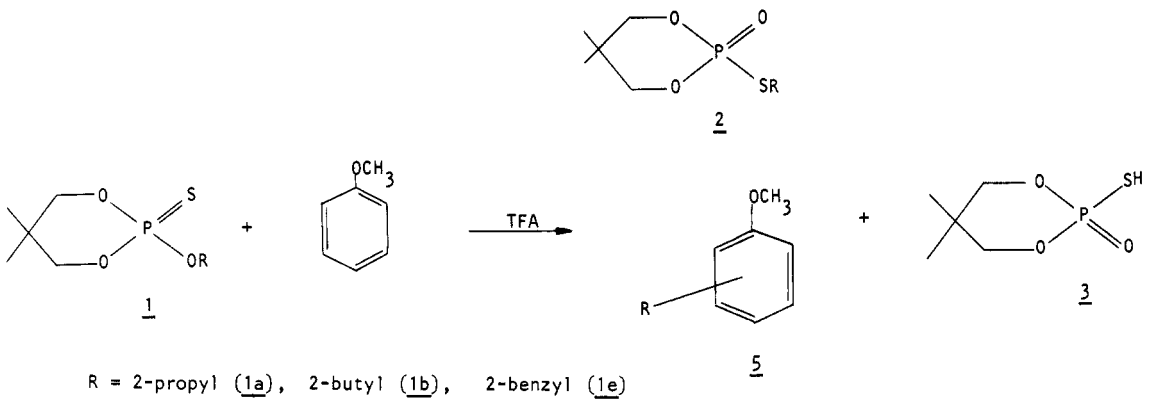
Table II. Contribution of the Elimination Process in the Rearrangement and Solvolysis of 1

no.	substrate 1	reaction conditions [acid and/or solvent, concn of 1 (M), temperature (°C), time]	deuterium abundance in 2[h,f]
1	a[a]	TFA-*d*, 0.05, 25, 9 days	16.1
2	b[b,d]	TFA-*d*-CH_2Cl_2 (1:1 v/v), 1.5, 25, 66 h	39.3
3	b[e]	TFA-*d*, 0.05, 25, 2 days	67.9
4	b[g]	TFA-*d*, 0.05, anisole 0.5, 25, 2 days	59.1
5	b	TFA-*d*, 1, 25, 2 days	45.0
6	e[c]	TFA-*d*, 0.05, 25, 5 h	1.9
7	f[c]	TFA-*d*, 0.05, 25, 10 min	1.3
8	f	AcOD, 0.1, 25, 7 days	<1

[a] Deuterium is incorporated in the 1-position of the 2-propyl group. [b] Deuterium is incorporated in the 3-position of the 2-butyl group. [c] Deuterium is incorporated due to the proton–deuterium exchange in the aromatic ring in the presence of strong acid.[13] [d] 2-Butyl trifluoroacetate isolated contained 24.9% of 3-deuterium-labeled compound. [e] 2-Butyl trifluoroacetate contained 68% of its 3-deuterated analogue. [f] Measurements were carried out by the use of mass fragmentography. [g] *o*- and *p*-(2-butyl)anisoles formed in this reaction contained a deuterated aliphatic chain; however, the presence of one and/or more deuterons in aromatic ring caused the impossibility of the determination of isotopic enrichment in 2-butyl side chain. [h] The extent of elimination is identical with deuterium enrichment of **2** with the assumption of a large excess of TFA-*d* to avoid isotope dilution.

(11) Shiner, V. J., Jr.; Dowd, W. *J. Am. Chem. Soc.* **1969**, *91*, 6528. Shiner, V. J., Jr.; Fisher, R. D.; Dowd, W. *Ibid.* **1969**, *91*, 7748.
(12) Mason, I. J.; Norman, R. O. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 1840.
(13) Kresge, A. J.; Chiang, Y. *J. Am. Chem. Soc.* **1961**, *83*, 2877.
(14) (a) Weiner, H.; Sneen, R. A. *J. Am. Chem. Soc.* **1965**, *87*, 287. Streitwieser, A. Jr. *Ibid.* **1955**, *72*, 1117. Streitwieser, A., Jr.; Walsh, T. D.; Wolfe, J. R. *Ibid.* **1965**, *87*, 3682. (b) Tonellato, U.; Rosetto, O.; Fava, A. *J. Org. Chem.* **1969**, *34*, 4032. (C) Raber, D. J.; Harris, J. M.; Schleyer, P. v. R. "Ions and Ion-Pairs in Organic Reaction"; Wiley: New York, 1974; Vol. II, Chapter 3 and ref 162 and 164 cited therein.
(15) Nordlander, J. E.; Kelly, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 996.
(16) Pickard, R. H.; Kenyon, J. *J. Chem. Soc.* **1911**, 9945.
(17) Klyne, W.; Buckingham, J. In "Atlas of Stereochemistry. Absolute Configurations of Organic Molecules"; Oxford University Press: New York, 1974; p 5.
(18) Due to the observation of the enrichment of the sample of **1b** during its crystallization from hexane with the more abundant enantiomer it was necessary to determine the optical purity of **1b** obtained after several recrystallizations by means of the isotope-dilution method.[19]
(19) Allinger, N. L.; Elliel, E. L. *Top. Stereochem.* **1967**, *2*, 202.
(20) Salvadori, P.; Lardicci, L.; Stagi, M. *Gazz. Chim. Ital.* **1968**, *98*, 1400.

Scheme III

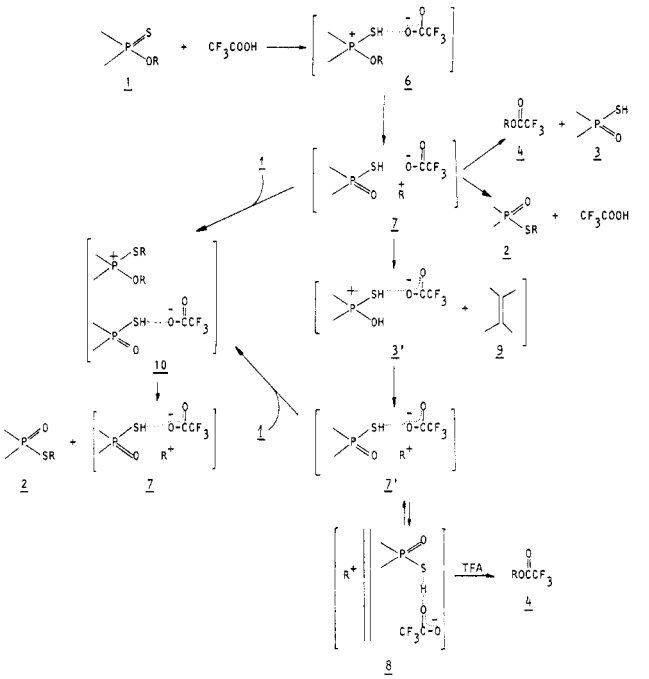


conditions were analogous to those of experiment 2 in Table II [**1b**, TFA-d_1/CH_2Cl_2 (1:1 v/v)][21] and the extent of elimination responsible for racemization was known, we calculated that "pure" rearrangement of **1b** → **2b** proceeds with 96% inversion. The starting material **1b**, of almost unchanged optical rotation[22] [7%, $[\alpha]^{20}_D$ −2.6° (*c* 8.8, acetone)], was isolated from the reaction mixture.

The assignment of optical purity of 2-butyl trifluoroacetate was essential for the mechanistic elucidation of the solvolysis of **1b** in TFA. The optical purity of isolated 2-butyl trifluoroacetate[23] when compared with that prepared independently from 2-butanol showed that solvolysis proceeds with 22% inversion at carbon. Correction of this value for elimination indicates that the stereospecificity of nucleophilic substitution at the carbon atom is 28% inversion. In the control experiment we have proved that **4b** is configurationally stable under the reaction conditions. The above-mentioned (Table II, no. 4) "trapping" experiment in which anisole was used as a "trap" for the cationoid intermediates deserves special comment.

This type of test for the presence of carbonium intermediates was described by Kevill et al.[24] and Trancik et al.,[25] who used nitrobenzene for the same purpose. The existence of the transient carbonium ion was postulated on the basis of the meta-alkylated nitrobenzene observed in the reaction mixture during the thermal decomposition of 2-adamantyl chloroformate in nitrobenzene-benzene medium. In this work, introduction of anisole into the reaction mixture resulted in the formation of both ortho- and para-alkylated anisole (**5**). This was observed during the rearrangement-solvolysis reactions of 2-butyl (**1b**), 2-propyl (**1a**), and benzyl (**1e**) esters. However, reactions performed with the methyl (**1h**), α-methylbenzyl (**1f**), and diphenylmethyl (**1g**) derivatives gave only the rearrangement product and no alkylation of anisole was observed (Scheme III). The differences observed between these two groups of compounds in this regard are believed to originate in the lower reactivity and higher selectivity[26] of the cationoid intermediates obtained from **1f** and **1g** relative to the ion pairs generated from the **1a, b,** and **e** derivatives. The lack of methylated anisoles among the products of reaction of **1h** carried out in the presence of anisole speaks also against intermediacy of ion pairs in protic acid catalyzed rearrangement of primary *O*-alkyl derivatives. The most probable mechanism for the overall rearrangement–solvolysis process for benzyl and simple secondary dialkyl phosphorothioates is illustrated in Scheme IV. Protonation of the nucleophilic phosphorothionate leads to the formation of the pseudophosphonium salt **6** which collapses to the ion pair **7**. Due to the low nucleophilicity of the reaction medium,[2] **7** is not stabilized by nucleophilic assistance.[2] Such ion pairs are highly reactive and exhibit lower selectivity. The reactivity of the ion pairs generated in solvolytic media depends substantially on the magnitude of nucleophilic assistance of the solvent. The stronger the nucleophilic assistance is the lower reactivity of the ion pairs is. Because of the complex equilibria between **1**,

Scheme IV



(21) The assumption of the same reaction condition for TFA-d_1-CH_2Cl_2 (1:1) and TFA-CH_2Cl_2 (1:1) was made.

(22) The change of optical rotation of recovered **1b** in relation with that of starting **1b** was close to the error limit of its measurements. However, the small degree of incorporation of the "external anion" to the substrate **1b** suggests that there is a very slow racemization of **1b** due to either external ion-pair return or O-addition of the phosphorothioic acid to butene.

(23) Compound **4b** was not isolated in pure state. It was obtained in methylene chloride solution only. The determination of the concentration of **4b** in this solution allowed us to calculate its optical rotation and the steric course of trifluoroacetolysis.

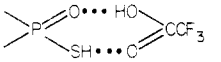
(24) Kevill, D. N.; Weitl, F. L. *J. Am. Chem. Soc.* **1968, 90**, 6416.

(25) Trancik, R. J.; Beak. P. "Abstracts of Papers", 154th National Meeting of the American Chemical Society, Chicago, IL, Sept 1967; American Chemical Society: Washington, DC, 1967; S164.

(26) For a general review of reactivity–selectivity principle, see: Pross, A. *Adv. Phys. Org. Chem.* **1977**, *14*, 69; Johnson, C. D. *Chem. Rev.* **1975**, *75*, 755.

CF_3COOH, and **6**, precise assessment of the effective concentration of **1**, which undergoes reaction with **7**, is difficult, and rendering the application of a quantitative approach to reactivity–selectivity rule is impossible.[27] However, analysis of the extent of solvolysis of **1a,b,e** was precise enough and allows the postulate that nucleophilic species attack the more reactive intermediates in this case compared to those existing in the reaction of *O*-diphenylmethyl (**1g**) and *O*-(α-methylbenzyl) (**1f**) phosphorothioates (see Table I). Although the nucleophilic reactivity of neutral phosphorothionate and trifluoroacetic acid is different, the high reactivity of the ion pair **7** is responsible for the parallel formation of **2** and alkyl trifluoroacetate. However, the stereochemical results provide evidence suggesting that the attack of the phosphorothionate and trifluoroacetate ions does not occur at the same intermediate. The more nucleophilic unprotonated **1** attacks the internal ion pair **7**. This results in high stereospecificity (96%) and inversion of configuration at the O→S migrating carbon atom. The less nucleophilic trifluoroacetate attacks the more loosely bound and more reactive **8**, and the resulting alkyl trifluoroacetate is formed with lower stereospecificity. Lowering the concentration of **1** in solvolytic medium increases the lifetime of ion pair **7**, which in the case of **1a,b,f** may collapse to the olefin **9**, thioacid **3**, and trifluoroacetic acid. The reverse process, addition of carboxylic acids and dialkyl phosphorothioic acids to olefins, is well-known[8,11,12] and in our work was documented by deuterium-labeling experiments. This must, in principle, restore the intervention of **7′** which is identical with that of original **7**. Experiment 3 in Table II clearly indicates the same degree of deuterium incorporation into **2b** and 2-butyl trifluoroacetate (**4b**) which may also be interpreted in terms of both nucleophiles **1** and TFA equally attacking the ion pairs **7** and **7′**. The addition of the phosphorothioic acid to olefin leading to the phosphorothionate **1** does not occur in the investigated reaction because the optical purity of "unreacted" recovered **1b** was unchanged.[22] Furthermore, this fact indicates that under the given reactions, ion pair return is very limited. As pointed out in our earlier work,[1a] the "primer" ion pair **7** reacts with unprotonated **1** to give the phosphonium salt **10**[28] with the liberation of dialkyl hydrogen phosphorothioate **3** associated with the anion of TFA. The phosphonium salt **10** may similarly collapse to **2**, regenerating the ion pair **7**. Replication of the reaction sequence **7** + **1** → **10** → **2** + **7** is primarily responsible for the thiono-thiolo rearrangement.[29]

This process can be stopped by the intervention of dialkyl phosphorothioate ion present at low concentration in the reaction mixture. However, as proved in an independent experiment, incorporation of the external (nucleophilic) dialkyl phosphorothioate ion even when present in high concentration occurs only to a limited extent (ca. 10%). This implies a novel route for the disappearance of olefin in the reaction mixture. If the protonated olefin reacts with phosphorothioate anion, the extent of incorporation of the "external" anion into the product would be even higher than the values reported in the Table II. From the small degree of "external" anion incorporation it is clear that ion pair **7′** which is formed after protonation of the olefin must preferentially react with the phosphorothionate molecule **1**. This fact can be only explained if one assumes the existence of the thioacid **3** in the weak nucleophilic form of a heterodimer (**11**) with trifluoroacetic



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acid. What is the role of the acidic component in the thiono–thiolo rearrangement of simple secondary alkyl esters of phosphorothioic acids? It is not only limited to the activation of the substrate **1** and the stabilization of the leaving group during its departure by protonization or hydrogen bonding.[30] This type of interaction causes "shielding" of the nucleophilic sulfur atom within the ion pair **7** which effectively stops the recombination of the ion pair leading to **2** with retention of configuration.[1a] The efficiency of the interaction between the hydrogen atom of the parent acid and sulfur in the pseudophosphonium complex and the solvent polarity are factors of primary importance influencing recombination within **7**, attack of the external nucleophile, and separation of the ion pair **7**. In a strongly acidic medium like CF_3COOH, the sulfur atom in **7** is very effectively shielded and its nucleophilicity so reduced that attack by external (unprotonated) **1** becomes more favored. This is not the case with acetic acid. In this solvent, proton binding to sulfur is not so effective, and recombination within the ion pair of type **7** is a more important route.

Experimental Section

All melting and boiling points are uncorrected. Solvents and commercial reagents were distilled and dried by conventional methods before use. Methylene chloride used in the studies on product distribution in the solvolysis–rearrangement reaction was rigorously purified[31] and was stored in sealed ampules over a sodium mirror. Commercial trifluoroacetic acid (Fluka) and acetic acid were dried and purified as described previously.[1a] Hexafluoroisopropyl alcohol (Merck) was rectified on a helix-packed column and was stored in sealed ampules to avoid contact with moisture. Trifluoroethanol (Fluka) was rectified and stored in sealed ampules. Trifluoroacetic acid-*d* was prepared by the reaction of deuterium oxide with an excess of trifluoroacetic anhydride. The crude acid was then purified as its undeuterated analogue. Acetic acid-d_1 was prepared by being distilled from a mixture of sulfuric acid-d_2 and anhydrous sodium acetate. Anisole was dried with sodium hydride and distilled before use. ^1H NMR spectra were recorded at 60 MHz with a Perkin-Elmer R12B spectrometer. ^{31}P NMR spectra were obtained on a JEOL FX-60 spectrometer operating at 24.3 MHz with external H_3PO_4 as the reference. Positive chemical shifts are assigned for compounds absorbing at lower field than H_3PO_4. Mass spectra were obtained on an LKB 2091 spectrometer at a 70-eV ionizing energy. GC analyses were performed on a Varian Aerograph 1520 chromatograph equipped with an electronic integrator. Product purities were also determined by TLC (silica gel F_{254}, standard glass plates). Optical activity measurements were made with a Perkin-Elmer 241MC photopolarimeter. Measurements of deuterium content in labeled compounds were accomplished by using mass fragmentography.[32] The deuterium contents reported are the mean values of at least five repetitive determinations which differ one from another by no more than 1% of their absolute values.

(27) The calculation of the selectivity values requires the knowledge of the effective concentration of the free base–nucleophile **1**. Its assignment is difficult due to complex equilibria between **1** and TFA which involve proton transfer and hydrogen bonded complexes.

(28) In reactions of primary *O*-alkyl and *O*-allyl esters of phosphylthioic acid in TFA, phosphonium salt type intermediates are present at concentrations which allow their direct observation: Bruzik, K.; Stec, W. J., to be submitted for publication.

(29) Catalysis of the thiono–thiolo rearrangement by phosphonium salts derived from phosphorothionates was suggested by Teichmann, H.; Hilgetag, G. *Chem. Ber.* **1963**, *96*, 1454.

(30) Bentley, T. W.; Schleyer, P. v. R. *Adv. Phys. Org. Chem.* **1977**, *14*, 1.

(31) Cheradame, H.; Mazza, M.; Hung, N. A.; Sigwalt, P. *Eur. Polym. J.* **1973**, *9*, 375.

(32) Gordon, A. E.; Frigerio, A. *J. Chromatogr.* **1972**, *73*, 401.

Table III. Yield,[a] Physical, and Spectroscopic Data of Compounds 1, 2, and 2-Alkoxy-5,5-dimethyl-1,3,2-dioxaphosphorinanes

R	bp, °C (mmHg)	mp, °C	yield, %	$\delta^{31}P$[e]	mp, °C	$\delta^{31}P$[e]
CH_3[b]	60 (18)[b]	93-94[b]	92	62.2	b	21.8
2-C_3H_7[b]	not isolated	86-88	90[c]	60.6	oil	
2-C_4H_9[d]	88-92 (0.8)	62-64.5	50	59.8	oil, bp 125-130 (0.15)[g]	20.4
1-C_4H_7	70-75 (0.8-0.9)	50-52	65	61.7	not isolated	20.9
2-C_4H_7	78-80 (8)	60-62	55	60.4	in pure state	19.3
CH_2Ph	not isolated	44-45	94.5[c]	60.9	78-80	19.7
CH-(CH_3)Ph[f]	96-100 (0.01)[f]	102-103	65	59.6	64-65	18.6
$CHPh_2$	solid	102-105	20	61.3	115-116	19.3

[a] Joint yield of the condensation of phosphorochloridite with alcohol, addition of sulfur, and purification, relative to alcohol. [b] Literature[34] value. [c] Yield of product purified by column chromatography. [d] *dl* form. [e] In chloroform solution. [f] (*R*)-(+) enantiomer. [g] Pressure (mmHg) in parentheses.

Starting Materials. 2-Chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane, its 4,4,6,6-tetradeuterio analogue, and 2-alkoxy-5,5-dimethyl-1,3,2-dioxaphosphorinanes were obtained as described in the literature.[33] Yield, physical, and spectroscopic data of compounds 1 and 2 are listed in the Table III. 2-Butyl alcohol was resolved into its enantiomers as described by Pickard and Kenyon.[16] 2,2-Dimethyl-1,1,3,3-tetradeuteriopropane-1,3-diol was obtained from diethyl dimethylmalonate by means of reduction with lithium aluminium deuteride in 71% yield. 2-Butyl and benzyl trifluoroacetates were prepared from the corresponding alcohols and trifluoroacetic anhydride. 2-Hydroxy-2-thiono-5,5-dimethyl-1,3,2-dioxaphosphorinane (3) was obtained from **1h** by its demethylation with trimethylamine and chloroform extraction of 3 from an acidified solution of its tetramethylammonium salt: soild; mp 72–73 °C;[34] ^{31}P NMR δ 57.8 (CH_2Cl_2).

Analysis of Product Distribution in the Solvolysis–Rearrangement Reactions of 1. A weighed amount of 1 was placed in an NMR tube equipped with a stopcock. The tube was then connected to a vacuum line, and a known volume of acid solution in CH_2Cl_2 or acid alone was added from the vacuum buret. The resulting sample tube was immersed in liquid N_2 and sealed by flame. The sample was then warmed, and the tube was placed in a thermostat. The reaction was monitored by means of ^{31}P NMR and/or ^{19}F NMR. Due to media dependence of the chemical shift of 3 in different acids, the identity of this signal had to be proved by addition of a small amount of authentic 3 to the reaction mixture. The extent of solvolysis was estimated from the integrated ^{31}P NMR spectra. The relative error in integration of the spectra is dependent on the concentration of the sample and varies in the limit of 1% for 0.5-mol/L and 5% for 0.1-mol/L concentrations.

Investigation of the Elimination–Addition Process during the Solvolysis–Rearrangement Reactions of 1. To a weighed amount of 1 in an ^{31}P NMR tube was added a known volume of a CH_2Cl_2 solution of CF_3COOD, CF_3COOD alone, or CH_3COOD under vacuum-line conditions. The progress of the reaction was monitored by means of ^{31}P NMR spectroscopy. The reaction was quenched by evaporation of the acid and neutralization of the residue with dry gaseous ammonia. Crude 2 was purified by means of preparative thin-layer chromatography on silica gel. The products and regenerated substrates were analyzed for deuterium content by using mass fragmentography (gas chromatography/mass spectroscopy system). Samples were chromatographed on glass columns packed with OV-1 (2.7 m) on Chromosorb WAW. At least five repetitive runs were performed for each analysis.

In the cases where the solvolysis reactions were observed, the reaction mixture was worked up in a different way. Di-*n*-butyl ether was added to the reaction mixture, and the acid was neutralized with an aqueous solution of sodium bicarbonate. The organic layer was separated and dried with anhydrous $MgSO_4$. Solutions containing alkyl trifluoroacetate or alkyl acetate and phosphorus compounds were analyzed by means of gas chromatography using columns filled with a mixture of SE-30 (3%) and DEGS (5%) on Chromosorb WAW. Calculations of the abundance of deuterated compounds were performed on the basis of the relative intensity of the M + 1 ion and the molecular ion after substraction of the intensity of M + 1 ion arising from natural isotope abundance.

Assignment of Stereochemistry and Stereospecificity of Rearrangement of (*R*)-(−)-1b in CF_3COOH/CH_2Cl_2 Solution. (*R*)-(−)-**1b** (9.0 g, 0.038 mol; mp 62–64 °C; $[\alpha]^{20}_D$ −2.68° (*c* 8.7, acetone); 38.2% ee) was placed in the flask connected to a vacuum line. A mixture of CF_3COOH (11.1 g, 7.5 mL) and CH_2Cl_2 (7.5 mL) was added. After the sample was warmed to room temperature, it was placed in a thermostat at 23 °C. After 13 days at 23 °C, 92% of **1b** was converted to products as determined by ^{31}P NMR assay. The reaction was quenched and worked up as usual. The crude mixture of the product and unreacted substrate was separated and purified by column chromatography on silica gel with benzene–petroluem ether–acetone (10:10:1) as the developing system to yield **2b**: 6.5 g (72%); bp 125–130 °C (0.15 mmHg); n^{25}_D 1.4867; $[\alpha]^{20}_D$ +6.02 (neat); ^{31}P NMR 20.4; mass spectrum, *m/e* (relative intensity) 238 ($M^{+\cdot}$, 17), 183 (28), 182, (27), 115 (52), 68 (base peak). The **1b** [600 mg (7%); mp 61–63 °C; $[\alpha]^{20}_D$ 2.6° (*c* 8.8, acetone)] isolated from the reaction mixture was essentially the same as starting **1b**.

Compound **2b** [6.5 g (0.027 mol); $[\alpha]^{20}_D$ +6.02 (neat)] was hydrolyzed as described earlier.[1] The ethereal solution of liberated 2-butanethiol was treated with NaH and ethyl iodide (20 g). The mixture was stirred overnight, and the suspension of NaCl and an excess of NaH were separated by means of centrifugation. The resulting clear solution was concentrated, and (*S*)-(+)-2-butyl ethyl sulfide was separated by means of preparative gas chromatography: 0.7 g; $[\alpha]^{25}_D$ +7.12° (neat); 22.3% ee;[20] mass spectrum, *m/e* (relative intensity) 118 ($M^{+\cdot}$, 31), 89 (base peak).

Stereochemistry of Trifluoroacetolysis of (*S*)-(+)-1b. (*S*)-(+)-**1b** [7.92 g (0.033 mol); $[\alpha]^{20}_D$ +1.16° (*c* 12, acetone); 16.5% ee] was dissolved in a mixture of CF_3COOH (9.76 g, 6.55 mL) and CH_2Cl_2 (6.55 mL). After 13 days at 23 °C the reaction was quenched by distilling off the volatile fraction of the reaction products. This fraction was neutralized with an aqueous solution of sodium carbonate, and the organic layer was then concentrated by removal of CH_2Cl_2 through a Vigreax column, yielding a solution of 2-butyl trifluoroacetate (**4b**) in CH_2Cl_2 (600 μL; $[\alpha]^{20}_{313.5}$ −0.179°). Attempts to separate the trifluoroacetate **4b** from CH_2Cl_2 by means of preparative gas chromatography have failed. The concentration of **4b** in this solution was determined by using gas chromatography with automatic integration of the peak areas. Determination of the concentration of (−)-**4b** in CH_2Cl_2 was performed on the basis of the calibration curve obtained for four solutions of different concentrations of trifluoroacetate (+)-**4b** in CH_2Cl_2. The calculated concentration of the solution was equal to 66 mg of **4b** in 1 mL of CH_2Cl_2. This corresponds to a specific rotation of pure 2-butyl trifluoroacetate of $[\alpha]^{20}_{313.5}$ −2.71° (*c* 6.6, CH_2Cl_2).

(*S*)-(+)-2-Butyl Trifluoroacetate (4b). (*S*)-(+)-2-Butyl alcohol [2 g (0.027 mol); $[\alpha]^{20}_D$ +8.26° (neat); 59.4% ee[16]] was added dropwise with stirring to trifluoroacetic anhydride (5.8 g, 0.027 mol) at 10 °C. The mixture was stirred for an additional

(33) Edmundson, R. S. *Tetrahedron* **1965**, *21*, 2379.
(34) Edmundson, R. S. *Tetrahedron* **1964**, *20*, 2781.

1 h, and diethyl ether (15 mL) was added. The solution was washed with aqueous sodium carbonate and water and was dried with anhydrous Na_2CO_3. Ether was removed by distillation through small helix-packed column. The residual fraction was distilled and the fraction with a boiling point of 65–67 °C was collected: yield 1.5 g; $[\alpha]^{20}_D$ +12.9° (neat), $[\alpha]^{20}_{313.5}$ +44.2° (c 6.4, CH_2Cl_2).

Determination of Optical Purity of 1b. Determination of optical purity of (–)-**1b** was accomplished by using isotope dilution method.[19] 2-(2-Butoxy)-2-thiono-4,4,6,6-tetradeuterio-5,5-dimethyl-1,3,2-dioxaphosphorinane (**1b**-*4,4,6,6-d*$_4$) as the labeled racemate was used. **1b**-*4,4,6,6-d*$_4$ was obtained analogously as the compounds listed in the Table III 3 from 2,2-dimethyl-1,1,3,3-tetradeuteriopropane-1,3-diol. For **1b**-*4,4,6,6-d*$_4$: yield 70%; mp 63–64 °C; deuterium content 100%; ^{31}P NMR δ 59.8.

Compound **1b**-*4,4,6,6-d*$_4$ (241.5 mg, 0.998 mmol) and (*R*)-(–)-**1b** [202.8 mg (0.852 mmol); $[\alpha]^{20}_{589}$ –6.66° (c 9.7, acetone)] were dissolved in acetone, and then the solvent was evaporated. The optical rotation of the residue has been assigned. The residue was dissolved in warm hexane and allowed to crystallize. The crystals were filtered off, were washed twice with cold ether, and were analyzed for deuterium content and optical rotation. Calculations of the maximum optical rotation of phosphorothionate **1b** were performed according to formula shown in eq 1, where $[A]$ is the absolute rotation of phosphorothionate, S_i is

$$[A]^2 = \frac{S_i n^2[\alpha]^2 - S_0 mn[\alpha][\alpha]_i}{S_i(m+n) - S_0 m(m+n)} \quad (1)$$

the content of the labeled compound in the recrystallized sample (S_i = 0.499), n is the weight of the test sample of phosphorothionate (n = 0.2028 g), m is the weight of labeled racemate added to the test sample (m = 0.2415 g), $[\alpha]$ is the rotation of the test sample of phosphorothionate $[\alpha]^{20}_{589}$ –6.66 (c 9.7, acetone), $[\alpha]_i$ is the rotation of the recrystallized sample $[\alpha]_i{}^{20}_{589}$ –4.117° (c 10, acetone), S_0 is the content of labeled compounds in the starting racemate (S_0 = 1.0 mol of D/mol of compound). The calculated absolute rotation of pure enantiomer of phosphorothioate **1b** is $[\alpha]_{589}$ ±7.02 ± 0.08.

The following control experiment was performed. Racemic phosphorothioate **1b** and phosphorothionate **1b**-*4,4,6,6-d*$_4$ were mixed together, and the sample was analyzed for deuterium content. The mixture was then recrystallized (vide supra) from hexane, and the deuterium content analysis was performed again. This analysis clearly showed that the deuterium content of the recrystallized sample was essentially the same as that of the starting mixture.

Solvolysis–Rearrangement Reactions of Phosphorothionates 1 in the Presence of the Anisole. The corresponding phosphorothioates **1a,b,e–h** (1.5×10^{-4} mol) were dissolved in a mixture (3 mL) of the anisole (162 mg, 1.5×10^{-3} mol) and trifluoroacetic acid under vacuum-line conditions. Reactions were carried out at 25 °C. The progress of the reactions was followed by ^{31}P NMR. In the reactions of compounds **1a,b,e** besides signals from corresponding rearrangement products **2a,b,e** the appearance of the signal from **3** was observed. After the reaction was more than 90% complete, the samples were worked up in the usual manner. The products of the reactions were analyzed by means of gas chromatography/mass spectrometry (glass column, 10% OV-101 on Chromosorb WAW). The presence of the two isomers of alkylated anisole **5** was proved in the products of the reactions of compounds **1a,b,e**. The reaction mixture resulting from the reactions of compounds **1h,f,g** did not contain any traces of methylated, methylbenzylated, or diphenylmethylated anisoles, respectively. Mass spectrum for **5**, *m/e* (relative intensity): **5a** (slow) 150 ($M^{+\cdot}$, 22), 135 (base peak), (fast) 150 ($M^{+\cdot}$, 25), 135 (base peak); **5b** (slow) 164 ($M^{+\cdot}$, 20), 136 (base peak), (fast) 164 ($M^{+\cdot}$, 22), 136 (base peak); **5e** (slow) 198 ($M^{+\cdot}$, base peak), (fast) 198 ($M^{+\cdot}$, base peak).

"External" Phosphorothioate Anion Incorporation Measurements. Compound **1b**-*4,4,6,6-d*$_4$ (48.4 mg, 0.2 mmol) and the tetramethylammonium salt of **3** (53 mg, 0.2 mmol) were dissolved in 2 mL of anhydrous TFA under vacuum. From time to time a small portion of this solution was sampled through a Teflon stopcock and was worked up in the usual manner. The mixture was divided by means of preparative TLC, and both the recovered substrate and the product were subjected to deuterium analysis. Incorporation of an "external anion" into the product is essentially constant (10.5% incorporated nondeuterated **2b**). A small amount of nondeuterated **1b** was detected in the regenerated substrate (1.5% after 2 days).

Determination of the Relative Concentration of Styrene during the Rearrangement of 2f in Trifluoroethanol. A 0.2 M solution of **2f** in trifluoroethanol at 23 °C was subjected to GC analysis (2-m column filled with 10% OV-101 on Chromosorb WAW). Styrene concentrations were measured on the basis of the peak areas corresponding to styrene and an internal standard (cumene). This analysis showed a continuous increase in the concentration of styrene which achieved a maximum after 90 min and then slowly decreased.

Acknowledgment. This project was financially assisted by the Polish Academy of Sciences, Grant no. M.R.-I-12.1.7.

Registry No. 1a, 62891-12-7; (*R*)-(–)-**1b**, 75768-20-6; (*S*)-(+)-**1b**, 75768-21-7; (±)-**1b**, 75801-56-8; (±)-**1b**-*4,4,6,6-d*$_4$, 75768-22-8; **1c**, 75716-64-2; **1d**, 75716-65-3; **1e**, 75768-23-9; (*R*)-(+)-**1f**, 71719-69-2; **1g**, 75768-24-0; **1h**, 1005-97-6; **2a**, 75768-25-1; (*S*)-(+)-**2b**, 75768-26-2; (±)-**2b**, 75801-57-9; **2c**, 75716-66-4; **2d**, 75716-67-5; **2e**, 75768-27-3; (*R*)-(+)-**2f**, 71719-72-7; **2g**, 75768-28-4; **2h**, 1005-98-7; **3**, 45734-11-0; **4a**, 400-38-4; (*R*)-(–)-**4b**, 66585-35-1; (*S*)-(+)-**4b**, 66585-22-6; **4c**, 6864-58-0; **4d**, 37729-50-3; **4e**, 351-70-2; (*R*)-(+)-**4f**, 58287-20-0; **5a** (*o*-iosmer), 2944-47-0; **5a** (*p*-isomer), 4132-48-3; **5b** (*o*-isomer), 18272-71-4; **5b** (*p*-isomer), 4917-90-2; **5e** (*o*-isomer), 883-90-9; **5e** (*p*-isomer), 834-14-0; 2,2-dimethyl-1,1,3,3-tetradeuteriopropane-1,3-diol, 75768-29-5; diethyl dimethylmalonate, 1619-62-1; (*S*)-(+)-2-butanethiol, 20407-74-3; ethyl iodide, 75-03-6; (*S*)-(+)-2-butyl ethyl sulfide, 20407-75-4; (*S*)-(+)-2-butyl alcohol, 4221-99-2; 2-methoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane, 1005-69-2; 2-isopropoxy-5,5-dimethyl-1,3,2-dioxaphosphorinane, 1009-82-1; (±)-2-(1-methylpropoxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane, 75768-30-8; 2-(2-butenyloxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane, 75768-31-9; 2-(1-methyl-2-propenyloxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane, 75768-32-0; 2-benzyloxy-5,5-dimethyl-1,3,2-dioxaphosphorinane, 75768-33-1; (*R*)-(+)-2-(α-methylbenzyloxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane, 71719-77-2; 2-(α-phenylbenzyloxy)-5,5-dimethyl-1,3,2-dioxaphosphorinane, 75768-34-2; 2-chloro-5,5-dimethyl-1,3,2-dioxaphosphorinane, 2428-06-0; methanol, 67-56-1; 2-propanol, 67-63-0; (±)-2-butanol, 15892-23-6; 2-buten-1-ol, 6117-91-5; 3-buten-2-ol, 598-32-3; benzyl alcohol, 100-51-6; (*R*)-(+)-α-methylbenzyl alcohol, 1517-69-7; α-phenylbenzyl alcohol, 91-01-0.