Reaction of Thiolo and Selenolo Esters of Phosphorus Acids with Halogens. 1. Stereochemical and ^{31}P NMR Studies of Reaction of *S*-Methyl *tert*-Butylphenylphosphinothiolate with Elemental Chlorine and Sulfuryl Chloride[1]

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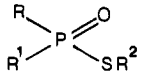
Reaction of *S*-methyl *tert*-butylphenylphosphinothiolate (4) with elemental chlorine and sulfuryl chloride involves chlorolysis of the P–S bond and formation of the *tert*-butylphenylphosphinochloridate 5. It is demonstrated here that the stereoselectivity of the reaction of chiral ester 4 depends on the parameters of the reaction, and the favored stereochemistry is retention of the configuration at the phosphorus atom. Three intermediate products, [*t*-BuPhP(O)S(Cl)Me]$^+$Cl$^-$, 6, [*t*-BuPhP(SMe)OP(O)PhBu-*t*]$^+$Cl$^-$, 7, and [*t*-BuPhP(Cl)OP(O)PhBu-*t*]$^+$Cl$^-$, 8, were detected by ^{31}P NMR studies; they are responsible for the stereochemical course of the reaction. The salt 7 is formed by nucleophilic attack of 4 on 6, while 8 is generated by ligand exchange in the salt 7. Structures of 7 and 8 were confirmed by independent synthesis from a P^{III}–O–P^{IV} anhydride via Arbuzov-type reaction with methanesulfenyl chloride and elemental chlorine.

The thiolo esters of phosphorus acids 1 show interesting chemistry,[2] stereochemistry,[3] and biological activity.[4] Some of these compounds have been manufactured on an industrial scale as pesticides[4] and others have excited military interest.[5] Thiolo esters 1 can be prepared by a



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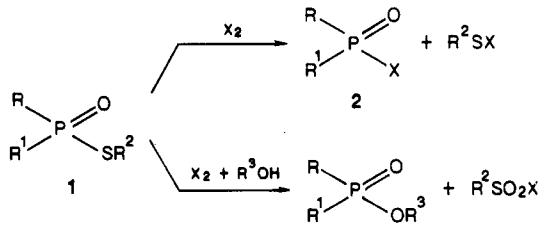
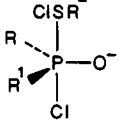
variety of methods.[2] Since the group of optically active monothio acids $RR^1P(S)OH$ is readily available, alkylation leading to optically active 1[3] is the preparative method of choice.

The reactions of 1 with halogenating reagents such as elemental chlorine, bromine,[6] and sulfuryl chloride[7b] have been known for almost 30 years. These reactions proceed via different pathways, depending on the reaction medium.[6,7] Optically active chloridates 2 have been successfully



R^3 = H or alkyl

synthesized by the reaction of 1 with elemental chlorine and sulfuryl chloride in inert solvents.[7] This kind of reaction is often interpreted by Scheme I, but in this case and others[7b,f-h] the accumulated experimental facts are not consistent with it. Scheme I consists of electrophilic attack of halogen on the sulfur atom with formation of the corresponding chlorosulfonium salt 3 (step a) which subsequently decomposes by nucleophilic attack of the chloride anion on the phosphorus atom (step b). When groups R and R^1 are alkyl or aryl, the strongly electronegative ligands $-(Cl)^+SR^2$ and Cl would be likely to take the apical positions of the intermediate pentacoordinate species with trigonal-bipyramid geometry in step b. This should result



in inversion of configuration at the phosphorus center. Contrary to this prediction, retention of configuration was observed,[7b,f-h] and in many cases it was accompanied by considerable racemization. The stereochemical course of the chlorinolysis was influenced by factors such as solvent, halogenating agent, and addition of mercuric chloride.

The aim of this investigation was to examine the stereochemical course of the chlorinolysis reaction of organic phosphorus thiolo esters by using a model which, due to the presence of a sterically crowded phosphorus atom, should reduce the rate of any intermediate step involving nucleophilic displacement at the reaction center. This would increase the chances of detecting intermediates by spectroscopy. Our paper is devoted to detailed stereochemical and spectroscopic studies of the chlorinolysis reaction of the *S*-methyl *tert*-butylphenylphosphinothiolate, 4. In addition to steric hindrance at the phosphorus center, another advantage of the model thiolate 4 is the lack of side reactions which may occur when alkoxy

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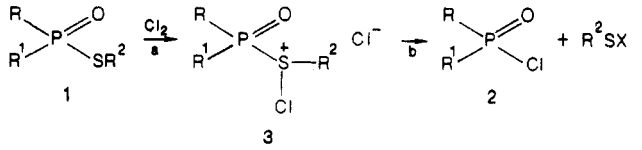
Table I[a]

$$t\text{-BuPhP(O)SMe} \xrightarrow[(SO_2Cl_2)]{Cl_2} t\text{-BuPhP(O)Cl} + MeSCl$$
4 5

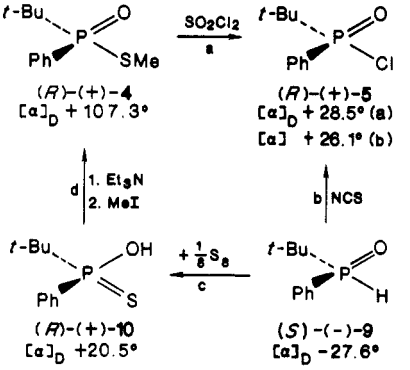
no.	$[\alpha]^{25}_D$, deg	opt purity, %	config	$[\alpha]^{25}_D$, deg	opt purity, %	config	stereochemistry	stereoselectivity	solvent	chlorinating agent
1	+107.3	66	*R*	+28.5	57	*R*	ret.	86	C_6H_6	SO_2Cl_2
2	−106.9	66	*S*	−30.6	61	*S*	ret.	92	C_6H_6	SO_2Cl_2
3	+89.1	55	*R*	+9.4	19	*R*	ret.	34	CH_2Cl_2	Cl_2
4	−131.9	81	*S*	−20.2	40	*S*	ret.	49	CH_2Cl_2	SO_2Cl_2
5	+154.0	95	*R*	+40.6	81	*R*	ret.	85	CCl_4	Cl_2
6	−162.0	100	*S*	−20.0	40	*S*	ret.	43	CH_2Cl_2/CCl_4	Cl_2
7[b]	−162.0	100	*S*	+19.0	38	*R*	inv.	38	CH_2Cl_2	SO_2Cl_2

[a] All optical rotation measurements were made in benzene (*c*, 0.01–0.05 g/1 mL). Determinations of optical purities were based on assumption that the *tert*-butylphenylphosphinic chloride (**5**) with $[\alpha]^{23}_D$ +49.8° (highest known value) is optically pure. For the thiolate **4** the specific rotation value of (±) 162.6° corresponding to 100% of its optical purity was estimated from that of optically pure *tert*-butylphenylphosphinothioic acid. [b] Experiment carried out in the presence of mercuric chloride (2 mol $HgCl_2$/1 mol of **4**).

Scheme I

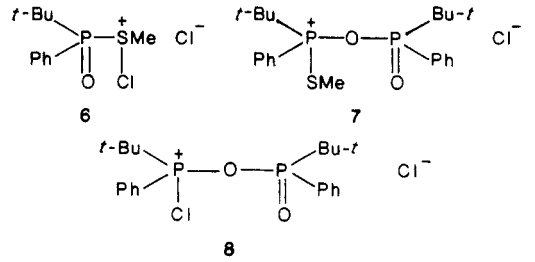


Scheme II[a]



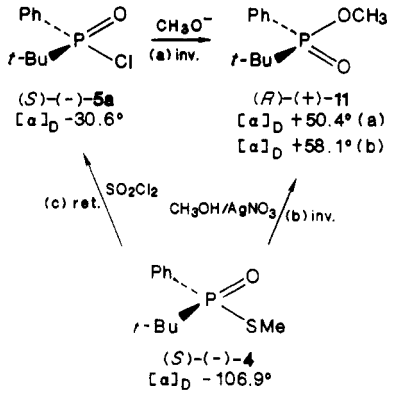
[a] NCS = *N*-chlorosuccinimide.

or aryloxy groups are present. The work is arranged in the following sequence: After establishing the stereochemical course of the reaction between **4** and elemental chlorine or sulfuryl chloride leading to the chloridate **5**, results of ^{31}P FT NMR spectroscopic studies are discussed. These studies demonstrate the formation of intermediates containing a single phosphorus atom **6** related to the salt **3** and two types of intermediates **7** and **8** in which two



phosphorus atoms are bridged by an oxygen atom. It is shown that all three intermediates **6**, **7**, and **8** are responsible for the stereochemical course of the chlorinolysis of **4** and formation of organophosphorus side products other than **5**.

Scheme III



Results

Stereochemical Course of the Chlorinolysis of 4. The optically active thiolates **4** were prepared by S-methylation of the corresponding *R*-(+) and *S*-(−) phosphinothioic acids *t*-BuPhP(S)OH. Their optical purity and absolute configuration is known from our previous stereochemical studies and those of other authors.[8]

Specific rotations and optical yields for chlorination reactions performed at 293 K are collected in Table I.

It can be seen from Table I that the dominating stereochemistry is retention of configuration accompanied in many cases by considerable racemization. Inversion is observed only when the chlorination reaction is carried out in the presence of mercuric chloride. It is also evident that retention of configuration is favored when weakly polar solvents, such as benzene, carbon tetrachloride, and sulfuryl chloride as chlorinating reagent, are used. This is in agreement with the observations of Hall and Inch.[7f] Evidence of the reaction stereochemistry has been based on two stereochemical cycles exemplified in Schemes II and III, connected with the experiment Nr 1 and 2, respectively (see Table I). Scheme II consists of the podal diligostatic cycle[9] involving reactions preceeding with retention of configuration. The *tert*-butylphenylphosphine oxide (**9**) of known configuration[10] was transformed by action of *N*-chlorosuccinimide (NCS) into the chloridate **5**[10a] (reaction b). The same oxide was transformed into *tert*-butylphenylphosphinothioic acid (**10**) by addition of elemental sulfur (reaction c).[10a,b] The latter was methylated to form the thiolate **4** (reaction d). Reactions b and

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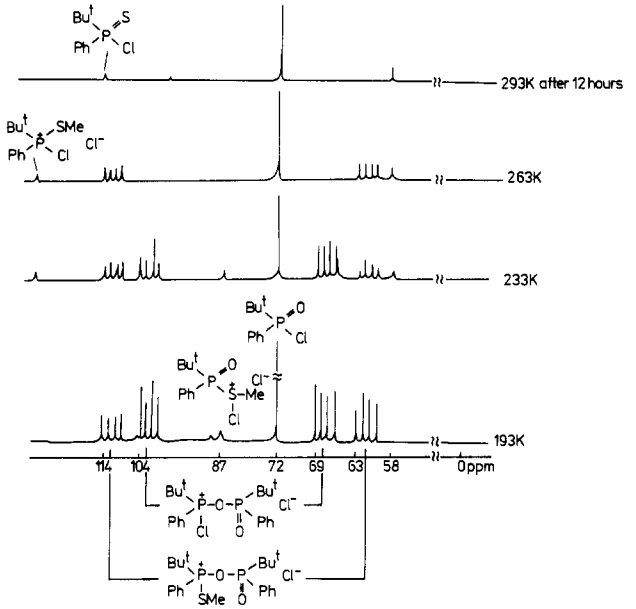

Figure 1. ^{31}P NMR spectra of (R,S)-**4** + Cl_2. The sample was dissolved in CH_2Cl_2 and spectra were run on a JEOL JNM-FX 60 FT spectrometer. 85% H_3PO_4 was used as external standard. The spectra were monitored at 1/2 h intervals unless otherwise stated.

c are known to proceed with retention of configuration.[10] The same applies to the reaction d which does not affect any bond attached to the chiral phosphorus atom. Since there is no ligand metathesis in the cycle, the reaction (a) representing the chlorinolysis of the phosphorus–sulfur bond of **4** occurs with retention of configuration. The cycle shown in Scheme III as a three-reaction podal triligostat cannot involve ligand metathesis.[9] Reactions a and b involving transformation of **5** into **11** by methoxide ion and **4** into **11** by methanol in the presence of silver nitrate are most likely to proceed with inversion of configuration.[3,11] The cycle is podal; therefore, reaction c must proceed with retention of configuration.

The reaction of *S*-methyl *tert*-butylphenylphosphinothiolate (**4**) with sulfuryl chloride performed in methylene chloride solution in the presence of mercuric chloride (reaction 7, Table I) led to the chloridate **4** of opposite configuration. Therefore, this reaction proceeds with inversion of configuration at the phosphorus atom. Obvi-

$$\underset{[\alpha]_D\ -162.0^\circ}{(S)\text{-}(-)\text{-}\mathbf{4}} \xrightarrow[2HgCl_2]{SO_2Cl_2} \underset{[\alpha]_D\ +19.0^\circ}{(R)\text{-}(+)\text{-}\mathbf{5}}$$

ously this stereochemical data cannot be rationalized on the basis of the mechanisms in Scheme I involving the chlorosulfonium salt **3a** (R = *t*-Bu, R^1 = Ph, R^2 = Me). It will be rationalized in the following section together with ^{31}P NMR spectroscopic results.

^{31}P NMR Spectroscopic Studies. Intermediates Containing Two Phosphorus Atoms. ^{31}P FT NMR studies of the reacting system **4** + Cl_2 (SO_2Cl_2) were performed in the temperature range 173 to 293 K in methylene chloride or toluene. Substrates dissolved in the appropriate solvent were cooled in liquid nitrogen under dry argon and then mixed together. The spectra were usually monitored at 1/2 h intervals. Concentrations of the starting material **4**, intermediates **6**, **7**, and **8**, and final product **5** were estimated by integration of the corresponding signals. These studies are tedious since reproducibility of results depends on many factors which are

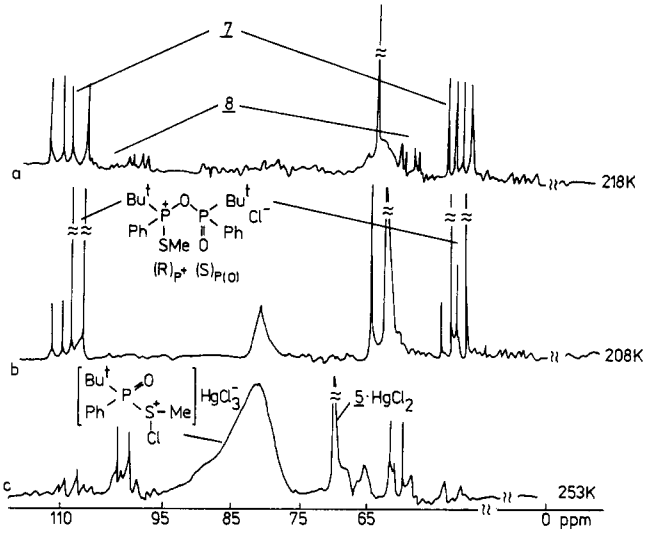

Figure 2. ^{31}P NMR spectra of reaction mixture of (a) (R,S)-**4** with SO_2Cl_2; (b) (R)-(+)-**4** (ee 68%) with SO_2Cl_2; (c) (R)-(+)-**4** (ee 68%) with SO_2Cl_2 and $HgCl_2$ (1:1:1). All solution ca. 1 M in CH_2Cl_2.

not always easy to control. For this reason only those spectra with a high reproducibility factor were taken into account.

Figure 1 depicts a typical set of spectra taken at various temperatures for the racemic (R,S)-**4** reacting with elemental chlorine in methylene chloride. A similar spectroscopic pattern was observed for the systems (R,S)-**4** + SO_2Cl_2 – CH_2Cl_2; (R)-(+)-**4** + SO_2Cl_2 – CH_2Cl_2, and (R)-**4** + SO_2Cl_2 + $HgCl_2$ – CH_2Cl_2. Selected spectra are presented in Figure 2. The spectra of toluene medium indicate the same intermediates as in methylene chloride but in somewhat different proportions. However, reproducibility of spectra in toluene is poor due to difficulties connected with the precipitation of reaction intermediates at low temperatures. It is reasonable to assume that signals in the region 114–100 ppm correspond to phosphonium-type structures and those at 68–60 ppm to species containing a phosphoryl group. The presence of two different phosphorus atoms bridged by oxygen is manifest in the multiplicity of spectral terms and coupling constants. The characteristic doublet of doublets is multiplied by two because salts **7** and **8** are formed as pairs of diastereoisomers. Signals 114.09 ppm and 62.36 ppm, $^2J_{PP}$ = 42.97 ± 1.95 Hz, are tentatively assigned to the diastereoisomer **7a**; signals 111.00 ppm and 61.12 ppm, $^2J_{PP}$ = 46.88 ± 1.95 Hz, to the diastereoisomer **7b**, signals 104.06 ppm and 68.65 ppm, $^2J_{PP}$ = 41.02 ± 1.95, to the diastereoisomer **8a**; and signals 102.63 ppm and 67.68 ppm, $^2J_{PP}$ = 46.88 ± 1.95, to the diastereoisomer **8b**. Although all these data are consistent with the presence of two species containing two different phosphorus atoms bridged by oxygen, a definite structural assignment was lacking. For this reason an independent synthesis of compounds **7** and **8** was undertaken. Employing our previous experience in chemistry of mixed anhydrides with tricoordinate and phosphoryl centers,[12a–c] the anhydride **14** was prepared by condensation of *tert*-butylphenylchlorophosphine (**12**) with *tert*-butylphenylphosphinic acid (**13**) in the presence of triethylamine under argon in methylene chloride. The anhydride **14** was formed, according to the ^{31}P NMR spec-

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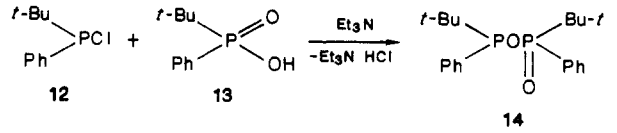
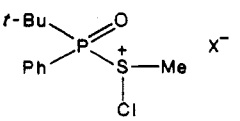


trum, in almost quantitative yield. After the reaction was complete no starting materials were detected, and only a small amount of the acid chloride **5** derived from the oxidation of **12**. The multiplicity and position of phosphorus atoms signals (Figure 3, spectrum a) are consistent with the observations of Lucenko et al.[12d] for similar anhydrides and are of sufficient diagnostic value for definite assignment of structure. The crude anhydride **14** was immediately used for further transformations. Scheme IV represents reactions of **14** with methanesulfenyl chloride and with elemental chlorine in methylene chloride solution. At 200 K the reaction between anhydride **14** and methanesulfenyl chloride led to the compound **7** which, on the basis of its ^{31}P NMR spectrum, was identical with that detected in the system (*R,S*)-**4** + Cl_2. The reaction of **14** with elemental chlorine was analogous. The ^{31}P NMR spectrum of the product **8** obtained had the same characteristics as the corresponding part of the spectrum of the system (*R,S*)-**4** + Cl_2. Superposition of spectra for synthetic products **7** and **8** gave the same picture as the system (*R,S*)-**4** + Cl_2, except for those peaks which corresponded to a species containing one phosphorus atom. This is clearly visible by comparison of spectra in Figures 1 and 3. It is evident from spectrum a (Figure 2) that, of the two intermediates containing two phosphorus atoms formed when (*R,S*)-**4** is allowed to react with sulfuryl chloride in methylene chloride solution, the salt **7** is predominant. Furthermore, a relatively low degree of racemization is observed in this case (Table I). The system (*R*)-(+)-**4** + SO_2Cl_2 + $HgCl_2$ in methylene chloride (spectrum c, Figure 2) is of special interest because, in contrast to other cases, inversion of configuration is observed at the phosphorus center. After addition of an equivalent amount of mercuric chloride at 195 K, it is evident from the chemical shift in 70.50 ppm region that the starting thiolo ester (*R*)-(+)-**4** ($\delta_P(CH_2Cl_2)$ +66.3 ppm) is complexed. The complex is stable at ambient temperature and further addition of the salt does not cause any changes in chemical shift. In the presence of sulfuryl chloride, chemical changes are observed at 243 K. The characteristic spectrum c at 253 K is shown in Figure 2. The broad band in the region 80–90 ppm can be assigned to the salt **15** in equilibrium with other species such as **6**.

Interestingly, careful monitoring of the ^{31}P NMR spectrum of the substrate (*R,S*)-**4** interacting with an excess of elemental chlorine in methylene chloride in the temperature range 178 K to 263 K (Figure 4) gave the following picture. Two distinct signals at 93.67 ppm and 86.71 ppm were observed at 178 K at lower field than the corresponding substrate **4**; they gradually coalesced at 213 K into a single peak at 88.21 ppm which vanished at 263 K. The signal at 93.67 ppm, for which structure **16** is assumed, is close to that observed for the (*R,S*)-**4** + SO_2Cl_2 + $SbCl_5$ system in which the salt **17** is formed. The signal at 86.71



15 (X = $HgCl_3^-$), 95.32 ppm at 263 K
16 (X = Cl_3^-), 93.67 ppm at 173 K
17 (X = $SbCl_6^-$), 92.42 ppm at 203 K

ppm close to that assigned for the sulfonium salt **15** is likely to be a CT-type complex. This type of species in

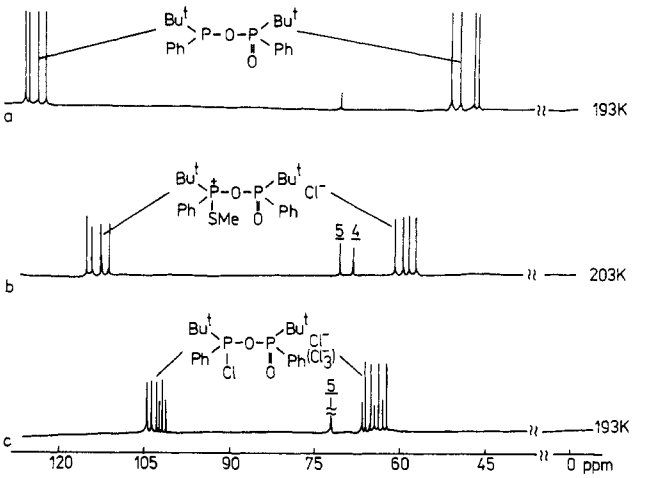


Figure 3. ^{31}P NMR spectra of (a) freshly prepared anhydride **14** in CH_2Cl_2; (b) after addition of CH_3SCl into this solution; (c) the sample of anhydride **14** after addition of elemental chlorine (excess).

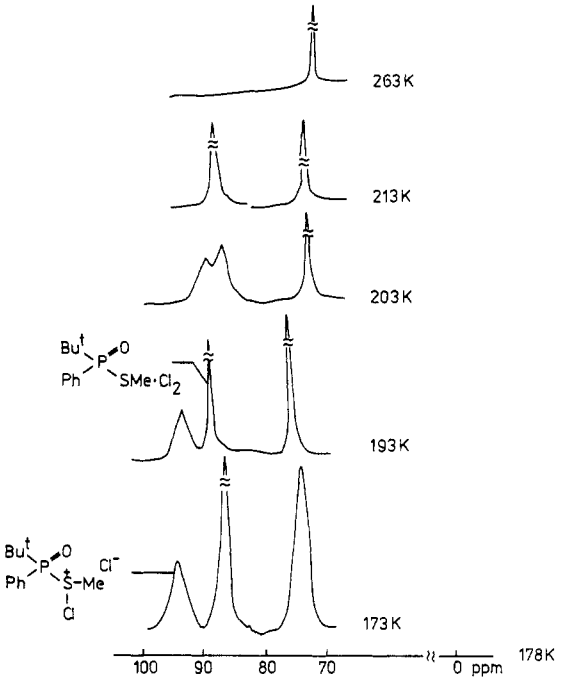
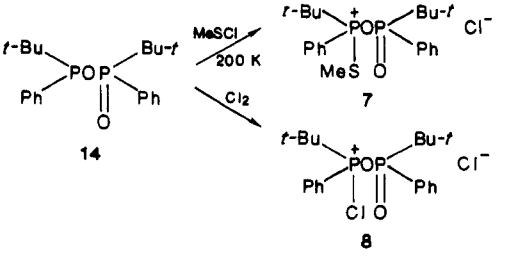


Figure 4. Fragment of ^{31}P NMR spectrum of (*R,S*)-**4** + Cl_2.

Scheme IV

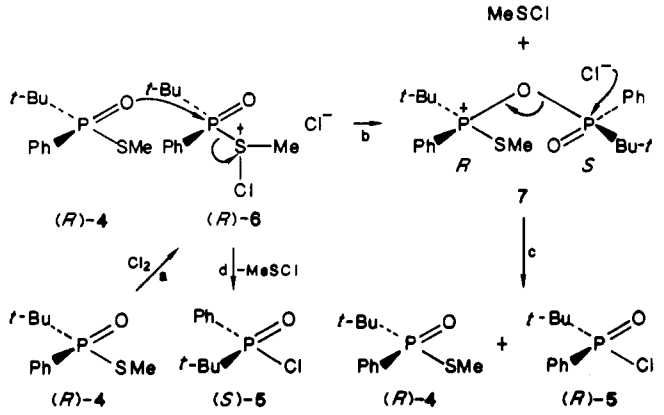


equilibrium with sulfonium salts is known in organic sulfur chemistry[13] and similar equilibria are likely to occur in this case.

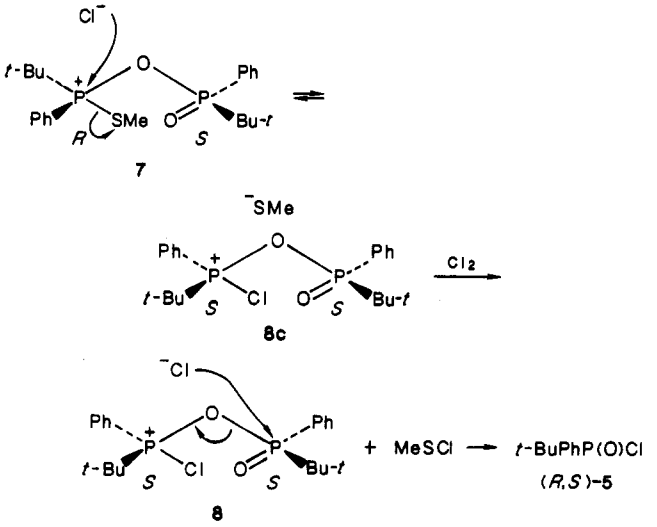
In addition to the main products **5** and the intermediates already discussed, three other compounds containing

(13) (a) Marino, J. P. In *Topics in Sulfur Chemistry*; Senning, A., Ed.; Georg Thieme: Stuttgart, 1976; p 32. (b) Wilson, G. E., Jr. *Tetrahedron* **1982**, *38*, 2597–2625. (c) Wilson, G. E., Jr.; Chang, M. M. Y. *J. Am. Chem. Soc.* **1974**, *96*, 7533–7537.

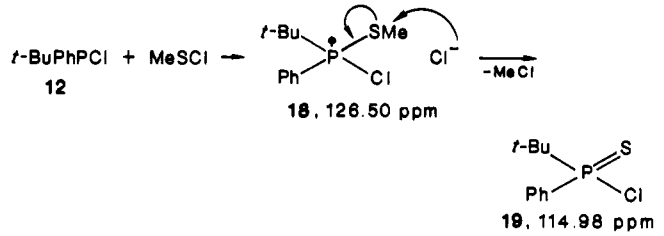
Scheme V



Scheme VI



phosphorus were noticed. The signal at 115.8 ppm (Figure 1) corresponds to the *tert*-butylphenylphosphinothioic chloride (**19**). The signal at 126.66 ppm (Figure 1), which gradually diminishes, is attributed to the phosphonium salt **18**, which is believed to be precursor of **19** (Figure 1). The structure of **18** was confirmed by independent synthesis from *tert*-butylchlorophenylphosphine (**12**) and methanesulfenyl chloride. It was found that the phosphonium



salt **18** decomposes thermally into the chloridate **19** by nucleophilic attack of the chloride anion on the methyl group. The origin of the phosphonium salt **18** will be discussed later. The signal δ 57.4 corresponds to *tert*-butylphenylphosphinic acid.

Discussion

It has been shown in the first part of this paper that, in the case of the model thiolo ester **4** with a sterically crowded phosphorus atom, intermediate products **7** and **8** are formed which contain two phosphorus atoms bonded through an oxygen bridge. This allows a rational mechanistic explanation of the somewhat unexpected stereochemical course of the reaction. It is clear that the intermediate **7** can only be formed by nucleophilic attack of a phosphoryl-group oxygen[15] of the thiolo ester **4** on the sulfonium salt **6** containing an excellent leaving group as in Scheme V. Intermediate **7** collapses into the starting thiolo ester **4** and the chloridate **5**. There is good evidence, mentioned in the introductory part of this paper, that all known reactions of the system *t*-BuPhP(O)X with nucleophiles proceed with inversion of configuration at phosphorus.[18b] Therefore, reaction between **4** and **6** (reaction b) should occur with inversion of configuration at the phosphoryl center. There is no bond breaking in the formation of the phosphonium center and consequently retention of configuration is expected there. The decomposition of intermediate **7** by nucleophilic attack of chloride ion (reaction c) also should proceed with inversion of configuration at the phosphoryl center and retention at the phosphonium center. The phosphonium group acts as an excellent leaving group. The net stereochemical outcome of the reaction series a, b, and c presented on Scheme V is formation of the chloridate **5** having the same configuration as the starting thiolo ester **4** following two consecutive inversions at the same phosphorus atom. On the other hand, the mechanistic scheme presented above consistent with retention does not account for the high degree of racemization observed. Three sources of racemization can be considered. The key intermediate **6** is likely to undergo nucleophilic displacement as a free ion pair to yield the chloridate **5** with inversion of configuration at the phosphorus center (Scheme V, reaction d). It is difficult to estimate the importance of this reaction from our present experimental evidence compared with that between **4** and **6** leading to **7** which is responsible for retention. Some evidence comes from the observation that when sulfuryl chloride is employed as chlorinating agent, the degree of racemization is noticibly lower. It is likely that at a relatively low temperature the counterion $^{-}O_2SCl$ is present, and this ion shows lower nucleophilicity toward a tetracoordinate phosphorus atom than the chloride anion. So the decomposition of the ion pair **6** with chloride anion replaced by the $^{-}O_2SCl$ is slow but the reaction between **4** and **6** responsible for retention is not affected. It is also likely that predominant inversion observed when the reaction proceeds in the presence of mercuric chloride has its origin in electronic and steric factors favoring decomposition of the complexed intermediate of the type **6**

(14) Łopusiński, A.; Michalski, J.; Stec, W. J. *Liebigs Ann. Chem.* **1977**, 924–947.

(15) Nucleophilic and basic character of the phosphoryl group oxygen is well-known and its interaction with hard electrophiles leads to phosphonium salts.[16] Recently Dormoy and Castro (*Tetrahedron* **1981**, *37*, 3699–3706) have been able to disclose an intermediate **21** by low temperature ^{31}P NMR spectroscopy. Similar intermediates have been postulated in polymerization of organophosphorus compounds.[17]

$$(Me_2N)_3P^{+}OP(O)Cl_2Cl^{-}$$
21

(16) (a) Edmundson, R. S. In *Comprehensive Organic Chemistry*; Barton, D., Ollis, W. E., Eds.; Vol. 2, Sutherland, I. O., Ed.; Pergamon Press: Oxford, New York, Toronto, Sydney, Paris, Frankfurt, 1979; Chapter 10.5., p 1273, 1283. (b) Kosolapoff, G. M.; Watson, R. M. *J. Am. Chem. Soc.* **1951**, *73*, 4101–4102. (c) Kosolapoff, G. M. *Science (Washington, D.C.)* **1948**, *108*, 485. (d) Toy, A. D. F. *J. Am. Chem. Soc.* **1949**, *71*, 2268. (e) Simpson, P.; Zwierzak, A. *J. Chem. Soc., Perkin Trans. 1* **1975**, 201–204. (f) Auberg, T.; Gramstad, T.; Husebye, T. *Tetrahedron Lett.* **1979**, 2263–2264.

(17) Vogt, W. *Macromol. Chem.* **1973**, *163*, 89–109.

(18) (a) Michalski, J.; Mikołajczak, J.; Skowrońska, A. *J. Am. Chem. Soc.* **1978**, *100*, 5386–5390. (b) Krawiecka, B.; Michalski, J.; Skrzypczyński, Z. *J. Chem. Soc., Chem. Commun.* **1974**, 1022. (c) Retention of configuration in the first ligand exchange shown in Scheme VI cannot be excluded according to earlier work of Trippett et al. (*J. Chem. Soc. D* **1971**, 717). In such a case this route would also contribute to the product with retained configuration.

Table II.[a] ^{31}P NMR Analysis of the Reaction of 4 with Elemental Chlorine, SO_2Cl_2, and SO_2Cl_2 in the Presence of $HgCl_2$

		relative intensity of ^{31}P NMR signals											
		193 K			233 K			263 K			293 K		
compound	no.	i	ii	iii	i	ii	iii	i	ii	iii	i	ii	iii
t-BuPhP(O)SMe	4		55	100[b]		19[c]	100[b]						
t-BuPhP(O)SMe·XCl		6	12						4				
[*t*-BuPhP(O)S(Cl)Me]$^+X^-$	6									13			
[*t*-BuPhP(SMe)OP(O)*t*-BuPh]$^+X^-$	7	21	27		23	58		10	58				
[*t*-BuPhP(Cl)OP(O)*t*-BuPh]$^+Cl^-$	8	39			32	8			9	45			
t-BuPhP(O)Cl	5	34	5		37	14		70	26	42	80	68	100[d]
[*t*-BuPhP(SMe)]$^+Cl^-$	18				5			3				5	
t-BuPhP(S)Cl	19				3			2			5	3	
t-BuPhP(O)OH	13							15			15	18	

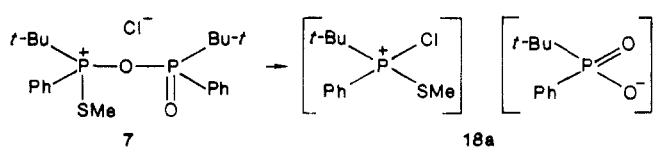
[a] X = Cl, $ClSO_2$, or $HgCl_3$; solvent CH_2Cl_2; (i) 4 + Cl_2 (1:1); (ii) 4 + SO_2Cl_2 (1:1); (iii) 4 + SO_2Cl_2 + $HgCl_2$ (1:1:1). [b] Complex with $HgCl_2$ and SO_2Cl_2, δ_P 74.29. [c] Broadened signals of complexed 4, δ_P 78.5. [d] Complex *t*-BuPhP(O)Cl·$HgCl_2$, δ_P 80.57 (prepared from *t*-BuPhP(O)Cl + $HgCl_2$ in CH_2Cl_2, δ_P 71.21).

rather than its reaction with the substrate 4.

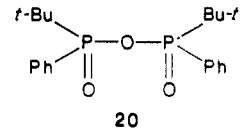
Another source of racemization is likely to be compound 8, which contains two phosphorus atoms. Compound 8 is formed from 7 via ligand exchange[18a] with inversion of configuration at the phosphonium center to give 8c which then reacts further (Scheme VI). Ligand exchange is facilitated by shifting the equilibrium from 7 toward salt 8c by converting the anions MeS^- by reaction with Cl_2-(SO_2Cl_2) to give MeSCl and Cl^-. Finally, the phosphonium salt 8 undergoes nucleophilic displacement at the phosphoryl center leading to two molecules of the chloridate 5. A racemic mixture is formed in this step since nucleophilic substitution at the phosphoryl center should occur with inversion of configuration providing two molecules of 5 with opposite configuration.[18c] Use of SO_2Cl_2 as chlorinating reagent may also reduce racemization because both the phosphoniums salt 7 and 8 are more stable in the presence of the counterion ^-O_2SCl. It is impossible without further experimental studies to estimate the participation of chlorine–chlorine exchange at the phosphonium center of 8. If such exchange is significant, it should lower the degree of racemization, providing a mixture of diastereoisomers *R,S* + *S,S*.

All these intermediates involved in the stereochemical control of the reaction are connected with displacements at tetracoordinate phosphorus centers. Even in acyclic organophosphorus compounds such displacements are difficult to rationalize in a very precise and definite manner in terms of electronic, steric, and solvent effects. A better understanding can only be gained by further kinetics studies of the reacting system. It is clear from our preliminary experiments, however, that chlorine–chlorine exchange in the chloridate 5 is so slow, even at ambient temperature, that its contribution toward racemization can be neglected.[19]

It has already been mentioned that side reaction is observed leading to *t*-BuPhP(S)Cl, 19, and *t*-BuPhP(O)OH, 13. The formation of the acid could be partly due to traces of water in the reacting system. It is almost certain that the appearance of 19 is inherently linked to formation of phosphonium salt 18a which results from decomposition of the compound 7. The acid 13 can also be formed from 18a. No evidence could be found for the formation *O*-methyl *tert*-butylphenylphosphinate. Therefore, it is reasonable to suppose that the salt 18a undergoes exchange of anion with other salts containing chloride as counterion to form 18, which decomposes into the chloride 19 and methyl chloride. The presence of methyl chloride was confirmed by ^1H NMR spectroscopy. The anion derived from the *tert*-butylphenylphosphinic acid (13) is likely to be the source of pyrophosphinates 20, through phosphorylation by species such as 6, 7, or 8 but not by 5, which is not reactive enough.



7 18a



20

Experimental Section

All melting and boiling points are uncorrected. Solvents and commercial reagents were purified by conventional methods before use. Solutions were dried over $MgSO_4$. NMR spectra were recorded with JEOL JNM-FX60FT (60 MHz, ^1H; 24.3 MHz, ^{31}P), Bruker HX-72 (90 MHz, ^1H; 36.4 MHz ^{31}P), and Tesla BS487 (80 MHz, ^1H) spectrometers; positive chemical shifts are downfield from external 85% H_3PO_4 and internal Me_4Si. Products were identified with a LKB Model 2091 gas chromatograph–mass spectrometer and/or ^{31}P NMR. Optical rotations were measured at 589 nm and 20 ± 2 °C on a Perkin-Elmer 141 polarimeter in benzene solution unless specified otherwise.

Starting Materials. *tert*-Butylphenylphosphinothioic acid was synthesized and resolved into optical antipodes by known methods.[8a,b,20] Methanesulfenyl chloride[21] was prepared from the corresponding disulfide by chlorination with sulfuryl chloride, and crude product was used in subsequent reactions.

Low-Temperature ^{31}P NMR Measurements. A 10-mm NMR tube (cooled N_2 liquid or acetone–CO_2) was charged with equimolar amounts (unless stated otherwise) of *S*-methyl *tert*-butylphenylphosphinothiolate (4) (ca. 0.5–1.0 mmol) and the chlorinating agent in toluene or methylene chloride. All operations were carried out in a dry argon atmosphere. The tube was sealed off and the progress of the reaction was monitored periodically by ^{31}P NMR FT. The temperature was gradually increased from 173 K (193 K) to room temperature. The spectra were recorded 1 h after the substrates were mixed and then in 1/2 h intervals, and in some cases spectra were recorded during the next day. Table II shows the results of ^{31}P NMR analysis of the reaction mixtures at 193, 233, 263, and 293 K; in Table III are given ^{31}P NMR chemical shifts of the intermediate products 7 and 8.

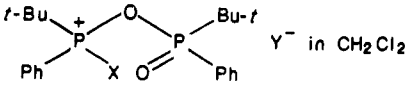
***S*-Methyl *tert*-Butylphenylphosphinothiolate (4).** To a solution of *tert*-butylphenylphosphinothioate (6.42 g, 0.03 mol) in benzene (50 mL) were added triethylamine (3.03 g, 0.03 mol) and iodomethane (5.00 g, 0.035 mol) successively at 20 °C. The

(19) Optically active 5 (concn 0.1 M) mixed with $Et_4N^+Cl^-$ (concn 0.02 M) at 298 K has not changed its optical rotation value during more than 7 h.

(20) Hoffmann, H.; Schellenbeck, P. *Chem. Ber.* **1966**, *99*, 1134–1142.

(21) Schöberl, A.; Wagner, A. In *Methoden der Organischen Chemie (Houben-Weyl)*; Müller, E., Ed.; Georg Thieme: Stuttgart, 1955; Vol. 9, p 271.

Table III. ^{31}P NMR Chemical Shifts[a] and Coupling Constants of Phosphonium Salts 7a–f and 8a–e



no.	X	Y⁻	δ_{P^+}, ppm	$\delta_{P(O)}$, ppm	$J_{P^+OP(O)}$, Hz	temp,[f] K
7a[b]	SMe	Cl	113.8 (d)	61.7 (d)	45	253 (273
7b			111.4 (d)	61.1 (d)	47	
7c	SMe	$HgCl_3$	113.6 (d)	61.7 (d)	45	243 (293)
7d			110.7 (d)	60.0 (d)	47	
7e[c]	SMe	SO_2Cl	113.5 (d)	61.6 (d)	45	223
7f			110.7 (d)	60.6 (d)	47	
7a[d]	SMe	Cl	113.7 (d)	61.8 (d)	45	193
7b			110.7 (d)	60.5 (d)	47	
8a[b]	Cl	Cl	103.8 (d)	68.3 (d)	41	253 (253)
8b			102.9 (d)	67.7 (d)	47	
8d	Cl	$HgCl_3$	103.5 (d)	67.9 (d)	43	263 (273)
8e			102.7 (d)	67.2 (d)	49	
8a[e]	Cl	$Cl(Cl_3)$	103.5 (d)	67.8 (d)	41	193
8b			102.1 (d)	67.1 (d)	47	

[a] The dynamic situation encountered in the reactions is responsible for the variations in the ^{31}P NMR shift values. [b] From reaction of **4** with Cl_2. [c] From reaction of **4** with SO_2Cl_2. [d] From reaction of **14** with MeSCl. [e] From reaction of **14** with Cl_2. [f] Temperature at which the spectrum was measured; in parentheses are given the highest temperatures at which the corresponding salt was observed in the ^{31}P NMR spectrum.

precipitation of triethylammonium iodide was observed immediately. The reaction mixture was kept overnight, triethylammonium iodide was filtered off, and the filtrate was washed with water (3 × 10 mL), dried, concentrated, and distilled at 84 °C/0.03 mmHg to give *S*-methyl *tert*-butylphenylphosphinothiolate (**4**) (5.55 g, 81%): mp 36–38 °C (hexane); ^1H NMR (CCl_4) δ 1.10 (9 H, d, $^3J_{HP}$ = 16 Hz), 2.07 (3 H, d, $^3J_{HP}$ = 10 Hz), 7.53–7.91 (5 H, m); ^{31}P NMR (CH_2Cl_2) δ +66.63, +63.25 (toluene) (lit.[8a] bp 118–122 °C/0.6–0.7 mmHg, ^1H NMR τ 8.74 (9 H, d, J_{PH} = 17 Hz), 7.82 (3 H, d, J_{PH} = 11 Hz), 1.8–2.6 (5 H, m)). Anal. ($C_{11}H_{17}POS$) C, H, P, S. Starting from (*R*)-(+)- or (*S*)-(−)-*tert*-butylphenylphosphinothioic acid, $[\alpha]_D$ +17.50° (*c* 1.96, methanol) and $[\alpha]_D$ −20.72° (*c* 1.56, methanol), (*R*)-(+)- or (*S*)-(−)-*S*-methyl *tert*-butylphenylphosphinothiolate (**4**), $[\alpha]_D$ +107.73° (*c* 0.75) and $[\alpha]_D$ −106.90° (*c* 1.94), were obtained, respectively.

Chlorinolysis of *S*-Methyl *tert*-Butylphenylphosphinothiolate (4). (a) With Sulfuryl Chloride. A solution of sulfuryl chloride (4.0 g, 0.03 mol) in benzene (5 mL) was added dropwise to a stirred solution of **4** (6.4 g, 0.028 mol) in benzene (50 mL) at 0–5 °C. The stirring was continued for 4 h at room temperature, and then the reaction mixture was concentrated in vacuo and distilled at 70 °C/0.15 mmHg to give *tert*-butylphenylphosphinic chloride (**5**) (5.0 g, 78%), solidified after distillation: mp 57–60 °C; ^1H NMR ($CDCl_3$) δ 1.23 (9 H, d, $^3J_{PH}$ = 18 Hz), 7.49–8.10 (5 H, m); ^{31}P NMR (benzene) δ +70.70 (lit.[8c] bp 103–104 °C/0.1 mmHg; ^1H NMR δ 1.25 (9 H, d, $^3J_{PH}$ = 19 Hz), 7.8 (5 H, m); lit.[14] bp 84–88 °C/1.5 mmHg; ^{31}P NMR (CH_2Cl_2) δ 69.4; ^1H NMR δ (CH_2Cl_2) 1.2 (9 H, d, $^3J_{HP}$ = 18 Hz), 7.5–7.8 (m). Anal. ($C_{10}H_{14}POCl$) C, H, P. Starting from (*S*)-(−)-**4**, $[\alpha]_D$ −106.90° (*c* 1.94), or (*R*)-(+)-**4**, $[\alpha]_D$ +107.73° (*c* 0.75), (*S*)-(−)-**5**, $[\alpha]_D$ −30.63° (*c* 4.69), or (*R*)-(+)-**5**, $[\alpha]_D$ +28.50° (*c* 1.93), was obtained, respectively. Using methylene chloride as the solvent from (*S*)-(−)-**4**, $[\alpha]_D$ −131.90° (*c* 2.38), (*S*)-(−)-**5**, $[\alpha]_D$ −20.20° (*c* 3.91), was obtained; literature[8c] reports **5**, $[\alpha]^{23}_D$ +49.8° (*c* 2.77 benzene), from reaction of (*R*)-(+)-*tert*-butylphenylphosphinothioic acid (**10**), $[\alpha]_D$ +28.6 (methanol), with thionyl chloride.

(b) With Elemental Chlorine. Into a cooled (−10 to −5 °C) and stirred solution of **4** (2.33 g, 0.01 mol) in tetrachloromethane (10 mL) was added chlorine (2.16 g, 0.03 mol) dropwise in the same solvent. The stirring was continued for 1.5 h at room temperature. The solvent and the excess chlorine were removed in vacuo, and the residue was distilled to give *tert*-butylphenylphosphinic chloride (**5**) (1.90 g, 86%). From (*R*)-(+)-**4**, $[\alpha]_D$ +154.0° (*c* 2.349), chloride (*R*)-(+)-**5**, $[\alpha]_D$ +40.6° (*c* 2.11), was obtained. With the mixture of solvents CH_2Cl_2/CCl_4 (5:1), from (*S*)-(−)-**4**, $[\alpha]_D$ −150.6° (*c* 3.14, dichloromethane), (*S*)-(−)-**5**, $[\alpha]_D$ −20.38° (*c* 5.2 dichloromethane), was obtained.

(c) With Sulfuryl Chloride in the Presence of Mercuric Chloride. To a cooled (0–10 °C) and stirred solution of **4** (1.6 g, 0.007 mol) and mercuric chloride (3.96 g, 0.014 mol) in methylene chloride (19 mL) was added sulfuryl chloride (0.96 g, 0.007 mol) dropwise in the same solvent (5 mL). The stirring was continued for 2 h at room temperature. The solvent was removed, the residue was diluted with benzene (5 mL), and then triethylamine (1.10 g, 0.01 mol) was added. Two layers were formed. The upper one was separated and concentrated in vacuo. The residue was distilled at 117–119 °C/0.2 mmHg to give *tert*-butylphenylphosphinic chloride (**5**) (0.5 g, 31%). From ester (*S*)-(−)-**4**, $[\alpha]_D$ −162.22 (*c* 2.25), chloride (*R*)-(+)-**5** $[\alpha]_D$ +19.08 (*c* 2.30), was obtained.

Reaction of (*S*)-(−)-5 with Sodium Methoxide. Into the stirred solution of sodium methoxide (prepared from 0.12 g, 0.005 mol of sodium) in methanol (25 mL) was added *S*-(−)-**5**, $[\alpha]_D$ −30.63° (*c*, 4.69), dropwise at room temperature. The stirring was continued for 3 h. After the evaporation of methanol, the residue was dissolved in benzene (30 mL) and washed with water (3 × 5 mL). The benzene solution was dried and the solvent evaporated. The distillation of the residue gave *O*-methyl *tert*-butylphenylphosphinate (**11**) (0.93 g, 78%) as a solid product: mp 64–66 °C; $[\alpha]_D$ +50.43° (*c* 1.84); NMR δ_H ($CDCl_3$) 1.01 (9 H, d, $^3J_{PH}$ = 15 Hz), 3.64 (3 H, d, $^3J_{PH}$ = 11 Hz), 7.37–7.92 (5 H, m) (lit.[22] δ_P (C_6H_6) +50.1; $[\alpha]_D$ +42.3° (*c* 0.6, C_6H_6)).

Reaction of (*R*)-(+)-4 with $CH_3OH/AgNO_3$. The procedure described by Stec[11] was used (reflux 5 h). Starting from **4**, $[\alpha]_D$ −106.9°, after distillation a mixture was obtained containing 35% of **4**. The mixture was separated by using preparative GC to give two fractions: *O*-methyl *tert*-butylphenylphosphinate (**11**), $[\alpha]_D$ +58.08° (*c* 0.92), and **4**, $[\alpha]_D$ −49.96° (*c* 0.66).

Preparation of Salts 7 and 8 from Bis(*tert*-butylphenyl)phosphinophosphinic Anhydride (14). Anhydride **14** was prepared for each experiment in an NMR tube from equimolar amounts of *tert*-butylphenylphosphinic acid (**13**) and *tert*-butylchlorophenylphosphine (**12**) in the presence of the corresponding amount of triethylamine in methylene chloride (3 mL). The reaction was monitored by ^{31}P NMR. After the reaction was completed, triethylammonium chloride was filtered off and crude anhydride was used for further reaction: NMR (CH_2Cl_2) **14a** $\delta_{P^{III}}$ + 126.7 (d), $\delta_{P(O)}$ +49.8 (d), $^2J_{PP}$ = 18 Hz; **14b** $\delta_{P^{III}}$ +129.2 (d), $\delta_{P(O)}$ +48.5 (d), $^2J_{PP}$ = 8 Hz. Anhydride **14** was contaminated in some cases with small amounts (5%) of *tert*-butylchlorophenylphosphine, δ_P +107.7, and **5**, δ_P +70.5.

(a) Reaction of 14 with Methanesulfenyl Chloride. To the solution of anhydride **14** (0.4 mmol) in CH_2Cl_2 (3 mL) was added methanesulfenyl chloride (0.0366 g, 0.4 mmol) at −80 °C. The ^{31}P NMR spectrum showed the absence of anhydride **14** and the presence of **7a,b** (71%), **5**, δ_P +72.4 (15%), and **4**, δ_P +69.4 (13%). ^{31}P NMR chemical shifts of **7a** and **7b** are given in Table III.

(b) Reaction of 14 with Chlorine. Reaction was carried out

(22) Omelańczuk, J.; Mikołajczyk, M. *J. Am. Chem. Soc.* **1979**, *101*, 7292–7295.

according to the procedure described above, starting from anhydride (0.64 mmol) and elemental chlorine (0.0681 g, 0.96 mmol) in methylene chloride (3 mL). At −80 °C ^{31}P NMR analysis revealed the presence of **8a,b**. ^{31}P NMR chemical shifts are given in Table III.

Acknowledgment. This research was supported by the Polish Academy of Sciences (Project MR.I.12.).

Registry No. (*R*)-(+)-**1** (R = Bu-*t*, R^1 = Ph; R^3 = H), 55705-77-6; (*S*)-(−)-**1** (R = Bu-*t*, R^1 = Ph, R^3 = H), 54100-47-9; (*R*)-(+)-**4**, 51584-30-6; (*S*)-(−)-**4**, 51584-29-3; (*R,S*)-**4**, 76380-86-4; (*R*)-(+)-**5**, 75213-02-4; (*S*)-(−)-**5**, 75213-01-3; **7** (isomer 1), 104092-20-8; **7** (isomer 2), 104153-59-5; **8** (isomer 1), 104092-21-9; **8** (isomer 2), 104154-51-0; (*R*)-(+)-**11**, 33586-26-4; **12**, 29949-69-7; **13**, 4923-86-8; **14**, 104092-22-0; **15**, 104114-64-9; **16**, 104092-24-2; **17**, 104092-25-3; **18**, 104114-65-0; **19**, 62839-84-3.

Preparation of 2,3-Dimethylene-2,3-dihydrobenzofuran by the Flash Vacuum Pyrolysis of (2-Methyl-3-benzofuryl)methyl Benzoate[1]

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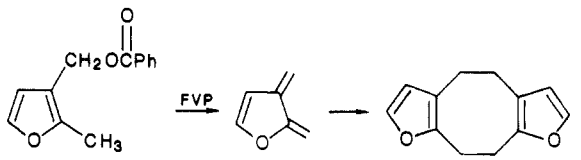
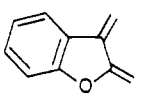
Pyrolysis of (2-methyl-3-benzofuryl)methyl benzoate (**7**) gives a 30% yield of two dimers of 2,3-dimethylene-2,3-dihydrobenzofuran (**4**), a [4 + 2] dimer (**12**) and a [4 + 4] dimer (**13**), in a ratio of 4.1 to 1. It is shown, by low-temperature ^1H NMR spectroscopy, that the primary pyrolysis product from **7** is **4**, which forms **12** and **13** upon warming. The structure of the [4 + 2] dimer **12** is confirmed by a deuterium-labeling experiment. Compound **4** can be trapped with methyl acrylate to form a 3.0 to 1 ratio of two Diels–Alder adducts.

During the past few years, 2,3-dimethylene-2,3-dihydrofuran (**1**), the furan analogue of *o*-xylylene,[2] has been actively investigated by our research group.[3,4] Compound **1** can be conveniently prepared by the flash vaccum pyrolysis (FVP) of (2-methyl-3-furyl)methyl benzoate (**2**). Compound **1** in solution at temperatures above −30 °C dimerizes rapidly and quantitatively to the head-to-head [4 + 4] dimer **3**.[3,4]



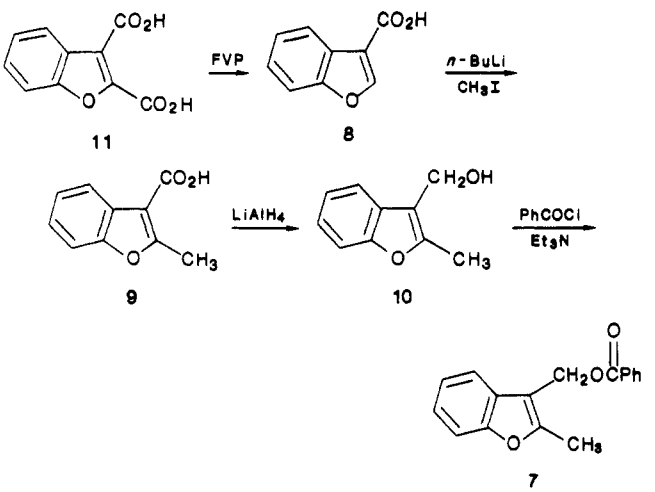
As part of our study of quinodimethanes, we selected for study the benzo analogue of **1**, 2,3-dimethylene-2,3-dihydrobenzofuran (**4**). We anticipated that **4**, as a result



4

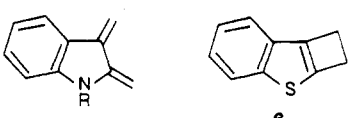
of the aromaticity of its benzene ring, would be less reactive than **1** and hence more amenable to study. Also, **1** and some substituted 2,3-dimethylene-2,3-dihydrofurans are the only known *o*-quinodimethanes that favor [4 + 4] dimerization over [4 + 2] dimerization and we wished to probe the effects of the fused benzene ring on the mode

Scheme I



of dimerization of the furan *o*-quinodimethane system.

Prior to our work, **4** had not been prepared although indole-2,3-quinodimethanes **5** have been reported[5–18] and



5 **6**

(1) Based on work by C. H. Chou in partial fulfillment of the requirements for the Ph.D. Degree at Iowa State University.
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