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Halogenolysis of *Se*-Methyl Phosphinoselenoates*

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ABSTRACT

The reaction of the title phosphinoselenolates with sulfuryl chloride and halogens was investigated stereochemically and spectroscopically (^{31}P NMR at variable temperatures). Differences were observed in the reaction course when compared to the behavior of sulfur analogs towards the same reagents. The good donor character of the selenium atom and the leaving ability of the $-Se^{+}(R)X$ group explain well the results of the investigation.

INTRODUCTION

In the previous paper [1] of this series, it was demonstrated that the reaction of dialkyl phosphoroselenoates with halogens and sulfuryl chloride involves the formation of the same type of intermediates as described earlier [2] for the sulfur analogs. However, considerable differences in the pathways of the decomposition of intermediates to the reaction products were noticed.

From the preliminary studies on phosphinoselenoates [3] and from the previous work concerning the reactions of phosphinothiolates with halogens [2], we gathered that *Se*-methyl *t*-butylphenylphosphinoselenoate **1a** should be a useful model for both stereochemical and spectroscopic investigations. The advantage of this model is the lack of the side reactions that occur when alkoxy groups are present. Moreover, since the environment around the phosphorus atom is sterically congested, the rate of any intermediate step involving nucleophilic displacement at the reaction center should be reduced. The aim of this investigation was to examine the stereochemical course of the chlorinolysis reaction of ester **1a** in order to compare the results with those obtained for the sulfur analog. Stereochemistry will be discussed in terms of the results of ^{31}P NMR spectroscopic studies. In order to recognize the effect of the structure of the substituent at the selenium atom on the reaction course (which was demonstrated to be dramatic for the sulfur analog), the reaction of *Se*-phenyl *t*-butylphenylphosphinoselenoate **1b** was also investigated. As a second series, esters **2a** and **2b** with two bulky group at the phosphorus atom were used.

RESULTS

Stereochemical Course of the Chlorinolysis of **1a** *and* **1b**

The optically active selenolates **1a** were prepared by *Se*-methylation of the corresponding (*R*)(+) and (*S*)(−)-phosphinoselenoic acids Bu^{t}PhP(Se)OH **3**. The optically active ester **1b** was obtained from the reaction of the enantiomeric *t*-butylphenylphosphine oxide **5** with benzeneselenenyl chloride:

$$\underset{\mathbf{4}}{Bu^tPhP(S)OH} \xrightarrow{Ni(R)} \underset{\mathbf{5}}{Bu^tPhP(O)H} \xrightarrow{PhSeCl} \mathbf{1b}$$

The optical purity and the absolute configuration of optically active **1a** and **1b** was estimated on the basis of the previous stereochemical studies from this laboratory [4, 5].

Specific rotations and optical yields for chlorination (and bromination) reactions performed at 278–293 K are collected in Table 1.

* Reaction of Thiolo- and Selenolo Esters of Phosphorus Acids with Halogens, Part 5. For Part 4, see Ref. [1].

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It can be seen from Table 1 that the dominating stereochemistry is retention of configuration accompanied usually by considerable racemization.

The stereochemistry stems from the previous investigations. It was shown [5] that both *S*-methyl *t*-butylphenylphosphinothioate and *Se*-methyl *t*-butylphenylphosphinoselenoate **1a** undergo the chlorinolysis reaction with sulfuryl chloride in benzene with the same stereochemistry. On the basis of the two stereochemical cycles [2], it was evidenced that both reactions involve retention of configuration under the above-mentioned conditions.

The comparison of the stereochemical results obtained for the ester **1a** and its sulfur analog shows that the stereoselectivity is reduced approximately by half in the case of the selenoester. This observation will be rationalized in the following section together with ^{31}P NMR results.

^{31}*P NMR Spectroscopic Studies*

^{31}P NMR studies of the reacting system **1** + X_2 and **1** + SO_2Cl_2 were performed in the temperature range from 173 to 293 K in methylene chloride, or in toluene in the same manner as described for the sulfur analogs [2]. Concentrations of starting materials **1(2)**, intermediates **6–8**, **9–11**, **16–18**, **19**, and final products **12(13)** were estimated by integration of the corresponding signals.

(*a*) *Intermediates Containing One Phosphorus Atom*

In the ^{31}P NMR spectra of all the reacting systems (**1a** with SO_2Cl_2, **1a** or **1b** with chlorine or bromine), there are signals which can be assigned to the intermediates containing one or two phosphorus atoms.

In most of the ^{31}P NMR spectra two distinct signals from monophosphorus intermediates are observed; both signals or only one of them occur in the reaction mixtures, depending on the nature of the reacting system. The following picture based on ^{31}P NMR spectra of the reaction of ester (*R*, *S*): **1a** with SO_2Cl_2 *in* CH_2Cl_2 in the temperature range 173–243 K was obtained. Two distinct signals at $\delta = +93.4$ and $+87.6$ were observed at 173 K; they gradually coalesced and at 213 K only the peak $\delta = +94.1$ was visible as a sharp signal, but at 233 K it vanished and the signal with $\delta = +86.7$ appeared. The latter was still visible at 243 K.

For the reacting system **1a** + Cl_2 in CCl_4-toluene (1 : 4), only the peak with $\delta = +90.8$ could be observed in the temperature range 173–223 K.

An interesting picture could be seen for the reacting system **1b** + Cl_2 in CH_2Cl_2. At 173 K, two signals were observed at $\delta = +85.4$ and $+84.5$ and one peak at $\delta = +78.4$. At higher temperatures, the latter decreased and became very broad, while two other signals coalesced. At 253 K, one signal with $\delta = +84.7$ was visible. A very similar picture was observed for the reacting system **1b** + Br_2 in CH_2Cl_2 in the temperature range 193–253 K and for the system **1b** + SO_2Cl_2 in CH_2Cl_2 between 213–223 K.

On the basis of the experience with the reactions of the sulfur analog of **1a** and **2a** [2], it may be assumed that the signal with δ *ca.* 93 corresponds to the haloselenonium salt **9a**, while the one of δ *ca.* 87 may be attributed to a CT complex between reactants. Due to the strong affinity of

TABLE 1 Stereochemistry of the Reaction of **1a–b** $\xrightarrow{XY}$ **12a–b** Depending on the Reaction Conditions

1					12				
R	$\lvert\alpha\rvert^{20}$,[a] deg.	e.e.,[b] %	Config	X_2	$\lvert\alpha\rvert^{20}$,[a] deg.	e.e.,[b] %	Config	Stereochem.	Stereoselect.[g]
Me	+157.80	94	R	SO_2Cl_2[c]	+18.57	37	R	ret.	39
Me	−155.60	93	S	SO_2Cl_2[d]	−12.64	25	S	ret.	27
Me	+156.50	93	R	Cl_2[e]	+15.26	31	R	ret.	33
Me	−158.0	94	S	Cl_2[f]	−16.40	33	S	ret.	35
Ph	−173.33	78	S	SO_2Cl_2[c]	−10.64	21	S	ret.	27
Me	+153.30	91	R	Br_2[d]	+6.06	12	R	ret.	13

[a] All optical rotation measurements were made in benzene (c, 0.005–0.02 g / 1 mL).

[b] Determinations of optical purities were based on the assumption, that *t*-butylphenylphosphinochloridate with $\lvert\alpha\rvert^{23}$ +49.8 (highest known value) is optically pure. For the selenoate **1a** the specific rotation value of 167.7 (100% op) was estimated as corresponding to the optically pure *t*-butylphenylphosphinoselenoate **3**. Optical purity of **1b** was roughly estimated from the optical purity of *t*-butylphenylphosphinothioate **4**, used in the reactions sequence: **4** → **5** → **1b**, assuming that both reactions: desulfurization **4** to **5** and the reaction of **5** with benzeneselenenyl chloride are stereospecific. Optical purity of bromide **12b** was estimated similarly on the basis of the bromination reaction of **5** with *N*-bromosuccinimide.

[c] In benzene.

[d] In methylene chloride.

[e] In CCl_4.

[f] In the mixture CCl_4—CH_2Cl_2 (1 : 10).

[g] Stereoselectivity was calculated as ratio of e.e. of **12** to e.e. of **1**.

selenium to form the structure with higher valency [6], the participation of phosphoryl selenurane **9'** in the equilibrium (Scheme 1) cannot be excluded.

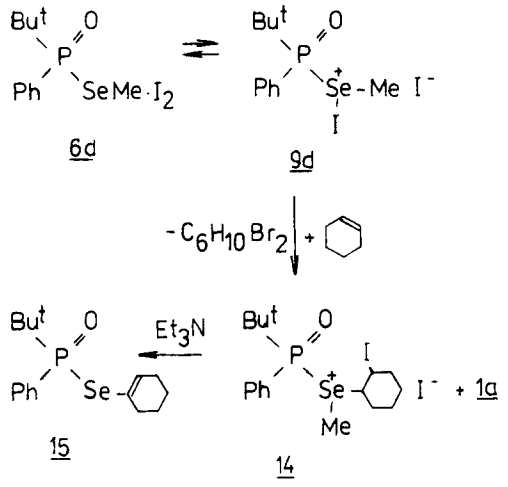
The splitting of the peak δ_P *ca.* 85 into two close signals observed for the system **1b** + X_2 requires some comment. It seems to be likely that the chemical shift of selenonium salt **10** is *ca.* 85 ppm, while for that of the CT complex **7**, $\delta = +78$. Two distinct but very close signals in the region 84–85 ppm might be the result of the participation of two diastereomeric selenonium salts (due to two chiral centers at phosphorus and selenium atoms).

The ^{31}P NMR spectroscopic data of the chosen salts **9–11** and complexes **6–8** are shown in Table 2.

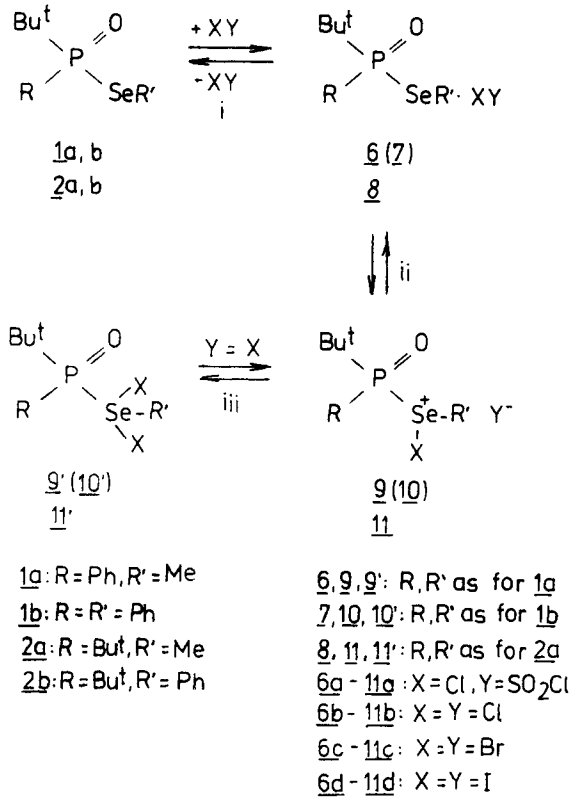
It is known [7] from the literature that bromosulfonium bromides such as R^1—$S^+(R^2)Br\ Br^-$ add to olefins giving sulfonium salts.

In the course of these studies, experiments were conducted to prove whether the iodophosphorylselenonium salt **9d** (observable at room temp.) undergoes a similar reaction.

In the reacting system **1a** + I_2 in CH_2Cl_2, 7 days after the reagents were mixed, according to the ^{31}P NMR spectrum, the following compounds were observed: **6d** ⇄ **9d**, δ +88.56 (52%), pyrophosphinate **24** (27%) and *t*-butylphenylphosphinoiodidate, **12c** (21%). Then cyclohexene was added until the mixture decolorized, with subsequent addition of an excess of triethylamine. The solution was decanted from a white solid that had formed, and the residue was analyzed by the GC/MS method. In addition to the recovered ester **1a**, a product with m/z 342 was found, which could be *Se*-cyclohexenyl *t*-butylphenylphosphinoselenoate. The latter might have been formed *via* the following reaction sequence (Scheme 2):



SCHEME 2



SCHEME 1

(*b*) *Intermediates Containing Two Phosphorus Atoms*

^{31}P NMR spectra of reaction mixtures of (*R*, *S*)-**1a** and (*R*, *S*)-**1b** with SO_2Cl_2, Cl_2 and Br_2 show, in every case, the presence of two types of diphosphorus intermediates. A characteristic doublet of doublets multiplied by two, due to the formation of two pairs of diastereoisomers, is observed for each of these intermediates.

An intermediate with chemical shifts *ca.* 100–104 and 68–66 is known from the studies on the sulfur analog of **1a** [2]. It has the structure of the chloro(phosphoryloxy)phosphonium salt **19a**. Its spectroscopic data are given in Table 3.

The signals in the region 115–110 (for the reacting system **1a** + X_2), 107–110 (for **1b** + X_2) and 62–60 ppm (for both **1a–b** + X_2) correspond to the methylseleno(phosphoryloxy)phosphonium salts **16a–d** and phenylseleno(phosphoryloxy)phosphonium salts **17a–d**, respectively. Their chemical shifts (given in Table 3) are very similar to those observed for the thioanalog described previously [2].

Phosphonium salts **16(17)** and **19** are observed in the wide temperature range (173–273 K) in CH_2Cl_2. In toluene, the reaction mixtures become homogeneous above 220 K and then the salts **16(17)** and **19** are also observed. The proportions of **16(17)** versus **19** are strongly dependent on the nature of

the solvent and the nucleophilicity of the counteranion. It has been observed that while for the reacting system **1a** + SO_2Cl_2 in CH_2Cl_2 at 223 K the ratio of **16a:19a** is 54:4, for **1a** + Cl_2 in CCl_4—CH_2Cl_2 (1:2) at the same temperature it reverses (**16b:19a** = 13:81). This striking difference demonstrates that SO_2Cl_2 generates originally an anion different from Cl^-. Such a phenomenon was observed as well in the course of the previous studies concerning the chlorinolysis reactions of phosphorus thioloesters [1, 8]. It was assumed that at the low temperature the $ClSO_2^-$ anion could be formed, which should undergo subsequent dissociation, that is, $ClSO_2^- \rightarrow Cl^- + SO_2$. The example of a phosphonium salt with the $ClSO_2^-$ anion and its transformation into the corresponding salt with the Cl^- anion has been described by Appel *et al.* [9].

It is noteworthy that the bromo(phosphoryloxy)phosphonium salt **19b** was not observed during the reaction of the corresponding thioloester with bromine [10]; therefore, its participation in the reaction systems **1a(1b)** + Br_2 must be the result of the presence of alkyl(aryl)seleno groups at phosphorus.

TABLE 2 ^{31}P NMR (24.3 MHz) Chemical Shifts of **6–8** and **9–11** in CH_2Cl_2

No of compd.	R	R'	X	Y[i]	δ_P	Temp.[a] K
6a	Ph	Me	Cl	SO_2Cl	87.6	173
9a	Ph	Me	Cl	SO_2Cl	93.4	173
9b	Ph	Me	Cl	Cl_3	92.5[b]	173
9e	Ph	Me	Cl	$AlCl_4$	89.8[c]	293
$9c_1$	Ph	Me	Br	Br_3	92.9[d]	263
$9c_2$					90.0	
9d	Ph	Me	I	I_3	90.1[e]	293[h]
$10a_1$	Ph	Ph	Cl	SO_2Cl	85.0	213
$10a_2$					84.5[b]	
$10b_1$	Ph	Ph	Cl	Cl_3	85.4[b]	173
$10b_2$					84.5	
$10c_1$	Ph	Ph	Br	Br_3	85.0	203
$10c_2$					84.5	
10c	Ph	Ph	Br	Br_3	96.7[d]	253
7d	Ph	Ph	I	I	82.9[e,f]	293
10d	Ph	Ph	I	I_3	88.4[e]	293
11c	Bu[t]	Me	Br	Br_3	114.5[g]	293
8d	Bu[t]	Me	I	I	97.9[g,h]	293

The dynamic situation in the reactions is responsible for the variation in the ^{31}P NMR shifts values. All chemical shifts are positive.

[a] Temperature of measurement.
[b] In CH_2Cl_2—CCl_4 (5:1).
[c] J_{P-Se} = 500 Hz (ΔJ_{P-Se} 115 Hz).
[d] In toluene.
[e] δ_P (121.5 MHz, $CDCl_3$).
[f] J_{P-Se} = 471 Hz (ΔJ_{PSe} 84 Hz), after 4 months.
[g] In benzene.
[h] After 5 months.
[i] Existence of X_3^- anions was confirmed by UV spectra [10].

Intermediates **16d(17d)** and **19c** were also observed in the course of the reaction of **1a(1b)** with iodine; however, the spectroscopic picture is strongly dependent on the concentration of the starting esters. This problem will be discussed below.

The reacting systems **2a(2b)** + SO_2Cl_2 were investigated spectroscopically only at room temperature and in the case of **2a** + SO_2Cl_2, a trace amount of the diphosphorus intermediate **18a** was observed. However, phosphonium salt **18c** could be observed in higher (*ca.* 20%) concentration during the reaction of **2a** with bromine.

Final Products

The phosphorus selenoloesters **1a–b** and **2a–b** in the reaction with sulfuryl chloride, chlorine, and bromine give, as main products, the phosphinochloridate **12a**, **13a** and bromidate **12b**, **13b**, respectively. The reaction of **1a–b** with iodine results in the formation of 20–25% of the corresponding phosphinoiodidate **12c**, in addition to intermediates **6d(7d)**, **9d(10d)** and/or **16d(17d)** and **19c**, depending on the concentrations of substrates used. Esters **2a–b** do not produce the corresponding iodidate. The only products observed are intermediates **8** and side products.

The side products are the products of hydrolysis: phosphinates **27(28)** and pyrophosphinates **24(25)** in the case of all models. The pyrophosphinate **24** can be formed also by the reaction pathways shown in Scheme 3. Reaction of ester **1a** with SO_2Cl_2, Cl_2, and Br_2 leads additionally to the formation of minute amounts of chloro(bromo)-*t*-butylphenyl(methylseleno)phosphonium chloride (bromide) **22a(22b)** which decompose giving *t*-butylphenylphosphinoselenochloridate **23a** and bromidate **23b**, respectively. The same types of side products were observed during the corresponding reactions of sulfur analogs of **1a** [2].

DISCUSSION

(a) Reaction Course

The first step of the reaction of **1** with halogenating agents is the formation of halophosphorylselenonium salt **9(10)**, and this step is reversible. The second step can occur according to two different reaction pathways: (i) selenonium salt **9(10)** may be attacked by a halide anion at the electrophilic phosphoryl center giving as the result the reaction product **12** with inversion of configuration (Scheme 3, pathway v); (ii) the selenonium salt **9(10)** undergoes a nucleophilic attack by the phosphoryl oxygen atom of the starting ester leading to the formation of the diphosphorus intermediate **16(17)** (Scheme 3, pathway i). The latter can decompose according to several reaction pathways.

TABLE 3 ^{31}P NMR (24.3 MHz, CH_2Cl_2) Chemical Shifts and Coupling Constants of Phosphonium Salts **16a–d**, **17a–d**, **18a**, **b** and **19a–c**

No of compds	*R*	*X*	*Y* [e]	δ_P +	$\delta_{P(O)}$	J_{P-O-P}, Hz	*Temp., K* [a]
16a$_1$ 16a$_2$	Ph	SeMe	SO_2Cl	115.8(d) 112.3(d)	61.8(d) 60.8(d)	42.5[b] 43.9	213
16b$_1$ 16b$_2$	Ph	SeMe	$Cl(Cl_3)$	115.7(d) 112.5(d)	61.1(d) 60.4(d)	43.9[c] 46.4	203
16e$_1$ 16e$_2$	Ph	SeMe	$HgCl_3$	114.8(d) 111.9(d)	61.2(d) 60.9(d)	43.9 46.4	293
16c$_1$ 16c$_2$	Ph	SeMe	$Br(Br_3)$	115.1(d) 111.8(d)	61.3(d) 60.8(d)	43.0 44.9	273
16d$_1$ 16d$_2$	Ph	SeMe	$I(I_3)$	115.6(d) 112.2(d)	61.7(d) 61.1(d)	41.5 43.9	293
17a$_1$ 17a$_2$	Ph	SePh	SO_2Cl	108.9(d) 107.9(d)	61.3(d) 62.7(d)	52.2 53.7	233
17b$_1$ 17b$_2$	Ph	SePh	$Cl(Cl_3)$	108.6(d) 107.7(d)	61.0(d) 62.6(d)	51.3[c] 48.9	193
17c$_1$ 17c$_2$	Ph	SePh	$Br(Br_3)$	109.4(d) 108.5(d)	62.1(d) 63.2(d)	51.3 48.9	233
17d$_1$ 17d$_2$	Ph	SePh	$I(I_3)$	109.82(d) 109.29(d)	62.64(d) 63.51(d)	52.0[d] 51.2	293
18b	Bu^t	SeMe	$Br(Br_3)$	135.29(d)	92.75(d)	77.2[d]	293
18a	Bu^t	SeMe	SO_2Cl	129.8(d)	93.0(d)	76.6[d]	293
19a$_1$ 19a$_2$	Ph	Cl	$Cl(Cl_3)$	103.8(d) 103.0(d)	68.0(d) 67.6(d)	43.9[c] 48.8	253
19b$_1$ 19b$_2$	Ph	Br	$Br(Br_3)$	102.3(d) 101.5(d)	66.6(d) 64.9(d)	46.9 48.8	293
19c$_1$ 19c$_2$	Ph	I	$I(I_3)$	82.6(d) 81.9(d)	65.2(d) 65.0(d)	46.4 48.8	293

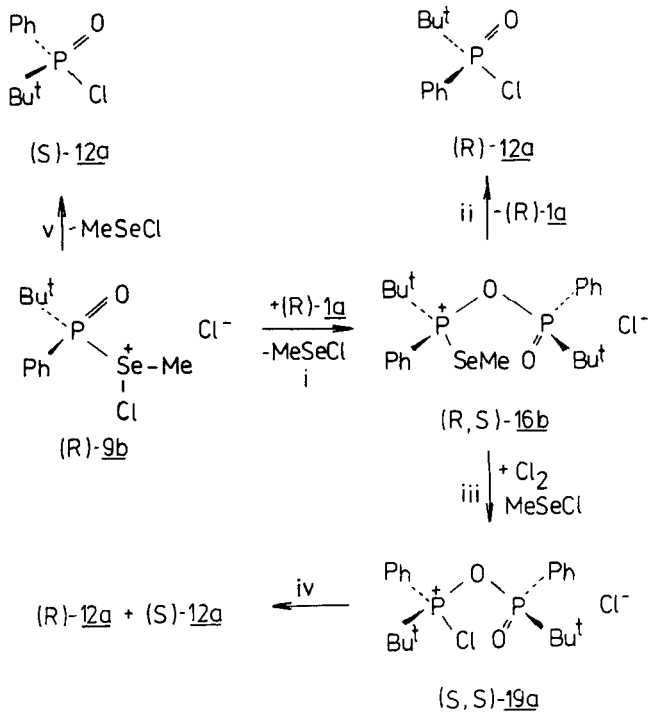
The dynamic situation in the reactions is responsible for the variation in the ^{31}P NMR chemical shifts values.
[a] Temperature of measurement.
[b] In experiment carried out in toluene J_{P-Se} value was measured: 610 Hz and 595 Hz for diastereomers **16a**$_1$ and **16a**$_2$, correspondingly.
[c] In CH_2Cl_2—CCl_4 (5 : 1).
[d] δ_P (121.5 MHz, $CDCl_3$).
[e] Existence of X_3^- anions was confirmed by UV spectra [10].

The counteranion may attack the phosphoryl phosphorus atom with the departure of the starting ester and the formation of the reaction product **12** with retention of configuration (Scheme 3, reaction pathways i, ii). The ligand exchange at the phosphonium center of the salt **16(17)**, followed by the halogenation of the anion RSe^- leads to the intermediate **19** (Scheme 3, pathways i, iii). This intermediate decomposes when attacked by the anion at the phosphoryl phosphorus atom giving the racemic reaction product **12** (Scheme 3, pathway iv).

Another ligand exchange at the phosphonium centre leading to the salt **20** · **21** (Scheme 4, pathway i) is the source of the side products **22** and **23**, analogically, as it was proposed for the reaction of the sulfur analog of **1a** [2]. The attack of anion **21** on the phosphoryl center of **9(10)**, **16(17)**, **19** or **12** can give the pyrophosphinate **24**.

(*b*) *Stereochemistry*

As described above, the stereochemical studies of the chlorinolysis reaction of the optically active **1a** show that the latter reacts with chlorinating agents less stereoselectively than its sulfur analog [2]. Tak-



SCHEME 3

ing into account that the reaction product **12a** is optically relatively stable [2], two sources of racemization may be considered on the basis of the proposed reaction scheme.

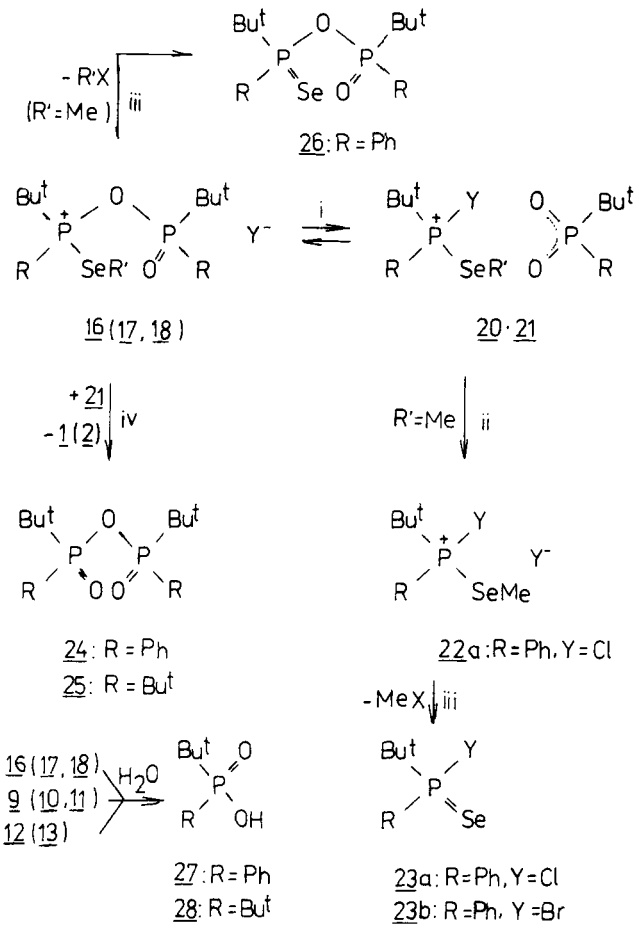
Racemization can be the result of two parallel reaction pathways one of which occurs with retention of configuration while the other with inversion.

Another source of the racemic product may be the phosphonium salt **19a**, which decomposes forming two molecules of product **12a**, with opposite configurations.

Each of the reactions contributing to the racemization pathways discussed above is facilitated when compared to the sulfur analogs, due to the presence of a better leaving group, that is, $-Se^{+}(R)X$. Therefore, it is reasonable to assume that, in the various reacting systems, both these racemization pathways participate to a different extent, depending on the reaction condition.

(c) *Comparison of the Reactivity of* **1a** *with That of Its Sulfur Analog*

Although the disappearance of **1a** from the reacting system **1a** + SO_2Cl_2 in CH_2Cl_2 is considerably faster than for its sulfur analog, the rate of formation of the final reaction product **12a** is not very much increased. The same situation occurs in the reacting system **1a** + Cl_2 in CH_2Cl_2—CCl_4. A more striking difference is observed in the behavior of both models **1a** and **1b** towards bromine. While



SCHEME 4

$Bu^tPhP(O)SMe$ forms > $P^{+}(SMe)OP(O)$ < Br^{-} as the only diphosphorus intermediate and **19b** was never observed for this system [10], **1a** + Br_2 in CH_2Cl_2 forms also **19b**, which in the temperature range 193–293 is observed to be present in 21–28% yield. Moreover, the formation of *t*-butylphenylphosphinobromidate **12b** from the corresponding thioloester required several months [10], while from **1a** bromidate **12b** is formed after several hours.

Due to the fact that the optically active *t*-butylphenylphosphinobromidate **12b** is formed from **1a** with retention of configuration similar to the chloride **12a** (Table 1), it seems reasonable to assume that its formation follows the same reaction pathways. The observed low reaction stereoselectivity may be caused by the same reasons as those discussed for the chlorinolysis reaction.

In the paper concerning the reaction of *S*-methyl *t*-butylphenylphosphinothiolate with higher halogens [10], it was assumed that the rate determining step of the reaction with iodine is the formation of the corresponding iodosulfonium salt. It seems not to be the case for the reacting systems **1** + I_2 which form relatively readily intermediates **6(7)** ⇄ **9(10)** and/or **16(17)**, leading stepwise to

TABLE 4 ^{31}P NMR Data[a,b,c] of the Reaction Products

Compound	δ_P, ppm	Solvent	Lit.
12a	+70.7[a]	CH_2Cl_2	+69.4 (CH_2Cl_2) [2]
12b	+71.9[a]	CH_2Cl_2	+72.4 (CH_2Cl_2) [10]
12c	+54.49[b]	$CDCl_3$	
13a	+95.62[c]	$CDCl_3$	+94.7 [14]
13b	+102.94[c]	$CDCl_3$	+102.5 [14]
22a	+121.5[a]	CH_2Cl_2	
23a	+110.7[a]	CH_2Cl_2	
23b	+105.5[a]	CH_2Cl_2	

[a] δ_P (24.3 MHz).
[b] δ_P (81 MHz).
[c] δ_P (121.5 MHz).

t-butylphenylphosphinoiodidate **12c**. The latter was never observed when sulfur analogs of **1** were reacted with iodine [10].

Careful inspection of the spectroscopic data obtained for the systems **1a(b)** + xI_2 (x = 1–3) showed dramatic dependence of the spectroscopic picture on the concentration of **1a(b)** in the reaction mixture. It has been found that, if the concentration of **1a(b)** was below 0.1 M, only a monophosphorus intermediate was observed. However, when the concentration of **1a(b)** was 0.11–0.4 M, typical diphosphorus intermediates **16d(17d)** and even **19c** were observed, which after reaching *ca.* 30% of the reacting mixture (4 days after mixing of the substrates) disappeared stepwise. After 10 days the reacting mixture contained no intermediate **16d(17d)** and **19c**, but 34% of **6(7)** ⇄ **9(10)** and 31% of the iodidate **12c**. If the reaction of **1a** was stopped by the removal of iodine with Et_3N, demethylation of **16d** occurred at the same time, giving the selenopyrophosphinates **26**. The latter compounds were observed also when the reaction mixture of **1a** + I_2 was analyzed by the GC/MS method.

CONCLUSION

The greater reactivity of phosphinoselenoates versus thiolates towards halogens is evident in view of the good donor properties of the selenium atom. The presence of this element in the molecule of the phosphorus reactant facilitates all of the reaction steps involved in the reaction course.

The formation of intermediates **7–11** is promoted by the higher affinity of selenium towards halogens, when compared to the sulfur atom [6].

The nucleophilic displacement step at the electrophilic phosphorus center is supported by the better leaving ability of the $-Se^+(X)R$ group. It enhances the nucleophilic attack of both nucleophiles present in the reaction medium: a halide anion and the phosphoryl oxygen of the starting ester. This results in the decrease of the stereoselectivity of the reaction and the increase of the participation of the diphosphorus intermediates **16(17)** and **19**.

The behavior of the selenoesters towards higher halogens demonstrates the operation of the symbiotic effect [11], which makes possible the nucleophilic attack of the weakly P-nucleophilic anions (Br^-, I^-) on the phosphorus atom attached to the $-Se^+(X)R$ leaving group.

EXPERIMENTAL

Melting points were taken on a Boetius PHMK apparatus and are uncorrected. Solvents and commercial reagents were purified by conventional methods before use. Organic extracts were dried over $MgSO_4$. NMR spectra were recorded with JEOL JNM-FX 60 FT (24.3 MHz, ^{31}P), Bruker MSL 300 (121.5 MHz, ^{31}P) and Bruker AC 200 (81 MHz, ^{31}P) spectrometers; positive chemical shifts are downfield from external 85% H_3PO_4. Products were identified by use of the 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

t-Butyl(phenyl)phosphinoselenoic acid was synthesized and resolved into optical antipodes by a known method [5]. Di-*t*-butylphosphinoselenoic acid was prepared by the addition of selenium to di-*t*-butylphosphine oxide under more drastic conditions than used for the former acid: the sodium salt of di-*t*-butylphosphine oxide was refluxed with selenium in ethanol for 2 hours. Mp 148°C. Analysis was found to be in agreement with that required for $C_8H_{19}POSe$ within ±0.15%. ^{31}P NMR δ (24.3 MHz, benzene) + 120.16. Di-*t*-butylphosphine oxide [12] and optically active *t*-butyl(phenyl)phosphine oxide **5** [4] were obtained by methods reported earlier. Benzeneselenenyl chloride [13] was prepared from the corresponding diselenide (commercial, from Aldrich) by chlorination with sulfuryl chloride. The crude product was used in subsequent reactions. *Se-Methyl di-t-butylphosphinoselenoate*, **2a** and *Se*-methyl *t*-butylphenylphosphinoselenoate, **1a**, were synthesized by the method described [2] for the sulfur analogs of the latter ester **1a**: mp 73–74°C; ^{31}P NMR: δ (24.3 MHz, CH_2Cl_2) +66.2, J_{P-Se} 385 Hz; **2a**: δ_P (121.5 MHz, $CDCl_3$) +86.86, J_{P-Se} 367.9 Hz; δ_P (24.3 MHz, benzene) +83.6, J_{P-Se} 359 Hz.

Se-Phenyl t-Butylphenylphosphinoselenoate **1b**

Into a stirred solution of *t*-butylphenylphosphine oxide **5** (1.820 g, 0.01 mol) in benzene (5 cm^3),

freshly prepared benzeneselenenyl chloride (1.815 g, 0.01 mol) was added dropwise at +5°C. The stirring was continued for 1 hour at room temperature. Hydrogen chloride and solvent were removed *in vacuo* and the residue was crystallized from hexane to give **1b** (2.494 g, 72%). Mp 65.0–65.5°C; ^{31}P NMR (121.5 MHz, $CDCl_3$) + 67.23, J_{P-Se} 390.6 Hz; δ (24.3 toluene) +63.7, J_{P-Se} 379 Hz.

Starting from (*S*)(−) *t*-butylphenylphosphine oxide **5**, $[\alpha]_D$ −19.94 (c 2.845), (*S*)-(−)-(**1b**), $[\alpha]_D$ −173.30 (c 1.8) was obtained.

Se-Phenyl Di-t-butylphosphinoselenoate **2b**

Di-*t*-butylphosphine oxide (1.69 g, 0.01 mol) was silylated with trimethylsilyl chloride (1.095 g, 0.01 mol) in the presence of triethylamine (1.01 g, 0.01 mol) in benzene (25 mL). Freshly prepared benzeneselenenyl chloride (1.815 g, 0.01 mol) in benzene solution (5 mL) was added dropwise at 10°C into the crude reaction mixture. The stirring was continued overnight at room temperature, then the reaction mixture (still colored from benzeneselenenyl chloride) was heated at 50° for 24 hours. Triethylammonium chloride (1.4 g, *ca.* 100%) was filtered off and the solvent was removed *in vacuo*. The crude product was chromatographed (Silica gel, eluent hexane-chloroform) to give *Se*-phenyl di-*t*-butylphosphinoselenoate **2b** (1.553 g, 49%), di-*t*-butylphosphinochloridate **13a** (0.511 g, 26%) and diphenyldiselenide (0.40 g). ^{31}P NMR of **2b**: δ_P (121.5 MHz, $CDCl_3$) +87.60, J_{P-Se} 373.2 Hz.

Low Temperature ^{31}P NMR Measurements

A 10 mm NMR tube (cooled in liquid N_2 or acetone, CO_2) was charged with equimolar amounts (unless stated otherwise) of phosphorus selenoester and halogen or sulfuryl chloride in toluene or methylene chloride. All operations were carried out in a dry argon atmosphere. The tube was closed tightly with a rubber septum and the progress of the reaction was monitored periodically by ^{31}P NMR spectroscopy. The temperature was gradually increased from 173 K (193 K) to room temperature.

Tables 2 and 3 show the ^{31}P NMR chemical shifts of the intermediates **6–8**, **9–11** and **16–19**, respectively; Table 4 gives the data for the final products.

Below are given the compositions of the reaction mixtures according to the ^{31}P NMR data for the chosen reacting systems.

The system **1a** + SO_2Cl_2 *in* CH_2Cl_2. Temp. 193 K: **1a** (29%), **6a** (9%), **9a** (17%), **16a** (44%). Temp. 253 K: **6a** (24%), **16a** (71%), **12a** (5%). Temp. 293 K: **6a** (20%), **12a** (29%), **22a** (9%), **23a** (6%), and an unidentified product with chemical shift δ +62.8 (11%).

System **1a** + Cl_2 *in* CCl_4—CH_2Cl_2 (1 : 2). Temp. 173 K: **9b** (27%), **16b** (21%), **19a** (52%); Temp. 203 K: **9b** (14%), **16b** (17%), **19a** (66%), **12a** (3%); Temp. 293 K: **12a** (77%), **24** (8%), **22a** (3%), and an unidentified product with δ +62.8 (13%).

System **1b** + SO_2Cl_2 *in* CH_2Cl_2. Temp. 193 K: **1b** (75%), **17a** (13%), **19a** (12%); Temp. 253 K: **17a** (50%), **19a** (16%), **12a** (26%), **24** (8%); Temp. 293 K: **12a** (54%), **24** (28%), **27** (18%).

System **1a** + Br_2 *in* CH_2Cl_2. Temp. 193 K: **6c** (13%), **16c** (64%), **19b** (15%); Temp. 273 K: **6c** (10%), **16c** (70%), **19b** (9%), **12b** (2%); Temp. 293 K: **1a** (12%), **6c** (10%), **12b** (35%), **23b** (10%). After 1 month: **6c** (16%), **12b** (79%).

System **1b** + Br_2 *in* CH_2Cl_2. Temp. 193 K: **1b** (16%), **10c** (15%), **17c** (57%). Temp. 213 K: **7c** (11%), **10c** (13%), **17c** (58%); Temp. 293 K: **12b** (62%), **24** (22%), **27** (15%).

System **1a** + I_2 *in* CH_2Cl_2. Ratio 1 : 1. After 168 h: **6d** (72%), **12d** (14%). Ratio 1 : 2. After 24 h: **9d** (2%), **16d** (34%), **19c** (39%), **12c** (14%). Ratio 1 : 3. After 2 h: **6d** (21%), **16d** (72%), **12c** (8%).

The experimental details are given below for the experiments where optically active esters **1a–b** were used and in the cases when the components in the reaction mixtures were additionally identified by GC/MS or elemental analysis.

Chlorinolysis of Se-Methyl t-Butylphenylphosphinoselenoate

(*a*) *With Sulfuryl Chloride in Benzene.* A solution of sulfuryl chloride (0.0196 g, 0.145 mol) in benzene (5 mL) was added dropwise to a stirred solution of **1a** (0.040 g, 0.145 mol) in benzene (5 mL) at 0–5°C. The stirring was continued for 3.5 hours at room temperature and then the reaction mixture was concentrated *in vacuo* and purified by crystallization from hexane or chromatographed on silica gel. Yield 0.0140 g (45%). Spectral data are given in Table 4.

Starting from (*R*)(+)-**1a**, $[\alpha]_D$ +157.80° (c 1.0), (*R*)-(+)-**12a**, $[\alpha]_D$ + 18.57° (c 0.70) was obtained. Using methylene chloride as the solvent from (*S*)-(−)-**1a**, $[\alpha]_D$ −155.60°, (*S*)-(−)-**12a**, $[\alpha]_D$ −12.64° (c 1.21) was obtained.

(*b*) *With Elemental Chlorine.* Into a cooled (−5–0°C) and stirred solution of **1a** (0.164 g, 0.599 mmol) in carbon tetrachloride (15 mL) chlorine was added (5 mL, 3 g in 10 mL) in the same solvent. The stirring was continued for 3 hours at room temperature. The solvent and the excess of chlorine were removed *in vacuo* and the residue was purified as stated above to give **12a** (0.0992 g, 76%).

From (*R*)-(+)-**1a**, $[\alpha]_D$ +156.50 (c 1.0), chloride (*R*)-(+)-**12a**, $[\alpha]_D$ +15.26 (c 4.96) was obtained. Using methylene chloride as the solvent from (*R*)-(+)-**1a**, $[\alpha]_D$ +156.5°, (*R*)-(+)-**12a**, $[\alpha]_D$ +7.42 (c 1.86), was obtained.

Brominolysis of (R)-(+)Se-Methyl t-Butylphenylphosphinoselenoate

A solution of elemental bromine (0.1724 g, 1.36 mmol) in methylene chloride (5 mL) was added dropwise to a stirred solution of **1a** (0.2970 g, 1.08 mmol), $[\alpha]_D$ +153.3° in methylene chloride (10 mL). The stirring was continued for 2 hours at room temperature and then the reaction mixture was concentrated *in vacuo*. The efforts to crystallize the reaction product from pentane failed; G.C. showed in the mixture **12b** (40%), the pyrophosphinate **24** (10%) and the selenopyrophosphinate **26** (14%) in addition to the methaneselenenyl bromide and its decomposition products. The fraction of product obtained by extraction with pentane was 77% pure according to G.C. analysis and it had $[\alpha]_D$ + 6.06° (c 0.33).

Chlorinolysis of Se-Phenyl t-Butylphenylphosphinoselenoate

Reaction was carried according to the same procedure as described for *Se*-methyl ester **1a**. From (*S*)-(−)-**1b**, $[\alpha]_D$ −173.30, reacting with SO_2Cl_2 in benzene, (*S*)-(−)-**12a**, $[\alpha]_D$ −5.64° (c 0.585) was obtained.

Reaction of Se-Methyl t-Butyl(phenyl)phosphinoselenoate **1a** *with Iodine*

(*a*) *In Methylene Chloride.* To a solution of **1a** (0.1574 g, 0.57 mmol) in CH_2Cl_2 (4 mL), the elemental iodine was added (0.1357 g, 0.53 mmol) in one portion. The progress of the reaction was monitored periodically by means of ^{31}P NMR spectroscopy. After the reaction mixture had been stored at room temperature during 154 hours, its composition did not change. ^{31}P NMR spectrum showed the presence of selenonium salt **9**, δ (24.3 MHz) +88.2 (J_{P-Se} 476 Hz) (52%), **12c**, δ +57.0 (21%) and two diasteromers of bis(*t*-butylphenyl)pyrophosphinate **24**, complexed with iodine, δ +64.3, δ +63.2 (27%). To the reaction mixture cyclohexene (excess) was added until the mixture decolorized. The ^{31}P NMR spectroscopy of the reacting system showed the following signals: **1a**, δ +75.7 (40%), δ +59.5 (9%), **24**, δ +57.7 and +57.4 (together 17%) and **12c**, δ +54.2 (42%). Then triethylamine (excess) was added. A pale-yellow precipitate formed immediately. The solution decanted from the solid was investigated by ^{31}P NMR spectroscopy and GC/MS analysis. According to the ^{31}P NMR spectrum the mixture contained **1a** (37%), probably Bu^{t}PhP(O)SeC$_6$H$_9$, **15**, δ +61.4 (4%), **12c** (4%), bis(*t*-butylphenyl)pyrophosphinate **24**, δ +46.7, δ +46.5 (32%), and triethylammonium t-butylphenylphosphinate (22%).

GC/MS analysis showed the presence of **1a** m/z (70 eV) 278 (M^+ + 3, 1%), 277 (M^+ + 2, 1%), 276 (M^+ + 1, 6%), 275 (M^+, 0.6%), 274 (M^+ − 1, 4%), 220 (15), 181 (10), 125 (100), 77 (9), 57 (23) and Bu^{t}PhP(O)SeC$_6$H$_9$, **15**, m/z 343 (M^+ + 1, 1%), 342 (M^+, 0.5%), 341 (M^+ − 1, 4%), 81 (C_6H_9, 100) in addition to iodocyclohexane, diiodocyclohexane and 1-methylseleno-2-iodocyclohexane.

(*b*) *In Toluene.* To a solution of **1a** (0.2965 g, 1.07 mmol) in toluene (5 mL) iodine (0.5610 g, 2.2 mmol) was added in one portion. The ^{31}P NMR spectrum of the heterogeneous mixture showed the presence of **16d** (^{31}P NMR data are given in Table 2). A material insoluble in toluene was investigated by ^{31}P NMR spectroscopy in CH_2Cl_2 and shown to be a mixture of **16d** and **19c** (for ^{31}P NMR data see Table 2). The combined reaction mixture was treated with an excess of triethylamine to remove iodine. The solution was decanted from a pale-yellow solid and analyzed by the ^{31}P NMR spectroscopy and GC/MS method.

^{31}P NMR spectrum showed only *t*-butylphenylphosphinoiodidate **12c** and bis(*t*-butylphenyl)pyrophosphinate **24**. According to GC/MS analysis the mixture contained: **12c**, m/z (70 eV) 309 (M^+ + 1, 1%), 181 (M^+-I, 56%), 125 (100), 77 (24), 57 (38); pyrophosphinate, **24a**$_1$: m/z 381 (M^+ + 2, 1%), 379 (M^+ + 1, 2%), 378 (M^+, 1%), 323 (15), 322 (66), 321 (44), 267 (11), 266 (77), 265 (97), 201 (37), 188 (17), 125 (100), 77 (39), 57 (81); **24a**$_2$: 381 (M^+ + 2, 3%), 379 (M^+ + 1, 0.7%), 323 (11), 322 (62), 321 (55), 266 (66), 265 (100), 222 (11), 202 (13), 201 (40), 188 (19), 141 (12), 125 (91), 77 (37), 57 (86), and two diastereoisomers of unsymmetrical bis(*t*-butylphenyl)selenopyrophosphinate, **26a**$_1$: m/z 445 (M^+ + 4, 1%), 444 (M^+ + 3, 3%), 443 (M^+ + 2, 4%), 442 (M^+ + 1, 15%), 441 (M^+, 3%), 386 (24), 384 (14), 338 (19), 306 (28), 305 (78), 265 (11), 189 (9), 188 (17), 186 (10), 185 (28), 125 (41), 111 (12), 107 (17), 77 (25), 57 (100); **26a**$_2$: m/z 445 (M^+ + 4, 1%), 444 (M^+ + 3, 4%), 443 (M^+ + 2, 6%), 442 (M^+ + 1, 17%), 441 (M^+, 3%), 440 (M^+ − 1, 11%), 386 (35), 385 (19), 384 (10), 306 (41), 305 (100), 265 (10), 189 (13), 188 (34), 186 (15), 185 (44), 125 (46), 109 (14), 108 (15), 107 (20), 77 (19), 57 (99).

Reactions of Se-Methyl and Se-Phenyl di-t-Butylphosphinoselenoates **2a, b** *with SO_2Cl_2 and Halogens. General procedure*

A 10 mm NMR tube was charged with solution of **2a** or **2b** in a proper solvent and closed with a

rubber septum. A solution of halogen or sulfuryl chloride in the same solvent was added from a syringe at room temperature. The ^{31}P NMR data on intermediates **8** ⇄ **11** and **18** are given in Tables 2 and 3, those on final products **13** in Table 4. The compositions of the reaction mixtures depended on the reaction time and solvent and are given below. The reacting system **2a** + SO_2Cl_2 in $CDCl_3$. After 1 h: **13a** (main product), additionally unmeasurable amount of **18a** was observed. The system **2a** + SO_2Cl_2 in toluene. After 1 h **13a** (100%). The system **2a** + Cl_2 in $CDCl_3$—CCl_4 (5:1): After 1 hour **13a** (100%). The system **2b** + SO_2Cl_2 in $CDCl_3$. After 1 hour **13a** (100%); $C_6H_5SeCl_3$ was separated as white crystals, mp 129–134 (lit. [13] reports 133–137). The same results were obtained for **2b** reacting with chlorine. The reacting system **2a** + Br_2 in benzene. After 3.5 hours: **13b** (7%), **8** ⇄ **11** (69%), **18b** (11%), **25** (13%); after 3 months: **13b** (69%), **11b** (15%), **25** (16%). The system **2a** + Br_2 in $CDCl_3$. After 12 hours: **13b** (58%), **8** ⇄ **11** (19%), **18b** (20%), **20** (3%). The system **2b** + Br_2 in $CDCl_3$. After 4 hours: **13b** (90%) traces of **18**, **25** (10%); additionally, crystalline $PhSeBr_3$ was separated. Mp 89–91 (lit. [13] reports mp 105). The reacting system **2a** + I_2 in benzene. After 6 months: **8** ⇄ **11** (89%), δ (24.3 MHz) +96.4, $\Delta\delta$ 12.7 (J_{P-Se} 413 Hz, ΔJ = 54 Hz), **25** (17%). **2a** + $2I_2$ in $CDCl_3$. After 6 months: **8** ⇄ **11** (84%), δ (24.3 MHz) 95.6, $\Delta\delta$ 12.0, J_{P-Se} 410 Hz, ΔJ 51; **25** (16%).

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