Reaction of three-coordinate phosphorus compounds with organophosphorus pseudohalogens. Part 4.[1] The mechanism of interaction between bis(phosphinoyl) diselenides $[R^1R^2P(O)Se]_2$ with three-coordinate phosphorus compounds

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The reaction of bis(phosphinoyl) diselenides $R^1R^2P(O)Se–SeP(O)R^1R^2$ **1** with P(III) compounds has been investigated and its mechanistic features have been elucidated by variable temperature ^{31}P NMR spectroscopy. These studies show that in most cases phosphonium intermediates $\left[>P(O)-Se-P^+< \quad {}^-O-P(Se)< \right]$ **7**, **13** and $\left[>P(Se)-O-P^+< \quad {}^-O-P(Se)< \right]$ **10**, **16** are involved. In the case when ligands on P(III) increase the stability of the five-coordinate structure, a phosphorane intermediate is observed. In the isomerization **7**→**10** and **13**→**16** the pathway of decomposition (deselenization, deoxygenation or dealkylation) to give stable end products is influenced by electronic and steric factors.

There has been a continued interest in organic and inorganic selenium chemistry. Many important biological functions for selenium have been demonstrated. Several proteins have been found to contain selenium and monoselenophosphoric acid $(HO)_3P{=}Se$ has been found to act as selenium donor for the synthesis of selenium-dependent t-RNA.[2–5] It has been known since 1947 that diselenides with phosphinoyl groups attached to the diselenide core $R^1R^2P(O)–Se–Se–P(O)R^1R^2$ exhibit typical properties of pseudohalogens.[6,7] The system which consists of triphosphate ATP, diphosphate ADP (pyrophosphate) and monophosphate AMP together with inorganic phosphates is of fundamental importance to the energy metabolism of all cells.

sym-Monoselenopyrophosphate $^{2-}O_2P(O)–Se–P(O)O_2^{2-}$ is a structural analogue of pyrophosphate (PP_i) which is a substrate for many enzymes. The synthesis and investigations of organophosphorus compounds with a sulfur bridging atom were developed in this laboratory.[8,9] Tetramethyl *sym*-monothiopyrophosphate prepared by the methodology of Michalski and co-workers was used to obtain *sym*-monothiopyrophosphate $^{2-}O_2P(O)–S–P(O)O_2^{2-}$ (MTP) as the probe for examining transition states of enzymatic reactions.[10–12] Preparation of analogous *sym*-monoselenopyrophosphate (MSP) requires, above all, efficient access to organophosphorus compounds containing the >P(O)–Se–P(O)< system. Sulfenyl chlorides $(RO)_2P(O)SCl$ are electrophilic thiophosphorylating reagents but methods based on them are not suitable because selenyl chloride analogues $(RO)_2P(O)SeCl$ are highly unstable.[9,13]

Therefore we turned our attention towards $R^1R^2P(O)–Se–Se–P(O)R^1R^2$ (**1**) systems. From earlier experience with analogous sulfur compounds we anticipated that their reactions with suitable tricoordinate phosphorus compounds might lead to the desired goal. Indeed the diselenides **1**, when allowed to react with dialkyl trimethylsilyl phosphites $R^3R^4POSiMe_3$ **2** under carefully chosen conditions, gave the *sym*-selenopyrophosphate systems $R^1R^2P(O)–Se–P(O)R^3R^4$ (**3**) in very good yield.[14]

$$\mathbf{1} + \mathbf{2} \xrightarrow[CH_2Cl_2]{-95\ ^\circ C} \mathbf{3} + \underset{\mathbf{4}}{R^1R^2P(Se)OSiMe_3}$$

The chemoselectivity of this reaction contrasts with those performed using other tricoordinate phosphorus esters. In the reaction between triethyl phosphite **5a** and bis(phosphinoyl) diselenide **1a** ($R^1 = R^2 = EtO$), performed in the days before NMR, two products were identified: tetraethyl *asym*-monoselenopyrophosphate $(EtO)_2P(Se)–O–P(O)(OEt)_2$ (**8a**) and *O*,*O*,*Se*-triethyl selenophosphate $(EtO)_2P(O)SeEt$ (**14a**).[15] Using ^{31}P NMR spectroscopy and column chromatography three more products have been recognized: *O*,*O*,*O*-triethyl selenophosphate $(EtO)_3PSe$ (**9a**), triethyl phosphate $(EtO)_3PO$ (**12a**) and tetraethyl *sym*-diselenopyrophosphate $(EtO)_2P(Se)–O–P(Se)(OEt)_2$ (**11a**). It became obvious that this reaction involves concurrent deselenization and deoxygenation.

We anticipated that NMR spectroscopy would reveal details of the mechanism of interaction between diselenides **1** and tricoordinate phosphorus compounds. We had already had success with the sulfur analogues of **1**.[1] In this report experiments are presented which clearly indicate the way in which products depend on reaction conditions and structural features of both the components involved.

Results and discussion

The diselenides **1** are readily available by iodine oxidation of the corresponding selenoacids **6**.[6] We improved this oxidation

$$R^1R^2P(O)H \xrightarrow[NEt_3]{[Se]} \underset{\mathbf{6}}{R^1R^2P(Se)O^-} \xrightarrow{I_2} \mathbf{1}$$

procedure by using sulfuryl chloride in methylene chloride as the oxidant.

Prior to detailed discussion of our results it is best to take a good look at Schemes 1 and 2.

The deselenization described in Scheme 1 (path a) proceeds by formation of the phosphonium intermediate **7** and its transformation into the *asym*-monoselenopyrophosphate **8** and the selenoester **9**. This transformation occurs *via* attack of the

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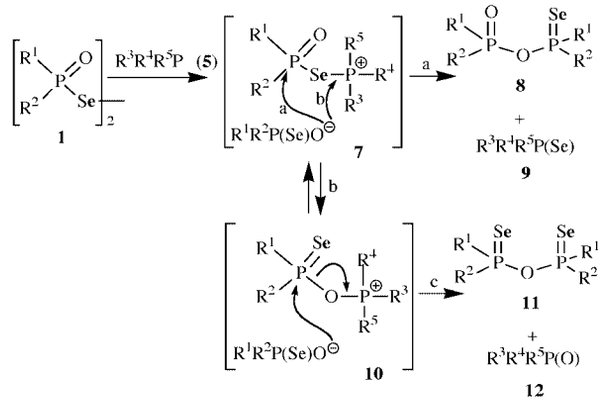
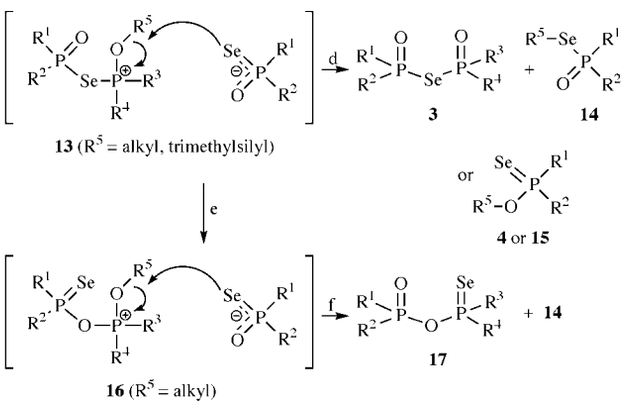


Scheme 1



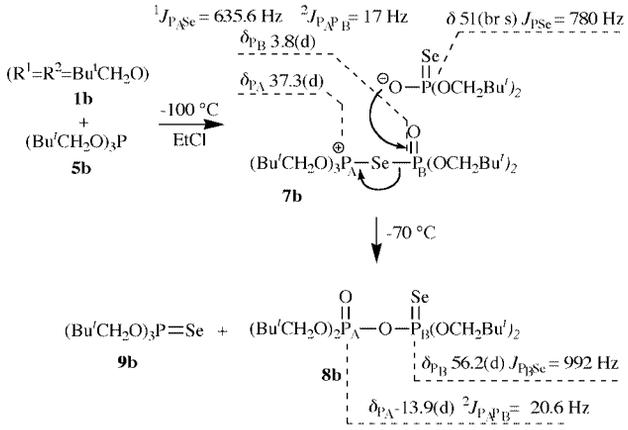
Scheme 2

counteranion derived from the corresponding selenoacids. Deoxygenation occurs in the isomerization of **7** into **10** and decomposition of isomeric ion pair **10** into the *sym*-diselenopyrophosphate-type structure **11** and the oxoester **12** (Scheme 1, paths b and c). Pathways a and c are only representative of the interaction of P(III) compounds where those compounds contain ligands immune to dealkylation or desilylation. When an alkoxy group is present in a P(III) system, the phosphonium intermediates **13** and **16** may undergo dealkylation as shown in the Scheme 2. In the first case the *sym*-monoselenopyrophosphate system **3** and *O*,*O*,*Se*-trialkyl selenophosphate **14** or *O*,*O*,*O*-trialkyl selenophosphate **15** are formed *via* path d. Similarly the formation of the *asym*-selenopyrophosphate system **17** and the selenoester **14** takes place by alkyl group transfer inside the ion pair **16** (path f). When $R^5 = Me_3Si$ in a P(III) system the decomposition of ion pair **13** proceeds chemoselectively *via* attack of the silyl group on the oxygen of the ambident monoselenophosphorate anion. As mentioned already, compounds **3** and **4** are formed in almost quantitative yield.

The reaction of the diselenides **1** with P(III) compounds is strongly exothermic and proceeds readily at −100 °C. The regioselectivity of this reaction depends on the ligands attached to the system **1** and at the tricoordinate phosphorus atom. It also depends to a striking extent on temperature. In contrast, the influence of solvents of different polarity such as pentane, dichloromethane and nitropropane is marginal.

Variable temperature studies provided compelling evidence about the nature of short-lived intermediates **7** and **10** and their interconversion and decomposition into final products. The experiments were performed in the temperature range −100 to 20 °C in dichloromethane or ethyl chloride. Only data reproducible in at least two experiments are presented here.

An example showing formation of the key phosphonium intermediate **7** containing a P–Se–P^+ bridge is presented in Scheme 3. The reaction between the diselenide **1b** ($R^1 = R^2 =$ Bu^{t}CH$_2$O) derived from neopentyl alcohol and trineopentyl phosphite takes the deselenization course (path a, Scheme 1).

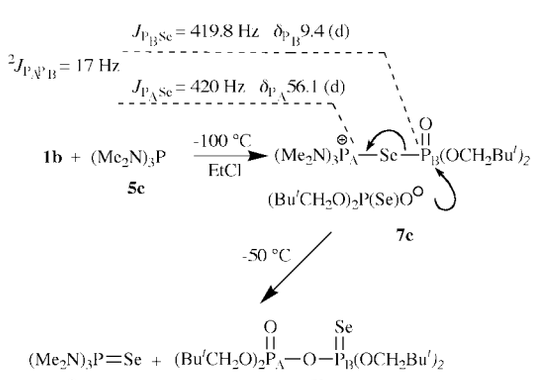


Scheme 3

At −100 °C formation of the intermediate **7b** was observed. Its structure is confirmed by ^{31}P NMR spectroscopy. The chemical shifts of the three different phosphorus centers are of the expected range and multiplicity. The most convincing evidence comes from typical coupling constants for singly-bonded selenium attached to the phosphorus center (J_{PASe} = 635.6 Hz) and two phosphorus atoms bridged by selenium ($^2J_{PAPB}$ = 17 Hz). The values of phosphorus selenium coupling constants are diagnostic for single P–Se and double P=Se bonds.[16] The phosphonium intermediate **7b** decomposes at −70 °C into the tetraneopentyl *asym*-monoselenopyrophosphate **8b** *via* nucleophilic displacement at P_B by the ambident anion of dineopentylphosphoroselenoic acid (hard–hard interaction). It is amazing that this reaction is very fast at −70 °C, in spite of steric hindrance caused by neopentoxy groups. The structure of **8b** is confirmed by coupling constants $^2J_{PAPB}$ 20.6 Hz and $^1J_{PBSe}$ 992 Hz. The coupling constants of two phosphorus atoms connected by a selenium or sulfur bridge are substantially lower than those of the pyrophosphate system bridged by oxygen.[17–19] The yield of the monoselenopyrophosphate **8b** was almost quantitative.

A similar deselenization course is observed in the reaction between the diselenide **1b** and tris(dimethylamino)phosphine **5c**. The relatively stable phosphonium salt **7c** was formed at −100 °C and then disappeared at −50 °C to give the selenopyrophosphate **8b**.

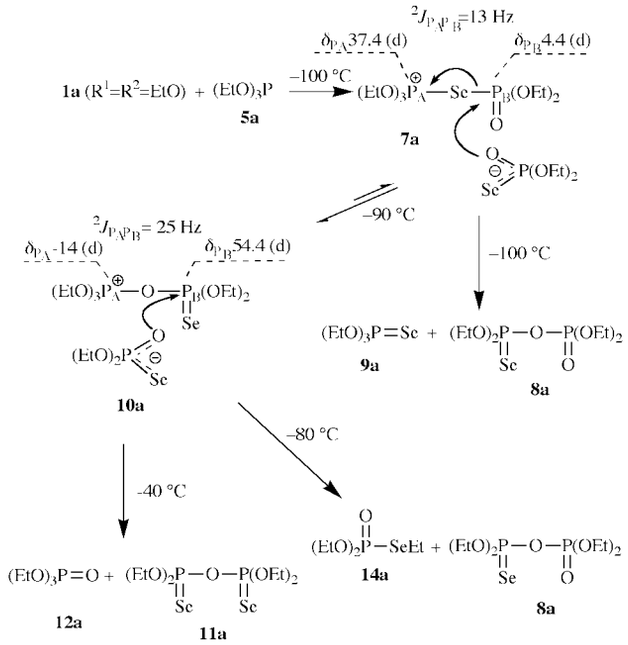
The structure of the salt **7c** (Scheme 4) containing two differ-



Scheme 4

ent phosphorus centers bridged by selenium is evident from the ^{31}P NMR spectra. The *asym*-monoselenopyrophosphate **8b** shows spectral ^{31}P NMR properties identical to those described in Scheme 3.

The reaction between triethyl phosphite **5a** and diselenide **1a** ($R^1 = R^2$ = EtO) proceeds *via* both deselenization and deoxy-

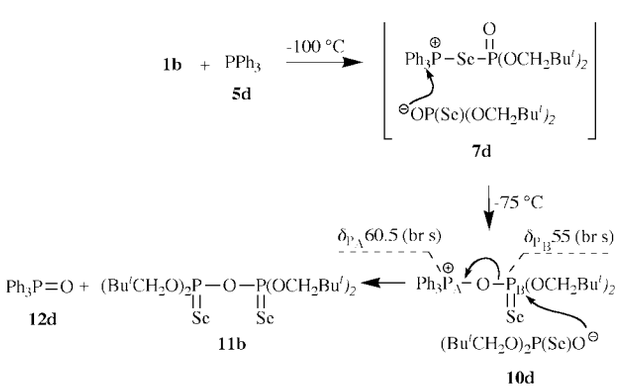


Scheme 5

genation (Scheme 5, paths a and c in Scheme 1). We were able to observe two isomeric transient phosphonium salts **7a** and **10a** by ^{31}P NMR spectroscopy. The former is involved in deselenization. The latter, which is formed by isomerization of salt **7a**, decomposes (deoxygenation) to give triethyl phosphate $(EtO)_3P(O)$ **12a** and tetraalkyl *sym*-diselenopyrophosphate **11a** at −40 °C. However at −80 °C dealkylation takes place giving *O*,*O*,*Se*-triethyl selenophosphate **14a** and tetraethyl *asym*-monoselenopyrophosphate **8a**. Both intermediate phosphonium salts **7a** and **10a** are readily recognized by the chemical shifts of the corresponding phosphorus centers. The system containing two phosphorus centers bridged by selenium has a typically low coupling constant $^2J_{PAPB} = 13$ Hz, while the isomeric system containing two phosphorus centers bridged by oxygen has a much higher coupling constant $^2J_{PAPB} = 25$ Hz. Similar values of coupling constants are observed for the corresponding selenopyrophosphates.

It is most likely that isomerization of the phosphonium salt **7a** into **10a** proceeds *via* nucleophilic attack of the counterion $(EtO)_2P(Se)O^-$ on the phosphonium center of the salt **7a**. The involvement of a pentacoordinate intermediate is not excluded. This question is discussed in detail later in this paper.

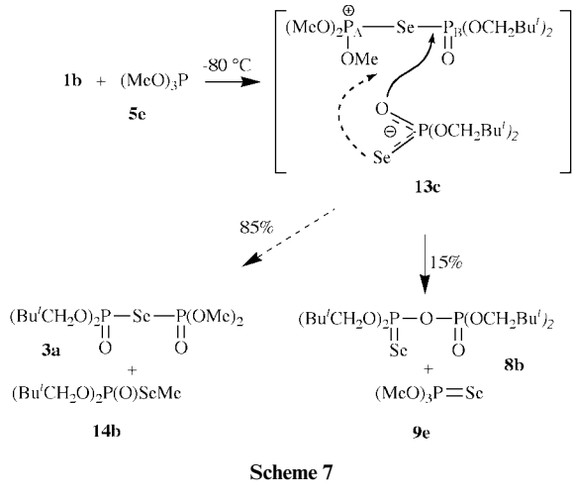
The reaction between diselenide **1b** and triphenylphosphine **5d** takes the deoxygenation course (Scheme 6, Scheme 1, path c). In this case we did not observe at −100 °C by ^{31}P NMR the primary phosphonium salt **7d**. It was possible however, to observe the isomeric phosphonium salt **10d**.



Scheme 6

The deoxygenation reaction presented in Scheme 6 proceeds in almost quantitative yield and can be applied to other diselenides as a preparative method for *sym*-diselenopyrophosphate type compounds **11**. An alternative way to the compound **11** ($R^1 = R^2 = EtO$) based on the reaction of tetraethyl pyrophosphite with elemental selenium seems to be of low preparative value and is not verified by ^{31}P NMR spectroscopy.[20]

It is of interest to compare the reactions described in Schemes 3 and 4 with the interaction of the trimethyl phosphite **5e** with diselenide **1b**, where dealkylation (85%) prevails over deselenization (~ 15%). The mechanistic explanation of this reaction course is given in Scheme 7.

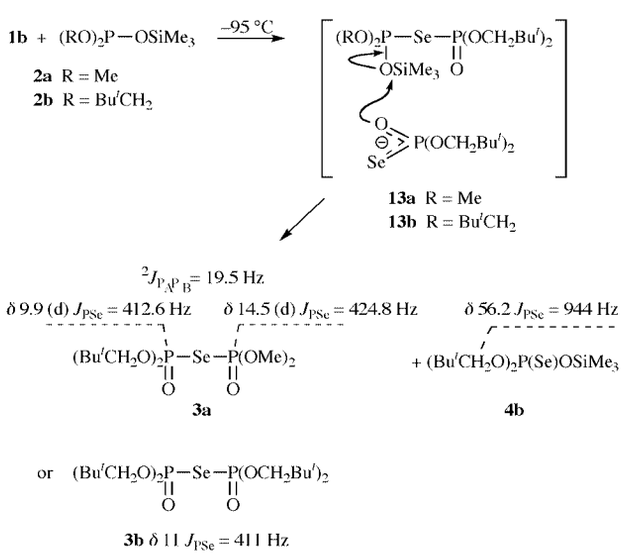


Scheme 7

The similar reaction with triethyl, rather than trimethyl phosphite leads to the *sym*-monoselenopyrophosphate $(Bu^tCH_2O)_2P(O)–Se–P(O)(OEt)_2$ in only 20%. This is not surprising, because nucleophilic displacement at an ethoxy carbon atom is known to occur at a considerably slower rate than at a methoxy carbon.

The reaction between dialkyl trimethylsilyl phosphites $(RO)_2P–OSiMe_3$ **2** and diselenide **1b** proceeds with full chemoselectivity.[14]

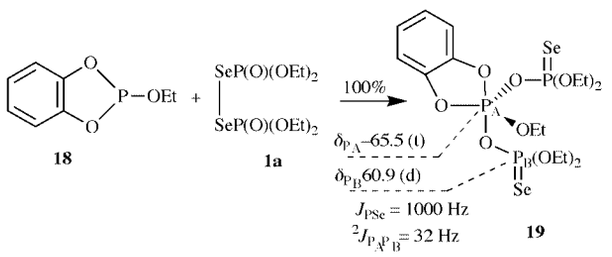
Tetraalkyl *sym*-monoselenopyrophosphates are formed in very high yield at −95 °C. Our attempts to detect the phosphonium salts **13a**,**b** failed. On the basis of other observations described in this paper, however, we can confidently accept the mechanistic Scheme 8. The decomposition of the intermediate phosphonium salt **13a**,**b** leading to *sym*-monoselenopyrophates **3a**,**b** takes place *via* a transsilylation pathway. Interestingly the



Scheme 8

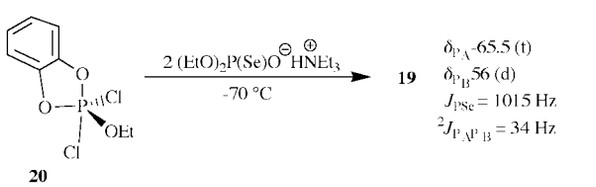
same reaction performed at temperatures higher than −95 °C leads to a mixture of products.

It is well known that five-membered ring and aryloxy ligands increase the stability of five-coordinate phosphorus compounds. Therefore we decided to employ P(v) esters derived from 1,3,2-benzodioxaphosphole system. In earlier studies formation of five-coordinate intermediates has been observed in the reaction of 2-neopentyloxy-1,3,2-benzodioxaphosphole with diethoxyoxophosphoranesulfenyl chloride.[21] The interaction of diselenide **1a** with 2-ethoxy-1,3,2-benzodioxaphosphole **18** leads to the adduct **19** which is stable at room temperature (Scheme 9). The structure of the phosphorane **19** is



Scheme 9

strongly supported by ^{31}P NMR spectroscopic data (chemical shifts, coupling constants values and multiplicity of spectral signals) (Scheme 9) and independent synthesis (Scheme 10).

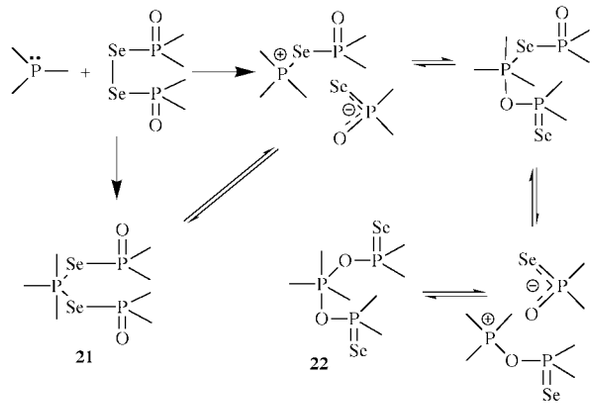


Scheme 10

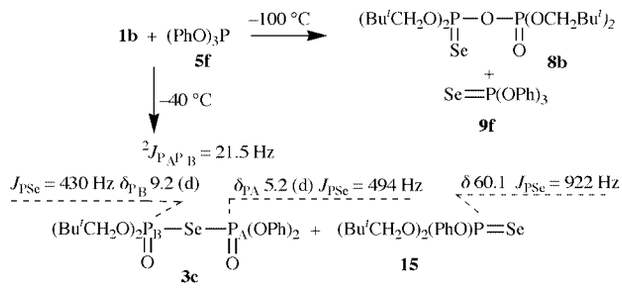
It is not easy to define the stereochemical course of the reaction described in Scheme 9, or that of all other oxidative additions of diselenides **1** to tricoordinate phosphorus compounds. However, this addition is most likely to involve formation of the primary pentacoordinate intermediate **21** in a single step procedure. Such addition can result in an orientation which is both apical, both equatorial or one apical and one equatorial. The frontier orbital method shows that axial–equatorial is forbidden, while the other two products that can be formed are allowed.[22] The feasible possibility is that the primary phosphorane **21** has an e–e structure which, after dissociations and redissociations, is transformed into the isomeric structure **22**. The a–a arrangement for phosphorane **22** is excluded because the five-membered ring is likely to occupy a–e positions. The e–e structure is supported by lack of different signals for the two selenophosphoryl groups in ^{31}P NMR (121.5 MHz). However, fast ligand exchange for the a–e structure would lead to the same spectral pattern.

We were unable to observe the formation of the pentacoordinate intermediate $(PhO)_3P[O–P(Se)(OCH_2Bu^t)_2]_2$ or phosphonium type intermediates in the reaction of $(PhO)_3P$ **5f** with the diselenide **1b**. We looked for them because these intermediates have been observed in analogous reactions with phosphinoyl disulfides.[1]

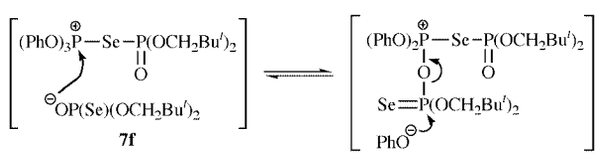
Formation of the products **8b** and **9f** at −100 °C can be readily explained by a pathway analogous to that described in Schemes 3 and 4. It seems likely that at a higher temperature (−40 °C) ligand exchange may occur in the intermediate phosphonium salt **7f** leading to new intermediate phosphonium salt **23**. The latter decomposes by the nucleophilic attack of phenoxy anion on the selenophosphoryl phosphorus center to give compounds **3c** and **15**.



Scheme 11



Scheme 12



All the reactions described so far must be performed under strictly anhydrous conditions; phosphonium salts **7**, **10** and **13**, **16** and phosphorane **19** are very readily hydrolyzed.

In conclusion, consideration of the interaction between three-coordinate phosphorus compounds and diselenides by studies at low temperature ^{31}P NMR and full characterization of final reaction products allows a rational mechanistic description. In consequence guidelines are generated for the rational synthesis of compounds containing groups >P(O)–Se–P(O)< and >P(Se)–O–P(Se)<.

The chemoselectivity of the reaction between bis(phosphinoyl) diselenides **1** and P(III) can be influenced by ligands at the P(v) and P(III) centres and the temperature of reaction. The phosphonium intermediates **7, 10** and **13, 16** which are of great importance for the outcome of the reaction are most likely in dynamic equilibria with P(v) phosphoranes. The equilibria favour the phosphonium structure except when phosphorus contains ligands which stabilize the P(v) species. But in every case the reaction seems to advance *via* phosphonium intermediates.

Experimental

General

Melting points were uncorrected. Solvents and commercial reagents were purified and dried by conventional methods. All reactions were performed under Ar. Products were identified with ^{31}P NMR spectroscopy by comparision with authentic samples (unless specified otherwise). ^{31}P NMR spectra were recorded on a FT JEOL FX-60H spectrometer at 24.3 MHz and on a Bruker MSL 300 spectrometer at 121.5 MHz. Positive

NMR chemical shifts were reported in parts per million (ppm) downfield from 85% H_3PO_4 as external standard. IR spectra were taken with ATI MATTSON INFINITY FTIR 60 spectrometer. MS spectra were measured with LKB 2091 GCMS spectrometer. Microanalyses were obtained on a Carlo Erba CHNS-OEA 1108 Elemental Analyzer.

Low-temperature ^{31}P NMR measurements

A 10 mm NMR tube (cooled in liquid N_2 or acetone–solid CO_2) was charged with the compounds (0.5–1 mmol) in dichloromethane or ethyl chloride. All operations were carried out in a dry argon atmosphere. The tubes were closed tightly with rubber septa under argon. Variable temperature spectra were monitored usually at intervals of 10 °C and 10 min.

Materials

The following were prepared by literature procedures: tris(dimethylamino)phosphine,[23] trineopentyl phosphite,[23] dimethyl trimethylsilyl phosphite,[24] dineopentyl trimethylsilyl phosphite,[24] ethyl *o*-phenylene phosphite,[25] di-*O*-ethyl hydrogen phosphoroselenoate.[26]

Bis[diethoxy(phosphinoyl)] diselenide[6] 1a. (75%) (Found: C, 22.62; H, 4.99; P, 13.45. Calc for $C_8H_{20}O_6P_2Se_2$: C, 22.24, H, 4.66; P, 14.34%); δ_P (24.3 MHz, $CDCl_3$) 13.0 ($^1J_{PSe}$ 580) prepared by chlorination of the potassium salt of di-*O*-ethyl hydrogen phosphoroselenoate with half molar amount of sulfuryl chloride at −25 °C in CH_2Cl_2.

Bis[dineopentoxy(phosphinoyl)] diselenide[27] 1b. (80%); δ_P (24.3 MHz, $CDCl_3$) 10.1 ($^1J_{PSe}$ 490) (lit.,[27] 10.9. $^1J_{PSe}$ 496) prepared by chlorination of the triethylammonium salt of di-*O*-neopentyl hydrogen phosphoroselenoate with half molar amount of sulfuryl chloride at −25 °C in CH_2Cl_2.

Reactions of bis(phosphinoyl) diselenides 1 with three-coordinate phosphorus compounds 5: General procedure

A solution of compound **5** (5 mmol) in methylene chloride (20 cm^3) was added dropwise at −80 °C to a stirred solution of diselenide **1** (5 mmol) in CH_2Cl_2 (20 cm^3) under a dry argon atmosphere. After 2 h of stirring at −80 °C, the reaction mixture was allowed to warm to ambient temperature. Evaporation of solvent gave the crude reaction mixture which was analysed by ^{31}P NMR spectroscopy.

Reaction of bis[diethoxy(phosphinoyl)] diselenide 1a with triethyl phosphite 5a

Following the general procedure compounds **1a** (2.17 g, 5 mmol) and **5a** (0.83 g, 5 mmol) gave the mixture which was analysed by ^{31}P NMR and was found to contain the following compounds: tetra-*O*-ethyl *asym*-monoselenopyrophosphate **8a** (30%), *O*,*O*,*O*-triethyl selenophosphate **9a** (12%), *O*,*O*,*Se*-triethyl selenophosphate **14a** (15%), triethyl phosphate **12a** (21%) and tetra-*O*-ethyl *sym*-diselenopyrophosphate **11a** (22%). All compounds were isolated by flash chromatography (silica gel) 70–230 mesh, eluent: C_6H_6 to C_6H_6–EtOAc (1:1), graduated change in concentration.

8a δ_P (24.3 MHz, $CDCl_3$) −13.9 (d, *J* 25.4, P_A), 54.2 (d, *J* 25.4, $^1J_{P_BSe}$ 1000, P_B) (lit.[28] −15.5, 58.5, $^1J_{PSe}$ 1020, *J* 24). **14a** δ_P 20.5 ($^1J_{PSe}$ 496) (lit.[16] 19.6, $^1J_{PSe}$ 468). **9a** δ_P 71.0 ($^1J_{PSe}$ 940) (lit.[16] 71.8, $^1J_{PSe}$ 935). **12a** δ_P −2.6 (lit.[29] −1.3). **11a** δ_P 54.8 ($^1J_{PSe}$ 890).

Reaction of bis[dineopentoxy(phosphinoyl)] diselenide 1b with trineopentyl phosphite 5b

According the general procedure with **1b** (3 g, 5 mmol) and **5b** (1.46 g, 5 mmol) the crude mixture was obtained and found by means of its ^{31}P NMR spectrum to contain tetra-*O*-neopentyl *asym*-monoselenopyrophosphate **8b** (50%), and *O*,*O*,*O*-trineopentyl selenophosphate **9b** (50%). Flash chromatography (eluent: C_6H_6 and C_6H_6–EtOAc 2:1) gave:

8b (2.3 g, 90%) δ_P (24.3 MHz, $CDCl_3$) −13.9 (d, *J* 20.6, P_A), 56.2 (d, *J* 20.6, $^1J_{P_BSe}$ 992, P_B) (lit.[27] 57.2, −14.3, $^1J_{PSe}$ 1014, *J* 21.5); *m*/*z*: 522 [M^+(^{80}Se), 10.7%], 520 [M^+(^{78}Se), 5.5%], 43 (100), 242 (91.8). **9b** (1.6 g, 87%) (Found: C, 48.3; H, 8.62; P, 7.98. Calc. for $C_{15}H_{33}O_3PSe$: C, 48.52; H, 8.95; P, 8.34%); δ_P 69.9 ($^1J_{PSe}$ 932.7) (lit.[25] 72.6).

Reaction of bis[dineopentoxy(phosphinoyl)] diselenide 1b with tris(dimethylamino)phosphine 5c

From **1b** (3 g, 5 mmol) and **5c** (0.8 g, 5 mmol) a mixture of **8b** (50%) and hexamethylphosphoroselenoic triamide **9c** (50%) was obtained.

9c δ_P (24.3 MHz, $CDCl_3$) 82.4 ($^1J_{PSe}$ 790) (lit.[30] 83.2, $^1J_{PSe}$ 780).

Reaction of bis[dineopentoxy(phosphinoyl)] diselenide 1b with triphenylphosphine 5d

^{31}P NMR analysis of the crude reaction mixture, obtained from **1b** (3 g, 5 mmol) and **5d** (1.3 g, 5 mmol) revealed the presence of triphenylphosphine oxide **12d** (50%), and tetra-*O*-neopentyl *sym*-diselenopyrophosphate **11b** (50%). Compound **11b** was purified by preparative chromatography (R_f = 0.6, hexane–EtOAc 3:1).

11b (2.3 g, 80%), mp 87–89 °C (Found: C, 40.6; H, 7.16; P, 11.4. Calc. for $C_{20}H_{44}O_5P_2Se_2$: C, 41.1; H, 7.59; P, 10.6%). δ_P (24.3 MHz, $CDCl_3$) 55.4 ($^1J_{PSe}$ 852); ν_{max}(film)/cm^{-1} 1017 (P–O–P) and 573 (P=Se); *m*/*z*: 586, 584, 582 (ratio 10:9.5:4.2) [<1%, M^+ (2 × ^{80}Se), M^+ (^{78}Se^{80}Se), M^+ (2 × ^{78}Se)].

Reaction of bis[dineopentoxy(phosphinoyl)] diselenide 1b with trimethyl phosphite 5e

From **1b** (3 g, 5 mmol) and **5e** (0.6 g, 5 mmol) the crude mixture was obtained and found by means of its ^{31}P NMR spectrum to contain **8b** (8%), *O*,*O*,*O*-trimethyl selenophosphate **9e** (7%), *O*,*O*-dineopentyl *Se*-methyl selenophosphate **14b** (42%), and *O*,*O*-dimethyl *O*,*O*-dineopentyl *sym*-monoselenopyrophosphate **3a** (43%). Compound **3a** is stable in solution for 4 h at room temperature. All attempts to isolate pure compound **3a** failed.

9e δ_P (121.5 MHz, $CDCl_3$) 72.2 ($^1J_{PSe}$ 945) (lit.[31] 78.1, $^1J_{PSe}$ 955.6). **3a** δ_P 14.5 (d, *J* 19.5, $^1J_{PSe}$ 424.8, P_A), 9.9 (d, $^1J_{PSe}$ 412.6, *J* 19.5, P_B). **14b** δ_P 21.8 ($^1J_{PSe}$ 490) (lit.[32] 23.4, $^1J_{PSe}$ 473.2).

Reaction of bis[dineopentoxy(phosphinoyl)] diselenide 1b with dimethyl trimethylsilyl phosphite 2a

From **1b** (3 g, 5 mmol) and **2a** (0.9 g, 5 mmol) a mixture of **3a** (50%) and of *O*,*O*-dineopentyl *O*-trimethylsilyl selenophosphate **4b** (50%) was obtained.

4b δ_P (121.4 MHz, $CDCl_3$) 56.2 ($^1J_{PSe}$ 944) (lit.[33] 55.2, $^1J_{PSe}$ 940).

Reaction of bis[dineopentoxy(phosphinoyl)] diselenide 1b with dineopentyl trimethylsilyl phosphite 2b

From **1b** (3 g, 5 mmol) and **2b** (1.5 g, 5 mmol) a mixture of products was formed and found by ^{31}P NMR analysis to contain **3b** (50%), and **4b** (50%). Tetra-*O*-neopentyl *sym*-monoselenopyrophosphate **3b** was purified by flash chromatography (silanised silica gel 60, eluent: benzene–$CHCl_3$ 1:1).

3b[13,14] (2 g, 78%) mp 45 °C (Found: C, 46.5; H, 9.1; P, 12.3. Calc. for $C_{20}H_{44}O_6P_2Se$: C, 46.1; H, 8.5; P, 11.9%); δ_P (121.5 MHz, $CDCl_3$) 11.0 ($^1J_{PSe}$ 411); ν_{max} (film)/cm^{-1} 490 (P–Se–P) and 1256 (P=O).

Reaction of bis[dineopentoxy(phosphinoyl)] diselenide 1b with triphenyl phosphite 5f

From **1b** and **5f** the crude reaction mixture was obtained and found by means of ^{31}P NMR and of GCMS spectrometry, to contain *O*,*O*,*O*-triphenyl selenophosphate **9f** (20%), tetra-*O*-neopentyl *asym*-monoselenopyrophosphate **8b** (22%) and *O*,*O*-dineopentyl *O*,*O*-diphenyl *sym*-monoselenopyrophosphate **3c** (30%), and *O*,*O*-dineopentyl-*O*-phenyl selenophosphate **15**.

8b δ_P (121.5 MHz, $CDCl_3$) −14.0 (d, *J* 21, P_A), 56.5 (d, *J* 21, $^1J_{PSe}$ 993, P_B); *m*/*z*: 522 [M^+ (^{80}Se), 8.5%], 520 [M^+(^{78}Se), 4.5%]. **9f** δ_P 58.1 ($^1J_{PSe}$ 1086) (lit.[31] 58.6, $^1J_{PSe}$ 1027); *m*/*z*: 390 [M^+(^{80}Se), 6.6%], 388 [M^+(^{78}Se), 12.1%]. **15** δ_P 60.1 ($^1J_{PSe}$ 922); *m*/*z*: 378 [M^+(^{80}Se), 4.7%], 376 [M^+(^{78}Se), 2.3%]. **3c** δ_P 9.2 (d, *J* 21, $^1J_{PSe}$ 430.5, P_B), 5.2 (d, *J* 21, $^1J_{PSe}$ 494, P_A); *m*/*z*: 534 [M^+(^{80}Se), 8.3%], 532 [M^+(^{78}Se), 4.1%].

Reaction of bis[diethoxy(phosphinoyl)] diselenide 1a with ethyl *o*-phenylene phosphite 18

The reaction of **1a** (0.33 g, 1 mmol) and **18** (0.18 g, 1 mmol) in CH_2Cl_2 (7 cm^3) was performed at −60 °C. The reaction mixture, analysed by ^{31}P NMR spectroscopy, showed the presence of unchanged substrates (80% recovery) and the phosphorane **19** (20%), δ_P (121.5 MHz, $CDCl_3$) −65.5 (t, *J* 32, P_A), 60.9 (d, *J* 32, $^1J_{PSe}$ 1000, P_B). Complete conversion of substrates into compound **19**, stable for 2 h in solution at room temperature, was achieved after raising the temperature to −10 °C.

Reaction of 2,2-dichloro-2-ethoxy-1,3,2λ^5-benzodioxaphosphole 20 with di-*O*-ethyl hydrogen phosphoroselenoate 6 in the presence of triethylamine

A solution of di-*O*-ethyl hydrogen phosphoroselenoate **6** (0.44 g, 2 mmol) and triethylamine (0.2 g, 2 mmol) in methylene chloride (2 cm^3) was added at −90 °C to a solution of 2,2-dichloro-2-ethoxy-1,3,2λ^5-benzodioxaphosphole **20** (0.125 g, 1 mmol), freshly prepared from ethyl *o*-phenylene phosphite and chlorine at −100 °C in ethyl chloride (3 cm^3). The reaction mixture was stirred at −70 °C until the ^{31}P NMR spectrum indicated the complete conversion (3 h) of 2,2-dichloro-2-ethoxy-1,3,2λ^5-benzodioxaphosphole **20** into the adduct **19** (100%), δ_P (24.3 MHz, $CDCl_3$) −65.5 (t, *J* 34, P_A), 56 (d, *J* 34, $^1J_{PSe}$ 1015, P_B).

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