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Mercury trifluoroacetate-catalyzed conversion of *Se*-alkyl phosphoroselenolates into the corresponding phosphates

Lucyna A. Wozniak *

Department of Bioorganic Chemistry, Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Lodz, PL 90-363, Sienkiewicza 112, Poland

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Abstract

The role of mercuric trifluoroacetate as reactive agent and activator in reactions of various *Se*-alkyl phosphoroselenoates with O- and N-nucleophiles is examined. The formation of mercury-complexed intermediates of putative mixed anhydride-like structure is indicated.

Keywords: Mercuric trifluoroacetate; Mixed anhydrides; Nucleophilic substitution; Phosphoroselenoates; Phosphorothioates

1. Introduction

Mercuric trifluoroacetate (**1**) has become an important reagent in modern synthetic chemistry, mostly due to its use in oxymercuration/peroxymercuration reactions. These are often focused on diastereoselective syntheses of natural products [1,2] or site-specific fluorescent labeling of proteins [3] as well as on the Lewis acid catalysis of cyclization reactions [4]. However, its potential as acylating agent has been rarely explored so far [5].

We have found that stereospecific solvolysis of *S*-alkyl and *Se*-alkyl phosphorothio(seleno)lates (**2**) into the corresponding phosphates is catalyzed efficiently by $(CF_3COO)_2Hg$ [6]. This prompted us to further investigate the function of mercury in this process.

In this report, we discuss some of the aspects of solvolysis of phosphoroselenolates in the presence of mercuric trifluoroacetate, including both synthetic applications of **1** for stereospecific synthesis of phosphate analogues, and a plausible mechanism of these reactions.

Solvolysis of **2** has been postulated previously to proceed via trifluoroacetic-phosphoric mixed anhydrides **3** as reactive intermediates. Stereochemical results of the solvolysis of these intermediates led us to the conclusion that compounds **3** were formed stereospecifically with retained configuration at the phosphorus center [6] (see Scheme 1).

Some reactive intermediates of mixed phosphorus-carboxylic anhydride structure (**3**) have been postulated based upon ^{31}P NMR analysis [7]. However, *in situ* generated intermediates of putative mixed anhydride-like structures possess phosphorylating properties towards alcohols. In these reactions, *O*-alkyl esters **4** are formed almost exclusively. This observation is at variance with the studies of Michalski and coworkers [8], who reported acylating rather than phosphorylating properties of the isolated phosphoryl trifluoroacetates towards alcohols. Therefore, the formation of mixed anhydrides in reactions mediated by mercury trifluoroacetate has been questioned [8a].

* Tel.: +48-42-6816970; fax: +48-42-681-5483.
E-mail address: lwozniak@bio.cbmm.lodz.pl.

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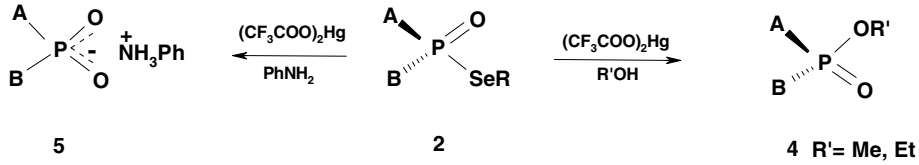


5 2 4 R'= Me, Et

a: AB = 4-methyl-1,3,2-dioxaphosphorinan-yl
b: A = B = OEt R = Et
c: A = B = OMe R = Me
d: A = OMe B = NHPh

Scheme 1.

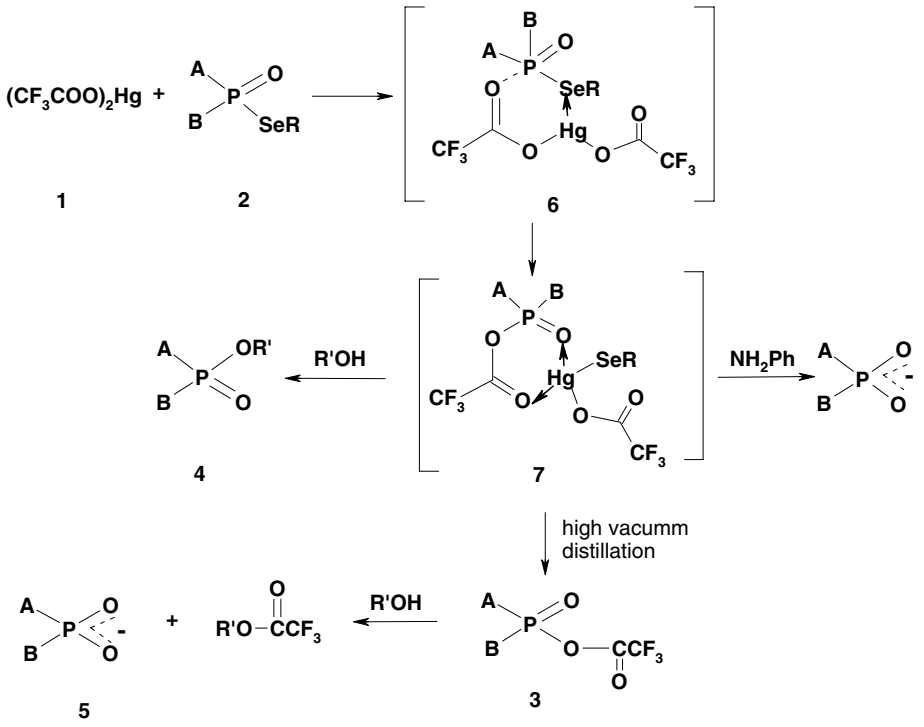
The reactivity of mixed phosphorus-carboxylic anhydrides is complex and depends not only on the relative electrophilicity of both phosphorus and carbon centers and on steric hindrance [9], but also on the acidity of the leaving groups [10]. It is well known that the reactivity of mixed phosphorus-carboxylic anhydrides also depends on the nature of the nucleophile. In general, nitrogen nucleophiles attack on the carbonyl center while oxygen attacks at the phosphoryl center [10b,11]. Recently, we have demonstrated that in the case of 2,4,6-trimethylbenzoyl phosphonothioates it is possible to activate either carbonyl or phosphoryl center using selected tertiary amines [12]. *O*-alkyl or *S*-aryl substituted phosphonates or phosphonothioates were formed almost exclusively when DBU was used as activator but *O*-alkyl benzoates were produced in case of DMAP activation [13]. This observation revealed broad potential for tuning the properties such mixed anhydrides and led us further to reinvestigate the reaction between *Se*-alkyl phosphoroselenolates and mercury trifluoroacetate. We have assumed that mercury complexation could be responsible for enhancement and diversion of reactivity of the intermediates formed in these reactions, in comparison to the isolated mixed anhydrides, in a manner analogous to the effect of strong amines on 2,4,6-trimethylbenzoyl phosphonothioates [12].

We therefore verified the possibility of formation of non-complexed mixed anhydrides in the reported reactions and considered the possibility of an alternative reaction pathway depending on the extent of mercury^{II} catalysis/complexation.

2. Results and discussion

Systematic investigation on reactions of *Se*-alkyl phosphoroselenolates with $(CF_3COO)_2Hg$ indicated that trifluoroacetyl phosphates were obtained almost quantitatively in neutral solvents, and they could be isolated by distillation. As reported, in the absence of mercury derivatives, trifluoroacetyl phosphates elicited exclusively acylating properties [8b].

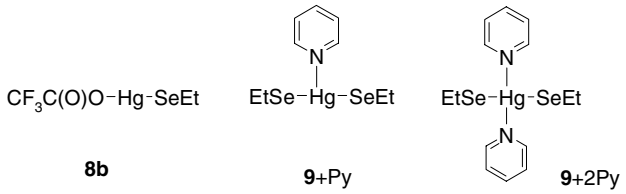
The reaction of *O,O,Se*-trimethyl phosphoroselenolate (**2c**) (^{31}P NMR δ: 27.13, $^{1}J_{PSe}$ = 484 Hz) with an equimolar amount of mercuric trifluoroacetate, after removal of solvent and careful distillation under reduced pressure (30 °C/0.005 mm Hg), furnished *O,O*-dimethyl-*O*-trifluoroacetyl phosphate (**3c**) (^{31}P NMR δ: −6.61 in CH_2Cl_2) in high yield. Treatment of this isolated product with methanol caused slow conversion of the mixed anhydride **3c** into *O,O*-dimethyl phosphate (**5c**) (^{31}P NMR δ: 3.1 in CH_2Cl_2) and methyl trifluoroacetate, respectively (^{19}F NMR δ: −76.98). Moreover, addition of an excess of mercury trifluoroacetate to the distilled trifluoroacetyl phosphate **3c**, followed by methanolysis also provided *O,O*-dimethyl phosphate (**5c**). In an independent set of experiments, it was confirmed that reaction of *O,O,Se*-trimethyl phosphoroselenoate (**2c**) with $Hg(OCOCF_3)_2$ in CH_2Cl_2 resulted in a rapid disappearance of **2c**, accompanied by formation of compound with chemical shift of −6.7 ppm, which after addition of methanol was quantitatively converted into *O,O,O*-trimethyl phosphate (**4c**). The same results were observed for reaction of **2c** with $(CF_3COO)_2Hg$ and methanol added simultaneously. Reaction between **2c**, and mercury trifluoroacetate (molar ratio 1:1) in CH_2Cl_2 is very fast, even at low temperatures (−90 °C), and ^{31}P NMR spectrum recorded at that temperature immediately after mixing the reagents revealed complete disappearance of the resonance for substrate **2c**, and the appearance of a new resonance at about −7 ppm as a broadened signal with a high-field chemical shift characteristic for mixed anhydrides. This signal was deprived of any satellite lines expected from a spin–spin $^{1}J_{PSe}$ coupling, thus indicating cleavage of the P–Se bond. This transformation was accompanied by immediate precipitation of an insoluble compound from the reaction mixture. Notably, even before distillation, the ^{31}P NMR spectrum of the reaction mixture did not show any ^{31}P–^{77}Se coupling, providing that one equivalent of the salt **1** was used. In case of an excess of phosphoroselenolate **2** used, the amount of a high-field product corresponded to amount of **1** in the reaction mixture, and an excess of substrate **2** was detected. Both chemical shift and coupling constant J_{P-Se} of **2** were almost unchanged. Therefore, one can postulate that the immediate coordination of mercury salt **1** to phosphoroselenoate **2** (Scheme 2) leads to formation of the first



Scheme 2.

reactive intermediate (complex) **6** where mercury interacts with selenium of phosphoroselenolate. The interaction between the phosphorus center and the trifluoroacetate ligand originating from mercury trifluoroacetate eventually results in formation of anhydride bond, accompanied with breaking of the P–Se bond and resulting in formation of an "anhydride-like" intermediate of putative structure **7** without selenium linked to phosphorus (Scheme 2). Most probably, a complex of *O,O*-dimethyl *O*-trifluoroacetate **3c** with mercuric salt formed *in situ*, possesses carbonyl and phosphoryl oxygens involved in interactions with mercury as bidentate ligands [14]. However, numerous literature data give information about supramolecular [15] or polymer structures of complexes between alkyl mercury derivatives and organophosphorus compounds [16] observed in crystalline structures, therefore in this case intermolecular coordination with ligands of the neighbouring molecules cannot be excluded.

The immediate formation of precipitates in this reaction is of special interest (formed as white solid, slowly darkening during separation from a reaction mixture and drying in dark on vacuum). Structure of one of these species was studied in detail using NMR. Efforts to get crystals suitable for X-ray diffraction analysis have failed because of low stability of the crystals obtained. Therefore, due to very limited solubility of these compounds, tentatively identified as $RSeHgOCOCF_3$ (**8**), we isolated precipitate formed in the reaction of $(EtO)_2PSeEt$ (**2b** A = B = OEt, R = Et) with $(CF_3COO)_2Hg$ and analyzed a pyridine solution of $EtSeHgOCOCF_3$ (**8b**) [17]. NMR analysis is in agreement with the proposed structure of **8b** (^{19}F NMR δ: −71.55; ^{13}C NMR δ: 22.22 and 20.75 (CH_3CH_2), 162.60 ($^2J_{CF} = 50.34$ Hz, (O)C), 120.2 ($^1J_{CF} = 442.8$ Hz, CF_3).



Mass spectrometry analysis (FAB^+) of pyridine solutions of **8b** revealed peaks at 417.0 identified as EtSeHgSeEt (**9**) [18], accompanied by signals of higher molecular weight, assigned to complexes of symmetrical product **9** with pyridine (M + Py): 495.6 and (M + 2Py): 575.7. In contrast, partial dissolution of the primary precipitate **8b** in *i*PrOH, yielded signals (FAB^+MS) corresponding to EtSeHgO*i*Pr (M + H): 369.5, evidence for ligand exchange under these conditions. The aforementioned analysis suggests a limited stability of **8b** in pyridine or *i*PrOH, caused by formation of different secondary complexes [14].

As demonstrated, complex **7c** could be destroyed by distillation [19,20] but it reacted with alcohols as a phosphorylating agent, with replacement of trifluoroacetate group and formation of *O,O,O*-trimethyl phosphate **4c**.

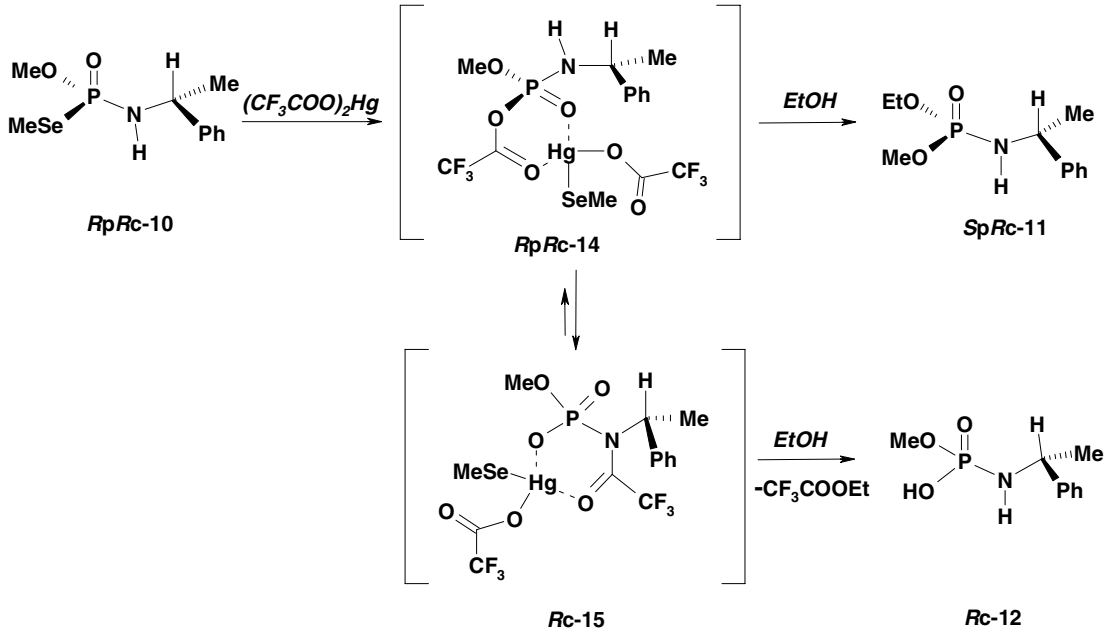
It was also found that the reactions of **2** with aniline in the presence of $(CF_3COO)_2Hg$ occurred with an attack at the carbonyl center, yielding anilinium salts of *P*-achiral phosphoric acids **5** and trifluoracetanilide, respectively.

Analogously, when *O,Se*-dimethyl-*N*-phenyl phosphoramidoselenolate (**2d**) (^{31}P NMR δ: 21.35, $^1J_{PSe}$ = 446 Hz, MeCN/C_6D_6) reacted with equimolar amount of mercuric trifluoroacetate in acetonitrile at room temperature, immediate appearance of a single product was observed. Based upon the chemical shift (δ: 2.66), and the absence of ^{77}Se satellites, we consequently assigned the structure of this intermediate as *O*-methyl-*O*-trifluoroacetyl phosphoranilidate forming a complex with mercury in solution (**7d**). Addition of an excess of methanol to this reaction mixture caused quantitative formation of *O,O*-dimethyl phosphoranilidate **4d** (δ: 5.63, MeCN/C_6D_6). The same product **4d** was formed, when **1** was added to a solution of **2d** and methanol in acetonitrile. Diastereomerically pure R_PR_C-*O,Se*-dimethyl-*N*-(α-methylbenzyl) phosphoramidoselenolate (**10**) [21] (δ: 22.86, $^1J_{PSe}$ = 420 Hz, MeCN) when treated with ethanol in the presence of **1** yielded in S_PR_C-*O*-methyl-*O*-ethyl-*N*-(α-methylbenzyl) phosphoramidate (**11**) (δ: 10.36) in high isolated yield (>95%) (Scheme 3) [22].

In contrast, when the same substrate R_PR_C-**10** first was treated with mercury trifluoroacetate **1**, and subsequently ethanol was added, exclusive P-achiral product, namely R_C-*O*-methyl-*N*-(α-methylbenzyl) phosphoramidate (**12**) (^{31}P NMR δ: 8.44) was formed. The presence of free hydroxyl group in compound **12** was confirmed via its reaction with trimethylsilyl chloride and triethylamine, leading to *O*-trimethylsilyl *O*-methyl *N*-(α-methylbenzyl) phosphoramidate (**13**) with a diagnostic upfield shift of ^{31}P NMR signal of the corresponding silyl ester **13** (δ: 0.6 ppm) [23].

When stoichiometric amounts of pure R_PR_C-**10** and **1** were mixed together in MeCN at room temperature, formation of two products was observed (^{31}P NMR δ: 2.59 and δ: 2.2, MeCN-d_3), in ≈3:4 ratio. This mixture of two intermediates reacted either with ethanol or with aniline at room temperature to form exclusively phosphoramidate **12** [24].

To explain the difference of reactivity of phosphoramidoselenoate **10** in comparison to **2**, we performed low temperature ^{31}P NMR investigations of the two-step process, when the reaction between substrate R_PR_C-**10** and mercuric trifluoroacetate (**1**) was treated as the first step, and ethanolysis of formed intermediates was the second one. These studies revealed that reaction between phosphoramidoselenolate **10** and **1** proceeded rapidly even at temperatures as low as −90 °C in dichloromethane, or −40 °C in MeCN. After 5 min, only traces of substrate **10** were detected in both experiments, with two new up field resonating products observed. We assume that the initially formed intermediate of putative structure **14**, analogous to the previously postulated **7**, resonating at δ: 1.77 ppm is capable to isomerise to compound **15** resonating at δ 2.80 ppm (reaction in CH_2Cl_2). Molecular ratios between **14** and **15** varied from ≈3:1 at −90 °C (immediately after the solvent melted) to ca. 3:4 when the reaction mixture was warmed up to room temperature. Addition of ethanol to the reaction mixture at low temperature (−40 °C in MeCN) caused formation of two P-containing products,



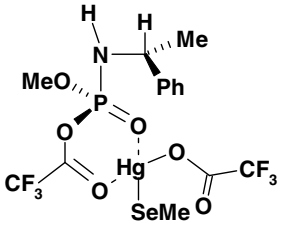
Scheme 3.

identified as phosphoramidates S_PR_C-**11** and R_C-**12**, in 2:3 ratio, while aniline added under the same reaction conditions resulted in a single product, identified as R_C-**12** (Scheme 3). A mixture of **11** and **12** was alkylated with diazoethane, giving the expected single product as diastereomeric mixture ($R_PR_C + S_PR_C$)-*O*-methyl-*O*-ethyl-*N*-(α-methylbenzyl) phosphoramidate **11** (^{31}P NMR δ: 9.63, 9.08) in high yield.

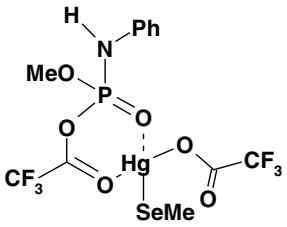
Based upon these results we postulate that complexed R_PR_C-*O*-methyl-*O*-trifluoroacetyl-*N*-(α-methylbenzyl) phosphoramidate **14** with retained configuration at phosphorus has been formed as a primary reactive intermediate [25]. This supports the mechanism described previously, involving coordination of mercuric trifluoroacetate to selenium, facilitating nucleophilic attack of the trifluoroacetic moiety at the phosphorus center. The second intermediate, appearing even at low temperatures, is now presumed to be complexed *N*-trifluoroacetyl-*O*-methyl-*N*-(α-methylbenzyl) phosphoramidate (**15**) and most likely results from an intramolecular rearrangement of **14**, involving trifluoroacetyl group migration from oxygen to nitrogen. The function of mercury at this stage is still obscure, and is a subject of further study.

While the ethanolysis of **14** occurs at the phosphorus center, and yields exclusively the expected *O*-ethyl ester **11**, a second intermediate **15** must react via an attack of nucleophile at the carbonyl carbon atom resulting in formation of ethyl trifluoroacetate (as confirmed by GC chromatography), and the corresponding phosphoramidate **12** [26].

The striking feature of the process under investigation is a comparison of the migratory aptitude of trifluoroacetyl group in compounds **7d** and **14**, indicating the influence of substituents at nitrogen on the process of $O \rightarrow N$ acyl migration [27].



RpRc-14



7d

It is known that sp^2 hybridization of nitrogen atom in phosphoranilidates **3d** prevents migration of the trifluoroacetyl group, while sp^3-like hybridization of nitrogen in phosphoramidates **14** facilitates such migration, even at low temperatures, and enables the rearrangement **14**→**15** [28]. This observation is consistent with the body of existing data documenting electrophililic assistance in the rearrangement of *O,O*-dialkyl-*N*-benzoyl-phosphoranilidates into *O,O*-dialkyl phosphoric-*N*-iminobenzoic anhydrides, with the reversed process occurring in the absence of electrophilic catalyst [29].

In conclusion, we have demonstrated a significant influence of complexed mercury (II) species in reactions of various *Se*-alkyl phosphoroselenolates and mercuric trifluoroacetate on their reactivity and stereochemistry. The detailed structure of these complexes remains obscure. Based on spectrometric criterion, and the isolation of mixed phosphoric-trifluoromethylcarboxylic anhydrides **3b**, we anticipate their close structural analogy to regular mixed phosphoric–carboxylic anhydrides.

3. Experimental

Reactions were carried out under positive pressure of dry argon. Solvents and reagents were purified according to standard laboratory techniques and distilled directly to reaction vessels. $(CF_3COO)_2Hg$ was purchased from Aldrich, and was dried under vacuum (150 °C/0.01 mm Hg) for several hours. Synthesis and isolation of $(MeO)_2P(O)OC(O)CF_3$ (**3b**) was carried out using vacuum line techniques. Column chromatography and TLC analyses were performed on a silica gel (Kieselgel 60, 240–400 mesh), and silica gel HP TLC precoated F_{254} plates, purchased from E.Merck Inc. All melting and boiling points are uncorrected. NMR spectra were recorded on a Bruker Advance DRX 500 spectrometer, operating at 500.13 MHz (^{1}H), 202.46 MHz (^{31}P), and 212 MHz (^{19}F) and 200.13 MHz (^{13}C). Chemical shifts (δ) are reported relative to TMS (^{1}H), 85% H_3PO_4 (^{31}P) and pyridine (^{13}C) as external standards. Positive chemical shift values were assigned to compounds resonating at lower fields than standards. Mass spectra were recorded on a Finnigan Mat 95 (nba, Cs^+ gun operating at 13 keV).

O,O,Se-trimethyl phosphoroselenolate (***2b***) was prepared in a reaction of *O,O*-dimethyl phosphoroselenoate (ammonium salt) (^{31}P NMR δ: 54.66, $^1J_{PSe}$ = 777 Hz in MeOH-d_3), prepared according to [30] with methyl iodide in CH_2Cl_2, followed by distillation (bp = 85–90 °C/0.01 mm Hg, ^{31}P NMR: 26.1, $^1J_{PSe}$ = 472 Hz in C_6D_6).

O,O-dimethyl N-phenyl phosphoramidoselenoate (^{31}P NMR δ: 72.5, $^1J_{PSe}$ = 955 Hz in $CDCl_3$) was subjected to MeI assisted isomerization to yield **2d** in 67% yield after a silica gel column chromatography. ^{31}P NMR, $CDCl_3$ δ: 23.25, $^1J_{PSe}$ = 446 Hz, ^{1}H NMR: 2.11 (d, $^2J_{PH}$ = 13.83, CH_3O), 3.84 (d, $^2J_{PH}$ = 13.13, $^2J_{HSe}$ = 148.59 CH_3Se). MS CI: 266.1; Calc. 265.16 (^{80}Se).

O,O-dimethyl O-trifluoroacetyl phosphate (***3c***). Into 0.1 mmol of **2c** (0.2 ml), 2.5 ml of CH_2Cl_2 was distilled, and a solution of 0.1 mmol (0.42 g) of **1** in CH_2Cl_2 (0.25 ml) was transferred at room temperature. Immediate

formation of precipitate of $RSeHgOCOCF_3$ was observed. After 5 min solvent and volatile products were distilled (30 °C/0.005 mm Hg, liquid nitrogen cooled trap). ^{31}P NMR, C_6D_6, δ: −6.6; ^{19}F NMR δ: −75.95.

R_PR_C-(+)-Se-methyl-O-methyl-N-(α-methylbenzyl) phosphoramidoselenolate (***10***) was prepared according to literature [21].

Starting from *R*(+)α-methylbenzylamine, *O,O*-dimethyl phosphorochloridite and elemental selenium, *R*(+)-*O,O*-dimethyl-*N*-(α-methylbenzyl) phosphoramidoselenoate was obtained, and purified by a silica gel column chromatography. [^{31}P NMR, $CDCl_3$ δ: 75.6, $^1J_{PSe}=890$ Hz; ^1H NMR δ: 1.49 (d, 3H, $^3J_{HH}=6.8$ Hz, CH_3–CH), 3.43, 3.67 (2d, 6H, $^2J_{PH}=14.4$ Hz, CH_3O), 3.6 (m, 1H, NH), 4.44 (m, 1H, CH–CH_3), 7.4 (m, arom)], and rearranged into **10** by a Pischimuka type rearrangement with MeI. Pure R_PR_C-**10** was crystallized from acetone (mp = 112–120 °C). ^{31}P NMR, $CDCl_3$ δ: 27.9, $^1J_{PSe}=435$ Hz; ^1H NMR δ: 2.0 (d, 3H, $^3J_{PH}=13.1$ Hz, CH_3Se), 3.6 (d, 3H, $^3J_{PH}=13.0$ Hz CH_3O), 4.47 (m, 1H, CH–NH), 7.3 (m, arom); MS FAB [M + H] 292.1 (^{78}Se), 294.1 (^{80}Se).

($R_PS_C+S_PS_C$)-O-methyl-O-ethyl-N-(α-methylbenzyl) phosphoramidate (***11***). ^{31}P NMR δ: 9.63, 9.08. In MS FIB (Cs^+, 13 keV) spectrum of the reaction mixture after alkylation of **11** with diazoethane, signals [*m*/*z*] 244 (100%) (M + 1) of **11**, and [*m*/*z*] 216 (30%) assigned to $CF_3CONHCHPhMe$ were identified.

General procedure of reactions activated by mercury trifluoroacetate. Into a solution of 0.1 mmol of **2** or **10** in dry solvent (MeCN or CH_2Cl_2, 0.25 ml), a solution of 0.1 mmol of **1** in the same solvent (0.25 ml) was added. Immediate formation of white precipitate, darkening in the reaction medium, was observed. After filtration of precipitate, an excess (5 equiv.) of nucleophile was added. Final products were isolated by a silica gel column chromatography (Kieselgel 60, 70–230 mesh, Merck, chloroform–ethanol used as an eluent).

Analysis of mercury (II) compound **8b**. Solid product **8b**, which was precipitated in the above reaction was centrifuged, separated and washed with small portions of the same solvent, followed by wash with hexane (grey powder). It was dried at high vacuum, and kept in dark ampoule. For analytical reasons it was dissolved in dry pyridine (240 mg/ml). ^{19}F NMR δ: −71.55; ^{13}C NMR δ: 22.22 and 20.75 (CH_3CH_2), 162.60 ($^2J_{CF}=50.34$ Hz, (O)C), 120.2 ($^1J_{CF}=442.8$ Hz, CF_3). MS FAB+, Cs+, 13 keV, nba: (M + H) 417.0, 495.6 (M + Py) and 575.7 (M + 2Py).

Low temperature studies of reaction between R_PR_C-(+)-Se-methyl-O-methyl-N-(α-methylbenzyl) phosphoramidoselenolate **10** *and mercury trifluoroacetate.* Reactions were prepared in NMR tubes equipped with argon supply device. A solution of 0.05 mmol of **10** in 250 μl of solvent (CH_2Cl_2 or MeCN) was placed in NMR tube, and frozen in liquid nitrogen. Then a solution of **1** in 250 μl of the same solvent was transferred to this tube and frozen likewise as separated layer. Tubes were placed in NMR device, and kept rotated at melting temperatures (−90° and −45 °C, for CH_2Cl_2 and MeCN, respectively) until solvents were melted and the reagents were mixed. Spectra were recorded in the range of temperatures −90–30°, or −45–30 °C.

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Appendix A. Supplementary material

Supporting Information Available: General procedures and synthetic procedures for **2b**, **2d**, **3c**, **8**, **10** and **11**; ^1H NMR, ^{31}P NMR and Mass Spectra. Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.jorganchem.2004.06.003.

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