Synthesis of Thiol, Selenol, and Tellurol Esters by the Reaction of Organochalcogeno Mercurials with Acid Chlorides

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Summary: Thiol, selenol, and tellurol esters were prepared by the reaction of bis(organochalcogeno)mercurials with acid chlorides in chloroform or carbon tetrachloride and in the presence of tetrabutylammonium halides as catalysts.

Bis(organochalcogenyl)mercury compounds have been long known, but aside from applications related to inorganic chemistry[1] or solid-state chemistry in the development of semiconductors,[2] no organic chemistry has been associated with this class of compounds. In contrast, related parent compounds such as (organochalcogenyl) cadmium,[3] lead,[4] thallium,[5] and silver[6] reagents have proved to be useful sources of nucleophilic moieties. Reasoning that those mercury compounds have never been reported as nucleophiles due to their poor reactivity and low yields attained under classical reaction conditions,[3−6] it was decided to explore the scope and limitations of the reaction of bis(organochalcogenyl)mercury compounds with acyl chlorides, as an approach to the synthesis of organochalcogenol esters.

Thiol, selenol, and tellurol esters are useful synthetic intermediates employed as mild acyl-transfer reagents,[5a,7] building blocks for heterocyclic compounds (oxazole,[8] β-lactone[9]), and precursors of acyl radicals[10] and anions[11] and for asymmetric aldol reactions.[12] These compounds are usually available by the reaction of acyl halides with mercaptans,[13] selenols,[14] or dichalcogenides,[15] as well as their alkali metal salts.[16] In addition, carboxylic acids are also transformed into thiol and selenol esters by treatment with arylthio- or arylselenocyanates and tributyl phosphine in dichloromethane.[17] Group IIIA organyl chalcogenides (B and Al) convert carboxylic acid esters into their thiol[18] and selenol[19] analogues. Also, aldehydes react under Tishchencko-type conditions to afford all of the isologues.[20] Thiol esters have been prepared by the acid-catalyzed hydrolysis of thioacetylenes.[21] Miscellaneous methods are summarized in ref 22.

Since many of these methodologies require vigorous reaction conditions, often dealing with moisture- or air-sensitive reagents and due to the growing interest in new organic strategies for the production of chalcogenol ester compounds, we wish to report here a new method for their synthesis based on the reaction of bis(organochalcogenyl)mercury compounds with acyl chlorides under tetrabutylammonium halide catalysis, as shown in eq 1. The starting mercurials, bis(phenylthiolate)Hg (**1**), bis(phenylselenolate)Hg (**2**), bis(*n*-butyltellurolate)-Hg (**3**), bis(ethanethiolate)Hg (**4**), and bis[(2-methyl)-2-propanethiolate)]Hg (**5**), are stable solids, easily prepared by the reaction of metallic Hg with the corresponding thiols, diphenyl diselenide, or di-*n*-butyl ditelluride,

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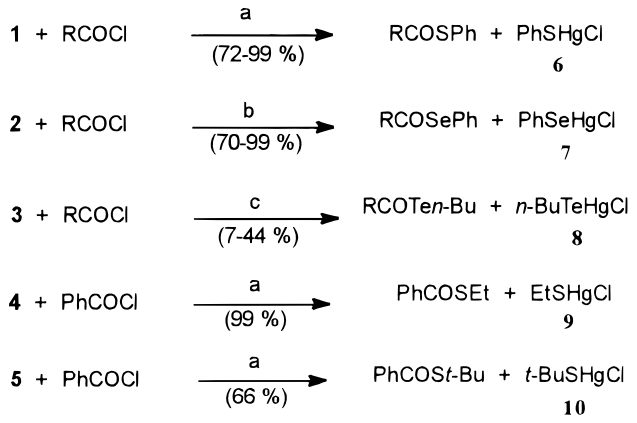
Scheme 1



Conditions: (a) *n*-Bu_4NBr, $CHCl_3$, reflux, 4 h. (b) *n*-Bu_4NBr, $CHCl_3$, rt, 5 h. (c) *n*-Bu_4NCl, CCl_4, rt, 2 h.

Table 1. Synthesis of Chalcogenol Esters[a] by Reaction of Bis(organochalcogenyl)mercury with Acyl Chlorides

entry no.	R	C_6H_5S (yield, %)	C_6H_5Se (yield, %)	*n*-BuTe (yield, %)
1	C_6H_5	98	99[b]	39
2	*p*-ClC_6H_4	99	74	44
3	*p*-$NO_2C_6H_4$	99	79	
4	*p*-$MeOC_6H_4$	98	81[c]	
5	$C_6H_5CH_2$	99	94	35
6	$(C_6H_5)_2CH$	72	74	
7	CH_3	72	70	
8	$ClCH_2$	97	82	
9	*t*-C_4H_9	94	81	7
10	*n*-C_5H_{11}	72	70	

[a] Isolated yields. [b] 4 h at reflux. [c] 17 h at room temperature.

according to literature procedures.[1,2] The mercury−bis(organochalcogenide) can deliver only one YR^1 group under the present conditions. The organochalcogen and Hg moieties can be easily recovered from the R^1YHgCl by a procedure described previously.[23]

$$Hg(YR^1)_2 \xrightarrow{RCOCl} RCOYR^1 + R^1YHgCl$$
$$Y = S, Se, Te$$

The reactions studied are outlined in Scheme 1 and are performed in chloroform or carbon tetrachloride. Bis(organochalcogenates)Hg exhibit different reactivities. Thus, compound **1** furnishes very high yields of the products by reaction in chloroform at reflux for 4 h, regardless of the structure of the acid chloride. Compounds **4** and **5** as well as **2** react at room temperature in chloroform and in the presence of a catalytic amount of *n*-Bu_4NBr (vide infra). The reactions as monitored by TLC are completed after 5 h. Compound **3** (Te derivative) reacted best in carbon tetrachloride, and the use of *n*-Bu_4NCl instead of *n*-Bu_4NBr was required.

The yields obtained are summarized in Table 1. The reaction was studied in detail with compounds **1**−**3.** **C**ompounds **1** and **2** reacted well with several acid chlorides, furnishing the desired products in medium to high yield. Fewer examples were studied with **3** since lower yields were obtained in its reactions, mainly because of its instability under the employed experimental conditions.

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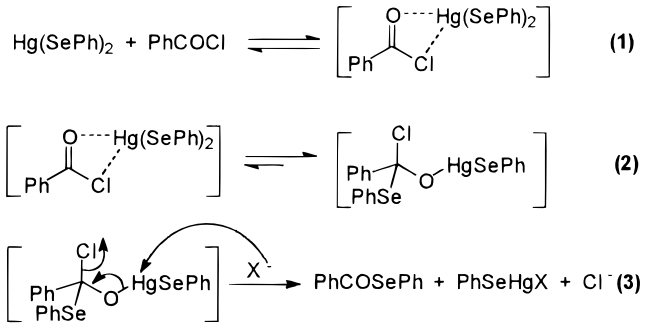
Scheme 2



It was observed that the yield is related to the reactivity of both the acyl chloride and the mercury reagent. The change from S to Se and Te was accompanied by a decrease in yield. The addition of the ammonium halide catalyst greatly improved the efficiency of the reaction. In the absence of *n*-Bu_4NBr, the reaction of benzoyl chloride with bis(phenylseleno)Hg **2** gave only a 53% yield, even after a 24 h reaction period. The reaction between benzoyl chloride and **2** in chloroform mediated by *n*-Bu_4NBr was monitored by IR spectroscopy,[24] in order to obtain an insight into the reaction course. It was observed that at the start of the reaction the C=O stretching frequency of benzoyl chloride was barely changed ($\cong$5 cm^{-1}); it was consumed at such a rate that less than 10% remained after 1 h. Unexpectedly, however, no sign of the product (1680 cm^{-1}) was detected. The characteristic band of PhCOSePh began to appear only after 1.5 h. At that time, the presence of the selenol ester was also detected by TLC. These observations rule out an anionic catalyst effect[25] on $Hg(SePh)_2$ to produce a more intense selenol ester band. Instead, strong absorptions at 1530, 1475, and 1425 cm^{-1} were observed, which could not be attributed to $Hg(SePh)_2$ or to ClHgSePh when compared with authentic spectra. Therefore, we tentatively suggest that this transformation might follow a pathway as depicted in Scheme 2: (step 1) coordination of the mercury with the carbonyl and chlorine moieties to form a complex in rapid equilibrium with reactants (the magnitude of $\Delta\nu \approx 5$ cm^{-1} suggests a weak interaction); (step 2) the complex collapses into an intermediate ($\nu \approx$ 1530, 1475, and 1425 cm^{-1} attributed to this intermediate); (step 3) a halide anion reacts irreversibly the intermediate, giving rise to the products. Here one can see the important role played by the *n*-Bu_4NX catalyst.

Experimental Section

^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra were obtained with a Bruker AC-200 spectrometer in $CDCl_3$ with TMS as the internal standard. IR spectra were recorded on a Bruker IFS-28 or Perkin-Elmer 1310 spectrometer. Low-resolution mass spectra were obtained with a Hewlett-Packard 5988−8/5890 GC/MS spectrometer, operating at 70 eV. Elemental

(24) IR experiment: [ ] $\cong 4 \times 10^{-2}$ M in a NaCl cell of 0.2 mm (Teflon) path, double-beam spectrophotometer, $CHCl_3$ spectroscopic grade, and all reagents were treated by extended time in a vacuum to avoid humidity.

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analyses were performed on a Vario EL analysensysteme, at UFSM. Column chromatography was carried out with Merck silica gel (230−400 mesh). Thin-layer chromatography (TLC) was performed on silica gel 60 F-254. All solvents used were previously dried and distilled according to the usual methods.[27] Phenylthiol, ethanethiol, and *tert*-butylthiol were purchased from Aldrich. Diphenyl diselenide[28] and di-*n*-butyl ditelluride[29] were prepared by literature procedures. The acid chlorides were prepared by standard techniques[30] from the carboxylic acids obtained from commercial sources. All operations were carried out in oven-dried glassware under an inert atmosphere of dry argon.

Caution! The toxicity of mercury compounds is well-known, and so, all operations should be carried out under a well-ventilated hood, with all requirements for appropriate waste disposal. Approximately up to 90% of total mercury was recovered. Also, we suggest treatment with nitric acid and recovering the mercury by reduction of the resulting salts with metallic Fe.

Preparation of 1, 4, and 5. To a stirred solution of $Hg(OAc)_2$ (1 equiv) in EtOH under argon at room temperature was added RSH (2.05 equiv). After a few minutes, the suspension was filtered and the solids were washed with EtOH, acetone, and ether. The solids were dried in vacuo. The yields were from 80 to 100%.

Di(phenylsulfenyl)mercury (1): white solid; mp 149.8−152.1 °C (lit.[1a] mp 152.5−153.5 °C); ^{1}H NMR (DMSO-d_6) δ 7.36 (d, J = 7.0 Hz, 2H), 7.19−7.06 (m, 3H); IR (KBr) 3080, 3000, 1440, 1310, 1030, 1010, 910, 740, 690 cm^{-1}.

Di(ethylsulfenyl)mercury (4): white solid; mp 75.2−76.8 °C (lit.[1b] mp 76 °C); IR (KBr) 2950, 2918, 2856, 1441, 1365, 1260, 972, 769, 407 cm^{-1}.

Di(*tert*-butylsulfenyl)mercury (5): white solid; mp 157.9−159.4 °C (dec); IR (KBr) 2969, 2955, 2889, 1454, 1362, 1163, 1025, 575 cm^{-1}.

Preparation of 2 and 3. [1f,g] To a solution of diphenyl diselenide or di-*n*-butyl ditelluride (1 equiv) in dioxane (3 mL/mmol) was added metallic mercury (1.4 equiv). The solution was vigorously stirred under argon for 30 min (for the tellurium derivative) or 4 h (for the selenium derivative). The solid product was filtered, washed with benzene and ether, and dried in high vacuo. The yields were nearly quantitative.

Di(phenylselenenyl)mercury (2): greenish solid; mp 146−148 °C (dec) (lit.[1f] mp 152−153 °C); IR (KBr) 3052, 1573, 1471, 1435, 1299, 1070, 1018, 999, 902, 731, 688, 468 cm^{-1}.

Di(*n*-butyltellurenyl)mercury (3): light-brown-yellow solid; mp 106.2 °C (dec); IR (KBr) 2954, 2869, 1637, 1459, 1376, 1242, 1155, 883, 703, 617 cm^{-1}. Anal. Calcd for $C_8H_{18}HgTe_2$: C, 16.86; H, 3.18. Found: C, 16.74; H, 3.32.

General Procedure for the Reaction of 1 with Acyl Chlorides. To a stirred suspension of **1** (l mmol) in chloroform (4 mL) under argon atmosphere at room temperature was added *n*-Bu_4NBr (0.04 mmol). After 2 min of stirring the acyl chloride (1 mmol; dissolved in 1 mL of solvent) was added slowly by a syringe. The reaction mixture was refluxed for 4 h, then cooled to room temperature and evaporated in vacuo. The solid was resuspended in ethyl acetate and filtered through Celite.[31] The organic phase was evaporated, and the crude product was purified by silica gel column chromatography, eluting with hexanes followed by ethyl acetate, to give the thiol ester.

General Procedure for the Reaction of 2, 4, and 5 with Acyl Chlorides. To a stirred suspension of **2**, **4**, or **5** (1 mmol) in chloroform (4 mL) under an argon atmosphere at room temperature was added *n*-Bu_4NBr (0.04 mmol). After stirring for 2 min, the acyl chloride (1 mmol; dissolved in 1 mL of solvent) was added by syringe. The reaction mixture was stirred for 5 h, and the liquid phase was then evaporated in vacuo. The solid residue was dissolved in ethyl acetate and filtered through Celite.[31] The organic phase was evaporated, and the crude product was purified by silica gel column chromatography, eluting with hexanes followed by ethyl acetate, to give the appropriate alkanethiol or phenylselenol ester.

General Procedure for the Reaction of 3 with Acyl Chlorides. To a stirred suspension of **3** (1 mmol) in carbon tetrachloride (4 mL) under an argon atmosphere at room temperature was added *n*-Bu_4NCl (2 mmol; 2 equiv). After stirring for 2 min, the acyl chloride (1 mmol, dissolved in 1 mL of solvent) was added by syringe. The reaction mixture was stirred for a maximum period of 2 h, and the liquids then were poured into 5% deactivated neutral alumina suspended in CCl_4 and filtered rapidly. The orange filtrate was evaporated in vacuo, and the resulting crude liquid was purified by silica gel column chromatography eluting with hexanes followed by ethyl acetate, to afford the tellurol ester.

***S*-Ethyl thiobenzoate:** yield 99%, colorless oil. Spectroscopic data were in good agreement with the literature.[22c]

***S*-*tert*-Butyl thiobenzoate:** yield 66%, white solid, mp 123.8−130.5 °C (dec); bp 75 °C/7 mmHg (lit.[18a] 110 °C/28 mmHg).

***S*-Phenyl thiobenzoate:** yield 98%, white solid, mp 54.8−55.1 °C (lit.[17] mp 55−56 °C). ***S*-Phenyl *p*-chlorothiobenzoate:** yield 99%, white solid, mp 80.6−81.8 °C (lit.[17] mp 79.5−81.5 °C).

***S*-Phenyl *p*-nitrothiobenzoate:** yield 99%, pale brownish solid, mp 151.3−153.0 °C (lit.[13c] mp 160 °C).

***S*-Phenyl *p*-methoxythiobenzoate:** yield 98%, pale yellow solid, mp 93.3−94.7 °C (lit.[17] mp 94−95 °C).

***S*-Phenyl 2-phenylethanethioate:** yield 99%, white solid, mp 33.0−34.6 °C (lit.[17] mp 33.0−33.5 °C).

***S*-Phenyl 2,2-diphenylethanethioate:** yield 72%, white solid, mp 87.6−89.2 °C (lit.[22g] mp 84−85 °C).

***S*-Phenyl ethanethioate:** yield 72%, colorless oil. Spectroscopic data were in good agreement with literature.[5b]

***S*-Phenyl 2-chloroethanethioate:** yield 97%, white solid, mp 39.3−41.2 °C (lit.[15a] 43−43.5 °C).

***S*-Phenyl 2,2-dimethylpropanethioate:** yield 94%, colorless oil. Spectroscopic data were in good agreement with literature.[13b]

***S*-Phenyl hexanethioate:** yield 72%, colorless oil. Spectroscopic data were in good agreement with literature.[22d]

***Se*-Phenyl selenobenzoate:** yield 99%, yellowish solid, mp 38.3−39.8 °C (lit.[3] mp 38.5−39.5 °C).

***Se*-Phenyl *p*-chloroselenobenzoate:** yield 74%, white solid, mp 81.1−82.1 °C (lit.[17] mp 83.5−84.5 °C).

***Se*-Phenyl *p*-nitroselenobenzoate:** yield 79%, pale green solid, mp 136.5−138.2 °C (lit.[13c] mp 137 °C).

***Se*-Phenyl *p*-methoxyselenobenzoate:** yield 81%, white solid, mp 60.3−61.6 °C (lit.[17] mp 62−63 °C).

***Se*-Phenyl 2-phenylethaneselenoate:** yield 94%, yellowish solid, mp 42.5−43.0 °C (lit.[22a] mp 41−43 °C).

***Se*-Phenyl 2,2-diphenylethaneselenoate:** yield 99%, yellowish solid, mp 71.6−72.6 °C; ^{1}H NMR δ 7.48−7.28 (m, 15H), 5.29 (s, 1H); ^{13}C NMR δ 200.0, 137.5, 135.6, 129.3, 129.1, 128.9, 128.7, 127.7, 126.9, 68.2; LRMS *m*/*z* (relative intensity) 195 (M^+ − SePh, 5), 167 (100); IR (KBr) 3025, 1755, 1665, 1555, 1475, 1285, 1070, 950, 825, 775, 605 cm^{-1}. Anal. Calcd for $C_{20}H_{16}OSe$: C, 68.27; H, 4.33. Found: C, 68.38; H, 4.59.

***Se*-Phenyl ethaneselenoate:** yield 70%, yellow oil. Spectroscopic data were in good agreement with literature.[5b]

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(31) The solid residue from the filtration consisted of PhYHgX (X = Cl, Br), isolated in high yield (≅90%), from which PhYYPh and Hg can be recovered (see ref 23).

***Se*-Phenyl 2-chloroethaneselenoate:** yield 82%, yellow solid (mp 35.5−36.9 °C); ^{1}H NMR δ 7.45−7.32 (m, 5H), 4.14 (s, 2H); ^{13}C NMR δ 196.6, 135.9, 129.5, 129.3, 125.3, 51.4; IR (film) 3080, 2960, 1720, 1580, 1445, 1260, 1055, 970, 700 cm^{-1}. Anal. Calcd for C_8H_7ClOSe: C, 41.14; H, 3.02. Found: C, 41.05; H, 2.99.

***Se*-Phenyl 2,2-dimethylpropaneselenoate:** yield 81%, yellowish oil; ^{1}H NMR δ 7.50−7.45 (m, 2H), 7.38−7.34 (m, 3H), 1.28 (s, 9H); ^{13}C NMR δ 207.7, 136.3, 129.1, 128.6, 126.3, 49.9, 27.0; LRMS *m*/*z* (relative intensity) 242 (M$^+$, 2), 57 (100); IR (film) 3058, 2967, 1719, 1579, 1475, 1364, 1227, 1022, 907, 737, 689, 482 cm^{-1}. Anal. Calcd for $C_{11}H_{14}OSe$: C, 54.54; H, 5.95. Found: C, 54.87; H, 5.85.

***Se*-Phenyl hexaneselenoate:** yield 70%, yellowish oil. Spectroscopic data were in good agreement with literature.[22e]

***Te*-*n*-Butyl tellurobenzoate:** yield 39%, yellow oil. Spectroscopic data were in good agreement with literature.[20]

***Te*-*n*-Butyl *p*-chlorotellurobenzoate:** yield 44%, yellow oil. Spectroscopic data were in very good agreement with literature.[20]

***Te*-*n*-Butyl 2-phenylethanetelluroate:** yield 35%, yellow oil. Spectroscopic data were in good agreement with literature.[22f]

***Te*-*n*-Butyl 2,2-dimethylpropanetelluroate:** yield 7%, yellow oil. Spectroscopic data were in good agreement with literature.[20]

Benzenesulfenylmercuric chloride (6): white solid, mp 198 °C (dec); IR (KBr) 3047, 1571, 1476, 1436, 1021, 908, 738, 686, 482 cm^{-1}.

Benzeneselenenylmercuric chloride (7): photosensitive yellow solid, mp 174−180 °C (dec); ^{1}H NMR (DMSO-d_6) δ 7.53−7.49 (m, 2H), 7.15−7.13 (m, 3H); ^{13}C NMR (DMSO-d_6) δ 134.2, 128.9, 128.5, 125.7; IR (KBr) 3070, 2980, 1580, 1480, 1440, 1020, 1005, 730, 690 cm^{-1}.

***n*-Butyltellurenylmercuric chloride (8):** yellowish solid, mp 130.8−132.6 °C; ^{1}H NMR (DMSO-d_6) δ 3.18 (t, J = 7.0 Hz, 2H), 1.85 (quint, J = 7.0 Hz, 2H), 1.35 (sext, J = 7.0 Hz, 2H), 0.96 (t, J = 7.0 Hz, 3H); IR (KBr) 2954, 2869, 1618, 1459, 1244, 1180, 887, 617, 487 cm^{-1}. **1-Ethanesulfenylmercuric chloride (9):** white solid, mp 208−210 °C (dec); LRMS *m*/*z* (relative intensity) 297 (M$^+$, 47), 236 (10), 232 (14), 202 (100), 101 (10), 61 (98); IR (KBr) 3080, 1450, 1390, 1260, 1050, 980, 780, 640 cm^{-1}.

2-Methyl-2-propanesulfenylmercuric chloride (10): photosensitive white solid, mp 135−150 °C (dec); LRMS *m*/*z* (relative intensity) 325 (M$^+$, 3), 236 (1), 202 (47), 101 (7), 57 (100); IR (KBr) 2780, 1460, 1370, 1160 cm^{-1}.

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