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Efficient synthesis of selenol esters from acid chlorides mediated by indium metal

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ABSTRACT

This article describes an efficient and easy one-pot route for the synthesis of a wide range of selenol esters from acyl chloride with diselenides in the presence of indium metal. A variety of functional groups can be tolerated within the diorgano diselenide and the acyl chloride coupling partner.

1. Introduction

Great advances on organoselenium chemistry have been made during the last decades. Selenium compounds have shown an important role in organic chemistry, acting as versatile and useful reagents in organic synthesis[1] as well as in asymmetric catalysis.[2] In this way, organoselenium compounds have emerged as an exceptional class of structures due to their pivotal role in the synthesis of a large number of biological compounds (e.g., selenocarbohydrates, selenoamino acids, and selenopeptides).[3]

2. Results and discussion

In this context, selenol esters are important intermediates in several organic transformations. Selenol esters have been used as precursors of acyl radicals[4] and anions,[5] mild acyl transfer reagents,[6] intermediates in the synthesis of ketones,[7] and for asymmetric aldol reactions.[8] In addition to their synthetic applications, these compounds have also attracted considerable attention for the design, synthesis, and investigation of new molecular materials, especially for conducting or superconducting materials and for liquid crystals.[9] Applications of this class of compounds have been expanded into the synthesis of proteins by chemical ligation of chalcogenol esters[10] as well as substrates to undergo facile and efficient radical decarbonylation in the synthesis of the alkaloid (+)-geissoschizine.[11] Therefore, a convenient method for the synthesis of these compounds with stable reagents under neutral conditions is still called for.[12]

Selenol esters are usually available by the reaction of acylhalides with selenols[13] or dichalcogenides,[14] as well as their alkali metal salts.[15] In addition, carboxylic acids are also transformed into thiol and selenol esters by treatment with arylselenocyanates and tributyl phosphine in dichloromethane.[16] Group IIIA organyl chalcogenides (B and Al) convert carboxylic acid esters into their selenol analogues.[17] Also, aldehydes react under Tishchenko-type conditions to afford these compounds.[18] Miscellaneous methods are summarized in Ref. 19.

It is well known that the selenium anions are generated in situ via chemical Se–Se bonds' cleavage to avoid handling unstable reagents such as selenols. Thus, research to improve these transformations is of current interest[20] as observed in the reports concerning use of indium iodide(I) for the cleavage of diselenides.[21] In recent years, more attention has been paid to the development of new synthetic methods using indium metal due to its remarkable efficiency in various synthetic operations, unique properties, such as stability toward air and moisture compared with other metals, its nontoxic nature, and its availability in pure form.[22]

As part of our studies with indium mediated reactions, we recently reported the synthesis of a new set of chiral α-seleno-amines[23a] and β-seleno-amides[23b] in straightforward procedures involving stereoselective ring-opening reactions with indium(III)-chalcogenolates, obtained from indium iodide(I) and diorganoyl diselenides. Additionally, by these methods, it was possible to synthesize various selenocysteine derivatives in good to excellent yields.[23] Thus, we propose herein a simple experimental procedure, with metallic indium system, easy to handle, less expensive than those with indium(I), and active enough to promote the direct coupling of diselenides and acyl chlorides[21a,b,24] (Scheme 1). The study resulted in an efficient synthesis of selenol ester derivatives under mild and neutral conditions.

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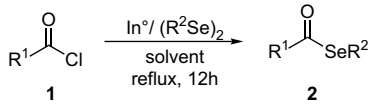


Scheme 1. General synthesis of selenol esters.

The conditions for carrying out the reaction were optimized by using benzoyl chloride and PhSeSePh in the presence of indium metal in different solvents (Table 1).

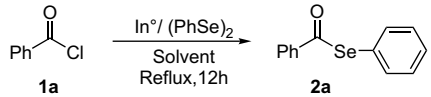
The first experiment was performed using CH_2Cl_2 and 1.0 equiv of indium metal and the desired product was obtained in 86% yield (Table 1, entry 1).

When dioxane was used as solvent a small decrease in the yield compared with DCM was observed, affording the corresponding product in 83% yield (entries 1 vs 2). A number of different solvents, including DMF, THF, and DMSO, were also investigated, and they were all less effective than dichloromethane (entries 3–5). Subsequently, the amount of In° was reduced to 0.8 mol equiv yielding **2a** in 64% in relation to benzoyl chloride (entry 6).

Using the optimized conditions, the scope and limitations of this new methodology were examined as shown in Table 2. A variety of diorganyl diselenides reacted with benzoyl chloride to generate the selenol esters in good to excellent yields. Electronic effects showed a remarkable influence in this reaction; electron withdrawing aryl diselenides and benzoyl chloride reacted easily (Table 2, entries 1 and 3) while electron rich aryl diselenides, which have a stronger Se–Se bond, gave the corresponding selenol ester in lower yields (entries 2 and 4). It is well known that diaryl diselenides are more reactive than aliphatic ones, and much more easily cleaved.[25] We also extended this method to prepare selenol ester starting from aliphatic diselenides. Applying the same methodology and using dibenzyl diselenide as source of selenolate anion, the coupling reaction with benzoyl chloride furnished the desired product in good yield (entry 5) whereas using diethyl diselenide as selenium source, the product was obtained in satisfactory yield (entry 6).

The combination of a wide range of acyl chlorides with diphenyl diselenide was also checked in our reaction system (Table 2, entries 7–11). Electron withdrawing substituent attached at the benzoyl chloride moiety showed a negative effect in the yields, affording the desired products in moderated yields (entries 7 and 8). The ability to couple alkyl groups prompted further exploration of this reaction. By using 2,2-dimethyl-propionyl chloride **1d** afforded the product in a low yield (entry 9), while the similar 3-chloro-2,2-dimethylpropanoyl chloride **1e** furnished the corresponding selenol ester in satisfactory yield (entry 10). Unfortunately, acetyl

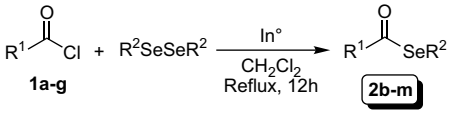
Table 1
Optimization of the reaction conditions[a]

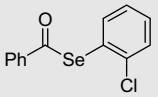
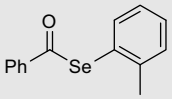
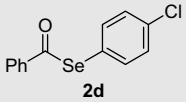
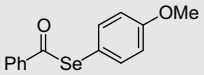
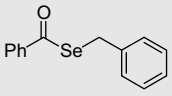
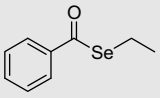
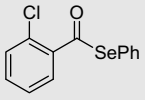
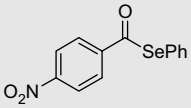
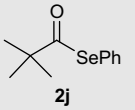
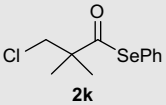


Entry	Solvent	Yield[b] (%)
1	CH_2Cl_2	86
2	1,4-Dioxane	83
3	DMF	62
4	THF	62
5	DMSO	51
6[c]	CH_2Cl_2	64

[a] Reaction was performed using benzoyl chloride, 1 mol equiv of In° and 0.5 mol equiv of diphenyl diselenide at reflux for 12 h.
[b] Isolated yield.
[c] Reaction was performed using 0.8 mol equiv of In°.

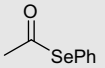
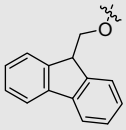
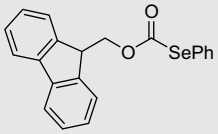
Table 2
Indium cleavage of diorganyl diselenides to selenol esters



Entry	R^1	R^2	Product	Yield[a] (%)
1	Ph, **1a**	*o*-ClPh	 **2b**	91
2	Ph, **1a**	*o*-MePh	 **2c**	65
3	Ph, **1a**	*p*-ClPh	 **2d**	90
4	Ph, **1a**	*p*-OMePh	 **2e**	58
5	Ph, **1a**	Bn	 **2f**	80
6	Ph, **1a**	Et	 **2g**	69
7	*o*-ClPh, **1b**	Ph	 **2h**	66
8	*p*-NO_2Ph, **1c**	Ph	 **2i**	63
9	*t*-Bu, **1d**	Ph	 **2j**	34
10	$ClCH_2CMe_2$, **1e**	Ph	 **2k**	55

(*continued on next page*)

Table 2 (*continued*)

Entry	R^1	R^2	Product	Yield[a] (%)
11	Me, **1f**	Ph	 **2l**	—
12	 **1g**	Ph	 **2m**	>99

[a] Yields related to pure isolated products characterized by spectroscopic data.

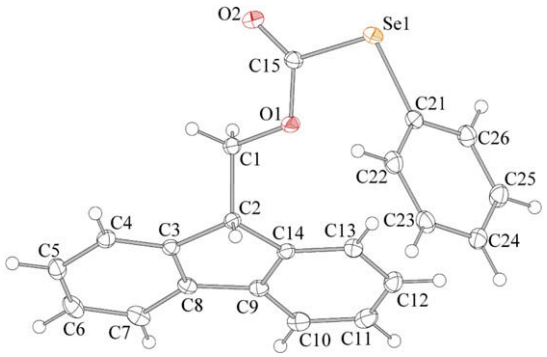
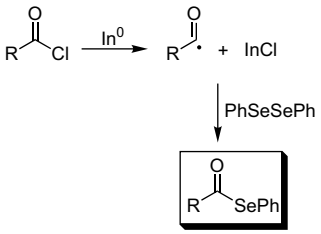


Figure 1. X-ray structure of **2m**. Selected bond distances: (Å): Se1–C15 1.9288(12), Se1–C21 1.9224(12), C15–O1 1.3304(14), C15–O2 1.2030(15), C15–Se1–C21 101.13(15), Se1–C15–O1 112.29(8), O1–C15–O2 126.27(11), Se1–C15–O2 121.42(9), O1–C1–C2 106.78(9), C21–Se1–C15–O1 −1.41(9); C2–C1–O1–C15 −170.84(9).

chloride **1f** did not produce the desired selenol ester (entry 11). As a further extension, we attempted to synthesize selenocarbonate **2m** bearing interesting functionalities. To our delight, when we used 9-fluorenylmethyl chloroformate and benzyl chloroformate, the corresponding selenocarbonate **2m** was obtained in quantitative yield (entry 12).

The selenocarbonate **2m** was confirmed by a single crystal X-ray study of the crystalline solid. The molecular structure is shown in Figure 1 with selected bond lengths in the caption of the figure. There are very few examples of structural studies of compounds containing the selenocarbonate moiety. Just two metallo-selenocarbonates have been reported in literature.[26] This is the first organic selenocarbonate structure reported. The bond lengths and angles within the organic parts of **2m** are normal. The selenocarbonate moiety adopts a synperiplanar conformation around the oxygen atom and antiperiplanar around the selenium atom. This contrasts to the *syn*/*syn* conformation for the similar dimethyl thiocarbonate.[27]

The reaction pathway for the formation of acyl phenyl selenides is believed to occur firstly through the single-electron transfer (SET) from indium to acyl chloride with generation of an acyl radical and indium(I) chloride salt. The acyl radical thus formed reacts with $(PhSe)_2$ in an S_H2 reaction affording respective selenol esters (Scheme 2).[28]



Scheme 2. Proposed mechanism for the synthesis of selenol esters.

Exploratory experiments revealed the ability of the Fmoc modified substrate **2m** as an efficient protecting group for selenium organic coumpounds.[29] As depicted in Scheme 3, the Fmoc group was removed in DMF using piperidine as base furnishing diphenyl diselenide in 85% yield.

Scheme 3.

3. Conclusion

In summary, a simple efficient and broadly applicable general method for the preparation of selenol esters from readily available and inexpensive starting materials is reported. Features of this method include the following: (i) easily accessible acylating agents were used; (ii) metal indium is stable toward air and moisture, its nontoxic nature, available in pure form; (iii) neutral conditions; (iv) various functional groups can be tolerated within the diorgano diselenide and/or the acyl chloride coupling partner; (v) good to excellent yields of selenol esters were obtained. Studies dealing with the application of this methodology in the synthesis of liquid crystals and application of selenol esters as appropriated protecting groups for biologically relevant selenium compounds are currently in progress in our laboratory.

4. Experimental section

IR spectra were recorded in the range of 4000–600 cm^{-1} using a Nicolet Magna 550 Spectrometer, and were measured as KBr or as neat oils. ^1H and ^{13}C NMR spectra were recorded at 400 and 100 MHz, respectively, with tetramethylsilane as internal standard. High-resolution mass spectra were measured at the Institute of Plant Biochemistry, Halle-Saale, Germany, with a Bruker BioApex 70e FT-ICR (Bruker Daltonics, Billerica, USA) instrument in ESI mode. Melting points were determined on an MQ APF – 302 digital melting point apparatus and are uncorrected. Column chromatography was performed using Merck Silica Gel (230–400 mesh) following the methods described by Still et al.[30] Thin layer chromatography (TLC) was performed using Merck Silica Gel GF_{254}, 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light, or stained with iodine vapor, or acidic vanillin. Dichloromethane was refluxed under P_2O_5 and after distilled. The diselenides were conveniently prepared from classical procedures.[31] Temperatures above room temperature were maintained by use of a mineral oil bath with an electrically heated coil connected to a Variac controller.

4.1. General procedure for the synthesis of selenol esters

In a two neck flask, equipped with reflux condenser, under an argon atmosphere, indium powder (1 mmol, 0.115 g), appropriate diselenide (0.5 mmol) and acyl chloride (1 mmol) were stirred in dry dichloromethane (8 mL) at reflux for 12 h. After this time, the mixture was cooled to room temperature and quenched with a solution of HCl 1 M, extracted with CH_2Cl_2 and the combined organic fractions were collected, dried over $MgSO_4$

and filtered; the solvent was then removed in vacuo yielding the crude products **2a**–**m**, which were purified by flash chromatography.

*4.1.1. Se-Phenyl selenobenzoate **2a***

Yield: 0.224 g (86%); yellow solid, mp 37–38 °C, IR (KBr) 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.94–7.92 (m, 2H, Ph); 7.63–7.58 (m, 3H, Ph); 7.50–7.42 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=193.7 (CO); 138.9 (Ph); 138.4 (Ph); 136.7 (Ph); 134.2 (Ph); 129.7 (Ph); 129.4 (Ph); 129.3 (Ph); 127.7 (Ph); 126.1 (Ph). HRMS-ESI *m*/*z* calcd for $C_{13}H_{10}OSe+Na^+$ 284.9794, found 284.9788.

*4.1.2. Se-2-Chlorophenyl selenobenzoate **2b***

Yield: 0.269 g (91%); yellow liquid; IR (liquid film) 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.93–7.24 (m, 9H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=191.4 (CO); 138.7 (Ph); 137.8 (Ph); 133.6 (Ph); 130.8 (Ph); 130.3 (Ph); 129.9 (Ph); 129.3 (Ph); 129.1 (Ph); 128.9 (Ph); 127.4 (Ph). HRMS-ESI *m*/*z* calcd for $C_{13}H_9ClOSe+Na^+$ 318.9405, found 318.9409.

*4.1.3. Se-o-Tolyl selenobenzoate **2c***

Yield: 0.178 (65%); yellow liquid; IR (liquid film) 1685 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.96–7.80 (m, 2H, Ph); 7.50–7.20 (m, 7H, Ph); 2.35 (s, 3H, Me). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=192.7 (CO); 142.5 (Ph); 138.6 (Ph); 137.7 (Ph); 133.7 (Ph); 130.4 (Ph); 129.8 (Ph); 128.8 (Ph); 127.2 (Ph); 127.2 (Ph); 126.5 (Ph); 22.9 (CH_3). HRMS-ESI *m*/*z* calcd for $C_{14}H_{12}OSe+Na^+$ 298.9951, found 298.9958.

*4.1.4. Se-4-Chlorophenyl selenobenzoate **2d***

Yield: 0.266 g (90%); yellow solid; mp 84–85 °C, IR (KBr) 1690 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.91–7.89 (m, 5H, Ph); 7.61–7.59 (m, 2H, Ph); 7.50–7.37 (m, 2H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=192.4 (CO); 138.2 (Ph); 137.9 (Ph); 136.4 (Ph); 133.7 (Ph); 129.2 (Ph); 128.6 (Ph); 127.0 (Ph); 123.6 (Ph). HRMS-ESI *m*/*z* calcd for $C_{13}H_9ClOSe+Na^+$ 318.9404, found 318.9410.

*4.1.5. Se-4-Methoxyphenyl selenobenzoate **2e***

Yield: 0.169 g (58%); white solid; mp 60–62 °C, IR (KBr) 1675 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.93–7.90 (m, 2H, Ph); 7.59–7.37 (m, 3H, Ph); 6.96–6.94 (m, 2H, Ph); 6.80–6.78 (m, 2H, Ph); 3.82 (s, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=194.2 (CO); 160.4 (Ph); 137.8 (Ph); 135.4 (Ph); 134.5 (Ph); 133.7 (Ph); 128.9 (Ph); 127.3 (Ph); 114.3 (Ph); 55.7 (CH_3). HRMS-ESI *m*/*z* calcd for $C_{14}H_{12}O_2Se+Na^+$ 314.9900, found 314.9904.

*4.1.6. Se-Benzyl selenobenzoate **2f***

Yield: 0.220 g (80%); yellow liquid; IR (liquid film) 1664 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.87–7.84 (m, 2H, Ph); 7.49–7.32 (m, 3H, Ph); 7.24–7.17 (m, 5H, Ph); 4.30 (s, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=194.5 (CO); 138.9 (Ph); 138.7 (Ph); 133.6 (Ph); 128.9 (Ph); 128.9 (Ph); 128.7 (Ph); 127.1 (Ph); 126.9 (Ph); 29.1 (CH_2). HRMS-ESI *m*/*z* calcd for $C_{14}H_{12}OSe+Na^+$ 298.9951, found 298.9945.

*4.1.7. Se-Ethyl selenobenzoate **2g***

Yield: 0.147 (69%); brown liquid; IR (liquid film) 1660 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.90–7.40 (m, 5H, Ph); 3.08 (q, 2H, CH_2); 1.50 (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=195.0 (Ph); 138.8 (Ph); 133.2 (Ph); 130.2 (Ph); 127.0 (Ph); 19.4 (CH_2); 15.8 (CH_3). HRMS-ESI *m*/*z* calcd for $C_9H_{10}OSe+Na^+$ 236.9794, found 236.9789.

*4.1.8. Se-Phenyl 2-chlorobenzoselenoate **2h***

Yield: 0.195 g (66%); yellow solid; mp 59 °C, IR (KBr) 1741 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.65–7.59 (m, 4H, Ph); 7.37–7.18 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=190.1 (CO); 136.3 (Ph); 135.7 (Ph); 135.0 (Ph); 132.3 (Ph); 131.5 (Ph); 130.9 (Ph); 129.1 (Ph); 128.6 (Ph); 127.7 (Ph); 126.5 (Ph). HRMS-ESI *m*/*z* calcd for $C_{13}H_9ClOSe+Na^+$ 318.9404, found 318.9411.

*4.1.9. Se-Phenyl 4-nitro selenobenzoate **2i***

Yield: 0.193 g (63%); yellow solid; mp 136–138 °C, IR (KBr) 1741 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=8.35–8.33 (m, 2H, Ph); 8.17–8.00 (m, 2H, Ph); 7.66–7.40 (m, 2H, Ph); 7.30–7.23 (m, 3H, Ph). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=192.5 (CO); 150.6 (Ph); 143.0 (Ph); 136.1 (Ph); 131.5 (Ph); 129.6 (Ph); 128.1 (Ph); 124.9 (Ph); 124.2 (Ph). HRMS-ESI *m*/*z* calcd for $C_{13}H_9NO_3Se+Na^+$ 329.9645, found 329.9639.

*4.1.10. Se-Phenyl 2,2-dimethylpropaneselenoate **2j***

Yield: 0.08 g (34%); brown oil; IR (liquid film) 1731 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.49–7.46 (m, 2H, Ph); 7.37–7.33 (m, 3H, Ph); 1.29 (s, 9H, $(CH_3)_3$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=207.9 (CO); 136.4 (Ph); 129.1 (Ph); 128.8 (Ph); 126.4 (Ph); 50.0 ($C(CH_3)_3$); 27.2 ($(CH_3)_3$). HRMS-ESI *m*/*z* calcd for $C_{11}H_{11}OSe+Na^+$ 265.0107, found 265.0113.

*4.1.11. Se-Phenyl 3-chloro-2,2-dimethylpropaneselenoate **2k***

Yield: 0.151 g (55%); yellow liquid; IR (liquid film) 1700 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.49–7.35 (m, 5H, Ph); 3.64 (s, 2H, CH_2); 1.38 (s, 6H, $C(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=204.8 (CO); 135.8 (Ph); 128.9 (Ph); 128.5 (Ph); 125.2 (Ph); 53.9 (CH_2); 51.0 ($C(CH_3)_2$); 22.8 ($(CH_3)_2$). HRMS-ESI *m*/*z* calcd for $C_{11}H_{13}ClOSe+Na^+$ 298.9717, found 298.9712.

*4.1.12. O-(9H-Fluoren-9-yl)methyl Se-phenyl carbonoselenoate **2m***

Yield: 0.379 g (100%); yellow solid; mp 113.1–114.6 °C; IR (KBr) 1772 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ=7.78–7.26 (m, 13H, Ph); 4.53 (d, *J*=7.6 Hz, 2H, CH_2); 4.12 (t, *J*=7.2 Hz, 1H, CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ=166.5 (CO); 134.8 (Ph); 129.3 (Ph); 128.1 (Ph); 127.4 (Ph); 126.9 (Ph); 124.9 (Ph); 119.9 (Ph); 64.9 (CH_2); 50.2 (CH). HRMS-ESI *m*/*z* calcd for $C_{21}H_{16}O_2Se+Na^+$ 403.0213, found 403.0216.

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Supplementary data

General experimental procedures, IR, HRMS, ^1H, and ^{13}C NMR spectral data for all isolated compounds. This material is available free of charge via the Internet at http://sciencedirect.com. CCDC 681177 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.03.069.

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