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Synthesis of Selenol Esters from Acid Chlorides and Organic Diselenides in the Presence of the $Zn/AlCl_3$ System

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Summary. Treatment of diphenyl and dibenzyl diselenides with aliphatic and aromatic acid chlorides in the presence of $Zn/AlCl_3$ affords selenol esters. Availability, low costs, and lack of toxicity of the catalysts, simple reaction work-up, and high yields under relatively mild condition are distinct advantages of this method.

Keywords. Selenol esters; $Zn/AlCl_3$; Zinc selenoate; Reductive cleavage of diselenides.

Introduction

Selenol esters have been successfully used as liquid crystals [1] and in the syntheses of steroids and sex hormones [2]. These compounds exhibit also a higher and more selective reactivity toward nucleophiles than their O-analogs. These properties make selenol esters a valuable acyl transfer agent and permit selective transformations in complex molecules. They are usually synthesized by one of the five main methods: (i) reaction of carboxylic acids with diaryl diselenides [3] or aryl selenocyanates [4], (ii) acylation of selenols [5] and their metal salts [6], (iii) reaction of aroylhydrazine with benzeneseleninic acid [7], (iv) alkylation of selenocarboxylates [8], and (v) reaction of aldehydes with diisobutylaluminum selenoate [9]. These methods suffer from laborious removal of by-products such as diaryl diselenide, or in some cases, unavailability of reagents. *Kato et al.* [10] reported a simple method for preparation of *Se*-aryl selenol esters via *Se*-aryl acylmethanesulfenoselenoates, which, in turn, are prepared both from reactions of acylsulfenyl bromides with diaryl diselenides and from reactions of metal thiocarboxylates with areneselenylbromides.

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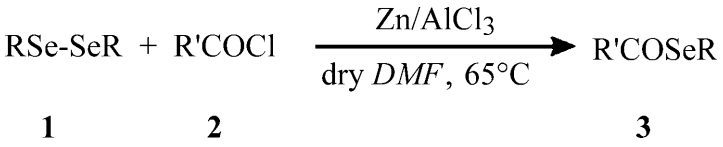


Scheme 1

We now describe a new method for preparation of *Se*-aryl and *Se*-alkyl selenol esters **3** which involves treatment of diselenides **1** and different acid chlorides **2** with the $Zn/AlCl_3$ system in dry dimethylformamide (*DMF*) at 65°C (Scheme 1).

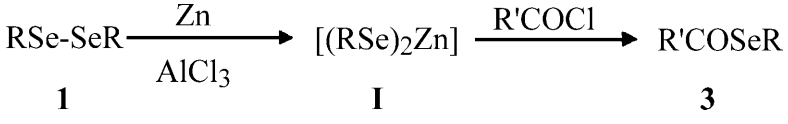
Results and Discussion

As seen in Table 1, both diaryl and dialkyl diselenides, diphenyl and dibenzyl diselenides, were treated with various acid chlorides to afford the corresponding selenol esters in high yields. Selenole esters prepared from aryl diselenides generally give higher yields than those produced from alkyl diselenides. In the case of the aromatic acid chlorides a longer reaction time is generally required (**3d**, **e**, and **j**, Table 1) which is due to their lower reactivity towards nucleophiles compared to aliphatic acid chlorides. It is observed that during the course of reaction the zinc dust is gradually consumed. This means that reductive cleavage of the Se–Se bond may lead to the zinc selenoate intermediate **I**, which further undergoes nucleophilic displacement with acid chloride in the presence of aluminum chloride to afford the selenol esters (Scheme 2).

In conclusion, the selenol ester synthesis described above is a valuable alternative for all processes where direct transformation of a carboxylic acid to the

Table 1. Selenol esters **3** from diselenides **1** and acid chlorides **2**

Product	R	R′	Reaction time/h	Isolated yield/%
3a	Ph	CH_3	0.75	89
3b	Ph	CH_3CH_2	2	86
3c	Ph	$CH_3CH_2CH_2$	2	87
3d	Ph	Ph	3	85
3e	Ph	4-ClC_6H_4	4.5	80
3f	$PhCH_2$	CH_3	1.5	81
3g	$PhCH_2$	CH_3CH_2	2	82
3h	$PhCH_2$	$CH_3CH_2CH_2$	3	80
3i	$PhCH_2$	Ph	2	74
3j	$PhCH_2$	4-ClC_6H_4	3	76



Scheme 2

corresponding selenol ester is not required. This methodology complements other methods, offering several advantages such as the greater availability of the starting materials, simple reaction work-up, and higher yields.

Experimental

Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra were recorded on a Jeol JNM-EX90A in $CDCl_3$ solutions. IR spectra were obtained using a Shimadzu IR-408. Mass spectra were recorded with a Shimadzu GC-MS QP 1100EX instrument.

General Procedure for Synthesis of Selenol Esters from Acid Chlorides

A mixture of the 1 mmol diselenide, 4.6 mmol zinc powder, 2.0 mmol anhydrous $AlCl_3$, and 15 cm^3 dry *DMF* were stirred at room temperature for 10–15 min. 4.0 mmol Acid chloride was then added at once and stirring was continued for the specified time (Table 1) at 65°C. Progress of the reaction was monitored by TLC. After addition of ethyl ether (20 cm^3) the mixture was washed with water (2×25 cm^3), dried over anhydrous Na_2SO_4, and the ether evaporated. The resulting crude product was purified by preparative thin layer chromatography (silica gel, eluent *n*-hexane : ethyl ether = 6 : 1) to afford the desired ester.

Se-Phenyl Ethaneselenoate (**3a**, C_8H_8OSe)

Oil ([4a]: bp 80°C at 0.5 Torr); IR (neat): $\bar{\nu} = 1730$ (C=O), 940 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 2.4$ (s, 3H, CH_3), 7.3–7.7 (m, 5H, Ph) ppm.

Se-Phenyl Propaneselenoate (**3b**, $C_9H_{10}OSe$)

Oil; IR (neat): $\bar{\nu} = 1725$, 930 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.2$ (t, 3H, CH_3, $J = 8$ Hz), 2.7 (q, 2H, CH_2, $J = 8$ Hz), 7.2–7.7 (m, 5H, Ph) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 9.3$, 40.9, 126.3, 128.7, 129.2, 135.7, 200.9 ppm; MS: m/z (%) = 213 (M^+, 0.6), 156 (4), 57 (29), 44 (100).

Se-Phenyl Butaneselenoate (**3c**, $C_{10}H_{12}OSe$)

Oil; IR (neat): $\bar{\nu} = 1723$, 940 cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 1.0$ (t, 3H, CH_3, $J = 8$ Hz), 1.8 (sext, 2H, CH_3CH_2, $J = 8$ Hz), 2.7 (t, 2H, CH_2CO, $J = 8$ Hz), 7.2–7.7 (m, 5H, Ph) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 13.1$, 18.6, 48.9, 126.4, 128.4, 128.9, 135.4, 199.4 ppm; MS: m/z (%) = 227 (M^+, 2), 156 (71), 77 (100), 71 (46), 51 (68).

Se-Phenyl Selenobenzoate (**3d**, $C_{13}H_{10}OSe$)

Oil ([4a]: mp 37–38°C); IR (neat): $\bar{\nu} = 1690$ cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.3$–7.7 (m, 8H, Ph), 7.8–8.1 (m, 2H, Ph) ppm.

Se-Phenyl 4-Chlorobenzeneselenoate (**3e**, $C_{13}H_9ClOSe$)

Mp 83°C ([4a]: mp 83.5–84.5°C); IR (KBr): $\bar{\nu} = 1690$ cm^{-1}; ^{1}H NMR ($CDCl_3$): $\delta = 7.4$–7.8 (m, 7H, Ph), 7.8–8.1 (m, 2H, Ph) ppm.

Se-Benzyl Ethaneselenoate (**3f**, $C_9H_{10}OSe$)

Oil; IR (neat): $\bar{\nu} = 1715\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 2.4$ (s, 3H, CH_3), 4.2 (s, 2H, PhCH_2), 7.3 (s, 5H, Ph) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 29.2$, 34.3, 126.8, 128.5, 128.8, 139.1, 197.2 ppm; MS: m/z (%) = 213 (M^+, 2), 170 (5), 91 (100), 65 (55), 43 (100).

Se-Benzyl Propaneselenoate (**3g**, $C_{10}H_{12}OSe$)

Oil; IR (neat): $\bar{\nu} = 1710$, $930\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.2$ (t, 3H, CH_3, $J = 8$ Hz), 2.6 (q, 2H, CH_3CH_2, $J = 8$ Hz), 4.2 (s, 2H, PhCH_2), 7.2 (s, 5H, Ph) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 9.4$, 28.6, 41.2, 126.8, 128.5, 128.8, 139.2, 202.0 ppm; MS: m/z (%) = 227 (M^+, 0.3), 91 (100), 57 (10).

Se-Benzyl Butaneselenoate (**3h**, $C_{11}H_{14}OSe$)

Oil; IR (neat): $\bar{\nu} = 1708$, $950\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 1.0$ (t, 3H, CH_3, $J = 8$ Hz), 1.7 (sext, 2H, CH_3CH_2, $J = 8$ Hz), 2.6 (t, 2H, CH_2CO, $J = 8$ Hz), 4.2 (s, 2H, PhCH_2), 7.3 (s, 5H, Ph) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 13.2$, 18.8, 28.6, 49.5, 126.7, 128.4, 128.7, 139.2, 200.9 ppm; MS: m/z (%) = 242 (M^+, 25), 91 (100), 71 (97), 43 (92).

Se-Benzyl Selenobenzoate (**3i**, $C_{14}H_{12}OSe$)

Oil; IR (neat): $\bar{\nu} = 1670\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 4.4$ (s, 2H, PhCH_2), 7.2–7.7 (m, 8H, Ph), 7.8–8.1 (m, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 29.0$, 126.9, 127.1, 128.5, 128.7, 128.9, 133.6, 138.9, 194.2 ppm; MS: m/z (%) = 275 (M^+, 3), 105 (91), 91 (100), 77 (96), 51 (78).

Se-Benzyl 4-Chlorobenzeneselenoate (**3j**, $C_{14}H_{11}ClOSe$)

Mp 70–71°C; IR (KBr): $\bar{\nu} = 1675$, $950\,cm^{-1}$; ^1H NMR ($CDCl_3$): $\delta = 4.4$ (s, 2H, PhCH_2), 7.2–7.6 (m, 7H, Ph), 7.7–8.0 (m, 2H, Ph) ppm; ^{13}C NMR ($CDCl_3$): $\delta = 29.3$, 127.1, 128.5, 128.6, 129.1, 137.1, 138.6, 140.0, 193.2 ppm; MS: m/z (%) = 310 (M^+, 3.8), 139 (100), 91 (79).

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