Reductive cleavage of the Se–Se bond in the presence of a Zn/AlCl$_3$ system: synthesis of selenol esters

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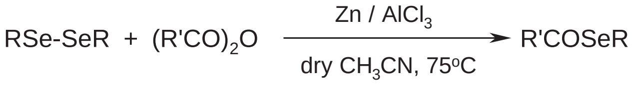
Selenol esters were prepared in good yields by reacting diselenides with carboxylic acid anhydrides in dry acetonitrile in the presence of a Zn/AlCl$_3$ system.

Keywords: selenol esters, carboxylic acid anhydrides, Zn/AlCl$_3$, reductive cleavage of diselenides, zinc selenoate

Organoselenium compounds have attracted considerable attention as reagents and intermediates in organic synthesis.[1] For instance, selenol esters are a type of activated esters due to their weaker C–Se bonds. They are very useful for the synthesis of naturally occuring macrocyclic lactones and lactams.[2] They have also been used as precursors of acyl radicals[3] and acyl cations[4] and can be converted easily into the corresponding acids,[5] esters,[5] amides,[5a] ketones,[6] aldehydes,[7] and alkenyl selenides.[8] Selenol esters have been prepared by: (i) acylation or aroylation of selenols and their metal salts;[9] (ii) alkylation of selenocarboxylates;[10] (iii) reaction of carboxylic acids with selenocyanates or *N*-phenylselenophthalimide;[11] (iv) reaction of esters or aldehydes with aluminum selenolates;[4b,5a,6d,12] (v) transition-metal-catalysed carbonylation of diselenides;[13] (vi) reaction of carboxylic acids with diaryl diselenides;[14] and other miscellaneous methods.[15-24] These methods suffer from laborious removal of by-products such as diaryl diselenides, or in some cases, unavailability of reagents.

We now introduce another procedure for the preparation of selenol esters from carboxylic acid anhydrides and organic diselenides by reductive cleavage of the Se–Se bond with a Zn/AlCl$_3$ system in dry acetonitrile at 75°C (Scheme 1).

The development of a convenient and efficient method for the synthesis of selenol esters has attracted considerable attention because they are used as liquid crystals[25] and in the syntheses of steroids and sex hormones.[26] The study of the reaction of diselenides with various carboxylic acid anhydrides was undertaken (Table 1). To study the efficiency of the reaction, acetonitrile was the solvent of choice. The treatment of diaryl diselenides with various acid anhydrides under the reaction conditions generally gave higher yields (**3a–f**, Table 1) than those produced from dialkyl (dibenzyl) diselenides. In the cases of aromatic, benzoic anhydride (**3d** and **3j**, Table 1), and bulky, pivalic anhydride (**3e** and **3k**, Table 1), carboxylic acid anhydrides longer reaction times are required which is due to their lower reactivities toward nucleophiles compared to the other aliphatic anhydrides. Recently, cleavage of diselenides with Zn/ZrCl$_4$ and subsequent conjugate addition has been reported.[27] In another report it has been proposed that the reduction of the Se–Se bond by zinc, with the aid of aluminium trichloride, leads to a zinc selenoate intermediate;[28] this anionic species then undergoes nucleophilic displacement with carboxylic acid anhydrides in the presence of aluminium trichloride to afford the selenol esters.



$$\underset{\mathbf{1}}{\mathrm{RSe\text{-}SeR}} + \underset{\mathbf{2}}{(\mathrm{R'CO})_2\mathrm{O}} \xrightarrow[\text{dry } CH_3CN,\ 75^{o}C]{Zn\ /\ AlCl_3} \underset{\mathbf{3}}{\mathrm{R'COSeR}}$$

Scheme 1

In summary, the selenol ester synthesis described above is a valuable alternative in all processes where direct transformation of a carboxylic acid to the corresponding selenol ester is not required. The current methodology offers several advantages such as the ready availability of the starting materials, neutral reaction conditions, simple reaction work-up, and moderate to good yields.

Experimental

Typical procedure: In a two-neck flask fitted with a reflux condenser, were placed dibenzyl diselenide (170 mg, 0.5 mmol), zinc powder (180 mg, 2.75 mmol), anhydrous AlCl$_3$ (333 mg, 2.5 mmol), and dry acetonitrile (10 ml). The mixture was stirred at room temperature for 2 hours; pivalic anhydride (420 mg, 2.25 mmol) was then added at once to the solution and stirring was continued for 8.5 hours at 75°C in an air atmosphere. Progress of the reaction was monitored by TLC. After completion of the reaction, ethyl ether (20 ml) was added. The combined ether / CH$_3$CN solution was then washed with 10% NaHCO$_3$ (10 ml), and water (3 × 20 ml), and dried over anhydrous Na$_2$SO$_4$. The solvent was evaporated *in vacuo* to give the

Table 1 Synthesis of selenol esters by reaction of diselenides with acid anhydrides

Product	R	R'	Reaction time/h	Isolated yield/%[a]	M.p. or b.p. (obs/°C (m.p. lit/°C or b.p. (lit/°C, mm)
3a	C_6H_5	CH_3	5	75	Oil / 80, 0.5[2]
3b	C_6H_5	CH_3CH_2	5.5	72	Oil/ oil[28]
3c	C_6H_5	$CH_3CH_2CH_2$	7.5	69	Oil/ oil[22]
3d	C_6H_5	Ph	8	71	Oil/ 37-38[2]
3e	C_6H_5	t-C_4H_9	8.5	74	Oil/ oil[29]
3f	4-ClC_6H_4	Ph	7	82	75/ 74–75[9c]
3g	$C_6H_5CH_2$	CH_3	4	65	Oil/ oil[28]
3h	$C_6H_5CH_2$	CH_3CH_2	6	68	Oil/ oil[28]
3i	$C_6H_5CH_2$	$CH_3CH_2CH_2$	7	60	Oil/ oil[28]
3j	$C_6H_5CH_2$	Ph	7.5	66	Oil/ oil[30]
3k	$C_6H_5CH_2$	t-C_4H_9	8.5	60	Oil/ oil[30]

[a] All products were identified by comparison of their IR and ^{1}H NMR spectra with the literature or with authentic samples and for **3f** by m.p. comparison.

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corresponding selenol ester which was purified by preparative thin layer chromatography (silica gel, eluent *n*-hexane: ethyl ether = 6:1 or CCl_4 : Petroleum ether = 1:1) to afford **3k** (Table 1) (153 mg, 60%) as an oil. IR (neat): 1720, 1690 cm^{-1}; ^{1}H NMR (90 MHz, $CDCl_3$) δ: 1.33 (s, 9H), 4.12 (s, 2H), 7.32 (s, 5H).[30]

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