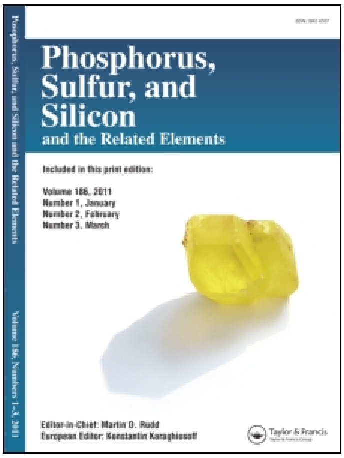

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SYNTHESIS AND STABILITY OF SELENOTHIOIC AND DISELENOIC ACID ESTERS

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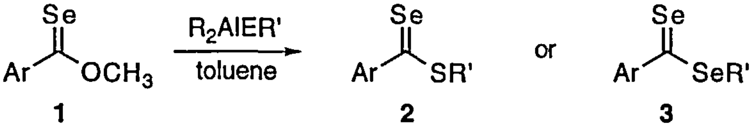
Abstract: The reaction of selenoic acid *O*-methyl esters with aluminum thiolates and selenolates proceeded smoothly to give a variety of selenothioic acid *S*-esters and diselenoic acid esters in moderate to good yields. The stability of the esters obtained were compared.

The chemistry of selenocarbonyl compounds is of great interest in recent years.[1] Very recently, we have synthesized and isolated selenothioic acid *S*-esters (RC(Se)SR')[2] and diselenoic acid esters (RC(Se)SeR')[3] for the first time. Extensive studies on their properties have been continued.[4,5] The results have disclosed that the esters are relatively stable purple to green compounds although their stability is highly dependent of the substituents next to selenocarbonyl group and sulfur or selenium atom. We report herein the reaction of selenoic acid *O*-methyl esters with aluminum chalcogenolates leading to a wide range of the esters and their relative stability.

Initially , reactions of aromatic selenoic acid *O*-methyl esters **1** with aluminum thiolates and selenolates were carried out. (eq 1). The results using a variety of **1** are listed in Table 1.



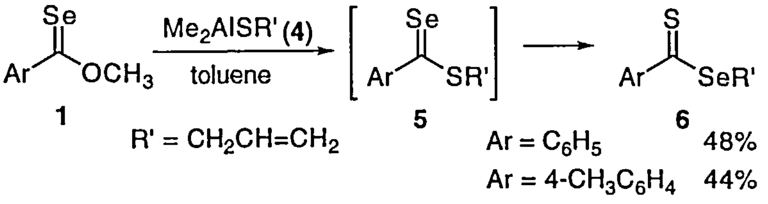
(1)

The reaction of selenobenzoic acid *O*-methyl ester **1** with aluminum methylthiolate proceeded smoothly to give the corresponding ester **2a** as a blue violet oil in 90% yield (entry 1). The use of aluminum thiolates derived from aliphatic thiols took place with high efficiency to afford **2b** - **2d** in good yields (entries 2 - 4). As for 4-methyl and 4-methoxy selenobenzoic acid *O*-methyl esters, the yields of the products decreased, whereas the reactions of **1** (Ar = 2-$CH_3C_6H_4$, 1-naphtyl) gave **2g** and **2i** in good yields (entries 7 and 9). Analogously, the reactions of **1** (Ar = C_6H_5) with aluminum selenolates afforded diselenoic acid esters **3a** - **3c** in moderate to good yields.

Table 1 Reaction of aluminum chalcogenolates with selenoic acid *O*-methyl esters [a]

entry	R_2AlER' R	R_2AlER' E	product	product Ar	product R'	yield, %
1	CH_3	S	**2a**	C_6H_5	CH_3	90
2	CH_3	S	**2b**	C_6H_5	C_2H_5	56
3	CH_3	S	**2c**	C_6H_5	C_4H_9-*n*	76
4	CH_3	S	**2d**	C_6H_5	C_4H_9-*t*	56
5	CH_3	S	**2e**	4-$CH_3C_6H_4$	C_4H_9-*n*	30
6	CH_3	S	**2f**	4-$CH_3OC_6H_4$	C_4H_9-*n*	13
7	CH_3	S	**2g**	2-$CH_3C_6H_4$	C_4H_9-*n*	80
8	CH_3	S	**2h**	4-$CH_3OC_6H_4$	C_6H_5	0
9	CH_3	S	**2i**	2-naphtyl	CH_3	72
10	CH_3	Se	**3a**	C_6H_5	CH_3	91
11	C_2H_5	Se	**3b**	C_6H_5	C_2H_5	46
12	*i*-C_4H_9	Se	**3c**	C_6H_5	C_4H_9-*i*	5
13	*i*-C_4H_9	Se	**3d**	C_6H_5	C_6H_5	0

[a] The reaction was carried out as follows: 1 (1 equiv), R_2AlER' (2 equiv), toluene (10 mL) at 0 °C - 25 °C for 2 - 5 h. [b] Isolated yields.

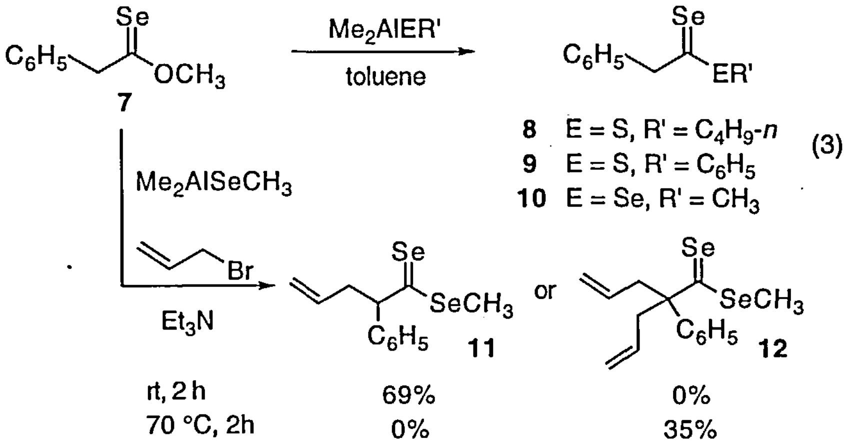


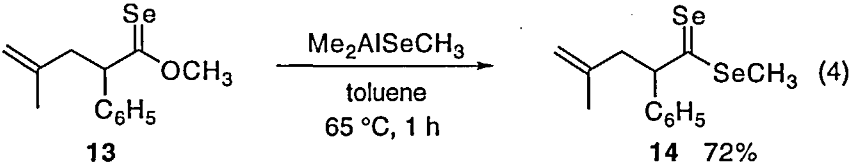
(2)

Aluminum allylthiolate **4** was also reacted with **1** (Ar = C_6H_5, 4-$CH_3C_6H_4$) (eq 2). The reaction mixture turned blue green at the earlier stage of the reaction. It gradually changed to brown to give *Se*-allyl esters **6** as a product without the contamination of **5**. In this case, *S*-allyl esters **5** may be initially formed. Then, **5** is likely to undergo 3,3-sigmatropic rearrangement to lead to **6**.

In these reactions the selenocarbonyl group of **1** survived under this reaction conditions, and selective substitution of the OMe group by organosulfur or organoselenium group has proceeded. No appreciable change of **2** and **3** bearing aliphatic substituents next to sulfur or selenium atom occurred during the chromatographic purification. On the contrary, reactions of **1** with aluminum benzene-thiolates and -selenolates failed to give the corresponding products **2h** and **3d**, although the reaction mixture turned blue or green,which was indicative of the formation of **2h** and **3d** (Table 1, entries 8, 13).

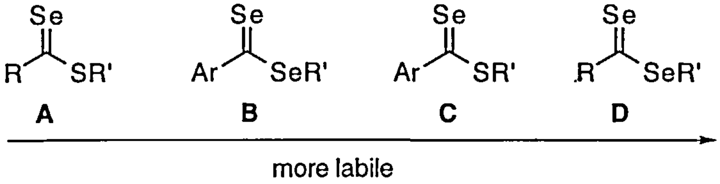
Secondly, the reaction of the aliphatic selenoic acid *O*-methyl ester **7** was examined. Similarily to the reactions described above, conversion of **7** to the ester **8** with aluminum thiolate derived from *n*-butanethiol took place, whereas the reaction of **7** with aluminum benzenethiolate did not give **9**, although the starting ester **7** was completely consumed. In the reaction of the aluminum methaneselenolate the ester **7** was efficiently converted to **10** in 65% yield. The blue violet fraction involving **10** was collected during the purification through a column chromatography. However, the ester **10** was not isolated as a pure form, and it involved about 20% of oligomers of **10**.





After several attempts to stabilize aliphatic diselenoic acid esters the treatment of the reaction mixture of **7** with aluminum methaneselenolate with allyl bromide and Et_3N prior to aqueous work-up was found to give the stable allylated esters **11** or **12** selectively by simply changing the reaction temperature and reaction time. The enhancement of the stability of the esters by introducing allylic group was further illustrated in eq 4. The reaction of **13** with aluminum methylselenolate gave **14** as a pure form in 72% yield.

On the basis of the synthetic results the relative stability of selenothioic acid *S*-esters and diselenoic acid esters have been qualitatively summarized below.



In a series of selenothioic acid *S*-esters aliphatic acid esters **A** are more stable than aromatic acid esters **C**, whereas aliphatic diselenoic acid esters **D** is more labile than aromatic derivatives **B**. When the lability of **B** and **C** under air was compared, **C** was oxidized to thioic acid *S*-esters more quickly than **B**.

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