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A new method for synthesis of *S*-aryl-*O*-alkyl thiolcarbonates: selenium-catalyzed reaction of alcohols with carbon monoxide and diaryl disulfides

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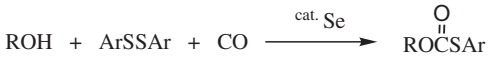
Abstract—A unique catalytic ability of selenium has been developed. When alcohols were allowed to react with diaryl disulfides in the presence of a catalytic amount of selenium under a pressurized carbon monoxide, *S*-aryl-*O*-alkyl thiolcarbonates were obtained in moderate to good yields.

The development of the process to replace the use of phosgene as a carbonylating reagent has received considerable attention in recent years in organic and industrial points of view. Carbon monoxide is one of the promising agents for the replacement of phosgene; the development of new methods for the carbonylation of various organic compounds with carbon monoxide could have a great impact in organic chemistry.[1] Thiolcarbonates were widespread used as synthetic intermediates,[2,3] polymerization initiators,[4] heat stabilizers for polymers,[5] precursors to polymercaptanes,[6] bioactive compounds,[7] and radiographic contrast agent.[8] Although many methods for the synthesis of thiolcarbonates have already been reported, there are some disadvantages of these methods: (i) the use of poisonous phosgene and carbonyl sulfide, (ii) the need of intolerable odorous thiol, (iii) the use of chloro thioformate having unstable against moisture, and (iv) multi-step procedures.[3b–r,9,10] In this letter, we wish to report a facile method for the synthesis of *S*-aryl-*O*-alkyl thiolcarbonates by the selenium-catalyzed reaction of alcohols with diaryl disulfides and carbon monoxide (Scheme 1).[11]



Scheme 1.

The treatment of ethyl alcohol with diphenyl disulfide in the presence of a catalytic amount of selenium (0.1 equiv) under the pressurized carbon monoxide (25 atm) at 25 °C for 6 h gave *S*-phenyl-*O*-ethyl thiolcarbonate (**1**) in almost quantitative yield (entry 1). The yield of **1** was diminished when the reaction was carried out under lower reaction temperature and carbon monoxide pressure. It is possible to reduce the amount of selenium still further under longer reaction time (15 h) giving **1** in 89% yield (entry 2). In order to know the application of the reaction, various alcohols were reacted with diphenyl disulfide and carbon monoxide (Table 1). The yields of product were influenced by the steric effect of alcohol used. *S*-Phenyl-*O*-methyl, *S*-phenyl-*O*-ethyl, and *S*-phenyl-*O*-butyl thiolcarbonates were formed by the reaction of methyl, ethyl, and butyl alcohol with diphenyl disulfide and carbon monoxide in good to excellent yields (entries 1, 3, and 4). Similarly, benzyl alcohol was coupled with diphenyl disulfide and carbon monoxide to give *S*-phenyl-*O*-benzyl thiolcarbonate in 77% yield (entry 5). When i-propyl alcohol was allowed to react with diphenyl disulfide and carbon monoxide under the similar reaction conditions to that of primary alcohol, the yield of *S*-phenyl-*O*-i-propyl thiolcarbonate was low (13%), however, the product yield was improved by using hash reaction conditions (at 80 °C, for 13 h under CO (70 atm)) (entries 6 and 7). Similarly, cyclohexyl alcohol was coupled with diphenyl disulfide and carbon monoxide giving *S*-phenyl *O*-cyclohexyl thiolcarbonate in moderate yield (entry 8). *S*-Phenyl-*O*-*tert*-butyl thiolcarbonate was not obtained on the reaction of *tert*-butyl alcohol (entry 9).

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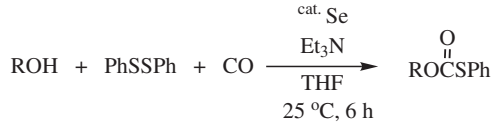
Table 1. Synthesis of *S*-phenyl-*O*-alkyl thiolcarbonates[a]

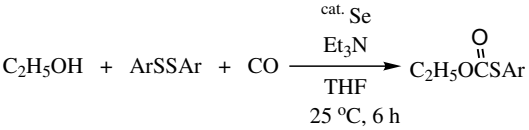


Entry	ROH	Yield/%[b]
1	C_2H_5OH	100
2[c]	C_2H_5OH	89
3	CH_3OH	100
4	C_4H_9OH	93
5	$PhCH_2OH$	77
6	$(CH_3)_2CHOH$	13
7[d]	$(CH_3)_2CHOH$	76
8[d]	*c*-$C_6H_{11}OH$	56
9	$(CH_3)_3COH$	Trace

[a] ROH (5 mmol), PhSSPh (5 mmol), Se (0.5 mmol), Et_3N (5 mmol), THF (2.5 mL), and CO (25 atm) at 25 °C for 5 h.
[b] GC yields based on alcohol.
[c] Se (0.1 mmol) at 25 °C 15 h.
[d] CO (70 atm) at 80 °C for 13 h.

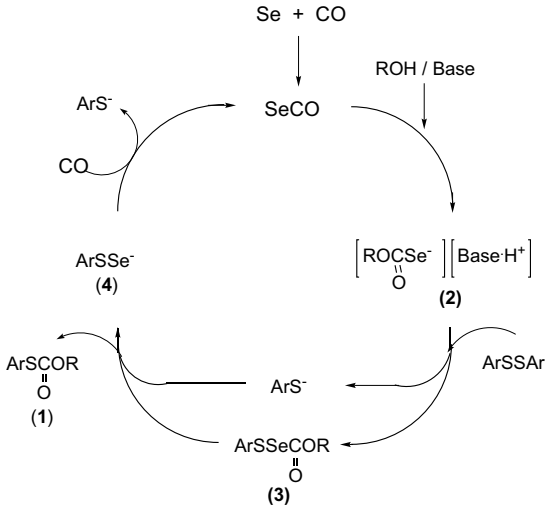
To know the scope and limitation of selenium-catalyzed synthesis of *S*-aryl-*O*-alkyl thiolcarbonates, various diaryl disulfides were reacted with ethyl alcohol and carbon monoxide in the presence of a catalytic amount of selenium. The results summarized in Table 2 showed that the reaction is amenable to the synthesis of various *S*-aryl-*O*-ethyl thiolcarbonates. In the case of di(3-methylphenyl), di(4-methylphenyl), di(4-bromophenyl), di(4-chlorophenyl), di(4-methoxy-phenyl), and di(2-napthyl) disulfide, the reaction proceeded efficiently giving the corresponding *S*-aryl-*O*-ethyl thiolcarbonates in good to excellent yields (entries 3–7 and 9). For the sterically hindered disulfide, di(2-methylphenyl), and di(2,6-dimethylphenyl) disulfide, the product yield was low (entries 1 and 2). For the reaction of di(4-nitrophenyl) disulfide, the corresponding thiolcarbonate was not obtained (entry 8).[12]

Table 2. Synthesis of *S*-aryl-*O*-ethyl thiolcarbonates[a]



Entry	Ar	Yield/%[b]
1	2-$CH_3C_6H_4$	32
2[c]	2,6-$(CH_3)_2C_6H_3$	Trace
3	3-$CH_3C_6H_4$	98
4	4-$CH_3C_6H_4$	95
5	4-ClC_6H_4	100
6	4-BrC_6H_4	100
7	4-$CH_3OC_6H_4$	87
8[c]	4-$O_2NC_6H_4$	Trace
9	2-$C_{10}H_7$	97

[a] C_2H_5OH (5 mmol), ArSSAr (5 mmol), Se (0.5 mmol), Et_3N (5 mmol), THF (2.5 mL), and CO (25 atm) at 25 °C for 5 h.
[b] GC yield based on ethyl alcohol.
[c] CO (70 atm) at 80 °C for 15 h.



Scheme 2.

Although we cannot clearly determine the catalytic reaction pathway for the synthesis of thiolcarbonates, catalytic cycle shown in Scheme 2 was suggested for the reaction. Nucleophilic addition of alcohol on selenium carbonyl, which was generated in situ by the reaction of elemental selenium with carbon monoxide under the basic conditions, formed selenolate (**2**) species as the first step in the reaction. The attack of **2** on sulfur atom of diaryl disulfide gave the intermediate (**3**) and arylthiolate. Aryl thiolate attacked on carbonyl carbon of intermediate **3** to give thiolcarbonate (**1**) and selenolate (**4**). Selenolate (**4**) was reacted with carbon monoxide to regenerate selenium carbonyl and arylthiolate.[13]

In summary, from the viewpoint of simple operation, mild reaction conditions, and good yields, the present reaction provides a useful method for synthesis of *S*-aryl-*O*-alkyl thiolcarbonates Furthermore, application of the reaction and elucidation of the reaction pathway are now in progress.

Acknowledgement

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11. It has reported that selenium acts as a catalyst on the reaction of secondary amine with disulfide and carbon monoxide giving thiocarbamates in moderate to good yields. See: Koch, P. *Tetrahedron Lett.* **1975**, 2087.
12. The treatment of di(4-nitrophenyl) disulfide (5 mmol), ethanol (5 mmol), and carbon monoxide (25 atm) in the presence of selenium (0.5 mmol) at 25 °C for 5 h, followed by alkylation with *n*-butyl iodide gave 4-nitrophenyl butyl sulfide (0.3 mmol). In addition, the formation of **3** was determined by GC–mass. From these results, it was suggested that the nucleophilic attack of 4-nitrophenylthiolate on **3** was suppressed by the lower nucleophilicity of thiolate.
13. When **2**, which was generated in situ by the reaction of ethyl alcohol with selenium and carbon monoxide in the presence of triethyl amine, was allowed to react with diphenyl disulfide at 65 °C for 5 h, *S*-phenyl-*O*-ethyl thiolcarbonate was obtained in 45% yield.