

A NEW SELENIUM CATALYZED SYNTHESIS OF S-ALKYL CARBONOTHIOATES
FROM ALCOHOLS, CARBON MONOXIDE, SULFUR AND ALKYL HALIDES

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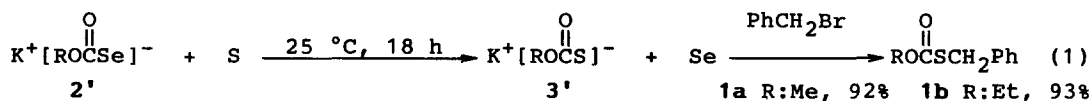
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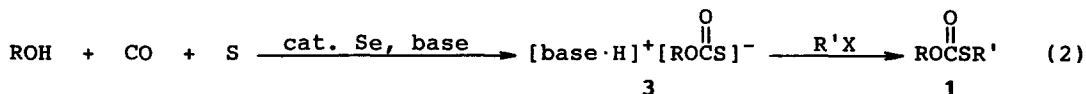
Selenium showed excellent catalytic activity for carbonothiolation of alcohols with carbon monoxide and sulfur under mild conditions. S-Alkyl carbonothioates were synthesized in good yields from various alcohols, carbon monoxide, elemental sulfur, and alkyl halides in the presence of selenium-catalyst.

During our continuing study on carbonylation with carbon monoxide, we recently found a novel catalysis of selenium, in which S-alkyl carbamothioates were produced from amines, carbon monoxide, sulfur, and alkyl halides in the presence of catalytic amount of selenium at room temperature under atmospheric pressure.¹ Our interest was focused on the further application of this novel catalysis of selenium to the other reactions. Then, we examined the selenium catalyzed reaction of alcohol with carbon monoxide and sulfur to generate S-alkyl carbonothioates 1.

At first, we attempted to elucidate whether the selenium-sulfur exchange reaction between salt of carbonoselenic acid 2 and elemental sulfur takes place smoothly or not. Because this exchange is considered to be a key step of our new catalytic reaction. Potassium salt of O-methylcarbonoselenic acid (2'), prepared from methanol, carbon monoxide, and elemental selenium in the presence of potassium carbonate,² was allowed to react with elemental sulfur at 25 °C for 18 h, and it was confirmed that corresponding potassium salt of O-methylcarbonothioic acid (3') was easily produced by the selenium-sulfur exchange accompanying deposition of selenium. Esterification of the salt (3') with benzyl bromide gave S-benzyl O-methylcarbonothioate (1a) in 92% yield, as shown in eq. 1. Recovery of elemental selenium suggests that the formation of salt of carbonothioates 3 from alcohols, carbon monoxide, and sulfur may be catalyzed by a catalytic amount of selenium.



Coupled this selenium-sulfur exchange reaction with selenium-catalyzed carbonylation of alcohols with carbon monoxide,³ a new method for synthesis of **1** using catalytic amount of selenium has been established, in which carbonothiolation of alcohols with carbon monoxide and sulfur under mild conditions was performed to give **3**. Esterification of resulting salts **3** gave S-alkyl carbonothioates (**1**) in good yields (eq. 2).⁴



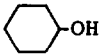
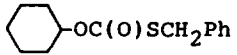
The typical procedure is as follows: methanol (4.1 mL, 100 mmol), elemental sulfur (0.32 g, 10 mmol), metallic selenium (8 mg, 0.1 mmol), triethylamine (7.0 mL, 50 mmol), and THF (20 mL) were placed in a 100 mL stainless steel autoclave with a magnetic stirring bar. The apparatus was then flushed with carbon monoxide several times, and finally charged with carbon monoxide at 10 kg/cm², and was maintained at 60 °C for 1 h with stirring. After carbon monoxide was purged, a small portion of sulfur (32 mg, 1 mmol) was added into the resulting solution of **3a** under nitrogen atmosphere with stirring at 25 °C to complete the deposition of selenium.⁷ Then, benzyl bromide (1.3 mL, 11 mmol) was added dropwise at 0 °C, and the solution was kept at 25 °C for a few hours. S-Benzyl O-methylcarbonothioate (**1a**)⁸ was given by distillation in 69% yield (1.26 g).

S-Alkyl carbonothioates (**1a-j**) were prepared from alcohols, carbon monoxide, elemental sulfur, and alkyl halides by the similar procedure using selenium-catalyst (1 mol%) as shown in Table 1. It was observed that addition of a small amount (1 mol%) of selenium accelerated extremely the carbonothiolation of alcohols in which simultaneous incorporation of carbon monoxide and sulfur took place. It is quite noteworthy that S-alkyl carbonothioates **1** were not obtained in the absence of selenium catalyst.

The path of present selenium-catalyzed reaction is postulated as follows (Scheme 1). The salt of carbonoselenic acid **2** is initially formed from alcohol, carbon monoxide, and selenium. Then, carbon oxide selenide (**4**), which is in equilibrium with **2**, reacts with sulfur to afford thermodynamically stable carbon oxide sulfide (**5**). Subsequent reaction of **5** with alcohol gives the salt of carbonothioic acid **2**.^{9,10}

From a viewpoint of simple operation, mild reaction conditions, good yields, and high purities of products, the present reaction provides with a useful method for synthesis of S-alkyl carbonothioates **1** from alcohols, carbon monoxide, sulfur, and alkyl halides using selenium-catalyst.

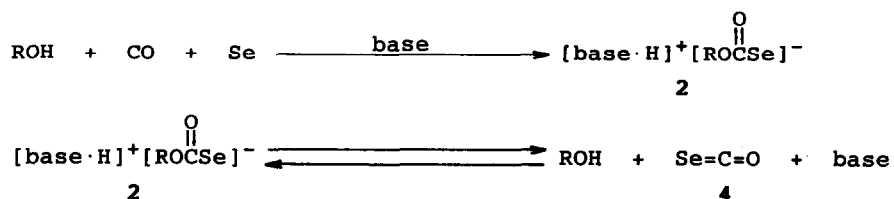
Table 1. Synthesis of S-Alkyl Carbonothioates (1a-j)

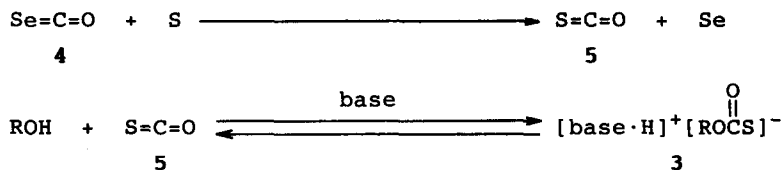
alcohol	alkyl halide	product		yield, % ^a
MeOH	PhCH ₂ Br	MeOC(O)SCH ₂ Ph	1a	69
EtOH	PhCH ₂ Br	EtOC(O)SCH ₂ Ph	1b	61 0 ^b 73 ^c
EtOH	n-BuI	EtOC(O)SBu-n	1c	33
EtOH	CH ₂ =CHCH ₂ Br	EtOC(O)SCH ₂ CH=CH ₂	1d	46
n-PrOH	PhCH ₂ Br	n-PrOC(O)SCH ₂ Ph	1e	60 ^d 0 ^{b,d}
n-BuOH	PhCH ₂ Br	n-BuOC(O)SCH ₂ Ph	1f	65 ^d
 -OH	PhCH ₂ Br		1g	62
CH ₃ OCH ₂ CH ₂ OH	PhCH ₂ Br	CH ₃ OCH ₂ CH ₂ OC(O)SCH ₂ Ph	1h	71
CH ₂ =CHCH ₂ OH	PhCH ₂ Br	CH ₂ =CHCH ₂ OC(O)SCH ₂ Ph	1i	61
t-BuOH	PhCH ₂ Br	t-BuOC(O)SCH ₂ Ph	1j	0

^a Isolated yield based on sulfur used. ^b Without selenium-catalyst.

^c 10 mol% of selenium was used. ^d Reaction time : 1.5 h.

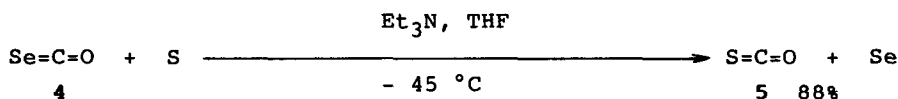
Scheme 1. A Possible Reaction Path





References and Notes

- 1) N. Sonoda, T. Mizuno, S. Murakami, K. Kondo, A. Ogawa, I. Ryu, and N. Kambe, *Angew.Chem.Int.Ed.Engl.*, **28**,452(1989).
- 2) Potassium carbonate affects as a base. The same type of carbonylation of alcohol using potassium carbonate did not occur at all in the absence of carbon monoxide under similar reaction conditions.
- 3) K. Kondo, N. Sonoda, and H. Sakurai, *Bull.Chem.Soc.Japan*, **48**,108(1975).
- 4) Preparation of 1 is generally performed by alkylation of salts of carbonothioic acids 3, which are formed by the reaction of carbon oxide sulfide (5) with alkaline alcohols.⁵ As another preparative method for 1, we reported a non-selenium route via salts of carbonothioic acids 3 generated by the direct carbonothiolation of alcohols with carbon monoxide and sulfur in the presence of a base such as DBU,⁶ however, this method requires more intense reaction conditions.
- 5) For a review, see R.J. Ferm, *Chem.Revs.*, **57**,621(1957).
- 6) T. Mizuno, I. Nishiguchi, T. Hirashima, A. Ogawa, N. Kambe, and N. Sonoda, *Tetrahedron Lett.*, **29**,4767(1988).
- 7) The remaining amine salt of O-methylcarbonoselenoic acid (2a) was completely exchanged by further addition of elemental sulfur to the reaction mixture, and metallic selenium used as the catalyst was recovered. GLC analysis showed the product S-benzyl O-methylcarbonothioate (1a) was entirely pure, and Se-benzyl O-methylcarbonoselenoate was not detected (<0.01%).
- 8) 1a : colorless oil; bp 145 °C/4 torr; IR (neat) 1705 (C=O), 1140 cm⁻¹ (C-O); ¹H-NMR (CDCl₃) δ 3.80 (s, 3H), 4.08 (s, 2H), 7.28 (s, 5H); MS m/z(%) 182 (M⁺, 40), 91 (100); exact mass calcd. 182.0402, found 182.0400.
- 9) Rapid conversion of carbon oxide selenide (4) to carbon oxide sulfide (5) by the reaction with elemental sulfur in the presence of triethylamine at low temperature has been observed.¹



- 10) One of the reasonable paths may be as follows.

