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Facile Synthesis of S,S-Dialkyl Dithiocarbonates from Water, Sulfur, Carbon Monoxide, and Alkyl Halides

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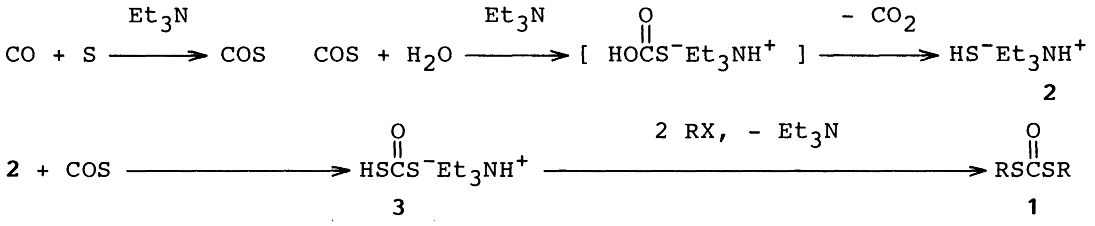
S,S-Dialkyl dithiocarbonates were easily synthesized in good to excellent yields by the reaction of carbon monoxide with sulfur in the presence of water and triethylamine, followed by alkylation of the resulting salts with alkyl halides.

S,S-Dialkyl dithiocarbonates (**1**) are versatile reagents for thioalkylation with alkyl halides,[1] α,β-unsaturated alkenes, and alkynes.[2] These reagents (**1**) are usually prepared from thiols and phosgene.[3] Other routes for preparation of **1** were reported, which involve selenium-catalyzed carbonylation of thiols with carbon monoxide,[4] rearrangement of O,S-dialkyl dithiocarbonates,[3] and carbonylation using carbonyl sulfide.[5]

Recently, we found sulfur-assisted O-carbonylation of alcohols with carbon monoxide in the presence of an appropriate base.[6] We now wish to report a facile synthesis of **1** by the reaction of carbon monoxide with elemental sulfur in the presence of water and triethylamine. This preparative method for **1** is straightforward and convenient, which does not need toxic phosgene and thiols having nasty smell.



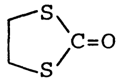
$$\mathrm{CO + S \xrightarrow{Et_3N} COS \qquad COS + H_2O \xrightarrow{Et_3N} [\ HO\overset{\overset{O}{\|}}{C}S^-Et_3NH^+\ ] \xrightarrow{-\ CO_2} \underset{\mathbf{2}}{HS^-Et_3NH^+}}$$

$$\mathrm{\mathbf{2} + COS \longrightarrow \underset{\mathbf{3}}{HS\overset{\overset{O}{\|}}{C}S^-Et_3NH^+} \xrightarrow{2\ RX,\ -\ Et_3N} \underset{\mathbf{1}}{RS\overset{\overset{O}{\|}}{C}SR}}$$

Various derivatives of **1** were synthesized from the corresponding alkyl halides under similar reaction conditions (Table 1).[7]

From a viewpoint of simple operation, good yields and high purities of products, and easy availability of reagents, the present reaction may provide with a useful method for synthesis of **1** from water, sulfur, carbon monoxide, and alkyl halides. Further study on this sulfur-assisted carbonylation is in progress.

Table 1. Synthesis of **1** from Water, Sulfur, Carbon Monoxide, and Alkyl Halides

Entry	RX	Product		Yield/%[a)]
1	$PhCH_2Br$	$(PhCH_2S)_2C=O$	**1a**	88
2	EtI[b)]	$(EtS)_2C=O$	**1b**	69
3	n-BuI[b)]	(n-BuS)$_2$C=O	**1c**	92(29)[c)]
4	n-HexI[b)]	(n-HexS)$_2$C=O	**1d**	77
5	n-OctI[b)]	(n-OctS)$_2$C=O	**1e**	63
6	$CH_2=CHCH_2Br$	$(CH_2=CHCH_2S)_2C=O$	**1f**	76
7	4-$MeC_6H_4CH_2Cl$	(4-$MeC_6H_4CH_2S)_2C=O$	**1g**	80
8	3,4-$Me_2C_6H_3CH_2Cl$	(3,4-$Me_2C_6H_3CH_2S)_2C=O$	**1h**	100
9	$BrCH_2CH_2Br$[b,d)]		**1i**	35

a) Isolated yields based on alkyl halides. b) DBU (20 mmol) was added at the alkylation step. c) Without DBU. d) RX (5 mmol) was used.

References
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7) The typical procedure is as follows : in a 100 mL stainless steel autoclave, water (0.18 mL, 10 mmol), sulfur (0.96 g, 30 mmol), triethylamine (4.18 mL, 30 mmol), and THF (10 mL) were placed under nitrogen atmosphere. The autoclave was charged with carbon monoxide at 30 kg/cm^2 at room temp. The reaction was carried out 80 °C for 4 h with vigorous stirring.[8)] After the reaction, subsequent alkylation of **3** with benzyl bromide (1.19 mL, 10 mmol) under ordinary pressure followed by purification by short-column chromatography (silica gel, hexane:benzene = 2:1) gave 1.21 g of **1a**[9)] (88% yield, based on benzyl bromide).

8) Complex products were afforded in the presence of DBU or N-methylpyrrolidine. Yields of **1a** lowered at 60 °C (68%) or 100 °C (76%).

9) **1a** : mp 42.9 °C (lit.[3)] 45-46 °C); IR (neat) 1640 cm^{-2} (C=O); ^{1}H-NMR ($CDCl_3$) δ = 4.22 (4H,s), 7.26 (10H,s); MS (70 eV) m/z (rel intensity) 274 (M^+;12), 214(16), 123(32), 91(100); exact MS (70 eV) m/z calcd. 274.0486, obsd. 274.0481.

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