Conversion of Xanthates to *O,O*-Dialkyl Thiocarbonates

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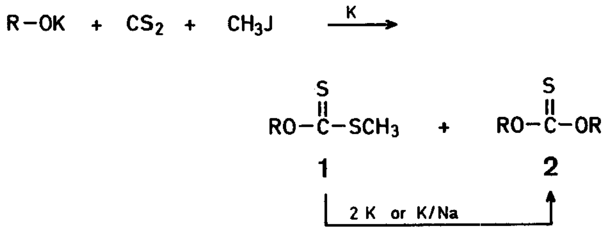
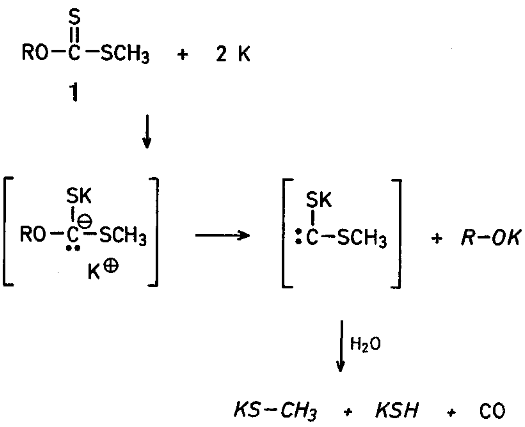
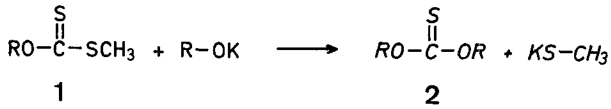
As potassium reacts easier than sodium with some higher alcohols to afford alkali alkoxides, potassium alkoxides have sometimes been used in the preparation of *S*-methyl xanthates (**1**) from alkoxide ion, carbon disulfide, and methyl iodide. If this reaction is not carried out properly, i.e. when more than 1 equivalent of potassium is used or carbon disulfide and methyl iodide are added before all the potassium has dissolved, *O,O*-dialkyl thiocarbonates (**2**) are formed as side products. This result is not observed in the analogous reaction with sodium.



In order to investigate the above side reaction (formation of **2**), we treated a variety of *S*-methyl alkylxanthates (*O*-alkyl *S*-methyl dithiocarbonates, **1**) with potassium in boiling benzene (Method A). It was found that two equivalents of potassium are required to achieve complete conversion of **1** into **2**. It was also found that in the case of *prim*-alkylxanthates potassium-sodium alloy (Method A') is advantageous over potassium; the reverse result is observed for *sec*-alkyl xanthates (see Table).





Incidentally, the formation of decanol was observed in the reaction of *O*-decyl *S*-methyl dithiocarbonate (*S*-methyl decylxanthate) with potassium-sodium alloy. This suggests that the conversion **1**→**2** might proceed via attack of potassium alkoxide (formed from the xanthate and potassium) on the xanthate. This assumption was proven by experiments using potassium alkoxides; further experiments revealed that the conversion **1**→**2** can also be achieved by treatment with

Table. *O,O*-Dialkyl Thiocarbonates (**2**) obtained from *O*-Alkyl *S*-Methyl Dithiocarbonates (**1**) by Reaction with Potassium (A), Potassium-Sodium Alloy (A'), or Sodium Alkoxides (RONa) (B)

R	Method	Yield (%)	b.p./torr[a]	I.R. (neat)[b] ν (cm⁻¹)	^{1}H-N.M.R. (CCl_4)[c] δ (ppm)	Elemental analysis			
n-C_3H_7	A'	30	91°/22	1228	4.33 (t, 4H, $-OCH_2-$)	$C_7H_{14}O_2S$	calc.	C 51.81	H 8.69
	B	74				(162.3)	found	51.85	8.72
i-C_3H_7	A	7	78°/20	1243	5.36 (h, 2H, $-OCH<$)	$C_7H_{14}O_2S$	calc.	C 51.81	H 8.69
	B	66				(162.3)	found	52.14	8.67
n-C_4H_9	A	6.3	122°/22	1238	4.35 (t, 4H, $-OCH_2-$)	$C_9H_{18}O_2S$	calc.	C 56.80	H 9.53
	A'	42				(190.3)	found	56.92	9.79
	B	80							
sec-C_4H_9	A	41	100°/22	1240	5.21 (m, 2H, $-OCH<$)	$C_9H_{18}O_2S$	calc.	C 56.80	H 9.53
	A'	trace				(190.3)	found	57.05	9.57
	B	72							
n-C_5H_{11}	A'	50	149°/21	1233	4.34 (t, 4H, $-OCH_2-$)	$C_{11}H_{22}O_2S$	calc.	C 60.50	H 10.15
	B	81				(218.4)	found	60.29	10.09
c-C_6H_{11}[d]	A	62	116°/0.8	1228	5.09 (broad, 2H, $-OCH<$)	$C_{13}H_{22}O_2S$	calc.	C 64.42	H 9.14
	B	70				(242.4)	found	64.55	9.20
n-C_8H_{17}	A'	38	151°/0.7	1228	4.34 (t, 4H, $-OCH_2-$)	$C_{17}H_{34}O_2S$	calc.	C 67.49	H 11.32
	B	66				(302.5)	found	67.66	11.40
n-C_9H_{19}	A'	32	167°/0.7	1234	4.34 (t, 4H, $-OCH_2-$)	$C_{19}H_{38}O_2S$	calc.	C 69.03	H 11.58
	B	60				(330.6)	found	69.12	11.68
n-$C_{10}H_{21}$	A'	26	183°/0.7	1234	4.35 (t, 4H, $-OCH_2-$)	$C_{21}H_{42}O_2S$	calc.	C 70.33	H 11.80
	B	54				(358.6)	found	70.61	11.92

[a] Boiling points were uncorrected.
[b] I.R. spectra were recorded with a JASCO DS-701G spectrometer.
[c] N.M.R. spectra were obtained with a JEOL PS-100 spectrometer at 100 MHz using TMS as an internal standard.
[d] In addition to the spectrometrical data, further proof of the structure of this compound was obtained by conversion to dicyclohexyl carbonate with lead(IV) acetate (see procedure).

sodium alkoxides containing the same alkyl group as **1**. The results given in the Table indicate that this conversion can be regarded as a useful method for the synthesis of *O,O*-dialkyl thiocarbonates (**2**) from *O*-alkyl *S*-methyl dithiocarbonates (*S*-methyl xanthates, **1**).

It has been reported[1] that thiobenzophenone reacts with two equivalents of sodium to form a dianion complex. This report together with our findings presented here support the following mechanism for the conversion of *O*-alkyl *S*-methyl dithiocarbonates (**1**) into *O,O*-dialkyl thiocarbonates (**2**) by reaction with potassium. The products detected are shown in italics.

Preparation of *O*-Alkyl *S*-Methyl Dithiocarbonates (1):
O-Propyl[2], *O-isopropyl*[3], *O-butyl*[4], *O-(2-butyl)*[5], *O-pentyl*[6], *O-cyclohexyl*[7], *O-octyl*[8], and *O-decyl*[9] *S-methyl dithiocarbonates* were prepared by known methods.

S-Methyl O-nonyl dithiocarbonate was prepared by the usual method from nonanol, potassium hydroxide, carbon disulfide, and methyl iodide in dimethylformamide; yield: 52%; b.p. 101°/0.4 torr.

$C_{11}H_{22}OS_2$	calc.	C 56.36	H 9.45
(234.4)	found	56.28	9.48

I.R. (liquid film): ν_{max} = 1219 (C—O), 1061 cm⁻¹ (C=S).

Reaction of *O*-Alkyl *S*-Methyl Dithiocarbonates (1) with Potassium or Potassium-Sodium Alloy (1:1): General Procedure:
A mixture of the *O*-alkyl *S*-methyl dithiocarbonate (**1**; 0.1 mol), potassium (0.2 g-atom) or potassium-sodium alloy (total: 0.2 g-atom), and dry benzene (200 ml) is heated cautiously. A vigorous reaction sets in immediately and then gradually subsides. The mixture is gently refluxed for 4 h, then filtered, the filtrate washed with water, dried with magnesium sulfate, and evaporated to dryness. The residue is distilled repeatedly under reduced pressure to give the *O,O*-dialkyl thiocarbonate **2** (see Table).

Conversion of *O*-Alkyl *S*-Methyl Dithiocarbonates (1) to *O,O*-Dialkyl Thiocarbonates (2) with Sodium Alkoxides; General Procedure:
To a suspension of powdered sodium (0.045 g-atom) in anhydrous benzene (50 ml), the alkanol (0.060 mol) is added and the mixture refluxed while stirring. After the sodium has completely dissolved a solution of the *O*-alkyl *S*-methyl dithiocarbonate (**1**; 0.030 mol) in anhydrous benzene (30 ml) is added while stirring and the solution refluxed for 4 h. After cooling, the solution is washed with water, dried with anhydrous magnesium sulfate, and evaporated to dryness. The residue is distilled repeatedly under reduced pressure to give the *O,O*-dialkyl thiocarbonate **2** (see Table).

Dicyclohexyl Carbonate from *O,O*-Dicyclohexyl Thiocarbonate and Lead(IV) Acetate:
A mixture of *O,O*-dicyclohexyl thiocarbonate (2.4 g, 0.10 mol) and lead(IV) acetate (5.3 g, 0.12 mol) in anhydrous benzene (200 ml) is stirred at room temperature for 1 h. The mixture is washed with water, dried with anhydrous magnesium sulfate, and evaporated to dryness. The residue is distilled under reduced pressure to give dicyclohexyl carbonate which crystallizes; yield: 1.4 g (62%); b.p. 99°/0.7 torr; m.p. 42°, from petroleum ether.

$C_{13}H_{22}O_3$	calc.	C 68.99	H 9.79
(226.3)	found	68.89	9.80

I.R. (KBr): ν_{max} = 1736 cm⁻¹ (C=O).

^{1}H-N.M.R. (CCl_4): δ = 4.48 (broad, 2H, $-OCH<$), 1.1–2.1 ppm (m, 20H, $-CH_2-$).

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